THE CRYSTAL STRUCTURE AND
CRYSTAL CHEMISTRY OF SCAPOLITES

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By

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SCOPE AND CONTENTS:

The X-ray diffraction symmetry of scapolite solid solution series has thoroughly been investigated. The structural analyses and refinements of three scapolites (ON8, 20% Me; XL, 52% Me; ON45; 93% Me) have been carried out by using 3-dimensional intensity data collected by integrated precession film techniques and an automated X-ray single-crystal diffractometer, and by using the full-matrix least-squares method. The ambiguities arising from the previous studies have been clarified. The real nature of the crystal structure and crystal chemistry of the scapolites have been elucidated, with emphases on (1) the space group problem, (2) the significance of the weak reflection violating the body-centred symmetry, (3) the order-disorder, (4) the structural variation, and (5) the stoichiometry.

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ABSTRACT

The systematic investigation of the X-ray diffraction symmetry of scapolites covering the whole range of solid solution show that all scapolites possess space group $P4_2/n$, except the pure end-members, marialite and meionite, which will possess space group $I4/m$, if they exist. The intensity of the weak superlattice reflections violating the body-centred symmetry, continuously increases from zero at the marialite end-member as Me% increases, reaches a maximum around 37%±2% Me then approximately symmetrically decreases to 75% Me followed by a slower decrease to zero at the meionite end-member. Hence, all the intermediate scapolites of the marialite-meionite series actually have a pseudosymmetric structure, i.e., a pseudobody-centred structure, and as the chemical composition approaches both end-members, the scapolite structure approaches the structure with a body-centred lattice. The weak superlattice reflections are directly related to the following two correlated factors: (1) the relative order-disorder of Al and Si distribution in the tetrahedral framework, and (2) the structural distortion from the body-centred symmetry. Accompanied with the above facts is the systematic deviation of cell dimensions from the linear regression in such a way that the further the structure deviates from the body-centred symmetry, the smaller the cell volume and the a_o become relative to the

evaluated one from the linear regression. Scapolites are regarded as a continuous, perfect solid solution with a long-range disordering, and unlikely to be composed of submicroscopic twins or different domains.

The structural analyses and refinements of three scapolites (ON8, 20% Me; XL, 52% Me; ON45, 93% Me) have been carried out by using 3-dimensional intensity data collected by integrated precession film techniques (ON8, ON45) and an automated single-crystal diffractometer (XL), and using the full-matrix least-squares method. The result has clarified the ambiguities arising from the previous studies and showed that the crystal structure is essentially continuous along the marialite-meionite series, with a slight structural variation as a function of chemical composition and ordering of Al,Si.

Several important quantitative relationships regarding the crystal structure and crystal chemistry of the scapolite solid solution series have been established, namely,

(1) the relationship between the superlattice intensity ratio $r(\Sigma I_{h+k+\ell=2n+1}/\Sigma I_{h+k+\ell=2n})$ and the chemical composition index % Me.

(2) the exponential relationship between the superlattice intensity ratio r and the atomic displacement from the mirror plane consistent with the space group I4/m.

(3) The linear relationship between the superlattice intensity

ratio r and the difference of Al occupancy between T_2 and T_3 sites.

(4) The Al occupancy (%) of tetrahedral sites as a function of the chemical composition of scapolites.

The ordering of Al-Si, the c-axis displacement of (Ca,Na), the tilting of CO_3 and the relative amount of CO_3 and Cl in the same scapolite are all inter-related. The mechanism to cause all such related structural phenomena and even the abnormal stoichiometry of scapolite can all be interpreted in terms of the internal strain created by the two greatly different anions, Cl^- and $CO_3^=$, sharing the same set of equivalent sites.

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CHAPTER 1

INTRODUCTION

The studies of the crystal structure of scapolites have been initiated by Gossner and Brückl (1928) and then subsequently done by Pauling (1930), Schiebold and Seumel (1932), Scherillo (1935), Papike and Zoltai (1965) and Papike and Stephenson (1966). Nevertheless, some problems concerning the crystal structure and crystal chemistry of scapolites still remained uncertain or unresolved. Even their space group has been very controversial.

Scapolite is particularly of interest, not only for its relative structural complexity, difficulty of synthesis (Fyfe 1958; Burley et al, 1961) and stoichiometrical anomalies (Evans, Shaw and Haughton, 1969), but also as an important rock-forming mineral with a wide variety of geological occurrence. Without complete, correct data on its crystal structure and crystal chemistry, the geological significance of scapolites can not be fully assessed. The availability of detailed structural information on scapolites will certainly be helpful in understanding its mineralogical properties, stoichiometry and its paragenesis in mineral assemblages, and perhaps in constructing and interpreting phase diagrams of petrological systems containing scapolites.

Indeed scapolites have not received intensive modern mineralogical, petrological or geochemical studies as other important groups of rock-forming minerals. So far, only two modern structural analyses have been reported by Papike and Zoltai (1965), and Papike and Stephenson (1966) respectively. The results of their refinements basically confirmed the structural model proposed by Schiebold and Seumel (1932). However, their work still has left some discrepancies and ambiguities. These uncertainties include (1) the high R value of mizzonite reported (15.7%); (2) the presence of weak reflections violating body-centered symmetry; (3) the abnormally negative isotropic temperature factor of (Si,Al) in mizzonite; (4) the co-ordination of (Na, Ca) atoms; (5) the crystal-chemical role of the carbonate group; (6) the order-disorder problem; (7) a rather low value for the Al-O distance derived from Papike's refinement of marialite ON8, when comparing with other reported mean Al-O distance. In addition, before learning that Papike and Stephenson (1966) also reported the presence of weak reflections violating body-centered symmetry, which obviously has led other previous investigators to assign a primitive space group (Gossner and Brückl, 1928; Burley, Freeman and Shaw, 1961) to scapolite, the writer in a preliminary survey also found a scapolite from the McMaster departmental collection showed very distinct and rather strong non body-centered spectra (hereafter,the non body-centered reflections refer to the reflections violating the body-centered symmetry). Even marialite (ON8), the same specimen studied by Papike and Zoltai (1965), surprisingly displayed exactly the same non body-centered reflections. This experimental fact quite surprised and inspired the writer to decide to thoroughly reinvestigate the crystal structure of scapolites covering the whole range of the solid solution series.

The intention of the present studies is to provide data on the structural parameters of scapolites with different chemical composition ($Ma_{80}Me_{20}$, $Ma_{48}Me_{52}$, $Ma_{7}Me_{93}$) in order to clarify the ambiguities arising from previous studies, to reveal the real nature of the crystal structure and crystal chemistry of scapolites and to provide answers to such pertinent questions as the following:

(1) Why is the space group of scapolites so controversial? Which one is the true space group? Is it a function of chemical composition or of thermal history? Or is it an "averaging effect" resulting from submicroscopically twinned aggregates or the disordered domains of lower symmetry?

(2) What is the nature of the order-disorder transformation involved in scapolite solid solution series? Does it only involve continuous changes of atomic arrangement within a single phase or does it involve unmixing?

(3) What are the nature and significance of the weak

reflections violating the body-centered symmetry? How are they related to the structural state of scapolites?

(4) Is there any obvious change of structural state in the scapolite series, either transitional or abrupt? What are the basic factors to cause structural variations?

(5) What is the relationship between crystal structure and stoichiometry of scapolite? Does any variation of structural property correspondingly reflect the characteristics of the scapolite stoichiometry?

This work was carried out first through the careful, systematic examination of space groups of eleven specimens; then, based on the determined space groups, 3-dimensional structural analyses and refinements of three specimens were undertaken. Finally the polymorphism and crystal chemistry of scapolites in the light of the structural information was investigated.

CHAPTER 2

HISTORICAL REVIEW

1) Chemical Composition and Chemical Formula:

The previous work and problems regarding the mineralogy of the scapolites have been extensively reviewed and discussed by D. M. Shaw (1960).

Scapolites are a group of framework aluminosilicates containing volatile components such as CO_3, Cl, SO_4 and possessing tetragonal symmetry. Various forms of the general chemical formula for scapolite group were suggested. In the absence of complete structural information, Shaw (1960) gives the following formula as provisionally suitable:

$$W_4Z_{12}O_{24}\cdot R$$

where W is mainly Ca, Na and K, but may include small amounts of other metals; Z is Si and Al, often with excess Si and deficient Al; R is (a) CO_3, SO_4, O_2H_2, Cl_2 or F_2 for meionite components (the calcium rich end-member) or (b) Cl, F, HCO_3, HSO_4 of OH for marialite (the sodium rich end-member).

Although other kinds of end-members have been suggested and scapolites could be really a solid solution with a number of end members, scapolite is tentatively accepted by most workers (e.g., Borgstrom, 1915; Winchell, 1924; Barth, 1927; Strunz, 1949; Shaw, 1960a; Deer et.al. 1963), in its simplest form, as a binary solid solution of two main end-members, namely, marialite $Na_4Al_3Si_9O_{24}$ Cl and meionite $Ca_4Al_6Si_6O_{24}CO_3$; the coupled substitution is $Ca_4Al_3CO_3$ for Na_4Si_3Cl. Shaw (1960) has defined an index of chemical composition % Me as the following ratio:

$$\text{Atomic per cent Me} = \frac{Ca+Mg+Fe+Mn+Ti}{Na+K+Ca+Mg+Fe+Mn+Ti}$$

The nomenclature is accepted as marialite, Me_0-Me_{20}; dipyre, Me_{20}-Me_{50}; mizzonite, Me_{50}-Me_{80}; meionite Me_{80}-Me_{100}. Papike (1964) evaluated % Me in three different ways: (1) as a function of Ca/(Ca+Na), (2) as a function of Al/Si and (3) as a function of $CO_3/(Cl+CO_3)$, and gave systematically divergent results. He stated that charge balance in the structure is maintained by excessive carbonate anion and deficient aluminum, and that the anion site is filled with CO_3 at about 80% Me. He also concluded that the proposed formula for the meionite end-member is not satisfactory. Ingamells and Gittins (1967) evaluated the available chemical data, and inferred a value of 7/2 for Ca/C, and proposed a formula of $Ca_7Si_{12-h}Al_{10+h}(C,S,Si)_2O_{50}H_h$ for the meionite end-member, but their proposal is not consistent with the known structural models. One needs good crystal structure determination to elucidate these problems. In a recent paper of Evans, Shaw and Haughton (1969), the anomalies of scapolite stoichiometry based on the model of a simple binary system were discussed and it was shown that the statistical curve of stoichiometry deviated from the ideal curve and showed an inflexion around Me %=75%. They suggested that, over the range Ca/(Ca+Na) from zero to 0.75, scapolites vary linearly between $Na_4Al_3Si_9O_{24}Cl$ and $NaCa_3Al_5Si_7O_{24}CO_3$, by means of a coupled replacement of Na_3Si_2Cl by $Ca_3Al_2CO_3$, and from 0.75 to 1.00, scapolites vary between $NaCa_3Al_5Si_7O_{24}CO_3$ and $Ca_4Al_6Si_6O_{24}CO_3$, by means of a coupled replacement of NaSi by CaAl. As the authors stated, this is really a unique feature for a mineralogical solid solution series, but no laws of crystal chemistry seem to be violated.

2) Unit Cell and Space Groups:

Investigations of the unit cell dimensions and space group of scapolites have been pursued by many people. Their results are summarized in Table (1).

The point group has been uncertain for a long time. The groups 4/m, 4 and $\bar{4}$ have all been suggested. Gossner and Brückl (1927), as a result of a single crystal investigation of a scapolite (41% Me), considered the space group to be either I4/m or $I4_1/a$, and again in 1928, the space group to be either $P4_2/m$ or $P4_2/n$. Later both Pauling (1930) and Scherillo (1935), as a result of a preliminary structural analysis, sug-

Table 1. Previous Results of Cell Dimensions and Space Group of Scapolites

Composition	Cell size (Å)		Space group	Reference	Sample Locality
	c	a			
41% Me	7.65	12.21	$I4/m$ or $I4_1/a$	Gossner and Brückl (1927)	Grasse Lake N.Y.
41% Me	7.65	12.21	$P4_2/m$ or $P4_2/n$	Gossner and Brückl (1928)	Grasse Lake N.Y.
Meionite medium scapolite	7.66	12.27	$I4/m$, $I4$ or $I\bar{4}$	Pauling (1930)	Vesuvius and Bedford, Ont.
69% Me	7.54	12.13	$I4/m$	Jakob et al. (1931)	Tessin
50% Me Meionite	7.580 7.619	12.09 12.19	$I4/m$, $I4$ or $I\bar{4}$	Schiebold and Seumel (1932)	Arendal, Norway, Mt. Somma Italy
62% Me and 87% Me	7.59	12.24	$I4/m$	Scherillo (1935)	Vesuvius
66% Me Meionite	7.51	12.055	$P4/m$	Burley, Freeman and Shaw (1961)	Quebec
	7.60	12.11			Mt. Somma
	7.548	12.25			Pianura
50% Me	7.571	12.095	$I4/m$	Gibbs and Bloss (1961)	Grenville, Canada
70% Me	7.569	12.163			Arendal, Norway
20% Me	7.572	12.060	$I4/m$	Papike and Zoltai (1965)	Gooderham, Ontario
70% Me	7.569	12.169	$I4/m$	Papike and Stephenson (1966)	Grenville, Quebec

gested the space group to be I4/m. Schiebold and Seumel (1932) again as a result of the single crystal measurements decided that the point group must be 4/m or $\bar{4}$. They also tested their crystals for piezoelectricity and obtained no effect. Similarly, Hettich and Steinmetz (1932) were unable to obtain any indication of piezoelectricity. Greenwood (1935) tested two crystals of scapolites of which one was colorless and the other pink; the colorless variety gave a piezoelectric effect and the pink variety did not. Greenwood concluded that scapolite belonged to one of the acentric point groups, either $C_4(4)$ or $S_4(\bar{4})$ and that the impurity causing the pink colour suppressed the piezoelectric effect. Unfortunately, Greenwood did not provide the chemical composition of his samples. Gibbs and Bloss (1961) also studied the piezoelectricity of a 50% Me scapolite at 50°C intervals between the boiling temperature of liquid nitrogen and 20°C and obtained no indication of acentricity. Burley, et. al. (1961) were the first to apply the Roger's statistical N(Z) test for centrosymmetry to two scapolites (Pianura R.O.M. M5432, Monte Somma R.O.M. M9122) and concluded that their scapolites were centric. Further, as a result of indexing a powder pattern of a scapolite (Q85, 65.9% Me), they found that the indices were compatible with a primitive lattice and not a body-centered lattice. So combining this result with that of the centrosymmetry test, they concluded that the most probable space group is P4/m. More recently, Papike and Zoltai (1965) also applied the statistical test for centrosymmetry proposed by Wilson (1949) and Howells et. al. (1950) and obtained a centric distribution. Therefore, they combined their result of a study of diffraction symmetry with the centric test to conclude that the most probable space group of the Gooderham scapolite (ON8) appeared to be I4/m.

Later Papike et. al. (1966) also reported that a few very weak and diffuse reflections were observed from another scapolite which apparently violated body-centered symmetry. However, they still ignored the significance of these weak reflections and continued to refine the structure of scapolite by using the body-centered space group I4/m.

Eugster, Prostka and Appleman (1962) presented refined cell dimensions for six analyzed natural scapolites covering most of the compositional range. The result showed that the a-axis linearly increased in length as Me content increased, while the c-axis remained invariant, and therefore a regular increase in unit cell volume with increase in % Me could be used to determine the composition of scapolite. This work was again confirmed by Papike (1964) and Haughton (1967).

3) Previous Work on Crystal Structure of Scapolite:

Preliminary work has been done by Gossner and Brückl (1928), Pauling (1930), Schiebold and Seumel (1932), and Scherillo (1935). The structures suggested do not differ greatly.

The general feature is that the Si-Al tetrahedra are joined in four-fold rings perpendicular to the c-axis and these rings are further linked into groups, four at a time, to form four oval shaped channels running parallel to the c-axis. A central cavity is occupied by anions (Cl,CO_3, SO_4) and the vertical channels are occupied by cations (Na, Ca, K).

Gossner and Brückl (1928) studied the structure of a 41% Me scapolite by using the Laue method. They used the space group $P4_2/m$ and proposed an incomplete set of coordinates in which they obviously make no attempt to group Al and Si together in the same tetrahedral site.

Pauling (1930) took oscillation and Laue photographs of a meionite scapolite and an intermediate one, and concluded that the possible space groups are I4/m, I4 or $I\bar{4}$. He determined the unit cell content to be two formula weights, and proposed a (Si,Al)-O framework consistent with the cell dimensions and space group I4/m. He also tested his model by comparing the estimated intensities of seven (00ℓ) type reflections with the calculated intensities, and showed that the agreement was good enough to confirm the proposed model. So the main contributions of Pauling to the determination of the crystal structure of scapolite were (1) the design of a tetrahedral linkage scheme and (2) the anticipation of the disorder of Si and Al in the tetrahedral sites.

Schiebold and Seumel (1932) studied a 50% Me crystal from Arendal, Norway and a meionite scapolite from Mt. Somma, Italy and suggested that the possible space groups are I4/m, I4 and $I\bar{4}$. After they failed to find ordered structure models which would be consistent with these space groups, they in turn supported Pauling's proposal on the disordered distribution of Si and Al atoms in the tetrahedral framework, and proposed a model which is practically identical to that of Pauling. Nevertheless, they are the first to present a complete set of atomic coordinates with reasonable accuracy. Their proposed atomic coordinates are listed in Table (2). However, they believed their model left the possibility open that scapolite might be a pseudotetragonal crystal consisting of submicroscopically twinned aggregates. This twinning hypothesis obviously stemmed from the difficulty in finding an ordered distribution for Si and Al which would be consistent with the observed symmetry (Papike, 1964).

Scherillo (1935) investigated an 88% Me scapolite from Mt. Somma, Italy and stated that his data appeared to be in agreement with the structural model proposed by Schiebold and Seumel (1932).

More recently with the availability of computers, Papike et.al. (1965) attempted to conduct a modern refinement of the crystal structure of marialite scapolite (ON8; 20% Me) from Gooderham, Ontario, starting from the Pauling-

Table 2. Atomic Coordinates and Temperature Factors of Scapolites

Atom	Coordinate	Schiebold-Seumel (1932) (Å)	Total Change	Papike and Zoltai (1965)	
				(Å)	B
Na	X	.13	+0.004	0.1340 ± .0003	2.65
	Y	.23	-0.0187	0.2113 ± .0002	
	Z	0	0	0	
Si 1	X	.334	+0.0048	0.3388 ± .0001	.82
	Y	.409	+0.0014	0.4104 ± .0001	
	Z	0	0	0	
$(Si,Al)_2$	X	.358	+0.0206	0.3374 ± .0001	.76
	Y	.069	+0.0161	0.0851 ± .0001	
	Z	.177	+0.0290	0.2060 ± .0002	
O 1	X	.466	+0.0027	0.4587 ± .0005	1.60
	Y	.350	-0.0017	0.3483 ± .0004	
	Z	0	0	0	
O 2	X	.307	-0.0004	0.3066 ± .0006	2.14
	Y	.093	+0.0276	0.1206 ± .0004	
	Z	0	0	0	
O 3	X	.051	+0.0007	0.0517 ± .0003	1.55
	Y	.353	-0.0030	0.3500 ± .0002	
	Z	.250	-0.0352	0.2148 ± .0006	
O 4	X	.234	-0.0047	0.2293 ± .0003	1.37
	Y	.129	-0.0001	0.1289 ± .0002	
	Z	.323	+0.0051	0.3281 ± .0006	
Cl	X	0	0	0	-
	Y	0	0	0	
	Z	0	0	0	

Schiebold-Seumel model, assuming the space group to be I4/m. However, they claimed that initial tests on the validity of the Pauling-Schiebold-Seumel structure model showed rather poor agreement between calculated and observed intensities which were collected with an equi-inclination, single-crystal diffractometer, and thus decided to attempt a complete structure determination. Their refined structure turned out to be similar to that of Schiebold and Seumel, with a maximum shift of 0.0352 Å or a "r.m.s." shift of 0.063 Å in the atomic coordinates from the model of Schiebold and Seumel (Table 2) and a residual index R = 11.97%.

Later, Papike and Stephenson (1966) refined the crystal structure of another scapolite (M730; 70.1%) from Grenville, Quebec in the space group I4/m using 3-dimensional intensity data collected by integrated Weissenberg film technique. The refined structure is basically the same as that of marialite with differences in the aluminum distribution in the tetrahedral sites of the framework and the crystal-chemical role of the carbonate ion. The final R value is 15.7%, and their refined atomic coordinates and temperature factors are listed in Table 3.

However, during their investigation of this 70.1% Me scapolite, they also found a few weak non-body-centred reflections which had led the previous workers (Gossner and Brückl, 1928; Burley et al., 1961) to assign a primitive space

Table 3. Atom Coordinates and Temperature Factors of a Mizzonite (70.1% Me) (Papike and Stephenson, 1966)

Atoms	X	Y	Z	B(Å^2)
(Ca,Na,K)	0.1428(3)	0.2170(3)	0	1.13
(Si,Al)1	0.3391(3)	0.4084(3)	0	-0.08
(Si,Al)2	0.3374(3)	0.0866(3)	0.2069(4)	0.03
O 1	0.4581(7)	0.3480(7)	0	0.58
O 2	0.3120(8)	0.1280(8)	0	0.87
O 3	0.0510(5)	0.3489(5)	0.2081(10)	0.84
O 4	0.2332(5)	0.1354(5)	0.3263(11)	0.79
(Cl,C,S)	0	0	0	1.80

group to the scapolite group. Unfortunately they ignored this experimental fact at that time and reported that the occurrence and significance of these reflections violating body-centered symmetry were being investigated subsequently by M. G. Bown and J. J. Papike. Finally, again as Schiebold and Seumel (1932) did, they suggested that the apparent 4/m symmetry of scapolites may be an averaging effect resulting from ordered domains of lower symmetry simply because their observed space group is not compatible with the hypothetical ordering scheme for the end-member meionite. As mentioned previously, the refinements of Papike et al. basically confirmed the model of Schiebold and Seumel (1932), but still left many ambiguities to be clarified and confirmed. Moreover, the composition of their sample becomes in doubt after the microprobe analysis of the same sample done by Eavans et.al. (1969).

4) Synthesis and Petrological Occurrence of Scapolites

Scapolite is noted for its difficulty of synthesis. Many workers have met with failure. Among earlier investigators, only Eitel (1925) reported the synthesis of meionite as a reaction rim on anorthite. The meionite reaction rim was identified only by optical means. This synthesis of meionite, however, needs confirmation. More recently, Fyfe (1958) was unable to synthesize scapolite in the system anorthite-$CaCO_3$-$CaCl_2$ at H_2O pressures of 500Kg/cm^2 in the region

400-700° C. Burley et al. (1961) failed to synthesize scapolites with numerous different starting materials over a range of temperature of 200°C to 800°C and a water pressure range of 10,000 psi to 35,000 psi. Their experiments were also conducted under total CO_2 and H_2O. Eugster et al. (1960) reportedly synthesized marialite from dry mixtures of $Na_2O \cdot 6SiO_2$, Al_2O_3 and NaCl at 1 atmosphere between 700°C and 850°C. Meionite was also reportedly formed at 1 atmosphere at 850°C from SiO_2, Al_2O_3 and $CaCO_3$. The authors also note that marialite melts incongruently at 860°C to albite plus NaCl-rich liquid. Seeding with natural scapolite was however necessary and it is therefore uncertain whether equilibrium was obtained. Recently, P. M. Orville (1970) reportedly was able to synthesize the scapolite and found it stable relative to the assemblage plagioclase + calcite + halite in the albite-anorthite - $CaCO_3$ - NaCl system at 750°C and 4 kb. The end-members scapolites marialite and meionite, however, are unstable. The chloride-free scapolite is reported stable under hydrothermal conditions ($P_{H_2O} = P_{total}$) whereas the chloride-bearing scapolite solid solution is thought not. This work has not yet been published other than in Abstract form.

The scapolite group is a common mineral phase widely spread in regional metamorphic terrains, especially in Precambrian rocks all over the world. Its origin and occurrence have been extensively reported on in a thorough review by Shaw (1960). The major modes of occurrence of scapolite are the following:

a) in blocks ejected from volcanoes by volcanic action;
b) in contact skarns where sedimentary marbles have been influenced by nearby plutonic bodies;
c) in altered igneous rocks especially gabbro and diabase altered by the effect of hydrothermal or pneumatolytic fluids (possibly also by ground water action, as claimed by LaCroix for scapolite from the Pyrenees);
d) in metamorphic rocks of regional distribution especially marbles, calcareous gneisses and granulites;
e) in metamorphosed salt deposits (Serdyuchenko, 1955);
f) in pegmatites and anorthosites.

Modes (b) and (d) are probably the most common ones.

The conditions of formation of scapolite are observed to cover a wide P.T. range and under high P_{CO_2}, P_{Cl_2} or P_{SO_2} which is often induced by pegmatitic, pneumatolytic or hydrothermal action.

Summing up the above, all piezoelectric experiments and statistical tests have indicated that scapolites are unlikely to be acentric, except Greenwood's work which was, ambiguous. Therefore, the conclusion that scapolites are centric in crystal symmetry has become accepted by most people, but the space group of scapolites is still uncertain.

CHAPTER 3

UNIT CELL AND SPACE GROUP

1) Introduction

As discussed previously, the space group of scapolite is still uncertain. Various space groups have been assigned for scapolites by investigators. Seven space groups, namely, I4, $I\bar{4}$, I4/m, $I4_1/a$, $P4_2/m$, $P4_2/n$ and P4/m have been reported. There are several possible reasons why the space group of scapolite has been so controversial. Firstly, some of these space groups only differ in the presence or absence of a centre of symmetry and the existence of this symmetry element is difficult sometimes to determine. A good X-ray technique enabling this to be done has only been available for about fifteen years. As more experiments, tests and structural analyses have been done, it has become certain now that scapolites are centric. Secondly, a most important reason is that some previous investigators have missed the weak reflections violating body-centred symmetry and some, though they have observed these weak non body-centred reflections, have ignored them. Previous workers failed to observe these weak non body-centred reflections, probably because of the following: (1) their exposures were not long enough to reveal these weak non body-centred reflections; (2) the experimental arrangements were not suitable to observe these weak non body-centred reflections; (3) the samples used were too few to reveal the changing nature of the space group of the scapolite solid solution series. A systematic survey of the scapolite space group has not been done before.

Because of the controversy about the scapolite space group and the importance of the space-group information to a correct crystal structure analysis, a very careful, complete and systematic examination of the scapolite space group was carried out as the initial part of the present study. Then the most reliable space group determined was used as a basis to determine the crystal structure of scapolite which in turn provided a counter test of the validity of the space group determined.

2) Specimen Descriptions

Since synthetic scapolites are not available, all the samples used for this study were natural scapolites. The suitable single crystals of scapolites were selected according to the following criteria:

a) Samples should be fresh, homogeneous and free from any inclusions or other imperfections.

b) Samples should have had a reliable chemical analysis.

c) Samples should cover a large range of chemical composition and approximately represent the whole solid solution series of scapolite.

d) Samples should be obtained from various localities and from various types of geological occurrences in order to examine any possible variation arising from the local environment of formation.

e) Samples should have sufficient quantity for further study.

f) Samples studied by previous workers were used in order to help to understand their problems and also to compare the results obtained by different workers.

Eleven specimens of scapolites were used to observe the x-ray diffraction symmetry. One of the specimens (M637) was obtained from the departmental collection of minerals; two of them (XL and 615011) were provided by Dr. B. J. Burley, and all the rest were supplied by Dr. D. M. Shaw. Generally speaking, these specimens are of good quality, suitable for x-ray crystallographic study and meet most of the requirements of the above mentioned criteria for selection. Among them, ON70 and XL are superior, transparent, single gem crystals; ON45 is a colorless, transparent, tiny single crystal bounded with prominent second order prisms and first order pyramids. However, attention must be paid to the inhomogeneities (inclusions, alternation zoning or intimate intergrowths) of some specimens (GL, M730, M637, ON47, 615011). The specimen M730 appears to be the most seriously affected. A careful examination under a binocular microscope has revealed that M730 consists of two different parts: one part is whitish, translucent, brittle and glassy but slightly dull in luster; the other part is yellowish, transparent, compact and glassy but slightly greasy in luster. A precession photo has shown that the yellowish part is a genuine single crystal of scapolite while the whitish part is not a single crystal but an aggregate composed of many minute crystalline particles. Furthermore, the powder diffraction pattern of this whitish part gave some poor weak reflection peaks which are not compatible with scapolite. These two parts intimately intergrow together, with variable size up to several millimeters in length or width. The boundary between these two parts is irregular, intricate and indistinct, while structural continuity is still preserved; the cleavages continue through the boundaries of these two parts. Along the cleavage planes, both parts contain reddish brown inclusions or staining (or radioactive minerals). From these evidences, the yellowish part of the fresh scapolite seems to be the relict and the whitish part of the poorly crystalline aggregates seems to be the product of an alteration from an originally large, single crystal of scapolite. Electron microprobe studies have also noted the inhomogeneity of scapolites (Evans et. al., 1969). Specimens used for the present study came from various type localities in the world. However, the occurrences of most of these specimens are pegmatitic skarn or pegmatites, this is apparently affected by the fact that only scapolites of these occurrences are generally free from impurities and give sufficient quantity of samples with rather constant composition for full chemical analysis and further study. Table (4) briefly lists the occurrences, mineral assemblages, appearances and localities of these specimens. The data of chemical analyses by means of conventional analysis and electron microprobe are available for most of the specimens (Tables 5 and 6). The specimens ON8 and ON45 respectively represent the most Na-rich scapolite and the most Ca-rich scapolite ever found in nature. There is generally a good agreement between microprobe and conventional analysis data. In case any prominent discrepancy occurs or contamination is doubted, such as in the case of M730, the microprobe data is preferred, because of its advantage of analyzing phases virtually free from contamination. The carbon contents were obtained from the conventional chemical analysis. For those specimens with unknown chemical composition, their % meionite were estimated by an optical method (Shaw, 1960) and then checked by X-ray method (Burley et. al., 1961, and Papike et. al., 1964). It is wise to normalize atomic proportions of scapolites to $Z = 12.0$ because of its adaptability in dealing with a discussion of the crystal chemistry of scapolites (Table 6).

Table 4. Occurrences and Localities of Scapolite Samples

Sample	Appearance	Mineral Assemblage	Occurrence	Locality
ON8	Bluish grey; massive; compact	Scapolite Feldspar Nepheline	syenite-pegmatite	Glamorgan Twp. Ontario
GL	Blue with whitish spots	Scapolite Amphibole Plagioclase	Zoned skarn in marble	Pontefract Twp. Quebec
ON6A	Colorless to slightly yellowish, transparent	Scapolite pyroxene sphene	Scapolite-pyroxene granulite	Monmouth Twp. Ontario
ON70	Pale-yellowish, transparent Single crystal gem-quality	Scapolite Quartz	Druses in quartzo-feldsparthic gneiss	Mpwapwa, Tanzania
XL	Honey-yellow transparent single, prismatic crystal, gem-quality	Scapolite Beryl & other radioactive minerals	pegmatite	Tsarasaotra, Madagascar
Q85	White, Brittle, non-translucent	Calcite Amphibole Diopside	pegmatitic skarn	Huddersfield Twp. Quebec
M637	Coarse, columnar aggregates, white, massive		pegmatite ?	New York U.S.A.
M730	Honey-yellow, translucent; Altered.		pegmatitic skarn	Granville, Quebec

(continued next page)

Sample	Appearance	Mineral Assemblage	Occurrence	Locality
ON47	White, brittle, Bladed			Slyndyanka Siberia U.S.S.R.
ON45	Tiny, single, prismatic crystal, colorless		Ejected blocks in tuff with lava flow	Monte Somma, Italy
615011	Coarse,massive columnar aggregates, white	Scapolite Quartz (massive)	pegmatitic ?	California U.S.A.

Table 5. Chemical Composition of Scapolite Samples

Wt. %	ON8	GL	ON6A	ON70	Q85
SiO_2	57.89	5.48	54.6	53.06	47.6
Al_2O_3	21.62	23.1	22.8	23.20	26.3
Fe_2O_3	0.07	0.00	0.10	0.19	0.04
MnO	0.01	0.00	0.01	0.02	0.00
MgO	0.03	0.01	0.01	0.02	0.05
CaO	4.81	8.55	8.75	9.88	15.70
Na_2O	10.50	9.1	8.40	7.65	4.5
K_2O	1.16	0.11	1.01	0.95	0.26
BaO	0.00	0.07	0.00	0.00	0.00
SrO	0.01	0.08	0.08	0.07	0.29
Cl	2.96	2.32	2.28	1.90	0.82
SO_3	0.03	0.19	0.33	1.10	1.43
CO_2	1.11	1.90[c]	1.69[c]	2.18	2.66[c]
H_2O^+	0.44	-	-	0.08	-
H_2O^-	0.06	-	-	0.03	-
Less O≡Cl,F	0.67	0.52	0.51	0.43	0.18
Sum	100.03	99.71	99.55	99.99	99.48

(a) Microprobe analyses of Gl, ON6A, Q85, M730 and ON45 are from Evans et.al. (1969); conventional analyses of ON70 and ON47 are from Haughton (1967); conventional analysis of ON8 are from Shaw (1960a); and the microprobe analyses of M637 and XL are from the present study.

(continued next page)

Wt. %	M637	XL	M730	ON47	ON45
SiO_2	50.75	49.80	44.9	44.05	39.6
Al_2O_3	24.62	25.16	28.5	28.67	30.7
Fe_2O_3	-	-	0.01	0.08	0.16
MnO	-	-	0.00	0.01	0.00
MgO	-	-	0.03	0.07	0.08
CaO	12.43	12.80	18.2	18.65	21.8
Na_2O	6.37	5.82	3.1	2.55	0.64
K_2O	0.75	1.17	0.49	0.24	0.47
BaO	-	-	0.00	0.00	0.00
SrO	-	-	0.16	0.19	0.08
Cl	1.38	1.43	0.02	0.03	0.10
SO_3	0.00	1.68	1.46	1.63	0.22
CO_2	3.16[b]	2.15[b]	2.86[c]	3.20	
H_2O^+	-	-	-	0.26	-
H_2O^-	-	-	-	0.13	-
Less O=CL,F	-	-	0.00	0.01	-
Sum	99.46	99.91	99.73	99.75	

(b) Data derived by using the crystal-chemical relationship that the total atomic proportions of C,S and Cl is equal to 1.0, based on Si+Al = 12.0.

(c) Data available from the conventional analyser.

Table 6. Atomic Proportions and Physical Properties of Scapolites [Based on Si+Al = 12,000]

Atom	ON8	GL	ON6A	ON70	Q85
Si	8334	8017	8044	7919	7272
Al	3666	3983	3956	4081	4729
Fe	8	0	11	21	5
Mn	1	0	1	2	0
Mg	7	2	2	4	11
Ca	744	1340	1382	1580	2568
Na	2934	2581[1]	2400[1]	2213[1]	1332
K	214	20	190	181	57
Ba	0	4	0	0	0
Sr	1	7	7	6	26
Cl	721	575	570	480	212
S	3	21	36	123	164
C	218	379	339	444	555
H	422	-	-	79.6	-
ΣNa	3148	2601	2590	2394	1383
ΣCa	760	1349	1403	1607	2610
AN	942	975[1]	945[1]	1047[1]	931
% Me	19.4	34.2	35.1	40.3	65.3
n_m	1.545	1.553	1.554	1.558[H]	1.569
Sp.Gr.	2.619	-	2.660	2.67[H]	2.705

(1) ΣNa = Na+K; ΣCa = Ca+Fe+Mn+Sr+Ba+Mg; AN = C+Cl+S+F.

(continued next page)

Atom	M637	XL	M730	ON47	ON45
Si	7643	7522	5864	6790	6270
Al	4357	4478	5136	5109	5730
Fe	-	-	1	9	19
Mn	-	-	0	1	0
Mg	-	-	7	16	19
Ca	2001	2072	2982	3080	3699
Na	1856	1703	919	762	196
K	144	225	95	47	95
Ba	-	-	0	0	0
Sr	-	-	14	17	7
Cl	351	367	5	8	27
S	0	191	167	188	26
C	649	443	597	673	-
H	-	-	-	-	-
Σ Na	2000	1928	1014	809	291
Σ Ca	2001	2072	3004	3123	3744
AN	1000	1001	769	870	-
% Me	50.0	51.8	74.2	79.4	92.8
n_m	1.558^L	1.560^L	1.571	1.576	1.580
sp. gr.		2.69^L	2.703	-	2.79^L

(2) % Me = $[\Sigma Ca/(\Sigma Ca+\Sigma Na)]\times 100$; n_m = mean refractive index.

(3) L = measurement done by writer;
H = done by Haughton (1967); and the rest done by Shaw 1960a, 1960b, 1965).

3) Determination of Space Group:

The megascopically fresh specimens were crushed in an agate mortar. Fresh, homogeneous grains with suitable size and more or less block form were selected. These selected grains were further checked under a polarizing microscope to detect any inhomogeneity or fracture. Finally, the X-ray diffraction symmetry of these optically confirmed single-crystal samples were studied by the precession, Weissenberg and rotation methods. MoKα radiation was employed throughout this study. A portion of the selected grains of each specimen was used also for X-ray powder diffraction experiments for identification and the refinement of cell parameters.

In the first preliminary test, the precession photograph of the (0kℓ) layer of the specimen M637 (47% Me) unexpectedly showed up rather strong so-called non body-centred reflection spots. That is, the spectra with $h+k+\ell = 2n+1$ (n = integer) which violate the body-centred symmetry (Plate 1). Moreover, exposure of only a few hours (4-6 hrs.) easily revealed the weak non body-centred reflections.As these spectra are systematically weaker than the $h+k+\ell = 2n$ spectra insufficient exposure could be the most probable reason why the extra, weak reflections violating the body-centred symmetry were not reported for many scapolites. Keeping this in mind, the diffraction symmetry of the specimen ON8 (20% Me), was re-examined. This is the same mineral specimen studied by Papike

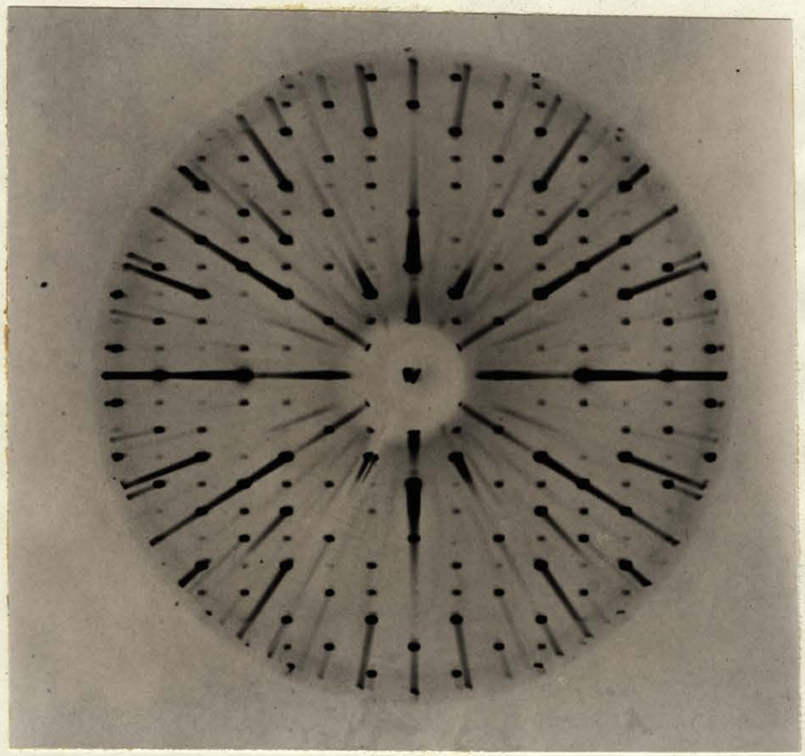


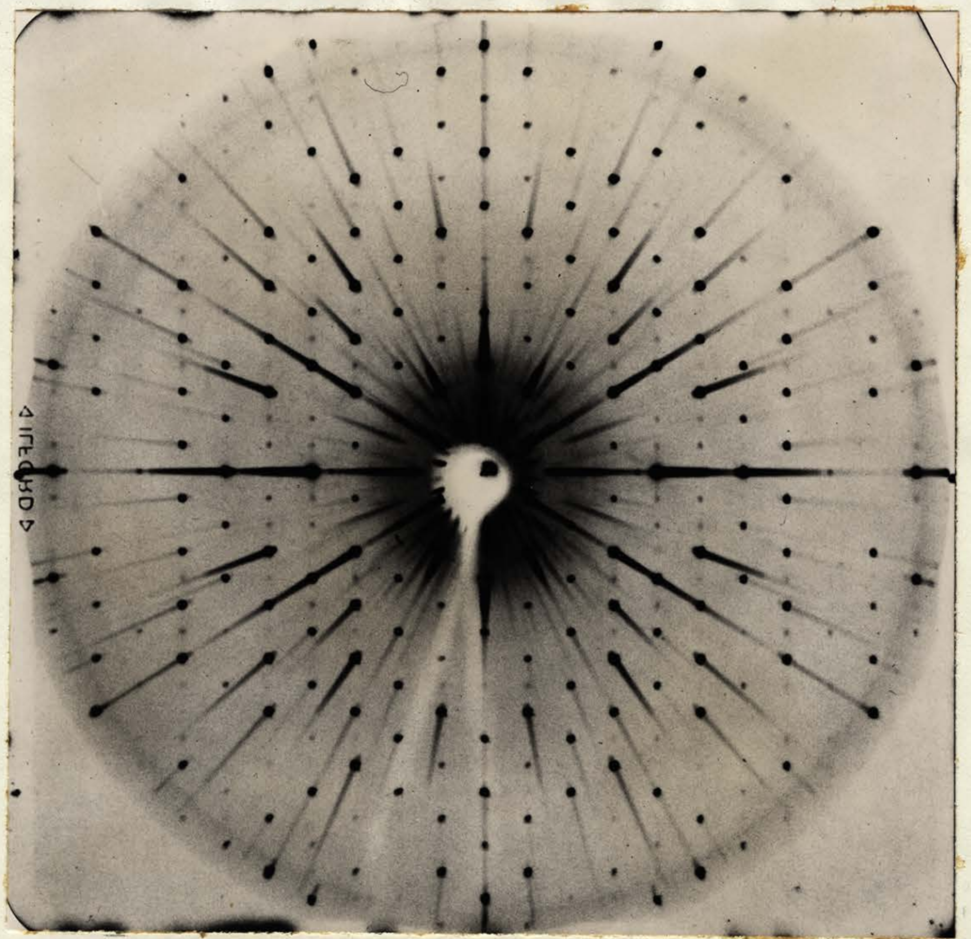
Plate 1. An (0kℓ) precession photograph of scapolite (M637, 50% Me), MoKα radiation, μ = 20°, 16 hrs.

(1965). Surprisingly, the photos showed the specimen ON8 is really primitive-celled in symmetry instead of being body-centred in symmetry (plate 2); the precession photographs of ON8 display exactly the same diffraction symmetry as shown by the former specimen M637, in such a way that the non body-centred reflections of both specimens not only have the same reflection indices ($hk\ell$), but also have about the same relative order of intensities within the class of the non body-centred reflections. That is to say, (043) reflection, for example, is the strongest of the non body-centred spectra of this specimen and is also the strongest reflection within the non body-centred spectra of the other specimens. However, the intensity of each non body-centred reflection relative to the body-centred reflection of specimen ON8 is systematically less than the intensity of the corresponding non body-centred reflection relative to the body-centred reflections of specimen M637. Therefore, it is necessary to take nearly six times as long an exposure to reveal the extra non body-centred reflections for specimen ON8 as that for specimen M637.

The size of the sample used in the above experiments for the specimens ON8 and M637 was relatively large, i.e., about 0.5×0.5×0.5 mm in size. In order to further confirm the result of the above-mentioned experiments for ON8 and M637, and also to test the effect of the sample size used on the results

Plate 2. An (0kℓ) precession photograph of a spherical crystal (0.5 mm in diameter) of scapolite (ON8, 19.4% Me) from Gooderham, Ontario. MoKα radiations, μ = 30°, 40 hrs.

Plate 3. An (0kℓ) precession photograph of a smaller crystal (0.15×0.15×0.2 mm) of scapolite (ON8, 19.4% Me) from Gooderham, Ontario. MoKα radiation, μ = 30°, 10 days.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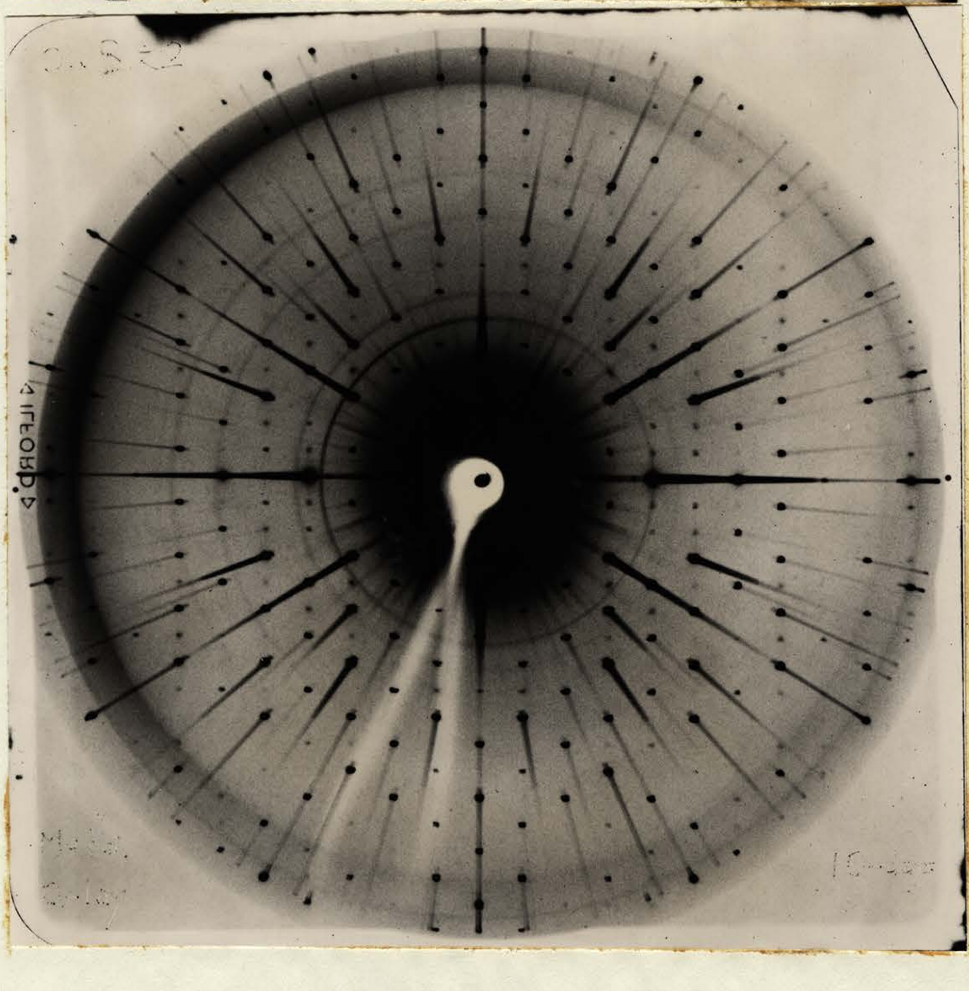
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of the diffraction experiments, samples with a small size about 0.15×0.15×0.20 mm were used to repeat the same experiments. The result obtained was exactly the same as that obtained from the preceding experiments using samples of relatively greater size, but the exposure necessary to reveal these weak non body-centred reflections was enormously increased (Plate 3). For ON8, it required more than one week to expose to about the same degree of intensity as that obtained in the preceding experiment using the sample with greater size. Hence the sample with greater size(0.3 mm - 0.5 mm in diameter) was preferred for taking X-ray diffraction photographs or for collecting intensity data in order to save time. At any rate, it has become evident that regardless of differences in composition or size of sample, the weak reflections violating body-centred symmetry are always present. As a matter of fact, a sample size of 0.3 mm - 0.5 mm in diameter is quite suitable since the optimum crystal size for X-ray photography calculated using the mass absorption coefficient for MoKα are 1.0 mm and 0.6 mm respectively for the marialite end-member and the meionite end-member (Buerger, 1966). CuKα radiation has been proved to take much longer exposure than MoKα radiation in revealing the weak non body-centred reflections of scapolites, probably because CuKα gives a linear absorption coefficient μ ten times greater than that given by

MoKα. Moreover CuKα gives a reflection sphere containing much fewer reciprocal lattice points than MoKα. So the optimum condition for observing the diffraction symmetry of these crystals is the precession method using hard MoKα radiation and relatively large size of crystal.

Likewise, all the precession photographs of higher layers (1kℓ), (2kℓ) etc. of M637 contain weak reflections inconsistent with the body-centred symmetry and thus it can be definitely concluded that there is no systematic extinction in (hkℓ) type spectra. Nevertheless, their precession photographs of the (hk0) layer, are consistent with body-centred symmetry, in other words, the so-called weak non body-centred reflections can not be found on these photographs at all, and therefore the systematically missing spectra are the (hk0) reflections with $h+k \neq 2n$. From the precession photographs of the (0kℓ) layer, another systematically missing spectra is observed, namely the (00ℓ) reflections with $\ell \neq 2n$. In order to check this latter systematic extinction, a long exposure of Weissenberg photograph of the (0kℓ) layer of M637 has been taken for a duration of one month to obtain back-reflections of (00ℓ) spectra with ℓ up to 20. The result has confirmed that (00ℓ) reflections with $\ell \neq 2n$ are extinct. Later, these systematic extinctions have been verified again during the collection of intensity data of the specimen XL using a single-crystal diffractometer.

Subsequently, in the same way, the diffraction symmetry of all the other specimens has been investigated by using the precession methods, and the results show that all specimens except one (ON45) display exactly the same diffraction symmetry as shown by the specimens M637 and ON8. Consequently, the identified systematic missing of spectra indicates that the general conditions limiting the possible reflections are the following:

$h\ k\ \ell$; No conditions
$h\ k\ 0$; $h+k=2n$
$0\ 0\ \ell$; $\ell=2n$.

Thus it is concluded that the real space group of all scapolite specimens except ON45 is unequivocally $P4_2/n$. It should be noted tht the space group $P4_2/n$ is uniquely determinable by extinctions.

Specimen ON45 is the most Ca-rich scapolite (93% Me) ever found in nature. It is the only scapolite that has not exhibited the weak reflections violating the body-centred symmetry, even in a photograph with a 10-day-long exposure. Nevertheless, this does not necessarily mean that ON45 should have a body-centred space group, e.g. $I4/m$; on the contrary, it is very likely that it really has a primitive space group $P4_2/n$, although it is very nearly body-centred $I4/m$, and can only produce very weak reflections inconsistent with the body-centred symmetry, which are not observable; in other words, they are "less than" (the background). This will be further discussed in a later section; and in effect, the specimen ON45 really has a primitive space group $P4_2/n$ and this has been verified later in the structural refinement of ON45.

4) Unit-Cell Dimensions of Scapolites:

The approximate unit cell dimensions can be directly measured from the precession photographs of each specimen, but these are too rough to be used as reliable data. The precise unit cell dimensions for each specimen were calculated from measurements taken from charts obtained from a Philips Geiger-counter X-ray goniometer unit, or from Debye-Scherrer photographs (114.6 diameter camera) if the quantity of specimen was limited, and refined on a digital computer, with a least squares refinement program*. In both methods CuKα radiation was employed. The powder diffraction charts were prepared on a scale of 1" per degree 2θ, using α-quartz as internal standard, so that accuracy in measurement of 2θ was ±0.01° and $K\alpha_1$ and $K\alpha_2$ peaks could often be distinguished, hence it gives **better** precision of measurements than that of Debye-Scherrer powder camera method. The determined cell dimensions and also cell volume are tabulated in Table 7.

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*An unpublished program written by H. D. Grundy, McMaster University.

Table 7. Cell Dimensions of the Scapolites

Specimen	Composition	a(Å)	c(Å)	V(Å^3)	Method
ON8	20% Me	12.059(1)[a]	7.587(2)	1103.22	chart[b]
GL	34% Me	12.060(3)	7.589(5)	1103.83	chart
ON6A	35% Me	12.071(4)	7.582(4)	1104.83	chart
ON70	40% Me	12.063(3)	7.585(3)	1103.77	chart
M637	50% Me	12.107(2)	7.577(3)	1110.70	chart
XL	52% Me	12.116(1)	7.581(2)	1112.98	chart
Q85	65% Me	12.147(2)	7.576(2)	1117.69	chart
M730	74% Me	12.156(4)	7.556(6)	1116.47	film[c]
ON47	80% Me	12.168(3)	7.571(4)	1120.86	chart
ON45	93% Me	12.194(4)	7.557(4)	1123.68	film

a) Estimated standard deviation enclosed in parentheses.

b) Chart from Philips Norelco powder diffractometer

c) Debye-Scherrer photographs.

The results of this study shown in Table 7 is illustrated in Figure (3). These plots are in general in agreement with the data of Eugster et al. (1962) and Papike (1964) but more closely agree with the findings of Haughton (1967). Although these approximately linear plots give no indication of abrupt structural change in scapolite solid solution series, the effect of the structural state on the cell dimensions and cell volume will be discussed in detail later.

Using these known cell dimensions and the specific gravities (Table 6) the cell contents may be calculated and shown to be 2 formula units.

CHAPTER 4

THE NON BODY-CENTRED REFLECTION AND ITS RELATIONSHIP TO THE CRYSTAL STRUCTURE OF SCAPOLITES

1) The Measurement of the Intensity of the Non Body-centred Reflections of Scapolites

As stated previously, the indices ($hk\ell$) of the non body-centred reflections ($h+k+\ell=2n+1$) are the same from specimen to specimen, while their intensities relative to the body-centred reflections ($h+k+\ell=2n$) are variable according to chemical composition. Moreover, the relative order of intensity within the class of the non body-centred reflections remains nearly the same from specimen to specimen. Thus it obviously implies that these non body-centred reflections ($h+k+\ell=2n+1$) are not just weak reflections violating the body-centred symmetry, but are systematic depending on a certain regular function of chemical composition and the interrelated structural parameters. This is the most important fact found in this study; it is the basis of elucidating the complicated structural problems of the scapolites.

This important relationship is best evaluated by plotting the ratio (r) of the total intensity (or mean intensity) of the non body-centred reflections to the total intensity (or mean intensity) of the ordinary body-centred reflections within the same reciprocal sphere (or space) of each specimen against the chemical composition. However, it is both excessive and unnecessary to measure the intensity of all the reflections contained in the reciprocal space for the radiation used. An easier alternative to derive the same result can be achieved by measuring the intensity of reflections, contained only in a certain limited reciprocal space for every specimen, and then take the ratio of the total intensity (or structure amplitude F_{obs}) of the non body-centred reflections to that of the body-centred reflections. Therefore, only the $(0k\ell)$ level of the reciprocal space, that is, the b^*c^* net of the reciprocal lattice was used in this study. The intensities were collected by the integrated Buerger's precession film technique,using Zr-filtered Mo radiation. Photometrically measured intensities were corrected for Lorentz and polarization factors[#], but no absorption corrections were made. The data of one of the specimens, XL, was collected by using a single-crystal diffractometer and agreed with its film data by checking some of the reflections. It is well known that the counter method is superior to the film method, especially for measuring weak reflections and for its directness and accuracy. Nevertheless, approximately accurate relative intensities of

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[#] Using an unpublished computer program written in the X-ray Crystallography Lab., Research Institute of Materials Science, McMaster University.

the weak reflections can still be measured by the film method. In fact, it turns out to be very satisfactory in this study. Moreover, to calculate the ratio of the total (or mean) intensity (or F_{obs}) of the non body-centred reflections to that of the body-centred reflections, the small error in intensity of the individual reflection can be averaged out by collecting a large number of reflections. In Table 8 are listed the observed relative intensities I_{obs} of $(0k\ell)$ spectra of the seven specimens measured.

2) Intensities of Non Body-centred Reflections and Their Relationship to the Chemical Composition of Scapolite:

Figure 1 shows the result of plotting the ratios of the total observed intensity of the non body-centred reflections to that of the body-centred reflections, i.e. $(\Sigma I_{obs})_{h+k+\ell=2n+1}/(\Sigma I_{obs})_{h+k+\ell=2n}$ against an index of chemical composition, i.e. % Me of the scapolites. As can be seen from this plot, the ratio (r) systematically increases and then decreases with the chemical composition. In order words, the intensity of the weak non body-centred reflections shows a systematic variation as a function of chemical composition; a maximum is reached around 37% Me, then declines toward the end-members, and becomes zero at both end-members, marialite and meionite. The extinction of the weak non body-centred reflection is inferred from the extrapolation of the experimental curve. As

Table 8. Observed Intensities of (0kℓ) Spectra of Scapolites

Specimen			ON8	GL	ON70	XL**	Q85	M730	ON47
% Me			20	34	40	52	65	74	80
h	k	ℓ	$I_{hk\ell}$	$I_{hk\ell}$	$I_{hk\ell}$	$I_{hk\ell}$	$I_{hk\ell}$	$I_{hk\ell}$	$I_{hk\ell}$
0	4	1	*0.15	0.29	0.33	0.94	*0.07	*0.01	*0.05
0	8	1	1.33	2.60	2.65	9.28	0.67	0.13	0.63
0	12	1	*0.29	0.55	0.60	1.03	*0.07	*0.01	*0.06
0	7	2	*0.22	0.42	0.58	1.01	*0.07	*0.01	*0.06
0	13	2	*0.27	0.51	0.55	0.80	*0.06	*0.01	*0.05
0	4	3	1.70	2.86	2.97	5.79	0.65	0.07	0.33
0	6	3	0.80	1.25	2.22	1.53	0.17	*0.02	*0.09
0	10	3	0.62	1.13	1.35	2.18	*0.07	*0.02	*0.08
0	1	4	1.15	2.39	2.19	4.79	0.37	0.05	0.17
0	3	4	0.39	0.76	0.81	1.50	0.22	0.08	0.27
0	5	4	1.55	3.20	3.33	7.94	0.89	0.16	0.72
0	7	4	*0.17	0.33	0.67	1.41	*0.14	*0.03	*0.08
0	15	4	*0.66	1.25	1.30	2.84	0.28	*0.06	*0.16
0	2	5	1.28	2.67	2.72	5.52	0.51	*0.11	0.35
0	4	5	0.85	1.59	1.78	3.74	0.35	*0.07	0.25
0	6	5	0.45	0.65	0.71	0.77	*0.07	*0.02	*0.04
0	8	5	0.60	0.66	0.81	1.56	*0.12	*0.03	*0.08
0	1	6	*0.55	0.78	0.70	0.48	*0.04	*0.01	*0.03
0	3	6	*0.13	0.25	0.48	0.56	*0.04	*0.01	*0.03
0	5	6	*0.14	0.26	0.39	0.56	*0.04	*0.01	*0.03
0	7	6	*0.35	0.66	0.80	1.57	*0.14	*0.03	*0.08
0	4	7	1.63	3.03	3.24	6.23	0.56	*0.13	0.19
0	6	7	2.10	4.03	4.51	7.74	0.68	0.16	0.33
0	8	7	1.03	2.06	2.26	4.34	0.45	0.10	0.33
0	10	7	1.22	2.48	2.57	4.65	0.48	0.12	0.20
0	5	8	*0.21	0.40	0.52	1.34	*0.12	*0.03	*0.07
0	7	8	*0.25	0.47	0.61	1.32	*0.12	*0.03	*0.07
0	2	9	*0.33	0.63	0.57	1.01	*0.08	*0.02	*0.05
0	1	10	0.78	2.96	2.98	5.26	0.43	*0.10	*0.20
0	3	10	*0.58	1.10	1.19	2.31	0.18	*0.04	*0.08
ΣI_{odd}			21.78	42.22	46.39	90.00	8.14	1.68	5.16
0	6	0	12.46	9.78	10.94	31.93	5.83	5.04	20.71
0	8	0	1.08	L 0.07	L 0.09	L 0.63	0.43	0.31	3.58
0	10	0	19.41	14.09	21.14	49.80	11.67	13.28	43.62
0	12	0	46.25	25.07	25.38	77.35	10.45	10.60	40.83
0	14	0	9.14	6.30	8.64	29.29	4.14	4.27	19.44
0	16	0	39.79	28.17	33.22	92.24	14.56	14.77	55.54
0	3	1	103.24	44.71	49.07	112.61	16.73	14.41	38.55

(continued next page)

Table 8 (cont'd)

Specimen h k ℓ	ON8	GL	ON70	XL	Q85	M730	ON47
0 5 1	2.11	1.07	0.82	1.35	0.12	0.20	0.45
0 7 1	4.46	2.71	3.87	9.17	1.53	2.02	6.48
0 9 1	49.77	28.06	33.39	97.91	14.86	12.74	49.84
0 11 1	2.73	2.61	4.75	12.70	2.65	3.46	14.11
0 13 1	7.32	2.95	2.70	4.79	0.29	0.37	0.70
0 15 1	19.20	12.25	13.02	39.51	4.65	4.28	19.61
0 2 2	2.72	2.10	4.13	8.29	2.53	2.83	9.54
0 4 2	6.17	3.28	2.53	9.90	0.80	0.59	3.30
0 6 2	12.52	7.02	8.42	26.04	4.03	3.68	15.35
0 8 2	12.90	9.21	6.93	22.43	2.50	1.88	10.03
0 10 2	17.93	7.75	6.69	18.95	1.96	1.71	6.97
0 12 2	20.25	12.86	12.61	35.11	4.20	4.31	17.13
0 14 2	L 0.34	L 0.11	L 0.14	1.22	L 0.07	0.10	1.33
0 1 3	3.01	1.28	0.72	5.83	0.28	0.07	0.72
0 3 3	137.57	74.79	101.86	196.31	49.11	48.01	112.45
0 5 3	54.83	32.43	37.16	99.38	15.03	14.05	46.92
0 7 3	101.61	52.43	67.52	165.74	29.82	29.36	84.42
0 9 3	26.80	14.40	14.68	39.30	4.59	4.46	16.18
0 11 3	59.74	40.03	55.50	130.28	24.51	25.14	83.91
0 13 3	1.09	L 0.11	L 0.14	1.25	0.76	0.97	5.70
0 15 3	3.14	3.29	2.88	11.37	1.45	1.38	7.74
0 2 4	1.28	0.21	L 0.09	0.68	0.12	0.13	1.35
0 4 4	98.93	52.51	62.23	140.52	26.81	29.60	72.76
0 6 4	13.48	9.01	8.72	29.33	4.27	3.65	16.16
0 8 4	8.71	3.25	3.45	9.53	0.75	0.65	1.97
0 10 4	1.15	0.71	1.41	4.01	0.71	0.88	3.31
0 12 4	16.24	8.40	8.03	21.93	2.51	2.58	9.82
0 14 4	1.37	0.81	1.31	6.83	0.94	1.00	6.02
0 1 5	1.50	0.82	0.58	2.55	L 0.05	L 0.02	0.22
0 3 5	162.97	75.65	82.95	177.34	32.75	30.74	81.68
0 5 5	37.02	20.46	19.30	42.11	6.57	6.31	20.18
0 7 5	69.49	37.15	45.85	109.33	19.11	18.25	60.58
0 9 5	48.27	28.54	31.62	84.18	12.97	12.50	46.42
0 11 5	0.61	L 0.11	L 0.13	L 0.03	L 0.07	0.07	0.53
0 13 5	7.42	3.96	4.52	10.02	1.04	1.22	3.97
0 2 6	8.17	5.45	6.13	17.27	2.64	3.00	12.54
0 4 6	21.28	10.41	12.83	32.79	4.78	5.08	17.84
0 8 6	2.81	2.09	1.83	5.48	0.76	0.75	3.38
0 10 6	L 0.33	0.28	1.07	2.30	0.65	0.97	4.05
0 12 6	1.07	0.22	0.37	1.88	0.15	0.21	0.85
0 1 7	22.76	12.31	10.83	27.34	3.16	2.93	10.21
0 3 7	15.19	8.41	10.17	27.72	4.61	5.57	20.02
0 5 7	35.56	20.52	22.15	61.72	8.83	8.35	32.95
0 7 7	53.23	26.33	31.31	83.48	11.94	11.94	43.21

(continued next page)

Table 8 (cont'd)

Specimen h k ℓ	ON8	GL	ON70	XL	Q85	M730	ON47
0 9 7	L 0.31	L 0.11	L 0.11	L 0.15	L 0.06	L 0.03	L 0.08
0 11 7	10.00	6.74	9.89	25.58	4.94	5.65	23.55
0 0 8	2.60	1.09	1.30	8.61	0.71	1.20	4.79
0 2 8	L 0.32	L 0.11	L 0.13	L 0.10	L 0.06	0.13	0.49
0 4 8	L 0.32	0.51	L 0.13	L 0.11	L 0.06	L 0.03	L 0.08
0 6 8	2.03	0.88	0.81	3.96	0.47	0.37	1.84
0 10 8	0.49	0.27	0.33	1.04	L 0.04	0.17	1.34
0 1 9	L 0.30	L 0.10	L 0.12	L 0.19	L 0.06	L 0.03	L 0.09
0 3 9	14.16	6.67	6.20	22.26	2.29	1.82	7.98
0 5 9	4.55	2.08	1.95	5.12	0.55	0.60	2.09
0 7 9	8.58	4.42	5.12	12.55	1.45	1.48	5.78
0 9 9	11.07	7.70	10.94	34.70	4.57	3.34	15.90
0 0 10	122.76	61.32	82.17	156.70	37.43	34.91	118.67
0 2 10	L 0.21	L 0.07	L 0.09	L 0.48	L 0.04	L 0.02	L 0.07
0 4 10	26.00	15.83	17.06	42.17	6.57	7.12	26.24
ΣI_{even}	1610.12	874.34	1032.17	2542.77	435.04	427.59	1414.16
$r = \frac{\Sigma I_{odd}}{\Sigma I_{even}}$	0.0135	0.0483	0.0449	0.0354	0.0186	0.0039 (0.0029)#	0.0036 (0.0027)#
$r \times 10^3$	13.5	48.3	44.9	35.4	18.6	3.9	3.6

Note: 1) odd: $h+k+\ell=2n+1$; even : $h+k+\ell=2n$.

2) All those unrealiable reflections affected by the beam stop, immersed in the white radiation streak, or near the margin of the photo are excluded, and only the reliable reflections ($h+k+\ell=2n$) common to all specimens are included.

3) * Unobservable non body-centred reflections ($h+k+\ell=2n+1$) whose values are approximately inferred from the nearest specimen in composition in which the corresponding reflection is observed or already inferred. All other unobservable non body-centred reflections are neglected because of their insignificant values.

4) ** Data collected by single-crystal X-ray diffractometer.

5) L "Less-than" belonging to the body-centred class of reflection.

6) # If only observed $I_{h+k+\ell=2n+1}$ are included.

mentioned previously, although the most Ca-rich natural scapolite, ON45, has a composition of 93% Me, its weak non body-centred reflections can no longer be observed. Nevertheless it probably exhibits non body-centred reflections that are so weak that they are unobservable because of the limitation of the experiment and it will have some non-zero inferred from the plot. It should be remarked that this plot may include some very small uncertainty regarding the % Me and the intensity data. Nevertheless it is believed to be accurate enough that the characteristic feature of this plot will not be changed.

There is a correlation in appearance between this r-% Me curve and the stoichiometric line of scapolite (Figure 1). The reason is not quite well known at this stage, but it could be tentatively explained as the following. This stoichiometric line was derived by plotting Cl atoms versus Ca+Sr atoms, on a basis of Si+Al=24.0 (Table 6) which is consistent with the calculated unit cell contents of scapolites. In this way the number of (Ca+Sr) atoms and the % Me can also be simply related to each other. It is known that the atoms of Na and Ca, and likewise the atoms of Si and Al, are so similar that they can replace each other in minerals without introducing any profound change of crystal structure. The coupled replacement of NaSi by CaAl in plagioclase is one example of this in minerals. On the other hand, the coupled replacement of Cl^- ion by $CO_3^=$

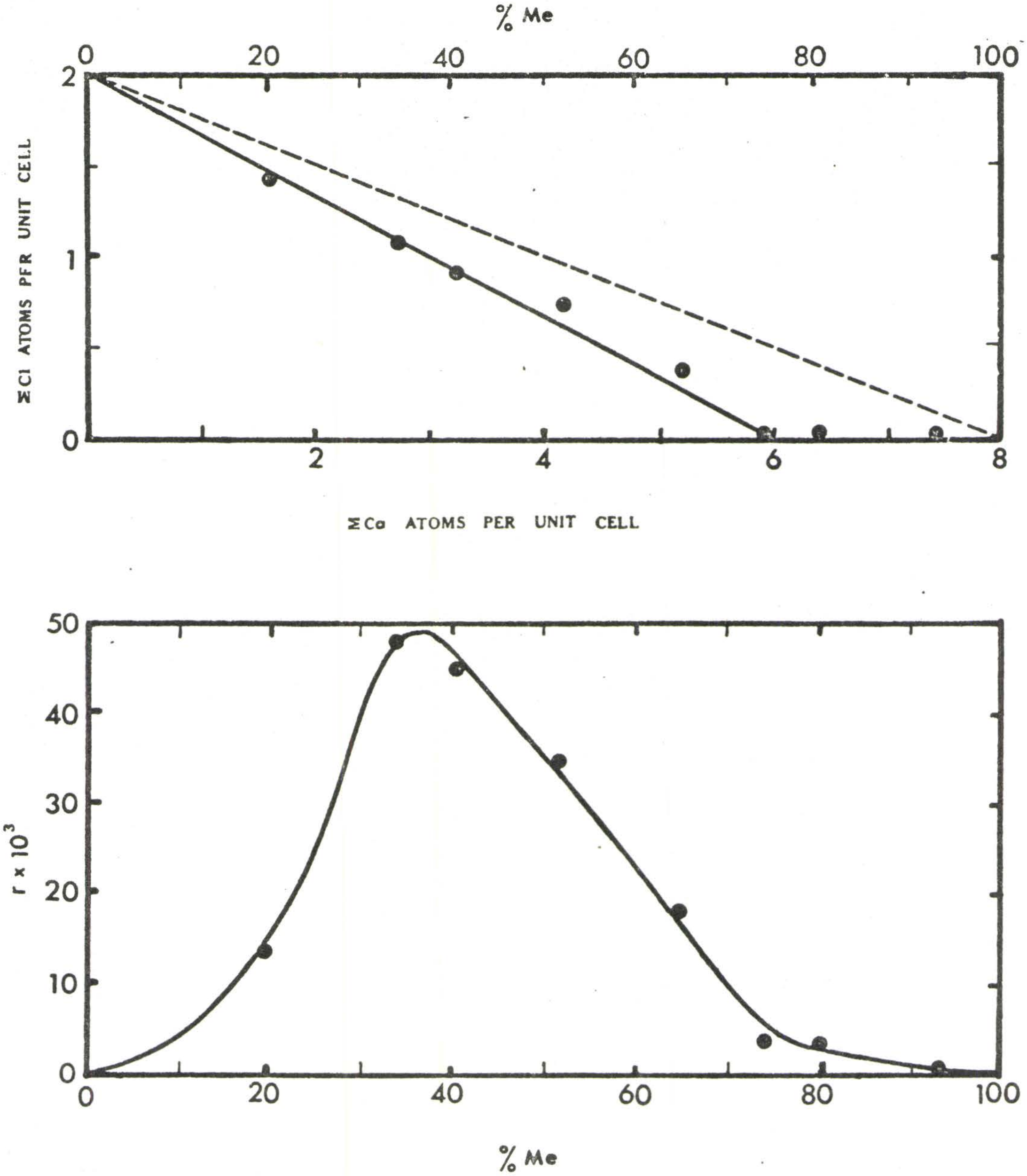


Fig. 1. Correlation between the stoichiometry of scapolites and the relationship derived by plotting the ratio $r(r = \Sigma I_{h+k+\ell}$ = odd/ $\Sigma I_{h+k+\ell\ =\ \mathrm{even}})$ vs. % Me of scapolites.

radical in scapolites is highly likely to introduce a change of the crystal structure of scapolites. Cl^- and $CO_3^=$ are both physically and chemically different; one is an anion of a single atom and the other one is a radical composed of a group of atoms with a specifically triangular planar molecular symmetry which is not compatible with the site symmetry within any tetragonal space group. The departure from the original structure of the end-members, namely that of pure marialite or pure meionite caused by the strain due to the difference between Cl^- and $CO_3^=$, will reach a maximum when both Cl^- and $CO_3^=$ are present in equal amount in the crystal. If the amounts of Cl^- and $CO_3^=$ are not equal, then the anion with the larger amount has a dominant effect; consequently, the net effect of the strain between Cl^- and $CO_3^=$ is to make the crystal structure of the scapolite approach that of the end-member to which it is closest in composition. Thus if Cl^- is dominant, then the crystal structure of scapolite will approach the structure of pure marialite; The departure from the structure of the end-member becomes smaller as its composition is approached.

Consider chlorine in Figure (1), the number of Cl atoms falls in a linear fashion to less than 0.1 at about Ca+Sr=6.0. That is, from about 75% Me to 100% Me scapolites contain almost only $CO_3^=$ as the anion (Evans et al., 1969). At about 37% Me, scapolites have an equal amount of Cl^- and $CO_3^=$, i.e., the anion sites are occupied half by Cl^- and $CO_3^=$ according to Evans et al. Consequently, such a scapolite would have a maximum structural departure from both the chlorine end-member (i.e., pure marialite $Na_4Al_3Si_9O_{24}Cl$) and the carbonate end-member (i.e., CO_3-meionite $Na_{1-0}Ca_{3-4}Al_{5-6}Si_{7-6}O_{24}CO_3$), at this composition. This corresponds to the apex of the r-% Me curve (Figure 1) which also occurs at about 37% Me. At the composition of 0% Me scapolite is free of $CO_3^=$ radical and correspondingly has no weak non body-centred reflections. Hence the chlorine end-member of the scapolite solid solution has a structure consistent with body-centred symmetry. Likewise, with a composition from 75% Me to 100% Me, scapolite is free from Cl^- anion and correspondingly also has a structure consistent with body-centred symmetry. Nevertheless, it should be noted that here the natural scapolites with composition from 75% Me to 100% Me, actually contain a quite significant amount of sulfur, in addition to very small amount of chlorine, for example, a ratio of S:C=3:10 in specimen M730, and with a ratio of S:C=3.5:10 in specimen ON47. In scapolites S occurs as $SO_4^=$ anion (Chappell and White, 1968 ; Lovering and Widdowson, 1968) whose molecular symmetry is consistent with the site symmetry $\bar{4}$ in the determined space group $P4_2/n$ by this study, and this is probably why specimens M730 and ON47 still show up very weak non body-centred reflections, i.e. the r-% Me curve does not fall down to zero between 75% Me and 100% Me.

Thus there is a significantly close relationship between the intensity of the weak non body-centred reflections and the chemical composition of the scapolite. As the % Me increases from zero, the structure of the scapolite deviates from the body-centred structure of the Cl-end-member ($Na_4Al_3Si_9O_{24}Cl$) and the intensity of the weak non body-centred reflections increases when the % Me reaches around 37% Me, the deviation of the structure from that of the Cl-end-member (or from that of carbonate-meionite, $Na_{1-0}Ca_{3-4}Al_{7-6}Si_{5-6}O_{24}CO_3$, because both have same body-centred structure) reaches a maximum as does the intensity of the non body-centred reflections. As the % Me continues to increase, the structure of scapolite approaches again the body-centred structure and the intensity of the non body-centred reflections decreases. It is obvious that the intensities of the non body-centred reflections are closely related to the structural departure from the body-centred structure, which is in turn induced by the variation of chemical composition, and the real nature of this structural departure will be elucidated and discussed in the following sections.

3) Superlattice Reflections and Pseudosymmetric Structure of Scapolites:

In X-ray photographs, certain classes of reflection are often observed to be systematically much weaker than the remainder. This phenomenon is ascribed to the existence of pseudosymmetry in the crystal and hence to the pseudosymmetric structure of the crystal, and the weaker reflections are called supperlattice reflections (Mackay, 1953). A pseudosymmetric structure or pseudo-structure can be defined as one in which the atoms are only slightly displaced from positions corresponding to a higher symmetry structure, usually termed the ideal structure. Thus the pseudosymmetric structure's space group is a subgroup of that corresponding to the ideal structure. The pseudosymmetric structure may be regarded as a slight distortion of the ideal structure. As a result of distortion of the ideal structure, the cell dimensions will be in general changed due to the loss of symmetry involved (Vousden, 1954). If the number of formula units in the unit cells of the pseudosymmetric structure and the ideal structure is the same, then the change will be quite small. If the unit cell of the pseudosymmetric structure contains more formula units than does the ideal structure, then the cell dimensions of the pseudosymmetric structure will be near to integral multiples of those of the ideal structure. In this latter case, the pseudosymmetric structure is also referred to as a superstructure, and the weak superlattice reflections thereby induced are sometimes also called "superstructure reflections". Taking into account the experimental results mentioned previously, the crystal structure of scapolite with the $P4_2/n$ space group is obviously a pseudo-symmetric structure, as a result of distortion of the ideal structure with space group I4/m. The superlattice reflections thereby induced are the previously mentioned weak non body-centred reflections ($h+k+\ell=2n+1$).

Superlattice reflections could be introduced from two types of origin:

(a) Difference in atomic distribution as a result of ordering of a disordered structure

For an alloy system with a simple lattice, atoms of one kind tend to segregate into one particular set of the lattice sites and thus lower the symmetry. Likewise, for more complicated compounds, similar atoms such as Al and Si in silicates tend to segregate into different parts in the unit cell. This kind of superlattice reflection is common in alloy systems, Cu_3Au and Fe_3Al and is a function of thermal history (Bragg and Williams, 1934). A pure case of this type of superlattice reflection can be recognized from the constancy of the ratio of the mean intensity of other reflections to the mean intensity of superlattice reflections for all ranges of θ (Mackay, 1953).

(b) Difference in atomic coordinates as a result of distortion of an ideal structure.

This type was already mentioned at the beginning of this section. The resulting superlattice reflections have intensities directly related to the atomic displacements from the ideal positions.

These two types are not mutually exclusive. On the contrary, they are often coexistent and interrelated in the crystal structure. The type (b) will often imply type (a) for a crystal containing crystallochemically similar atoms.

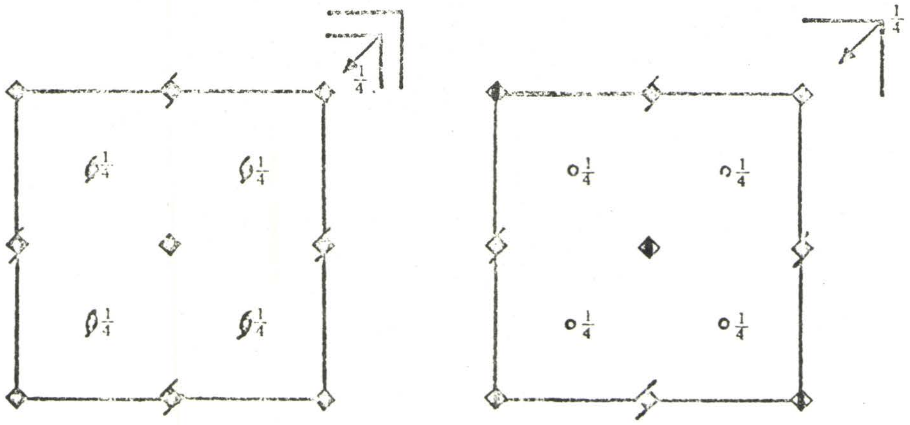
The intensity data of the $(0k\ell)$ layer of the specimen XL which shows the strongest superlattice reflection among the three structurally analysed crystals in this study, was used as an example to test the nature of the scapolite superlattice reflections by calculating the ratio of the mean intensity of the ordinary reflections to the mean intensity of superlattice reflections for all ranges of θ and also of $\sin\theta/\lambda$. Therefore, supposing the statement of Mackay (1953) is correct, then the result (Table 9) obviously indicates that the superlattice reflection of scapolite is of type (b) but at the same time could also be of type (a), since scapolite contains crystallochemically similar atoms such as Al and Si. In other words, the superlattice reflections of scapolite are

Table 9

θ	$R = \Sigma I_o/\Sigma I_s$	$\sin\theta/\lambda$	$R = \Sigma I_o/\Sigma I_s$
5° ∿ 10°	189.21	0.13 ∿ 0.26	45.12
10° ∿ 15°	18.11	0.26 ∿ 0.39	18.30
15° ∿ 20°	59.33	0.39 ∿ 0.52	39.71
20° ∿ 25°	12.22	0.52 ∿ 0.65	9.16
25° ∿ 30°	18.25	0.65 ∿ 0.78	19.94

due to the difference in atomic coordinates from those in the ideal structure having the space group I4/m. At the same time, the shift in atomic coordinates may also be accompanied with the related ordering of atoms of Al and Si in the tetrahedral framework of the scapolite structure. However, as implied from the regularity of the curve in Figure (1), the intensity of the superlattice reflections of scapolites is essentially dependent on the chemical composition rather than on the thermal history because the scapolites are from various geological environments and localities. Moreover, the X-ray photos of the heated scapolites (650°C, 10 days) remain exactly the same as the unheated one . Therefore, both the atomic displacement and the Al-Si ordering in scapolite are closely related to the variation of chemical composition. In short, the distortion of scapolite is essentially due to the variation of chemical composition as consequence of solid solution.

Next, the general features of the atomic displacement from the ideal positions consistent with the body-centred symmetry can best be understood from a comparison between the space group I4/m of the ideal structure and the space group $P4_2/n$ of the pseudosymmetric structure. The basic difference between space group I4/m and $P4_2/n$ (Figure 2) is that the former has mirror planes at $z = 0$ and $\frac{1}{2}$ in addition to the glide planes at $x = \frac{1}{4}$ and $\frac{3}{4}$, while the latter only has the glide planes at $z = \frac{1}{4}$ and $\frac{3}{4}$. The space group I4/m will be trans-



(a) I4/m (b) $P4_2/n$

Fig. 2. Comparison between the space group I4/m and the space group $P4_2/n$.

formed into the space group $P4_2/n$ through the loss of the mirror plane. Therfore the space group $P4_2/n$ is a subgroup of the space group I4/m.

As a result of lowering the degree of symmetry, the number of general equivalent sites is reduced from 16 for the space group I4/m to 8 for the space group $P4_2/n$. Consequently, the way to lose the mirror plane and hence to lower the symmetry degree is to separate each original set of the general equivalent sites in space group I4/m into two different sets of general equivalent sites and allow these two sets to displace independently. As shown before, scapolite has two formula weights in one unit cell, and both marialite and meionite end-members have space group I4/m, so the 8 Na atoms in marialite and 8 Ca atoms in meionite are originally on special sites, i.e. on the mirror plane. Likewise are some (Si,Al) atoms and some oxygen atoms. However, after one end-member is mixed more and more with the other end-member, those atoms such as Na or Ca, originally located on the mirror plane, begin to displace along the C-axis direction in addition to along horizontal directions, and thus come off the mirror plane. The original set of general equivalent atoms in the pure end-member segregate into two sets of general equivalent atoms, which then displace independently from the original ideal positions. Above all, the most important atomic displacement during the distortion is the movement along the z-axis direction (atomic co-ordinate), i.e., the c-axis direction of the scapolite. This is probably one of the essential factors which cause the systematic presence of those weak superlattice reflections violating the body-centred symmetry. Atomic displacement only in the horizontal direction will not introduce the superlattice reflection. Moreover, the intensity of the superlattice reflection will be proportional to the amount of displacement in the c-axis direction from the mirror plane.

Another essential factor causing the non body-centred superlattice reflection is the related substitutional ordering of Al and Si in the tetrahedral framework of scapolite. Especially in a crystal containing the crystallochemically similar atoms such as Al and Si, the distortion of the structure can, in fact, often be considered to be an accompanied phenomenon of the ordering-disordering of the crystallochemically similar atoms. The intensity of the superlattice reflection will be expected again to be proportional to the degree of ordering, since it is well known that a more ordered crystal structure generally has a lower symmetry. All these expected relationships will be verified in the structural determination of the three scapolite crystals reported on below.

The relationship between the atomic displacement and any order-disorder transition during the distortion from the ideal structure of scapolite and the basic mechanism to cause such atomic displacement or any order-disorder transition can only be fully evaluated after completing the 3-dimensional structural refinements covering the whole range of chemical composition to give a thorough understanding of the real nature of the crystal structure and crystal chemistry of scapolites.

4) The Nature of the Order-Disorder in the Solid Solution of the Scapolite

Scapolites have generally been regarded as a continuous solid solution series. It is well known that disorder is a common cause of solid solution, while a lowering temperature will often require ordering. If a crystal which must become completely ordered is a solid solution, then it becomes necessary for one phase to transform into two phases or multiple phases.

In other words, the complete ordering causes unmixing (Buerger, 1948). Mineral systems like feldspars, pyroxenes and many alloy systems are good examples.

Unlike some common rock-forming minerals, no microscopic twinning has so far been found to occur in the scapolite group. In addition to the optical homogeneity, the results of X-ray diffraction study are also in favor of the marialite-meionite series forming a continuous, homogeneous, isomorphous series. The nearly linear variation of the cell dimensions also suggests no sharp discontinuity of the crystal structure. The X-ray photos of the scapolites are all very similar in general appearance and only different in slight variation of intensity of reflections. This indicates that all the scapolites examined have the same space lattice. Moreover, the spots and the layer lines of reflections are very well-defined, and there are no typical evidences of submicroscopic twinning or oriented exsolution or even domain disordering, such as streaks, satellite reflections or diffuseness or complicated composite superlattice lines in rotation photos (Chao and Taylor, 1940; Laves, 1950; Morimoto and Tokonami, 1969; Papike and Zoltai, 1967). If scapolite exsolves into a random oriented composite mixture its X-ray photos will show a randomly superimposed pattern or more commonly powder concentric rings (when using precession method). If it is a regularly oriented composite mixture, the X-ray diffraction photos will be superimposed patterns of two or more kinds of reflection sets corresponding to two or more phases. Hence the reflection streak, satellite reflection, splitting reflection and weak superlattice lines (on rotation photos) will partly or all be present due to the different cell dimensions and/or different orientation of the different phases in the twinning aggregates. All single crystals of scapolites appear to be homogeneous, perfect mixed crystals, with long-range disordering, and the marialite-meionite series is believed to be a continuous, solid solution.

As discussed previously, the fact that the intermediate members possess weak reflections with $h+k+\ell=2n+1$ results from the progressive distortion and ordering within only one single phase as the chemical composition is progressively changed. Moreover and above all, neither submicroscopic twinning nor domain disordering can explain the observed experimental fact that the progressive variation of the intensity of the non body-centred reflections is a function of the chemical composition of the scapolite (Fig. 1).

5) Variation of Cell Dimensions of Scapolites

Cell dimensions also reflect the internal structure and chemical composition of crystals. As mentioned in Chapters 2 and 3, the a_o dimension of scapolite roughly increases as the % Me increases, while the c_o dimension slightly decreases in an approximately linear manner as % Me increases. The cell volume shows a relatively linear relationship to % Me (Figure 3). These phenomena can be explained by the following two basic factors: (1) Addition of aluminum content to the (Al,Si) tetrahedral framework as the % Me increases: because the Al-O bond length is greater than the Si-O bond and the framework structure basically remains the same throughout the whole scapolite solution series, the size of the whole framework increases with meionite percentage; hence the unit cell dimension a_o and unit cell volume also increase. (2) Addition of the large planar radical of $CO_3^{=}$ in place of the Cl^- ion in the cavity of the crystal structure as % Me increases. The $CO_3^{=}$ radical approximately lies parallel to the horizontal plane, i.e., the (001) plane and thus distorts the crystal structure in such a way that the horizontal axes of a_o and b_o are elongated whereas the vertical axis c_o is slightly shortened in spite of the simultaneous increase of Al atoms in the framework.

A close examination of Figure (3) shows that the points in the range between 25% Me and 50% Me are actually quite scattered and show systematic deviation from the regression lines. Obviously, the deviation can not be ascribed solely to the error of measurement. It is especially true in the plot-

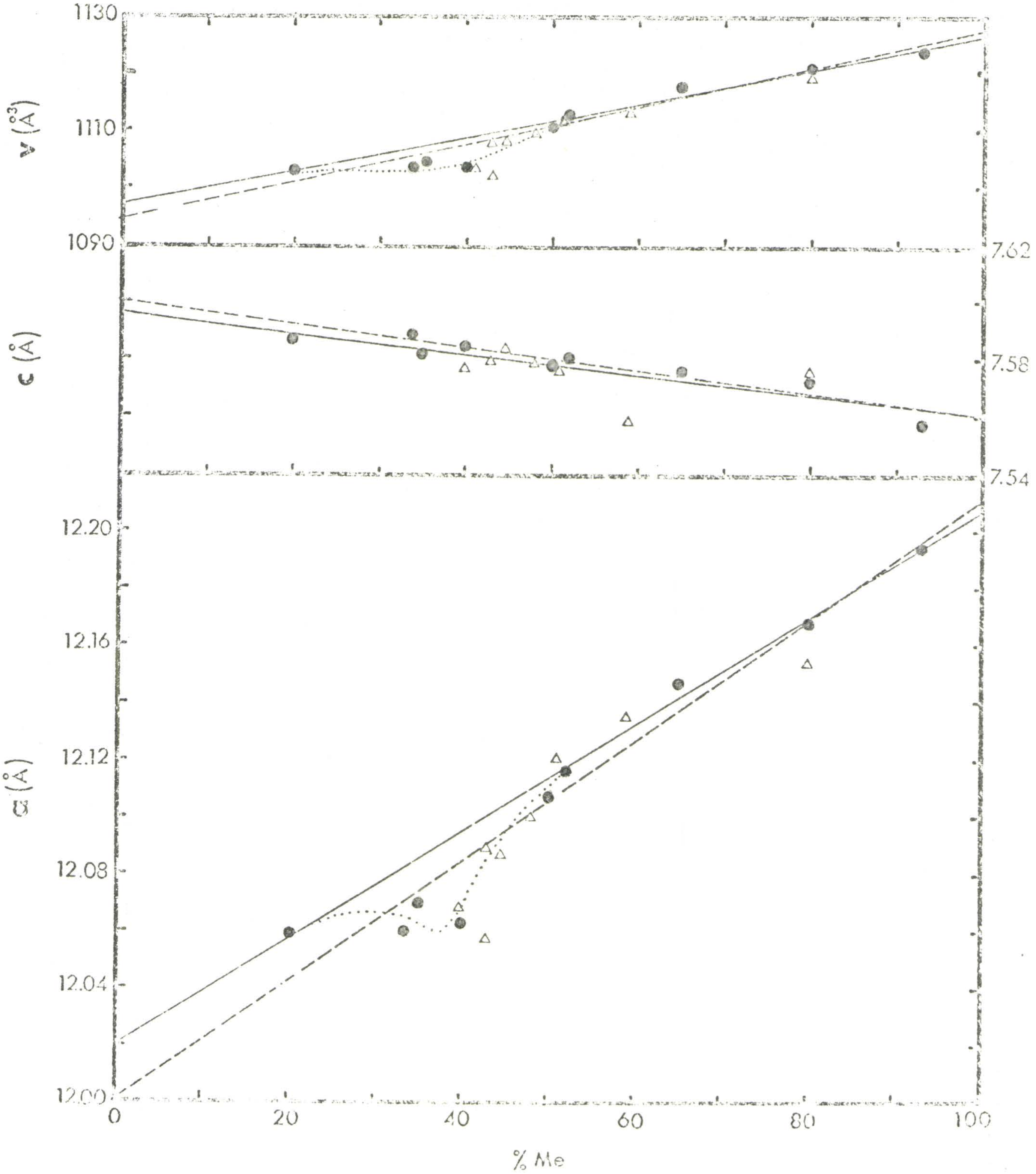


Fig. 3. The cell dimensions of scapolites as a function of the chemical composition (% Me). The dashed line represents the linear regression covering whole range of % Me, while the full line, the linear regression excluding the range of 25% Me ∿ 45% Me. Dots are data from present study and triangles are data from Haughton (1967).

tings of a_o dimension vs. % Me, and cell volume V($\mathring{A}^3$) vs. % Me. As a matter of fact, during the beginning stage of this study, the considerable departure of the cell dimensions of certain scapolites (specimens GL, ON6A and ON70) from the ideal slope line was immediately noticed by the writer. The a_o dimensions of the specimens GL and ON70 are shorter than those evaluated from the linearly increasing relationship with % Me. The c_o dimensions of these specimens do not show any very obvious relationship to the other plotted points, but may be slightly greater than those evaluated from the linearly decreasing relationship with % Me. The resulting cell volumes of these three specimens still obviously lie below the linear regression line, i.e., they are systematically smaller than those evaluated from the linearly increasing relationship with % Me. In order to confirm these differences, the determination of cell dimensions has been carefully repeated and the same result was obtained. Actually these differences can even be observed on the precession photos. Again a careful examination of the results of previous investigations made by Eugster et al (1962), Papike (1964), and Haughton (1967), shows that similar phenomena are shown in all their plottings. The a_o dimension and the cell volume of scapolites between 25% Me and 50% Me are systematically less than those evaluated from the linear regression. Actually, considering the mathematical relationship, $V = a_o^2c_o$, it is also obvious that the three variables v, a_o and c_o can not be all linear functions of composition, simultaneously, unless a_o is a constant, which it is not.

Moreover, as stated previously, the distortion of the ideal structure will in general result in a change in cell dimensions. The change will be quite small, say less than 5%, if the number of formula units in the unit all remains the same (Vousden, 1954). Because scapolite is a pseudo-body-centred structure,its cell dimensions should be as a result of the distortion of the ideal body-centred structure. In fact, in the structural analyses described later, the $CO_3^=$ planar radical in scapolite within the above-mentioned range of composition has been found to be considerably inclined to the horizontal plane (001) instead of being parallel to it, so the orientation of the $CO_3^=$ group is favorable for lengthening the c-axis and shortening the a-axis, contrary to the above remarks on the general effect of the CO_2 group. Moreover, the inclination of the $CO_3^=$ planar group is proportional to the intensity of the non body-centred reflections. So the CO_3 group will be most inclined to the horizontal at a composition around 37% Me. Therefore, the depression formed by the plotted points systematically deviating from the linear regression line in Figure (3) can be qualitatively explained as a result of the combined effect of the two different kinds of controlling factors described above, i.e., the first is the linear variations due to increasing amount of Al and $CO_3^=$ and the second is the variation due to the structural distortion resulting from the internal strain between $CO_3^=$ and Cl^- anions. In Figure (4), the line (a) represents the first kind of controlling factor and the curves (I, II, III) are supposed to be the possible types of curves representing the second kind of controlling factor. Then the ideal shape of the depression can be simply formed by combining the slope line (a) and curve I or II or III to get shape line I', II' or III'. Similarly, the corresponding depression of the plotting of cell volume vs. % Me (Figure 3) between 25% and 50% can also be ideally illustrated in the same way.

Since the deviation in the range between 25% Me and 50% Me in the plottings of a_o vs % Me and V vs. % Me is systematic and quite considerable, it is appropriate to draw two regression lines: one including all the plotted points over the whole range and another one excluding the plotted points between 25% Me and 45% Me. The latter has a better fit than the former one. The degree of change of cell dimensions from body-centred scapolite to primitive-celled scapolite can be estimated from the diagrams (Figure 3). The change of the a_o dimension is found to be 0.26% and 0.27% for specimens GL and ON70 respectively. The change of c_o dimension is negligible. The change of cell volume V is found to be 0.45% and 0.54% for GL and ON70 respectively. Therefore, one should be careful about this fact when applying cell dimensions and cell volume

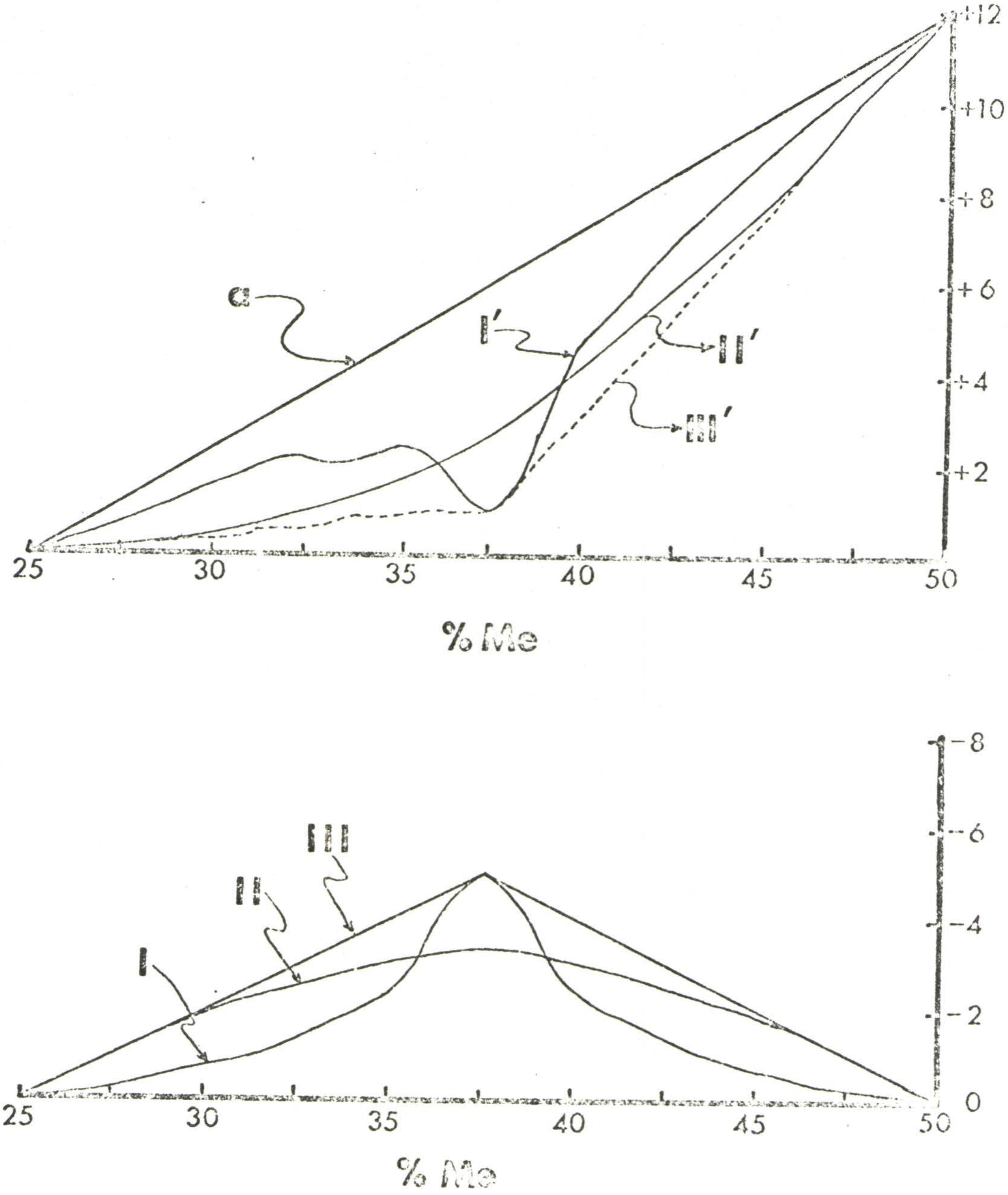


Fig. 4. Ideal illustration of the formation of the depression on the plot of a_o vs % Me, by combining two kinds of curves representing two kinds of controlling factors (see text).

in order to determine the chemical composition of scapolites. It should be noted that only the regression line of cell volume vs. % Me can be relatively safely used to estimate the % Me of unknown scapolite, because the precision of cell volume is good and always less than 1 $\mathring{A}^3$, i.e. about 5% Me, and the plotting is less scattered. So equation V=1097.75+0.2884 % Me may be applied for scapolites richer than 50% Me. Besides, the variation of cell dimensions could be further complicated by the considerable content of $SO_4^=$ or K^+, but their effects are difficult to be evaluated.

The variation in lattice parameter $(2\theta_{400}-2\theta_{112})_{CuK\alpha}$ with composition parameter % Me (Burley et al. 1961) can also be used as a convenient way for roughly estimating the chemical composition of scapolite. Unfortunately, the lattice parameter $(2\theta_{400}-2\theta_{112})_{CuK\alpha}$ seems to be highly sensitive to the instrumental condition of some unknown factor, because the standard deviation was in general found to be quite high, and sometimes the difference between the forward scan and backward scan was found to be up to 0.060. Nevertheless this is merely a reflection of antiquity of goniometer or sample preparation, nothing to do with method. Intrinsically this method is more accurate than measuring a_o and c_o because it is not an absolute measure but relative.

Both the averaged $(2\theta_{400}-2\theta_{112})_{CuK\alpha}$ observed from powder diffraction patterns and calculated $(2\theta_{400}-2\theta_{112})$ from the known cell dimensions, for each specimen, are plotted against the compositional parameter % Me together in Figure (5). The corresponding regression curves as a result of calculation based on the regression lines in the plots of cell dimensions vs. % Me (Figure 3) are also shown on the same Figure (5) and found to be practically straight lines. The line I corresponds to the case of regression including the whole chemical range , and the line II corresponds to the case of regression excluding the specimens within the range between 25% Me and 45% Me. Moreover, the deviation of the plotted points between 25% Me and 45% Me in Figure (5) corresponds to the systematic deviation of the cell dimensions in the same chemical range and this again proves that the cell dimensions of scapolites are not really linear functions of the chemical composition.

In short, the fact that the deviation of the cell dimensions coincides with the presence of the strong non body-centred reflections in the same compositional range (i.e., 20% Me $\sim$ 55% Me) implies that scapolite does have a continuous structural distortion as a function of chemical composition. The farther the structure deviates from the centred symmetry, the smaller the cell volume and the a_o become relative to the evaluated one from the linear regression. Correspondingly, this deviation of the cell dimensions will be one of the factors affecting the density variation of the scapolites, and the variation of the mean refractive index (n_m) of scapolites. The formation of a scapolite with chemical composition from 25% Me to 50% Me would be favored by high pressure.

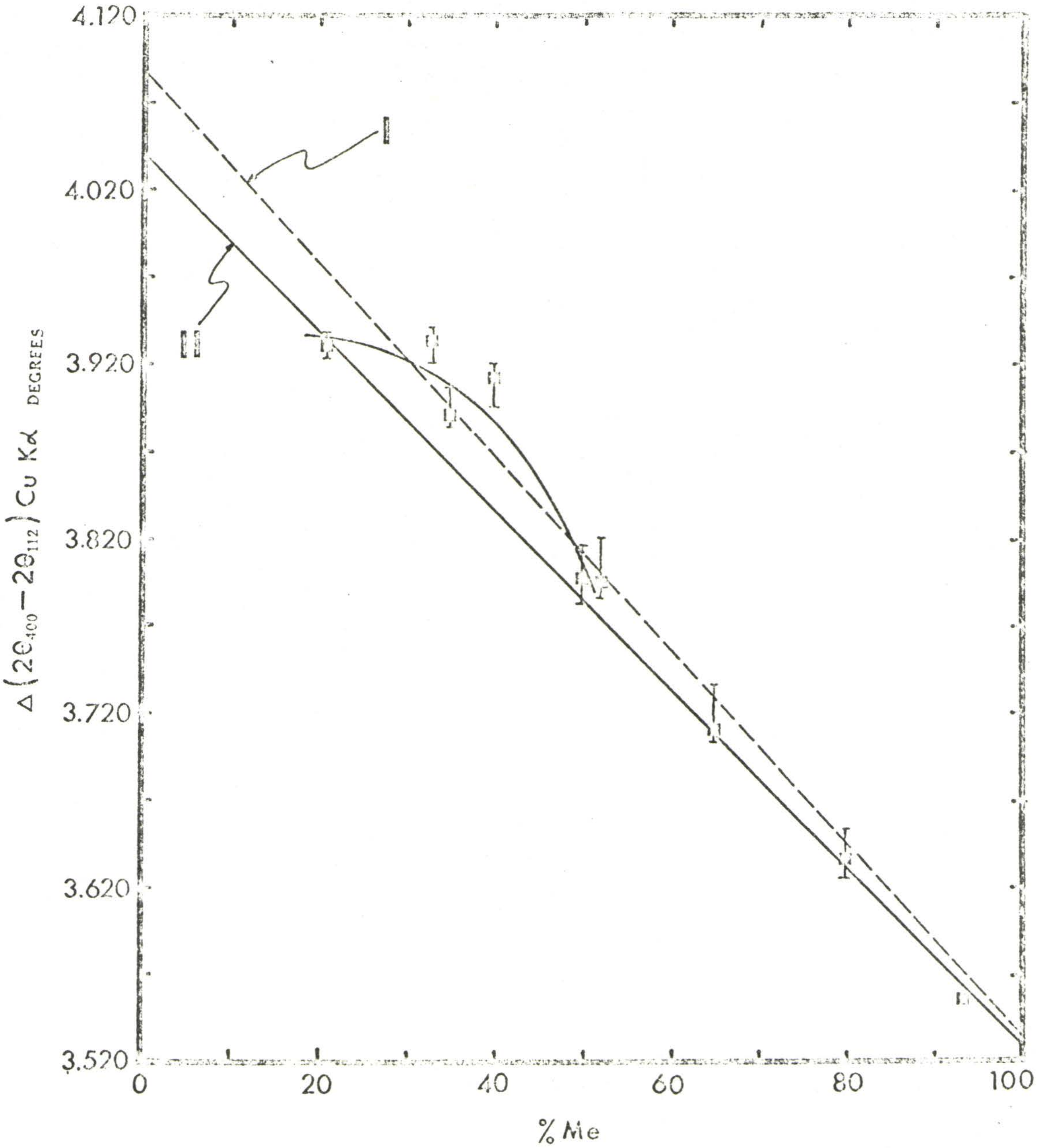


Fig. 5. Variation in lattice parameters $\Delta(2\theta_{400}-2\theta_{112})$ CuKα with composition. The squares are the data calculated from the known cell dimensions; I indicates the mean value with the standard deviation measured from the powder charts. The dashed line represents the regression covering the whole range of % Me, while the full line represents the regression excluding the range of 25% ∿ 45% Me.

CHAPTER 5

CRYSTAL STRUCTURE OF A SODIUM AND CHLORINE-RICH SCAPOLITE

1) Introduction

The explanation of the significance of the weak reflections violating the body-centred symmetry discussed above is used to help solve the crystal structure of three scapolite specimens ON8, XL and ON45, covering the whole range of the solid solution series. Further the successful refinement of these crystal structures will also be a confirmation of the correctness of the explanation regarding the weak non body-centred reflections.

As stated before, the specimen ON8, 19.4% Me scapolite from Gooderham, Ontario, obviously has a true space group of $P4_2/n$ (Chapter 3, Plate 2 and 3). This particular scapolite specimen was chosen because: (i) It is the most Na-rich scapolite ever found in nature, so its crystal structure is the closest to pure marialite ($Na_4Al_3Si_9O_{24}Cl$) and it is believed to represent the general features of the crystal structure of the Na-rich end of the scapolite solid solution. (ii) The crystal structure of this particular scapolite has also been studied by Papike and Zoltai (1965) on the assumption of a space group I4/m, so that their model can be compared with the structural model based on the space group $P4_2/n$, and the differences between the structures studied.

It was decided to at first refine the structural model proposed by Papike and Zoltai (1965) by using the full-matrix least-square method according to the new space group $P4_2/n$. If this attempt was not successful, the structural model of Schiebold and Seumel (1932) was to be tested by the same method. If the latter attempt still fails, then a complete structure analysis would have been initiated by using Patterson syntheses. etc. The unit cell contents were determined and shown in Table (10) using the known unit cell dimensions, and the chemical analysis stated in Chapter 3, and the specific gravity of 2.619 (Shaw, 1960). The cell contents are not significantly different from the product of the number of the formula weight (Z=2) and the atomic proportions calculated on a basis of 12.0 (Si+Al) (in Chapter 3). Therefore, the chemical formula per cell of the specimen ON8 is $(Na_{5.76}Ca_{1.67}K_{0.42}Fe_{0.002}Mn_{0.005}Sr_{0.002})(Si_{16.68}Al_{7.35})O_{48.55}[Cl_{1.45}(SO_4)_{0.007}(CO_3)_{0.44}]$.

2) Intensity Collection

A homogenous single crystal was ground into a sphere with an approximate diameter of 0.5 mm. The X-ray diffraction intensities were collected by integrated Buerger's precession film techniques, using Zr-filtered MoKα radiation. The (hk0) level and the (hkℓ) levels from h=0 through h=6 were photographed

Table 10. The Unit-Cell Contents of the Scapolite ON8 (19.4% Me; Gooderham, Ontario)

Atom	Number Per Cell				
	A		B		
Si	16.68	24.03	16.66	24.00	A = Result of calculation using sp.gr., cell dimension and chemical analysis
Al	7.35		7.34		
Na	5.76	7.86	5.76	7.86	
Ca	1.67		1.67		B = Result of multiplication of no. of formula wts. per cell and atomic proportions based on 12.0 (Si,Al).
K	0.42		0.422		
Sr	0.002		0.002		
Mn	0.005		0.004		
Fe	0.002		0.002		
O	48.55		(48.00)		
Cl	1.45	1.90	1.45	1.90	
CO_3	0.44		0.44		
SO_4	0.007		0.006		

to give 1255 total reflections. Of them, the "less-thans" were assigned values of $I_{min}/3$ (Hamilton, 1955). Then these photometrically measured intensities were corrected for Lorentz and polarization effects and converted into unscaled $|F_{obs}|$; however, no absorption correction was made, because the transmission factor is not significantly affected by the reflection angle θ (Evans and Ekstein, 1952).

3) Structure Refinement

The structure refinement was carried out on a CDC 6400 computer using a full matrix least-squares program (ORFLS) contained in the "X-ray 67" program system for X-ray crystallography (Kundell et. al., 1967). The scattering factor curves used during the refinement were as follows: Na^{1+}, K^{1+}, Ca^{2+}, Si^{0}, Al^{0}, Cl^{1-}, C^{2+} and O^{1-} (International Table for X-ray crystallography, Vol. III, 1962).

Structure refinement was initiated using the structural model of marialite of Papike and Zoltai (1965), in which the atomic coordinates were first transformed into a set of values based on the new space group $P4_2/n$ with origin at $\bar{1}$ at 1/4, 1/4, 1/4 from $\bar{4}$, and the temperature factor of Cl was assumed to be 2.0 since it was not included in the model of Papike and Zoltai (1965) and it was expected to be quite high due to the disordering of Cl and C atoms.

In the first two cycles of the least-squares refinement, only the eight scale factors, assigned for each level of reflection data were refined, giving an R value ($\Sigma\Big|\,|F_o|-|F_c|\,\Big|/\Sigma|F_o|$) of 14.9%. During the earlier stages of least-squares refinement, the "less thans" were ignored and all the weights of reflections were assigned as unity. Refinement was continued for three more cycles allowing atomic coordinates to vary in addition to scale factors, and the R dropped to 13.6%. After three additional cycles of refinement during which all the parameters including isotropic temperature factors, atomic coordinates, and scale factors were varied, the R value then dropped to 8.6% and the result showed a considerable change of temperature factors occurred. Na atom from 2.65 to 1.78; Clatom from 2.0 to 4.93, indicating a high disordering with C atom The temperature factors of all Si atoms and O atoms came within the normal range, i. e., temperature factor of Si atom is well below 1.0 and that of O atom is around 1.0.

Subsequently, a new scattering curve of $0.77\, f_{Cl^-} + 0.23 f_{C^{2+}}$ was prepared to replace the scattering curve of Cl^- atom, and three more cycles of refinement were executed, the R value then dropped to 8.0% and the temperature factor of (Cl,C) atom was reduced from 4.93 to 3.78. Similarly a new scattering curve of $0.8\, f_{Na^+} + 0.2\, f_{Ca^{2+}}$ was used for the (Na,Ca) atom and three cycles of refinement were run, the R value then dropped to 7.7% and the only prominent change was the temperaature factor of (Na,Ca) atom increasing from 1.55 to 2.28. At this stage, the dimensions of the three individual tetrahedra were calculated using the BONDLA program which is also contained in "X-ray 67" program systems for X-ray crystallography. Using the mean T-O bond length for each tetrahedron and a curve prepared by Smith and Bailey (1963), the Si-Al occupancy of each site was estimated. The results indicate that tetrahedron T_1 is Al-free, and tetrahedra T_2 and T_3 are partly occupied by Al atom. With the estimated occupancy of Al and Si among these three equipoints, three additional least-squares cycles were run, and the R value stopped at 7.6%.

Finally, the unobserved reflextions (i.e., "less thans") were included into the refinement and a modified Cruickshank weighting scheme was applied,

$$\text{Weight} = 1/(A+B\cdot F_o+C\cdot F_o{}^2)$$

where the coefficients A, B and C are all fixed by least-squares methods. Then following five cycles of least-squares refinement in which all scale factors, positional and thermal parameters were varied, the R value first slightly increased, then decreased and finally stayed at 7.5%. However, many parameters were more or less readjusted. Both Fourier synthesis $\rho(xyz)$ and difference synthesis $\Delta\rho(xyz)$ using the parameters from the last refinement cycle showed four broad peaks around the (Cl,C) atom and with a maximum on the (001) plane. These four peaks are formed by positional disordering of oxygen atoms of the $CO_3^=$ group. The coordinates of these four peaks were found to be essentially consistent with those found in the refined structural model of the ON45 (93% Me) specimen and with the x and y coordinates of the corresponding peaks in the structure of the specimen XL (52% Me). Thus the coordinates and the temperature factors of the oxygen atoms of the $CO_3^=$ group in the specimen ON45 were used as starting parameters for the corresponding peak revealed in the above-mentioned $\rho(xyz)$ and $\Delta\rho(xyz)$ maps, and included into the continued refinement of this scapolite crystal ON8. Following two additional cycles of refinement in which all parameters except multiplicity were allowed to vary, the R value was lowered again to 7.4% and all parameters essentially remained unchanged except that those of last included oxygen of the carbonate radical were slightly changed, i.e., changed by less than 1σ. The final, refined parameters from the last cycle of the least-squares refinement are listed with their standard deviations in Table (11), in which the coordinates of the Papike and Zoltai model are also given.

The observed and calculated structure factors are listed in Appendix (1).

4) Discussion of the Crystal Structure

In order to be consistent with the traditional descriptions of scapolite crystal structures, the final, refined parameters are transformed into those based on the origin at $\bar{4}$

Table 11. Atomic Coordinates and Temperature Factors of Marialite (19.4% Me; Gooderham, Ontario).

Papike and Zoltai (1965)		Present Study		
Atom	Parameters	Atom	Parameters	Total Change
	X 0.3660(3)		X 0.3659(3)	-0.0001
Na	Y 0.2887(2)	(Na,Ca)	Y 0.2884(3)	-0.0003
	Z 0.5		Z 0.5064(4)	+0.0064
	B 2.65		B 2.68 (6)	+0.03
	X 1/2		X 1/2	0
Cl	Y 1/2	(Cl,C)	Y 1/2	0
	Z 1/2		Z 1/2	0
	B -		B 3.85 (12)	-
	X 0.3388(1)		X 0.3390(1)	+0.0002
Si 1	Y 0.4104(1)	Si 1	Y 0.4100(1)	-0.0004
	Z 1.0		Z 0.9989(3)	-0.0011
	B 0.82		B 0.69 (3)	-0.13
	X 0.6626(1)		X 0.6621(2)	-0.0005
(Si,Al)2	Y 0.9149(1)	(Si,Al)2	Y 0.9152(2)	+0.0003
	Z 0.7940(2)		Z 0.7956(2)	+0.0016
	B 0.76		B 0.79 (4)	+0.03
	X 0.4149(1)		X 0.4145(2)	-0.0004
(Si,Al)2'	Y 0.8374(1)	(Si,Al)3	Y 0.8368(2)	-0.0006
	Z 0.7060(2)		Z 0.7085(2)	+0.0025
	B 0.76		B 0.63 (4)	-0.13
	X 0.4587(5)		X 0.4574(4)	-0.0013
O 1	Y 0.3483(4)	O 1	Y 0.3511(4)	+0.0028
	Z 0		Z 0.0011(7)	+0.0011
	B 1.60		B 1.39 (8)	-0.21
	X 0.6934(6)		X 0.6939(4)	+0.0005
O 2	Y 0.8794(4)	O 2	Y 0.8797(4)	+0.0003
	Z 0		Z 0.0048(7)	+0.0048
	B 2.14		B 1.25 (7)	-0.89
	X 0.3500(2)		X 0.3486(6)	-0.0014
O 3	Y 0.9483(3)	O 3	Y 0.9448(5)	-0.0035
	Z 0.7852(6)		Z 0.7898(6)	+0.0046
	B 1.55		B 1.48 (10)	-0.07
	X 0.5517(3)		X 0.5499(5)	-0.0018
O 3'	Y 0.8500(2)	O 4	Y 0.8475(6)	-0.0025
	Z 0.7148(6)		Z 0.7163(6)	+0.0015
	B 1.55		B 1.49 (10)	-0.06
	X 0.2707(3)		X 0.2706(5)	-0.0001
O 4	Y 0.3711(2)	O 5	Y 0.3699(5)	-0.0012
	Z 0.8281(6)		Z 0.8277(6)	-0.0004
	B 1.37		B 1.30 (9)	-0.07

(continued next page)

Table 11 (continued)

Papike and Zoltai (1965)		Present Study		
Atom	Parameters	Atom	Parameters	Total Change
O 4'	X 0.3711(])	O 6	X 0.3710(6)	-0.0001
	Y 0.7293(3)		Y 0.7282(6)	-0.0011
	Z 0.8281(6)		Z 0.8270(7)	-0.0011
	B 1.37		B 1.47 (10)	+0.10
-	-	O 7	X 0.3833(63)	-
			Y 0.4817(64)	-
			Z 0.5012(101)	-
			B 4.01 (1.28)	-
R factor	11.97%	R factor	7.4%	

and interpreted by referring to Fig. (6). It is also interesting to compare this refined model with the initial model based on the space group I4/m (Papike and Zoltai, 1965) to understand to what extent the structures differ so the parameters of Papike and Zoltai model were also included in the same table (Table 11). As expected, the difference between the ideal structure and the pseudosymmetric structure is very small. Comparison of the two models in Table (11) shows that the x and y coordinates of most atoms essentially remain the same, while the z coordinates generally have a small but significant change compared with the standard deviation σ; especially those atoms originally located on the mirror plane, e.g. Na, Si1, and O2 atoms. These atoms migrate from the mirror plane position as discussed in Chapter 4. Temperature factors are also more or less readjusted .

Although the distorted pseudosymmetric structure is symmetrically different from the undistorted ideal structure, the general physical features of the former are still similar to the latter but with some basic changes of geometrical relationship. Therefore, the pseudosymmetric structure of scapolite can also be described as a framework of (Si,Al)-O tetrahedra with a spherical cavity at the center of the unit cell, which is open to and surrounded by four oval shaped channels running parallel to the c-axis and arranged in a clockwise way. The central cavity contains the larger anions

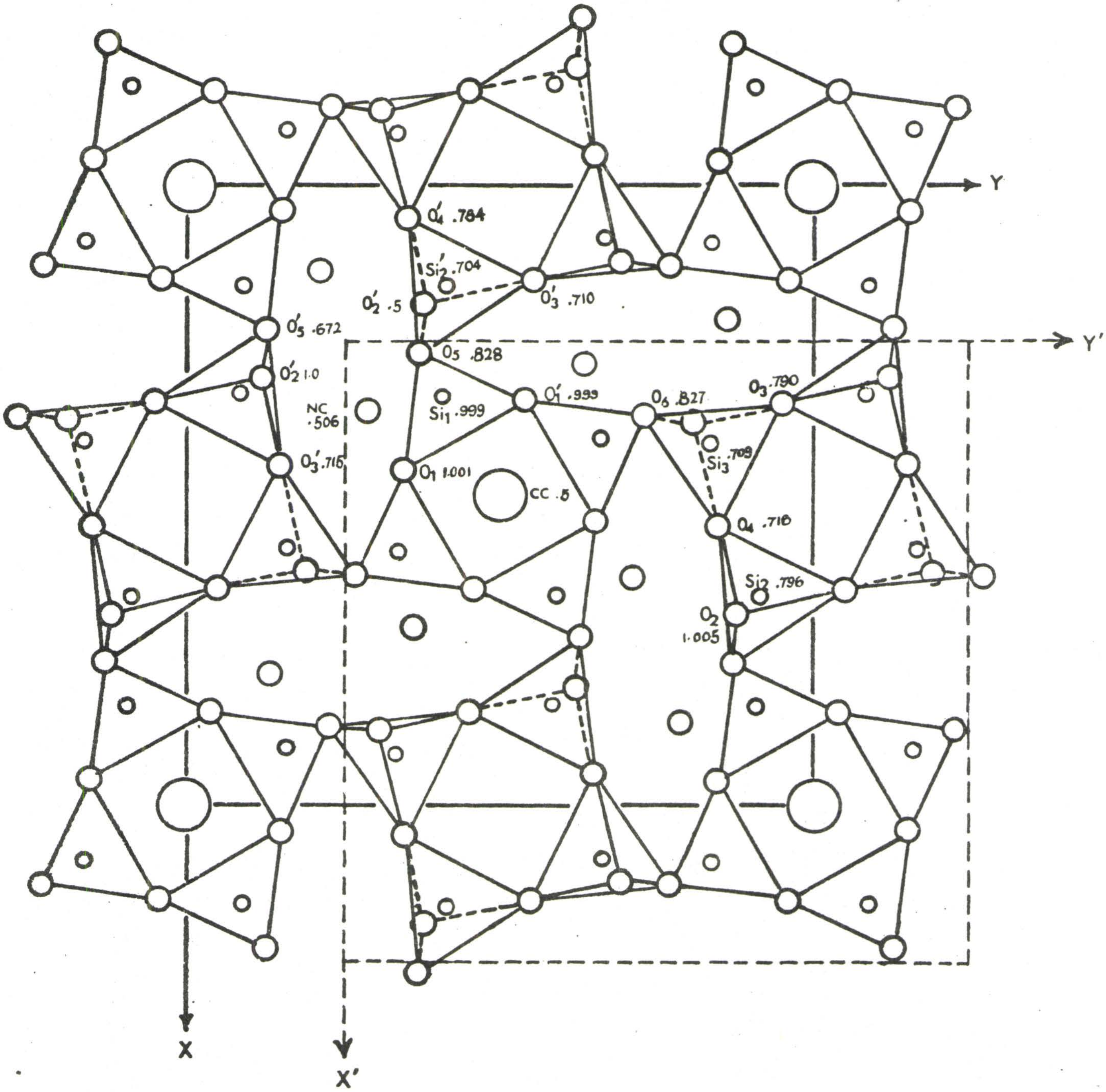


Fig. 6. Projection of the crystal structure of marialite (19.4% Me; Gooderham, Ontario). The long dashed lines indicate the unit cell boundary based on the origin at $\bar{1}$ at 1/4, 1/4, 1/4 from $\bar{4}$.

(Cl, CO_3, SO_4) and the vertical channels contain the smaller cations (Na, Ca, K). The framework is composed of two types of four-membered rings of (Si,Al)-O tetrahedra which are both parallel to the (001) plane, i.e., whose normals are both parallel to the c-axis. However, the (type 1) ring is made of only one kind of tetrahedra (T1) having one edge nearly parallel to the c-axis but Si atoms of alternate tetrahedra are above the (001) plane, and Si atoms of the other two tethedra are below, instead of lying on the same plane. This is illustrated in Figure (7) in which the difference in the horizontal positions between the O_5 and O_6 atoms is exaggerated for better presentation. On the other hand, the (type 2) ring is made of two kinds of tetrahedra, T_2 and T_3, pointing alternatively up and down. The (type 2) rings are connected together into multiple chains running parallel to the c-axis and are further held together by type 1 rings laterally. The details of the pseudo body-centred structure of this NaCl-rich scapolite is illustrated in Fig. (8) and is best presented by the stereographic drawing (Fig. 9) which was plotted by using the program ORTEP (Johnson, 1965).

The important interatomic distances and angles are listed in Tables (12a,b and 13) and may be interpreted by referring to Fig. (6) and Fig. (9).

Using the average (Si,Al)-O bond lengths of the three

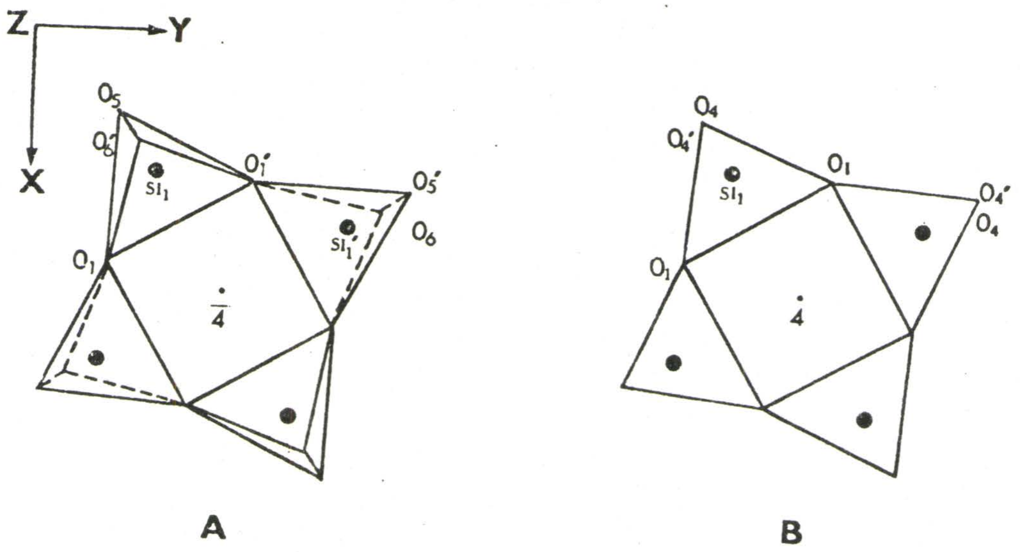


Fig. 7. Comparison between (A) the (type 1) ring based on the space group, $P4_2/n$, and (B) the (type 1) ring based on the space group $I4/m$.

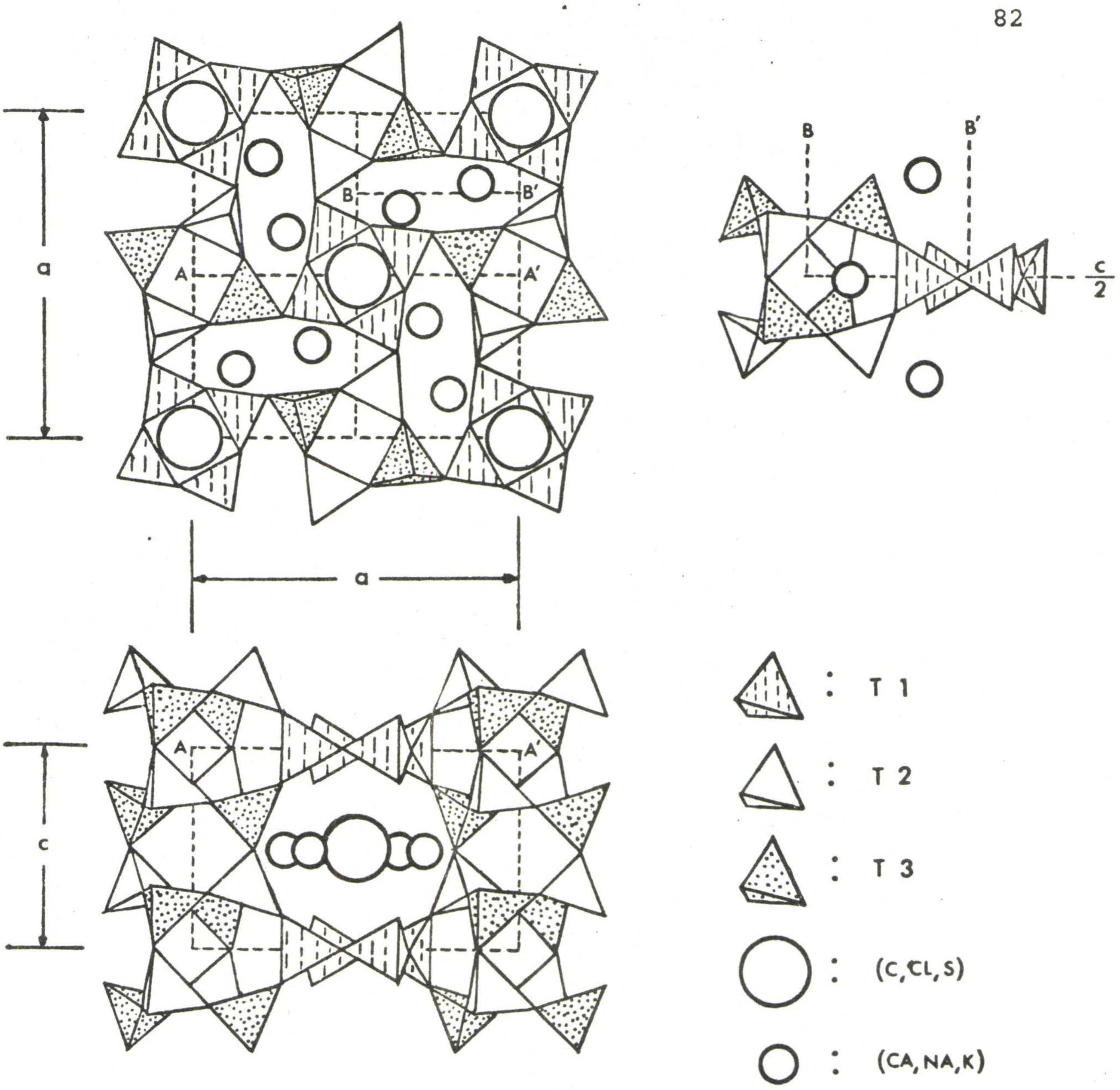


Fig. 8. The crystal structure of marialite (19.4% Me; Gooderham, Ontario).

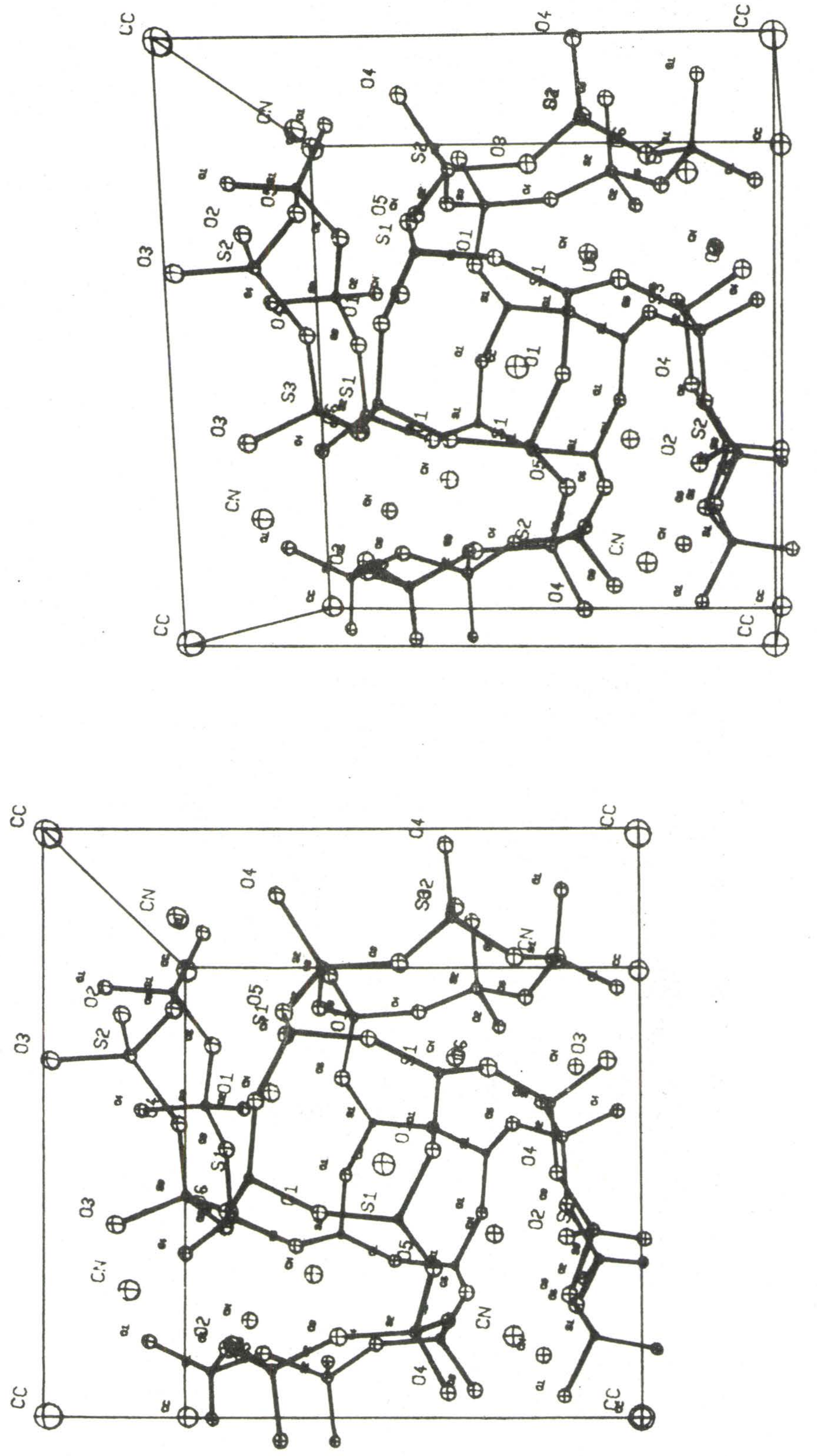


Fig. 9. The stereographic projection of crystal structure of scapolites.

Table (12). Interatomic Distances in Marialite (19.4% Me, ON8, Gooderham, Ontario)

(a) (Si,Al)-O and O-O Distances of Tetrahedra:

Tetrahedron	T-O Distance (Å)			O-O Distance (Å)		
	Atoms	Multiplicity	Distance	Atoms	Multiplicity	Distance
T_1	O_1	1	1.594(5)	O_1-O_5	1	2.618(8)
	O_5	1	1.612(6)	O_1-O_1'	1	2.642(7)
	O_1'	1	1.607(5)	O_1-O_6'	1	2.601(8)
	O_6'	1	1.619(6)	$O_1'-O_5$	1	2.640(8)
				$O_1'-O_6'$	1	2.635(8)
				O_5-O_6'	1	2.620(7)
	Average		1.608(5)	Average		2.626(8)
T_2	O_2	1	1.688(5)	O_2-O_4	1	2.820(8)
	O_4	1	1.690(7)	O_2-O_3'	1	2.720(8)
	O_3'	1	1.693(7)	O_2-O_5'	1	2.689(7)
	O_5'	1	1.699(6)	O_4-O_5'	1	2.695(9)
				O_4-O_3'	1	2.842(9)
				$O_3'-O_5'$	1	2.802(8)
	Average		1.693(6)	Average		2.761(8)
T_3	O_3	1	1.646(7)	O_3-O_4	1	2.754(9)
	O_4	1	1.639(7)	O_3-O_6	1	2.642(9)
	O_6	1	1.673(7)	O_3-O_2'	1	2.760(8)
	O_2'	1	1.644(5)	O_4-O_6	1	2.726(9)
				O_4-O_2'	1	2.653(8)
				O_6-O_2'	1	2.621(7)
	Average		1.651(6)	Average		2.693(8)

(b) Selected Interatomic Distances:

Type	From	To	Multiplicity	Distance(Å)
(Na,Ca,K) Coordination Polyhedron	(Ca,Na,K)	Cl	1	3.021(3)
		O_2'	1	2.350(6)
		O_3'	1	2.516(7)
		O_4'	1	2.500(7)
		O_5	1	2.868(6)
		O_5'	1	2.817(7)
		O_6'	1	2.882(7)
		O_6'	1	2.945(6)
Anion Cage Diagonals	O_1	O_1'	4	8.457
	O_5	O_6'	4	8.055
	O_2'	O_2'	2	7.933

Table (13). Interatomic Angles in Marialite (19.4% Me, Gooderham, Ontario).

Type	Atoms	Angle ± σ
O-T_1-O Angles,	O_1-T_1-O_5	109.43±0.31
(T_1 tetrahedra)	O_1-T_1-O_1'	111.22±0.28
	O_1-T_1-O_6'	108.04±0.31
	O_5-T_1-O_1'	110.20±0.31
	O_5-T_1-O_6'	108.35±0.32
	O_1'-T_1-O_6'	109.52±0.31
O-T_2-O Angles	O_2-T_2-O_4	113.23±0.28
	O_2-T_2-O_3'	107.08±0.26
(T_2 tetrahedra)	O_2-T_2-O_5'	105.13±0.28
	O_4-T_2-O_3'	114.30±0.34
	O_4-T_2-O_5'	105.38±0.31
	O_3'-T_2-O_5'	111.40±0.33
O-T_3-O Angles	O_3-T_3-O_4	113.93±0.35
	O_3-T_3-O_6	105.47±0.32
(T_3 tetrahedra)	O_3-T_3-O_2'	114.03±0.29
	O_4-T_3-O_6	110.78±0.34
	O_4-T_3-O_2'	107.79±0.27
	O_6-T_3-O_2'	104.41±0.29
T-O-T Angles	T_1-O_1-T_1'	158.77±0.37
	T_2-O_2-T_3'	140.22±0.35
	T_3-O_3-T_2'	146.61±0.41
	T_2-O_4-T_3	147.98±0.42
	T_1-O_5-T_2'	137.78±0.42
	T_3-O_6-T_1'	137.63±0.43

types of tetrahedra presented in Table (12a) and the curve prepared by Smith and Bailey (1963), the Al,Si occupancy of each tetrahedral site was estimated = T_1 (0% Al, 100% Si); T_2 (59.3% Al, 40.7% Si); T_3(29.3% Al, 70.7% Si). Therefore, Al only disorderedly distributes in T_2 and T_3 tetrahedral sites partially replacing Si. The Al content in the unit cell derived as the sum of the products of the Al occupancy in each tetrahedral site times the number of equipoints of each corresponding site was found to be 7.10 atoms per unit cell which is reasonably consistent with the unit cell content of Al, 7.35 atoms, calculated by using specific gravity, cell volume, and a chemical analysis. Again applying the same method as Smith and Bailey (1963) and Papike and Zoltai (1965), a plot of % Al in a tetrahedron versus average T-O distance (Fig. 10) can be constructed by using two available points:

(1) Average distance of T_1-O:

$[(Si_{1.0}Al_{0.0})\text{-}O] = 1.608$ Å

(2) Average distance of T_2-O and T_3-O

$[(Si_{0.54}Al_{0.46})\text{-}O] = 1.672$ Å .

The linear extrapolation to 100% Al gives a theoretical mean T-O distance for a pure AlO_4 of 1.747 Å which is significantly longer than 1.732 Å given by Papike and Zoltai (1965) for the same crystal. The same type of extrapolation for the feldspars gives 1.750 Å (Smith and Bailey, 1963). This might

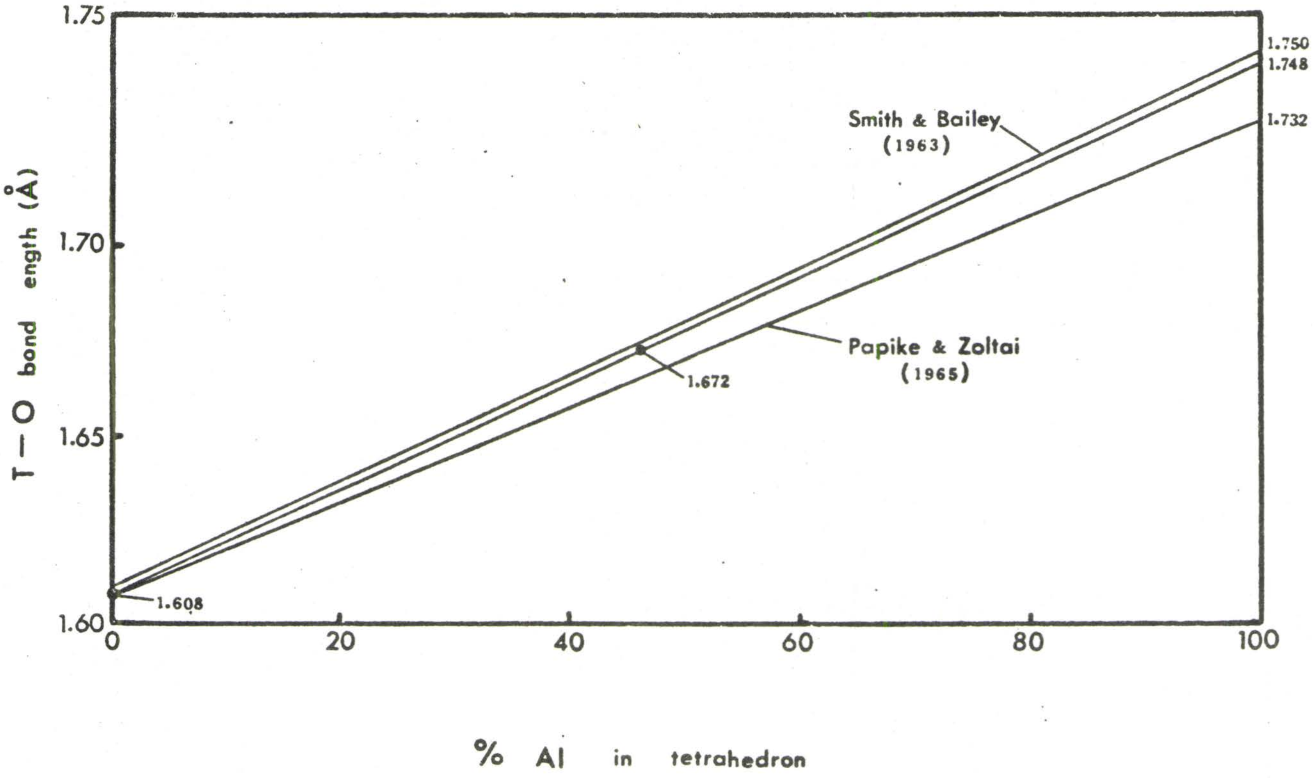


Fig. 10. Determinative curves for aluminum tetrahedral occupancies.

suggest that the T-O bond in scapolites behaves very similarly in character to the T-O bond in feldspars and the effect of the crystal symmetry on the mean sizes of tetrahedra of framework silicates is probably insignificant.

Since the pseudosymmetric structure results from distortion of the more symmetric ideal structure, all the coordination polyhedra in this marialite are found to be more distorted. Moreover, (type 2) and (type 3) (Si-Al)-tetrahedra are more distorted than (type 1) tetrahedra. The shorter O-O distances of (type 2) and (type 3) tetrahedra are the edges that are shared with the (Na,Ca) polyhedron (Table 12). In the (type 3) tetrahedron, the T_3-O_6 bond length is considerably longer than the mean T_3-O bond length. This is because O_6 is coordinated to T_3, T_1 and two additional (Na,Ca) cations which are shifted away from each other during the distortion from the ideal structure, i.e., the scapolite structure with the I4/m space group. The coordination environment of O_6 is best evaluated in Figure (12) with reference to Figures (6 and 9). Both (Na,Ca) cations attract the O_6 anion and will drag O_6 further away from T_3 if both (Na,Ca) cations shift away from each other. Moreover, T_1 contains more Si than T_3 does, therefore, T_1 is more electropositive than T_3 and will have a stronger attracting force to the O_6 anion. It is evident that the resultant force of these three above mentioned attracting forces tends to drag O_6 away from T_3, and thus increases the T_3-O_6 distance. On the other hand, the other oxygen atoms bonded to T_3,are only bonded to one (Na,Ca) atom and the less electropositive T_2 which contains 59.3% Al.

The (Na,Ca) coordination polyhedron in marialite is also rather distorted. The interatomic distances from the central atom (Na,Ca), to the coordinated atoms range from 2.35 to 3.02 Å. Papike and Zoltai (1965) stated that the Na atoms are coordinated by 1 chlorine atom and 5 oxygen atoms. This statement is erroneous because the (Na,Ca) atom in marialite is actually coordinated by 7 oxygen atoms from the tetrahedral framework, together with 1 chlorine atom or 1 oxygen atom from the carbonate radical $CO_3^{=}$ (Table 12b). Therefore, rather than 6, the coordination number of (Na,Ca) in marialite is 8 which is quite common among sodium containing silicates (Prewitt and

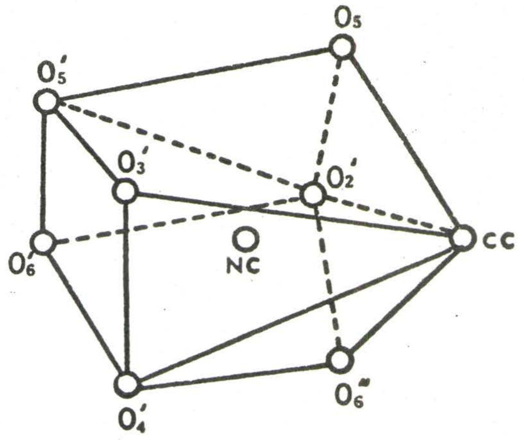


Fig. 11. Coordination polyhedron for (Na,Ca) in marialite, when looking at the (Na,Ca) atom at $x = 0.3659$, $y = 0.2884$ and $z = 0.5064$ along the x-axis direction, i.e., the long diagonal of the oval shape channel, where NC = (Na,Ca), CC = (Cl,C).

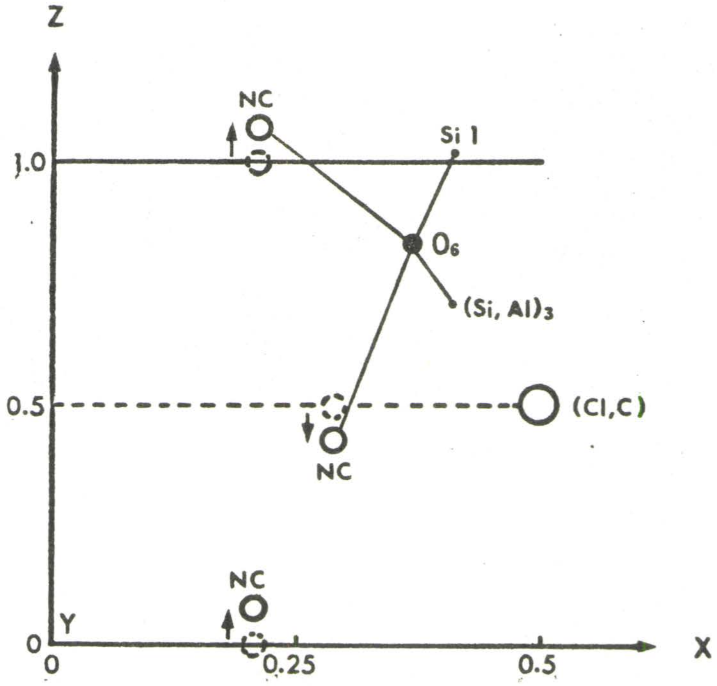


Fig. 12. Environment of chemical bonding of O_6 ($x = 0.3710$, $y = 0.7282$, $z = 0.8270$) when viewed horizontally along the y-axis direction.

Burnham, 1966). The geometrical relationship of the (Na,Ca) coordination polyhedron can be fully illustrated by viewing the surrounding of the (Na,Ca) atoms in the stereographic drawing (Fig. 9) and its physical appearance can be represented by Fig. (11). On the other hand, each (Cl, CO_3, SO_4) anion is coordinated by 4 (Na,Ca,K) atoms.

It seems that the classic electrostatic valency principle (Pauling, 1960) still holds for the (Na,Ca,K) atoms in scapolites. By taking into account the coordination of atoms, the chemical substitution and the Al distribution, the negative charge contributed to the (Na,Ca,K) from the anions can be calculated as follows:

$$\begin{array}{rl@{\qquad}l}
(Cl, CO_3, SO_4) & = -0.293 & T_2 = 0.593/4 = 0.148 \\
O_2 & = -0.221 & T_3 = 0.293/4 = 0.073 \\
O_3 & = -0.221 & O_3 = O_4 = o.148+0.073 = 0.221 \\
O_4 & = -0.221 & O_2 = 0.148+0.073 = 0.221 \\
(\frac{1}{2})(2)O_5 & = -0.148 & O_5 = 0.148 \\
(\frac{1}{2})(2)O_6 & = -0.073 & O_6 = 0.073 \\
\hline
 & -1.177 \approx 1.18 &
\end{array}$$

This negative charge is well balanced by the positive charge of the (Na,Ca,K) cation +1.19. It should be noted that each O_5 and O_6 are coordinated to two (Na,Ca,K) simultaneously.

The final, refined temperature factors of atoms in this crystal structure are found to be rather high, and to fall into three distinguishable size groups according to the crystal-chemical nature of the atoms in marialite (Table 11). The three groups are: (1) temperature factors of the tetrahedral Si and (Si,Al) range from 0.63 to 0.79; (2) temperature factors of the tetrahedral framework oxygen atoms, ranging from 1.25 to 1.49; (3) temperature factors of metallic ions (Na,Ca,K) anion, chlorine and oxygen atoms of the CO_3 radical, ranging from 2.68 to 4.01.Undoubtedly, the abnormally high temperature factors of (Na,Ca,K) and (Cl,C) are due to the substitutional disordering of the involved atoms. Each atomic species involved has only partial occupancy of its site. On the other hand, the abnormally high thermal parameter of the oxygens of the CO_3 group is due to the positional disordering which also makes the concerned oxygen sites only partially occupied (Stout and Jensen, 1968; Prewitt and Burnham, 1966). These phenomena are non-thermal in reality,but are due to the nature of a disordered crystal. Furthermore, the refined isotropic temperature factors listed in Table (11) for Si, (Si,Al) and the framework oxygen atoms are generally larger than the previously determined values in well-refined, ordered silicate structures (Burnham, 1965). Again this may be partly because of the disordering of the crystal and partly because of the inherent internal strain which induces the distortion of the ideal structure (Chapter 4). As a matter of course, this latter cause is also merely a result of the former cause, i.e. the disordering, i.e. the basic cause of solid solution, and this will be discussed in more detail later.

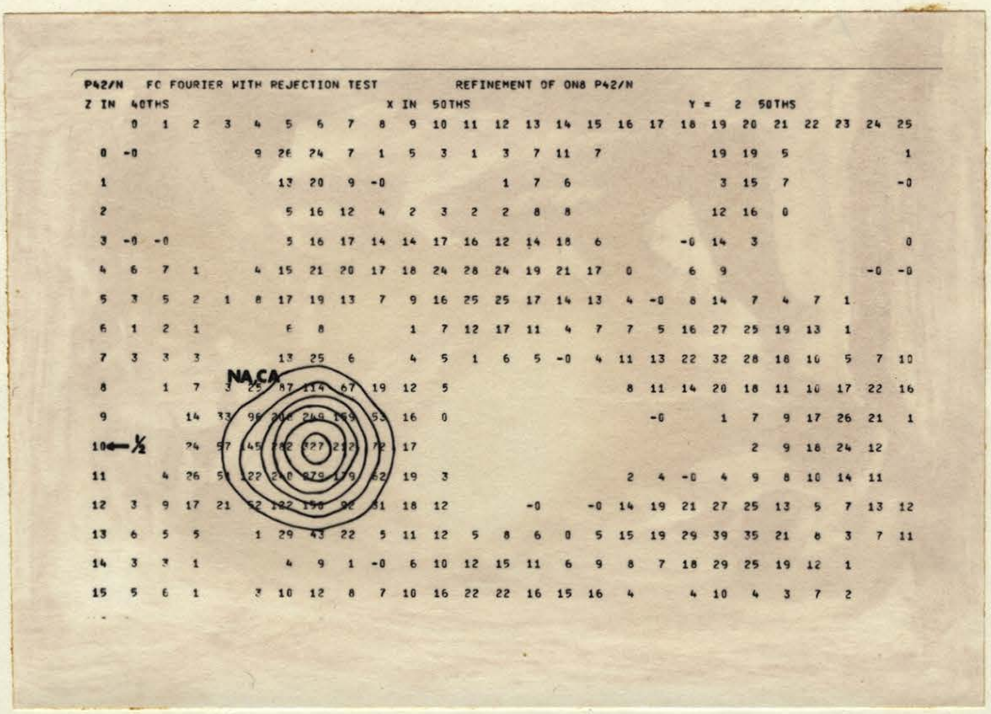
As already discussed, those atoms originally located on the mirror plane in the ideal structure, i.e. the I4/m space group, do migrate away from the mirror plane when refined according to the $P4_2/n$ space group, and this is evidenced by comparing the z-coordinate shifts from the mirror plane with the corresponding standard deviation σ of the z-coordinates. In order to test this fact further, a vertical electron-density section was prepared and showed up the well-defined peak of (Na,Ca,K) clearly located away from the central mirror plane, (plate 4) and there is no evidence to indicate that the (Na,Ca,K) atom occurs as a split atom (Papike and Zoltai, 1965).

This marialite ON8 described contains the least amount of CO_3 among the natural scapolites, but still nearly one fourth of the central cavity is occupied by a carbonate group and this is shown in both the Fourier synthesis and difference synthesis in which four small peaks around the origin (000) and mainly on the (001) plane are present (plate 5). However, some of the CO_3 group are believed to be tilted from (001) plane, as evidenced by the broad peaks present on the vertical electron-density maps and the large temperature factor. Although these peaks are not well enough defined, their position parameter, especially the x,y coordinates are

Plate 4. Vertical section of F_o synthesis to cut through the (Na,Ca) atom. Section run $x = 0 \rightarrow 25/50$ across and $z = 0 \rightarrow 15/40$ down, at $y = 2/50$. Contoured at arbitrary intervals.

Plate 5. Horizontal section of F_o synthesis to show the CO_3 group disordered in the central anion cage. Section run $x = 0 \rightarrow 25/50$ down, $y = 0 \rightarrow 25/50$ across, at $z = 10/40$.

Note: These sections of F_o synthesis were calculated based on space group $P4_2/n$ with origin at $\bar{1}$ at 1/4,1/4,1/4 from $\bar{4}$.



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P42/N   FC FOURIER WITH REJECTION TEST          REFINEMENT OF ON8 P42/N
Z IN  40THS                                X IN  50THS                            Y =   2  50THS
       0   1   2   3   4   5   6   7   8   9  10  11  12  13  14  15  16  17  18  19  20  21  22  23  24  25

 0    -0                   9  26  24   7   1   5   3   1   3   7  11   7              19  19   5               1

 1                            13  20   9  -0               1   7   6                   3  15   7              -0

 2                             5  16  12   4   2   3   2   2   8   8                  12  16   0

 3    -0  -0                   5  16  17  14  14  17  16  12  14  18   6          -0  14   3                   0

 4     6   7   1           4  15  21  20  17  18  24  28  24  19  21  17   0       6   9                  -0  -0

 5     3   5   2   1   8  17  19  13   7   9  16  25  25  17  14  13   4  -0   8  14   7   4   7   1

 6     1   2   1               6   8           1   7  12  17  11   4   7   7   5  16  27  25  19  13   1

 7     3   3   3              13  25   6           4   5   1   6   5  -0   4  11  13  22  32  28  18  10   5   7  10

 8         1   7   3  25  87 114  67  19  12   5                           8  11  14  20  18  11  10  17  22  16

 9            14  33  96 208 249 169  53  16   0                              -0       1   7   9  17  26  21   1

10←½          24  97 145 282 327 212  72  17                                               2   9  18  24  12

11         4  26  58 122 240 279 179  62  19   3                           2   4  -0   4   9   8  10  14  11

12     3   9  17  21  52 122 190  92  31  18  12          -0      -0  14  19  21  27  25  13   5   7  13  12

13     6   5   5       1  29  43  22   5  11  12   5   8   6   0   5  15  19  29  39  35  21   8   3   7  11

14     3   3   1           4   9   1  -0   6  10  12  15  11   6   9   8   7  18  29  25  19  12   1

15     5   6   1       3  10  12   8   7  10  16  22  22  16  15  16   4       4  10   4   3   7   2
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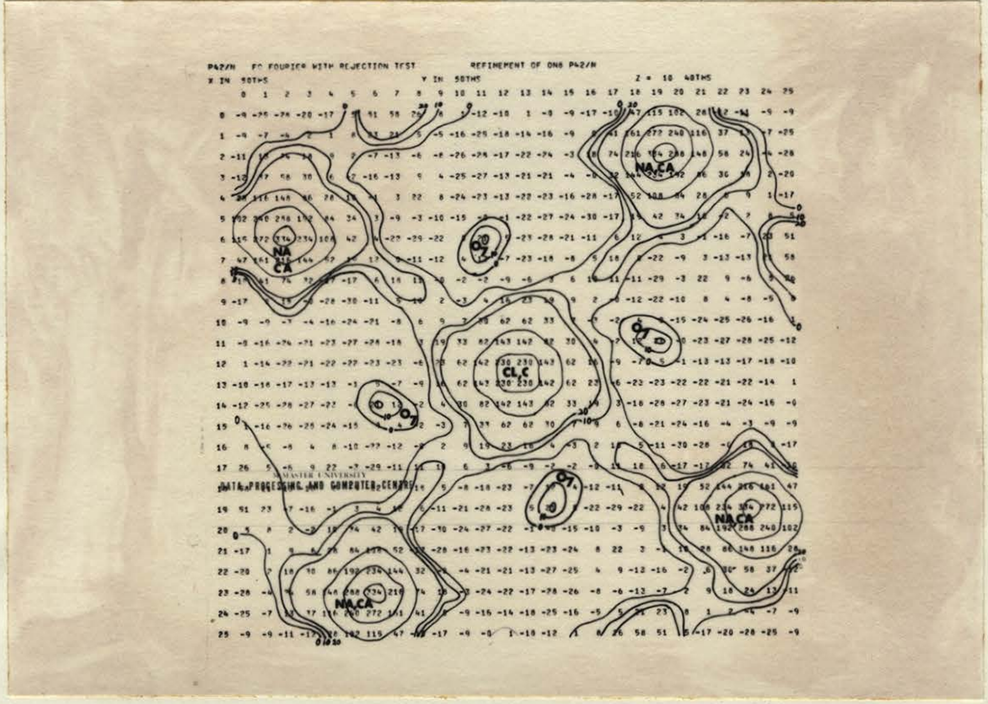

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P42/N   FC FOURIER WITH REJECTION TEST          REFINEMENT OF ON8 P42/N
X IN  50THS                           Y IN  50THS                         Z =  10  40THS
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comparable with the corresponding findings in the structure refinements of the carbonate-rich scapolite specimens XL and ON45 to be described subsequently.

CHAPTER 6

THE CRYSTAL STRUCTURE OF MEIONITE

1) Introduction

Once the pseudosymmetric structure of the sodium and chlorine-rich scapolite was established through a successful structural refinement of the Gooderham scapolite (20% Me; ON8), it became interesting to investigate the crystal structure of the other end of the scapolite solid solution, viz. the calcium-carbonate-rich scapolite. Various significant structural differences from the marialite-rich scapolite were expected. Therefore, a meionite-rich scapolite from Monte Somma, Italy (93% Me; ON45) was selected for structural analysis and refinement.

As discussed in Chapter 3, the scapolite (ON45) is the only one examined that shows no reflections violating body-centred symmetry. Though the apparent space group is $I4/m$, it is believed that the real space group may still be $P4_2/n$. It was hoped to determine its real space group by investigation of its crystal structure and crystal chemistry.

One of the main aims in studying the crystal structure of meionite-rich scapolite is to determine the Al-Si distribution in the tetrahedral framework which has a high Al/Si ratio, and hence to understand its possible relationship to the intensity of the non body-centred reflections ($h+k+\ell = 2n+1$).

The scapolite (ON45; 93% Me) is the most calcium and carbonate-rich one ever found in nature. Therefore, the structural change due to a large compositional difference can be evaluated by comparing this structure with the structure of the Gooderham scapolite (ON8, 20% Me). Moreover, the crystal-chemical role of the CO_3 group can be more easily assessed because there is little if any interference from Cl anion or SO_4 radical (both Cl and S are nearly absent from the specimen ON45). The environment of the Ca atom can also be studied.

2) Space Group and Unit Cell

The scapolite specimen (ON45) is a transparent, colorless, tiny single crystal bounded with prominent second order prisms and first order pyramids. It occurs in ejected blocks - in lava flow on Monte Somma, part of the famous volcano of Vesuvius, Italy.

The weak, extra reflections violating the body-centred symmetry can not be observed from the X-ray photographs of scapolite ON45. It was therefore concluded that scapolite (ON45) has the apparent space group $I4/m$ but probably has a real space group of $P4_2/n$, because the non body-centred reflections may be just too weak to be recorded (see Chapters 3 and 4).

The density of scapolite (ON45) was measured as 2.78 g/cm^3 by using a Berman Torsion Balance and its cell parameters have been determined to be a = 12.194(4) Å, c = 7.557(4) Å, by least-squares refinement of data derived from a Debye-Scherrer powder film. A microprobe analysis of scapolite (ON45) conducted by Evans et. al. (1969) gave a partial analysis. Assuming this analysis is satisfactory, and also assuming the anion sites are only occupied by Cl, SO_4 and CO_3, then by combining the microprobe analysis data together with the data on cell volume and specific gravity, the unit cell content of the scapolite ON45 may be calculated and is listed in Table (14). Consequently, the formula per cell of the scapolite ON45 was derived as $(Ca_{7.32}Na_{0.39}K_{0.19}Fe_{0.038}Mg_{0.004}Sr_{0.015})(Si_{12.4}Al_{11.33})O_{48.51}$ $[Cl_{0.053}(SO_4)_{0.052}(CO_3)_{1.895}]$.

3) Intensity Collection

The single-crystal X-ray diffraction data were collected by integrated Buerger's precession film techniques, using Zr-filtered MoKα radiation. The (hk0) level and the (hkℓ) levels from h=0 through h=5 were photographed to give 688 total reflections. Of these, 166 have intensities less than the minimum observable value and were assigned a value equal to $I_{min}/3$. Then the photometrically measured intensities were corrected for Lorentz and polarization effects and converted into unscaled $|F_{obs}|$, but no absorption corrections were applied, because the transmission factor is not significantly affected

Table (14). Unit Cell Content of Scapolite ON45.

Cation	Number Per Cell	Cation	Number Per Cell	Anion	Number Per Cell	Anion	Number Per Cell
Si	12.41	Ca	7.32	O	48.51	Cl	0.053
Al	11.33	Na	0.39			SO_4	0.052
		K	0.19			CO_3	1.895
		Fe	0.038				
		Mg	0.004				
		Sr	0.015				
Total	23.74		7.96		48.51		4.00

by the reflection angle θ (Evans and Ekstein, 1952).

4) Structural Analysis and Refinement.

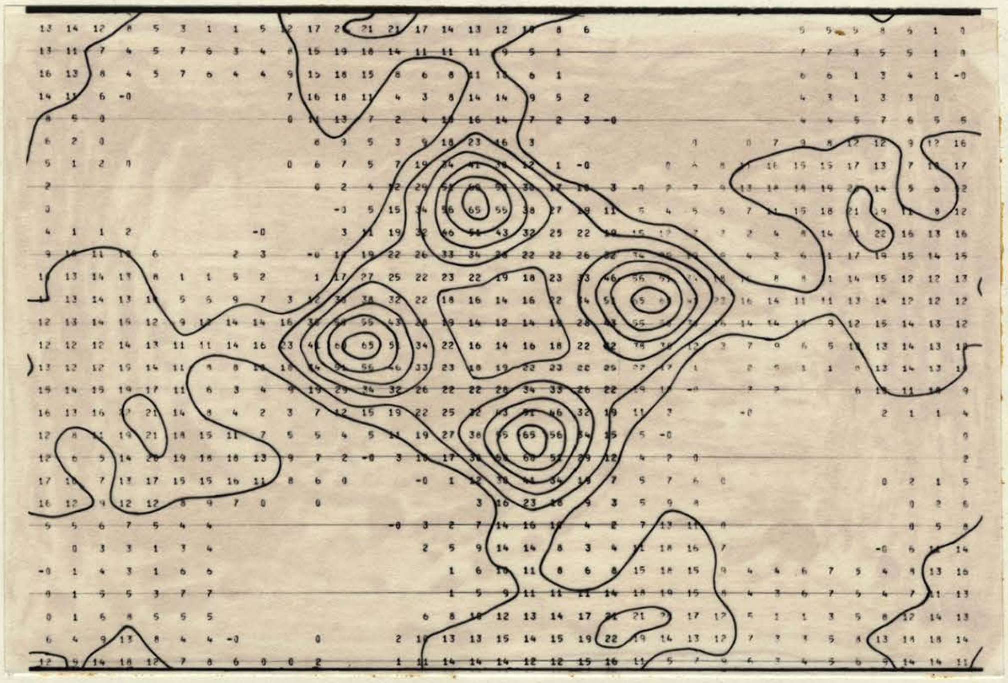
The structural model was formed by transforming some of the positional parameters and corresponding thermal parameters of the scapolite specimen ON8 into a unit cell based on the space group I4/m with origin at 4/m, and resetting the z coordinates of (Si,Al)3, O1 and O2 atoms so that they are on the mirror plane. The carbonate group was not included. This trialmodel was refined for six cycles of a full-matrix least-squares refinement by using the "ORFLS" program contained in the "X-ray 67" program for X-ray crystallography (Computer Science Center, University of Maryland) and allowing the coordinates, isotropic temperature factors and scales to be varied. The R factor for all unscaled data before refinement was found to be 1.18 and the final R after the above-mentioned six cycles was 0.096. Both a horizontal series ($\parallel$ plane (001)) and a vertical series ($\perp$ plane (001)) of $\rho(xyz)$ and $\Delta\rho(xyz)$ sections were then calculated in an attempt to learn the spatial distribution of the carbonate group (CO_3) in the anion cavity. In addition to the peaks corresponding to the atoms included in the calculation of the $\rho(xyz)$ sections, both the $\rho(xyz)$ and the $\Delta\rho(xyz)$ sections revealed four well-defined peaks around (000) on the (001) plane and a broad plateau at (000). These electron-density highs were interpreted as being ascribed to the carbonate groups with positional disordering statistically to fit the 4/m site symmetry. Thus the trial atomic coordinates of oxygen of CO_3 group were assigned to be $x = 0.400$, $y = 0.4800$, $z = 1/2$ and that of C to be $x = 1/2$, $y = 1/2$, $z = 1/2$ inferred from these three-dimensional $\Delta\rho(xyz)$ sections (Plates 6 and 7).

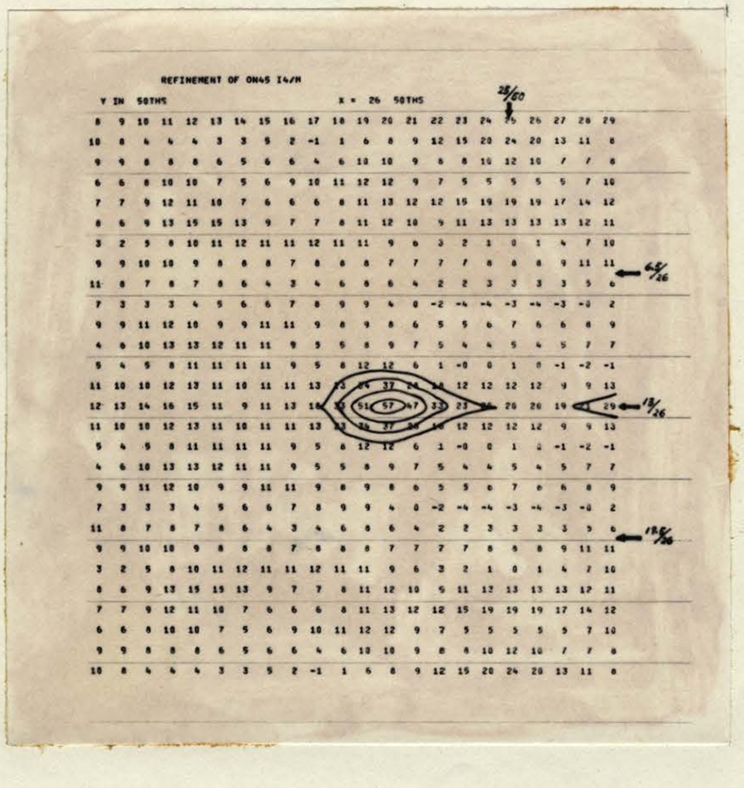
Including the contribution from the carbonate group, the least-squares refinement was continued for three more cycles in which various parameters were varied, and the result showed the R value dropped to 0.081 and the coordinates of the oxygen of the CO_3 group essentially remained unchanged but its isotropic temperature factor drastically increased to 6.54,

Plate 6. Section of ΔF_o synthesis to reveal the O_7 position of the disordered CO_3 groups. Section run x = 12/50 → 40/50 down, y = 8/50 → 42/50 across, at z = 13/26.

Plate 7. Section of ΔF_o synthesis to reveal the z coordinates of O_7 atom of the disordered CO_3 group. Section run y = 9/50 → 29/50 across, z = 0 → 26/26 down, at x = 26/50.

Note: These sections of ΔF_o synthesis were calculated based on I4/m with original $\bar{1}$.





REFINEMENT OF ON45 I4/M

Y IN 50THS X = 26 50THS

25/50

8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	
10	8	4	4	4	3	3	5	2	-1	1	6	8	9	12	15	20	24	20	13	11	8	
9	9	8	8	8	6	5	6	6	4	6	10	10	9	8	8	10	12	10	7	7	8	
6	6	8	10	10	7	5	6	9	10	11	12	12	9	7	5	5	5	5	5	7	10	
7	7	9	12	11	10	7	6	6	6	8	11	13	12	12	15	19	19	19	17	14	12	
8	6	9	13	15	15	13	9	7	7	8	11	12	10	9	11	13	13	13	13	12	11	
3	2	5	8	10	11	12	11	11	12	11	11	9	6	3	2	1	0	1	4	7	10	
9	9	10	10	9	8	8	8	7	8	8	8	7	7	7	7	8	8	8	9	11	11	
11	8	7	8	7	8	6	4	3	4	6	8	6	4	2	2	3	3	3	3	5	6	← 6.5/26
7	3	3	3	4	5	6	6	7	8	9	9	4	0	-2	-4	-4	-3	-4	-3	-0	2	
9	9	11	12	10	9	9	11	11	9	8	9	8	6	5	5	6	7	6	6	8	9	
4	6	10	13	13	12	11	11	9	5	5	8	9	7	5	4	4	5	4	5	7	7	
5	4	5	8	11	11	11	11	9	5	8	12	12	6	1	-0	0	1	0	-1	-2	-1	
11	10	10	12	13	11	10	11	11	13	23	24	37	28	18	12	12	12	12	9	9	13	
12	13	14	16	15	11	9	11	13	18	33	51	57	47	33	23	26	26	26	19	[illegible]	29	← 13/26
11	10	10	12	13	11	10	11	11	13	23	24	37	28	18	12	12	12	12	9	9	13	
5	4	5	8	11	11	11	11	9	5	8	12	12	6	1	-0	0	1	0	-1	-2	-1	
4	6	10	13	13	12	11	11	9	5	5	8	9	7	5	4	4	5	4	5	7	7	
9	9	11	12	10	9	9	11	11	9	8	9	8	6	5	5	6	7	6	6	8	9	
7	3	3	3	4	5	6	6	7	8	9	9	4	0	-2	-4	-4	-3	-4	-3	-0	2	
11	8	7	8	7	8	6	4	3	4	6	8	6	4	2	2	3	3	3	3	5	6	← 19.5/26
9	9	10	10	9	8	8	8	7	8	8	8	7	7	7	7	8	8	8	9	11	11	
3	2	5	8	10	11	12	11	11	12	11	11	9	6	3	2	1	0	1	4	7	10	
8	6	9	13	15	15	13	9	7	7	8	11	12	10	9	11	13	13	13	13	12	11	
7	7	9	12	11	10	7	6	6	6	8	11	13	12	12	15	19	19	19	17	14	12	
6	6	8	10	10	7	5	6	9	10	11	12	12	9	7	5	5	5	5	5	7	10	
9	9	8	8	8	6	5	6	6	4	6	10	10	9	8	8	10	12	10	7	7	8	
10	8	4	4	4	3	3	5	2	-1	1	6	8	9	12	15	20	24	20	13	11	8	

suggesting great positional disordering. Two more cycles were run to include the "less thans" into the refinement and the R factor stayed at 0.081 with oscillatory changes in parameters. At this point a modified Cruickshank weighting scheme was introduced. After three cyles of refinement, the positional parameters remained unchanged or only very slightly changed, while all the thermal parameters were generally somewhat decreased. The dimensions of individual tetrahedra were then calculated and the Al-Si occupancy of each tetrahedral site was estimated by using the mean T-O bond length and the regression line of Smith and Bailey (1963). Finally the new scattering curves were prepared according to the estimated Al,Si occupancy and three more least-squares cycles were run, giving a final R = 7.9%. Moreover, almost all temperature factors continued to decrease slightly, especially those of (Al,Si)1, (Al,Si2), and the carbonate group.

As explained previously, the real space group of this meionite (93% Me) crystal is probably $P4_2/n$ rather than I4/m. However, it is well known that a pseudosymmetric or superstructure is quite difficult to completely refine by least-squares method due to the high correlation coefficient among parameters (Stout, G.H. and Jensen, C.H., 1968). A pseudosymmetric structure is only slightly distorted from the ideal structure which has a space group of higher symmetry. During refinement according to the real space group of lower symmetry;

attempts are made to adjust independently atoms which are nearly related by the higher symmetry, and these show large correlation coefficient. Before introducing the Cruickshank weighting scheme and reaching a final R during the above-mentioned refinement based on the space group I4/m, a refinement based on the space group $P4_2/n$ had been tried which failed; many parameters became non-positive and/or overflowed, but it should be noted that the "unobserved reflections" consistent with space group $P4_2/n$ had not been included into this refinement. Therefore all the "unobserved reflections" consistent with space group $P4_2/n$ were subsequently given a much smaller weight inferred from figure (1) in Ch. 4, and then included into a refinement based on $P4_2/n$ space group. In order to avoid the refinement collapsing again, the least-squares refinement was carefully conducted step by step. First of all, fixing the isotropic temperature factors of all the atoms and the z-coordinates of all oxygen atoms the R factor dropped from 13.5% to 8.6% after one cycle of least-squares and only a few positional parameters, mostly of oxygen atoms, had changed over one standard deviation σ, namely the y coordinate of O^-6 with 22σ. In the next cycle of refinement, only the temperature factors were fixed and the R value continued to drop to 7.5%. Again in the next cycle least-squares refinements in which scales, temperature factors and atomic coordinates were all allowed to vary the R value was only slightly lowered to 7.4% and most of the temperature factors only slightly increased while some slightly decreased. T-O bond lengths were then calculated and the Al-Si distribution was assigned to form new atomic scattering curves for the tetrahedral sites. Finally using these new atomic scattering curves and applying the modified Cruickshank weighting scheme, three additional least-squares cycles were executed, giving a final R = 7.2% for all observations including those $|F_o|<|F_{o\ min}|$.

The scattering curves and the computer programs used during the refinement of this structure are the same as those used in the structural refinement of the Gooderham marialite (ON8) in the last chapter.

5) Results and Discussion

The parameters resulting from the refinement based on the space group $P4_2/n$ is selected as the final, refined values for the crystal structure of this meionite. However, they are listed together with those resulting from the refinement of the same crystal based on space group I4/m and the atomic coordinates of marialite(ON8, Gooderham, Ontario) , in Table (15) for comparison. The scaled F_{obs} and F_{cal} are listed in Appendix (2). The important interatomic distances and angles are given in Tables (16 and 17). All these tables can be used in conjunction with Fig. (13). The details of the crystal structure can also be investigated by referring to Figs. (8) and (9) of Chapter 5.

Table (15). Atomic Coordinates and Temperature Factors of Meionite (93% Me, Mt. Somma, Italy). Standard Deviations, σ, given in parentheses

Specimen / Atom		1	2	3	Difference between	Difference between
		Meionite ($P4_2/n$)	Meionite I4/m	Marialite (ON8)	1 & 2	1 & 3
(Ca,Na, K)	X	0.3565(2)	0.3565(2)	0.3659(3)	0.0000	-0.0094
	Y	0.2807(2)	0.2809(2)	0.2884(3)	-0.0002	-0.0077
	Z	0.5001(3)	1/2	0.5064(4)	0.0001	-0.0063
	B	1.79 (4)	1.54 (5)	2.68 (6)	0.25	-0.89
(C,Cl, S)	X	1/2	1/2	1/2	0	0
	Y	1/2	1/2	1/2	0	0
	Z	1/2	1/2	1/2	0	0
	B	1.97 (29)	1.36 (40)	3.85 (12)	0.61	-1.88
(Si,Al)1	X	0.3395(2)	0.3395(3)	0.3390(1)	0.0000	0.0005
	Y	0.4074(2)	0.4071(3)	0.4100(1)	0.0003	-0.0026
	Z	1.0000(3)	1	0.9989(3)	0.0000	0.0011
	B	0.47 (4)	0.29 (5)	0.69 (3)	0.18	-0.22
(Si,Al)2	X	0.6599(2)	0.6598(2)	0.6621(2)	0.0001	-0.0022
	Y	0.9129(2)	0.9134(2)	0.9152(2)	-0.0005	-0.0023
	Z	0.7930(3)	0.7934(2)	0.7956(2)	-0.0004	-0.0026
	B	0.51 (5)	0.32 (3)	0.79 (4)	0.19	-0.28
(Si,Al)3	X	0.4130(2)		0.4145(2)		-0.0015
	Y	0.8401(2)		0.8368(2)		0.0033
	Z	0.7072(3)		0.7085(2)		-0.0013
	B	0.51 (5)		0.63 (4)		-0.12
O1	X	0.4593(5)	0.4591(7)	0.4574(4)	0.0002	0.0019
	Y	0.3475(5)	0.3484(7)	0.3511(4)	-0.0009	-0.0036
	Z	0.9999(10)	1	1.0011(7)	-0.0001	-0.0012
	B	1.33 (9)	1.13 (14)	1.39 (8)	0.20	-0.03
O2	X	0.6871(5)	0.6873(6)	0.6939(4)	-0.0002	-0.0068
	Y	0.8732(5)	0.8726(7)	0.8797(4)	0.0006	-0.0065
	Z	0.9999(9)	1	1.0048(7)	-0.0001	-0.0049
	B	0.98 (8)	0.57 (12)	1.25 (7)	0.41	-0.27
O3	X	0.3491(5)	0.3482(4)	0.3486(6)	0.0009	0.0005
	Y	0.9495(5)	0.9510(4)	0.9448(5)	-0.0015	0.0047
	Z	0.7941(9)	0.7965(6)	0.7898(6)	-0.0024	0.0043
	B	1.09 (10)	0.84 (9)	1.48 (10)	0.25	-0.39
O4	X	0.5504(5)		0.5499(5)		0.0005
	Y	0.8491(5)		0.8475(6)		0.0016
	Z	0.7055(9)		0.7163(6)		-0.0108
	B	1.11 (10)		1.49 (10)		-0.38

(continued next page)

Table (15) (continued)

Specimen / Atom		1	2	3	Difference between 1 & 2	Difference between 1 & 3
		Meionite ($P4_2/n$)	Meionite I4/m	Marialite (ON8)		
O5	X	0.2674(5)	0.2669(4)	0.2706(5)	0.0005	-0.0032
	Y	0.3645(6)	0.3647(4)	0.3699(5)	-0.0002	-0.0054
	Z	0.8245(7)	0.8293(7)	0.8277(6)	-0.0048	-0.0032
	B	1.42 (12)	1.10 (9)	1.30 (9)	0.32	0.12
O6	X	0.3643(6)		0.3710(6)		-0.0067
	Y	0.7345(5)		0.7282(6)		0.0063
	Z	0.8269(7)		0.8270(7)		-0.0001
	B	1.48 (12)		1.47 (10)		0.01
O7	X	0.3995(16)	0.3961(16)	0.3833(62)	0.0034	0.0162
	Y	0.4865(16)	0.4822(19)	0.4817(64)	0.0043	0.0048
	Z	0.5001(25)	1/2	0.5012(101)	0.0001	-0.0011
	B	6.42 (41)	6.27 (52)	4.01 (1.28)	0.15	2.41

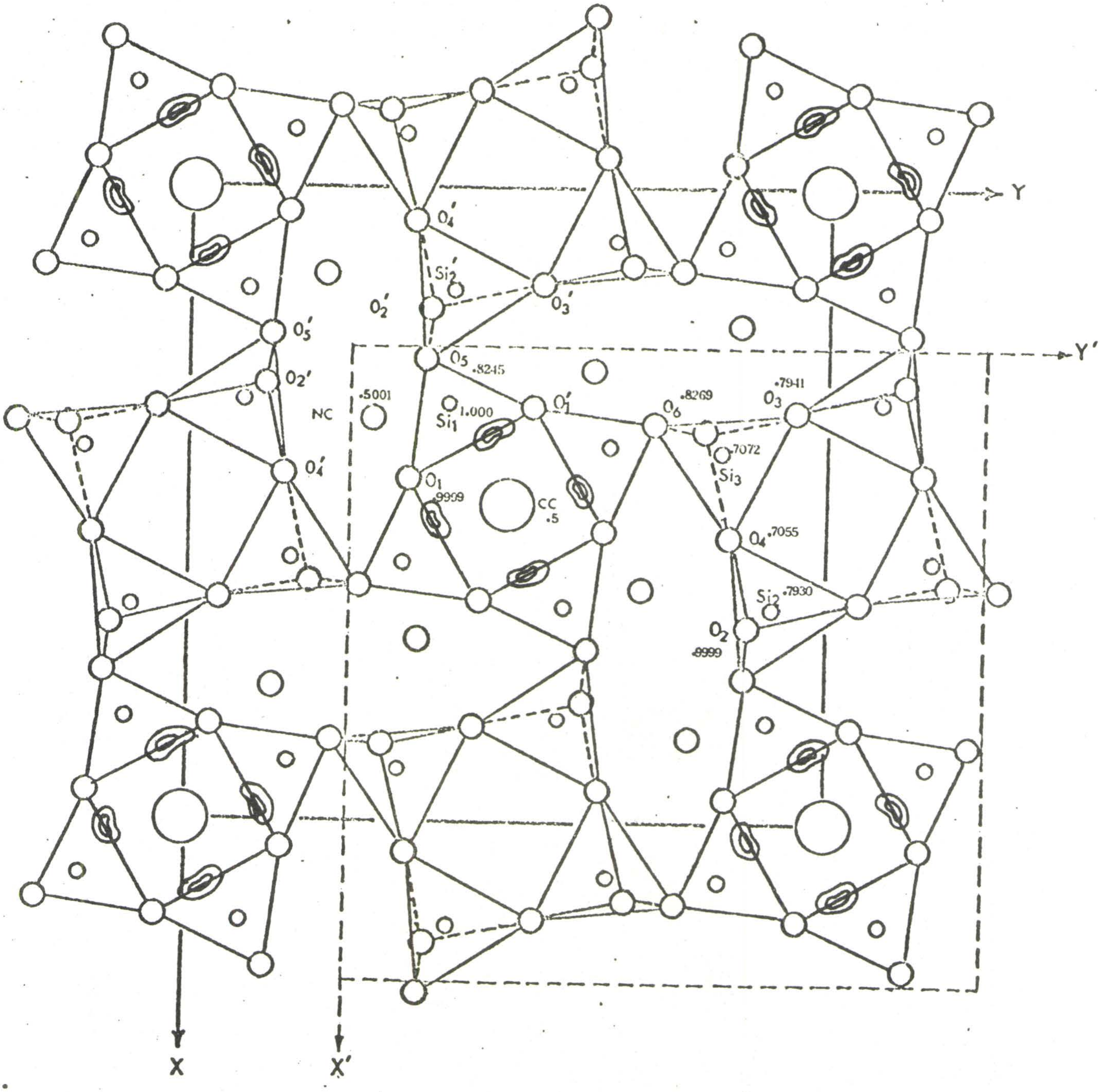


Fig. 13. Projection of the crystal structure of meionite (ON45, 93% Me). Dashed lines indicate the cell boundary consistent with the space group $P4_2/n$ having the origin at $\bar{1}$ from 1/4,1/4,1/4 from $\bar{4}$.

Table (16) Interatomic Distances in Meionite (93% Me,
Monte Somma, Italy)

(a) (Si,Al)-O and O-O Distances of Tetrahedra

Tetrahedron	T-O Distances (Å)			O-O Distances (Å)		
	Atoms	Multiplicity	Distance	Atoms	Multiplicity	Distance
T_1	O_1	1	1.634(6)	O_1-O_5	1	2.697(9)
	O_5	1	1.674(6)	O_1-O_1'	1	2.721(9)
	O_1'	1	1.628(6)	O_1-O_6'	1	2.709(10)
	O_6'	1	1.674(6)	O_1'-O_5	1	2.707(10)
				O_1'-$O_{6'}$	1	2.709(9)
				O_5-O_6'	1	2.635(8)
	Average		1.653(6)	Average		2.696(9)
T_2	O_2	1	1.670(7)	O_2-O_4	1	2.796(9)
	O_4	1	1.681(7)	O_2-$O_{3'}$	1	2.699(9)
	$O_{3'}$	1	1.681(7)	O_2-$O_{5'}$	1	2.642(8)
	$O_{5'}$	1	1.690(7)	O_4-$O_{5'}$	1	2.663(9)
				O_4-$O_{3'}$	1	2.825(9)
				$O_{3'}$-$O_{5'}$	1	2.822(10)
	Average		1.681(7)	Average		2.741(9)
T_3	O_3	1	1.679(7)	O_3-O_4	1	2.824(9)
	O_1	1	1.680(7)	O_3-O_6	1	2.640(9)
	O_6	1	1.682(6)	O_3-$O_{2'}$	1	2.699(9)
	$O_{2'}$	1	1.673(7)	O_4-O_6	1	2.819(10)
				O_4-$O_{2'}$	1	2.698(9)
				O_6-$O_{2'}$	1	2.652(8)
	Average		1.679(7)	Average		2.722(9)

Table (16) (continued)

(b) Selected Interatomic Distances:

Type	From	To	Multiplicity	Distance (Å)
Cation Coordination polyhedron	(Ca,Na,K)	C,Cl	1	3.196(2)
		O_2'	1	2.353(6)
		O_3'	1	2.493(7)
		O_4'	1	2.490(7)
		O_5	1	2.870(6)
		O_5'	1	2.679(7)
		O_6'	1	2.655(7)
		O_6'	1	2.893(6)
		O_7'	1	2.402(20)
Anion Cage Diagonals	O_1	O_1'	4	8.480
	O_5	O_6'	4	8.223
	O_2	O_2'	2	8.234
Carbonate Group	C	O_7	3	1.236(20)

Table (17): Interatomic Angles in Meionite (93% Me, Monte Somma, Italy)

Type	Atoms	Angle ± σ (degree)
	$O_1-T_1-O_5$	109.22 ± 0.37
$O-T_1-O$ Angles	$O_1-T_1-O_1'$	113.09 ± 0.34
	$O_1-T_1-O_{6'}$	109.98 ± 0.37
(T_1 tetrahedron)	$O_5-T_1-O_{1'}$	110.12 ± 0.39
	$O_5-T_1-O_{6'}$	103.79 ± 0.31
	$O_{1'}-T_1-O_{6'}$	110.23 ± 0.39
	$O_2-T_2-O_4$	113.06 ± 0.34
$O-T_2-O$ Angles	$O_2-T_2-O_{3'}$	107.32 ± 0.33
	$O_2-T_2-O_{5'}$	103.66 ± 0.32
(T_2 tetrahedron)	$O_4-T_2-O_{3'}$	114.36 ± 0.34
	$O_4-T_2-O_{5'}$	104.33 ± 0.34
	$O_{3'}-T_2-O_{5'}$	113.70 ± 0.36
	$O_3-T_3-O_4$	114.44 ± 0.34
$O-T_3-O$ Angles	$O_3-T_3-O_6$	103.54 ± 0.34
	$O_3-T_3-O_{2'}$	112.93 ± 0.34
(T_3 tetrahedron)	$O_4-T_3-O_6$	113.98 ± 0.36
	$O_4-T_3-O_{2'}$	107.16 ± 0.33
	$O_6-T_3-O'_2$	104.44 ± 0.32
	$T_1-O_1-T_{1'}$	156.91 ± 0.45
	$T_2-O_2-T_{3'}$	138.85 ± 0.40
T-O-T Angles	$T_3-O_3-T_{2'}$	145.23 ± 0.44
	$T_2-O_4-T_3$	145.05 ± 0.44
	$T_1-O_5-T_{2'}$	135.56 ± 0.46
	$T_3-O_6-T_{1'}$	136.19 ± 0.47

As discussed in Chapter 4, the fact that weak reflections violating the body-centred symmetry were not observed in the photographs of this meionite (ON45) crystal may be due to the fact that their intensities are so weak that the reflection peaks are immersed in the background,and hence, the real space group of this meionite is likely to be $P4_2/n$ instead of the apparent I4/m. In order to confirm this, the crystal structure was also successfully refined based on the space group $P4_2/n$ to give a final R = 7.2% which is even lower than the final R = 7.9% given as a result of the refinement based on the space group I4/m. Though a lower R factor is by no means an absolute measure of the correctness of a crystal structure model, nevertheless,a successful refinement with a lower R does tend to favour the possibility of $P4_2/n$ being the real space group. However, another really surprising fact supporting $P4_2/n$ as real space group is the fact that the Al distribution in the (Si,Al)-framework derived from the refined parameters according to the space group $P4_2/n$ is consistent with Loewenstein's conclusion that Al-O-Al linkages are unstable in the framework silicates (Loewenstein 1956), whereas the refinement according to the space group I4/m does not support this conclusion.

Using the mean (Si,Al)-O bond lengths calculated from the refined models both based on space group I4/m and $P4_2/n$ (Table 16) and the curve prepared by Smith and Bailey (1963), the Al occupancy in each tetrahedral site was estimated as follows:

(A) Based on space group I4/m:

Tetrahedral Ring	Tetrahedral Sites	Mean (Si,Al)-O Distance (A)	Aluminum Occupancy (%)
Type 1	$(Si,Al)_1=T_1$	1.639	21
Type 2	$(Si,Al)_2=T_2$	1.687	55

(B) Based on space group $P4_2/n$:

Tetrahedral Ring	Tetrahedral Sites	Mean (Si,Al)-O Distance (A)	Aluminum Occupancy (%)
Type 1	$(Si,Al)_1=T_1$	1.653	30.1
Type 2	$(Si,Al)_2=T_2$	1.681	50.1
	$(Si,Al)_3=T_3$	1.679	49.3

As in the structure of the Gooderham scapolite described in Chapter 7, the (type 2) 4-membered tetrahedral ring is composed of four tetrahedra of $(Si,Al)_2$ if based on space group I4/m, while it is composed of two $(Si,Al)_2$-tetrahedra and two $(Si,Al)_3$-tetrahedra if based on space group $P4_2/n$ (Fig. 13).

Therefore, in the structure based on the space group I4/m the Al occupancy in the (type 2) ring will be 55%, i.e., even more than 50%, a compositional point which the (type 2) rings would have to start forming Al-O-Al linkages; a situation which Loewenstein (1954) has called unstable in framework silicates, whereas in the structure based on space groups $P4_2/n$, the Al occupancy in the (type 2) rings will be 49.7%, i.e., the average of the Al occupancies of T_2 and T_3 sites.

It is the author's belief therefore that meionite (ON45, 93% Me) has a space group $P4_2/n$. In contrast to the situation in the Na-rich and Cl-rich scapolite (represented by Gooderham scapolite with 20% Me, i.e., ON8) in which Al only distributes in a disordered manner between two tetrahedral sites T_2 and T_3, Al in the meionite-rich scapolite distributes in all three tetrahedral sites to partially replace Si. This is because the meionite-rich scapolite has a higher ratio of Al/Si. The average Al occupancy in (type 2) ring would be increased over 50% which is undesirable by Loewenstein's conclusion. Therefore, the T_1 sites are partially occupied by Al in order to decrease the probability of formation of the Al-O-Al linkage. Consequently, the present study seems also to support Loewenstein's conclusion.

The basic features of the meionite crystal structure are the same as those of the refined structure of the marialite (Chapter 5), but some significant differences in the atomic coordinates are observed (Table 15) and they are mainly due to the difference of chemical composition.

When looking along the c-axis, the structure can be considered to be composed of two types of four-membered rings (Fig. 13). The (type 1) rings made up of four T_1 tetrahedra are centered at (0,0,0) and have apparent symmetry 4/m. The

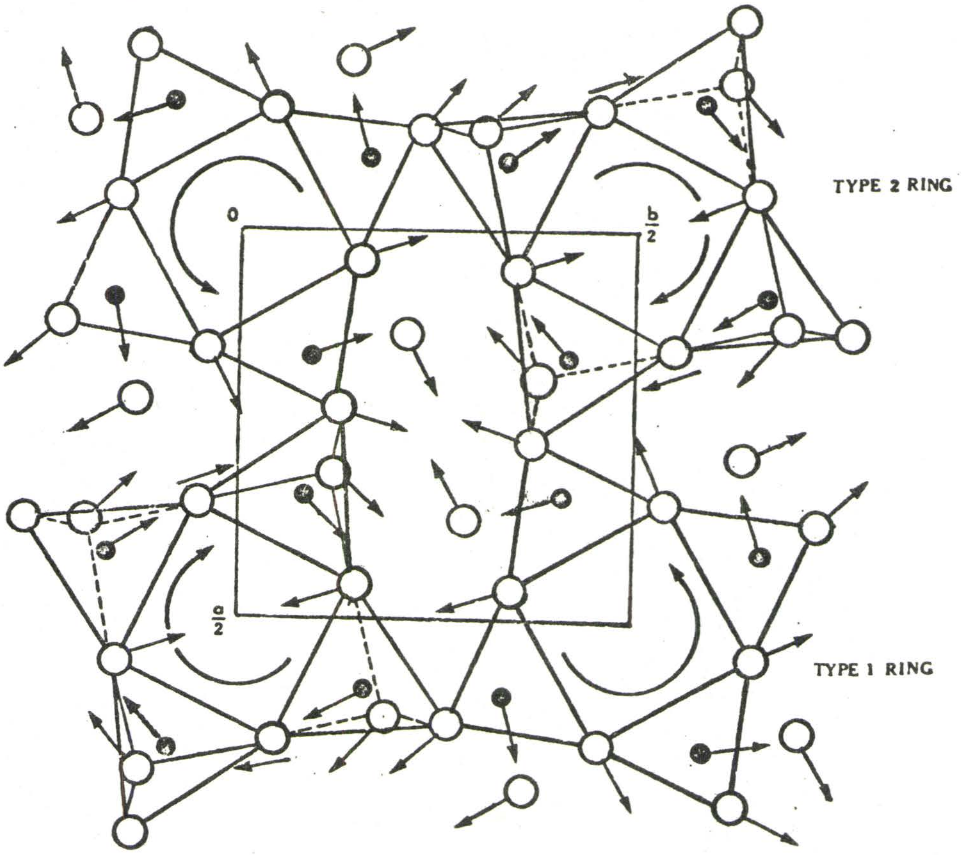


Fig. 14. Distortion of scapolite structure with chemical composition. The arrows indicate the direction of the atomic displacements and the ring rotations.

(type 2) rings made up of two T_2 tetrahedra and two T_3 tetrahedra are centered at (1/2,0,1/4) and have apparent symmetry $\bar{4}$. The directions of the horizontal atomic shifts and their total net effects are indicated in Fig. (14). Ignoring the vertical atomic shifts, the crystal structure of meionite can be considered as being derived from the marialite structure by rotating (type 1) rings in a counter-clockwise direction while rotating (type 2) rings in a clockwise direction (Fig. 14). Meantime, as a result of these coupled rotations, the oval-shaped cation-channels increase relatively their long diameters and decrease their short diameters. All these findings are consistent with those found in mizzonite by Papike and Stephenson (1966), though their refined structure was based on the space group I4/m and the composition of their crystal is in doubt (i.e., specimen M730 in Chapter 3).

The distortion of the central anion cage locate Cl and CO_3 anions, as a function of the chemical composition can also be evaluated from Table (18), by referring to Fig. 15 $\overline{O_2O_{2'}}$ is the horizontal diagonal of the cage, while $\overline{O_1O_{1'}}$ is an inclined diagonal more parallel to the c-axis. It is obvious that $\overline{O_2O_{2'}}$ is longer relative to $\overline{O_1O_{1'}}$, in other words, the cage becomes more equidimensional rather than being elongate, when the composition is richer in meionite. This fact is interpreted as a corresponding adjustment of the cage in order to accomodate the increasing planar group of CO_3. The variation of the ratio of $\overline{O_1O_1'}$ to $\overline{O_2O_2'}$ is also sympathetic with the variation of the axial ratio C_o/a_o, and it should be noted that the distance $\overline{O_1\ O_1}$ is equal to C_o in length.

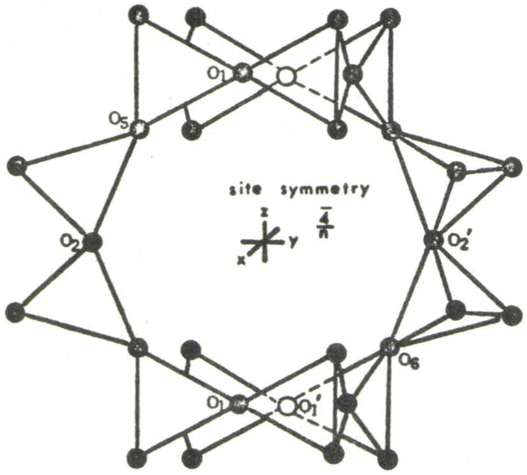


Fig. 15. The central anion cage of the scapolite structure

Table (18). Distortion of the Central Anion Cage as a Function of Chemical Composition of Scapolites

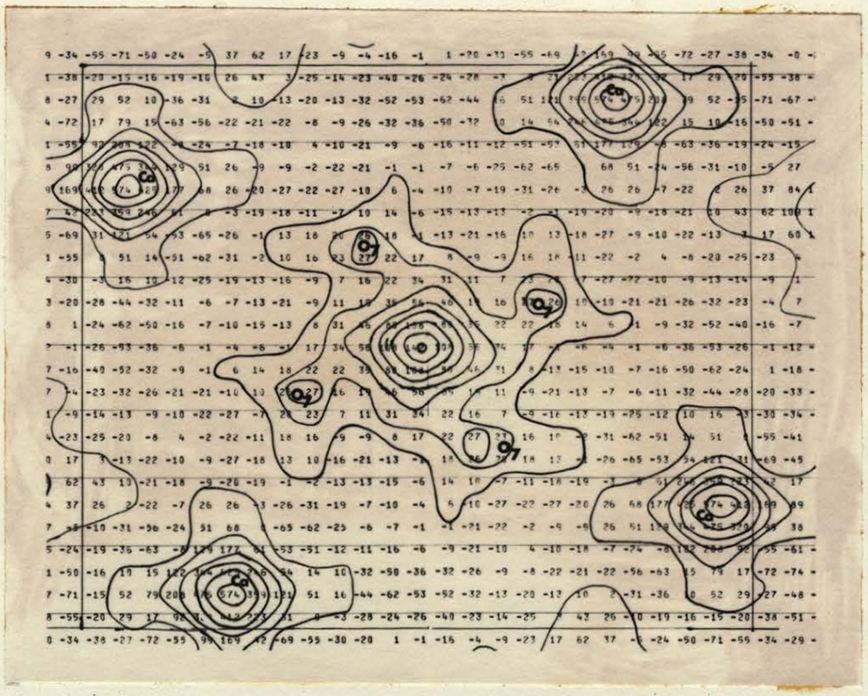
Scapolite	ON8(20% Me)	XL(52% Me)	ON45 (93% Me)
$\overline{O_1O_1'}$	8.457 Å	8.467 Å	8.480 Å
$\overline{O_5O_6}$	8.055 Å	8.131 Å	8.223 Å
$\overline{O_2O_2'}$	7.933 Å	8.091 Å	8.234 Å
$\overline{O_1O_1'}/\overline{O_2O_2'}$	1.066	1.046	1.030
C_o	7,587 Å	7.581 Å	7.557 Å
a_o	12.059 Å	12.116 Å	12.194 Å
C_o/a_o	0.629	0.626	0.620

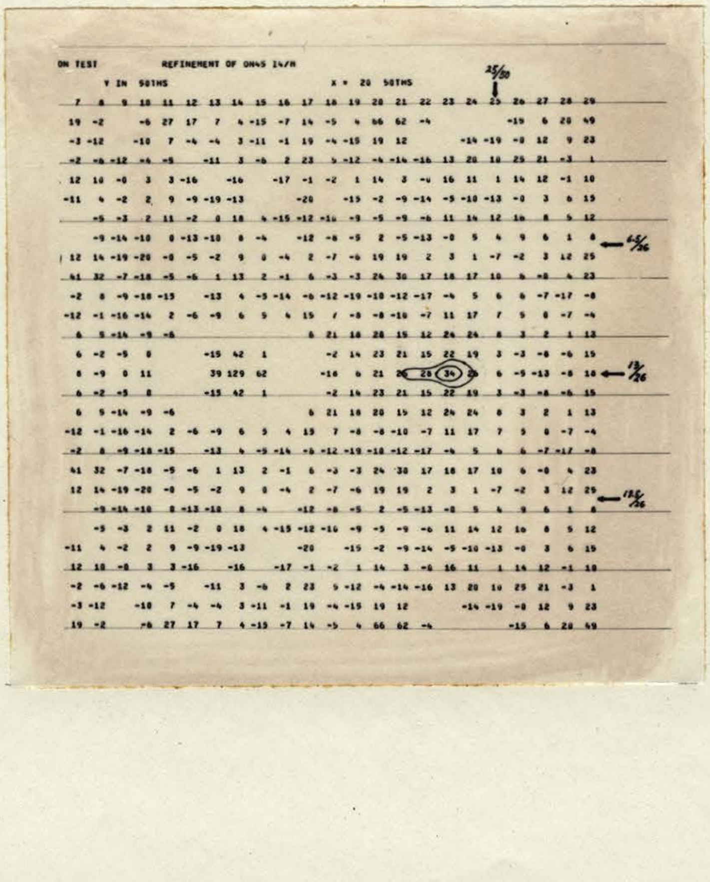
As a matter of fact, all these distortion effects arealso related to the increase of a_o cell dimension and decrease of c_o cell dimension as % Me increases or more basically, as a result of increase of CO_3 group as already discussed in Chapter 4. Moreover, it should be noted that it is not just a two-dimensional distortion but a three-dimensional one.

One of the most interesting problems in the crystal structure of the carbonate-rich scapolite is in regard to locating the triangular planar carbonate group ($CO_3^=$) with three fold molecular symmetry on a crystallographic site with four-fold symmetry. As stated in Section 4, during the structural analysis and refinement, a series of electron density sections or projections all consistently revealed four broad peaks on the ab plane and around the origin (0,0,0) and also a plateau centered at (0,0,0) on the ab plane (Plates 6, 7, 8 and 9). Thus the carbonate group found in this meionite seems to be similar to those found in mizzonite (Papike and Stephenson, 1966) which, however, also contains very little chlorine and only shows very weak non body-centred reflections. The result of the present study is also generally in favor of their suggested interpretation concerning the behaviour of the carbonate group in the scapolite structure. First, the carbonate group is essentially confined to the ab plane in meionite, though it could be slightly tilted away from the

Plate 8. Horizontal section of F_o synthesis to show O_7 of the disordered CO_3 groups. Section run x = 12/50→38/50 down, y = 11/50→39/50 across, at z = 13/26.

Plate 9 Vertical section of F_o synthesis to show O_7 of the CO_3 group. Section run y = 7/50→29/50 across, z = 0→26/26 down, at x = 20/50





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ON TEST          REFINEMENT OF ON45 I4/M
                                                                           25/50
      Y IN  50THS                            X =  20  50THS                  ↓
   7   8   9  10  11  12  13  14  15  16  17  18  19  20  21  22  23  24  25  26  27  28  29
  19  -2      -6  27  17   7   4 -15  -7  14  -5   4  66  62  -4             -15   6  20  49
  -3 -12     -10   7  -4  -4   3 -11  -1  19  -4 -15  19  12         -14 -19  -0  12   9  23
  -2  -6 -12  -4  -5     -11   3  -6   2  23   5 -12  -4 -14 -16  13  20  10  25  21  -3   1
  12  10  -0   3   3 -16     -16     -17  -1  -2   1  14   3  -4  16  11   1  14  12  -1  10
 -11   4  -2   2   9  -9 -19 -13         -20     -15  -2  -9 -14  -5 -10 -13  -0   3   6  15
      -5  -3   2  11  -2   0  18   4 -15 -12 -16  -9  -5  -9  -6  11  14  12  16   8   5  12
      -9 -14 -10   0 -13 -10   8  -4     -12  -8  -5   2  -5 -13  -0   5   4   9   6   1   8  ← 6.5/26
  12  14 -19 -20  -0  -5  -2   9   0  -4   2  -7  -6  19  19   2   3   1  -7  -2   3  12  25
  41  32  -7 -18  -5  -6   1  13   2  -1   6  -3  -3  24  30  17  18  17  10   6  -8   4  23
  -2   8  -9 -18 -15     -13   4  -5 -14  -6 -12 -19 -10 -12 -17  -4   5   6   6  -7 -17  -8
 -12  -1 -16 -14   2  -6  -9   6   5   4  15   7  -8  -8 -10  -7  11  17   7   5   0  -7  -4
   6   5 -14  -9  -6                       6  21  18  20  15  12  24  24   8   3   2   1  13
   6  -2  -5   0         -15  42   1          -2  14  23  21  15  22  19   3  -3  -8  -6  15
   8  -9   0  11          39 129  62         -16   6  21  26  28  34  26   6  -5 -13  -8  10  ← 13/26
   6  -2  -5   0         -15  42   1          -2  14  23  21  15  22  19   3  -3  -8  -6  15
   6   5 -14  -9  -6                       6  21  18  20  15  12  24  24   8   3   2   1  13
 -12  -1 -16 -14   2  -6  -9   6   5   4  15   7  -8  -8 -10  -7  11  17   7   5   0  -7  -4
  -2   8  -9 -18 -15     -13   4  -5 -14  -6 -12 -19 -10 -12 -17  -4   5   6   6  -7 -17  -8
  41  32  -7 -18  -5  -6   1  13   2  -1   6  -3  -3  24  30  17  18  17  10   6  -8   4  23
  12  14 -19 -20  -0  -5  -2   9   0  -4   2  -7  -6  19  19   2   3   1  -7  -2   3  12  25  ← 19.5/26
      -9 -14 -10   0 -13 -10   8  -4     -12  -8  -5   2  -5 -13  -0   5   4   9   6   1   8
      -5  -3   2  11  -2   0  18   4 -15 -12 -16  -9  -5  -9  -6  11  14  12  16   8   5  12
 -11   4  -2   2   9  -9 -19 -13         -20     -15  -2  -9 -14  -5 -10 -13  -0   3   6  15
  12  10  -0   3   3 -16     -16     -17  -1  -2   1  14   3  -4  16  11   1  14  12  -1  10
  -2  -6 -12  -4  -5     -11   3  -6   2  23   5 -12  -4 -14 -16  13  20  10  25  21  -3   1
  -3 -12     -10   7  -4  -4   3 -11  -1  19  -4 -15  19  12         -14 -19  -0  12   9  23
  19  -2      -6  27  17   7   4 -15  -7  14  -5   4  66  62  -4             -15   6  20  49
```

ab plane, as indicated by the very high temperature factor and the refined z coordinates of O_7 atom (Table 15). Second, the carbonate radical is not spinning at room temperature, though it is expected to start rotation at higher temperature. Third, the carbon atom is displaced from the center (0,0,0) in the ab plane, otherwise a trigonal carbonate group with carbon at the origin (0,0,0) and positionally disordered in a field with four-fold symmetry will form twelve equally spaced peaks rather than four. Moreover, the relatively high temperature factor of C atom (Table 15), the square-shaped plateau of electron density around the origin on the ab plane (Plates 6 and 8) and the slightly shorter bond length of the C-O bond (Table 16) also suggest that the C atom is displaced off and disordered around the origin (0,0,0) on the ab plane. Another piece of evidence supporting the positional disorderings of the carbonate group is the abnormally high temperature factor of the oxygen atom at O_7 of the CO_3 group (Table 15), which is of course not really due to thermal vibration of the said atom (Stout and Jensen, 1968). It is, therefore, concluded that, as indicated in Fig. (16), the carbonate group is disordered mainly in the ab plane, taking one of the possible positions in space and time in the structure of meionite.

The calcium coordination polyhedron in meionite is just like the sodium coordination polyhedron in marialite and has coordination number of eight (Chapter 5) instead of six

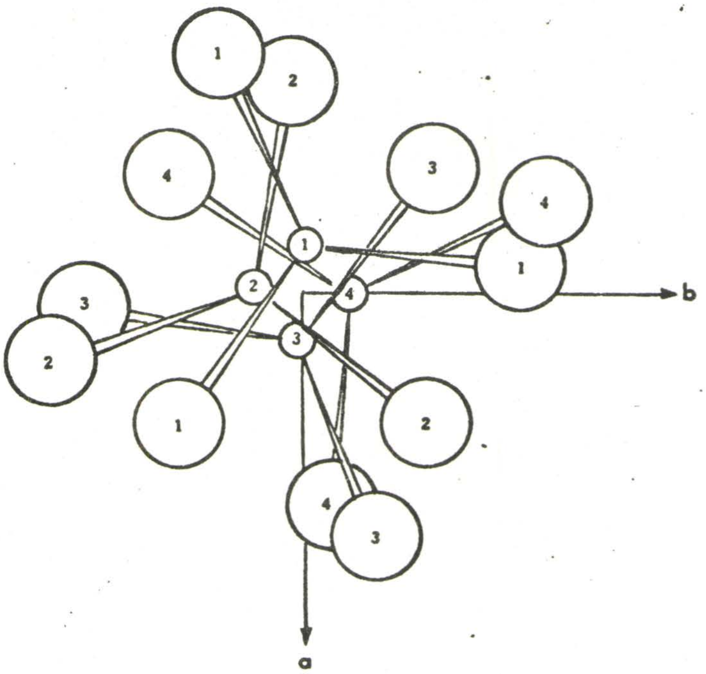


Fig. 16. The scheme of the positional disordering of carbonate group around the origin (0,0,0) and on the ab plane.

(Papike and Stephenson, 1966). The calcium atom in meionite is coordinated by seven oxygen atoms in the tetrahedral framework, together with an eighth oxygen atom of the carbonate group (Table 16b). As illustrated in Figure (17),two of the oxygen atoms are coordinated to one calcium atom each and the other oxygen is shared by two calcium atoms, for each one of the four disordered orientations of the carbonate group. The principal difference between the coordination of calcium in meionite and sodium in marialite is that in meionite the eighth atom in the cation-coordination polyhedra is oxygen (O_7) from the carbonate group, while in marialite the eighth atom is chlorine at the origin (0,0,0). Moreover, this principal difference is also a main factor producing a significant change between the x, y parameters of sodium in marialite and calcium in meionite, because the oxygen (O_7) in meionite and the chlorine in marialite are almost located on the (001) plane, but have greatly different x,y coordinates.

The final temperature factors refined according to the space group $P4_2/n$ are found to show a greater similarity to those of the scapolites ON8 and XL than those refined according to the space group I4/m. Likewise, these temperature factors also fall into three distinguishable size groups, related to the crystal chemical nature of the atoms, as already discussed in Chapter 5.

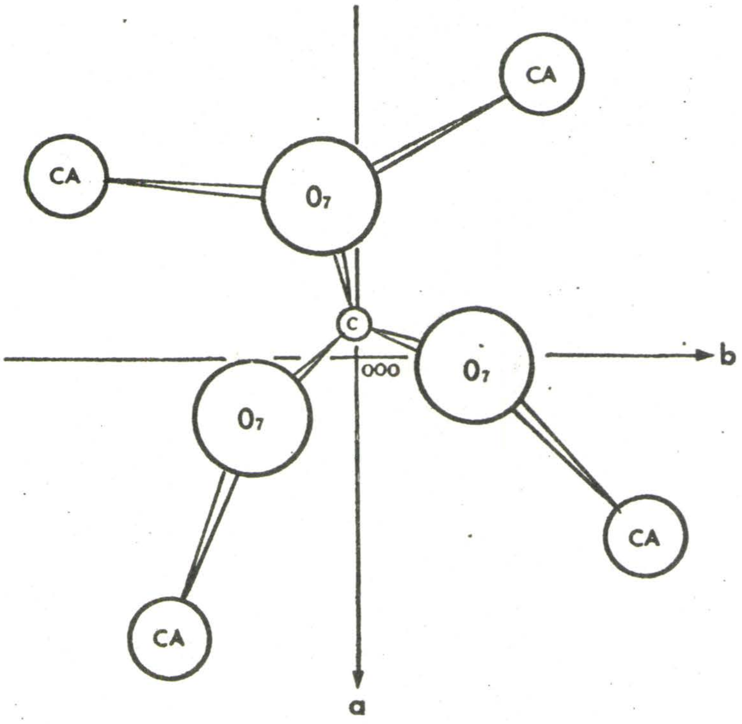


Fig. 17. The scheme of chemical bonding between the calcium atoms and the carbonate group in the scapolite structure.

CHAPTER 7

THE CRYSTAL STRUCTURE OF AN INTERMEDIATE SCAPOLITE

1) Introduction:

The successful least-squares refinement of the structure of scapolite ON8, described in Chapter 5, has shown that the crystal structure of ON8 can be considered as distorted, and hence deviates to some extent, from the body-centred structure. Although the refinement result of ON8 based on space group $P4_2/n$ turns out to be satisfactory and reasonable, it still necessitates further confirmation by systematic investigations of more scapolites, because it is well known that a precise determination of a pseudosymmetric crystal structure is difficult due to the much weaker extra reflections and the high correlation among the structural parameters. Therefore, a further sample, the well-known yellowish-gem scapolite of Tsarasaotra, Madagascar (specimen XL) was selected because of the following reasons:

(a) The superlattice reflection with $h+k+\ell=2n+1$ of this scapolite XL is much stronger than that displayed by the specimen ON8, so that the relationship between the structural distortion and the intensity of the extra non body-centred reflections will be better elucidated and of course, expected to confirm the determined pseudosymmetric structure of the specimen ON8.

(b) Scapolite XL has an intermediate composition around 50% Me with more Al atoms than scapolite ON8 has, and it should assist in understanding the relationship between the distribution of Al in the framework and the intensity of the non body-centred reflections. It has been suggested in Chapter 4 that the intensity of the superlattice reflections may be related to the ordering of the (Si,Al) atoms.

(c) Since the scapolite XL contains both chlorine anion and carbonate radical in about equal quantities, the internal strain caused by Cl, CO_3 substitution will become profound and maximum as suggested in Chapter 4. Therefore, a corresponding complexity in the environment of the site of the anion (Cl,CO_3) is expected and will be elucidated.

2) Unit Cell and Space Group:

As stated previously, the space group of the scapolite specimen XL of Tsarasaotra, Madagascar was clearly observed to be $P4_2/n$ with about three times stronger ($h+k+\ell=2n+1$) reflections than those of the scapolite (ON8) of Gooderham, Ontario.

The yellowish-gem scapolite of Tsarasotra, Madagascar has been reported to have an intermediate composition, i.e., around 50% Me (Lacroix, 1922; Gossner and Brückl, 1928). The present specimen XL is also a transparent, yellowish prismatic single-crystal having a size about 0.7 cm×0.7 cm×2 cm. The unit cell dimension was found to be $a = 12.1164$ Å, $c = 7.581$ Å, $V = 1112.98$ Å^3, by using a least-squares refinement of the powder pattern data. Its refractive indices were measured by using the immersion method, to be $\overset{n}{b}_o = 1.570$, $n_e = 1.549$, with a mean refractive index corresponding to a composition of 49.1% Me (Shaw, 1960a). However, more detail about the chemical composition should be known for a complete structural analysis and refinement of the crystal structure. The specimen XL was thus later analyzed by using an Acton electron microprobe with the scapolite specimen ON70 as a standard which has previously been analyzed (Evans et al., 1969) and is also yellowish of gem quality with a composition close to the specimen XL. The operating conditions for analysis were: 15 KV accelerating potential, 150 n amp specimen current, quartz $(10\bar{1}1)$ spectrometer for Ca, quartz $(10\bar{1}0)$ spectrometer for K, and mica spectrometer for the rest of elements to be analyzed; 10-second counts recorded digitally on scalers and reproduced on a typewriter. Likewise, the carbon content was obtained by using the crystallochemical relationship that the total number of anions (Cl) and radicals ($CO_3^=$ and $SO_4^=$) in one unit should be equal to two. Sodium was not analyzed since volatilization easily occurred. However, the sodium content can be well evaluated from the fixed crystallochemical relationship that the total number of metallic cations in the unit cell of scapolite structure should be equal to eight. All minor elements, such as Fe, Mg, Mn, Sr, etc., are neglected because of their practically insignificant quantities present in scapolites.

The results of the microprobe analysis of the specimen XL are shown in Table (19). A column represents the result with corrections for fluorescence, absorption and atomic number applied by using the computer program "EMPADR VII" (Rucklidge and Gasparrini, 1969). The B column represents the result without these corrections. Accordingly, the specimen scapolite XL has 52% Me according to the results of microprobe analysis. It can be seen that there is actually no significant difference between A and B.

The specific gravity of this scapolite was determined to be 2.69 on a Berman torsion balance. Using the determined specific gravity, the cell volume and the microprobe analysis in the A column of Table (19), its unit cell contents were calculated and listed in the Table (20).

Table (20) The Unit Cell Contents of the Scapolites of Tsarasaotra, Madagascar.

Cation 1	Number per cell	Cation 2	Number per cell	Anion 1	Number per cell	Anion 2	Number per cell
Si	14.986	Ca	4.172	O^-	51.9	Cl	0.732
Al	8.690	K	0.457			$SO_4^=$	0.374
		Na	3.310			$CO_3^=$	0.867
Total	23.676		7.939		51.9		1.973

Table (19). Microprobe Analysis of the Scapolite of Tsarasaotra, Madagascar

A*				B*			
Oxides & anion	Wt. %	Atomic proportions based on (Si+Al=12)		Oxides & anion	Wt.%	Atomic proportions based on (Si+Al=12)	
SiO_2	49.93	Si	7.596	SiO_2	49.80	Si	7.522
Al_2O_3	24.57	Al	4.404	Al_2O_3	25.16	Al	4.478
CaO	12.97	Ca	2.113	CaO	12.80	Ca	2.072
K_2O	1.19	K	0.231	K_2O	1.17	K	0.225
Na_2O	5.61	Na	1.656	Na_2O	5.82	Na	1.703
Cl	1.44	Cl	0.370	Cl	1.43	Cl	0.367
SO_3	1.67	S	0.191	SO_3	1.68	S	0.191
CO_2	2.11	C	0.439	CO_2	2.15	C	0.443
		O	26.304			O	26.255
Total	99.49			Total	99.91		

Note: *The scapolite (ON70) was used as standard and corrections for absorption, fluorescence, and atomic number have been applied.

**The scapolite (ON70) was used as standard but corrections for absorption, fluorescence, and atomic number have not been applied.

3) Intensity Data Collection

Single-crystal X-ray diffraction intensity data were collected with a normal beam single-crystal GE XRD6 diffractometer equipped with 1/4 circle scintillation counter and a pulse-height analyzer. Zr-filtered MoKα radiation was employed. Of the 1730 hkℓ reflections measured, 360 have intensities less than three standard deviations from the intensity of the background and were regarded as unobserved reflections. Those "observed" reflections were then corrected for Lorentz and polarization effects. The programs used in the crystallographic calculation for collecting diffraction data are all contained in "X-ray 67" Program System for X-ray Crystallography.

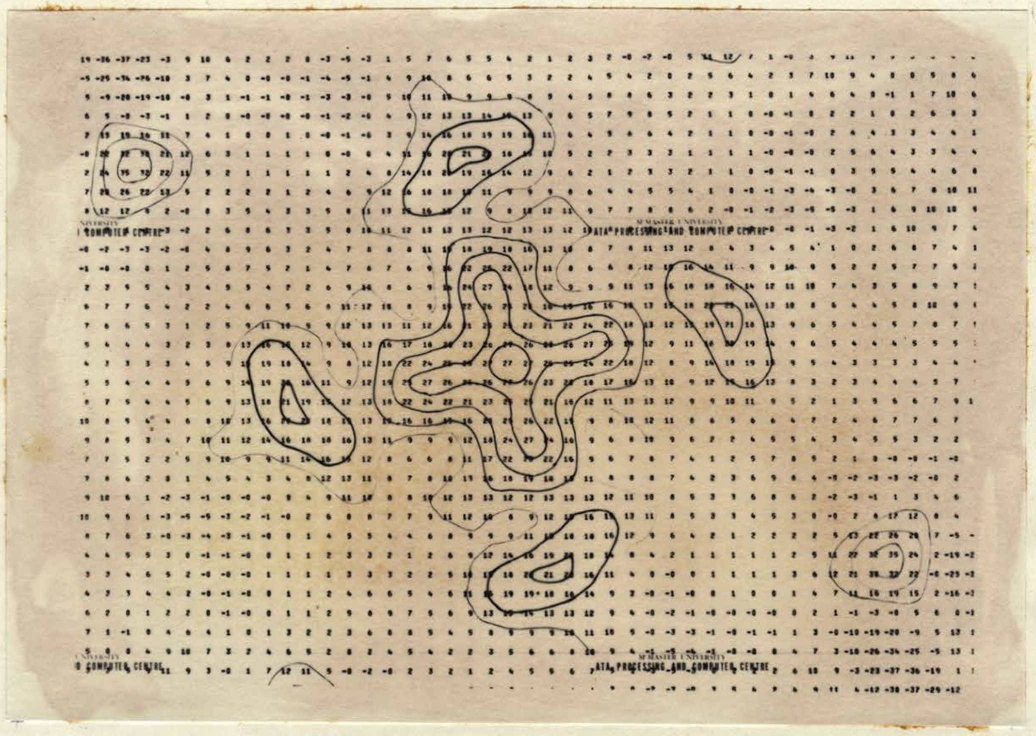
4) Structure Analysis and Refinement

All the atomic scattering curves and computer programs used for structural analysis and refinement of this scapolite (XL, 52% Me) are from the same sources as those used for the structural refinement of the Gooderham marialite (ON8, 19.4% Me; Chapter 5). "Less-thans" were included throughout the whole process of structural analysis and refinement.

The starting model used for this complete analysis and refinement of the scapolite XL was the refined structure of the scapolite (ON8, 19.4%) (Table 11). However some pre-adjustments were made; the coordinates of the oxygen of the carbonate group were not used and the Z coordinates of those atoms lying on the mirror plane in the ideal structure were deliberately placed on the xy planes at z = 0, 1/2. Two cycles of full-matrix least-squares refinement of the scale factors and the positional parameters lowered the R value from 27.4% to 15.7% and shifted all the atoms away from the xy planes at z=0, 1/2. The refinement was continued for six cycles to refine the scale factor, positional and thermal parameters and the R value dropped to 11.4%. Each reflection has been assigned a weight of unity up to this stage of refinement. In order to obtain preliminary information about the disposition of the carbonate group in this crystal, a set of electron density sections were calculated using the parameters from the last refinement cycle. On the $\Delta\rho(xyz)$ section parallel to (001) plane and passing through (0,0,0), four equal peaks around (0,0,0) and one electron-density high at (0,0,0) similar to the features found in the meionite (ON45, 93% Me) (Plate 10) were noted and thought to be contributed from the missing carbonate group. However, the vertical $\Delta\rho(xyz)$ sections parallel to the (100) plane and cutting through these four electron-density peaks present in the above-mentioned horizontal $\Delta\rho(xyz)$ section, have each showed that vertical regions of high electron-density with two unequal peaks each at the opposite end (Plate 11) and the four higher peaks from each of the four electron-density high regions corresponding to

Plate 10. Section of ΔF_o synthesis, parallel to (001) plane and at z = 0.5. The grid positions of the central peak is x = 50/100, y = 50/100, and z = 30/60.

Plate 11. Sections of ΔF_o synthesis, perpendicular to (001) plane and at (a) x = 0.39, and (b) x = 0.53. Note that these sections were actually calculated based on $P4_2/n$ with origin at $\bar{1}$ at 1/4,1/4,1/4 from $\bar{4}$, and x in 100ths y in 100ths and z in 60ths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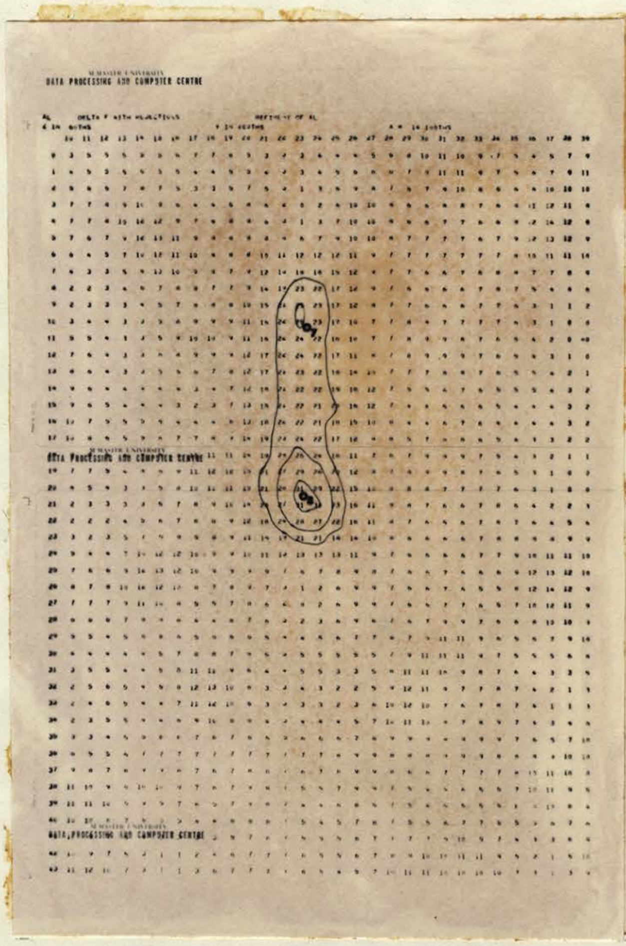
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08
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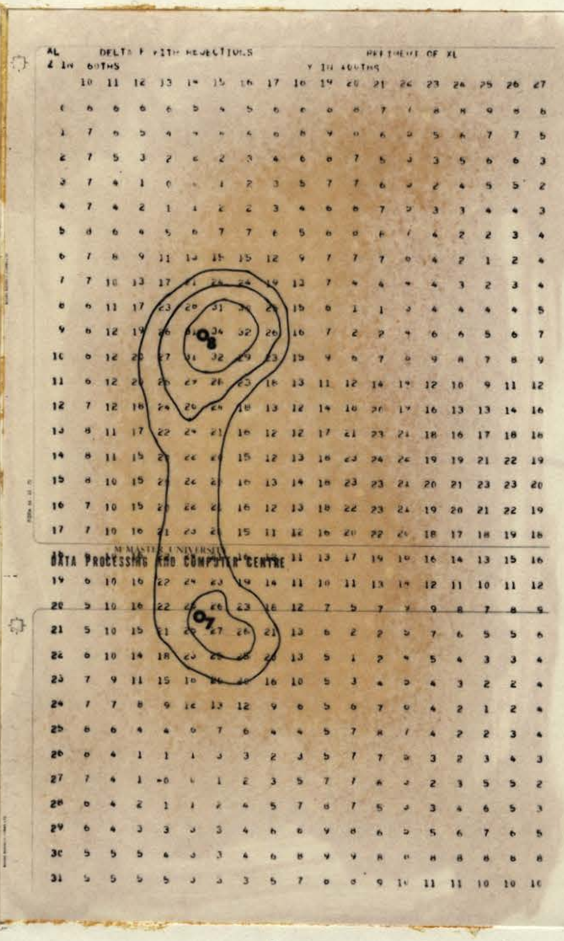
a


AL
DELTA F WITH REJECTIONS
REFINEMENT OF XL
X IN 60THS
Y IN 60THS
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DATA PROCESSING AND COMPUTER CENTRE
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b

the four peaks around (000) in the (001) plane (Plate 10) are alternatively above and below the (001) plane. It is quite unlike the case of the carbonate group in the meionite (specimen ON45), in which the carbonate group is obviously disordered and confined to the (001) plane (Chapter 6). Because the orientation of the carbonate group was rather uncertain at that moment, the writer has anticipated a change of attitude of the carbonate group in order to correspond to the change of the space group. It was thus decided not to conclude this problem until more confirmation was obtained in the later stages. Therefore, the least-squares refinement was continued for three more cycles by using a modified Cruickshank weighting scheme and the R value dropped to 9.9%. At this point, analysis of data revealed that some intense reflections, especially those at low reflection angles, appeared to be seriously affected by extinction effects (Stout and Jensen, 1968). With deletion of these bad data, the R factor dropped to 9.2% after one cycle of least-square refinement. Then the same set of electron-density sections used to reveal the position of the carbonate group as mentioned above were prepared again using the parameters derived in the last cycle. They still displayed exactly the same features as just described above. As a preliminary test the oxygen atoms of the carbonate group were then assumed to disorder in only one set of equivalent sites with starting parameters: x = 0.39, y = 0.45, z = 0.50, B = 6.0, Allowing z to vary two cycles of least-squares refinement were then executed and the result showed that 0^- of the carbonate group significantly moved away from the xy plane at z = 0, 1/2 (i.e., equivalent to the mirror plane in I4/m space group) with a change of z from 0.50 to 0.52, and meanwhile, its temperature factor abnormally increased to 11.96, although the R value slightly decreased to 8.8%.

With the results of these tests, combining the geometrical analysis of the possible disordered pattern of CO_3 groups and (Ca,Na) cations (this will be illustrated in the next section (5)), the writer concluded that the trigonal-planar carbonate groups become inclined to the (001) plane in this intermediate scapolite instead of being parallel to the (001) plane as in the meionite crystal (ON45), and the two highs in the vertical sections of the electron-density (Plate 11) do represent the images of oxygen atoms resulting from disordering of inclined carbonate group taking one of the four possible tilted positions in space and time. Therefore, the oxygens of the carbonate group were separately assigned to two different sets of equivalent sites. They are:

O_7^-: x=0.395, y=0.480, z=0.400, B-6.0, m=0.14

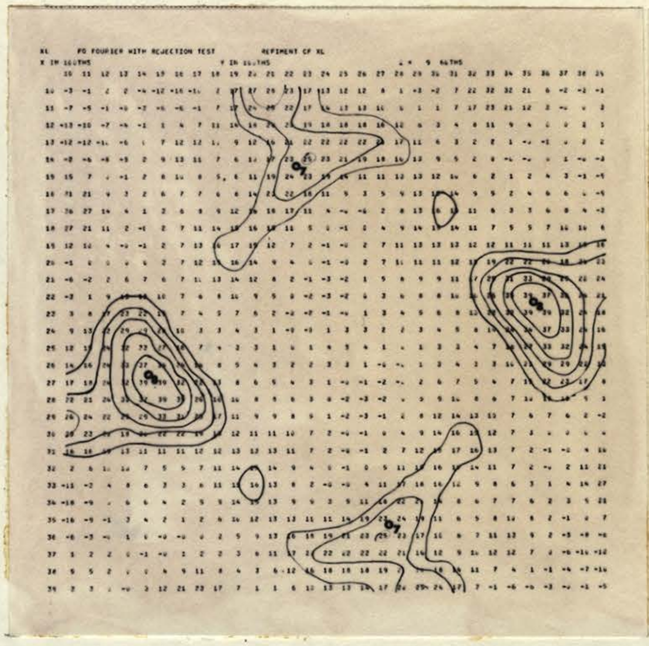
O_8^-: x=0.395, y=0.480, z=0.600, B=6.0, m=0.28

where m is the population ratio and is inferred from the content of CO_3 in the crystal, the approximate relative ratio between areas and heights of the two electron density peaks (Plate 11) and the disordering configuration of the carbonate group to conform with the observed electron density distribution (discussed in next section). When the contribution from these two oxygen atoms O_7^- and O_8^- is included, the R value dropped from 9.2% to 8.7% before the subsequent refinement was executed, while one subsequent cycle of refinement further reduced the R value to 8.6%, and the temperature factors of both O_7^- and O_8^- decreased to 3.1 and 4.0 respectively. $\rho(xyz)$ sections at z=0.4, 0.5, 0.6 were then calculated to show the spatial distribution of the carbonate group (Plates 12,13a) while the corresponding peaks formerly present in the corresponding $\Delta\rho(xyz)$ sections largely disappeared except the one at $z = 0.5$.

In order to test the validity of the population ratios (m) of O_7^- and O_8^-, one cycle of least-squares was run in which population ratios of O_7^- and O_8^-, all positional and thermal parameters except those of O_7^- and O_8^- were allowed to vary, the result showed that both population ratios of O_7^- and O_8^- and R remained nearly the same (M of $O_7^- = 0.16$, M of $O_8 = 0.28$, $R = 8.6\%$).

The dimensions of individual tetrahedra were then calculated by using a set of parameters derived in the cycle before the last cycle. Then by applying the curve prepared by Smith & Bailey (1963), the Al, Si occupancy of each tetrahedral site was assigned. With these assignments four additional

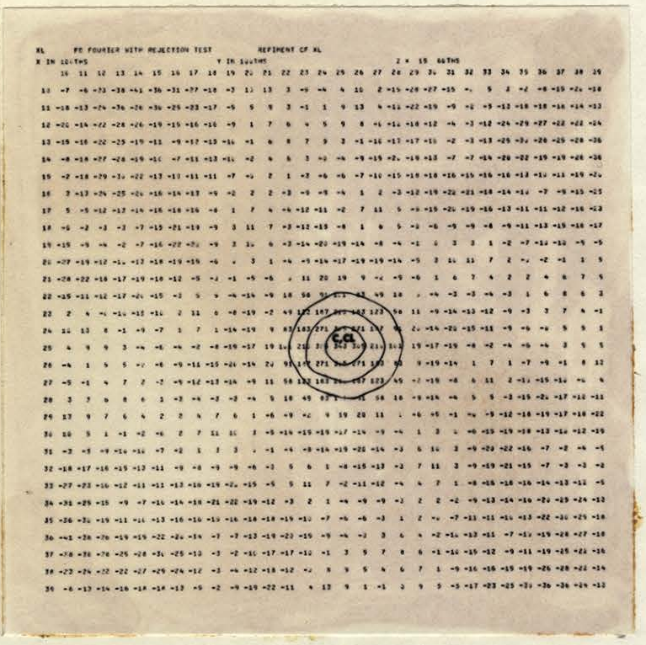
Plate 12. Adjacent sections of an F_o synthesis. Sections run x = 35/100→64/100 down, y = 35/100→64/100 across, at (a) z = 0.4, (b) z = 0.5, and (c) = 0.6.



XL FO FOURIER WITH REJECTION TEST REFIMENT OF XL

X IN 100THS Y IN 100THS Z = 9 60THS

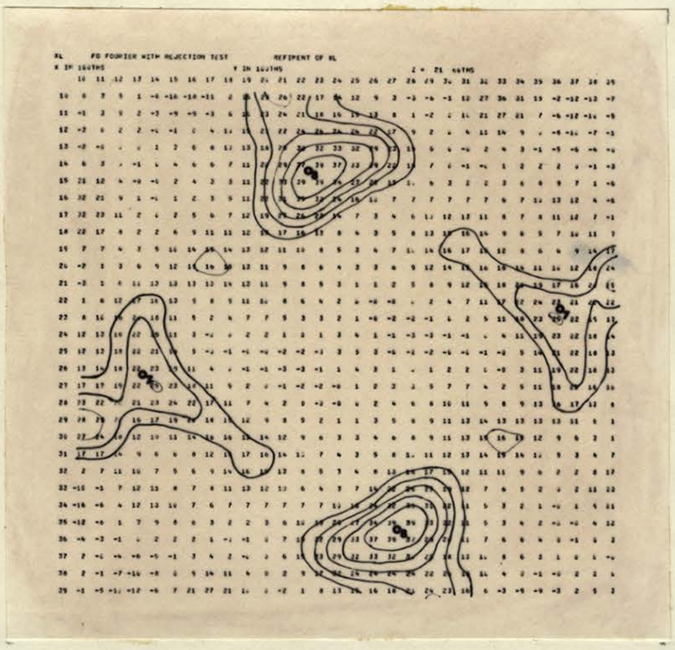
a



XL FO FOURIER WITH REJECTION TEST REFIMENT OF XL

X IN 100THS Y IN 100THS Z = 15 60THS

b



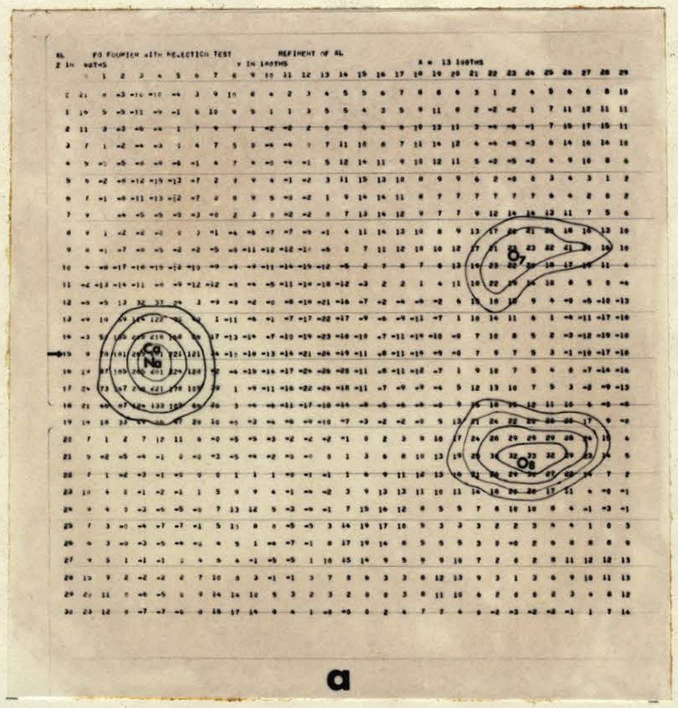
XL FO FOURIER WITH REJECTION TEST REFIMENT OF XL

X IN 100THS Y IN 100THS Z = 21 60THS

c

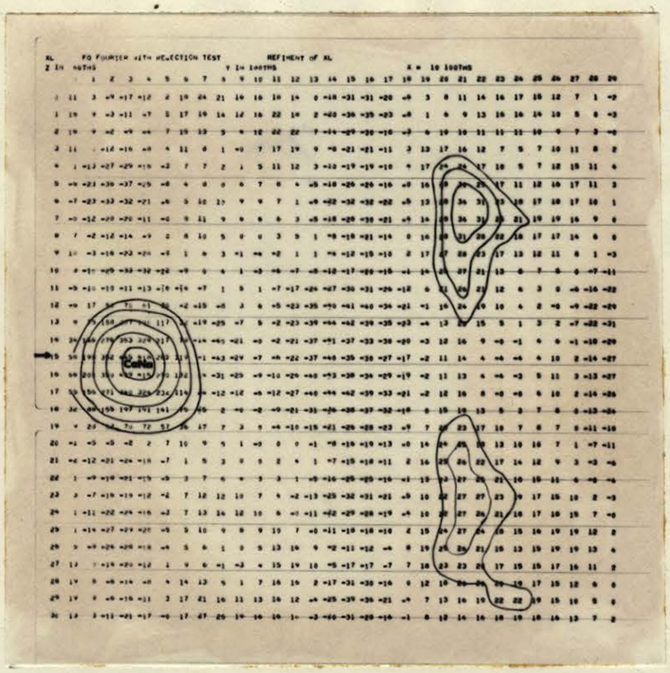
Plate 13. Adjacent sections of an F_o synthesis. Sections run y = 25/100→49/100 across, z = 15/60→45/60 down at (a) x = 38/100, and (b) x = 35/100.

Note: All these sections of F_o synthesis were actually calculated based on $P4_2/n$ with origin at $\bar{1}$ at 1/4, 1/4, 1/4 from $\bar{4}$.



XL FO FOURIER WITH REJECTION TEST REFINEMENT OF XL
Z IN 60THS Y IN 100THS X = 13 100THS

a



XL FO FOURIER WITH REJECTION TEST REFINEMENT OF XL
Z IN 60THS Y IN 100THS X = 10 100THS

b

cycles of least-squares were run, giving a final R = 8.3% for all observations including those with $|F_o|<|F_{o_{min}}|$.

5) Result and Discussion

The final refined parameters of the crystal structure of the scapolite (52% Me) of Tsarasaotra, Madagascar are listed in Table (21), together with those of the scapolite (19.4% Me) of Gooderham, Ontario (Chapter 5). The calculated structure factors and the scaled observed structure factors from the last cycle of least-squares refinement are listed in the Appendix (III). The important interatomic distances and angles are respectively contained in Tables (22 and 23), and can be fully evaluated by referring to Figures (18), (8) and (9).

The geometrical features of the crystal structure of this 52% Me scapolite which has strong superlattice reflections is the same as the scapolite (ON8, 19.4% Me) which was already described in Chapter 5, except that the former deviates more from the body-centred structure. The vertical edges of the T_1 tetrahedra of which the (type 1) four-membered ring are composed, deviate from being parallel to the c-axis, and of course, these four T_1 tetrahedra also no longer lie on the same (001) plane because both $(Si,Al)_1$ atoms and the O_1 atoms migrate away from the (001) plane. The difference in

Table (21). Final Atomic Coordinates and Isotropic Temperature Factors in Scapolites

Atoms	Parameters	ON8	XL	Changes
(Na,Ca,K)	X	0.3659(3)	0.3603(2)	0.0056
	Y	0.2884(3)	0.2841(2)	0.0043
	Z	0.5604(4)	0.5126(3)	-0.0062
	B	2.68 (6)	1.89 (3)	0.79
(Cl,C,S)	X	1/2	1/2	
	Y	1/2	1/2	
	Z	1/2	1/2	
	B	3.85 (12)	1.88 (7)	1.97
$(Si,Al)_1$	X	0.3390(1)	0.3390(1)	0.0000
	Y	0.4100(1)	0.4092(1)	0.0008
	Z	0.9989(3)	0.9978(3)	0.0011
	B	0.69 (3)	0.51 (2)	0.18
$(Si,Al)_2$	X	0.6621(2)	0.6593(2)	0.0028
	Y	0.9152(2)	0.9155(2)	-0.0003
	Z	0.7956(2)	0.7967(2)	-0.0011
	B	0.79 (4)	0.61 (3)	0.18
$(Si,Al)_3$	X	0.4145(2)	0.4125(1)	0.0020
	Y	0.8368(2)	0.8363(1)	0.0005
	Z	0.7085(2)	0.7103(2)	-0.0018
	B	0.63 (4)	0.57 (2)	0.06
O_1	X	0.4574(4)	0.4576(3)	-0.0002
	Y	0.3511(4)	0.3503(3)	0.0008
	Z	1.0011(7)	1.0019(7)	-0.0008
	B	1.39 (8)	1.03 (5)	0.36
O_2	X	0.6939(4)	0.6902(5)	0.0037
	Y	0.8797(4)	0.8757(5)	0.0020
	Z	0.0048(7)	0.0088(7)	-0.0040
	B	1.25 (7)	1.13 (8)	0.12
O_3	X	0.3486(6)	0.3498(4)	-0.0012
	Y	0.9448(5)	0.9420(4)	0.0028
	Z	0.7898(6)	0.7947(6)	-0.0049
	B	1.48 (10)	1.38 (7)	0.10
O_4	X	0.5499(5)	0.5459(5)	0.0040
	Y	0.8475(5)	0.8472(5)	0.0003
	Z	0.7163(6)	0.7160(7)	0.0003
	B	1.49 (9)	1.25 (8)	0.24

(continued on next page)

Table (21) (continued)

Atoms	Parameters	ON8	XL	Changes
O_5	X	0.2706(5)	0.2677(5)	0.0029
	Y	0.3699(5)	0.3667(5)	0.0032
	Z	0.8277(6)	0.8307(7)	-0.0030
	B	1.30 (9)	1.45 (8)	-0.15
O_6	X	0.3710(6)	0.3703(5)	0.0007
	Y	0.7282(6)	0.7287(5)	0.0000
	Z	0.8270(7)	0.8256(7)	0.0014
	B	1.47 (10)	1.28 (8)	0.19
O_7	X		0.3978(50)	
	Y		0.4793(52)	
	Z		0.4598(78)	
	B		4.63 (1.03)	
O_8	X		0.4007(30)	
	Y		0.4819(30)	
	Z		0.5871(46)	
	B		3.99 (64)	

Table (22). Interatomic Distances in Scapolite (52% Me; Tsarasaotra, Madagascar)

(a) (Si,Al)-O and O-O Distances of Tetrahedra:

Tetrahedron	T-O Distances (Å)			O-O Distance (Å)		
	Atoms	Multiplicity	Distance	Atoms	Multiplicity	Distance
T_1	O_1	1	1.604(4)	O_1-O_5	1	2.648(7)
	O_5	1	1.617(6)	$O_1-O_{1'}$	1	2.666(5)
	$O_{1'}$	1	1.620(4)	$O_1-O_{6'}$	1	2.620(7)
	$O_{6'}$	1	1.639(6)	$O_{1'}-O_5$	1	2.674(7)
				$O_{1'}-O_{6'}$	1	2.656(7)
				$O_5-O_{6'}$	1	2.606(8)
	Average		1.620(5)	Average		2.645(7)
T_2	O_2	1	1.720(6)	O_2-O_4	1	2.847(7)
	O_4	1	1.717(6)	$O_2-O_{3'}$	1	2.784(7)
	$O_{3'}$	1	1.730(6)	$O_2-O_{5'}$	1	2.743(8)
	$O_{5'}$	1	1.734(6)	$O_4-O_{5'}$	1	2.722(8)
				$O_4-O_{3'}$	1	2.912(8)
				$O_{3'}-O_{5'}$	1	2.882(8)
	Average		1.725(6)	Average		2.815(8)
T_3	O_3	1	1.620(6)	O_3-O_4	1	2.705(8)
	O_4	1	1.622(6)	O_3-O_6	1	2.607(8)
	O_6	1	1.651(6)	$O_3-O_{2'}$	1	2.713(7)
	$O_{2'}$	1	1.623(6)	O_4-O_6	1	2.698(8)
				$O_4-O_{2'}$	1	2.631(7)
				$O_6-O_{2'}$	1	2.596(7)
	Average		1.629(6)	Average		2.658(7)

Table (22) (continued)

(b) Selected Interatomic Distances

Type	From	To	Multiplicity	Distance (Å)
Environment of (Na,Ca,K)	(Ca,Na,K)	(Cl,C)	1	3.117(2)
		$O_{2'}$	1	2.347(5)
		$O_{3'}$	1	2.518(6)
		$O_{4'}$	1	2.491(6)
		O_5	1	2.842(6)
		$O_{5'}$	1	2.675(6)
		$O_{6'}$	1	2.838(6)
		$O_{6'}$	1	2.971(6)
		$O_{7'}$	1	2.391(63)
		$O_{8'}$	1	2.494(36)
Carbonate Group	C	O_7 or O_8	3	$\leq$1.345(48)
Anion Cage Diagonals	O_1	$O_{1'}$	4	8.467
	O_5	$O_{6'}$	4	8.131
	$O_{2'}$	$O_{2'}$	2	8.091

Table (23). Interatomic Angles in Scapolite (52% Me; Tsarasaotra, Madascar)

Type	Atoms	Angle ± σ
	$O_1-T_1-O_5$	110.60±0.29
$O-T_1-O$ Angles	$O_1-T_1-O_{1'}$	111.54±0.21
	$O_1-T_1-O_{6'}$	107.73±0.28
(T_2 tetrahedra)	$O_5-T_1-O_{1'}$	111.32±0.30
	$O_5-T_1-O_{6'}$	106.30±0.29
	$O_{1'}-T_1-O_{6'}$	109.14±0.28
	$O_2-T_2-O_4$	111.82±0.24
$O-T_2-O$ Angles	$O_2-T_2-O_{3'}$	107.59±0.24
	$O_2-T_2-O_{5'}$	105.11±0.26
(T_2 tetrahedra)	$O_4-T_2-O_{3'}$	115.24±0.28
	$O_4-T_2-O_{5'}$	104.10±0.28
	$O_{3'}-T_2-O_{5'}$	112.56±0.29
	$O_3-T_3-O_4$	113.07±0.29
$O-T_3-O$ Angles	$O_3-T_3-O_6$	105.67±0.29
	$O_3-T_3-O_{2'}$	113.50±0.26
(T_3 tetrahedra)	$O_4-T_3-O_6$	111.03±0.29
	$O_4-T_3-O_{2'}$	108.35±0.25
	$O_6-T_3-O_{2'}$	104.91±0.26
	$T_1-O_1-T_{1'}$	158.43±0.28
	$T_2-O_2-T_{3'}$	139.45±0.28
T-O-T Angles	$T_3-O_3-T_{2'}$	145.30±0.36
	$T_2-O_4-T_3$	147.83±0.35
	$T_1-O_5-T_{2'}$	137.07±0.40
	$T_3-O_6-T_{1'}$	137.61±0.37

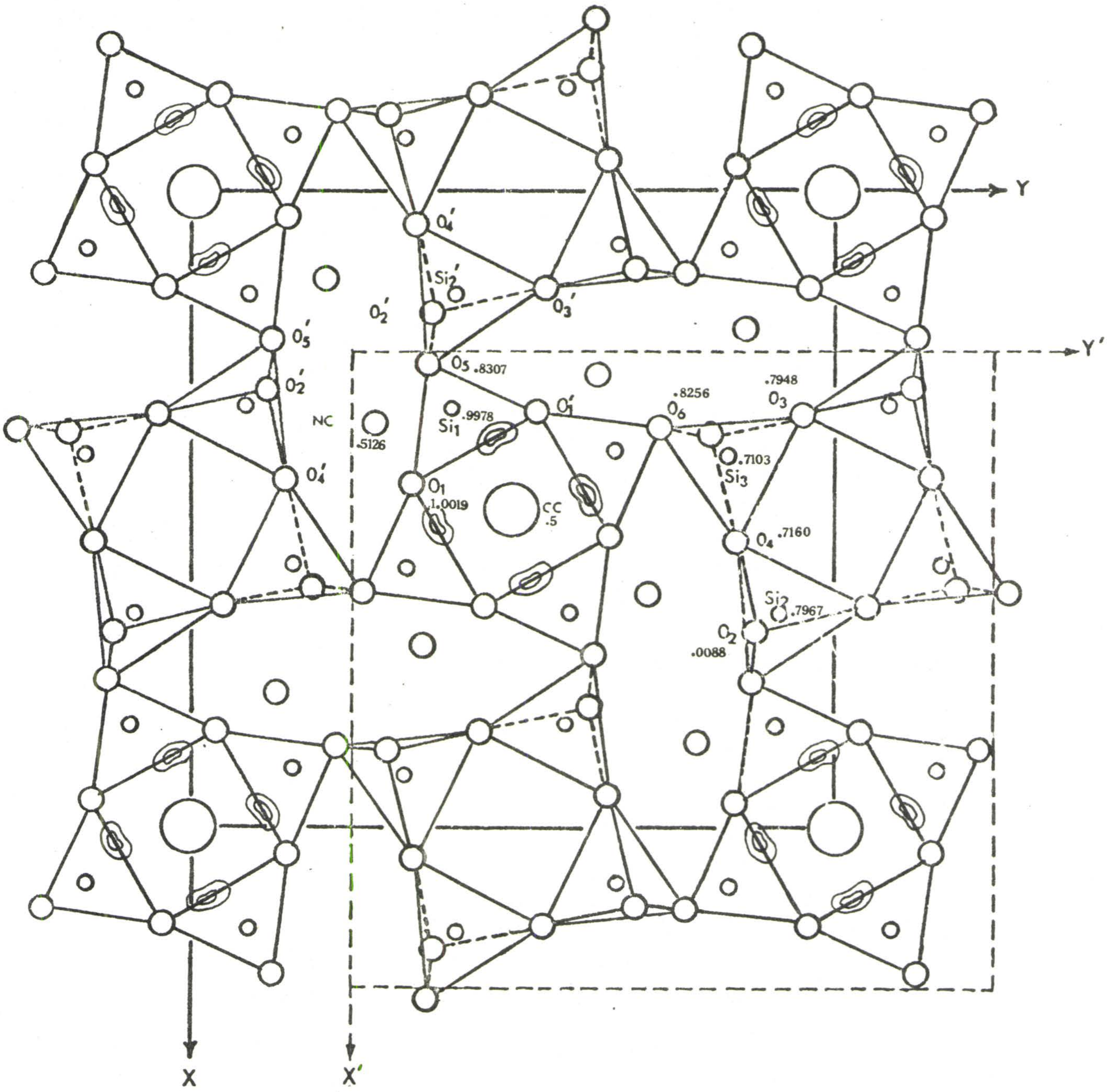


Fig. 18. Projection of the scapolite structure (XL, 52% Me, Madagascar)

physical appearance between the type 1 ring of the real structure and that of the body-centred structure of the scapolite is also illustrated in Figure (7), in which the difference in the horizontal positions between O_5 and O_6 atom is exaggerated for better presentation.

As discussed in Chapter 4, one of two factors causing the superlattice reflections which violate the body-centred symmetry of the scapolite structure, ~~is~~ the factor that those atoms originally located on the mirror planes in the ideal structure displace along the c-axis direction and thus move away from the xy planes at z=0, and 0.5. Moreover, it is to be expected that the intensity of the superlattice reflections will be proportional to the amount of displacement in the c-axis direction from the mirror plane. In Chapter 5, the result of the structure refinement of the NaCl-rich scapolite (19.4% Me) does show that the atoms (Na,Ca), $(Si,Al)_1$, O_1, O_2 more or less all migrate from xy planes at z=0 and 0.5. In this chapter, the result of the structure refinement of the present intermediate scapolite (52% Me) with strong superlattice reflections, again shows that these same atoms mentioned above not only displace in the same direction along the c-axis but also move farther away from the xy planes at z=0 and 0.5 (Table 21). This experimental fact thus confirms the conclusion from theoretical considerations in Chapter 4, and this is one of the main aims in studying this scapolite (XL) with strong superlattice reflections. Figure (19) illustrates the proportional relationship between the intensity of superlattice reflection and the atomic displacement from the xy planes at z=0 and 0.5. All these curves pass through the origin in Figure (19), because the atoms concerned will remain on the mirror planes at z=0 and 0.5, if no superlattice reflection violating the body-centred symmetry occurs. Obviously, these empirical plottings are not likely to be linear, considering the complex mathematical relationship which is of no point to be attempted. In addition to the exponential relationship between the intensity of the superlattice reflection and the related atomic displacement along the c-axis direction, the Figure (19) also implies that the z coordinate of the (Ca,Na,K) atom is the most easily affected during the distortion of crystal structure; the next is the O_2 atom, and so on. In another way, it implies that a small z-coordinate displacement of the atoms O_1 and $(Si,Al)_1$ will enormously increase r, the ratio of the total intensity of the superlattice reflection $(h+k+\ell=2n+1)$ to the ordinary reflection $(h+k+\ell=2n)$.

Similarly to the structures of the NaCl-rich scapolite (ON8, 20% Me) and the $CaCO_3$-rich scapolite (ON45, 93% Me), the T_2 and T_3 tetrahedra are more distorted than the T_1 tetrahedron. Even the sequences of the lengths of the edges and the cation-anion distances in each of the coordination polyhedra

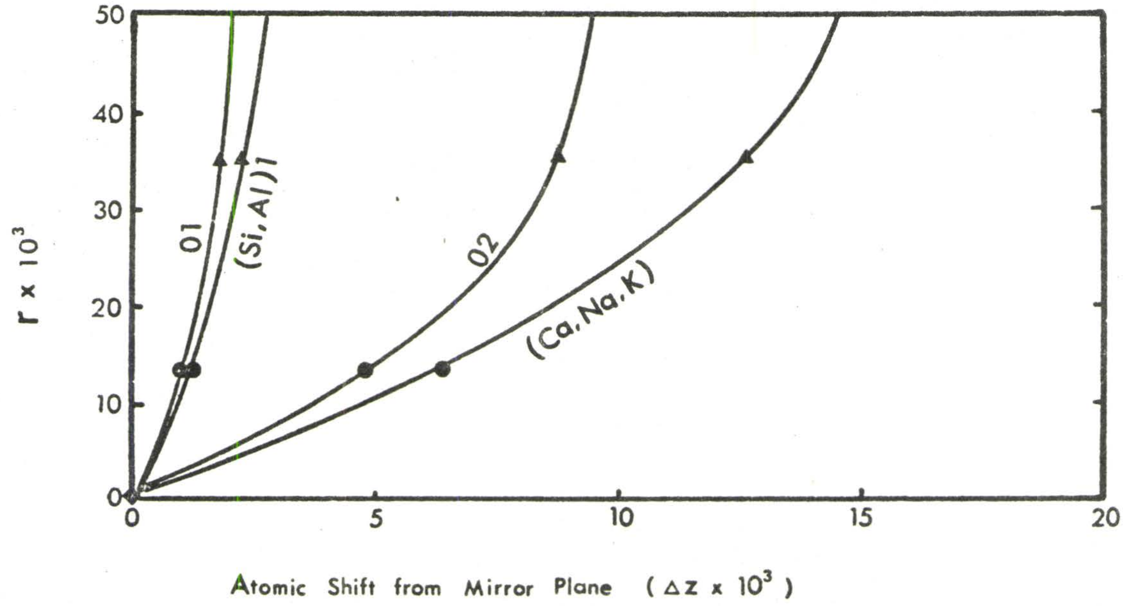


Fig. 19 Relationship between the intensity ratio of superlattice reflections to ordinary reflections, namely $r = \Sigma I_{h+k+\ell=odd} / \Sigma I_{h+k+\ell=even}$, and the atomic displacement from the mirror plane consistent with the space group I4/m. Triangles represent the data of scapolite XL; dots represent the data of scapolite ON8, and the square represents the case of scapolite with no, or extremely weak, superlattice reflection.

are almost the same as those in the corresponding coordination polyhedra in the other two scapolites mentioned above. All these facts indicate that the structural refinements of these three scapolites are in good consistency, because corresponding bonds and edges of the coordination polyhedra in each similar structure should have a similar local environment, e.g., corresponding edges shared by two coordination polyhedra should be generally shorter than those unshared, and likewise, the relatively long T_3-O_6 and T_1-O_6 bonds can be explained in the same way as proposed in Chapter 5.

Using the mean (Si,Al)-O bond lengths of the three tetrahedra (Table 22) and the curve prepared by Smith and Bailey (1963), the Al, Si occupancy of each tetrahedral site was estimated and listed together with those assigned for the corresponding tetrahedral sites in the crystal structures of the marialite-rich specimen (ON8, 20% Me) and the meionite-rich specimen (ON45, 93% Me) as in Table (24).

The results show that in the 52% Me scapolite XL, Al atoms already start to enter into T_1 sites, as noted in Chapter 6, in order to decrease the probability of forming the unstable Al-O-Al linkage in type 2 rings because there are now about 8.7 atoms of Al in the unit cell of the scapolite XL. Table (24) also shows that Al atoms tend to concentrate in the T_2 sites and at the same time Si atoms tend to concentrate in

Table (24). Al Occupancy (%) in the Tetrahedral Sites and Rings of Scapolites

Scapolite Specimens	Me %	$r\times10^3$	T_1 (Si,Al)1	Type 1 ring	T_2 (Si,Al)2	T_3 (Si,Al)3	Type 2 ring
Marialite (ON8)	20	13.5	0	0	59.3	29.3	44.3
Intermediate Scapolite (XL)	52	35.4	7.4	7.4	82.0	13.5	47.8
Meionite (ON45)	93	*	30.1	30.1	50.1	49.3	49.7

*Extremely small because reflections with $h+k+\ell=2n+1$ could not be observed (see Chapters 3 and 4).

the T_3 sites in the intermediate scapolite which has relatively strong non body-centred superlattice reflections. In other words, the intermediate scapolite has a higher degree of ordering in the distribution of Al, Si atoms than marialite and meionite. As discussed in Chapter 4, the intensity of the superlattice reflections will be proportional to the degree of the substitutional ordering of the Al and Si in the tetrahedral framework of scapolite. The relationship between them can be evaluated through the following comparison. When the scapolite structure based on the ideal space group I4/m is transformed into that based on the pseudosymmetric space group $P4_2/n$ (whether as a result of ordering of Al, Si and/or distortion), a close investigation will reveal an important special feature that the geometrical configuration of the T_1 tetrahedral sites still remains exactly the same (if only ordering occurs) or virtually remains unchanged (if distortion accompanies the ordering), for the following reasons (by referring to Fig. 8):

a) The total number of the equivalent T_1 sites in the unit cell still remains unchanged and is equal to eight.

b) All the equivalent T_1 sites are still on their original position or only slightly off their original mirror positions which are symmetrical, distributed in relation to all those atoms lying on the mirror plane, such as (Na,Ca,K), O_2, etc.

c) T_1 tetrahedra only form the (type 1) four-membered tetrahedral rings in both ideal and pseudosymmetric structures of scapolite.

Therefore, the Al occupancy in the T_1 site will have no contribution to the intensity of superlattice reflection when the ideal structure (I4/m) transforms into the real structure ($P4_2/n$) at a given Al occupancy in the T_1 site and hence is not involved in the relationship between the intensity of superlattice reflection and the order-disorder of Al, Si atoms. On the other hand, the Al occupancies in the T_2 and T_3 tetrahedral sites are directly related to the order-disorder of Al, Si atoms in the scapolite structure. As noted previously (Chapters 4 and 5) in the body-centred structure

(I4/m), the (type 2) tetrahedral four-membered ring is composed of only one kind of tetrahedral site, while in the real structure $P4_2/n$, the same type of tetrahedral ring is composed of two kinds of tetrahedral sites, namely T_2 and T_3. It is obvious that the smaller the difference between the Al occupancy of T_2 site and that of T_3 site the lower is the degree of ordering of the Al and Si atoms, and hence the weaker the intensity of the superlattice reflections. In the extreme case, the Al occupancies of both sites T_2 and T_3 approach equivalence, then T_2 and T_3 sites become identical and the real structure ($P4_2/n$) automatically transforms into the body-centred structure (I4/m). Hence the superlattice reflections violating the body-centred symmetry disappear. So, the intensity of the superlattice reflection must be related in some way to the difference between the Al occupancy of the T_2 site and that of the T_3 site.

The ratios of $\Sigma I(h+k+\ell=2n+1)/\Sigma I(h+k+\ell=2n)$ of scapolite ON8 and XL (Chapter 4) were then plotted against the corresponding differences between the Al occupancy of T_2 and that of T_3 in Figure (20). The line connecting the plotting points of ON8 and XL must go through the origin which corresponds to the case of the body-centred structure (I4/m), and the relationship between them is considered to be virtually linear. However, even more surprising is the outcome

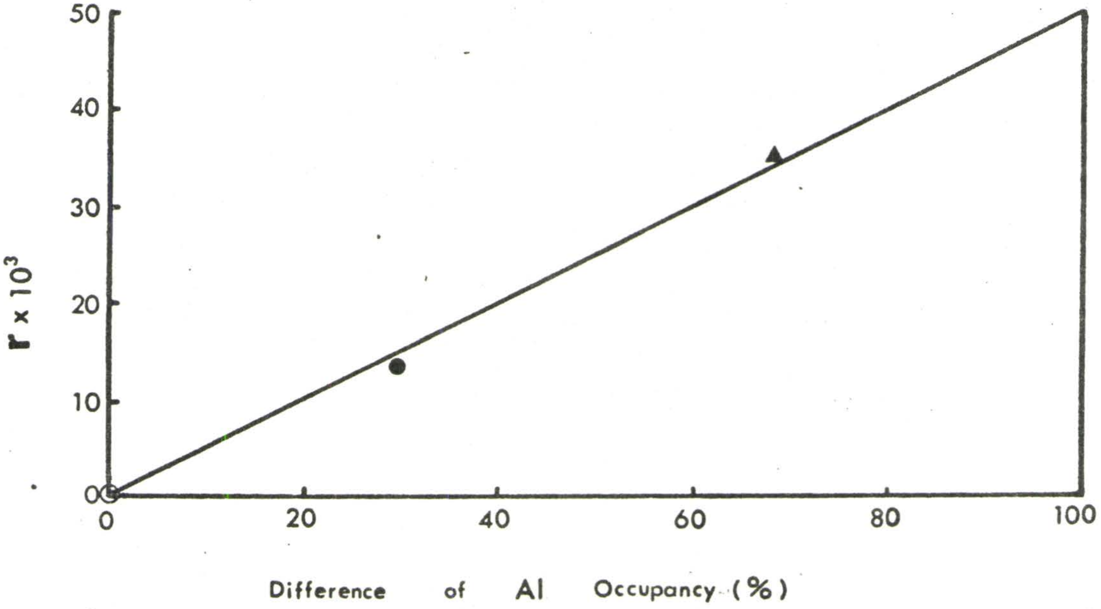


Fig. 20. Relationship between the intensity ratio of superlattice reflections to ordinary reflections and the difference of Al occupancies between T_2 and T_3 sites, where $r = \Sigma I_{h+k+\ell=odd}/\Sigma I_{h+k+\ell=even}$ of (okℓ) spectra (Chap. 4). The triangle represents the data of scapolite XL; the dot represents scapolite ON8; and the circle represents the case of I4/m which has no superlattice reflection.

which the writer had not expected, viz. that when the line is extrapolated to 100% of difference of Al occupancy, the corresponding ratio was found to be 0.05 which is just about equal to the maximum ratio at about 37% Me obtained in Figure (1) of Chapter 4. This good internal consistency indicates that, first, at about 37% Me, scapolite reaches its highest degree of ordering of the Al, Si distribution, i.e. 100% Al in the T_2 site and 0% Al (namely 100% Si) in the T_3 site thus having a 100% difference in Al occupancy; second, 0.05 is probably the highest ratio of $\Sigma I(h+k+\ell=2n+1)/\Sigma I(h+k+\ell=2n)$ (total intensities of superlattice reflections to the total intensities of ordinary reflections), which a scapolite can ever reach; third, the experimental results so far are reliable.

The crystal chemical role of the carbonate group was one of the objects of the study of this intermediate scapolite. The role of the carbonate group in meionite containing very little chlorine and sulphur has been studied in the last chapter, and the results show that the carbonate group is disordered mainly on the xy planes at z=0 and 1/2 taking one of four possible positions in space and time. However, the disposition of the carbonate group in this intermediate scapolite (52% Me) is expected to be more complex than in meionite, because the former contains a significant amount of chlorine to occupy the same crystallographic sites and has strong superlattice non body-centred reflection. So the main concerns are how to locate a group with trigonal molecular symmetry on a crystallographic site with $\bar{4}$ symmetry, and how two very different anions Cl^- and $CO_3^=$ replace each other in an essentially disordered crystal. As pointed out in Chapter 4, there is a sympathetic relationship between the intensity of the superlattice reflection and the amounts of chlorine present in the scapolite. Thus to study the behaviour and environment of the anions is also a key to understanding the relationship between them.

As anticipated, the present study shows that the behaviour of the carbonate group in the intermediate scapolite with strong superlattice reflection is far more complex than in the meionite.

The horizontal sections of $\Delta\rho(xyz)$ and $\rho(xyz)$ show that the oxygens of the carbonate group have the same horizontal coordinates and peak shape as those found in meionite (Chapter 6), while the vertical sections of $\Delta\rho(xyz)$ and $\rho(xyz)$ cutting through these four peaks present on the above-mentioned horizontal sections of electron density, have revealed that each of these four peaks actually has a vertically elongated electron-density high with two unequal peaks at opposite ends (Plate 11). Moreover, the stronger peaks which are about twice as strong as the weaker ones lie alternatively above and below the central xy plane passing through the (C,Cl) site. Therefore it is obvious that the planar carbonate groups in the intermediate scapolite become tilted instead of being parallel to the (001) plane, and their resulting disordered configuration also becomes consistent with the $\bar{4}$ symmetry required by the crystallographic site. In order to interpret the observed electron-density distribution, various possible disordered schemes of the inclined carbonate group have been tried and only scheme (a) has been found to be consistent with the observed electron-density distribution and the required symmetry. The disordered scheme can be neatly demonstrated by the following way, referring to Figure (21).

a)

Quarter Group	I	II	III	IV
1	A	A		B
2	A	B	B	
3		B	A	A
4	B		A	B
Total	2A+B	A+2B	2A+B	A+2B

Where Roman figures represent each quarter on the xy plane; the Arabic figures represent each carbonate group possessing one of the possible orientations; finally A means the oxygen atom of the carbonate group is located above the xy plane at $z=0,1/2$ and B means the said atom is located below the mentioned plane. The resulting configuration of this proposed disordered scheme is consistent with the observed electron-density distribution and the $\bar{4}$ site symmetry. The following are several other unfavorable schemes:

b)

Quarter Group	I	II	III	IV
1	B	A		A
2	B	A	B	
3		A	B	A
4	B		B	A
Total	3B	3A	3B	3A

This one (b) is consistent with $\bar{4}$ symmetry but not with the observed electron density.

c)

Quarter Group	I	II	III	IV
1	A	B		A
2	A	A	B	
3		A	A	B
4	B		A	A
Total	2A+B	2A+B	2A+B	2A+B

This one (c) is neither consistent with the $\bar{4}$ symmetry nor with the observed electron density.

d)

Quarter / Group	I	II	III	IV
1	B	B		A
2	A	B	A	
3		A	B	B
4	A		A	B
Total	2A+B	A+2B	2A+B	A+2B

This one (d) is not completely consistent with $\bar{4}$ symmetry, although it is consistent with the observed electron density.

Another scheme that should be mentioned is a combination in unequal proportions of the scheme (a) and the following scheme (e) which is actually the reverse of scheme (a).

e)

Quarter / Group	I	II	III	IV
1	B	B		A
2	B	A	A	
3		A	B	B
4	A		B	A
Total	A+2B	2A+B	A+2B	2A+B

This combined scheme can also be concordant with the $\bar{4}$ symmetry and even the observed electron-density distribution. However, it seems unlikely to have a significant portion of the scheme (e) in this scapolite (XL) because the observed electron-density ratio of O_7 to O_8 and the refined multiplicity

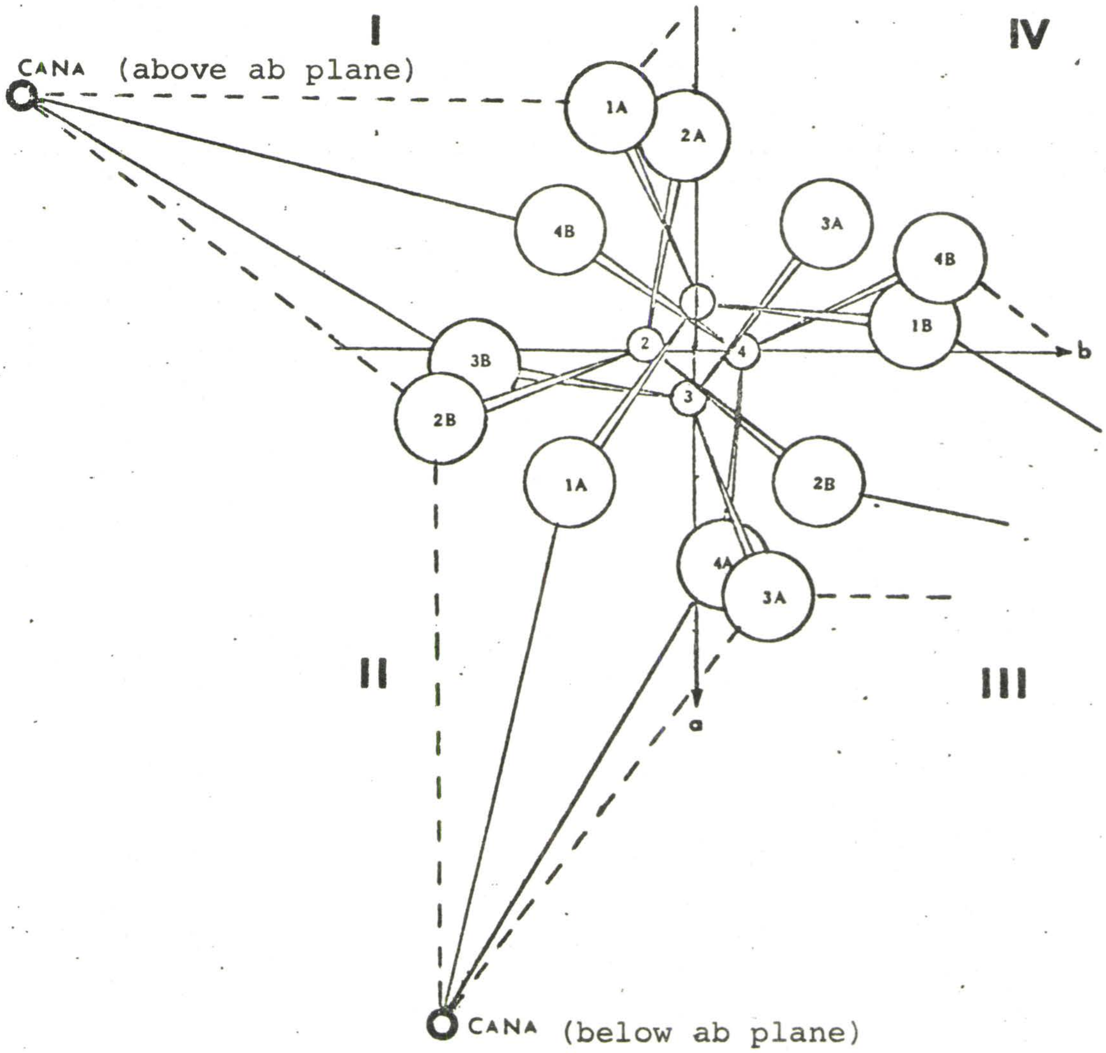


Fig. 21. The disordered scheme of the tilted carbonate groups in the intermediate scapolite.

ratio (or population ratio) of O_7 to O_8 are both nearly 1:2.

The inclined angle to the horizontal plane (001) of majority of the carbonate planar group, taking any of the four orientations according to the disordered scheme (a) and the refined coordinates, was calculated to be 39°, meanwhile, their distance off the crystallographic center (0,0,0) was found to be 0.147 Å. The latter is coincident with the requirement that the carbon of the carbonate groups disordered in the four-fold field should be displaced from the center (0,0,0) in order to give rise to eight peaks rather than twenty four peaks for the same reason as given in Chapter 6.

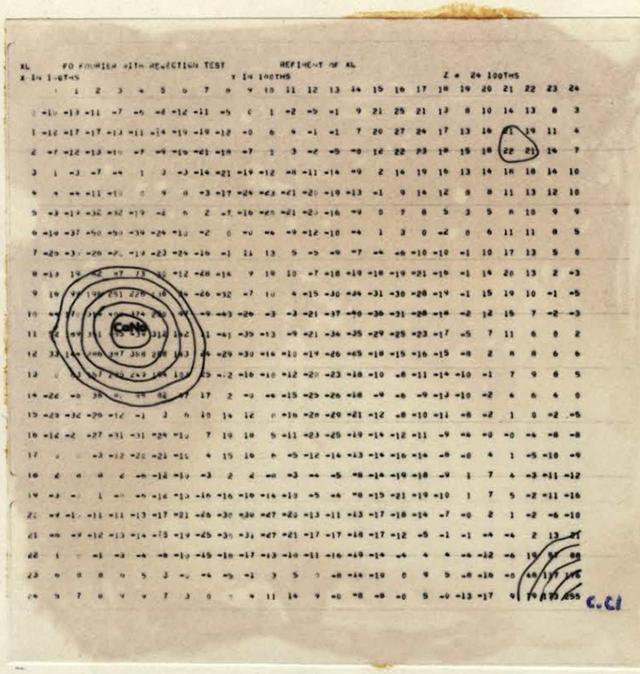
The real C-O bond length of the carbonate group should be slightly less than the mean value of the distance between O_7 atom and the crystallographic center (000) (or $\frac{1}{2},\frac{1}{2},\frac{1}{2}$) and the distance between O_8 atom and the same center, that is $\frac{1}{2}(1.300\ \text{Å} + 1.380\ \text{Å}) = 1.345\ \text{Å}$, because, as mentioned above, the planar carbonate group is slightly off the center by a distance of 0.147 Å. The distance between the O_7 and O_8 atoms both above or below the horizontal plane at $z = 0$ or $\frac{1}{2}$, was found to be 1.788 Å, while the distance between the O_7 and O_8 atoms both in the same quarter was found to be 0.966 Å.

Although $\rho(xyz)$ sections at and near $z=0$ or $\frac{1}{2}$ do not show any peak corresponding to peaks which are shown on the corresponding $\Delta\rho(xyz)$ sections and have similar horizontal coordinates to the carbonate group, it is believed that the inclined angle of the carbonate group could vary in a rather wide range but with the most probable angle of 39° as evidenced by the ΔF(xyz) maps (Plates 11 and 14). The difference of 0.05 between the least-squares refined z coordinate of O_7 atom and that of the O_7 peak on the ρ(xyz) map is not quite certain to be whether due to Fourier shift or not. Besides,according to the microprobe analysis, this intermediate scapolite also contains some sulphate ion ($SO_4^{=}$) in the anion cage, but their atomic positions could not be definitely revealed on the ρ(xyz) and Δρ(xyz) maps. A number of spurious peaks are also present in the anion cavity. In short, the environment of the anion cavity is very complex and still not very certain in the intermediate scapolite in which many anions are all disordered together. Nevertheless, it is obvious that the carbonate group in the intermediate scapolite with strong superlattice reflection becomes tilted, and the present proposed disordering scheme (a) of carbonate group seems to be the most probable one to interpret the observed electron-density and to fit the required symmetry.

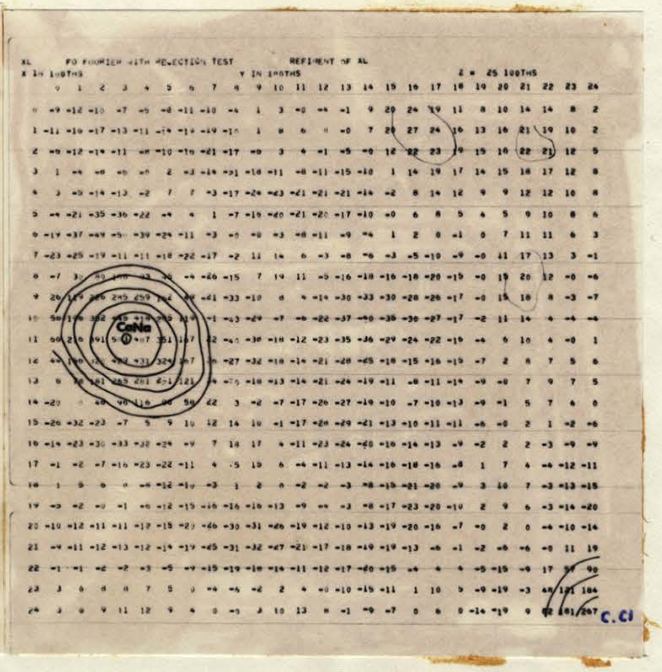
Although the peaks of (Ca,Na,K) atom present in the vertical section of F_o synthesis (i.e. ||(100) plane) appear to be well-defined, non-split, and above the xy plane at z=0 or $\frac{1}{2}$ (Plate 13), the peaks of the same (Ca,Na,K) atom present in the horizontal sections of F_o synthesis (i.e., ||(001) plane) appear to be somewhat elongated along [110] direction, and probably split because the highest point is also not at

Plates 14 a, b, c

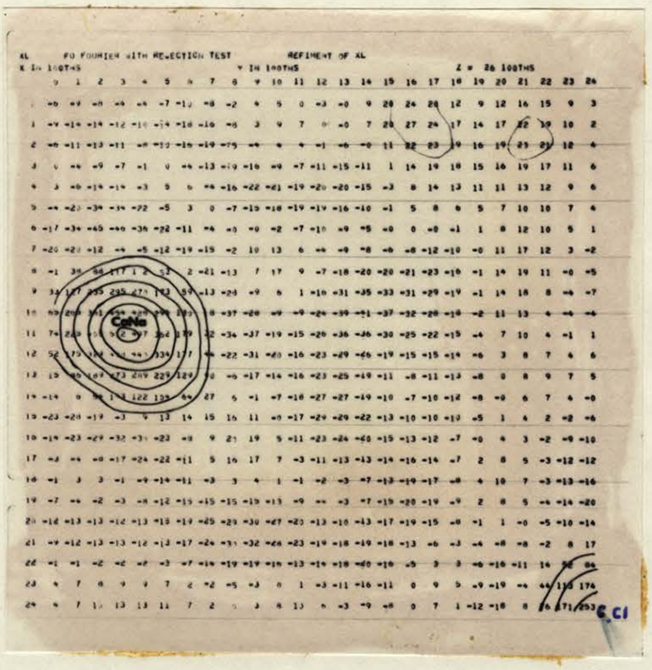
Adjacent sections of an F_o synthesis. Sections run x = 25/100 → 49/100 down, y = 25/100 → 49/100 across, at (a) z = 0.49, (b) z = 0.50, and (c) z = 0.51. Note that these sections of F_o synthesis were actually calculated based on $P4_2/n$ with origin at $\bar{1}$ at $\frac{1}{4},\frac{1}{4},\frac{1}{4}$ from $\bar{4}$.


XL FO FOURIER WITH REJECTION TEST REFINEMENT OF XL
X IN 100THS Y IN 100THS Z = 24 100THS
CaNa
C.Cl

a


XL FO FOURIER WITH REJECTION TEST REFINEMENT OF XL
X IN 100THS Y IN 100THS Z = 25 100THS
CaNa
C.Cl

b


XL FO FOURIER WITH REJECTION TEST REFINEMENT OF XL
X IN 100THS Y IN 100THS Z = 26 100THS
CaNa
C.Cl

c

the center of the whole peak (Plate 14). This phenomenon could be interpreted as the following. The (Ca,Na,K) atoms in some unit cells are coordinated to (C,Cl) atoms at (0,0,0) or $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ site, while (Ca,Na,K) atoms in some other unit cells are coordinated to the oxygen of the CO_3 group. The sum of $\overline{(Ca,Na,K)-O} + \overline{C-O} = 3.7$ Å is much longer than the distance (Ca,Na,K)-Cl $\doteq$ 2.9 Å. Therefore, the (Ca,Na,K) atom coordinated to Cl atom would be closer to the (0,0,0) or $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ site, while those coordinated to oxygen of CO_3 group would be further away from these sites, even when the planar group tilts to offset its larger sum of the vectors $\overrightarrow{(Ca,Na,K)-O} + \overrightarrow{C-O}$ than the vector $\overrightarrow{(Ca,Na,K)-Cl}$.

CHAPTER 8

THE CRYSTAL CHEMISTRY OF THE SCAPOLITE SOLID SOLUTION SERIES

1) General Statement

As a result of the investigation of the space group of eleven scapolites, and the crystal structures of three scapolites as described in the foregoing chapters, the crystal chemistry of the scapolite solid solution series can be fully evaluated. The results show that all scapolites possess the space group $P4_2/n$, except the pure end-members, marialite and meionite, which will possess space group $I4/m$ if they exist. The intensity of the weak superlattice reflections which violate the body-centred symmetry, namely, the spectra with $h+k+\ell=2n+1$ have a sympathetic correlation with the chemical composition of the scapolite. Their intensity continuously increases from zero at the marialite end-member as Me % increases, and reaches a maximum around 37% ± 2% Me, then more or less symetrically decreases to 75% Me, followed by a slower decrease to zero at the meionite end-member. Therefore, all the intermediate scapolites of the marialite-meionite series actually have a pseudosymmetric structure, i.e., a pseudobody-centred structure which really has a primitive lattice, and as the chemical composition approaches both end-members, the structure of the intermediate scapolite approaches the ideal structure with a body-centred lattice. The weak superlattice reflections violating body-centred symmetry are directly related to the following two structural factors: (1) the relative order-disorder of Al and Si distribution in the tetrahedral framework and (2) the structural distortion from the body-centred symmetry. Specifically, the intensity of these non-body centred reflections is almost linearly proportional to the difference of Al occupancy between T_2 and T_3 tetrahedral sites, and is exponentially proportional to the c-axis direction displacements of some atoms, e.g., Na, Ca, etc., from the mirror planes which are consistent with the space group I4/m. As evidenced from the various X-ray photographs and experimental facts, all the scapolites are homogeneous single crystals with long-range disordering, and thus the marialite-meionite series is a continuous, perfect solid solution (isomorphous) series. Submicroscopic twinning and the domain disordering are unlikely, and of course, unmixing will not occur in the marialite-meionite series. The order-disorder operating in the scapolite system, unlike that in the feldspar system, only involves continuous changes of atomic arrangement essentially within a single homogeneous phase which is again further controlled by basic crystallochemical factors. Hence there is only a continuously transitional, and slight structural variation in the unit cell as both composition and temperature change, without any abrupt change of the crystal structure. The so-called basic crystallo-chemical factors which control the ordering-disordering and hence the structure variation involved in the scapolite system will be further elucidated in the following sections.

2) The Al-Si Distribution in the Marialite-Meionite Solid Solution Series and its Relationship to Unstable Al-O-Al Linkages

Although only three scapolites have been structurally analyzed, the Al-Si distribution in the tetrahedral sites along the entire range of the marialite-meionite solid solution series can be well established through consideration of the following relationships and results:

(a) The relationship between the superlattice intensity ratio $r(\Sigma I_{h+k+\ell=2n+1}/\Sigma I_{h+k+\ell=2n})$ and the chemical composition index % Me (Fig. 1, Chapter 4).

(b) The relationship between the same ratio r and the difference between Al occupancy at T_2 and T_3 site (Fig. 20, Chapter 7).

(c) The mean Al occupancies (%) of T_2 site and T_3 site can not be greater than 50% (Chapter 5).

(d) The results of the structural analyses and refinements of the three scapolites, namely, samples of ON8 (Chapter 5), ON45 (Chapter 6) and XL (Chapter 7).

(e) The result of chemical analyses of scapolites (Chapter 3).

(f) The stoichiometry of the marialite-meionite solid solution series (Chapter 2).

Figure (22) is such a diagram constructed on the above-mentioned criteria. First of all, the Al occupancies of the three scapolite samples (from (d)) were plotted. It shows that Al does not occupy the T_1 site in the 20% Me scapolite . Then from (a), the maximum r was found to be around 37% Me, and the difference in the Al occupancy between T_2 and T_3 corresponding to this composition was also found to be about 100% from (b), namely, T_2 = 100% Al and T_3 = 0% Al. Now, from the stoichiometry either theoretical or real, the number of Al atoms in one unit cell of a scapolite with about 37% Me will be near to eight, hence the Al occupancy (%) of the T_1 site must be nearly equal to zero. Moreover, the result of (d) shows that Al atoms still do not enter the T_1 sites of the scapolite ON8 (20% Me). According to theoretical stoichiometry, scapolite should contain exactly eight Al atoms at 33% Me and have T_1 = 0% Al, T_2 = 100% Al, T_3 = 0% Al. However, according to the experiment, the corresponding composition of the scapolite is slightly greater than 33.3% **Me**, because of the Al deficiency in scapolites (Fig. 27). It can be, therefore, concluded that the Al atoms only enter into T_2 and T_3 sites between 0% Me and 37% Me. As mentioned previously, both pure marialite and pure meionite have the space group I4/m and thus r equal to zero. Then from the above-mentioned relationship (b), the Al occupancy of T_2 site and that of T_3 site will be equal in pure marialite and meionite. So at the pure marialite end, T_1 will be = 0% Al and T_2=T_3=37.5% Al, and at the pure meionite end T_1=T_2=T_3=50% Al as discussed in Chapter 6. With this information, the general trend of the Al distribution curves of T_1, T_2 and T_3 can be estimated from 0% Me to 37% Me. The details of the T_2 and T_3 curves can be defined with reference to the above-mentioned facts (b) and (e), because the difference between Al % of T_2 and that of T_3 is known from (b), while their sum is known from (e).

The general trend of the T_1, T_2 and T_3 Al distribution curves in the range from 37% Me to 100% Me can also be derived from the experimentally determined and inferred values at 37% Me, 52% Me, 93% Me and from relationship (b). As discussed previously, in compositions more meoinite rich the 37% Me Al atoms enter into the T_1 site in order to keep the total number of Al atoms in T_2 and T_3 sites not greater than eight per unit cell; in other words to keep the mean Al occupancy of T_2 and T_3 not greater than 50%. Otherwise, the unstable Al-O-Al linkage must start to form. In fact, as shown by the experimental results, the mean Al occupancy of T_2 and T_3 essentially stays at 50%. Therefore, the Al occupancy of T_1 may also be simply derived by dividing the difference between the total Al atoms in one unit cell and eight atoms with the number of

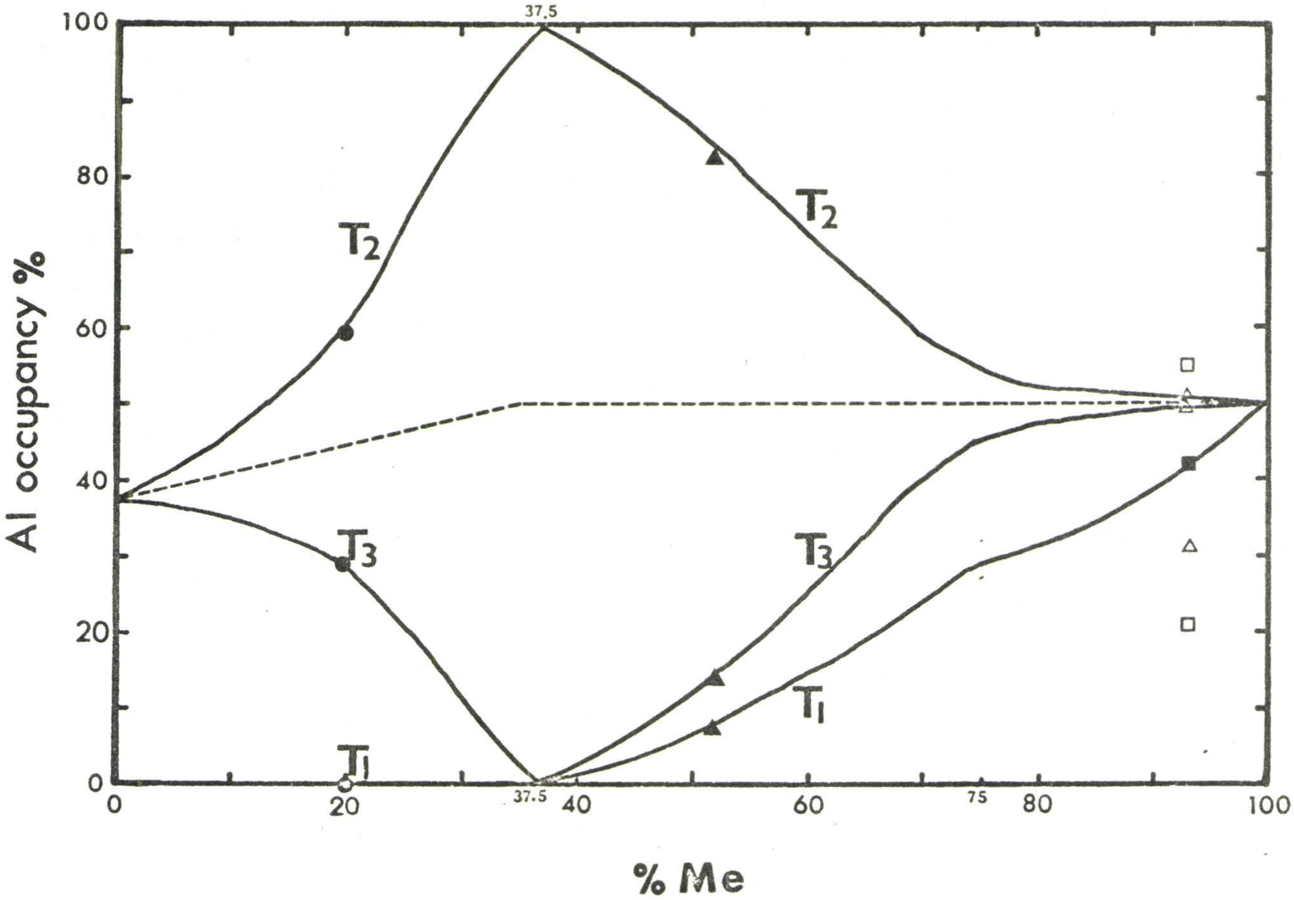


Fig. 22. The Al occupancy (%) of the tetrahedral sites as a function of the chemical composition of scapolites. The dashed line indicates the averaged Al occupancy of T_2 and T_3 sites. Dotes represent ON8; solid triangles represent XL; triangles represent the data from structure refinement of ON45 based on $P4_2/n$, while squares based on $I4/m$. The solid square is derived by dividing the difference between the total Al atoms per unit cell and eight atoms with the number of the general equivalent points.

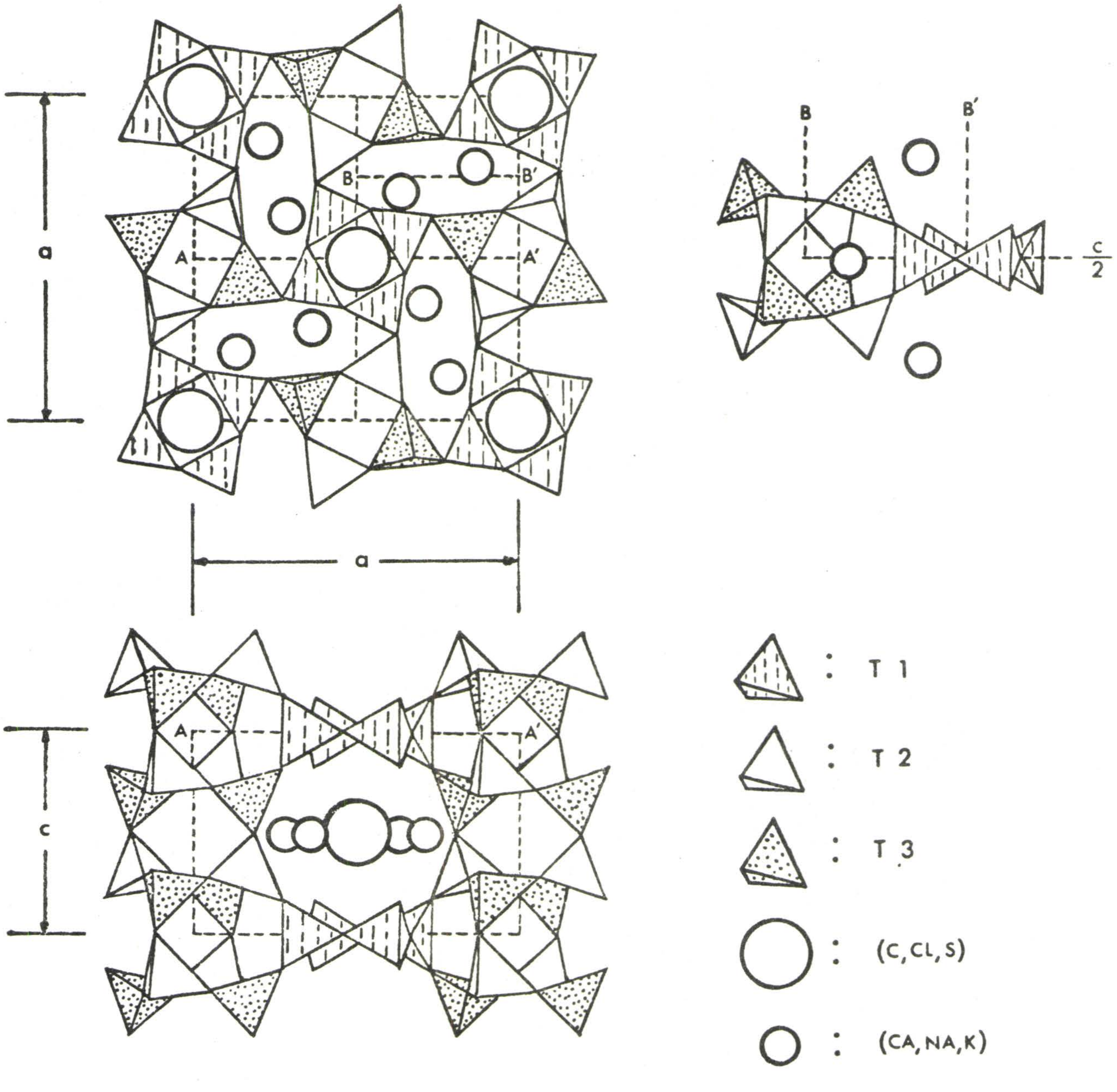


Fig. 23. The crystal structure of scapolites.

the general equivalent points. This forms a smooth curve with an inflection at 75% Me as a result of scapolite stoichiometry. The Al occupancy of T_2 and T_3 sites can also indirectly be known, because the sum of them is equal to 100% Al and the difference between them can be obtained by using the relationships of (a) and (b). The values thus derived, together with the experimentally determined ones form smooth curves with similar inflections as a result of the scapolite stoichiometry to those described by Evans et al. 1969. At 93% Me the discrepancy between the Al % of T_1 derived by the indirect way and that directly from the structure refinement of the scapolite specimen ON45 (Chapter 6) may be ascribed to the various experimental uncertainties or due to a really shorter Al-O bond in scapolite than that given by Smith and Bailey (1963). In fact, it is actually equivalent to a very small discrepancy of about one electron per unit cell. The structure refinement of scapolite with high % Me is difficult because of the unobserved weak superlattice reflections and the high correlation among the structural parameters. The values from the structural refinement of scapolite (ON45, 93% Me) based on space group I4/m are in Figure (22) for comparison.

It would be very interesting and significant to know why the Al atoms distribute in the tetrahedral sites of the scapolite structure according to the manner shown in Figure (22). It is well known that, thermodynamically, an orderly arrangement has a lower entropy and a lower free energy than that of the disorderly one at a lower temperature, and hence is more stable at the lower temperature (Bragg and Williams, 1934; Buerger, 1948). Therefore, the crystal will always tend to crystallize in the more ordered state in order to be as stable as it possibly can.

It is known that within the entire solid solution range, scapolite possesses the most ordered state with $T_1 = Al_{0\%}Si_{100\%}$, $T_2 = Al_{100\%}Si_{0\%}$ and $T_3 = Al_{0\%}Si_{100\%}$ at 37% Me (Figures 22 and 23). However, after 37% Me, the Al atoms must start to enter into T_1 and/or T_3 because the total Al atoms per unit cell will be more than eight as the meionite percentage increases beyond 37%. Now, there is a question why after 37% Me the Al atoms do not continue to occupy all of the T_2 sites, and at the same time, the increasing Al atoms only enter into either T_1 or T_3, or even both of them, in order to keep the configuration of Al and Si as ordered as possible. In other words, why is it that the Al occupancy of T_2 decreases, while those of T_1 and T_3 increase in such a way that all of them are gradually approaching each other and finally all reach the same Al occupancy (i.e., 50% Al) at the pure meionite end-member, thus gradually increasing the degree of disordering? Obviously, the answer to this question is also the answer to the following question. What are the basic factors that cause the structural variation of scapolites or that control the order-disorder transformation across the marialite-meionite isomorphous series?

One of the structural characteristics of scapolite is a ring made up of five tetrahedra (Figure 23). Therefore after 37% Me, no matter whether the increasing Al atoms enter the T_1 site or T_3 site or both of them, the so-called "unstable Al-O-Al linkages" in the framework silicates (Loewenstein, 1954) will be inevitably formed and the density of the Al-O-Al linkage continuously increases all the way up to 100% Me, as long as all the T_2 sites are continuously occupied by Al atoms, i.e., $T_2 = Al_{100\%}Si_{0\%}$. This is why the Al occupancy (%) of T_2 must decrease while those of T_1 and T_3 increase in such a way that the Al occupancies of T_1, T_2 and T_3 sites are approaching each other in order to decrease the density of the Al-O-Al linkage, and all ultimately reach 50% Al at the pure meionite end-member which consequently has a body-centred lattice. In this case, the five-membered ring and the Al-O-Al linkage seem to be the "structural barrier" to inhibit the scapolite solid solution from being more ordered in its atomic arrangement. This is also probably why meionites exist in the disordered state and the completely ordered pure meionite is very unlikely to exist (Chapter 6).

However, in the range from $Ma_{100}Me_0$ to $Ma_{64}Me_{37}$, a more ordered state in which all Al atoms only go into T_2 sites, thus making its Al occupancy increase from 75% to 100%, is found to be not contradictory to the above-mentioned "structural barrier" because the Al-O-Al linkages are not formed. Moreover, even in the range from $Ma_{63}Me_{37}$ to Ma_0Me_{100}, the above-mentioned "structural barrier" does not require that the curves of the Al occupancy of T_2 and T_3 should have the inflections at 75% Me. In other words, the Al occupancy of T_2 and T_3 can linearly approach each other without inflections at 75% Me as long as their mean Al occupancy is not greater than 50%. These phenomena suggest that some other more fundamental crystallochemical factor is controlling the explicit distribution of Al atom in scapolites, and hence the structural distortion of the scapolites.

3) The Al-Si Distribution in the Marialite-Meionite Series and its Relationship to the Strain Between Cl^- and $CO_3^=$

The coordination in the metallic ions (Na,Ca) in scapolites has been discussed and illustrated in Chapter 5 and 6. The (Na,Ca) ion is coordinated by seven oxygen atoms (O_2, O_3, O_4, $2O_5$, and $2O_6$) from $(Al,Si)O_2$-tetrahedral framework, together with chlorine anion or one oxygen of the $CO_3^=$ group in the central anion cage. The coordination polyhedron of (Na,Ca) is believed to be essentially ionic in nature, as evidenced by the satisfaction of Pauling's electrostatic valency principle (Chapter 5). In fact, this proof can be generalized as the following. Let the general formula of the unit cell of scapolite be $(Ca_PNa_{8-P})[Al_{X+Y+Z}Si_{24-(X+Y+Z)}]O_{48}[(CO_3)_QCl_{2-Q}]$ and the x, y and z be the Al occupancy respectively at T_1, T_2 and T_3 tetrahedral sties, then

$x=X/8$, $y=Y/8$, $z=Z/8$.

The total positive electrostatic valencies should be equal to the total negative electrostatic valencies, i.e. the unit cell formula is neutral, so that $X+Y+Z=6+P-Q$ (1)

As stated above, the metallic cation (Ca,Na) is coordinated to O_2,O_3,O_4, two O_5, and two O_6 atoms from the (Si,Al)O_2tetrahedral framework, together with Cl^- or $Co_3^=$ anions (Figs. 9 and 11). Then the electrostatic charges on each of the coordinated atoms are:

$$O_2=O_3=O_4=(-y/4)-(z/4)=-(Y+Z)/32$$

$$O_5=(-x/2)-(y/4)=-(2X+Y)/32$$

$$O_6=(-x/2)-(z/4)=-(2X+Z)/32$$

$$(CO_3,Cl)=-[2(Q/2)+1(2-Q)/2]/4=-(Q+2)/8$$

$$(Ca,Na)=2(P/8)+1(8-P)/8=(P+8)/8$$

Now if the (Ca,Na) coordination polyhedron is ionic, then it should be neutral in respect to electrostatic charges, i.e., the following formula must be equal to zero,

$$(P+8)/8-(Q+2)/8-3(Y+Z)/32-(2X+Y)/32-(2X+Z)/32$$

$$= (P+8)/8-(Q+2)/8-(X+Y+Z)/8$$

(from equation (1))

$$= (P+8)/8-(Q+2)/8-(6+P-Q)/8 = 0$$

It thus becomes evident that the electrostatic charge of this (Ca,Na) coordination polyhedron is always balanced no matter how

Al substitutes for Si in the tetrahedral framework. However, the analysis of the balanced system of the electrostatic forces acting upon the (Ca,Na) atom shows them to be related to the distribution of Al atoms in the $(Al,Si)O_2$ tetrahedral framework.

Figure (24) shows the spatial positions of the oxygen atoms coordinated with (Ca,Na) atom, when viewing the (Ca,Na) coordination polyhedron (Figs. 9 or 11) along the X direction. All the oxygen atoms O_2, O_3 and O_4 are located symmetrically to the xy plane at z = 0, 1/2 on which the (Ca,Na) atom would be located if scapolite had the ideal space group I4/m instead of the real space group $P4_2/n$ as a result of distortion, but the oxygen atoms of O_5 and O_6 respectively possess a spatial distribution asymmetrical to the above-mentioned xy plane and likewise to the (Ca,Na) atom. As shown above, O_2, O_3 and O_4 will have the same negative charge, while O_5 always has a greater negative charge than O_6, because of the Al occupancy of the T_2 site always being found greater than that of the T_3 site (Fig. 22). That is the (Ca,Na) polyhedron is electrostatically polarized in respect to the xy plane at z = 1/2 or 0. Consequently the (Ca,Na) atom will be more strongly attracted by the oxygen atoms of O_5 than by the oxygen atoms at O_6, and thus the (Ca,Na) atom is shifted away from the xy plane at z=0, 1/2. As already discussed in Chapter 4, the displacement along the c-axis of those atoms originally located on the mirror plane at z=0, 1/2 which is consistent with the space group I4/m, may be related to the

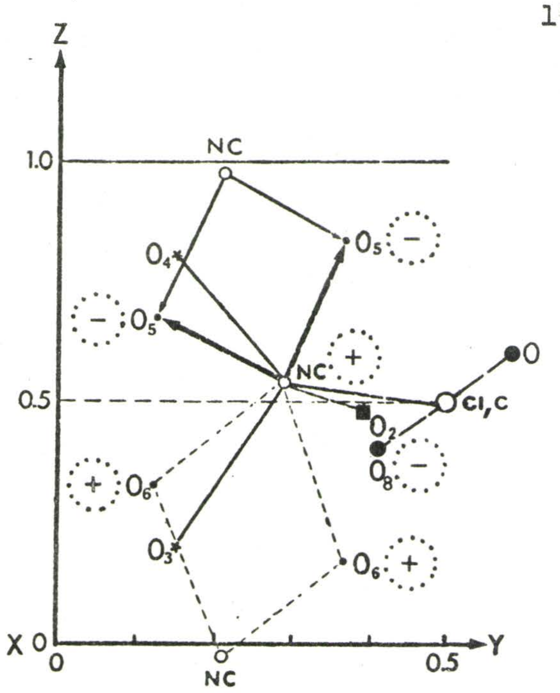


Fig. 24. The electrostatically polarized polyhedron of (Ca,Na) cation ($x < 0.5$, $y < 0.5$, $z > 0.5$), when viewed horizontally along the x-axis direction. Where O_5 atoms are more electrostatically negative than O_6 atoms, and O_2, O_3 and O_4 atoms all have the same electrostatic charge, as a result of Al distribution in the tetrahedral framework to replace Si. NC=(Ca,Na) cation.

ordering of Al in the scapolite. In fact, the proportional relationship between these two structural factors has been verified by the results of the structural analysis and the refinement of three scapolites (Chapters 5, 6 and 7) and is illustrated in Figure (25). Specifically, the displacement along the c-axis of (Ca,Na) atom is proportional to the difference between the Al occupancy (%) of T_2 and that of T_3 (Chapter 7), while the latter is, in turn, related to the net negative electrostatic charges distributed on the oxygen atoms of O_5 and O_6. However, this kind of coupling between the displacement of (Ca,Na) atom and the ordering of Al, in the $(Al,Si)O_2$ framework is considered to be originated from the complexity of the central anion cage,because as already discussed in the last section, the explicit pattern of Al ordering along the scapolite solid solution (Fig. 22) can not be explained in terms of the Al-O-Al linkage.

The complex environment of the central anion cage is created by (1) the internal strain between the two drastically different anions Cl^- and $CO_3^=$ which disorderly possess the same equivalent sites, (2) positional disordering of the trigonal-symmetry CO_3 group in a $\bar{4}$-symmetry field. Investigations of the crystal structures of scapolites (Chapters 5, 6 and 7) have all shown that the disordering of the CO_3 group forms four electron-density peaks with the same x,y coordinates. In fact, this seems to be the only horizontal configuration which will give each CO_3 group four approximately equal bonding

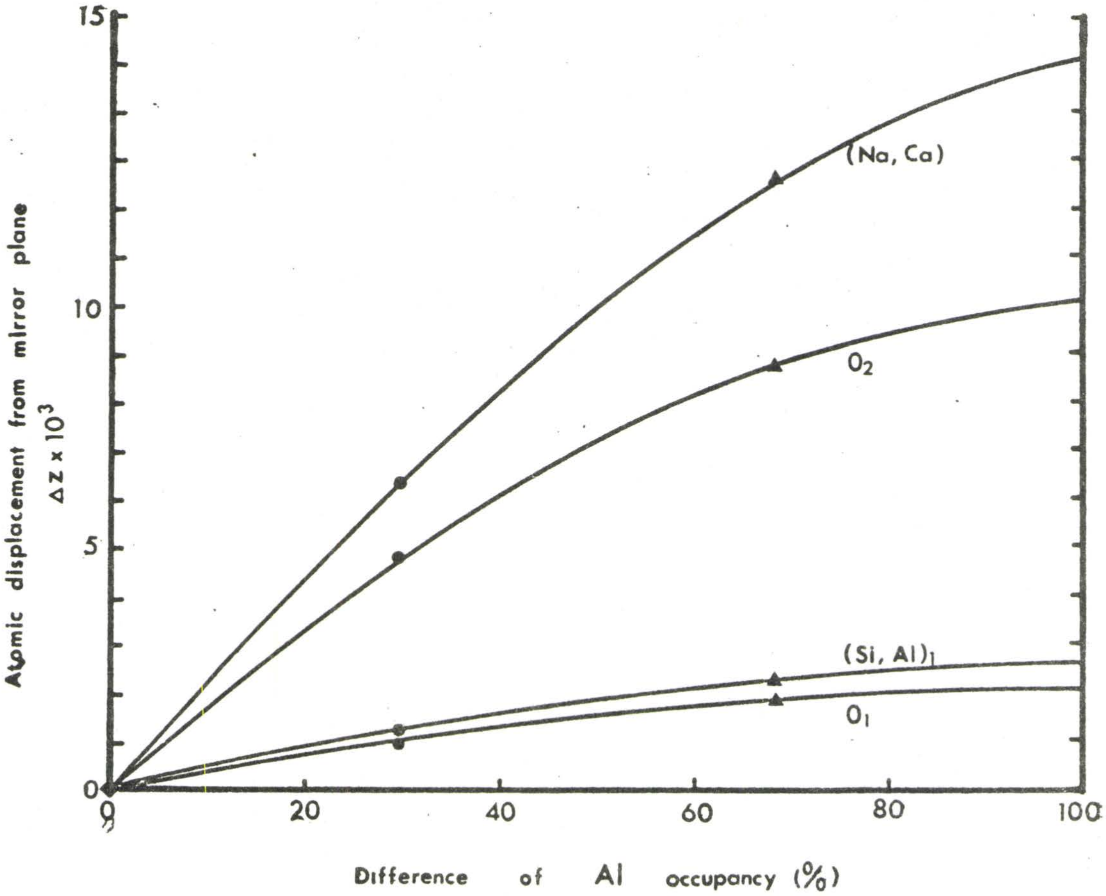


Figure 25. Relationship between the atomic displacement from xy plane at z=0 or 1/2, and the difference of Al occupancy between T_2 and T_3 sites. Triangles represent the data of scapolite (XL,52%Me), dots represent the data of scapolite (ON8, 20%Me); the diamond represents the case with space group I 4/m or with extremely weak superlattice reflection (ON45, 93%Me).

distances between oxygen and (Ca,Na) (Fig. 26). However, the vertical sections of electron density have shown that more CO_3 planar group becomes more inclined to the xy plane and forms a disordering configuration consistent with $\bar{4}$ symmetry when the non body-centred superlattice reflection becomes stronger, at the same time, the amount of Cl and of CO_3 approach each other (Chapter 4). This indicates that the ordering of Al-Si, the c-axis displacement of (Ca,Na), the tilting of CO_3 and the relative amount of CO_3 and Cl in the same scapolite are all inter-related.

As a result of the disordering of the CO_3 group by taking one of the four possible positions in space and time, each disordered Ca or Na atom will be bound to the oxygen of a CO_3 group through one of the four possible ionic bonds, p. q. r. s. as shown in Figure (26). So both (Ca,Na) and CO_3 groups have to adjust themselves in order to make the distances of the four possible bonds p.q.r.s as close to 2.4 A as possible.

In scapolites with composition more meionite rich than 75% Me, $CO_3^{=}$ becomes the dominant anion in the central cavity and Cl^- is insignificant. Therefore, the CO_3 groups are essentially disordered on the pseudomirror plane at z=0 or 1/2 (Chapter 6) (the designation A and B in Figure (26) should be ignored) and thus p.q.r. and s all lie in the same plane. In this case, the (Ca,Na)1 atom shifts (as evidenced in the Figure 14 of Chapter 6) to make p and s approach each other.

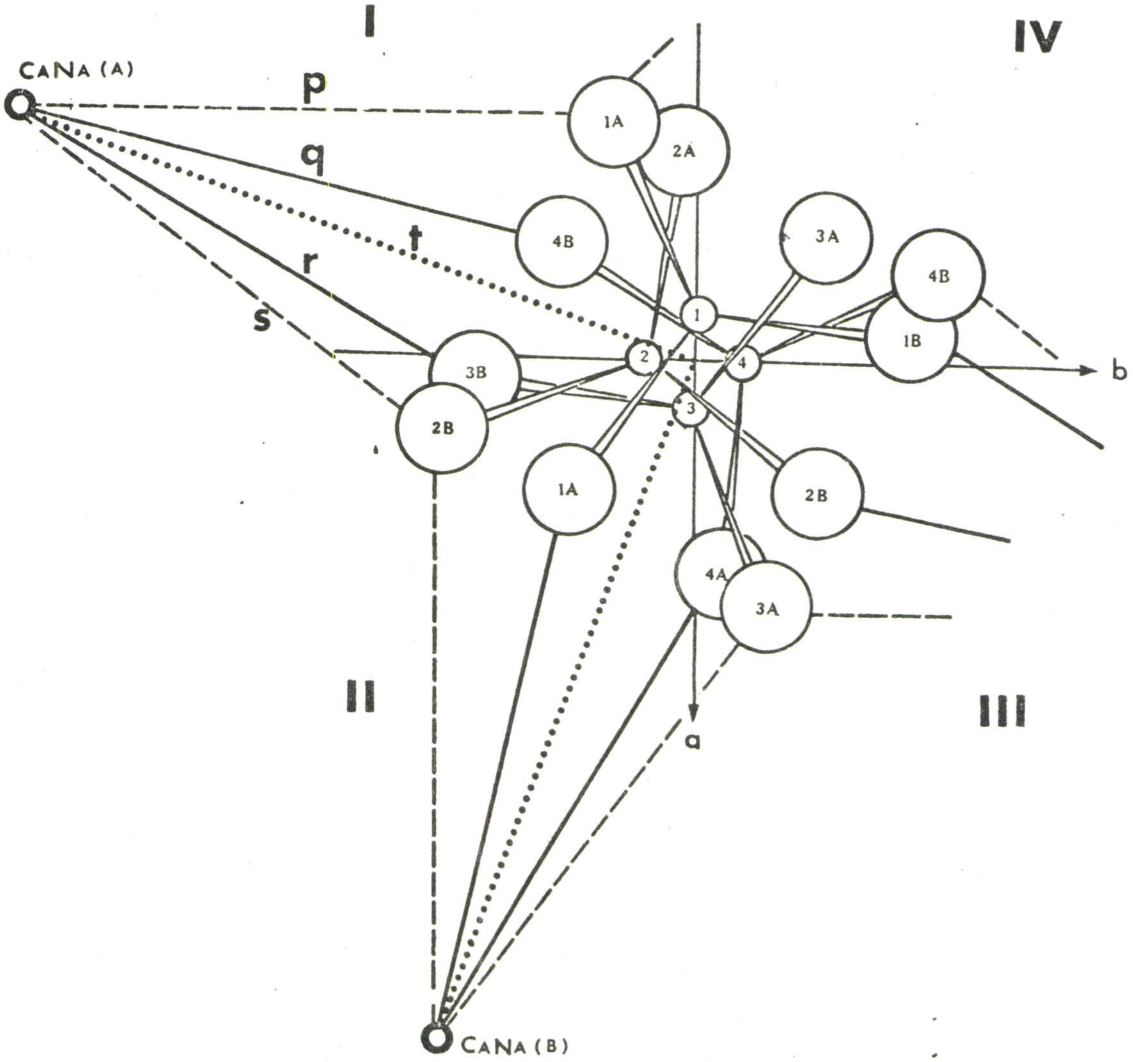


Fig. (26). The bonding relationship between the (Ca,Na) cation and the disordered CO_3 groups in the intermediate scapolite where Arabic figures indicate each single CO_3 group possessing one of four disordered orientations; Roman numerals represent the quarter; A means the oxygen or (Ca,Na) atom to locate above xy planes at z = 0,1/2, while B below the said planes. The lines both continued and dashed, e.g. p.q.r.s, refer to the bonding between the (Ca,Na) and oxygen of CO_3 group. The origin is at (0,0,0) or (1/2,1/2, 1/2) and with site symmetry $\bar{4}$. The two other (Ca,Na) atoms located in the quarters of III and IV are omitted. The Cl anion is also present at the origin and the bonding between the (Ca,Na) and Cl are designated by dotted line, e.g. t.

the atoms 3B and 4B (Fig. 26) are nearer to the origin in order to lengthen q and r so that they approach p and s. Thus 1A, 4B, 3B and 2B are approximately sitting on an arc rather than on a straight line, and (Ca,Na)1 is approximately on the focus to this arc. These are the basic reasons why the carbon atom of the disordered CO_3 groups is actually off its special position (0,0,0) or (1/2,1/2,1/2) in all scapolites and the (Ca,Na) atom displaces in the appropriate direction when a scapolite becomes rich in meionite (Chapter 6).

When both Cl^- and $CO_3^=$ are present in scapolites, the case becomes more complex, because the (Ca,Na) of the same equivalent set must simultaneously be coordinated to both Cl^- anion and the $CO_3^=$ radical whose C atom together with the Cl^- anion occupy the same special equivalent sites, i.e. (0,0,0) and (1/2,1/2,1/2). The typical radius of the concerned ions and the C-O covalent bond length of $CO_3^=$ radical are listed as follows:

$R_{Ca^{++}} = 0.99\text{Å}$, $R_{Na^+} = 0.95\text{Å}$, $R_{Cl^-} = 1.81\text{Å}$, $R_{O^=} = 1.40\text{Å}$ and $C\text{-}O = 1.3\text{Å}$, so the distance $\overline{(Ca^{++}, Na^+)\text{-}O^-} + \overline{C\text{-}O} = 3.7\ \text{Å}$ is much longer than the distance $\overline{(Ca^{++}, Na^+)\text{-}(Cl)} = 2.8\ \text{Å} \sim 3.0\text{Å}$ (the one found in the Cl-rich scapolite with 20% Me is equal to 3.02 Å). Therefore in this case, a 3-dimensional adjustment of the atomic positions of the (Ca,Na) and the oxygen of the CO_3 group has to occur in order to keep all the concerned coordination distances within the reasonable limit. Specifically, in Figure (26) the coordination distances p.q.r.s. and t. should be as near to the general values as possible. Consequently, this may be the reason why the planar CO_3 group is inclined to the xy plane at z=0,1/2. This 3-dimensional readjustment can also be called the "internal strain" between Cl^- and $CO_3^=$,which becomes stronger when the amount of Cl^- and that of $CO_3^=$ approach each other and when the superlattice reflection becomes stronger.

The inclination of CO_3 group will affect the position of (Na,Ca) atom and the distribution of the electrostatic charges on the surrounding $(Si,Al)O_2$ framework,hence the ordering of Al,Si. There are two possible mechanisms related to this: (1) the ordering of Al first responses to the inclination of CO_3 group, and then the polarized (Na,Ca) polyhedron attracts the (Na,Ca) cation off the xy plane at z = 1/2,0. (2) the inclination of CO_3 group directly necessitates the (Na,Ca) cation to shift along the c-axis direction, so that Al ordering is caused to polarize the (Na,Ca) polyhedron in order to attract the (Na,Ca) cation off the xy plane at z = 1/2,0. However, the first mechanism is more likely than the second one. No sound ground or fact has been found to support that the inclination of CO_3 group directly necessitates the displacement of (Ca,Na) cation along the c-axis direction from the xy plane at z = 1/2,0, while the first mechanism can be interpreted based on the local neutralization of the electrostatic charges. By referring to Figs. 24 and 26, when carbonate-group oxygens (O_7 and O_8) which carry much more amount of negative electrostatic charges (-0.67 e) than the framework oxygens coordinated to the same (Na,Ca) cation, lie on the xy plane at z = 1/2,0, the O_5 and O_6 both have the same electrostatic charges. However, when the carbonate-group oxygens become tilted from xy plane at z = 1/2,0, they statistically concentrate below or above the said xy plane. As shown in Figs. 24 and 26, three of the four carbonate-group oxygens statistically coordinated to the $(Na,Ca)_1$ cation, i.e. 2B, 3B, 4B, are located below the said xy plane. Then in order to keep the local neutrality of the electrostatic charge, the O_6 which is also located below the xy plane at z = 1/2,0, will decrease its negative charge, namely become relatively positive. On the other hand, the O_5 which is located above the said xy plane, will become relatively electrostatically negative. This process is accomplished by the ordering of Al in the tetrahedral framework, namely, more Al enter into T_2 sites. Hence, as illustrated in Fig. 24, the $(Na,Ca)_1$ cation is attracted upward and off the xy plane at z = 1/2.

Therefore, summing up the discussion given above, it appears that the ordering-disordering of Al is directly or indirectly related to the internal strain caused by the two greatly different anions, Cl^- and $CO_3^=$, sharing the same set of equivalent sites. The most ordered state of Al distribution in scapolites is coincident with the greatest strain state at 37.5% Me at which there are statistically one Cl^- and one $CO_3^=$ per unit cell, and perhaps these Cl^- and $CO_3^=$ anions even alternately occupy the (0,0,0) or (1/2,1/2,1/2) site.

4) The Possibility of Temperature-Dependent Structural Transitions

The regular relationship between the intensities of superlattice reflections and the chemical composition, as indicated by the smoothness of the curve in Figure (1), implies that the characteristic of this relationship depends on chemical composition rather than on the temperature of formation of the respective scapolite, especially in view of the fact that the samples are from various geological environments and localities. D.T.A. experiments have shown that scapolites do not have any major temperature-dependent structural inversions up to 1050°C except that CO_3 rich scapolites gave a small endothermic peak slightly above 700°C probably indicating the liberation of CO_2 (Kauffman and Dilling, 1950; Papike, 1964). In temperature-dependent disorder transformations the higher temperature yields the disordered structure and the lower temperature yields the ordered structure. The symmetry of the ordered form is a subgroup of that of the disordered form. All the natural scapolites except the pure end-members possess a relatively ordered form with space group $P4_2/n$ at room temperature, and could probably be transformed into a relatively disordered form with space group I4/m above a certain higher temperature. If this order-disorder transformation does exist, then the transition boundary on the temperature-composition phase diagram would be a continuous subsolidus solvus curve (or a transition zone rather than a transition line) extending from one pure end-member to the other end-member. In order to test any temperature-dependent disorder transformation, the scapolites have been heated in sealed capsules at 650°C for ten days and then quenched, however, the X-ray diffraction photos of these heated samples remain exactly the same as those of the unheated one. The intensity of the superlattice reflections has not been lessened. This result probably implies that there is no profound order-disorder transformation until near the dissociation point. Specifically, the $P4_2/n$ structure of scapolite may be stable all the way to dissociation. If there exists any order-disorder transformation, then it may be swift and non-quenchable but it will probably not be a simple substitutional disordering due to the thermal agitation, because generally, substitutional disordering is a gradual transition as a function of temperature and thus any increased dynamic disorder as a result of heating is easily quenched and becomes static disorder (Buerger, 1948). In fact, this is also favoured by the foregoing discussions on the non-random distribution of Al in the tetrahedral framework because of the "structural barriers". However, the possibility that the intensity of superlattice reflection varies as a function of temperature is by no means excluded. It may be because of this that scapolites are unlikely to have the inversion twinning, either microscopic or submicroscopic, which commonly occurs when a disordered crystal becomes ordered, e.g. the feldspars and many sulfide minerals. However, dynamic rotational disorder of CO_3 group might be expected at elevated temperature, especially near the temperature of liberation of CO_2 gas from scapolites.

5) Structural Formula and Stoichiometry of the Scapolite Solid Solution

Sulfur is present in scapolites as $SO_4^{=}$ anion, as has been shown by X-ray wavelength-shift studies (Chappell and White, 1968; Lovering and Widdowson, 1968). This fact is favored by the space group $P4_2/n$ determined as a result of the present study, because the molecular symmetry of SO_4 ions coincides with the site symmetry at the center of the unit cell based on the $P4_2/n$ space group. In scapolites, the SO_4 group behaves more like the CO_3 group than the Cl anion, for both of them are radicals with the same valency, and even are expected to have the same x,y coordinates of their oxygen atoms, although the exact location of the oxygen of the SO_4 ion is still not quite well known, due to its small amount and/or being superimposed upon by the disordered CO_3 group.

$SO_4^=$ ion is the third commonest anion present in the central cage of the scapolite structure and there seems no particular limit imposed on the amount of $SO_4^=$ except that of total anion proportions allowed by the formula. It has been found mainly to be of minor content, however, from the crystallochemical view point, a $SO_4^=$ dominant meionite is likely to exist or to be synthesized and doubtless, $Ca_4Al_6Si_6O_{24}(SO_4)$ could be another pure end-member of the scapolite solid solution. However, when treating the scapolite solid solution as a simple binary system of $Na_4Al_3Si_9O_{24}\cdot Cl$ and $Ca_4Al_6Si_6O_{24}\cdot CO_3$, the SO_4 proportion and the CO_3 proportion can be grouped together because of their comparatively similar crystallochemical role in scapolite. Nevertheless, the difference between them may still cause a slight adjustment of other atoms so violating the body-centred symmetry. This may be why those scapolites with CO_3 and SO_4 as the only essential anions still show very feeble superlattice reflections with $h+k+\ell=2n+1$. OH^- ion is another possible anion present in the central cavity of the scapolite structure, considering its similarity to the Cl^- ion and the usual excess of H_2O shown in the chemical analyses. However, it is minor as shown by the total proportions of anions.

The general formula of scapolites $W_4Z_{12}O_{24}R$, proposed by Shaw (1960) is also a structural formula, with two such chemical formulas in one unit cell. However, some amendments should be made. A number of end member components of scapolite solid solution have been suggested, but many of them are found not consistent with the crystal structure and should be discarded. For example, the following group (A) is not allowed because of the contradiction between the number of the specific ions per unit cell and the number of equivalent sites available to these ions in the space group.

Group (A)
$(Ab)_3\ Na_2Co_3$
$(Ab)_3 \cdot Na_2SO_4$
$(Ab)_3 \cdot NaHCO_3$
$(Ab)_3 \cdot NaHSO_4$
$(Or)_3 \cdot K_2CO_3$
$(An)_3 \cdot CaCl_2$
$(An)_3 \cdot Ca(OH)_2$
$(An)_3 \cdot CaF_2$
etc.

Group (B)
$(Ab)_3 \cdot Na(CO_3)_{1/2}$
$(Ab)_3 \cdot Na(SO_4)_{1/2}$
$(Or)_3 \cdot K(CO_3)_{1/2}$
$(An)_3 \cdot (CaCl_2)_{1/2}$
etc.

Group (C)
$(Ab)_3 \cdot NaCl$
$(Ab)_3 \cdot NaOH$
$(An)_3 \cdot CaCO_3$
$(An)_3 \cdot CaSO_4$
$(Or)_3 \cdot KCl$
$(Ab)_3 \cdot NaF$
etc.

where Ab = $Na\ Al\ Si_3O_8$, An = $CaAl_2Si_2O_8$ and Or = $KAl\ Si_3O_8$. It should be noted that these formulas listed here have no structural significance, but the concept of feldspars plus salt expresses concisely the composition of the scapolites. Group (B) is uncertain because some crystallographic sites must be vacant. However, considering the fact that Al and Cl are deficient in scapolite, and the number of anions (Cl^-, $CO_3^=$, and $SO_4^=$) per unit cell is usually less than that of available anion sites, scapolites could contain such molecules as $(Ab)_3Na(CO_3)_{1/2}$ and $(Ab)_3Na(SO_4)_{1/2}$. The resulting vacant anion sites could be occupied by water. Only group (C) formulas are consistent with the crystal structure of scapolite.

Moreover, the definition of the meionite percentage, given by Shaw (1960) and Evans et. al. (1969) should be unified from the viewpoint of crystal chemistry of the scapolites. The cations used in this expression should not only include the alkali and alkaline earth metals. All those cations whose ionic radii and valencies are comparable to those of the alkali or alkaline earth elements, should also be included, since they may replace Na,Ca, K etc. without deteriorating the scapolite structure. For example, Fe^{++} ion can replace Ca^{++} ion, and their presence both have the same crystal chemical effect, i.e. increase the amount of Al in scapolites. Therefore the % Me is better expressed as the following ratio of the atomic proportions:

$\%Me = (Ca+Sr+Ba+Fe^{++} + Mn^{++})/(Na + K + Ca + Sr + Ba + Fe^{++} + Mn^{++})$.

The Mg ion should be very carefully considered because of its smaller ionic radius and especially because it is often due to contamination. Furthermore, Ti should be excluded because its ionic size is quite small and its valencies are greater than two, thus it will go into tetrahedral sites to replace Si or Al rather than into octahedral sites to replace Ca, Na or K.

The present study throws some light on the cause of the abnormal stoichiometry of the scapolites as described in Chapter I (see Evans et. al. 1969). The stoichiometric anomaly in the scapolite solid solution is a unique feature; see Figure (27). Two substitutional schemes are operating, depending on the range of % Me:

(a) $0 \leq \% \text{ Me} \leq 75$: A coupled replacement of Na_3Si_2Cl by $Ca_2Al_2CO_3$, corresponding to a linear variation between $Na_4Al_3Si_9O_{24}Cl$ and $NaCa_3Al_5Si_7O_{24}CO_3$.

(b) $75 \leq \% \text{ Me} \leq 100$: A coupled replacement of NaSi by CaAl, corresponding to a variation between $NaCa_3Al_5Si_7O_{24}CO_3$ and $Ca_4Al_6Si_6O_{24}CO_3$.

As reported in Chapter 4, there exists a close correlation between the intensity of the superlattice reflections ($h+k+\ell=2n+1$) and the stoichiometry line of the scapolites. After the structural analyses were completed, it was realized that the distribution of Al in the various tetrahedral sites of the scapolite structure are closely related to the intensity of the superlattice reflections, which is also related to the relative abundance ratio of Cl to (CO_3+SO_4) ions in scapolites. The distribution of Al among the three different tetrahedral sites has been explained previously in terms of (1) the unfavorable Al-O-Al linkage, (2) the internal strain between the Cl ion and the (CO_3+SO_4) ion. It was found that the most orderly arrangement of Al in the scapolites is the one with T_2 = 100% Al, and $T_1 = T_3$ = 0% Al, i.e., eight Al atoms

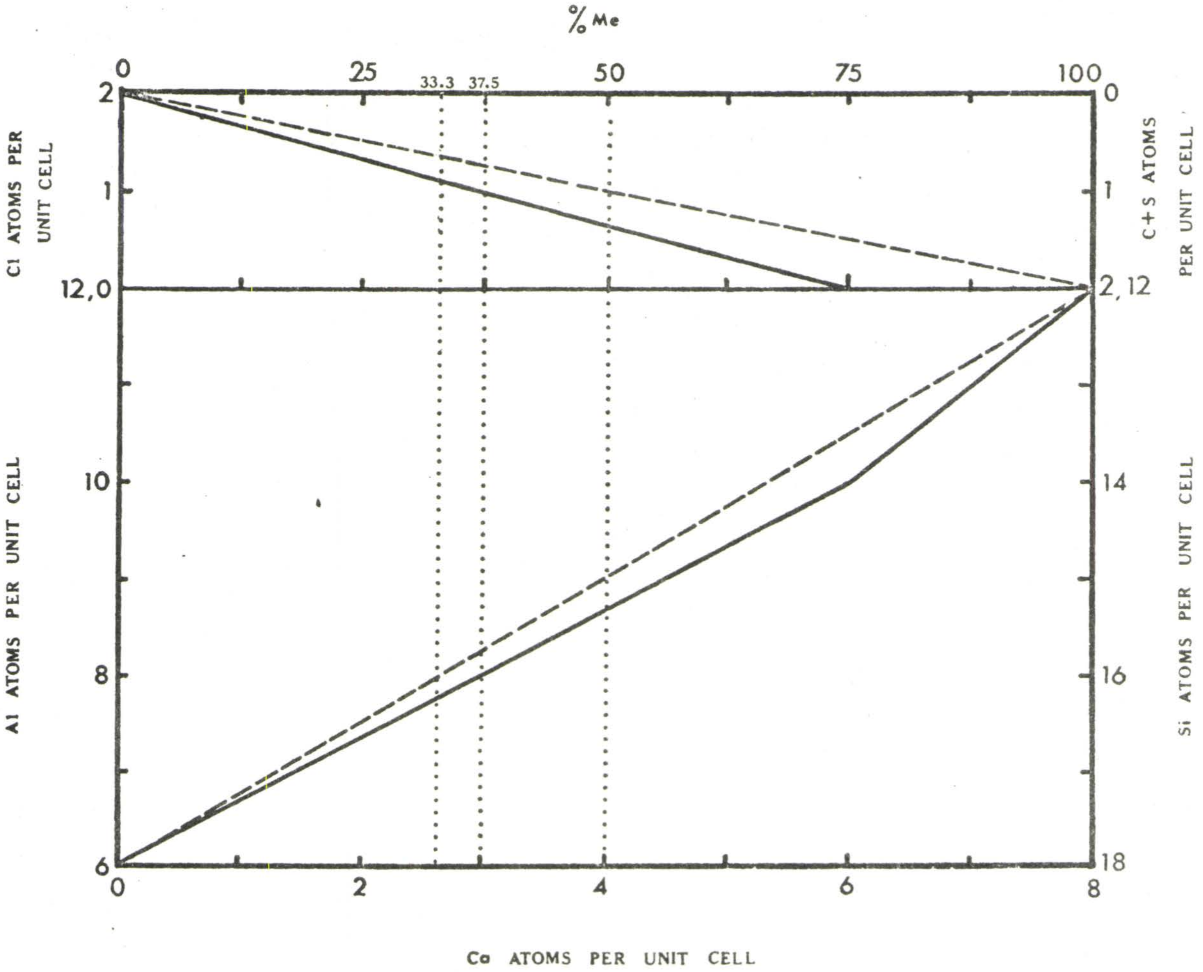


Fig. 27. The stoichiometry of the scapolite solid solution.

Dashed line = ideal stoichiometry
Full line = real stoichiometry

to occupy all eight T_2 sites in one unit cell. It has been shown that this most orderly arrangement of Al will have a maximum electrostatic force to pull (Na,Ca) and to tilt CO_3 from the mirror plane in the I4/m space group (Fig. 24). According to the real stoichiometry, scapolite happens to have eight Al atoms at 37.5% Me, half way between 0% and 75%, which is exactly corresponding to the greatest internal-strain state caused by one Cl and one CO_3 per unit cell, and hence to the maximum distortion state with the strongest superlattice reflections.

As shown in Fig. (27) according to the ideal stoichiometry scapolite will have one Cl and one CO_3 per unit cell at 50% Me, while it will have eight Al per unit cell at 33.3% Me. Now, in order to have the greatest strain state coincide with the maximum ordered distribution of Al and the maximum electrostatic force to pull (Na,Ca) and to tilt CO_3, the real stoichiometry must deviate from the ideal one, in such a way as to enable scapolite simultaneously to possess eight Al atoms, one Cl ion and one CO_3 ion per unit cell. As illustrated by Figure (27), when the stoichiometric line shifts to the left, i.e. scapolite is deficient in Cl ion, then the % Me corresponding to having one Cl and one CO_3 per unit cell will be lowered. On the other hand, a deficiency in Cl will also cause a deficiency in Al in scapolite, so that the stoichiometric line shifts to the right, and thus the % Me having eight Al atoms per unit cell will be increased. Then, there must be a certain % Me somewhere between 33.3% Me and 50% Me, at which the scapolite may simultaneously contain eight Al, one Cl and one CO_3 per unit cell. This particular % Me is found to be 37.5% Me. Furthermore, the internal strain is presumed to be symmetrical in the range from zero Cl ion to two Cl ions per unit cell, that is, presumably inversely proportional to the difference between the number of Cl ions and the number of CO_3 ions per unit cell. Thus the real stoichiometric line should pass through the point with two Cl and six Al at 0% Me, and another point with one Cl and eight Al at 37.5% Me, and that is the real one found experimentally.

It should be noted that the interpretation of stoichiometry given above is tentative, and a more thorough explanation seems to be beyond the X-ray crystallographic approach. A thermodynamic and experimental synthesis study of scapolites would give more information on this subject.

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APPENDICES

APPENDIX 1. The Observed Structure Factors(FO) and Calculated Structure Factors(FC) of the Scapolite(ON8,19.4% Me,Gooderham,Ontario).

H	K	L	GRP		FO	FC	H	K	L	GRP		FO	FC
0	2	0	1		59.39	53.00	0	14	3	1	L	5.59	.74
0	4	0	1		175.95	-199.38	0	15	3	1		17.30	-14.37
0	6	0	1		34.45	-37.53	0	0	4	1		274.30	281.54
0	8	0	1		10.14	-13.36	0	1	4	1		10.46	8.51
0	10	0	1		43.53	45.14	0	2	4	1		11.02	-5.51
0	12	0	1		66.38	73.45	0	3	4	1		6.12	3.59
0	14	0	1		29.51	-29.15	0	4	4	1		97.01	-92.10
0	16	0	1		61.55	-60.03	0	5	4	1		12.15	-9.16
0	1	1	1		35.91	46.05	0	6	4	1		35.81	-35.06
0	2	1	1		5.92	-4.30	0	7	4	1	L	5.04	-2.90
0	3	1	1		99.14	96.89	0	8	4	1		28.79	-29.42
0	4	1	1	L	3.33	-1.51	0	9	4	1	L	5.34	-1.17
0	5	1	1		14.18	13.61	0	10	4	1		10.47	11.05
0	6	1	1	L	3.98	-.57	0	11	4	1	L	5.59	1.48
0	7	1	1		20.60	-17.45	0	12	4	1		39.33	44.95
0	8	1	1		11.25	6.67	0	13	4	1	L	5.60	1.18
0	9	1	1		68.86	-67.21	0	14	4	1		11.46	-10.01
0	10	1	1	L	5.13	1.04	0	15	4	1	L	4.66	-2.80
0	11	1	1		16.11	-14.92	0	1	5	1		12.02	10.58
0	12	1	1	L	5.56	-2.21	0	2	5	1		11.03	-9.69
0	13	1	1		26.41	28.13	0	3	5	1		124.51	118.14
0	14	1	1	L	5.73	1.34	0	4	5	1		9.01	-6.62
0	15	1	1		42.77	40.31	0	5	5	1		59.34	55.68
0	0	2	1		7.14	.08	0	6	5	1		6.58	4.58
0	1	2	1	L	3.23	1.81	0	7	5	1		81.33	-82.09
0	2	2	1		16.07	-11.97	0	8	5	1		7.53	4.45
0	3	2	1	L	3.52	.25	0	9	5	1		67.79	-70.65
0	4	2	1		24.23	-23.54	0	10	5	1	L	5.57	.98
0	5	2	1	L	3.98	.61	0	11	5	1		7.63	6.74
0	6	2	1		34.52	32.62	0	12	5	1	L	5.56	-1.93
0	7	2	1	L	4.49	3.59	0	13	5	1		26.61	31.02
0	8	2	1		35.04	-36.07	0	14	5	1	L	4.83	-.40
0	9	2	1	L	5.00	-1.94	0	0	6	1		170.41	170.68
0	10	2	1		41.31	44.57	0	1	6	1	L	5.25	-4.54
0	11	2	1	L	5.44	.36	0	2	6	1		27.88	-30.11
0	12	2	1		43.92	45.99	0	3	6	1	L	5.30	-2.12
0	13	2	1	L	5.70	3.25	0	4	6	1		45.00	45.65
0	14	2	1	L	5.69	-4.45	0	5	6	1	L	5.38	3.73
0	15	2	1	L	5.46	.70	0	6	6	1		8.58	7.41
0	16	2	1		10.47	-10.71	0	7	6	1	L	5.49	3.38
0	1	3	1		16.93	-18.78	0	8	6	1		16.37	-17.41
0	2	3	1	L	3.97	-1.70	0	9	6	1	L	5.56	-.74
0	3	3	1		114.39	110.59	0	10	6	1	L	5.56	.34
0	4	3	1		12.70	9.32	0	11	6	1	L	5.49	2.04
0	5	3	1		72.23	74.76	0	12	6	1		10.08	-7.33
0	6	3	1		8.71	5.55	0	13	6	1	L	4.74	3.88
0	7	3	1		98.35	-97.94	0	14	6	1		7.23	8.81
0	8	3	1	L	4.96	-2.60	0	1	7	1		46.55	-46.35
0	9	3	1		50.52	49.87	0	2	7	1	L	5.49	-2.98
0	10	3	1		7.66	-5.00	0	3	7	1		38.02	38.29
0	11	3	1		75.43	73.93	0	4	7	1		12.45	8.54
0	12	3	1	L	5.64	-2.46	0	5	7	1		58.19	58.87
0	13	3	1		10.17	-6.55	0	6	7	1		14.13	9.79

H	K	L	GRP		FO	FC
0	7	7	1		71.21	-73.80
0	8	7	1		9.89	-7.45
0	9	7	1	L	5.48	-3.02
0	10	7	1		10.80	-7.49
0	11	7	1		30.93	29.86
0	12	7	1	L	4.37	-1.33
0	0	8	1		15.72	18.84
0	1	8	1	L	5.56	-1.13
0	2	8	1	L	5.55	-1.41
0	3	8	1	L	5.54	-1.61
0	4	8	1	L	5.53	-4.04
0	5	8	1	L	5.50	-4.29
0	6	8	1		13.92	-13.09
0	7	8	1	L	5.39	-2.60
0	8	8	1		8.31	2.38
0	9	8	1	L	5.02	1.95
0	10	8	1		6.88	-9.37
0	1	9	1	L	5.38	3.06
0	2	9	1	L	5.35	-4.27
0	3	9	1		36.78	34.86
0	4	9	1	L	5.24	-3.37
0	5	9	1		20.86	17.45
0	6	9	1	L	4.97	4.55
0	7	9	1		28.73	-30.12
0	8	9	1	L	4.18	1.58
0	9	9	1		36.05	-44.89
0	0	10	1		108.78	-111.15
0	1	10	1		8.67	-8.00
0	2	10	1	L	4.52	.92
0	3	10	1	L	4.36	-4.05
0	4	10	1		50.36	49.87
0	5	10	1		6.62	4.19
1	3	0	2		66.18	-61.97
1	-3	0	2		134.94	-172.76
1	4	0	2	L	2.39	-.00
1	-4	0	2	L	2.39	.00
1	5	0	2		62.68	-47.76
1	-5	0	2		26.31	34.92
1	6	0	2	L	2.99	.00
1	-6	0	2	L	2.99	.00
1	7	0	2		115.28	109.53
1	-7	0	2		111.87	132.42
1	8	0	2	L	3.51	-.00
1	-8	0	2	L	3.51	-.00
1	9	0	2		154.65	-150.33
1	-9	0	2	L	3.75	-7.05
1	10	0	2	L	3.99	.00
1	-10	0	2	L	3.99	.00
1	11	0	2		59.37	-62.69
1	-11	0	2		11.07	-7.35
1	12	0	2	L	4.42	.00
1	-12	0	2	L	4.42	-.00
1	13	0	2		26.03	25.41
1	-13	0	2	L	4.60	6.42
1	14	0	2	L	4.74	-.00
1	-14	0	2	L	4.74	.00
1	15	0	2		28.93	-28.31
1	-15	0	2		41.16	-39.16
1	16	0	2	L	4.80	-.00
1	-16	0	2	L	4.80	.00
1	0	1	2		36.20	46.05
1	2	1	2		23.98	-26.59
1	-2	1	2		25.24	-20.90
1	3	1	2		8.67	-4.37
1	-3	1	2	L	2.24	-.07
1	4	1	2		111.74	-110.61
1	-4	1	2	L	2.54	-1.00
1	5	1	2	L	2.81	-.37
1	-5	1	2	L	2.81	-1.38
1	6	1	2		46.50	-41.57
1	-6	1	2		120.12	116.81
1	7	1	2	L	3.32	.80
1	-7	1	2	L	3.32	2.59
1	8	1	2	L	3.56	-6.01
1	-8	1	2	L	3.56	-1.54
1	9	1	2	L	3.80	-1.70
1	-9	1	2		10.41	-7.45
1	10	1	2		33.93	31.91
1	-10	1	2		19.93	18.63
1	11	1	2	L	4.24	3.19
1	-11	1	2	L	4.24	-1.09
1	12	1	2		21.31	20.38
1	-12	1	2		26.47	23.05
1	13	1	2	L	4.62	.51
1	-13	1	2	L	4.62	2.99
1	14	1	2	L	4.75	-2.60
1	-14	1	2		16.46	12.86
1	15	1	2	L	4.82	2.12
1	-15	1	2	L	4.82	.42
1	16	1	2		34.62	-32.35
1	-16	1	2	L	4.78	-6.00
1	0	2	2	L	2.34	-1.81
1	1	2	2		194.58	206.56
1	-1	2	2		194.58	-206.56
1	2	2	2	L	2.54	6.09
1	-2	2	2	L	2.54	.98
1	3	2	2		41.59	44.70
1	-3	2	2		150.82	-161.55
1	4	2	2		8.85	7.16
1	-4	2	2	L	2.91	.88
1	5	2	2		49.12	-47.54
1	-5	2	2		48.28	-49.17
1	6	2	2	L	3.30	1.21
1	-6	2	2	L	3.30	-2.08
1	7	2	2		33.85	-34.69
1	-7	2	2		58.93	55.94
1	8	2	2	L	3.72	.72
1	-8	2	2	L	3.72	-.70
1	9	2	2		60.74	-66.00
1	-9	2	2		79.60	76.71
1	10	2	2	L	4.13	-.72
1	-10	2	2	L	4.13	-3.33
1	11	2	2		14.96	-16.35
1	-11	2	2		27.67	27.24
1	12	2	2	L	4.50	-1.76
1	-12	2	2	L	4.50	-.10
1	13	2	2		56.06	61.71
1	-13	2	2		61.24	-66.07
1	14	2	2	L	4.77	1.07
1	-14	2	2	L	4.77	2.54
1	15	2	2		26.57	25.09
1	-15	2	2		42.23	-42.61
1	16	2	2	L	4.73	-.34
1	-16	2	2	L	4.73	.76
1	0	3	2		17.56	-18.77
1	1	3	2		8.85	6.64
1	-1	3	2		8.58	6.64
1	2	3	2		18.42	-21.51
1	-2	3	2		9.13	-3.83
1	3	3	2		7.52	-4.58
1	-3	3	2	L	3.21	1.82
1	4	3	2		137.40	142.36
1	-4	3	2		75.27	71.67
1	5	3	2	L	3.46	-4.63
1	-5	3	2	L	3.46	.76
1	6	3	2		120.25	117.21
1	-6	3	2		68.48	65.48
1	7	3	2	L	3.76	1.79

H	K	L	GRP		FO	FC
1	-7	3	2	L	3.76	3.93
1	8	3	2		47.32	-45.76
1	-8	3	2		59.74	61.35
1	9	3	2	L	4.10	-1.73
1	-9	3	2	L	4.10	-3.95
1	10	3	2		20.25	-18.36
1	-10	3	2		105.18	-105.70
1	11	3	2	L	4.43	2.68
1	-11	3	2	L	4.43	.99
1	12	3	2		36.39	-39.15
1	-12	3	2		46.74	-44.16
1	13	3	2	L	4.70	.04
1	-13	3	2	L	4.70	2.66
1	14	3	2		67.20	-69.40
1	-14	3	2		46.14	45.27
1	15	3	2	L	4.78	-1.65
1	-15	3	2	L	4.78	-1.83
1	16	3	2		42.62	43.37
1	0	4	2		10.93	-8.52
1	1	4	2		14.00	-13.38
1	-1	4	2		14.00	13.38
1	2	4	2		9.83	-7.87
1	-2	4	2	L	3.59	.21
1	3	4	2		10.94	7.28
1	-3	4	2		17.68	-15.27
1	4	4	2	L	3.72	-2.52
1	-4	4	2		9.84	5.41
1	5	4	2		37.94	37.04
1	-5	4	2		57.35	55.97
1	6	4	2	L	3.92	-.25
1	-6	4	2	L	3.92	2.26
1	7	4	2		75.42	74.59
1	-7	4	2		59.59	52.52
1	8	4	2	L	4.16	1.22
1	-8	4	2	L	4.16	2.64
1	9	4	2		66.19	-67.95
1	-9	4	2		42.96	-41.47
1	10	4	2	L	4.43	-2.16
1	-10	4	2	L	4.43	.88
1	11	4	2		14.04	-14.99
1	-11	4	2		18.79	-16.16
1	12	4	2	L	4.67	-.98
1	-12	4	2	L	4.67	3.66
1	13	4	2		16.45	13.63
1	-13	4	2		25.13	21.77
1	14	4	2		7.98	4.98
1	-14	4	2	L	4.78	1.69
1	15	4	2		22.96	-25.98
1	-15	4	2		22.48	-21.40
1	0	5	2		14.00	10.58
1	1	5	2	L	3.97	-1.62
1	-1	5	2	L	3.97	-1.62
1	2	5	2		87.42	-84.06
1	-2	5	2		15.71	-16.08
1	3	5	2		11.38	-8.47
1	-3	5	2		6.86	5.14
1	4	5	2		45.01	-42.13
1	-4	5	2		24.28	22.38
1	5	5	2	L	4.14	-2.51
1	-5	5	2	L	4.14	2.41
1	6	5	2		48.38	48.67
1	-6	5	2		120.34	121.04
1	7	5	2		8.37	8.31
1	-7	5	2	L	4.29	-5.89
1	8	5	2		19.37	-19.79
1	-8	5	2		7.85	5.48
1	9	5	2	L	4.48	2.13
1	-9	5	2		13.07	-8.09
1	10	5	2		18.32	20.56
1	-10	5	2		45.79	-44.46
1	11	5	2	L	4.66	2.44
1	-11	5	2	L	4.66	1.71
1	12	5	2	L	4.72	6.40
1	-12	5	2	L	4.72	3.38
1	13	5	2	L	4.74	1.07
1	-13	5	2	L	4.74	4.12
1	14	5	2		33.78	-34.01
1	-14	5	2		36.29	33.95
1	0	6	2	L	4.29	4.54
1	1	6	2		48.82	46.70
1	-1	6	2		48.82	-46.70
1	2	6	2	L	4.32	7.17
1	-2	6	2	L	4.32	1.80
1	3	6	2		61.69	64.70
1	-3	6	2		10.71	8.52
1	4	6	2		10.70	7.81
1	-4	6	2	L	4.37	-4.66
1	5	6	2	L	4.41	5.93
1	-5	6	2		15.28	-15.17
1	6	6	2	L	4.46	.05
1	-6	6	2		9.77	-5.89
1	7	6	2		40.38	-40.44
1	-7	6	2		28.55	-25.92
1	8	6	2		7.38	-4.49
1	-8	6	2	L	4.58	.39
1	9	6	2		17.94	18.34
1	-9	6	2		23.63	22.80
1	10	6	2	L	4.68	1.64
1	-10	6	2		7.98	-4.75
1	11	6	2		23.84	23.58
1	-11	6	2		11.56	8.84
1	12	6	2	L	4.71	-1.73
1	-12	6	2	L	4.71	-1.88
1	13	6	2		22.27	23.53
1	-13	6	2		21.79	-24.63
1	0	7	2		48.14	-46.35
1	1	7	2	L	4.56	6.05
1	-1	7	2	L	4.56	6.05
1	2	7	2		78.75	-78.40
1	-2	7	2		9.34	7.15
1	3	7	2	L	4.58	-5.54
1	-3	7	2	L	4.58	2.37
1	4	7	2		76.40	80.40
1	-4	7	2		21.29	19.36
1	5	7	2	L	4.61	-4.71
1	-5	7	2	L	4.61	.37
1	6	7	2		95.45	100.97
1	-6	7	2		32.30	26.67
1	7	7	2	L	4.66	4.65
1	-7	7	2	L	4.66	-.13
1	8	7	2		35.72	-33.92
1	-8	7	2		27.74	27.56
1	9	7	2	L	4.70	-.86
1	-9	7	2	L	4.70	-.87
1	10	7	2		15.60	-14.11
1	-10	7	2		83.04	-76.80
1	11	7	2	L	4.66	1.23
1	-11	7	2	L	4.66	3.53
1	12	7	2		22.79	-21.51
1	-12	7	2		41.77	-38.61
1	0	8	2	L	4.71	1.13
1	1	8	2		48.73	-50.20
1	-1	8	2		48.73	50.20
1	2	8	2	L	4.71	-5.26
1	-2	8	2	L	4.71	-.61
1	3	8	2		16.67	-17.16
1	-3	8	2		47.15	51.12
1	4	8	2	L	4.71	-2.80

```
  H     K     L GRP        FO        FC    H     K     L GRP        FO        FC

  1    -4     8   2  L     4.71     -3.24    2     9     1   3       10.22     -7.32
  1     5     8   2       14.92     15.20    2    -9     1   3       64.16    -63.31
  1    -5     8   2  L     4.72      6.58    2    10     1   3  L     4.06     -4.33
  1     6     8   2  L     4.71     -1.74    2   -10     1   3  L     4.06      2.60
  1    -6     8   2  L     4.71       .50    2    11     1   3       26.41    -24.74
  1     7     8   2       22.82     21.15    2   -11     1   3       16.26     13.27
  1    -7     8   2       10.74     -9.11    2    12     1   3  L     4.54       .72
  1     8     8   2        8.12     -2.50    2   -12     1   3  L     4.54       .32
  1    -8     8   2  L     4.69      2.66    2    13     1   3       10.42     10.05
  1     9     8   2       24.34     21.21    2   -13     1   3       35.04     32.18
  1    -9     8   2       37.14    -34.21    2    14     1   3  L     4.94      4.48
  1    10     8   2  L     4.56       .93    2   -14     1   3  L     4.94      -.25
  1   -10     8   2  L     4.56      1.03    2    15     1   3       11.50    -10.50
  1    11     8   2       11.17     11.47    2   -15     1   3  L     5.09     -3.25
  1   -11     8   2       20.33    -17.40    2    16     1   3  L     5.17      -.40
  1     0     9   2  L     4.73      3.06    2   -16     1   3  L     5.17     -1.12
  1     1     9   2  L     4.73     -2.29    2     0     2   3       19.13    -11.97
  1    -1     9   2  L     4.73     -2.29    2     1     2   3  L     1.84      -.98
  1     2     9   2       53.30    -50.44    2    -1     2   3  L     1.84      6.09
  1    -2     9   2  L     4.73     -3.44    2     2     2   3       46.81    -46.14
  1     3     9   2  L     4.71     -4.91    2    -2     2   3       48.27    -46.14
  1    -3     9   2  L     4.71      4.13    2     3     2   3        7.79     -5.31
  1     4     9   2       30.09    -29.77    2    -3     2   3  L     2.52      4.09
  1    -4     9   2  L     4.70       .09    2     4     2   3       36.14     27.08
  1     5     9   2  L     4.67     -2.50    2    -4     2   3       56.42     61.69
  1    -5     9   2  L     4.67      2.70    2     5     2   3  L     3.06      1.06
  1     6     9   2       30.70     28.02    2    -5     2   3  L     3.06     -1.68
  1    -6     9   2       18.22     16.77    2     6     2   3       54.88     53.77
  1     7     9   2  L     4.57      5.89    2    -6     2   3        7.45     -3.51
  1    -7     9   2        8.16     -5.77    2     7     2   3        8.64      5.16
  1     8     9   2  L     4.46      2.68    2    -7     2   3  L     3.52     -4.34
  1    -8     9   2       19.71    -19.49    2     8     2   3      143.50    151.25
  1     9     9   2  L     4.29      1.70    2    -8     2   3      171.15   -167.92
  1    -9     9   2        6.37     -3.02    2     9     2   3  L     3.97       .40
  1     0    10   2       12.28      8.00    2    -9     2   3  L     3.97       .37
  1    -1    10   2       12.44      8.01    2    10     2   3       19.68    -19.09
  1     1    10   2       12.44     -8.01    2   -10     2   3       18.48    -14.75
  1     2    10   2  L     4.51      2.87    2    11     2   3  L     4.41     -2.83
  1     3    10   2       13.81     11.73    2   -11     2   3  L     4.41       .86
  1    -3    10   2       39.31     34.77    2    12     2   3       20.69    -20.29
  1     4    10   2        6.84      2.80    2   -12     2   3       34.46     32.87
  1    -4    10   2       12.51     -8.12    2    13     2   3  L     4.81     -2.75
  1     5    10   2       23.53    -22.64    2   -13     2   3  L     4.81     -2.16
  1    -5    10   2       29.07    -26.59    2    14     2   3       16.05     10.96
  2     4     0   3      102.12   -100.79    2   -14     2   3       25.37    -27.07
  2    -4     0   3        4.98     -1.32    2    15     2   3  L     5.11       .18
  2     6     0   3       81.55     83.99    2   -15     2   3  L     5.11       .13
  2     8     0   3       53.57     52.38    2    16     2   3       36.82    -41.06
  2    -8     0   3        7.22    -10.70    2   -16     2   3       56.72     54.61
  2    10     0   3       25.11    -26.60    2     1     3   3       10.88     -3.83
  2   -10     0   3       50.42    -60.70    2    -1     3   3       20.34     21.51
  2    12     0   3       25.65    -25.30    2     2     3   3  L     2.98     -3.53
  2   -12     0   3       52.57    -53.80    2    -2     3   3  L     2.98      3.53
  2    14     0   3       16.35     18.55    2     3     3   3       53.45     51.09
  2   -14     0   3       25.06    -22.97    2    -3     3   3       86.48    -83.31
  2    16     0   3       10.63      8.63    2     4     3   3  L     3.29     -1.65
  2   -16     0   3       30.64     30.13    2    -4     3   3        8.08      5.70
  2     3     1   3      190.44   -196.67    2     5     3   3       59.04    -55.14
  2    -3     1   3        6.65      9.83    2    -5     3   3       21.78    -23.34
  2     4     1   3  L     2.42      1.41    2     6     3   3  L     3.64     -3.78
  2    -4     1   3  L     2.42     -3.55    2    -6     3   3  L     3.64      2.49
  2     5     1   3       44.36    -41.58    2     7     3   3      101.35   -100.94
  2    -5     1   3       64.65    -62.35    2    -7     3   3        8.37     -4.36
  2     6     1   3  L     3.05     -1.90    2     8     3   3  L     3.99     -3.25
  2    -6     1   3  L     3.05       .58    2    -8     3   3  L     3.99     -3.22
  2     7     1   3       91.06     87.69    2     9     3   3       10.75      9.92
  2    -7     1   3       20.36     18.50    2    -9     3   3       32.82    -33.09
  2     8     1   3  L     3.58      3.44    2    10     3   3        9.28     -5.55
  2    -8     1   3  L     3.58     -2.76    2   -10     3   3  L     4.37      5.11
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H	K	L	GRP		FO	FC	H	K	L	GRP		FO	FC
2	11	3	3		81.12	86.76	2	-3	6	3	L	4.50	2.54
2	-11	3	3		15.12	-9.17	2	4	6	3		25.62	29.02
2	12	3	3	L	4.74	2.65	2	-4	6	3		40.09	38.74
2	-12	3	3	L	4.74	3.02	2	5	6	3	L	4.59	5.60
2	13	3	3		9.68	1.61	2	-5	6	3	L	4.59	-1.98
2	-13	3	3		42.87	49.95	2	6	6	3		24.87	-25.21
2	14	3	3	L	5.04	2.63	2	-6	6	3		24.59	-26.33
2	-14	3	3	L	5.04	-.11	2	7	6	3		12.15	7.68
2	15	3	3		38.16	-40.94	2	-7	6	3	L	4.72	1.31
2	-15	3	3	L	5.14	-.32	2	8	6	3		17.70	16.00
2	0	4	3		11.34	-5.51	2	-8	6	3		51.85	-50.84
2	1	4	3	L	3.53	-.21	2	9	6	3	L	4.88	-1.78
2	-1	4	3		10.66	-7.87	2	-9	6	3	L	4.88	1.59
2	2	4	3		27.73	-27.16	2	10	6	3	L	4.95	-3.13
2	-2	4	3		28.62	-27.16	2	-10	6	3		17.84	18.68
2	3	4	3	L	3.66	.83	2	11	6	3	L	5.02	-3.33
2	-3	4	3		7.25	-4.19	2	-11	6	3	L	5.02	.43
2	4	4	3		28.12	-32.05	2	12	6	3	L	5.08	-2.81
2	-4	4	3		21.44	20.02	2	-12	6	3		35.91	38.28
2	5	4	3	L	3.87	-3.37	2	13	6	3	L	5.10	-3.31
2	-5	4	3	L	3.87	2.97	2	-13	6	3	L	5.10	-3.60
2	6	4	3		22.32	19.49	2	0	7	3	L	4.77	2.98
2	-6	4	3		120.31	117.48	2	1	7	3		9.08	7.15
2	7	4	3	L	4.13	-1.51	2	-1	7	3		81.02	78.40
2	-7	4	3	L	4.13	.10	2	2	7	3	L	4.78	-3.37
2	8	4	3		33.38	-39.47	2	-2	7	3	L	4.78	3.37
2	-8	4	3		29.42	30.94	2	3	7	3	L	4.81	6.15
2	-9	4	3	L	4.42	-3.34	2	-3	7	3	L	4.81	1.51
2	9	4	3	L	4.42	-2.28	2	4	7	3	L	4.83	-3.54
2	10	4	3		25.78	-26.60	2	-4	7	3	L	4.83	3.70
2	-10	4	3		27.80	-27.49	2	5	7	3		11.33	-8.92
2	11	4	3	L	4.72	2.23	2	-5	7	3		30.36	-29.11
2	-11	4	3	L	4.72	1.78	2	6	7	3	L	4.90	-3.39
2	12	4	3		11.01	-9.19	2	-6	7	3	L	4.90	1.70
2	0	5	3		11.25	9.69	2	7	7	3		33.80	-39.98
2	1	5	3		14.57	-16.08	2	-7	7	3		11.18	-9.53
2	-1	5	3		91.11	84.06	2	8	7	3	L	4.98	-4.49
2	2	5	3		13.92	11.24	2	-8	7	3	L	4.98	-2.23
2	-2	5	3		15.39	-11.24	2	9	7	3	L	5.03	1.82
2	3	5	3		159.62	-161.26	2	-9	7	3		17.20	-19.35
2	-3	5	3		8.15	-6.10	2	10	7	3	L	5.07	-2.62
2	4	5	3	L	4.18	-1.01	2	-10	7	3	L	5.07	5.72
2	-4	5	3		14.69	-12.69	2	11	7	3		53.76	54.57
2	5	5	3		31.07	-33.72	2	-11	7	3		18.79	13.54
2	-5	5	3		47.18	-48.32	2	12	7	3	L	5.08	3.02
2	6	5	3	L	4.35	-2.74	2	-12	7	3	L	5.08	3.78
2	-6	5	3	L	4.35	-1.79	2	0	8	3	L	5.01	-1.41
2	7	5	3		63.94	66.34	2	1	8	3	L	5.02	.61
2	-7	5	3		18.94	16.86	2	-1	8	3	L	5.02	-5.26
2	8	5	3		8.99	6.13	2	2	8	3		8.72	4.67
2	-8	5	3	L	4.55	-2.49	2	-2	8	3		8.72	4.67
2	9	5	3		13.53	-13.13	2	3	8	3	L	5.03	2.51
2	-9	5	3		93.80	-96.13	2	-3	8	3		11.04	-8.10
2	10	5	3	L	4.77	-.72	2	4	8	3		27.85	26.76
2	-10	5	3	L	4.77	4.93	2	-4	8	3		34.46	-35.99
2	11	5	3		14.74	15.46	2	5	8	3	L	5.05	2.83
2	-11	5	3		21.93	18.41	2	-5	8	3	L	5.05	3.35
2	12	5	3	L	5.00	-.99	2	6	8	3		19.16	-14.44
2	-12	5	3	L	5.00	1.19	2	-6	8	3		18.72	16.42
2	13	5	3		18.29	15.57	2	7	8	3	L	5.08	-1.63
2	-13	5	3		76.86	69.21	2	-7	8	3		10.44	7.04
2	14	5	3	L	5.13	1.64	2	8	8	3		63.29	-68.77
2	-14	5	3	L	5.13	-2.93	2	-8	8	3		67.15	66.76
2	0	6	3		28.66	-30.11	2	9	8	3		9.26	-3.76
2	1	6	3	L	4.45	-1.80	2	-9	8	3	L	5.09	-2.62
2	-1	6	3		9.46	7.17	2	10	8	3	L	5.07	-.22
2	2	6	3	L	4.48	2.75	2	-10	8	3	L	5.07	-1.14
2	-2	6	3	L	4.48	2.75	2	11	8	3	L	5.02	3.08
2	3	6	3	L	4.50	-3.93	2	-11	8	3	L	5.02	-.25

H	K	L	GRP		FO	FC
2	0	9	3	L	5.14	4.27
2	1	9	3	L	5.14	-3.44
2	-1	9	3		51.26	50.44
2	2	9	3		9.77	6.48
2	-2	9	3		9.77	-6.48
2	3	9	3		57.67	-58.13
2	-3	9	3		21.12	22.49
2	4	9	3	L	5.14	-.59
2	-4	9	3		9.76	-7.65
2	5	9	3		9.33	9.38
2	-5	9	3	L	5.13	-2.24
2	6	9	3	L	5.11	-1.30
2	-6	9	3	L	5.11	-.69
2	7	9	3		47.98	50.99
2	-7	9	3		10.06	6.27
2	8	9	3	L	5.05	4.12
2	-8	9	3	L	5.05	-.93
2	0	10	3	L	5.11	.92
2	1	10	3	L	5.11	-2.54
2	-1	10	3	L	5.11	2.87
2	2	10	3		20.12	17.73
2	-2	10	3		20.12	17.73
2	3	10	3	L	5.08	-1.04
2	-3	10	3	L	5.08	-1.94
2	4	10	3		21.54	19.16
2	-4	10	3		20.75	-19.85
2	5	10	3		9.91	6.98
2	-5	10	3	L	5.01	-.56
3	5	0	4		86.75	-91.63
3	-5	0	4	L	2.07	5.49
3	7	0	4		29.82	-29.33
3	-7	0	4		51.24	-76.49
3	9	0	4		14.62	-8.65
3	-9	0	4		42.95	46.96
3	11	0	4	L	3.55	-2.10
3	-11	0	4		93.39	91.21
3	13	0	4		34.04	34.00
3	-13	0	4		24.40	23.83
3	15	0	4		8.63	-7.92
3	-15	0	4		21.14	19.99
3	4	1	4		72.42	62.24
3	-4	1	4		84.20	-87.54
3	5	1	4	L	2.17	5.28
3	-5	1	4	L	2.17	-.38
3	6	1	4		75.96	72.84
3	-6	1	4		44.44	45.91
3	7	1	4	L	2.72	.25
3	-7	1	4	L	2.72	2.99
3	8	1	4		26.51	-22.57
3	-8	1	4		26.67	28.33
3	9	1	4	L	3.16	1.55
3	-9	1	4	L	3.16	-.80
3	10	1	4		16.53	-17.44
3	-10	1	4		13.06	-13.06
3	11	1	4	L	3.58	-1.16
3	-11	1	4	L	3.58	-.91
3	12	1	4		46.35	47.21
3	-12	1	4		19.67	19.70
3	13	1	4	L	3.98	-1.65
3	-13	1	4	L	3.98	.92
3	14	1	4		24.64	23.28
3	-14	1	4	L	4.16	-5.27
3	15	1	4	L	4.33	-1.13
3	-15	1	4	L	4.33	-3.53
3	16	1	4	L	4.46	-7.44
3	-16	1	4		20.92	-21.65
3	3	2	4		45.95	-38.24
3	-3	2	4		43.81	38.23
3	4	2	4	L	2.12	1.31
3	-4	2	4	L	2.12	5.44
3	5	2	4		95.22	-92.70
3	-5	2	4		59.89	-63.70
3	6	2	4	L	2.67	-4.35
3	-6	2	4	L	2.67	.74
3	7	2	4		107.05	108.22
3	-7	2	4		96.64	-95.94
3	8	2	4	L	3.09	-.22
3	-8	2	4	L	3.09	3.24
3	9	2	4		9.31	5.39
3	-9	2	4		25.94	32.24
3	10	2	4	L	3.49	-1.67
3	-10	2	4	L	3.49	-.98
3	11	2	4		29.87	-30.62
3	-11	2	4		38.57	43.42
3	12	2	4	L	3.86	-.47
3	-12	2	4	L	3.86	-2.35
3	-13	2	4		26.84	-25.24
3	13	2	4		10.13	13.61
3	14	2	4	L	4.22	2.64
3	-14	2	4	L	4.22	.86
3	15	2	4		11.74	10.89
3	-15	2	4		21.39	-17.81
3	0	3	4		116.97	110.59
3	1	3	4	L	2.05	1.82
3	-1	3	4	L	2.05	-4.58
3	2	3	4		87.72	83.31
3	-2	3	4		51.18	51.09
3	3	3	4	L	2.41	-2.42
3	-3	3	4	L	2.41	-2.42
3	4	3	4		18.04	-14.97
3	-4	3	4		9.56	-7.91
3	5	3	4	L	2.79	-1.34
3	-5	3	4	L	2.79	.64
3	6	3	4		9.37	-9.14
3	-6	3	4		54.75	51.49
3	7	3	4	L	3.15	-1.22
3	-7	3	4	L	3.15	4.35
3	8	3	4	L	3.32	-7.57
3	-8	3	4		17.56	-18.53
3	9	3	4	L	3.49	.31
3	-9	3	4	L	3.49	3.31
3	10	3	4		16.34	17.07
3	-10	3	4		8.17	8.25
3	11	3	4	L	3.83	-1.68
3	-11	3	4	L	3.83	-1.13
3	12	3	4		9.15	-.90
3	-12	3	4		14.10	-10.27
3	13	3	4	L	4.15	-1.99
3	-13	3	4	L	4.15	-1.84
3	14	3	4		15.77	-14.14
3	-14	3	4		37.91	-36.69
3	1	4	4		18.13	15.27
3	-1	4	4		10.84	-7.28
3	2	4	4	L	2.86	-4.19
3	-2	4	4	L	2.86	-.83
3	3	4	4		19.16	-18.10
3	-3	4	4		19.16	18.10
3	4	4	4	L	3.07	-1.60
3	-4	4	4	L	3.07	-2.57
3	5	4	4		16.88	-20.74
3	-5	4	4		18.04	-18.94
3	6	4	4	L	3.32	2.07
3	-6	4	4	L	3.32	-5.78
3	7	4	4		49.83	-50.89
3	-7	4	4		43.87	-47.03
3	8	4	4	L	3.58	7.39
3	-8	4	4	L	3.58	1.32
3	9	4	4		13.14	-7.79
3	-9	4	4		9.77	-6.04
3	10	4	4	L	3.85	1.97

H	K	L	GRP		FO	FC
3	-10	4	4	L	3.85	-1.11
3	11	4	4		20.74	25.24
3	-11	4	4		30.12	31.42
3	12	4	4	L	4.13	.68
3	-12	4	4	L	4.13	1.81
3	13	4	4		25.20	26.67
3	-13	4	4		25.20	24.55
3	14	4	4	L	4.38	3.05
3	-14	4	4	L	4.38	2.53
3	15	4	4	L	4.46	-5.74
3	-15	4	4		16.11	15.05
3	0	5	4		123.30	118.14
3	1	5	4	L	3.32	5.15
3	-1	5	4		9.91	-8.46
3	2	5	4		8.40	6.10
3	-2	5	4		166.83	-161.26
3	3	5	4	L	3.42	1.42
3	-3	5	4	L	3.42	1.42
3	4	5	4		35.49	38.62
3	-4	5	4		111.75	-108.87
3	5	5	4		8.18	1.53
3	-5	5	4	L	3.56	5.17
3	6	5	4		76.53	79.91
3	-6	5	4		77.94	76.24
3	7	5	4		8.85	6.45
3	-7	5	4	L	3.74	-4.13
3	8	5	4		55.17	-56.17
3	-8	5	4		21.74	22.38
3	9	5	4	L	3.95	.82
3	-9	5	4	L	3.95	-1.69
3	10	5	4		36.28	-38.86
3	-10	5	4		7.37	3.70
3	11	5	4	L	4.16	-2.85
3	-11	5	4	L	4.16	-.89
3	12	5	4		48.34	54.11
3	-12	5	4		24.91	29.44
3	13	5	4	L	4.37	-.29
3	-13	5	4	L	4.37	-2.28
3	14	5	4		25.17	27.15
3	-14	5	4		31.46	-31.26
3	1	6	4		11.54	-8.52
3	-1	6	4		62.50	-64.70
3	2	6	4	L	3.75	2.54
3	-2	6	4	L	3.75	3.93
3	3	6	4		10.65	12.02
3	-3	6	4		9.73	-12.02
3	4	6	4	L	3.84	.04
3	-4	6	4	L	3.84	5.99
3	5	6	4		11.16	10.14
3	-5	6	4		32.52	33.57
3	6	6	4	L	3.95	-4.60
3	-6	6	4	L	3.95	3.91
3	7	6	4		36.37	41.18
3	-7	6	4		18.84	-17.68
3	8	6	4	L	4.09	-2.13
3	-8	6	4	L	4.09	1.39
3	9	6	4	L	4.16	-1.81
3	-9	6	4		24.65	-22.40
3	10	6	4	L	4.25	-2.36
3	-10	6	4	L	4.25	-4.61
3	11	6	4		7.05	-5.05
3	-11	6	4		19.33	-19.05
3	12	6	4	L	4.39	-.99
3	-12	6	4	L	4.39	-5.45
3	13	6	4		7.71	2.21
3	-13	6	4		15.55	-13.35
3	-4	6	4	L	3.84	5.99
3	0	7	4		37.21	38.29
3	1	7	4	L	4.07	2.37
3	-1	7	4	L	4.07	-5.54
3	2	7	4	L	4.08	-1.51
3	-2	7	4	L	4.08	6.15
3	3	7	4	L	4.10	-1.60
3	-3	7	4	L	4.10	-1.60
3	4	7	4		17.02	-15.46
3	-4	7	4		14.88	-11.95
3	5	7	4	L	4.16	-2.90
3	-5	7	4	L	4.16	2.97
3	6	7	4		9.95	4.66
3	-6	7	4		23.03	22.08
3	7	7	4	L	4.25	.60
3	-7	7	4	L	4.25	.83
3	8	7	4		23.13	-27.33
3	-8	7	4		20.61	-17.72
3	9	7	4	L	4.34	-1.89
3	-9	7	4	L	4.34	4.22
3	10	7	4		15.22	-10.36
3	-10	7	4		18.12	21.02
3	11	7	4	L	4.44	-2.44
3	-11	7	4	L	4.44	-1.13
3	12	7	4	L	4.46	.64
3	-12	7	4		12.56	11.96
3	1	8	4		46.33	-51.12
3	-1	8	4		19.32	17.16
3	2	8	4		10.24	-8.10
3	-2	8	4	L	4.33	-2.51
3	3	8	4		7.52	3.43
3	-3	8	4		7.88	-3.43
3	4	8	4	L	4.35	-5.32
3	-4	8	4	L	4.35	-1.99
3	5	8	4		38.64	39.47
3	-5	8	4		27.32	-27.18
3	6	8	4	L	4.39	5.13
3	-6	8	4	L	4.39	.02
3	7	8	4		36.17	-40.25
3	-7	8	4		26.89	24.50
3	8	8	4	L	4.44	-3.74
3	-8	8	4		8.07	-2.04
3	9	8	4	L	4.46	-4.68
3	-9	8	4		17.28	-13.25
3	10	8	4	L	4.48	2.26
3	-10	8	4	L	4.48	-1.94
3	0	9	4		35.64	34.86
3	1	9	4	L	4.49	4.13
3	-1	9	4	L	4.49	-4.91
3	2	9	4		20.58	-22.49
3	-2	9	4		57.18	-58.13
3	3	9	4	L	4.50	.99
3	-3	9	4	L	4.50	.99
3	4	9	4		7.80	4.53
3	-4	9	4		48.88	-45.72
3	5	9	4	L	4.50	-.87
3	-5	9	4		8.57	5.34
3	6	9	4		32.48	34.58
3	-6	9	4		22.06	21.32
3	7	9	4	L	4.50	4.04
3	-7	9	4	L	4.50	-3.59
3	8	9	4		33.92	-37.44
3	-8	9	4		10.63	6.91
3	1	10	4		37.51	-34.77
3	-1	10	4		14.29	-11.73
3	2	10	4	L	4.55	-1.94
3	-2	10	4	L	4.55	1.04
3	3	10	4	L	4.54	2.87
3	-3	10	4	L	4.54	-2.87
3	4	10	4	L	4.52	-2.49
3	-4	10	4	L	4.52	3.02
3	5	10	4		33.12	34.00

```
  H     K     L GRP       FO       FC    H     K     L GRP       FO       FC

  3    -5    10   4      17.15    15.65   4     5     5   5      39.40   -40.98
  4     6     0   5      82.87   -78.48   4    -5     5   5      37.26    33.37
  4    -6     0   5      26.52   -35.15   4     6     5   5       9.96    -7.50
  4     8     0   5     101.81    99.51   4     7     5   5      99.92   106.06
  4    -8     0   5      71.09    90.45   4    -7     5   5      26.17    28.50
  4    10     0   5      12.83   -15.79   4     9     5   5      13.36   -12.95
  4   -10     0   5      24.43    24.07   4    -9     5   5      53.30   -51.08
  4    12     0   5      47.06   -53.11   4    11     5   5   L   6.34     1.84
  4   -12     0   5      45.35   -48.09   4   -11     5   5      13.57   -12.28
  4    14     0   5      10.92    15.47   4    13     5   5   L   6.69     3.24
  4   -14     0   5      25.52   -25.27   4   -13     5   5      25.19    23.88
  4    16     0   5      36.15    41.54   4     0     6   5      45.47    45.65
  4   -16     0   5      50.36    47.80   4     1     6   5   L   5.56     4.66
  4     5     1   5      56.71   -53.02   4    -1     6   5      10.16     7.81
  4    -5     1   5      30.40   -27.88   4     2     6   5      36.72    38.74
  4    -6     1   5       8.19     5.51   4    -2     6   5      25.84    29.02
  4     7     1   5      74.50    71.21   4     4     6   5      21.02    22.47
  4    -7     1   5      22.10    24.25   4    -4     6   5      20.68    22.47
  4    -8     1   5       9.49    -6.76   4     6     6   5      16.35    16.85
  4     9     1   5       8.03     4.92   4    -6     6   5      16.80    14.87
  4    -9     1   5      30.35   -24.68   4     8     6   5      13.90   -18.08
  4    11     1   5      15.06    19.55   4    -8     6   5      40.54   -41.48
  4   -11     1   5      13.82   -12.30   4    10     6   5      24.06   -26.94
  4   -13     1   5      30.41    26.51   4   -10     6   5      13.24    11.23
  4    15     1   5      31.99   -33.85   4    12     6   5      11.54     9.78
  4    -4     2   5       8.80     4.94   4   -12     6   5      23.07    22.80
  4     6     2   5      11.65     6.51   4     1     7   5      21.38    19.36
  4    -6     2   5      34.40   -33.64   4    -1     7   5      79.06   -80.39
  4     8     2   5      27.76    30.18   4     3     7   5      14.47   -11.95
  4    -8     2   5      51.76   -52.82   4    -3     7   5      18.40    15.46
  4    10     2   5     102.25  -105.62   4     5     7   5      12.27    10.75
  4   -10     2   5      63.63    65.04   4    -5     7   5      75.89    72.69
  4    12     2   5      38.59   -43.38   4     7     7   5      50.34    51.12
  4   -12     2   5      12.98    -9.52   4    -7     7   5   L   6.50    -1.28
  4    14     2   5      80.46    80.58   4     9     7   5      16.91   -17.43
  4   -14     2   5      70.59   -67.49   4    -9     7   5      18.69   -19.07
  4     1     3   5      78.05    71.67   4   -10     7   5      10.52     6.06
  4     3     3   5       8.51    -7.91   4    11     7   5      30.03   -29.47
  4    -3     3   5      17.37    14.97   4   -11     7   5   L   6.86     1.25
  4     5     3   5      27.83   -30.72   4     0     8   5   L   6.61    -4.04
  4    -5     3   5     128.50   120.83   4     2     8   5      34.77   -35.99
  4     7     3   5      10.81     8.18   4    -2     8   5      27.40    26.75
  4    -7     3   5      41.77    40.06   4     4     8   5   L   6.69     4.71
  4     9     3   5      26.48   -28.37   4    -4     8   5   L   6.69     4.71
  4    -9     3   5   L   5.20    -5.24   4     6     8   5   L   6.78      .25
  4    11     3   5      42.78   -47.64   4    -6     8   5      11.89     9.30
  4   -11     3   5   L   5.74     4.47   4     8     8   5   L   6.87    -2.96
  4    13     3   5      21.80   -25.33   4    -8     8   5      14.98    17.77
  4   -13     3   5      16.69   -12.30   4    10     8   5      39.72    44.64
  4    15     3   5      16.29   -17.55   4   -10     8   5      31.16   -32.21
  4     0     4   5      97.84   -92.10   4     1     9   5   L   6.95      .09
  4     2     4   5      21.66    20.02   4    -1     9   5      28.74    29.77
  4    -2     4   5      29.53   -32.05   4     3     9   5      48.04   -45.72
  4     4     4   5      19.34    19.66   4    -3     9   5   L   6.97    -4.52
  4    -4     4   5      19.96    19.67   4     5     9   5   L   7.00     1.29
  4     6     4   5      30.80   -34.63   4    -5     9   5   L   7.00    -1.54
  4    -6     4   5      14.48    13.35   4     7     9   5      48.89    53.15
  4     8     4   5      40.47    43.29   4    -7     9   5   L   7.03    -4.18
  4    -8     4   5      56.07    57.45   4     0    10   5      51.50    49.87
  4    10     4   5      18.74    18.78   4     1    10   5      11.28     8.12
  4   -10     4   5       5.80    -7.47   4     2    10   5      19.53   -19.85
  4    12     4   5      16.15   -16.24   4    -2    10   5      20.07    19.16
  4   -12     4   5      14.57   -18.76   4     4    10   5      19.51   -17.82
  4    14     4   5      17.26   -16.66   4    -4    10   5      21.07   -17.82
  4   -14     4   5      13.65     7.14   2     0     0   6      52.29    53.00
  4     1     5   5      24.34    22.38   4     0     0   6     199.22  -199.38
  4    -1     5   5      43.96    42.13   6     0     0   6      36.98   -37.53
  4     2     5   5      14.83    12.69   8     0     0   6      15.03   -13.36
  4    -2     5   5   L   4.89     1.01  10     0     0   6      43.01    45.14
  4     3     5   5     113.11  -108.87  12     0     0   6      66.16    73.45
  4    -3     5   5      37.83   -38.62  14     0     0   6      33.66   -29.15
```

H	K	L	GRP		FO	FC	H	K	L	GRP		FO	FC
16	0	0	6		64.35	-60.03	9	11	0	6		35.09	38.81
1	1	0	6		30.09	36.56	9	13	0	6	L	4.27	3.68
1	3	0	6		60.41	-61.97	10	2	0	6		59.07	-60.70
1	5	0	6		60.08	-47.76	10	4	0	6		27.70	24.07
1	7	0	6		117.73	109.53	10	6	0	6		88.03	92.41
1	9	0	6		146.10	-150.33	10	8	0	6		49.73	-48.91
1	11	0	6		63.73	-62.69	10	10	0	6		21.44	-20.90
1	13	0	6		29.65	25.41	10	12	0	6		15.19	7.08
1	15	0	6		31.16	-28.31	11	1	0	6		14.90	7.35
2	2	0	6		63.16	-65.72	11	3	0	6		84.24	-91.21
2	4	0	6		107.45	-100.79	11	5	0	6		19.03	17.98
2	6	0	6		87.64	83.99	11	7	0	6		59.90	53.77
2	8	0	6		58.48	52.38	11	9	0	6		58.75	-61.26
2	10	0	6		29.63	-26.60	11	11	0	6		23.08	-15.13
2	12	0	6		29.65	-25.30	12	2	0	6		54.23	-53.80
2	14	0	6		18.22	18.55	12	4	0	6		47.38	-48.09
2	16	0	6		12.53	8.63	12	6	0	6		19.89	14.26
3	1	0	6		174.11	172.76	12	8	0	6		47.59	-40.60
3	3	0	6		84.91	-81.70	12	10	0	6		20.21	-10.92
3	5	0	6		84.46	-91.63	13	1	0	6		8.69	-6.43
3	7	0	6		32.80	-29.33	13	3	0	6		26.45	-23.83
3	9	0	6		18.29	-8.65	13	5	0	6		60.65	62.77
3	11	0	6		7.63	-2.10	13	7	0	6		65.27	64.27
3	13	0	6		37.60	34.00	13	9	0	6		51.72	-56.77
3	15	0	6		11.22	-7.92	14	2	0	6		25.86	-22.97
4	2	0	6	L	3.02	-1.32	14	4	0	6		28.71	-25.27
4	4	0	6		64.27	-52.14	14	6	0	6		28.78	26.15
4	6	0	6		81.34	-78.48	14	8	0	6		16.52	22.41
4	8	0	6		97.20	99.51	15	1	0	6		40.99	39.16
4	10	0	6		17.72	-15.79	15	3	0	6		22.72	-19.99
4	12	0	6		53.70	-53.11	15	5	0	6		49.09	-39.48
4	14	0	6		12.62	15.47	15	7	0	6		19.64	-14.40
4	16	0	6		41.31	41.54	16	2	0	6		32.36	30.14
5	1	0	6		29.28	-34.92	16	4	0	6		49.07	47.80
5	3	0	6		13.55	-5.49	5	7	0	7		30.47	25.66
5	7	0	6		31.41	25.66	5	-7	0	7		93.94	-123.82
5	9	0	6		115.51	127.67	5	9	0	7		114.54	127.67
5	11	0	6		22.19	-13.04	5	-9	0	7		67.97	73.83
5	13	0	6		56.17	-59.40	5	11	0	7		18.89	-13.04
5	15	0	6		52.97	49.68	5	-11	0	7		13.80	-17.98
6	2	0	6		174.72	177.37	5	13	0	7		53.54	-59.40
6	4	0	6		36.21	-35.15	5	-13	0	7		61.91	-62.77
6	6	0	6		169.47	-180.93	5	15	0	7		50.11	49.68
6	8	0	6		18.31	16.60	5	-15	0	7		48.98	39.48
6	10	0	6		85.01	84.88	5	6	1	7		49.21	53.85
6	12	0	6	L	4.86	-3.25	5	8	1	7		29.85	-20.61
6	14	0	6		13.93	-8.79	5	-8	1	7		21.83	-20.55
7	1	0	6		125.47	-132.41	5	-10	1	7		72.39	-67.09
7	3	0	6		71.30	76.50	5	-12	1	7		31.84	-26.07
7	5	0	6		115.14	123.82	5	-14	1	7		19.33	24.72
7	9	0	6		38.62	-39.75	5	5	2	7		38.84	-34.71
7	11	0	6		58.38	-56.92	5	-5	2	7		39.10	34.71
7	13	0	6		33.09	-32.03	5	7	2	7		67.55	68.98
7	15	0	6		73.39	76.80	5	-7	2	7		42.10	-40.35
8	2	0	6		10.55	-10.69	5	9	2	7		85.80	85.86
8	4	0	6		89.77	90.45	5	-9	2	7		35.91	-30.60
8	6	0	6		29.69	31.27	5	11	2	7		24.11	-27.85
8	10	0	6		10.06	2.27	5	13	2	7		35.50	-38.48
8	12	0	6		38.17	-39.10	5	-13	2	7		18.30	-11.74
8	14	0	6		21.53	-23.79	5	15	2	7		21.87	-20.83
9	1	0	6		11.06	7.04	5	-15	2	7		29.33	34.18
9	3	0	6		54.65	-46.96	5	-4	3	7		28.93	-30.72
9	5	0	6		75.73	-73.83	5	6	3	7		118.08	-121.19
9	7	0	6		20.61	-26.69	5	-6	3	7		23.67	-26.87
9	9	0	6		17.29	-3.00	5	8	3	7		72.81	69.53

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 H    K     L GRP       FO       FC    H    K     L GRP       FO       FC

 5   -8     3   7    63.91   -62.16    5   11     1   7  L    .99    -5.07
 5   10     3   7    23.43    23.97    5  -11     1   7  L    .99     1.59
 5  -10     3   7    68.95    65.20    5   12     1   7  L   4.29     5.56
 5   12     3   7    29.09    37.32    5   13     1   7  L   1.10      .59
 5  -12     3   7    55.16    48.76    5  -13     1   7  L   1.10      .31
 5   14     3   7    33.26    36.28    5   14     1   7  L   4.77   -15.01
 5  -14     3   7    44.83   -46.60    5    6     2   7  L    .67    -2.60
 5    0     4   7    11.21     9.16    5   -6     2   7  L    .67     2.41
 5    1     4   7    59.35   -55.97    5    8     2   7  L    .83      .69
 5   -1     4   7    37.78   -37.04    5   -8     2   7  L    .83      .92
 5    3     4   7    19.64    18.94    5   10     2   7  L    .95      .20
 5   -3     4   7    17.78    20.74    5  -10     2   7  L    .95      .88
 5   -5     4   7     8.78    11.11    5  -11     2   7  L   4.16    -5.21
 5    7     4   7    38.51   -38.78    5   12     2   7  L   1.07      .61
 5   -7     4   7    60.17   -57.60    5  -12     2   7  L   1.07     -.34
 5    9     4   7    31.32    37.68    5   14     2   7  L   1.18     -.76
 5   -9     4   7    44.13    43.34    5  -14     2   7  L   1.18     1.01
 5   13     4   7    23.41   -26.48    5    5     3   7  L    .68     -.63
 5  -13     4   7    25.28   -23.93    5   -5     3   7  L    .68     -.63
 5    0     5   7    61.94    55.69    5    7     3   7  L    .84    -2.37
 5    2     5   7    48.99    48.32    5   -7     3   7  L    .84    -4.12
 5   -2     5   7    35.25   -33.72    5    9     3   7  L    .95     3.39
 5    4     5   7    37.61   -33.37    5   -9     3   7  L    .95     4.49
 5   -4     5   7    42.69   -40.98    5   11     3   7  L   1.07    -1.94
 5   -8     5   7    55.69   -55.42    5  -11     3   7  L   1.07      .03
 5  -10     5   7    33.64   -30.36    5   13     3   7  L   1.16      .12
 5   12     5   7    26.56    24.35    5  -13     3   7  L   1.16     -.44
 5    1     6   7    16.01    15.17    5    2     4   7  L    .65     2.97
 5    3     6   7    35.16   -33.57    5   -2     4   7  L    .65     3.37
 5   -3     6   7     9.10   -10.14    5    4     4   7  L    .77     -.84
 5    5     6   7    16.64   -16.54    5   -4     4   7  L    .77    -5.76
 5   -5     6   7    17.06    16.54    5    6     4   7  L    .88     2.01
 5   -6     6   7    11.49     8.27    5   -6     4   7  L    .88    -6.57
 5   -7     6   7    12.00    14.64    5    8     4   7  L    .99     3.11
 5    9     6   7    12.34   -17.24    5   -8     4   7  L    .99    -2.06
 5   -9     6   7    38.43   -38.80    5   10     4   7  L   1.08      .42
 5  -11     6   7    11.63    11.04    5  -10     4   7  L   1.08     1.10
 5  -13     6   7    25.93    27.66    5   11     4   7  L   4.58     1.92
 5    0     7   7    62.21    58.87    5  -11     4   7  L   4.58    -6.46
 5    2     7   7    32.85    29.11    5   12     4   7  L   1.16     -.25
 5   -2     7   7     9.57    -8.91    5  -12     4   7  L   1.16     -.91
 5    4     7   7    74.42   -72.69    5   14     4   7  L   1.25    -3.00
 5   -4     7   7    11.36    10.75    5  -14     4   7  L   1.25     -.85
 5    6     7   7    65.48   -69.59    5    1     5   7  L    .85     2.41
 5   -6     7   7    17.46   -15.10    5   -1     5   7  L    .85    -2.51
 5    8     7   7    38.84    35.25    5    3     5   7  L    .90     5.17
 5   -8     7   7    58.94   -53.69    5   -3     5   7  L    .90     1.53
 5  -10     7   7    66.61    61.59    5    5     5   7  L    .97     1.72
 5   -1     8   7    17.50   -15.20    5   -5     5   7  L    .97     1.72
 5    3     8   7    27.89    27.18    5    6     5   7  L   4.08     5.37
 5   -3     8   7    42.29   -39.47    5    7     5   7  L   1.03    -2.27
 5    5     8   7    10.20    13.70    5   -7     5   7  L   1.03    -3.53
 5   -5     8   7    11.13   -13.70    5    8     5   7  L   4.39     7.56
 5    7     8   7    47.96   -44.55    5    9     5   7  L   1.10    -1.88
 5   -7     8   7    20.61    13.16    5   -9     5   7  L   1.10     3.74
 5    9     8   7    26.65   -30.82    5   10     5   7  L   4.69     8.32
 5   -9     8   7    24.11    21.66    5   11     5   7  L   1.18    -5.11
 5    0     9   7    21.97    17.45    5  -11     5   7  L   1.18     2.24
 5    6     9   7    14.41    16.28    5  -12     5   7  L   4.99     5.68
 5   -6     9   7    13.04    12.92    5    0     6   7  L   1.01    -3.72
 5    1    10   7    28.48    26.59    5   -1     6   7  L   4.14    -5.93
 5   -1    10   7    22.59    22.64    5    2     6   7  L   1.02    -1.98
 5    3    10   7    14.45   -15.65    5   -2     6   7  L   1.02    -5.60
 5   -3    10   7    36.06   -34.00    5    4     6   7  L   1.06    -4.19
 5    7     1   7  L   .71     1.25    5   -4     6   7  L   1.06     3.67
 5   -7     1   7  L   .71    -4.00    5    6     6   7  L   1.10    -1.88
 5    9     1   7  L   .86      .98    5   -6     6   7  L   1.10     8.27
 5   -9     1   7  L   .86     2.92    5    7     6   7  L   4.63     1.36
 5   10     1   7  L  3.78     8.46    5    8     6   7  L   1.16     2.89
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H	K	L	GRP		FO	FC	H	K	L	GRP		FO	FC
5	-8	6	7	L	1.16	.96	6	15	3	8		20.55	26.12
5	10	6	7	L	1.22	-1.01	6	-6	4	8		86.93	-90.80
5	-10	6	7	L	1.22	2.02	6	8	4	8		15.15	18.35
5	11	6	7	L	5.09	.10	6	-8	4	8		19.78	-18.15
5	12	6	7	L	1.28	.25	6	10	4	8		69.83	69.94
5	13	6	7	L	5.31	6.00	6	-10	4	8		29.83	29.24
5	1	7	7	L	1.14	.37	6	12	4	8		17.33	12.80
5	-1	7	7	L	1.14	-4.71	6	-12	4	8		11.77	8.41
5	3	7	7	L	1.15	2.97	6	-14	4	8		13.91	14.98
5	-3	7	7	L	1.15	-2.90	6	-1	5	8		40.49	-48.67
5	5	7	7	L	1.18	-2.19	6	3	5	8		77.00	76.24
5	-5	7	7	L	1.18	-2.19	6	-3	5	8		76.78	-79.91
5	7	7	7	L	1.22	-4.75	6	5	5	8		11.05	10.46
5	-7	7	7	L	1.22	-2.39	6	-5	5	8		8.25	-5.37
5	9	7	7	L	1.25	2.51	6	7	5	8		20.31	-21.74
5	-9	7	7	L	1.25	5.09	6	-7	5	8		31.85	34.81
5	11	7	7	L	1.30	.99	6	9	5	8		20.22	-23.10
5	-11	7	7	L	1.30	-1.17	6	-9	5	8		81.22	82.14
5	0	8	7	L	1.24	4.29	6	11	5	8		25.60	-23.26
5	2	8	7	L	1.24	3.35	6	-11	5	8		9.68	5.59
5	-2	8	7	L	1.24	-2.84	6	13	5	8		16.87	21.25
5	4	8	7	L	1.25	.68	6	-13	5	8		71.65	-63.84
5	-4	8	7	L	1.25	-2.29	6	0	6	8		13.50	7.41
5	6	8	7	L	1.28	2.58	6	2	6	8		25.92	-26.33
5	-6	8	7	L	1.28	-2.22	6	-2	6	8		27.98	-25.21
5	8	8	7	L	1.30	2.41	6	4	6	8		17.31	14.87
5	-8	8	7	L	1.30	-2.41	6	-4	6	8		17.75	16.85
5	10	8	7	L	1.32	-3.47	6	6	6	8		47.15	43.00
5	-10	8	7	L	1.32	1.61	6	-6	6	8		47.73	43.00
5	1	9	7	L	1.31	2.70	6	8	6	8		18.11	-17.08
5	-1	9	7	L	1.31	-2.50	6	-8	6	8		17.03	14.99
5	2	9	7	L	5.39	2.24	6	10	6	8		26.75	-26.38
5	-2	9	7	L	5.39	9.38	6	-10	6	8		34.83	-34.45
5	3	9	7	L	1.32	5.34	6	12	6	8		17.91	19.31
5	-3	9	7	L	1.32	-.87	6	-12	6	8		16.58	-16.20
5	4	9	7	L	5.41	1.54	6	1	7	8		32.57	26.67
5	-4	9	7	L	5.41	1.29	6	-1	7	8		101.08	-100.97
5	5	9	7	L	1.33	1.46	6	3	7	8		22.61	22.08
5	-5	9	7	L	1.33	1.46	6	5	7	8		15.71	-15.10
5	7	9	7	L	1.33	-.96	6	-5	7	8		68.77	69.59
5	-7	9	7	L	1.33	.61	6	7	7	8		29.71	30.71
5	0	10	7	L	1.37	-4.19	6	-7	7	8		37.58	-36.17
5	2	10	7	L	1.37	-.56	6	9	7	8		42.66	-39.97
5	-2	10	7	L	1.37	-6.98	6	11	7	8		40.76	-36.37
6	8	0	8		13.38	16.60	6	-11	7	8		19.96	21.36
6	-8	0	8		20.95	31.27	6	0	8	8		16.37	-13.09
6	10	0	8		84.12	84.88	6	2	8	8		17.52	16.42
6	-10	0	8		65.95	92.41	6	-2	8	8		19.13	-14.44
6	-12	0	8		10.63	14.26	6	8	8	8		13.15	15.61
6	14	0	8		10.81	-8.79	6	-8	8	8		36.46	-33.85
6	-14	0	8		25.57	26.15	6	1	9	8		16.49	16.77
6	9	1	8		18.30	15.52	6	-1	9	8		31.75	-28.02
6	-9	1	8		63.09	67.36	6	3	9	8		22.85	21.32
6	-11	1	8		13.49	-8.25	6	-3	9	8		35.67	-34.58
6	-13	1	8		46.82	-42.85	6	5	9	8		12.21	12.92
6	8	2	8		38.56	-37.88	6	-5	9	8		14.26	-16.28
6	10	2	8		26.30	-24.65	6	12	0	8	L	3.55	-3.25
6	-10	2	8		34.51	33.82	6	10	1	8	L	.74	3.48
6	12	2	8		7.75	10.52	6	11	1	8	L	3.33	-2.62
6	-12	2	8		19.24	-17.29	6	12	1	8	L	.87	-2.00
6	14	2	8		21.12	20.50	6	-12	1	8	L	.87	-.42
6	7	3	8		47.87	46.84	6	13	1	8	L	3.79	-2.50
6	-7	3	8		18.99	-17.90	6	9	2	8	L	.69	.61
6	9	3	8		39.58	-36.98	6	-9	2	8	L	.69	1.70
6	-9	3	8		7.50	2.81	6	11	2	8	L	.84	.31
6	11	3	8		34.15	-37.18	6	-11	2	8	L	.84	-.12
6	-11	3	8		23.18	19.63	6	13	2	8	L	.94	1.28
6	13	3	8		24.17	23.37	6	-13	2	8	L	.94	1.31
6	-13	3	8		15.28	-16.55	6	-14	2	8	L	4.03	-2.49

H	K	L	GRP		FO	FC
6	15	2	8	L	1.01	2.12
6	-15	2	8	L	1.01	-.96
6	8	3	8	L	.66	5.48
6	-8	3	8	L	.66	-.66
6	10	3	8	L	.82	1.02
6	-10	3	8	L	.82	.77
6	12	3	8	L	.93	-4.28
6	-12	3	8	L	.93	-1.64
6	14	3	8	L	1.00	-2.45
6	-14	3	8	L	1.00	-2.31
6	-15	3	8	L	4.17	-2.78
6	7	4	8	L	.67	-3.45
6	-7	4	8	L	.67	2.35
6	9	4	8	L	.82	-.99
6	-9	4	8	L	.82	-2.79
6	11	4	8	L	.92	1.12
6	-11	4	8	L	.92	-1.16
6	13	4	8	L	1.00	1.43
6	14	4	8	L	4.16	-6.91
6	2	5	8	L	.42	1.79
6	-2	5	8	L	.42	2.74
6	4	5	8	L	.60	-2.64
6	-4	5	8	L	.60	7.50
6	6	5	8	L	.74	-4.38
6	-6	5	8	L	.74	4.38
6	8	5	8	L	.85	.84
6	-8	5	8	L	.85	3.74
6	10	5	8	L	.93	2.12
6	-10	5	8	L	.93	-2.70
6	12	5	8	L	1.00	-1.56
6	-12	5	8	L	1.00	-1.72
6	1	6	8	L	.71	5.89
6	-1	6	8	L	.71	.05
6	3	6	8	L	.75	-3.91
6	-3	6	8	L	.75	-4.60
6	5	6	8	L	.82	-8.27
6	-5	6	8	L	.82	-1.88
6	7	6	8	L	.90	-1.52
6	-7	6	8	L	.90	2.31
6	9	6	8	L	.96	3.31
6	-9	6	8	L	.96	.82
6	11	6	8	L	1.01	1.19
6	-11	6	8	L	1.01	-1.03
6	2	7	8	L	.87	-1.70
6	-2	7	8	L	.87	3.39
6	-3	7	8	L	3.63	-4.66
6	4	7	8	L	.91	5.31
6	-4	7	8	L	.91	1.83
6	6	7	8	L	.95	6.42
6	-6	7	8	L	.95	-6.42
6	8	7	8	L	1.00	6.36
6	-8	7	8	L	1.00	1.06
6	-9	7	8	L	4.13	-2.01
6	10	7	8	L	1.03	-2.55
6	1	8	8	L	.96	-.50
6	-1	8	8	L	.96	-1.74
6	3	8	8	L	.98	-.02
6	-3	8	8	L	.98	5.13
6	4	8	8	L	4.05	9.30
6	-4	8	8	L	4.05	.25
6	5	8	8	L	1.01	2.22
6	-5	8	8	L	1.01	2.58
6	6	8	8	L	4.15	5.70
6	-6	8	8	L	4.15	5.70
6	7	8	8	L	1.03	-1.17
6	-7	8	8	L	1.03	-2.69
6	9	8	8	L	1.04	2.40
6	-9	8	8	L	1.04	-3.88
6	0	9	8	L	1.03	-4.56
6	2	9	8	L	1.03	.69
6	-2	9	8	L	1.03	1.30
6	4	9	8	L	1.04	-.63
6	-4	9	8	L	1.04	5.23
6	6	9	8	L	1.04	-3.24
6	-6	9	8	L	1.04	3.23

APPENDIX 2. The observed structure factors(FO) and Calculated
Structure Factors(FC) of the Scapolite(ON45, 93%
Me, Monte Somma, Italy)

```
  H      K      L     G  C F OBS    F CALC    H      K      L     G  C F OBS    F CALC
  2      0      0     1      79.36    86.86   16      6      0     1  R  11.09     8.91
  4      0      0     1  R 158.20 -213.12    1      7      0     1    108.40   104.04
  6      0      0     1      47.29   -50.14    3      7      0     1     32.35   -30.88
  8      0      0     1      19.86    15.74    5      7      0     1  L   3.90    -8.62
 10      0      0     1      84.02    84.08    7      7      0     1  R  39.55    17.84
 12      0      0     1      71.51    79.57    9      7      0     1     20.98    14.72
 14      0      0     1      53.12   -46.74   11      7      0     1     75.67    76.66
 16      0      0     1      99.38   -94.55   13      7      0     1     63.50    65.85
  3      1      0     1     115.13   133.66   15      7      0     1     18.32   -17.61
  5      1      0     1      54.04   -64.95    2      8      0     1     53.08    47.07
  7      1      0     1     158.22 -165.73    4      8      0     1     57.60    51.27
  9      1      0     1      20.91    17.74    6      8      0     1  L   4.13     6.64
 11      1      0     1      29.41    29.78    8      8      0     1  R  17.91     2.81
 13      1      0     1      10.08    -9.29   10      8      0     1     51.95   -48.13
 15      1      0     1      36.25    36.36   12      8      0     1     49.56   -40.21
  2      2      0     1      38.04   -34.97   14      8      0     1     18.46    30.18
  4      2      0     1      22.64    20.14    1      9      0     1    172.11 -168.17
  6      2      0     1     151.85   160.87    3      9      0     1     22.13   -20.86
  8      2      0     1      16.41     8.58    5      9      0     1    130.21   138.79
 10      2      0     1      20.45   -23.39    7      9      0     1     61.73    51.98
 12      2      0     1      36.94   -35.68    9      9      0     1     17.86    14.05
 14      2      0     1      34.32   -28.16   11      9      0     1     63.82   -66.48
 16      2      0     1      30.53    32.80   13      9      0     1     49.15   -56.11
  1      3      0     1      39.67   -38.21    2     10      0     1     26.31   -28.36
  3      3      0     1      75.28   -68.30    4     10      0     1  L   4.29    -3.59
  5      3      0     1      41.74   -39.90    6     10      0     1    129.78   123.34
  7      3      0     1      71.63    74.94    8     10      0     1     20.20    20.73
  9      3      0     1      59.96   -60.73   10     10      0     1     36.87   -38.45
 11      3      0     1     114.35 -112.20   12     10      0     1     30.60   -29.75
 13      3      0     1      49.20   -47.40    1     11      0     1     93.04   -84.86
 15      3      0     1      28.37   -26.00    3     11      0     1     20.78   -15.93
  2      4      0     1      95.98   -89.46    5     11      0     1     12.53    -8.42
  4      4      0     1     102.53   -94.63    7     11      0     1     48.37   -42.54
  6      4      0     1      36.39   -33.52    9     11      0     1     29.68    35.60
  8      4      0     1      98.67    94.83    7     11      0     1     48.37   -42.54
 10      4      0     1      45.50    39.74    9     11      0     1     29.63    35.60
 12      4      0     1      62.56   -59.83   11     11      0     1     42.29   -38.99
 14      4      0     1      45.23   -44.09   13     11      0     1  R  55.30   -54.04
 16      4      0     1      70.13    65.51    2     12      0     1     33.88   -35.95
  1      5      0     1      31.04   -21.42    4     12      0     1     41.78   -46.43
  3      5      0     1     123.05 -125.94    6     12      0     1     32.94    32.02
  5      5      0     1  R   20.75     1.33    8     12      0     1     12.24   -16.67
  7      5      0     1     140.52   146.06   10     12      0     1     17.22     7.08
  9      5      0     1      58.91   -55.08   12     12      0     1  R  56.98    57.04
 11      5      0     1      15.15    -7.35    1     13      0     1     25.14    23.05
 13      5      0     1      29.89    33.72    3     13      0     1     16.60    13.84
 15      5      0     1      67.88   -63.10    5     13      0     1     57.74   -61.20
  2      6      0     1      20.29    19.46    7     13      0     1     34.50   -29.63
  4      6      0     1     121.30 -113.22    9     13      0     1     14.93   -10.17
  6      6      0     1     196.33 -210.51   11     13      0     1  R  16.46     -.88
  8      6      0     1      46.63    50.90    2     14      0     1      9.21     1.85
 10      6      0     1      93.50    96.67    4     14      0     1  L   4.29     7.72
 12      6      0     1       7.74    -1.74    6     14      0     1     26.01   -24.28
 14      6      0     1  L    4.38     2.11    8     14      0     1     21.01   -27.89
```

H	K	L	G	C	F OBS	F CALC	H	K	L	G	C	F OBS	F CALC
1	15	0	1		36.27	-37.57	0	10	8	2	L	4.94	-10.81
3	15	0	1	L	4.09	-4.27	0	1	9	2	L	5.99	-1.39
5	15	0	1		68.09	67.56	0	3	9	2		29.25	21.90
7	15	0	1		84.05	86.23	0	5	9	2		15.48	13.66
2	16	0	1		13.18	-11.64	0	7	9	2		29.12	-32.49
4	16	0	1		34.76	38.33	0	9	9	2	R	46.75	-49.15
6	16	0	1	R	14.26	-10.54	0	0	10	2		139.50	-144.72
0	2	0	2	R	84.65	86.86	0	4	10	2		62.51	59.86
0	4	0	2		195.81	-213.12	0	4	1	2	L	.59	.12
0	6	0	2		50.25	-50.14	0	6	1	2	L	.71	-.48
0	8	0	2		17.38	15.74	0	8	1	2	L	.82	-.69
0	10	0	2		90.23	84.08	0	10	1	2	L	.89	-.12
0	12	0	2		76.30	79.57	0	12	1	2	L	.91	.12
0	14	0	2		52.06	-46.74	0	14	1	2	L	.91	-.53
0	16	0	2		97.69	-94.55	0	3	2	2	L	.57	.56
0	3	1	2		66.19	63.96	0	5	2	2	L	.69	.73
0	5	1	2		8.74	5.34	0	7	2	2	L	.78	.43
0	7	1	2		34.88	-29.82	0	9	2	2	L	.87	-.03
0	9	1	2		80.79	-75.05	0	11	2	2	L	.91	.25
0	11	1	2		49.59	-44.84	0	13	2	2	L	.91	.47
0	13	1	2	L	5.81	7.59	0	2	3	2	L	.62	.81
0	15	1	2		47.14	44.58	0	4	3	2	L	.69	1.13
0	0	2	2		73.63	-63.35	0	6	3	2	L	.78	.86
0	2	2	2		42.54	-38.58	0	8	3	2	L	.85	-.31
0	4	2	2		15.85	-18.27	0	10	3	2	L	.89	-.29
0	6	2	2		38.91	38.62	0	12	3	2	L	.91	.26
0	8	2	2		35.00	-34.24	0	14	3	2	L	.87	-.01
0	10	2	2		28.09	32.13	0	1	4	2	L	.66	.21
0	12	2	2		49.08	46.87	0	3	4	2	L	.71	.49
0	14	2	2		9.61	7.15	0	5	4	2	L	.78	.81
0	1	3	2	L	3.68	-1.39	0	7	4	2	L	.85	.25
0	3	3	2		149.22	143.69	0	9	4	2	L	.89	-.08
0	5	3	2		81.04	78.75	0	11	4	2	L	.91	.18
0	7	3	2		110.11	-106.14	0	13	4	2	L	.89	.64
0	9	3	2		42.31	42.64	0	2	5	2	L	.75	-.36
0	11	3	2		115.90	111.22	0	4	5	2	L	.80	.41
0	13	3	2		32.52	32.94	0	6	5	2	L	.85	.71
0	15	3	2		29.35	-26.52	0	8	5	2	L	.89	.34
0	0	4	2		288.90	317.76	0	10	5	2	L	.91	.12
0	2	4	2		14.16	20.85	0	12	5	2	L	.89	.08
0	4	4	2		113.95	-101.43	0	1	6	2	L	.82	-.40
0	6	4	2		40.42	-38.97	0	3	6	2	L	.85	-.50
0	8	4	2		11.87	-12.36	0	5	6	2	L	.87	.87
0	10	4	2		23.60	24.53	0	7	6	2	L	.91	1.16
0	12	4	2		36.34	42.20	0	9	6	2	L	.91	.35
0	14	4	2		27.79	-24.84	0	11	6	2	L	.89	.12
0	1	5	2	L	4.76	-1.34	0	2	7	2	L	.89	-.29
0	3	5	2		113.17	99.93	0	4	7	2	L	.91	-.20
0	5	5	2		49.52	46.09	0	6	7	2	L	.94	.51
0	7	5	2		96.00	-96.47	0	8	7	2	L	.94	.15
0	9	5	2		79.39	-80.56	0	10	7	2	L	.89	-.31
0	11	5	2		11.05	-10.25	0	1	8	2	L	.94	-.14
0	13	5	2		22.83	24.46	0	3	8	2	L	.94	-.09
0	15	5	2	R	44.17	45.66	0	5	8	2	L	.94	-.11
0	0	6	2		206.42	-207.29	0	7	8	2	L	.91	-.20
0	2	6	2		42.54	-48.91	0	2	9	2	L	.94	-.86
0	4	6	2		50.71	51.34	0	4	9	2	L	.94	-.97
0	6	6	2		19.76	16.85	0	6	9	2	L	.89	-.31
0	8	6	2		22.67	-25.11	0	8	9	2	L	.73	.20
0	10	6	2		27.47	-24.59	0	1	10	2	L	.85	-.22
0	12	6	2		9.65	-9.35	0	3	10	2	L	.80	-.33
0	1	7	2		34.70	-37.64	0	5	10	2	L	.64	-.12
0	3	7	2		54.21	57.93	1	3	0	3		38.95	-38.21
0	5	7	2		65.03	64.77	1	-3	0	3		119.04	-133.65
0	7	7	2		74.45	-76.35	1	5	0	3		31.19	-21.42
0	11	7	2		58.51	62.35	1	-5	0	3		58.33	64.95
0	0	8	2		25.71	31.82	1	7	0	3		100.36	104.04
0	2	8	2		11.62	16.28	1	-7	0	3		158.15	165.73
0	4	8	2	L	5.97	-4.93	1	9	0	3		157.00	-168.17
0	6	8	2		14.00	-15.62	1	-9	0	3		27.35	-17.74

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H     K      L    G  C  F OBS    F CALC     H      K      L    G  C  F OBS    F CALC
1    11      0    3      90.86   -84.86     1     -2      5    3      31.26   -35.04
1   -11      0    3      32.93   -29.78     1      4      5    3      35.35   -34.81
1    13      0    3  R   28.08    23.05     1     -4      5    3      26.77    23.74
1   -13      0    3  L    8.58     9.29     1      6      5    3      40.17    34.82
1    15      0    3      38.13   -37.57     1     -6      5    3     126.37   124.59
1   -15      0    3      35.07   -36.36     1      8      5    3      47.25   -46.66
1     2      1    3  R   17.12   -18.11     1     -8      5    3      22.04    24.05
1    -2      1    3  R   50.69   -46.88     1     10      5    3  L    8.49     -.25
1     4      1    3      93.28   -92.93     1    -10      5    3      48.03   -45.23
1     6      1    3      79.69   -74.14     1     12      5    3  L    8.66    12.97
1    -6      1    3     119.20   118.36     1    -12      5    3  L    8.66     3.82
1     8      1    3      35.75   -34.39     1     14      5    3      28.08   -24.93
1    -8      1    3      27.89    21.98     1    -14      5    3      57.53    58.25
1    10      1    3  L    8.04    11.09     1      1      6    3      45.44    41.55
1   -10      1    3      26.01    25.85     1      3      6    3      47.86    48.60
1    12      1    3      33.02    24.56     1     -3      6    3  L    7.41   -14.41
1   -12      1    3      24.48    23.29     1      5      6    3  L    7.76    -5.76
1    14      1    3  L    8.73     5.11     1     -5      6    3      27.24   -28.56
1   -14      1    3      27.19    25.47     1      7      6    3      41.11   -40.19
1    16      1    3      39.54   -34.61     1     -7      6    3      44.59   -42.11
1   -16      1    3  L    8.35     8.79     1      9      6    3      32.03    34.62
1     1      2    3  R  183.79   217.43     1     -9      6    3      20.79    22.48
1     3      2    3      34.15    33.20     1     11      6    3      37.44    38.55
1    -3      2    3     170.76-197.88      1    -11      6    3      18.04    18.25
1     5      2    3      97.63   -92.28     1     13      6    3      28.15    31.06
1    -5      2    3      80.84   -81.39     1    -13      6    3      25.71   -26.78
1     7      2    3      48.00   -46.62     1      0      7    3      37.02   -37.64
1    -7      2    3      29.31    26.77     1      2      7    3      86.86   -79.89
1     9      2    3      48.03   -50.61     1     -2      7    3      21.03    25.65
1    -9      2    3      69.24    61.78     1      4      7    3      82.81    83.98
1    11      2    3      19.12    13.96     1     -4      7    3      27.82    25.34
1   -11      2    3      28.46    25.89     1      6      7    3     118.80   128.05
1    13      2    3      70.44    78.83     1     -6      7    3      26.06    16.16
1   -13      2    3      69.62   -70.30     1      8      7    3      32.41   -24.81
1    15      2    3      27.75    29.17     1    -10      7    3      93.12   -89.81
1   -15      2    3      62.07   -60.40     1     12      7    3      27.07   -23.17
1     0      3    3  L    4.85    -1.39     1    -12      7    3      42.48   -40.50
1     2      3    3      26.91   -25.17     1      1      8    3      58.09   -57.38
1    -2      3    3  L    5.20    10.81     1      3      8    3      16.06   -18.40
1     4      3    3     145.61   148.00     1     -3      8    3      60.07    69.12
1    -4      3    3      79.10    78.20     1      5      8    3      34.95    36.82
1     6      3    3     156.79   166.25     1     -5      8    3      21.59    31.44
1    -6      3    3      58.24    50.53     1      7      8    3      32.88    26.54
1     8      3    3      40.36   -36.16     1     -7      8    3  L    8.73      .19
1    -8      3    3      46.31    43.57     1      9      8    3      16.77    13.57
1    10      3    3  L    8.21   -10.53     1     -9      8    3      36.74   -34.95
1   -10      3    3     112.00-111.56      1     11      8    3  L    8.19    -8.40
1    12      3    3      34.06   -29.93     1    -11      8    3      17.33   -16.15
1   -12      3    3      52.57   -48.89     1      0      9    3  L    8.80    -1.39
1    14      3    3      63.53   -64.53     1      2      9    3      54.36   -54.03
1   -14      3    3      53.46    52.41     1     -2      9    3  L    8.82    -9.94
1    16      3    3      51.06    49.19     1      4      9    2      33.17   -34.36
1   -16      3    3  L    8.04    13.14     1     -4      9    3  L    8.82    -1.72
1     1      4    3      25.54   -21.02     1      6      9    3      16.96    15.17
1     3      4    3      10.65     9.39     1     -6      9    3      23.99    29.11
1    -3      4    3  L    6.16     9.64     1      8      9    3  L    8.54    -8.49
1     5      4    3      67.06    64.04     1     -8      9    3  L    8.54   -10.31
1    -5      4    3      93.00    92.43     1      1     10    3  L    8.82   -12.95
1     7      4    3      79.22    79.89     1      3     10    3  L    8.75     4.28
1    -7      4    3      89.14    83.76     1     -3     10    3      36.20    25.57
1     9      4    3      83.83   -83.96     1      5     10    3      23.21   -25.57
1    -9      4    3      48.90   -45.20     1     -5     10    3      37.44   -41.46
1    11      4    3      46.55   -42.56     1      3      1    3  L      .54      .38
1   -11      4    3      26.01   -26.90     1     -3      1    3  L      .54      .57
1    13      4    3      16.75     9.60     1      5      1    3  L      .71     -.59
1   -13      4    3      36.71    27.48     1     -5      1    3  L      .71      .88
1    15      4    3      20.25   -25.21     1      7      1    3  L      .85     -.77
1   -15      4    3  L    8.28    -8.98     1     -7      1    3  L      .85      .14
1     0      5    3  L    6.44    -1.34     1      9      1    3  L      .94      .02
1     2      5    3      90.25   -83.51     1     -9      1    3  L      .94      .50
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H    K    L   G  C     F OBS    F CALC    H    K    L   G  C     F OBS    F CALC
1   11    1   3  L      1.01       .36    1    6    6   3  L       .96       .55
1  -11    1   3  L      1.01       .87    1   -6    6   3  L       .96       .32
1  -13    1   3  L      1.06       .62    1    8    6   3  L      1.01       .05
1   13    1   3  L      1.06       .28    1   -8    6   3  L      1.01      -.00
1   15    1   3  L      1.06      -.23    1   10    6   3  L      1.06      -.57
1  -15    1   3  L      1.06       .38    1  -10    6   3  L      1.06       .43
1    2    2   3  L       .54       .20    1   12    6   3  L      1.06      -.21
1   -2    2   3  L       .54      -.17    1  -12    6   3  L      1.06       .22
1    4    2   3  L       .68       .36    1   14    6   3  L       .96       .03
1   -4    2   3  L       .68      -.20    1    1    7   3  L       .96       .85
1    6    2   3  L       .80      -.30    1   -1    7   3  L       .96       .85
1   -6    2   3  L       .80       .27    1    3    7   3  L       .96      -.47
1    8    2   3  L       .92      -.71    1   -3    7   3  L       .96       .11
1   -8    2   3  L       .92       .05    1    5    7   3  L      1.01      -.02
1   10    2   3  L       .99      -.81    1   -5    7   3  L      1.01      -.36
1  -10    2   3  L       .99       .10    1    7    7   3  L      1.03       .83
1   12    2   3  L      1.06      -.12    1   -7    7   3  L      1.03      -.11
1  -12    2   3  L      1.06      -.31    1    9    7   3  L      1.06       .40
1   14    2   3  L      1.06       .00    1   -9    7   3  L      1.06      -.05
1  -14    2   3  L      1.06      -.44    1   11    7   3  L      1.06      -.14
1   16    2   3  L      1.01      -.43    1  -11    7   3  L      1.06      -.35
1  -16    2   3  L      1.01       .03    1    2    8   3  L      1.03      -.31
1    1    3   3  L       .61      -.69    1   -2    8   3  L      1.03       .46
1   -1    3   3  L       .61      -.69    1    4    8   3  L      1.03      -.42
1    3    3   3  L       .68      -.47    1   -4    8   3  L      1.03       .27
1   -3    3   3  L       .68       .32    1    6    8   3  L      1.06       .13
1    5    3   3  L       .78      -.21    1   -6    8   3  L      1.06       .01
1   -5    3   3  L       .78       .39    1    8    8   3  L      1.06       .23
1    7    3   3  L       .87      -.57    1   -8    8   3  L      1.06       .10
1   -7    3   3  L       .87      -.14    1   10    8   3  L      1.03       .08
1    9    3   3  L       .96      -.42    1  -10    8   3  L      1.03       .29
1   -9    3   3  L       .96       .01    1    1    9   3  L      1.08       .51
1   11    3   3  L      1.03      -.16    1   -1    9   3  L      1.08       .51
1  -11    3   3  L      1.03       .27    1    3    9   3  L      1.08      -.04
1   13    3   3  L      1.06      -.08    1   -3    9   3  L      1.08       .05
1  -13    3   3  L      1.06       .27    1    5    9   3  L      1.08      -.00
1   15    3   3  L      1.03      -.32    1   -5    9   3  L      1.08      -.31
1  -15    3   3  L      1.03       .10    1    7    9   3  L      1.06      1.02
1    2    4   3  L       .73      -.47    1   -7    9   3  L      1.06      -.05
1   -2    4   3  L       .73       .86    1    9    9   3  L      1.01       .61
1    4    4   3  L       .80      -.26    1   -9    9   3  L      1.01      -.24
1   -4    4   3  L       .80       .79    1    2   10   3  L      1.08       .31
1    6    4   3  L       .87      -.09    1   -2   10   3  L      1.08      -.46
1   -6    4   3  L       .87       .11    1    4   10   3  L      1.06       .26
1    8    4   3  L       .96      -.53    1   -4   10   3  L      1.06      -.60
1   -8    4   3  L       .96       .33    2    4    0   4         88.35    -89.46
1   10    4   3  L      1.01     -1.02    2   -4    0   4         18.87     20.14
1  -10    4   3  L      1.01       .68    2    6    0   4         19.93     19.46
1   12    4   3  L      1.06      -.37    2   -6    0   4        148.44    160.87
1  -12    4   3  L      1.06       .33    2    8    0   4         49.85     47.07
1    1    5   3  L       .80      -.82    2   -8    0   4         17.09      8.58
1   -1    5   3  L       .80      -.82    2   10    0   4         26.42    -28.36
1    3    5   3  L       .82      -.26    2  -10    0   4         21.87    -23.39
1   -3    5   3  L       .82      -.30    2   12    0   4         34.15    -35.95
1    5    5   3  L       .89      -.03    2  -12    0   4         40.28    -35.68
1   -5    5   3  L       .89       .04    2   14    0   4  L       9.24      1.85
1    7    5   3  L       .96       .41    2  -14    0   4         36.40    -28.16
1   -7    5   3  L       .96      -.40    2   16    0   4         15.12    -11.64
1    9    5   3  L      1.01      -.28    2  -16    0   4         33.24     32.80
1   -9    5   3  L      1.01      -.82    2    3    1   4        204.31   -227.19
1   11    5   3  L      1.06      -.37    2    5    1   4        103.86   -102.47
1  -11    5   3  L      1.06      -.47    2   -5    1   4         78.83    -74.38
1   13    5   3  L      1.06       .06    2    7    1   4         97.34     95.11
1  -13    5   3  L      1.06      -.12    2   -7    1   4         17.77    -15.68
1   15    5   3  L       .96       .07    2    9    1   4  L       7.78     -5.33
1  -15    5   3  L       .96       .03    2   -9    1   4         72.45    -73.86
1    2    6   3  L       .89      -.05    2   11    1   4         35.14    -33.67
1   -2    6   3  L       .89      1.10    2  -11    1   4         39.94     33.90
1    4    6   3  L       .92       .54    2   13    1   4  L       9.08     -1.17
1   -4    6   3  L       .92       .62    2  -13    1   4         65.20     57.84
```

H	K	L	G	C	F OBS	F CALC	H	K	L	G	C	F OBS	F CALC
2	15	1	4	L	9.29	-1.38	2	-6	6	4		34.66	-32.26
2	-15	1	4	L	9.29	-3.97	2	8	6	4		32.10	29.93
2	0	2	4		42.09	-38.58	2	-8	6	4		76.50	-75.46
2	2	2	4		56.80	-52.87	2	10	6	4	L	8.94	-5.72
2	4	2	4		28.85	20.98	2	-10	6	4	L	8.94	-3.80
2	-4	2	4		59.68	61.85	2	12	6	4	L	9.17	-.95
2	6	2	4		90.75	87.67	2	-12	6	4		38.82	38.33
2	-6	2	4	L	6.43	7.05	2	14	6	4	L	14.37	10.55
2	8	2	4		153.06	167.82	2	-14	6	4		15.97	13.35
2	-8	2	4		189.76	-206.94	2	1	7	4		21.73	25.65
2	10	2	4		26.17	-24.39	2	-1	7	4		85.21	79.90
2	-10	2	4		46.12	-40.85	2	3	7	4		11.12	22.10
2	12	2	4		30.40	-29.23	2	5	7	4	L	8.30	8.06
2	-12	2	4		50.97	46.76	2	-5	7	4		31.09	-27.11
2	14	2	4		42.98	39.28	2	7	7	4		33.51	-35.22
2	-14	2	4	L	13.82	-15.25	2	9	7	4	L	9.01	-3.10
2	16	2	4	R	14.37	-17.36	2	-9	7	4		15.17	-15.19
2	-16	2	4		46.83	43.37	2	11	7	4		66.32	61.95
2	-1	3	4		25.23	25.17	2	-11	7	4	L	10.64	3.87
2	3	3	4		83.84	84.60	2	0	8	4	L	10.80	16.28
2	-3	3	4		83.31	-77.62	2	2	8	4	R	13.13	10.54
2	5	3	4	L	8.90	-8.48	2	-2	8	4	R	12.72	10.54
2	-5	3	4		33.42	-30.69	2	4	8	4	R	12.08	9.70
2	7	3	4		104.31	-97.25	2	-4	8	4		38.20	-36.58
2	-7	3	4		26.31	24.01	2	6	8	4		30.22	-28.48
2	-9	3	4		27.79	-23.71	2	-6	8	4	L	8.92	10.34
2	11	3	4		82.35	86.03	2	8	8	4		73.11	-78.55
2	-11	3	4		37.75	-30.13	2	-8	8	4		91.94	93.05
2	13	3	4		21.18	15.07	2	10	8	4	L	9.20	2.93
2	-13	3	4		15.78	18.82	2	-10	8	4	R	13.29	13.49
2	15	3	4		67.64	-68.66	2	1	9	4	L	8.99	-9.94
2	-15	3	4	L	13.82	-16.53	2	-1	9	4		56.57	54.03
2	0	4	4		15.14	20.85	2	3	9	4		77.55	-84.36
2	2	4	4		17.13	-14.04	2	-3	9	4		14.43	15.74
2	4	4	4		41.25	-41.11	2	5	9	4	L	9.17	-7.96
2	-4	4	4		27.77	23.45	2	-5	9	4	L	11.71	-12.83
2	6	4	4		14.07	-9.37	2	7	9	4		55.93	58.27
2	-6	4	4		102.55	101.01	2	-7	9	4	L	9.24	-3.00
2	8	4	4		37.38	-40.85	2	0	10	4	L	9.33	-9.82
2	-8	4	4		52.68	52.17	2	2	10	4	R	13.98	14.62
2	10	4	4		29.56	-30.22	2	4	10	4		21.32	22.59
2	-10	4	4	L	8.56	-4.97	2	-4	10	4		19.08	-17.44
2	12	4	4		13.52	-14.71	2	4	1	4	L	.55	.50
2	-12	4	4		21.59	-19.03	2	-4	1	4	L	.55	-.52
2	14	4	4		20.47	-11.26	2	6	1	4	L	.75	-.16
2	-14	4	4	L	9.22	.44	2	-6	1	4	L	.75	-.90
2	1	5	4		30.65	-35.04	2	8	1	4	L	.89	-.13
2	-1	5	4		88.07	83.51	2	-8	1	4	L	.89	-1.00
2	3	5	4		175.69	-188.84	2	10	1	4	L	1.01	1.10
2	-3	5	4	L	9.33	-11.06	2	-10	1	4	L	1.01	-.77
2	5	5	4		68.67	-69.25	2	12	1	4	L	1.08	.89
2	-5	5	4		68.67	-66.92	2	-12	1	4	L	1.08	-.18
2	7	5	4		80.64	80.54	2	14	1	4	L	1.12	-.03
2	-7	5	4	L	7.89	-3.38	2	-14	1	4	L	1.12	-.16
2	9	5	4	L	10.36	-11.59	2	16	1	4	L	1.12	-.28
2	-9	5	4		98.32	-98.49	2	-16	1	4	L	1.12	-.41
2	11	5	4	L	8.94	3.70	2	1	2	4	L	.41	.17
2	-11	5	4		42.02	37.22	2	-1	2	4	L	.41	.20
2	13	5	4	L	9.20	10.53	2	3	2	4	L	.55	.74
2	-13	5	4		101.25	94.62	2	-3	2	4	L	.55	.53
2	15	5	4		37.24	-40.89	2	5	2	4	L	.71	.79
2	-15	5	4		21.11	-20.27	2	-5	2	4	L	.71	.05
2	0	6	4		44.45	-48.91	2	7	2	4	L	.85	.07
2	2	6	4	L	7.21	-5.08	2	-7	2	4	L	.85	.11
2	4	6	4		21.82	24.16	2	9	2	4	L	.95	-.05
2	-4	6	4		39.46	38.48	2	-9	2	4	L	.96	.63

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H    K     L    G  C     F OBS   F CALC    H    K     L    G  C     F OBS   F CALC
2   11     2    4  L      1.05      .26    2    4     7    4  L       .98     -.54
2  -11     2    4  L      1.05      .55    2   -4     7    4  L       .98      .28
2   13     2    4  L      1.12      .63    2    6     7    4  L      1.03     -.24
2  -13     2    4  L      1.12      .19    2   -6     7    4  L      1.03      .65
2   15     2    4  L      1.14      .58    2    8     7    4  L      1.08     -.06
2  -15     2    4  L      1.14      .15    2   -8     7    4  L      1.08      .53
2    2     3    4  L       .62     -.06    2   10     7    4  L      1.12     -.91
2   -2     3    4  L       .62      .06    2  -10     7    4  L      1.12      .73
2    4     3    4  L       .71      .88    2   12     7    4  L      1.12     -.74
2   -4     3    4  L       .71      .76    2  -12     7    4  L      1.12      .37
2    6     3    4  L       .82      .26    2    3     8    4  L      1.05     -.50
2   -6     3    4  L       .82      .20    2   -3     8    4  L      1.05     -.42
2    8     3    4  L       .94     -.25    2    5     8    4  L      1.08     -.17
2   -8     3    4  L       .94     -.65    2   -5     8    4  L      1.08     -.08
2   10     3    4  L      1.03      .13    2    7     8    4  L      1.10     -.34
2  -10     3    4  L      1.03     -.54    2   -7     8    4  L      1.10     -.38
2   12     3    4  L      1.10      .48    2    9     8    4  L      1.12     -.22
2  -12     3    4  L      1.10      .02    2   -9     8    4  L      1.12     -.38
2   14     3    4  L      1.12      .26    2   11     8    4  L      1.12     -.22
2  -14     3    4  L      1.12      .02    2  -11     8    4  L      1.12     -.12
2   16     3    4  L      1.10     -.06    2    2     9    4  L      1.10      .17
2  -16     3    4  L      1.10     -.14    2    4     9    4  L      1.12     -.84
2    1     4    4  L       .69     -.85    2   -4     9    4  L      1.12     -.80
2   -1     4    4  L       .69     -.47    2    6     9    4  L      1.12     -.48
2    3     4    4  L       .73     -.31    2   -6     9    4  L      1.12     -.19
2   -3     4    4  L       .73     -.18    2    8     9    4  L      1.12      .27
2    5     4    4  L       .82      .33    2   -8     9    4  L      1.12      .62
2   -5     4    4  L       .82     -.13    2    1    10    4  L      1.14      .46
2    7     4    4  L       .92     -.39    2   -1    10    4  L      1.14      .31
2   -7     4    4  L       .92     -.68    2    3    10    4  L      1.14      .35
2    9     4    4  L      1.01     -.28    2   -3    10    4  L      1.14      .11
2   -9     4    4  L      1.01      .37    2    5    10    4  L      1.14      .16
2   11     4    4  L      1.08      .09    2   -5    10    4  L      1.14      .21
2  -11     4    4  L      1.08      .66    3    5     0    5        128.77  -125.94
2   13     4    4  L      1.12      .86    3   -5     0    5         38.35    39.90
2  -13     4    4  L      1.12      .38    3    7     0    5         32.79   -30.88
2   15     4    4  L      1.12      .84    3   -7     0    5         70.27   -74.94
2  -15     4    4  L      1.12      .24    3    9     0    5         24.44   -20.86
2    2     5    4  L       .80      .40    3   -9     0    5         61.12    60.73
2   -2     5    4  L       .80     -.40    3   11     0    5         20.97   -15.93
2    4     5    4  L       .85      .03    3  -11     0    5        106.32   112.20
2   -4     5    4  L       .85     -.24    3   13     0    5         16.38    13.84
2    6     5    4  L       .92      .16    3  -13     0    5         50.02    47.40
2   -6     5    4  L       .92      .17    3   15     0    5  L       9.43    -4.27
2    8     5    4  L      1.01      .08    3  -15     0    5         28.67    26.00
2   -8     5    4  L      1.01      .22    3    4     1    5         43.81    37.72
2   10     5    4  L      1.08     -.04    3   -4     1    5  R    133.69  -129.47
2  -10     5    4  L      1.08      .20    3    6     1    5         73.20    68.59
2   12     5    4  L      1.12     -.01    3   -6     1    5         68.95    68.98
2   14     5    4  L      1.12      .21    3    8     1    5         47.11   -43.72
2  -14     5    4  L      1.12     -.11    3   -8     1    5         46.96    46.65
2    1     6    4  L       .87    -1.10    3   10     1    5         17.98   -15.81
2   -1     6    4  L       .87     -.05    3  -10     1    5         22.45   -21.23
2    3     6    4  L       .89     -.86    3   12     1    5         65.96    63.44
2   -3     6    4  L       .89      .42    3  -12     1    5  L       8.76    -3.09
2    5     6    4  L       .96      .25    3   14     1    5         56.70    52.15
2   -5     6    4  L       .96     -.71    3  -14     1    5  L       9.28      .26
2    7     6    4  L      1.01      .28    3   16     1    5  L       9.48    -6.92
2   -7     6    4  L      1.01     -.97    3  -16     1    5  L       9.48    -6.77
2    9     6    4  L      1.08     -.34    3    3     2    5  R      46.39   -35.95
2   -9     6    4  L      1.08     -.17    3   -3     2    5  R      46.39    35.95
2   11     6    4  L      1.12     -.48    3    5     2    5         80.99   -77.87
2  -11     6    4  L      1.12      .28    3   -5     2    5         19.52    20.69
2   13     6    4  L      1.12      .05    3    7     2    5         98.30    98.71
2  -13     6    4  L      1.12      .02    3   -7     2    5         98.30   -99.59
2    2     7    4  L       .96     -.49    3    9     2    5         54.68    55.52
```

H	K	L	G	C	F OBS	F CALC
3	-9	2	5		32.69	33.74
3	11	2	5	L	8.48	-5.21
3	-11	2	5		43.66	44.28
3	13	2	5	L	9.09	11.04
3	-13	2	5		51.49	-47.03
3	15	2	5	L	9.43	8.49
3	-15	2	5		53.77	-49.54
3	0	3	5	R	166.06	143.69
3	2	3	5		82.92	77.62
3	-2	3	5		80.16	84.60
3	4	3	5	L	5.34	4.97
3	-4	3	5		35.18	35.19
3	6	3	5		14.16	-10.38
3	-6	3	5		46.78	45.93
3	8	3	5		21.13	7.15
3	-8	3	5		20.93	-21.14
3	10	3	5		18.24	18.09
3	-10	3	5		28.41	26.78
3	12	3	5	L	8.89	-5.48
3	-12	3	5	R	14.58	6.10
3	14	3	5		30.99	-24.50
3	-14	3	5		45.57	-42.64
3	-16	3	5	R	70.79	-18.11
3	1	4	5	L	5.27	-9.64
3	-1	4	5		11.15	-9.38
3	3	4	5		18.00	-16.56
3	-3	4	5		19.04	16.56
3	5	4	5		39.65	-39.26
3	-5	4	5	L	6.42	3.56
3	7	4	5		53.25	-53.27
3	-7	4	5		38.67	-39.26
3	9	4	5		32.19	-29.43
3	-9	4	5	L	8.05	3.42
3	11	4	5	L	8.72	3.86
3	-11	4	5		45.22	44.31
3	13	4	5		18.83	19.87
3	-13	4	5		44.01	39.84
3	15	4	5	L	9.39	-1.52
3	-15	4	5		28.11	25.59
3	0	5	5		110.31	99.93
3	2	5	5	L	10.69	11.06
3	-2	5	5	R	211.28	-188.84
3	4	5	5		28.44	28.86
3	-4	5	5		126.13	-130.68
3	6	5	5		70.34	69.90
3	-6	5	5		91.53	95.69
3	8	5	5		65.55	-66.26
3	-8	5	5		38.48	37.55
3	10	5	5		40.82	-37.30
3	-10	5	5	L	8.63	-5.16
3	12	5	5		69.99	74.17
3	-12	5	5	L	9.11	9.42
3	14	5	5		56.59	57.06
3	-14	5	5		30.24	-27.29
3	1	6	5	L	6.79	14.41
3	3	6	5		18.70	21.22
3	-3	6	5		19.09	-21.22
3	5	6	5		14.51	13.45
3	-5	6	5	L	12.99	11.34
3	7	6	5		39.06	40.49
3	-7	6	5		15.27	-14.77
3	9	6	5		19.69	19.56
3	-9	6	5		29.41	-27.06
3	11	6	5	L	9.07	4.63
3	-11	6	5		29.74	-27.31
3	13	6	5	L	9.33	8.69
3	-13	6	5		35.09	-34.16
3	0	7	5		56.24	57.93
3	2	7	5	L	7.57	2.00
3	-2	7	5		14.34	22.10
3	4	7	5		16.64	-15.27
3	-4	7	5	L	7.87	5.21
3	6	7	5	L	8.26	7.48
3	-6	7	5		24.75	23.02
3	8	7	5		17.16	-15.87
3	-8	7	5		8.37	-22.05
3	10	7	5		18.26	-16.17
3	-10	7	5		20.78	24.15
3	12	7	5	L	9.30	-7.75
3	-12	7	5		17.98	17.22
3	1	8	5		42.82	-69.12
3	-1	8	5		20.45	18.40
3	3	8	5	L	8.33	-.79
3	-3	8	5	L	8.33	.79
3	5	8	5		38.56	34.46
3	-5	8	5		22.75	-17.45
3	7	8	5		44.59	-46.24
3	-7	8	5		36.42	31.39
3	9	8	5		20.39	-25.72
3	-9	8	5	L	15.88	-12.27
3	0	9	5		31.97	21.90
3	2	9	5	L	14.05	-15.74
3	-2	9	5		77.02	-84.36
3	4	9	5	L	8.98	3.18
3	-4	9	5		62.94	-63.20
3	6	9	5		33.55	30.72
3	-6	9	5		31.25	30.87
3	8	9	5		39.74	-40.27
3	-8	9	5		17.98	13.77
3	1	10	5		37.91	-25.57
3	-1	10	5	L	9.26	-4.28
3	3	10	5	L	9.33	12.20
3	-3	10	5	L	9.33	-12.20
3	5	10	5		41.64	36.72
3	-5	10	5	L	9.37	5.57
3	5	1	5	L	.56	-.66
3	-5	1	5	L	.56	.69
3	7	1	5	L	.78	-.94
3	-7	1	5	L	.78	-.14
3	9	1	5	L	.91	-.54
3	-9	1	5	L	.91	-.18
3	11	1	5	L	1.02	.01
3	-11	1	5	L	1.02	.49
3	13	1	5	L	1.11	-.01
3	-13	1	5	L	1.11	.43
3	15	1	5	L	1.15	-.71
3	-15	1	5	L	1.15	.02
3	4	2	5	L	.54	.61
3	-4	2	5	L	.54	-.61
3	6	2	5	L	.72	-.04
3	-6	2	5	L	.72	-.74
3	8	2	5	L	.87	-.72
3	-8	2	5	L	.87	-.25
3	10	2	5	L	.98	-.38
3	-10	2	5	L	.98	-.17
3	12	2	5	L	1.08	.12
3	-12	2	5	L	1.08	-.52
3	14	2	5	L	1.13	.11
3	-14	2	5	L	1.13	-.83
3	16	2	5	L	1.15	-.15
3	-16	2	5	L	1.15	-.53
3	1	3	5	L	.52	.32

H	K	L	G	C	F OBS	F CALC
3	-1	3	5	L	.52	-.47
3	3	3	5	L	.59	.65
3	5	3	5	L	.72	.03
3	-5	3	5	L	.72	.93
3	7	3	5	L	.85	-.48
3	-7	3	5	L	.85	.32
3	9	3	5	L	.95	-.67
3	-9	3	5	L	.95	.16
3	11	3	5	L	1.04	-.12
3	-11	3	5	L	1.04	.30
3	13	3	5	L	1.11	.15
3	-13	3	5	L	1.11	.37
3	15	3	5	L	1.15	-.17
3	-15	3	5	L	1.15	.26
3	2	4	5	L	.67	-.18
3	-2	4	5	L	.67	.31
3	4	4	5	L	.74	.58
3	-4	4	5	L	.74	-.38
3	6	4	5	L	.85	.98
3	-6	4	5	L	.85	-1.08
3	8	4	5	L	.93	.14
3	-8	4	5	L	.93	-.64
3	10	4	5	L	1.02	-.39
3	-10	4	5	L	1.02	.02
3	12	4	5	L	1.11	.18
3	-12	4	5	L	1.11	-.07
3	14	4	5	L	1.15	.23
3	-14	4	5	L	1.15	-.96
3	1	5	5	L	.74	-.30
3	-1	5	5	L	.74	-.26
3	3	5	5	L	.78	.25
3	5	5	5	L	.85	.64
3	-5	5	5	L	.85	.47
3	7	5	5	L	.93	.73
3	-7	5	5	L	.93	-.20
3	9	5	5	L	1.02	.07
3	-9	5	5	L	1.02	-.27
3	11	5	5	L	1.08	-.22
3	-11	5	5	L	1.08	-.09
3	13	5	5	L	1.13	.29
3	-13	5	5	L	1.13	-.07
3	2	6	5	L	.85	.42
3	-2	6	5	L	.85	.87
3	4	6	5	L	.89	.80
3	-4	6	5	L	.89	.65
3	6	6	5	L	.95	.95
3	-6	6	5	L	.95	-.25
3	8	6	5	L	1.02	.11
3	-8	6	5	L	1.02	-.10
3	10	6	5	L	1.08	-.19
3	-10	6	5	L	1.08	.28
3	12	6	5	L	1.13	.04
3	-12	6	5	L	1.13	.00
3	1	7	5	L	.91	.11
3	-1	7	5	L	.91	-.47
3	3	7	5	L	.93	-.56
3	5	7	5	L	.98	-.16
3	-5	7	5	L	.98	-.50
3	7	7	5	L	1.04	.52
3	-7	7	5	L	1.04	-.05
3	9	7	5	L	1.08	.20
3	-9	7	5	L	1.08	.37
3	11	7	5	L	1.13	-.11
3	-11	7	5	L	1.13	-.34
3	4	8	5	L	1.04	-.26
3	-4	8	5	L	1.04	.15

H	K	L	G	C	F OBS	F CALC
3	6	8	5	L	1.06	.68
3	-6	8	5	L	1.06	-.11
3	8	8	5	L	1.11	.69
3	-8	8	5	L	1.11	-.19
3	10	8	5	L	1.13	.05
3	-10	8	5	L	1.13	.22
3	5	9	5	L	1.11	-.14
3	-5	9	5	L	1.11	-.61
3	7	9	5	L	1.13	.74
3	-7	9	5	L	1.13	-.58
3	4	10	5	L	1.15	-.35
3	-4	10	5	L	1.15	.03
4	6	0	6		114.57	-113.22
4	-6	0	6		35.36	-33.52
4	8	0	6		52.45	51.27
4	-8	0	6		100.92	94.83
4	10	0	6	L	8.38	-3.59
4	-10	0	6		46.05	39.74
4	12	0	6		40.11	-46.43
4	-12	0	6		63.79	-59.83
4	14	0	6	L	10.10	7.72
4	-14	0	6		45.89	-44.09
4	16	0	6		34.32	38.33
4	-16	0	6		71.29	65.51
4	5	1	6		56.26	-52.84
4	-5	1	6		93.25	-86.05
4	7	1	6		81.16	77.93
4	-7	1	6		17.64	-13.80
4	9	1	6		39.53	40.12
4	-9	1	6		45.41	-40.79
4	11	1	6		33.39	34.64
4	-11	1	6	L	8.94	-9.48
4	13	1	6	L	9.80	7.66
4	-13	1	6		23.11	23.89
4	15	1	6		35.72	-34.51
4	-15	1	6	L	10.35	-1.87
4	4	2	6		47.00	45.19
4	6	2	6		13.88	9.69
4	-6	2	6		40.02	-34.89
4	8	2	6		63.18	67.46
4	-8	2	6		76.06	-77.27
4	10	2	6		94.72	-101.36
4	-10	2	6		36.99	33.91
4	12	2	6		53.38	-54.31
4	-12	2	6	L	9.49	-7.86
4	14	2	6		83.10	85.34
4	-14	2	6		71.70	-70.03
4	16	2	6	L	10.46	9.30
4	-16	2	6	L	10.46	-9.12
4	1	3	6		80.75	78.20
4	-1	3	6	R	115.91	-148.00
4	3	3	6		38.64	35.19
4	-3	3	6	L	4.62	-4.96
4	5	3	6		33.53	-32.79
4	-5	3	6		144.82	147.57
4	7	3	6	L	7.13	-3.66
4	-7	3	6		64.70	59.95
4	9	3	6		66.99	-68.36
4	-9	3	6	L	8.26	3.97
4	11	3	6		57.86	-61.69
4	-11	3	6	L	9.19	-.12
4	13	3	6		17.70	-20.39
4	-13	3	6	L	9.92	-3.75
4	15	3	6		18.50	16.37
4	-15	3	6	L	10.37	7.44
4	0	4	6		109.80	-101.43

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H    K    L   G  C  F OBS  F CALC    H    K    L   G  C  F OBS  F CALC
4    2    4   6       27.53  23.45    4   -5    9   6  L     9.73  -9.62
4   -2    4   6       40.07 -41.11    4    7    9   6       64.68  72.07
4    4    4   6  L     6.20  -4.26    4   -7    9   6  L    15.46 -19.20
4    6    4   6       47.31 -51.38    4    0   10   6       60.24  59.86
4   -6    4   6       20.60  18.23    4    2   10   6       17.16 -17.44
4    8    4   6  L     9.89   5.72    4   -2   10   6       22.21  22.59
4   -8    4   6       76.72  75.68    4    4   10   6  L    10.12  -9.91
4   10    4   6       21.23  21.99    4   -6    9   6  L     9.87    .10
4  -10    4   6       18.81  14.45    4    6    1   6  L      .66   -.63
4   12    4   6  L     9.73  -6.87    4   -6    1   6  L      .66   -.11
4  -12    4   6       26.03 -28.38    4    8    1   6  L      .88   -.06
4   14    4   6  L    10.26 -14.48    4   -8    1   6  L      .88    .13
4  -14    4   6  L    10.26    .10    4   10    1   6  L     1.04    .86
4    1    5   6       27.35  23.74    4  -10    1   6  L     1.04    .38
4   -1    5   6       36.24  34.81    4   12    1   6  L     1.15    .35
4    3    5   6      131.17-130.68    4  -12    1   6  L     1.15    .53
4   -3    5   6       27.05 -28.86    4   14    1   6  L     1.25    .05
4    5    5   6       48.97 -50.52    4  -14    1   6  L     1.25    .46
4   -5    5   6  L     7.31  -4.70    4    5    2   6  L      .61   -.00
4    7    5   6      118.42 121.09    4   -5    2   6  L      .61    .60
4   -7    5   6  L     8.10  -3.10    4    7    2   6  L      .81   -.52
4    9    5   6  L     8.90  11.95    4   -7    2   6  L      .81    .63
4   -9    5   6       68.77 -66.84    4    9    2   6  L      .97   -.33
4   11    5   6  L     9.60   8.54    4   -9    2   6  L      .97    .83
4  -11    5   6  L     9.60 -10.32    4   11    2   6  L     1.11   -.16
4   13    5   6  L    10.14   6.62    4  -11    2   6  L     1.11    .61
4  -13    5   6       30.63  29.36    4   13    2   6  L     1.20    .11
4    0    6   6       50.78  51.34    4  -13    2   6  L     1.20    .01
4    2    6   6       37.35  38.48    4   15    2   6  L     1.27   -.17
4   -2    6   6       21.14  24.16    4  -15    2   6  L     1.27    .09
4    4    6   6       40.16  43.29    4    4    3   6  L      .63    .18
4    6    6   6       38.62  40.00    4    6    3   6  L      .79   -.40
4   -6    6   6       18.77  18.34    4   -6    3   6  L      .79   -.27
4    8    6   6  L     8.92   -.51    4    8    3   6  L      .95   -.36
4   -8    6   6       47.54 -49.42    4   -8    3   6  L      .95   -.34
4   10    6   6       32.19 -33.91    4   10    3   6  L     1.06   -.04
4  -10    6   6  L     9.55   -.90    4  -10    3   6  L     1.06   -.01
4   12    6   6  L    10.07   3.49    4    5    4   6  L      .81    .45
4  -12    6   6       26.17  23.48    4   -5    4   6  L      .81    .75
4    1    7   6       27.64  25.34    4    7    4   6  L      .93   -.59
4   -1    7   6       83.63 -83.98    4   -7    4   6  L      .93    .42
4    3    7   6  L     8.15   5.20    4    9    4   6  L     1.04   -.71
4   -3    7   6       17.02  15.28    4   -9    4   6  L     1.04    .70
4    5    7   6  L     8.56  10.85    4   11    4   6  L     1.15   -.25
4   -5    7   6      101.40 100.79    4  -11    4   6  L     1.15    .51
4    7    7   6       43.69  41.12    4    6    5   6  L      .95    .02
4   -7    7   6       19.81  18.28    4   -6    5   6  L      .95   -.27
4    9    7   6       37.85 -41.24    4    8    5   6  L     1.04    .03
4   -9    7   6       18.20 -20.93    4   -8    5   6  L     1.04   -.32
4   11    7   6       46.16 -48.29    4   10    5   6  L     1.13   -.36
4  -11    7   6  L    10.05    .94    4  -10    5   6  L     1.13   -.44
4    0    8   6  L     8.63  -4.93    4   12    5   6  L     1.20   -.38
4    2    8   6       37.67 -36.58    4  -12    5   6  L     1.20   -.44
4   -2    8   6  L    13.47   9.70    4    5    6   6  L      .97   -.42
4    4    8   6  L     8.99  -7.07    4   -5    6   6  L      .97    .14
4    6    8   6  L     9.35  -6.97    4    7    6   6  L     1.04   -.10
4   -6    8   6  L     9.35  11.33    4   -7    6   6  L     1.04   -.07
4    8    8   6       25.31 -23.97    4    9    6   6  L     1.13   -.30
4   -8    8   6       30.81  36.02    4   -9    6   6  L     1.13    .57
4   10    8   6       42.47  46.64    4   11    6   6  L     1.20   -.79
4  -10    8   6       18.59 -14.98    4  -11    6   6  L     1.20    .90
4    1    9   6  L     9.37  -1.72    4    4    7   6  L     1.02   -.16
4   -1    9   6       33.39  34.36    4    6    7   6  L     1.09    .14
4    3    9   6       63.00 -63.20    4   -6    7   6  L     1.09   -.10
4   -3    9   6  L     9.49  -3.18    4    8    7   6  L     1.13    .43
4    5    9   6  L     9.73  -3.07    4   -8    7   6  L     1.13    .12
```

H	K	L	G	C	F OBS	F CALC
4	-10	7	6	L	1.20	.34
4	10	7	6	L	1.20	-.41
4	12	7	6	L	1.25	-.47
4	-12	7	6	L	1.25	-.17
4	5	8	6	L	1.11	.12
4	-5	8	6	L	1.11	.02
4	7	8	6	L	1.18	.11
4	-7	8	6	L	1.18	-.20
4	9	8	6	L	1.22	-.02
4	-9	8	6	L	1.22	-.23
4	4	9	6	L	1.18	-.19
4	6	9	6	L	1.20	.15
4	-6	9	6	L	1.20	.10
4	8	9	6	L	1.25	.74
4	-8	9	6	L	1.25	.38
5	-7	0	7	R	116.97	-146.05
5	9	0	7		121.62	138.79
5	-9	0	7		56.10	55.08
5	11	0	7		12.61	-8.42
5	-11	0	7		14.11	7.35
5	13	0	7		56.62	-61.20
5	-13	0	7		29.77	-33.72
5	15	0	7		72.23	67.56
5	-15	0	7		65.46	63.10
5	8	1	7		25.45	-13.49
5	-8	1	7		11.23	-7.83
5	10	1	7		15.28	12.46
5	-10	1	7		86.39	-82.64
5	12	1	7		30.50	27.85
5	-12	1	7		53.93	-49.46
5	14	1	7	L	6.73	5.54
5	-14	1	7		15.44	15.80
5	16	1	7	R	21.12	-6.50
5	-16	1	7	R	18.08	18.09
5	7	2	7		69.59	76.72
5	-7	2	7		28.64	-29.44
5	9	2	7		95.23	99.02
5	-9	2	7	L	5.07	1.99
5	11	2	7		24.04	-25.48
5	-11	2	7	L	5.98	.26
5	13	2	7		60.90	-64.39
5	-13	2	7		28.72	-22.98
5	15	2	7		34.27	-28.58
5	-15	2	7	R	18.06	22.26
5	6	3	7		129.54	-138.88
5	-6	3	7		15.14	-15.03
5	8	3	7		69.21	62.84
5	-8	3	7		60.74	-63.92
5	10	3	7		22.56	21.98
5	-10	3	7		91.44	91.57
5	12	3	7		12.83	15.56
5	-12	3	7		69.73	68.43
5	14	3	7		18.69	21.91
5	-14	3	7		57.49	-60.26
5	-3	4	7	R	40.21	39.25
5	5	4	7	L	4.03	.56
5	-5	4	7	L	4.03	-.56
5	7	4	7		43.59	-48.53
5	-7	4	7		81.41	-78.03
5	9	4	7		28.53	35.14
5	-9	4	7		19.27	18.85
5	11	4	7	L	6.32	-2.35
5	-11	4	7	L	6.32	-1.10
5	13	4	7		21.22	-19.68
5	-13	4	7	L	6.71	-7.71
5	15	4	7		46.85	44.46
5	-15	4	7		40.80	39.76
5	0	5	7		56.04	46.09
5	2	5	7		66.74	66.92
5	-2	5	7		70.69	-69.25
5	4	5	7		11.37	4.70
5	-4	5	7		50.44	-50.52
5	6	5	7	L	5.15	.60
5	-6	5	7		10.42	9.39
5	8	5	7		15.85	17.46
5	-8	5	7		49.75	-48.64
5	10	5	7		17.33	13.32
5	-10	5	7		41.67	-38.92
5	12	5	7		41.34	39.29
5	-12	5	7		13.09	-8.98
5	14	5	7		24.38	20.59
5	-14	5	7		10.48	-10.01
5	1	6	7		27.18	28.56
5	-1	6	7		8.84	5.76
5	3	6	7		13.25	-11.34
5	-3	6	7		15.91	-13.45
5	5	6	7		17.21	-17.06
5	-5	6	7		18.91	17.06
5	7	6	7		15.60	14.55
5	-7	6	7		29.43	30.49
5	9	6	7		15.22	-19.79
5	-9	6	7		31.33	-29.03
5	11	6	7	L	6.65	-8.29
5	-11	6	7	L	6.65	-4.36
5	13	6	7	L	6.75	-.71
5	-13	6	7	L	6.75	10.58
5	0	7	7		66.43	64.77
5	2	7	7		30.54	27.11
5	-2	7	7	L	5.57	8.06
5	4	7	7		101.59	-100.79
5	-4	7	7	L	5.80	10.85
5	6	7	7		77.29	-86.26
5	-6	7	7		18.08	-14.89
5	8	7	7		52.89	45.32
5	-8	7	7		59.50	-54.68
5	10	7	7	L	6.67	1.34
5	-10	7	7		82.71	83.05
5	1	8	7		25.64	-31.44
5	-1	8	7		35.02	-36.82
5	3	8	7		21.30	17.45
5	-3	8	7		37.92	-34.46
5	5	8	7		15.26	16.44
5	-5	8	7		13.74	-16.44
5	7	8	7		44.12	-40.30
5	-7	8	7		13.25	6.44
5	9	8	7		42.36	-41.53
5	-9	8	7	L	6.69	4.46
5	0	9	7		19.13	13.66
5	2	9	7		11.73	12.84
5	-2	9	7		10.03	-7.96
5	4	9	7	L	6.57	9.62
5	-4	9	7	L	6.57	-3.07
5	6	9	7		18.85	23.77
5	-6	9	7		10.32	8.99
5	1	10	7		38.95	41.46
5	-1	10	7		23.53	25.57
5	3	10	7		11.59	-5.57
5	-3	10	7		40.13	-36.72
5	9	1	7	L	.69	.28
5	-9	1	7	L	.69	-.80
5	11	1	7	L	.83	.74
5	-11	1	7	L	.83	-.72

H	K	L	G	C	F OBS	F CALC
5	13	1	7	L	.91	-.19
5	-13	1	7	L	.91	-.40
5	15	1	7	L	.97	-.81
5	-15	1	7	L	.97	-.54
5	8	2	7	L	.63	-.67
5	-8	2	7	L	.63	-.07
5	10	2	7	L	.79	.21
5	-10	2	7	L	.79	-.14
5	12	2	7	L	.89	.71
5	-12	2	7	L	.89	-.05
5	7	3	7	L	.61	-.08
5	-7	3	7	L	.61	.24
5	9	3	7	L	.75	.13
5	-9	3	7	L	.75	-.07
5	11	3	7	L	.87	.64
5	-11	3	7	L	.87	-.24
5	13	3	7	L	.93	.20
5	-13	3	7	L	.93	-.12
5	6	4	7	L	.63	.37
5	-6	4	7	L	.63	-1.05
5	8	4	7	L	.75	-.38
5	-8	4	7	L	.75	-.76
5	10	4	7	L	.85	.36
5	-10	4	7	L	.85	-.20
5	12	4	7	L	.93	.88
5	-12	4	7	L	.93	-.14
5	5	5	7	L	.69	.92
5	7	5	7	L	.77	.20
5	-7	5	7	L	.77	.39
5	9	5	7	L	.85	-.23
5	-9	5	7	L	.85	.41
5	11	5	7	L	.91	-.36
5	-11	5	7	L	.91	.23
5	13	5	7	L	.95	.16
5	-13	5	7	L	.95	.12
5	6	6	7	L	.79	.44
5	-6	6	7	L	.79	-.45
5	8	6	7	L	.87	-.35
5	-8	6	7	L	.87	-.53
5	10	6	7	L	.91	-.10
5	-10	6	7	L	.91	-.39
5	12	6	7	L	.95	.30
5	-12	6	7	L	.95	-.10
5	5	7	7	L	.83	-.48
5	7	7	7	L	.89	-.12
5	-7	7	7	L	.89	.03
5	9	7	7	L	.93	-.08
5	-9	7	7	L	.93	.85
5	11	7	7	L	.95	-.37
5	-11	7	7	L	.95	.48
5	6	8	7	L	.91	.22
5	-6	8	7	L	.91	-.33
5	8	8	7	L	.93	.26
5	-8	8	7	L	.93	-.36
5	10	8	7	L	.95	.03
5	-10	8	7	L	.95	-.09
5	5	9	7	L	.93	-.15
5	7	9	7	L	.95	-.12
5	-7	9	7	L	.95	-.29

APPENDIX 3. The Observed Structure Factors(FO) and Calculated Structure Factors(FC) of the Scapolite(XL, 52% Me, Tsarasaotra,Madagascar).

H	K	L	G	C	F OBS	F CALC
0	2	0	1		57.57	67.95
0	6	0	1		45.95	-44.35
0	8	0	1	L	6.46	1.25
0	10	0	1		57.40	59.79
0	12	0	1		71.52	76.31
0	14	0	1		44.02	-42.45
0	16	0	1		78.10	-77.57
0	18	0	1	L	3.98	1.11
0	2	1	1		11.19	-10.51
0	3	1	1		86.31	80.41
0	4	1	1		7.88	-11.29
0	5	1	1		9.44	7.26
0	7	1	1		24.62	-21.15
0	8	1	1		24.77	20.24
0	9	1	1		80.47	-75.02
0	11	1	1		28.99	-29.09
0	12	1	1		8.24	-8.16
0	13	1	1		17.79	17.59
0	15	1	1		51.12	48.20
0	17	1	1	L	6.51	-7.95
0	0	2	1		26.07	-24.08
0	2	2	1		23.42	-28.73
0	3	2	1	L	5.26	-7.71
0	4	2	1		25.59	-20.80
0	6	2	1		41.50	36.76
0	7	2	1		8.17	7.85
0	8	2	1		38.52	-36.01
0	10	2	1		35.40	35.60
0	12	2	1		48.19	48.30
0	13	2	1		7.28	7.43
0	14	2	1		8.99	7.39
0	16	2	1	L	6.48	-8.29
0	18	2	1	L	3.78	-2.02
0	20	2	1	L	9.73	-7.54
0	1	3	1		19.64	-20.38
0	2	3	1	L	4.82	-5.87
0	3	3	1		113.95	127.32
0	4	3	1		19.58	22.09
0	5	3	1		81.07	80.06
0	6	3	1		10.06	9.67
0	7	3	1		104.70	-101.65
0	9	3	1		50.66	49.81
0	10	3	1		12.02	-11.84
0	11	3	1		92.82	93.80
0	12	3	1		7.84	-8.33
0	13	3	1		9.08	9.84
0	15	3	1		27.42	-24.76
0	17	3	1		29.11	30.06
0	19	3	1	L	0.00	-4.98
0	1	4	1		17.80	16.90
0	2	4	1		6.73	10.44
0	3	4	1		9.96	9.30
0	4	4	1		96.40	-96.51
0	5	4	1		22.91	-25.47
0	6	4	1		44.05	-40.28
0	7	4	1		9.66	-12.27
0	8	4	1		25.11	-24.41
0	10	4	1		16.28	18.20
0	12	4	1		38.08	44.56
0	14	4	1		21.26	-20.15
0	15	4	1		13.70	-13.94
0	16	4	1		53.42	-49.25
0	18	4	1	L	2.09	.13
0	20	4	1		14.33	15.13
0	1	5	1		12.98	14.47
0	2	5	1		19.11	-20.03
0	3	5	1		108.30	108.35
0	4	5	1		15.72	-18.12
0	5	5	1		52.78	48.80
0	6	5	1	L	7.15	2.15
0	7	5	1		85.03	-87.36
0	8	5	1		10.16	9.62
0	9	5	1		74.62	-77.50
0	11	5	1	L	1.40	-1.47
0	13	5	1		25.74	26.50
0	15	5	1		53.78	51.52
0	17	5	1	L	3.56	1.26
0	1	6	1	L	5.65	-9.73
0	2	6	1		33.80	-40.13
0	3	6	1		6.07	-4.87
0	4	6	1		46.57	47.85
0	6	6	1		12.10	12.22
0	7	6	1		10.21	12.43
0	8	6	1		19.03	-20.74
0	10	6	1		12.32	-11.29
0	12	6	1		11.15	-8.22
0	14	6	1		20.09	19.57
0	16	6	1		20.98	21.58
0	18	6	1	L	0.00	-1.89
0	1	7	1		42.52	-48.55
0	3	7	1		42.82	44.17
0	4	7	1		20.29	22.04
0	5	7	1		63.89	65.17
0	6	7	1		22.63	24.33
0	7	7	1		74.31	-75.26
0	8	7	1		16.95	-17.80
0	9	7	1	L	3.17	-2.07
0	10	7	1		17.54	-18.57
0	11	7	1		41.13	42.88
0	13	7	1	L	3.65	.92
0	15	7	1		13.58	-13.78
0	17	7	1		18.76	20.86
0	0	8	1		23.86	26.00
0	2	8	1	L	2.61	4.26
0	4	8	1	L	2.64	-3.64
0	5	8	1		9.42	-11.18
0	6	8	1		16.18	-16.88
0	7	8	1		9.34	-12.35
0	8	8	1		11.73	4.95
0	10	8	1		8.29	-8.28
0	12	8	1		9.21	-9.89
0	14	8	1	L	6.14	-.49
0	16	8	1	L	4.48	-5.00
0	1	9	1	L	3.53	2.81
0	2	9	1		8.18	-8.74
0	3	9	1		38.37	33.87
0	5	9	1		18.40	15.35
0	7	9	1		28.81	-31.24
0	9	9	1		47.90	-50.99
0	11	9	1		16.64	-21.67
0	13	9	1		10.26	11.72
0	15	9	1		24.81	28.47
0	0	10	1		101.80	-125.29
0	1	10	1		18.66	-18.77
0	2	10	1	L	5.63	.48
0	3	10	1		12.37	-9.56
0	4	10	1		52.82	53.71
0	5	10	1		9.67	11.87

H	K	L	G	C	F OBS	F CALC
0	6	10	1		11.92	11.96
0	8	10	1		19.87	18.11
0	10	10	1	L	6.96	-11.71
0	1	11	1		19.39	-22.76
0	3	11	1		10.40	-9.61
0	4	11	1		13.11	14.34
0	5	11	1	L	6.98	12.04
0	7	11	1		10.85	-9.68
0	9	11	1	L	6.70	8.29
0	11	11	1	L	6.77	7.36
0	4	12	1		10.39	7.94
0	8	12	1		18.04	17.86
0	3	13	1	L	10.14	4.59
1	1	1	1	L	4.62	2.61
1	2	1	1		14.83	-21.70
1	3	1	1		13.26	-13.98
1	4	1	1		107.08	-105.34
1	6	1	1		61.22	-60.12
1	8	1	1		17.17	-20.41
1	10	1	1		32.22	26.25
1	11	1	1		8.46	8.07
1	12	1	1		26.86	23.31
1	14	1	1	L	2.86	2.82
1	16	1	1		38.96	-37.72
1	18	1	1	L	4.21	3.76
1	20	1	1		22.63	19.73
1	2	2	1		12.65	13.97
1	3	2	1		37.88	39.89
1	4	2	1		18.33	21.48
1	5	2	1		65.80	-65.66
1	7	2	1		40.60	-38.70
1	9	2	1		56.17	-55.47
1	11	2	1		6.77	-2.67
1	13	2	1		67.92	71.67
1	15	2	1		30.96	29.84
1	17	2	1	L	3.78	-5.57
1	1	3	1		16.66	20.59
1	2	3	1		17.74	-18.28
1	3	3	1		6.84	-5.09
1	4	3	1		143.31	146.72
1	5	3	1		12.29	-15.06
1	6	3	1		132.06	137.72
1	8	3	1		44.97	-38.93
1	10	3	1		17.86	-17.98
1	12	3	1		37.58	-36.32
1	14	3	1		73.43	-72.39
1	16	3	1		51.79	49.20
1	1	4	1		11.70	-8.81
1	2	4	1		15.06	-18.14
1	3	4	1		11.33	9.46
1	4	4	1		6.84	-10.19
1	5	4	1		44.05	48.02
1	7	4	1		82.06	79.17
1	9	4	1		77.06	-78.03
1	11	4	1		27.00	-27.98
1	13	4	1		12.97	9.41
1	14	4	1		12.12	11.86
1	15	4	1		21.68	-25.23
1	17	4	1		13.57	9.99
1	2	5	1		87.98	-88.55
1	3	5	1		17.64	-15.55
1	4	5	1		46.50	-42.94
1	6	5	1		48.75	43.89
1	7	5	1		14.63	16.43
1	8	5	1		30.52	-30.82
1	10	5	1		12.54	13.67
1	12	5	1	L	6.59	9.26
1	14	5	1		31.21	-28.58
1	16	5	1		16.99	-15.52
1	1	6	1		45.59	42.65
1	2	6	1		15.79	21.12
1	3	6	1		54.23	59.43
1	4	6	1		17.78	19.16
1	5	6	1	L	5.09	4.97
1	7	6	1		42.43	-41.73
1	8	6	1		11.84	-10.58
1	9	6	1		25.12	25.82
1	11	6	1		29.99	30.27
1	13	6	1		28.32	28.97
1	15	6	1		24.52	23.42
1	1	7	1		14.40	14.91
1	2	7	1		81.75	-81.56
1	3	7	1		10.11	-9.97
1	4	7	1		80.13	84.29
1	5	7	1		7.83	-10.01
1	6	7	1		102.72	112.24
1	8	7	1		35.83	-29.31
1	10	7	1		18.51	-16.94
1	12	7	1		24.10	-21.85
1	14	7	1		48.16	-44.45
1	1	8	1		54.12	-54.02
1	2	8	1		13.12	-15.95
1	3	8	1		17.56	-18.12
1	4	8	1		7.80	-10.28
1	5	8	1		17.95	20.76
1	7	8	1		25.11	25.75
1	8	8	1		10.95	-10.17
1	9	8	1		20.74	16.36
1	11	8	1	L	6.85	4.95
1	13	8	1		31.55	-28.66
1	2	9	1		49.94	-51.53
1	3	9	1		8.41	-7.98
1	4	9	1		31.93	-33.70
1	6	9	1		29.02	26.44
1	7	9	1		9.37	10.64
1	8	9	1	L	0.00	-1.14
1	10	9	1	L	3.81	4.12
1	1	10	1		9.01	-7.38
1	3	10	1		8.81	8.39
1	4	10	1	L	8.24	9.54
1	5	10	1		21.12	-22.77
1	7	10	1		43.12	-42.88
1	8	10	1		14.07	-14.30
1	9	10	1		44.46	47.56
1	11	10	1		16.57	17.27
1	2	11	1		13.03	-16.23
1	4	11	1		30.73	32.04
1	6	11	1		22.65	27.67
1	8	11	1	L	9.09	-10.26
1	10	11	1	L	7.92	-8.34
1	1	12	1		35.34	-39.57
1	3	12	1		24.97	-30.12
1	5	12	1	L	6.13	-7.40
1	2	13	1		15.93	11.82
2	2	0	1		46.06	-50.06
2	4	0	1		102.79	-97.99
2	6	0	1		59.70	52.82
2	8	0	1		54.52	48.20
2	10	0	1		25.30	-26.23
2	12	0	1		33.57	-31.94
2	14	0	1	L	5.20	8.85
2	16	0	1	L	4.49	2.46
2	18	0	1		46.23	45.14
2	20	0	1		12.63	9.91
2	1	1	1		27.39	-33.06
2	2	1	1		15.23	14.77
2	4	1	1		5.19	4.92
2	5	1	1		71.92	-72.30
2	6	1	1	L	5.48	-5.53
2	7	1	1		100.97	93.97
2	8	1	1		7.56	7.77
2	9	1	1	L	4.25	-2.68
2	10	1	1		11.88	-11.04
2	11	1	1		33.08	-30.87

H	K	L	G	C	F OBS	F CALC
2	13	1	1	L	4.61	6.58
2	14	1	1		10.17	9.90
2	15	1	1	L	5.37	-5.15
2	17	1	1		36.40	34.70
2	2	2	1		56.56	-50.83
2	3	2	1		10.92	-10.88
2	4	2	1		38.31	26.69
2	6	2	1		69.91	70.00
2	7	2	1		15.98	15.91
2	8	2	1		147.26	163.32
2	10	2	1		25.55	-23.90
2	11	2	1		8.38	-9.02
2	12	2	1		22.68	-20.88
2	13	2	1		8.44	-9.24
2	14	2	1		27.02	23.96
2	16	2	1		34.44	-33.70
2	18	2	1	L	6.26	1.22
2	1	3	1	L	1.87	8.48
2	2	3	1		7.14	-9.81
2	3	3	1		69.46	69.08
2	5	3	1		48.11	-36.53
2	6	3	1		6.40	-5.74
2	7	3	1		105.14	-101.10
2	8	3	1		5.82	-5.98
2	9	3	1	L	5.12	.97
2	10	3	1		17.61	-18.63
2	11	3	1		90.66	89.74
2	13	3	1	L	6.53	4.11
2	14	3	1		10.86	9.54
2	15	3	1		57.87	-53.32
2	17	3	1		25.07	-21.35
2	2	4	1		25.96	-23.49
2	4	4	1		40.69	-39.55
2	5	4	1		5.90	-7.21
2	6	4	1		18.37	10.43
2	8	4	1		41.45	-44.95
2	10	4	1		27.75	-27.93
2	12	4	1		13.80	-13.70
2	14	4	1	L	2.20	-2.26
2	16	4	1	L	5.50	-2.24
2	1	5	1		21.77	-27.40
2	2	5	1		23.58	22.92
2	3	5	1		156.69	-176.36
2	5	5	1		39.95	-44.13
2	6	5	1	L	5.85	-7.33
2	7	5	1		71.08	72.18
2	8	5	1		12.79	14.99
2	9	5	1		8.85	-9.53
2	11	5	1		11.56	8.77
2	13	5	1		17.54	16.17
2	15	5	1		40.29	-41.42
2	17	5	1		34.60	30.16
2	19	5	1		31.46	29.52
2	2	6	1	L	4.23	-.40
2	3	6	1		6.55	-4.93
2	4	6	1		28.34	29.52
2	5	6	1		11.37	11.79
2	6	6	1		19.91	-18.01
2	7	6	1		22.42	23.08
2	8	6	1		27.69	27.23
2	10	6	1		8.11	-5.68
2	11	6	1		8.43	-9.68
2	12	6	1	L	1.19	.21
2	13	6	1		11.39	-12.41
2	14	6	1	L	2.71	1.29
2	16	6	1		21.90	-22.62
2	18	6	1		18.75	-19.35
2	1	7	1		10.21	15.49
2	3	7	1		7.69	14.43
2	5	7	1		7.45	-3.81
2	7	7	1		33.85	-37.65
2	8	7	1		11.37	-12.19
2	9	7	1	L	2.25	-3.25
2	11	7	1		63.73	61.74
2	13	7	1		14.03	9.80
2	15	7	1		35.89	-40.19
2	17	7	1		15.86	-17.74
2	2	8	1		10.17	7.17
2	4	8	1		20.59	19.90
2	6	8	1		19.72	-15.39
2	8	8	1		70.92	-76.09
2	9	8	1		13.90	-12.87
2	10	8	1	L	3.14	2.04
2	12	8	1		9.60	9.46
2	16	8	1		13.28	14.56
2	1	9	1	L	2.82	-4.11
2	2	9	1		14.82	15.01
2	3	9	1		67.11	-70.95
2	5	9	1	L	.49	4.32
2	7	9	1		52.38	55.57
2	8	9	1		9.31	10.78
2	9	9	1		10.71	-9.73
2	11	9	1	L	7.75	-9.57
2	13	9	1	L	9.83	10.40
2	2	10	1		16.42	16.13
2	4	10	1		20.28	19.98
2	5	10	1		14.14	13.90
2	6	10	1		30.33	-27.50
2	7	10	1		13.73	14.10
2	8	10	1	L	6.89	.44
2	10	10	1		17.90	20.48
2	12	10	1	L	9.03	8.50
2	1	11	1	L	0.00	1.98
2	2	11	1		12.20	-12.21
2	3	11	1		21.62	26.21
2	5	11	1	L	3.37	4.62
2	7	11	1		18.00	-20.40
2	9	11	1	L	0.00	1.74
2	2	12	1		10.01	8.61
2	4	12	1		19.07	18.74
2	6	12	1	L	6.64	-3.98
2	1	13	1		10.27	-4.24
3	2	1	1		11.56	-8.06
3	4	1	1		62.92	52.20
3	5	1	1		11.49	12.17
3	6	1	1		80.22	73.39
3	8	1	1		35.81	-32.78
3	9	1	1		9.33	10.43
3	10	1	1		15.99	-16.32
3	12	1	1		62.46	60.38
3	14	1	1		39.58	36.59
3	16	1	1	L	7.08	-5.84
3	18	1	1	L	3.68	-.97
3	20	1	1	L	5.44	-6.16
3	2	2	1		6.79	6.15
3	3	2	1		44.25	-33.79
3	5	2	1		95.52	-88.76
3	6	2	1		10.51	-9.68
3	7	2	1		111.47	109.83
3	9	2	1		26.84	28.15
3	11	2	1		22.63	-19.64
3	13	2	1		6.97	8.58
3	15	2	1		8.30	9.31
3	17	2	1		45.07	-45.71
3	19	2	1	L	4.69	-1.29
3	2	3	1		89.38	83.10
3	3	3	1	L	5.29	-7.82
3	4	3	1		17.74	-12.43
3	6	3	1	L	4.58	-5.75
3	8	3	1	L	2.44	-1.31
3	10	3	1		16.81	17.09
3	12	3	1	L	6.05	-7.45

H	K	L	G	C	F OBS	F CALC
3	14	3	1		20.51	-19.65
3	16	3	1	L	1.30	-.61
3	18	3	1		19.21	18.57
3	20	3	1	L	5.62	-4.47
3	1	4	1		13.63	1.47
3	2	4	1		10.45	-13.03
3	3	4	1		24.59	-21.51
3	4	4	1	L	6.01	-10.11
3	5	4	1		18.41	-21.68
3	7	4	1		63.29	-60.74
3	8	4	1		15.03	16.55
3	9	4	1		21.32	-16.46
3	11	4	1		14.46	15.06
3	13	4	1		29.63	30.43
3	15	4	1	L	5.26	-2.34
3	17	4	1		8.09	-5.80
3	19	4	1	L	5.28	-3.55
3	1	5	1		7.61	7.93
3	2	5	1	L	2.42	5.41
3	4	5	1		40.65	39.42
3	6	5	1		70.64	71.97
3	7	5	1		15.05	15.78
3	8	5	1		59.33	-58.98
3	10	5	1		42.87	-40.98
3	12	5	1		64.14	67.91
3	14	5	1		37.57	38.83
3	16	5	1		8.20	-7.62
3	18	5	1	L	4.72	6.93
3	1	6	1		12.47	2.76
3	2	6	1		7.94	11.76
3	3	6	1		15.75	18.18
3	5	6	1		7.99	5.92
3	6	6	1		12.27	-14.54
3	7	6	1		44.14	46.99
3	9	6	1	L	4.88	5.60
3	11	6	1	L	2.01	-.30
3	13	6	1	L	1.60	.08
3	15	6	1		15.35	12.05
3	2	7	1	L	4.81	.40
3	4	7	1		19.06	-19.73
3	6	7	1		9.27	8.92
3	8	7	1		23.00	-23.70
3	10	7	1		16.64	-15.34
3	12	7	1		7.45	-5.41
3	14	7	1	L	6.79	-5.02
3	1	8	1		48.77	-56.94
3	2	8	1		18.58	-21.67
3	3	8	1	L	4.13	-.68
3	4	8	1		10.19	-12.33
3	5	8	1		40.69	40.87
3	6	8	1		8.74	8.35
3	7	8	1		43.45	-47.60
3	8	8	1		11.83	12.62
3	9	8	1	L	5.86	-11.29
3	11	8	1		19.40	17.90
3	13	8	1	L	2.14	-1.00
3	2	9	1		19.55	-22.39
3	4	9	1	L	3.63	6.47
3	6	9	1		34.39	33.57
3	7	9	1		9.40	10.43
3	8	9	1		36.58	-38.80
3	10	9	1		39.61	-39.55
3	12	9	1		20.18	24.27
3	1	10	1		39.49	-32.47
3	3	10	1	L	6.87	6.18
3	5	10	1		36.21	33.28
3	7	10	1		20.19	23.04
3	9	10	1	L	1.98	-1.07
3	13	10	1		33.04	-21.67
3	2	11	1	L	5.38	-7.52
3	4	11	1	L	6.34	-10.56
3	6	11	1		10.63	-10.45
3	10	11	1	L	3.38	3.43
3	1	12	1		28.28	-31.70
3	3	12	1	L	3.37	-.54
3	5	12	1		29.19	28.56
4	2	0	1	L	3.14	5.76
4	4	0	1		82.80	-72.42
4	6	0	1		97.18	-96.51
4	8	0	1		85.31	78.09
4	10	0	1		6.54	-8.05
4	12	0	1		47.24	-46.03
4	14	0	1		8.20	9.85
4	16	0	1		44.32	44.74
4	18	0	1		19.94	16.84
4	1	1	1	L	0.00	-2.04
4	2	1	1		7.76	6.83
4	3	1	1		104.62	-104.75
4	5	1	1		58.00	-54.12
4	7	1	1		79.18	75.99
4	9	1	1		23.27	24.89
4	11	1	1		26.70	29.75
4	12	1	1		7.49	7.04
4	13	1	1	L	4.28	3.76
4	15	1	1		39.15	-34.77
4	17	1	1		10.04	6.11
4	19	1	1		14.77	12.85
4	2	2	1		63.47	64.32
4	3	2	1		9.91	-9.41
4	4	2	1		17.65	21.57
4	6	2	1		15.92	15.26
4	8	2	1		43.16	45.91
4	10	2	1		109.14	-106.35
4	12	2	1		50.39	-54.47
4	13	2	1		8.49	-9.25
4	14	2	1		93.37	87.98
4	16	2	1	L	4.33	2.50
4	18	2	1		21.15	-20.38
4	1	3	1		79.25	75.17
4	2	3	1		10.91	-9.65
4	3	3	1		10.71	5.75
4	4	3	1		6.78	-7.54
4	5	3	1		24.57	-26.52
4	7	3	1	L	3.90	-1.12
4	9	3	1		45.50	-46.76
4	11	3	1		56.89	-58.98
4	13	3	1		22.91	-21.93
4	15	3	1		16.24	-17.30
4	17	3	1	L	.62	3.18
4	19	3	1		17.47	22.36
4	1	4	1		11.72	-8.66
4	2	4	1		20.99	20.93
4	3	4	1	L	5.56	6.11
4	4	4	1		22.67	16.00
4	5	4	1		14.20	15.74
4	6	4	1		52.01	-50.15
4	8	4	1		36.61	30.71
4	10	4	1		23.28	21.61
4	12	4	1		7.18	-7.91
4	14	4	1		19.55	-19.93
4	16	4	1		22.72	19.06
4	18	4	1		13.77	11.88
4	1	5	1		23.01	21.03
4	2	5	1		28.59	31.04
4	3	5	1		112.19	-113.26
4	5	5	1		51.44	-50.72
4	6	5	1		15.35	-14.97
4	7	5	1		117.92	119.03
4	8	5	1		9.25	10.00
4	9	5	1	L	5.24	-1.64
4	11	5	1	L	2.66	6.78
4	13	5	1	L	1.92	3.87

H	K	L	G	C	F OBS	F CALC
4	15	5	1		49.40	-50.17
4	17	5	1		15.19	10.27
4	1	6	1		11.24	12.90
4	2	6	1		40.34	41.92
4	3	6	1		10.88	-12.92
4	4	6	1		21.70	25.79
4	6	6	1		30.90	32.35
4	8	6	1		13.68	-12.37
4	10	6	1		30.59	-30.75
4	11	6	1		10.54	-10.68
4	12	6	1	L	7.15	3.63
4	14	6	1		30.85	28.72
4	16	6	1		20.24	-21.81
4	18	6	1		18.67	-14.83
4	1	7	1		25.32	23.05
4	2	7	1		13.39	-16.42
4	3	7	1		13.82	-10.13
4	5	7	1		13.10	15.18
4	7	7	1		50.00	45.21
4	9	7	1		25.08	-25.67
4	11	7	1		41.62	-40.27
4	13	7	1	L	1.98	-1.90
4	15	7	1	L	0.00	-4.98
4	17	7	1	L	6.63	5.98
4	2	8	1		37.68	-37.97
4	4	8	1	L	4.09	2.24
4	6	8	1	L	4.71	-5.37
4	8	8	1		10.33	-8.50
4	9	8	1		11.84	-10.59
4	10	8	1		43.69	45.04
4	12	8	1		16.00	19.92
4	14	8	1		51.37	-47.00
4	16	8	1	L	3.60	.37
4	1	9	1	L	2.31	-2.53
4	2	9	1		16.69	19.30
4	3	9	1		52.90	-51.13
4	5	9	1	L	3.53	-1.19
4	6	9	1		9.86	-9.06
4	7	9	1		57.26	63.12
4	9	9	1	L	2.93	-.33
4	11	9	1		11.45	12.92
4	13	9	1		14.48	15.81
4	1	10	1		17.06	15.71
4	2	10	1		18.47	-18.57
4	4	10	1		20.34	-19.07
4	6	10	1		11.49	16.59
4	8	10	1		20.56	-18.33
4	10	10	1	L	3.63	3.91
4	12	10	1		15.18	16.55
4	1	11	1	L	3.40	4.42
4	2	11	1		11.53	-13.76
4	3	11	1		16.41	14.77
4	5	11	1		12.62	10.97
4	7	11	1	L	0.00	2.44
4	9	11	1	L	4.76	-3.80
4	2	12	1		37.84	-41.49
4	4	12	1	L	9.73	-14.30
4	6	12	1	L	4.99	2.41
5	1	1	1	L	4.86	-7.52
5	2	1	1		79.27	71.21
5	4	1	1		57.65	54.04
5	5	1	1		10.06	11.03
5	6	1	1		54.01	55.57
5	8	1	1		26.31	-17.19
5	10	1	1		13.63	14.53
5	11	1	1		16.54	-16.62
5	12	1	1		17.86	14.68
5	14	1	1		8.29	-7.90
5	15	1	1		10.57	11.33
5	16	1	1		8.03	-8.23
5	18	1	1	L	9.55	12.29
5	20	1	1	L	1.97	.31
5	1	2	1		64.95	65.41
5	3	2	1		52.87	-45.95
5	4	2	1		10.10	-10.41
5	5	2	1		40.34	-37.81
5	7	2	1		71.65	69.61
5	9	2	1		94.31	91.10
5	11	2	1		28.00	-31.03
5	13	2	1		50.36	-48.23
5	15	2	1		34.51	-30.19
5	17	2	1		21.13	-20.25
5	19	2	1		20.43	21.33
5	2	3	1		22.05	21.90
5	4	3	1		130.34	-132.66
5	6	3	1		133.55	-134.85
5	8	3	1		77.08	69.94
5	10	3	1		22.80	20.31
5	12	3	1		25.82	27.38
5	14	3	1		31.56	31.40
5	15	3	1		9.47	11.01
5	16	3	1		36.83	-36.67
5	1	4	1		74.76	-74.20
5	3	4	1		16.80	12.33
5	5	4	1		10.44	-11.54
5	6	4	1	L	6.25	6.56
5	7	4	1		37.71	-40.81
5	8	4	1		14.76	16.58
5	9	4	1		33.15	37.24
5	11	4	1	L	5.30	3.22
5	13	4	1		24.88	-24.70
5	14	4	1		10.79	-10.68
5	15	4	1		42.94	39.97
5	17	4	1	L	0.00	5.96
5	2	5	1		59.65	57.95
5	3	5	1		12.45	10.69
5	4	5	1		29.34	-22.65
5	6	5	1		12.51	11.44
5	8	5	1		9.85	9.03
5	10	5	1		13.80	12.38
5	11	5	1		12.45	-13.20
5	12	5	1		33.03	31.20
5	14	5	1		11.03	8.54
5	16	5	1		35.28	-38.46
5	1	6	1		21.48	23.29
5	3	6	1		31.09	-27.71
5	4	6	1		8.93	-9.26
5	5	6	1		14.17	-14.78
5	7	6	1	L	2.86	1.53
5	9	6	1		15.53	-16.56
5	11	6	1	L	4.34	-4.65
5	13	6	1	L	3.51	4.41
5	15	6	1		40.28	-37.85
5	17	6	1		16.40	-15.80
5	2	7	1		28.64	26.77
5	3	7	1		7.32	7.01
5	4	7	1		83.71	-81.47
5	5	7	1		8.45	-8.23
5	6	7	1		74.29	-80.62
5	7	7	1		12.65	-12.87
5	8	7	1		48.41	42.72
5	10	7	1	L	1.64	-3.09
5	12	7	1		20.21	20.10
5	14	7	1		30.37	29.99
5	16	7	1		42.33	-43.75
5	1	8	1		10.44	-15.95
5	3	8	1		28.69	26.39
5	5	8	1		12.14	13.21
5	6	8	1		10.94	10.48
5	7	8	1		46.76	-42.74
5	8	8	1		11.61	14.46
5	9	8	1		33.29	-33.78

H	K	L	G	C	F OBS	F CALC
5	11	8	1		16.12	16.09
5	15	8	1		17.59	16.48
5	2	9	1		8.24	7.75
5	3	9	1		9.29	9.09
5	4	9	1	L	3.29	1.10
5	6	9	1		16.09	21.59
5	8	9	1	L	4.43	-8.05
5	10	9	1		9.75	-9.69
5	14	9	1	L	4.78	1.76
5	1	10	1		32.16	34.06
5	3	10	1		14.56	-14.78
5	5	10	1		8.71	9.32
5	7	10	1		12.40	12.62
5	9	10	1		30.58	-34.61
5	11	10	1	L	9.27	5.82
5	2	11	1	L	6.73	6.12
5	4	11	1		11.07	-14.11
5	6	11	1		24.07	-26.00
5	8	11	1	L	7.19	10.23
5	10	11	1	L	7.60	-5.61
5	3	12	1		19.68	19.02
5	5	12	1		13.53	17.50
5	7	12	1		16.97	-14.63
6	4	0	1		34.17	-32.64
6	8	0	1		11.74	14.30
6	10	0	1		109.36	107.49
6	12	0	1		11.05	10.49
6	14	0	1		16.52	-11.08
6	16	0	1		16.37	-12.79
6	18	0	1		43.90	-46.38
6	20	0	1	L	4.83	-4.71
6	1	1	1		124.63	122.89
6	3	1	1		60.03	56.38
6	4	1	1		17.16	-15.90
6	5	1	1		12.10	14.06
6	7	1	1		26.48	-24.78
6	8	1	1	L	5.10	5.23
6	9	1	1		33.52	31.93
6	10	1	1		11.70	11.10
6	11	1	1	L	6.01	5.61
6	13	1	1		7.34	-6.86
6	14	1	1		14.15	-14.48
6	15	1	1		9.37	-10.24
6	17	1	1	L	3.75	1.66
6	19	1	1		17.55	-18.74
6	1	2	1		10.80	10.52
6	2	2	1		6.28	.21
6	4	2	1		35.99	-32.31
6	5	2	1		10.83	-11.52
6	6	2	1		48.87	-49.52
6	7	2	1		8.62	-7.56
6	8	2	1		40.18	-40.97
6	10	2	1		34.17	-31.68
6	12	2	1	L	6.50	-3.18
6	14	2	1		14.40	12.00
6	16	2	1		11.97	9.34
6	18	2	1		28.29	-29.49
6	1	3	1		62.85	57.90
6	2	3	1		9.04	-11.86
6	3	3	1		60.13	49.96
6	5	3	1		25.86	-28.49
6	6	3	1		13.65	15.29
6	7	3	1		38.59	35.27
6	8	3	1		15.38	16.68
6	9	3	1		51.83	-48.78
6	11	3	1		41.04	-41.44
6	12	3	1		8.35	-7.22
6	13	3	1		34.10	31.31
6	15	3	1		37.92	40.27
6	17	3	1		21.24	-19.52
6	19	3	1	L	2.25	4.43
6	2	4	1		112.17	113.61
6	3	4	1		11.27	13.13
6	4	4	1		15.18	14.64
6	5	4	1		11.16	12.58
6	6	4	1		93.61	-93.28
6	7	4	1		9.20	-8.10
6	8	4	1		11.08	15.14
6	10	4	1		80.92	83.62
6	12	4	1		28.68	25.01
6	14	4	1	L	4.95	-4.46
6	16	4	1		10.83	-10.21
6	18	4	1		18.86	-20.20
6	1	5	1		117.53	124.13
6	2	5	1	L	5.12	8.34
6	3	5	1		81.69	83.13
6	5	5	1		10.72	13.98
6	6	5	1		11.34	-11.83
6	7	5	1		23.98	-23.17
6	9	5	1		11.13	-10.29
6	11	5	1		21.07	-19.14
6	13	5	1		16.18	18.90
6	15	5	1		18.97	19.53
6	17	5	1		10.08	-9.90
6	1	6	1		14.37	13.31
6	2	6	1		31.26	-27.35
6	3	6	1		10.85	-13.89
6	4	6	1		19.77	19.77
6	5	6	1		24.00	-26.19
6	6	6	1		50.57	46.64
6	7	6	1		9.57	-10.94
6	8	6	1		18.32	-18.46
6	10	6	1		35.92	-37.05
6	12	6	1		9.02	10.12
6	14	6	1		13.65	12.92
6	1	7	1		25.59	20.17
6	3	7	1		23.79	22.22
6	4	7	1		11.72	10.38
6	5	7	1		17.65	-18.64
6	6	7	1		12.09	13.49
6	7	7	1		28.05	29.29
6	8	7	1		11.99	12.71
6	9	7	1		48.48	-47.09
6	11	7	1		47.81	-43.06
6	12	7	1		11.03	-9.11
6	13	7	1		27.85	33.51
6	15	7	1		39.73	43.10
6	2	8	1		16.64	16.09
6	4	8	1		7.82	7.40
6	6	8	1		7.74	7.06
6	8	8	1		14.36	15.71
6	10	8	1		20.73	20.65
6	12	8	1	L	4.04	6.47
6	1	9	1		21.88	23.33
6	3	9	1		24.17	25.06
6	5	9	1		11.52	14.47
6	6	9	1		10.90	-11.61
6	7	9	1		17.17	-19.40
6	9	9	1		12.49	-15.23
6	11	9	1	L	8.69	-8.15
6	13	9	1		14.40	15.03
6	1	10	1		13.84	12.08
6	2	10	1		48.25	-50.65
6	3	10	1		11.93	-13.39
6	4	10	1	L	3.81	-1.59
6	5	10	1		21.32	-21.65
6	6	10	1		64.16	65.64
6	8	10	1	L	2.76	-5.95
6	10	10	1		41.47	-46.97
6	12	10	1	L	7.62	-8.41
6	1	11	1	L	8.09	-10.75
6	3	11	1	L	5.80	-10.20

H	K	L	G	C	F OBS	F CALC
6	5	11	1	L	.28	-5.35
6	7	11	1		14.66	17.84
6	9	11	1		11.01	-12.68
6	2	12	1		14.00	-14.53
6	4	12	1	L	6.50	-9.18
6	6	12	1		18.26	15.37
7	1	1	1		12.66	10.71
7	2	1	1		9.55	-2.06
7	3	1	1		9.77	8.17
7	4	1	1		6.71	-2.57
7	5	1	1		12.85	-12.06
7	6	1	1		46.79	-43.11
7	7	1	1		12.01	-11.71
7	8	1	1		12.33	17.50
7	10	1	1	L	4.59	7.62
7	12	1	1		15.36	-19.63
7	13	1	1		10.30	10.84
7	14	1	1		36.32	-39.19
7	16	1	1	L	5.52	5.69
7	18	1	1	L	7.30	-.64
7	1	2	1		53.36	-43.72
7	2	2	1		7.68	-9.54
7	3	2	1		107.46	99.85
7	5	2	1		34.84	31.00
7	6	2	1		11.81	12.16
7	7	2	1		109.32	-110.15
7	9	2	1		51.76	-52.00
7	10	2	1	L	7.40	-7.05
7	11	2	1		11.99	6.43
7	13	2	1		15.59	10.38
7	15	2	1		24.98	30.75
7	1	3	1		10.91	10.87
7	2	3	1		5.86	-9.48
7	3	3	1		11.05	12.95
7	4	3	1		54.91	-53.22
7	5	3	1		10.61	-9.48
7	6	3	1		7.94	4.89
7	7	3	1		11.10	-10.99
7	8	3	1		70.44	69.28
7	9	3	1		10.37	10.66
7	10	3	1		37.44	-35.34
7	11	3	1		12.52	11.61
7	12	3	1		58.72	-55.52
7	14	3	1		27.38	31.00
7	16	3	1	L	3.62	4.33
7	18	3	1		21.77	15.91
7	1	4	1		72.27	-68.41
7	2	4	1		6.42	7.86
7	3	4	1		43.39	43.48
7	5	4	1		74.12	71.94
7	6	4	1	L	5.91	7.34
7	7	4	1		13.72	11.59
7	8	4	1	L	7.08	-5.59
7	9	4	1		28.56	31.56
7	10	4	1		10.81	-11.25
7	11	4	1		34.53	-33.71
7	13	4	1		26.40	-27.43
7	15	4	1		38.37	32.59
7	1	5	1		11.79	-12.77
7	2	5	1		12.47	-6.41
7	3	5	1		7.47	-10.53
7	4	5	1		16.10	-12.11
7	5	5	1		6.96	-7.71
7	6	5	1		30.33	-31.56
7	7	5	1		7.64	-8.15
7	8	5	1		73.70	72.31
7	10	5	1	L	4.18	-4.45
7	12	5	1		54.27	-56.58
7	14	5	1		22.21	-27.98
7	18	5	1	L	6.18	6.99
7	1	6	1		28.93	31.64
7	3	6	1		19.33	19.10
7	5	6	1		20.74	-24.10
7	7	6	1		43.77	-47.48
7	9	6	1		38.21	-38.96
7	11	6	1		18.22	18.77
7	13	6	1		16.58	15.38
7	14	6	1		11.00	9.54
7	15	6	1		28.78	-24.36
7	2	7	1	L	2.56	3.43
7	4	7	1		10.27	-8.03
7	6	7	1		34.16	31.99
7	8	7	1		69.68	65.01
7	9	7	1		16.40	18.38
7	10	7	1		34.98	-34.73
7	11	7	1		9.93	10.55
7	12	7	1		44.51	-41.96
7	14	7	1		31.85	31.94
7	1	8	1		8.23	5.68
7	2	8	1		18.37	19.62
7	3	8	1		31.98	-28.96
7	5	8	1		15.44	-7.99
7	7	8	1		38.11	40.60
7	9	8	1		24.55	24.97
7	11	8	1		11.05	-10.15
7	13	8	1		10.42	-10.42
7	1	9	1		12.99	-15.90
7	2	9	1	L	6.98	-4.76
7	4	9	1	L	3.91	9.38
7	6	9	1	L	0.00	-1.13
7	8	9	1		37.88	36.70
7	10	9	1	L	6.76	4.52
7	12	9	1		14.41	-17.21
7	1	10	1		43.44	40.48
7	2	10	1		10.36	9.36
7	3	10	1		36.45	-35.89
7	5	10	1		39.04	-37.43
7	7	10	1		11.57	9.67
7	9	10	1		10.77	-11.36
7	11	10	1		17.38	19.44
7	2	11	1	L	5.84	5.30
7	4	11	1	L	6.17	5.02
7	6	11	1		18.31	19.69
7	8	11	1	L	7.77	9.04
7	3	12	1		35.97	-36.96
7	5	12	1		21.68	-18.57
8	2	0	1	L	2.67	-.86
8	4	0	1		109.59	102.66
8	6	0	1		34.29	39.83
8	8	0	1	L	0.00	3.04
8	10	0	1		8.14	7.40
8	12	0	1		24.46	-26.61
8	14	0	1		25.21	-27.32
8	16	0	1		14.82	20.82
8	1	1	1		5.49	8.62
8	2	1	1		7.42	4.98
8	3	1	1		41.81	38.42
8	4	1	1		17.51	16.35
8	5	1	1		21.03	-18.43
8	7	1	1		14.09	-16.19
8	8	1	1		15.96	-15.83
8	9	1	1		52.99	46.50
8	11	1	1		11.16	-13.44
8	13	1	1		70.56	-68.46
8	15	1	1		10.77	12.62
8	17	1	1		16.57	16.30
8	2	2	1		173.13	-187.18
8	3	2	1		9.72	-10.15
8	4	2	1		70.80	-71.42
8	6	2	1		98.73	92.77

H	K	L	G	C	F OBS	F CALC	H	K	L	G	C	F OBS	F CALC
8	7	2	1		10.56	10.70	8	7	9	1		19.22	-22.40
8	8	2	1		25.80	23.46	8	8	9	1		10.95	-12.02
8	9	2	1		8.77	9.87	8	9	9	1		26.81	24.55
8	10	2	1		53.94	57.24	8	11	9	1	L	9.09	-12.18
8	12	2	1		42.15	-38.76	8	13	9	1		37.16	-36.06
8	14	2	1		76.06	-73.85	8	2	10	1		11.30	4.43
8	16	2	1		34.94	32.55	8	4	10	1		30.04	-29.73
8	18	2	1		26.87	29.25	8	6	10	1	L	1.08	-.43
8	1	3	1		55.52	51.75	8	8	10	1	L	6.77	4.01
8	2	3	1		7.65	6.94	8	10	10	1	L	.75	-3.34
8	3	3	1		18.46	-19.34	8	1	11	1		11.68	10.64
8	4	3	1		12.04	11.68	8	3	11	1		13.60	-13.85
8	5	3	1		61.31	-60.33	8	5	11	1		14.26	-12.93
8	7	3	1		6.64	-5.70	8	7	11	1	L	9.66	-5.33
8	9	3	1		62.66	66.52	9	1	1	1		21.35	-21.14
8	11	3	1		47.42	45.47	9	2	1	1		70.21	68.62
8	13	3	1		47.51	43.78	9	4	1	1		34.39	30.52
8	15	3	1	L	3.40	.05	9	5	1	1		6.08	6.67
8	17	3	1		29.28	-31.26	9	6	1	1		70.00	-72.26
8	2	4	1		39.76	43.24	9	7	1	1		8.27	8.33
8	4	4	1		69.23	70.19	9	8	1	1		47.25	-45.14
8	6	4	1		17.34	-14.28	9	10	1	1		13.71	-9.51
8	7	4	1		9.18	7.82	9	12	1	1		9.41	-12.00
8	8	4	1		19.99	-15.09	9	14	1	1		29.02	25.64
8	10	4	1	L	4.18	-3.29	9	16	1	1		14.72	14.86
8	11	4	1		13.89	-14.29	9	18	1	1		27.52	-23.80
8	12	4	1	L	2.53	-.94	9	1	2	1		75.81	-71.96
8	14	4	1	L	5.70	3.06	9	3	2	1		32.34	-33.70
8	18	4	1		12.40	-9.87	9	5	2	1		26.19	21.19
8	1	5	1		9.90	13.06	9	7	2	1		85.81	-79.61
8	3	5	1		26.57	28.08	9	9	2	1		11.54	-7.00
8	4	5	1		9.18	6.60	9	11	2	1		43.26	39.44
8	5	5	1		54.59	-54.16	9	13	2	1		9.45	6.73
8	6	5	1		11.04	-11.15	9	15	2	1	L	5.49	-3.49
8	7	5	1		27.17	-33.05	9	17	2	1		28.89	32.96
8	8	5	1		18.84	-19.71	9	1	3	1		8.12	-6.27
8	9	5	1		93.74	87.29	9	2	3	1		32.84	29.85
8	11	5	1	L	3.65	-1.46	9	3	3	1		8.17	10.05
8	13	5	1		63.45	-63.97	9	4	3	1	L	3.84	1.19
8	15	5	1		15.95	17.58	9	5	3	1		9.66	8.41
8	17	5	1	L	6.51	-3.13	9	6	3	1	L	6.43	-1.15
8	2	6	1		63.89	-63.91	9	7	3	1		7.46	7.90
8	3	6	1		8.24	-8.94	9	8	3	1		13.35	14.83
8	4	6	1		47.73	-50.43	9	10	3	1		17.92	13.47
8	6	6	1		16.34	12.99	9	12	3	1		18.70	-14.82
8	7	6	1		12.61	13.61	9	14	3	1		29.26	-26.23
8	8	6	1	L	0.00	-.85	9	16	3	1	L	5.54	9.21
8	9	6	1		14.23	15.57	9	18	3	1	L	5.39	1.89
8	10	6	1		20.51	22.94	9	1	4	1		48.71	47.84
8	12	6	1	L	2.33	2.55	9	3	4	1		17.08	4.71
8	14	6	1		23.85	-22.32	9	4	4	1		20.05	-20.93
8	1	7	1		24.28	23.03	9	5	4	1		35.01	-36.02
8	3	7	1		23.80	-18.85	9	6	4	1		10.73	-11.13
8	5	7	1		57.43	-54.67	9	7	4	1		17.98	12.67
8	7	7	1		20.81	-22.60	9	9	4	1		11.06	8.99
8	9	7	1		37.29	37.75	9	10	4	1		8.80	7.96
8	11	7	1		20.66	24.07	9	11	4	1		23.93	25.23
8	13	7	1		24.55	25.78	9	13	4	1	L	5.49	1.61
8	15	7	1	L	3.60	-2.90	9	15	4	1		23.64	-27.29
8	2	8	1		78.62	77.31	9	1	5	1		19.16	-19.72
8	3	8	1		8.71	8.12	9	2	5	1		91.52	95.08
8	4	8	1		21.87	27.03	9	3	5	1		8.37	-9.65
8	5	8	1		10.25	9.28	9	4	5	1		59.92	60.04
8	6	8	1		38.80	-37.14	9	6	5	1		84.55	-84.90
8	8	8	1		9.70	-12.11	9	8	5	1		48.71	-50.00
8	10	8	1		22.87	-26.94	9	10	5	1		9.83	-3.97
8	12	8	1		18.29	15.69	9	12	5	1		15.43	-14.61
8	14	8	1		38.89	38.18	9	14	5	1		28.67	27.87
8	1	9	1		18.85	-18.67	9	16	5	1		27.71	29.82
8	3	9	1		14.01	10.91	9	1	6	1		23.88	-25.38
8	5	9	1		15.36	-14.90	9	3	6	1		26.84	25.76

H	K	L	G	C	F OBS	F CALC	H	K	L	G	C	F OBS	F CALC
9	5	6	1		38.11	37.84	10	7	3	1		17.09	18.95
9	7	6	1		25.38	-23.96	10	9	3	1	L	.91	1.84
9	9	6	1	L	4.56	1.59	10	11	3	1		16.09	-14.55
9	11	6	1		10.08	8.30	10	13	3	1		17.00	-24.46
9	13	6	1	L	6.71	4.31	10	15	3	1		14.23	11.52
9	15	6	1	L	6.49	8.51	10	17	3	1		24.18	24.21
9	2	7	1		14.73	17.11	10	2	4	1		23.30	-18.52
9	3	7	1		11.12	13.91	10	4	4	1	L	5.11	1.18
9	4	7	1		20.70	21.95	10	6	4	1		34.47	34.09
9	5	7	1		10.39	9.19	10	8	4	1		38.65	-37.09
9	6	7	1	L	1.91	3.78	10	9	4	1	L	7.86	-8.09
9	8	7	1	L	.59	.47	10	10	4	1		24.79	-23.28
9	10	7	1	L	5.18	7.08	10	11	4	1		8.54	-10.18
9	12	7	1	L	5.79	-2.41	10	12	4	1	L	2.29	-5.61
9	14	7	1	L	6.29	-5.15	10	14	4	1	L	0.00	-2.43
9	1	8	1		34.36	36.06	10	16	4	1		20.40	-14.56
9	3	8	1		14.39	13.49	10	1	5	1		46.46	-45.34
9	4	8	1		14.46	-15.53	10	2	5	1		8.49	-9.12
9	5	8	1		22.81	-21.31	10	3	5	1	L	0.00	-1.65
9	6	8	1		12.88	-14.16	10	5	5	1		36.02	-36.28
9	7	8	1		37.06	34.89	10	7	5	1		39.47	-42.03
9	9	8	1		9.65	7.71	10	9	5	1		64.25	64.04
9	10	8	1		10.97	10.26	10	11	5	1	L	6.60	5.29
9	11	8	1		11.26	-11.45	10	13	5	1		48.81	-46.56
9	13	8	1	L	2.35	1.78	10	15	5	1	L	4.84	4.25
9	2	9	1		43.92	43.44	10	1	6	1		12.64	14.01
9	4	9	1		36.35	37.12	10	2	6	1		12.47	10.41
9	6	9	1		32.18	-34.88	10	3	6	1		12.52	12.89
9	8	9	1		23.77	-25.02	10	4	6	1		12.00	9.58
9	10	9	1	L	3.03	-.85	10	6	6	1		36.29	-36.08
9	12	9	1	L	3.83	3.22	10	8	6	1		10.31	-9.37
9	1	10	1		12.97	-21.18	10	10	6	1		11.52	15.16
9	3	10	1	L	4.47	5.12	10	12	6	1	L	3.81	6.17
9	5	10	1		15.73	21.10	10	14	6	1		10.94	-10.88
9	7	10	1	L	7.56	8.00	10	1	7	1		87.03	-86.56
9	9	10	1	L	5.28	-3.32	10	3	7	1		18.41	23.06
9	2	11	1		13.01	-13.75	10	4	7	1		11.52	-11.18
9	4	11	1	L	1.63	-4.38	10	5	7	1		71.44	72.51
9	6	11	1		16.35	18.84	10	7	7	1		11.96	7.91
10	2	0	1		40.66	-41.58	10	9	7	1	L	1.90	-.57
10	4	0	1		30.01	29.05	10	11	7	1		11.69	-12.72
10	6	0	1		96.94	98.67	10	13	7	1		15.07	-20.59
10	8	0	1		53.50	-54.64	10	2	8	1	L	6.16	4.68
10	10	0	1		25.48	-31.14	10	4	8	1		31.41	-27.91
10	12	0	1		11.07	3.85	10	6	8	1		11.41	-9.55
10	14	0	1		7.84	6.13	10	8	8	1		16.65	14.52
10	16	0	1	L	2.72	3.18	10	10	8	1	L	2.15	-5.22
10	18	0	1		19.23	22.65	10	12	8	1		13.07	-14.00
10	1	1	1		27.82	25.67	10	1	9	1		12.39	-13.88
10	3	1	1		20.17	-21.55	10	3	9	1		8.50	8.80
10	5	1	1		82.87	-77.86	10	5	9	1		7.94	-10.88
10	7	1	1		46.12	-44.18	10	7	9	1		17.00	-19.01
10	9	1	1		53.63	50.52	10	9	9	1		25.70	27.80
10	11	1	1		13.59	11.17	10	11	9	1	L	0.00	2.31
10	13	1	1		31.05	-23.89	10	4	10	1		8.82	-6.34
10	15	1	1	L	2.60	-.80	10	6	10	1		35.25	-32.75
10	17	1	1	L	6.04	5.15	10	8	10	1		24.63	22.68
10	1	2	1		8.35	8.92	10	3	11	1	L	7.86	9.61
10	2	2	1		28.42	-30.18	10	5	11	1		26.29	29.81
10	4	2	1		58.16	55.73	11	1	1	1		8.07	-9.27
10	6	2	1		36.81	34.95	11	2	1	1		30.73	-30.57
10	8	2	1		34.25	-35.46	11	4	1	1		13.51	11.48
10	10	2	1		8.47	10.00	11	6	1	1		13.14	6.22
10	12	2	1		21.06	24.43	11	8	1	1		30.28	27.77
10	14	2	1	L	5.24	-6.48	11	10	1	1		8.71	-3.38
10	16	2	1		39.86	37.76	11	12	1	1		19.09	-13.36
10	18	2	1	L	6.90	6.11	11	14	1	1		16.52	9.03
10	1	3	1		108.57	-110.60	11	16	1	1		13.09	11.17
10	2	3	1		9.16	-9.13	11	1	2	1		30.16	-29.26
10	3	3	1		12.94	15.43	11	3	2	1		39.05	-39.71
10	4	3	1		8.09	-7.24	11	5	2	1		7.96	4.50
10	5	3	1		82.19	78.94	11	7	2	1		31.61	40.02

H	K	L	G	C	F OBS	F CALC	H	K	L	G	C	F OBS	F CALC
11	9	2	1		17.65	21.38	12	14	0	1		26.10	24.37
11	11	2	1		39.26	37.58	12	16	0	1		41.51	-40.18
11	13	2	1		15.75	-21.22	12	1	1	1		24.75	22.19
11	15	2	1		33.63	-34.40	12	3	1	1		14.13	13.63
11	17	2	1	L	0.00	.62	12	5	1	1		42.22	-39.41
11	2	3	1		24.10	24.37	12	7	1	1		14.78	-8.53
11	4	3	1	L	1.84	-3.32	12	9	1	1		15.14	-15.16
11	6	3	1		20.93	-15.96	12	11	1	1		19.34	17.46
11	8	3	1		42.83	-42.07	12	13	1	1		26.62	25.70
11	9	3	1		9.90	-10.43	12	15	1	1	L	4.96	6.09
11	10	3	1		73.14	66.40	12	17	1	1	L	4.03	-4.35
11	12	3	1		38.23	31.33	12	2	2	1		44.14	42.38
11	14	3	1		41.52	-37.00	12	3	2	1		8.29	7.59
11	16	3	1	L	5.24	-2.26	12	4	2	1		10.60	-8.26
11	1	4	1		18.35	19.85	12	6	2	1		14.55	-12.32
11	3	4	1		38.86	-40.10	12	8	2	1		11.67	8.04
11	5	4	1	L	6.39	4.26	12	10	2	1	L	6.40	-6.15
11	6	4	1		8.52	-8.88	12	12	2	1	L	6.56	4.87
11	7	4	1		26.32	23.62	12	14	2	1		23.06	22.77
11	9	4	1		41.55	-40.32	12	16	2	1	L	4.17	-7.84
11	11	4	1		15.75	-14.25	12	1	3	1		48.22	-44.73
11	13	4	1		15.24	18.82	12	2	3	1		9.37	-10.42
11	15	4	1		19.85	-19.17	12	3	3	1	L	4.95	-6.16
11	2	5	1		31.70	-30.09	12	4	3	1		9.17	-9.52
11	4	5	1		11.54	10.95	12	5	3	1		64.68	59.99
11	6	5	1	L	2.51	-7.36	12	7	3	1		23.85	-24.10
11	8	5	1	L	3.07	1.19	12	9	3	1		31.07	-28.12
11	10	5	1		22.13	29.36	12	11	3	1		24.43	-21.27
11	12	5	1	L	5.40	.75	12	13	3	1		34.46	-32.02
11	14	5	1	L	5.11	-9.42	12	15	3	1	L	0.00	-5.72
11	16	5	1		12.83	11.91	12	1	4	1		8.99	-9.31
11	1	6	1		14.30	-13.36	12	2	4	1		22.94	-24.27
11	3	6	1		24.53	24.72	12	4	4	1		18.19	-23.27
11	4	6	1		9.58	8.51	12	6	4	1	L	6.26	1.98
11	5	6	1	L	5.94	-5.15	12	8	4	1		34.53	-30.30
11	7	6	1		12.47	-9.72	12	10	4	1		10.32	-8.68
11	9	6	1		32.43	34.94	12	12	4	1		47.42	43.52
11	11	6	1		34.73	33.31	12	14	4	1	L	3.84	3.71
11	13	6	1	L	4.64	-9.62	12	16	4	1		32.12	-28.92
11	15	6	1	L	7.12	2.08	12	1	5	1	L	3.53	4.14
11	1	7	1		10.39	10.13	12	3	5	1		19.35	24.92
11	2	7	1		13.28	-7.81	12	5	5	1	L	1.66	-.64
11	4	7	1	L	2.64	-1.51	12	7	5	1		20.51	-19.36
11	6	7	1		16.16	-17.86	12	9	5	1		43.62	-40.94
11	8	7	1		49.64	-51.70	12	11	5	1		12.51	14.26
11	9	7	1		11.33	-10.33	12	13	5	1		24.42	23.94
11	10	7	1		44.11	45.46	12	15	5	1	L	9.41	8.10
11	12	7	1		28.62	29.66	12	2	6	1		40.52	41.01
11	14	7	1		27.83	-27.03	12	3	6	1		13.52	12.77
11	1	8	1		21.11	17.51	12	4	6	1		24.61	25.50
11	3	8	1		20.85	20.01	12	6	6	1		10.67	-10.71
11	5	8	1	L	2.45	-.40	12	7	6	1		13.26	-13.08
11	7	8	1		11.01	-15.07	12	8	6	1		14.31	13.17
11	9	8	1		12.42	-16.91	12	10	6	1	L	5.41	6.64
11	11	8	1		15.05	-14.33	12	12	6	1		23.86	-23.35
11	2	9	1		21.95	-22.30	12	14	6	1	L	3.51	-1.61
11	4	9	1		8.34	6.12	12	1	7	1		39.96	-40.18
11	6	9	1	L	5.75	-5.29	12	3	7	1		9.85	12.82
11	8	9	1	L	6.75	-6.05	12	4	7	1		9.72	-10.72
11	10	9	1	L	0.00	2.38	12	5	7	1		69.42	65.12
11	1	10	1	L	6.15	-7.52	12	7	7	1		10.30	-16.07
11	3	10	1		29.85	31.98	12	9	7	1		24.47	-24.04
11	5	10	1		12.69	-7.94	12	11	7	1	L	8.83	-4.49
11	7	10	1		22.70	-24.16	12	13	7	1		11.26	-12.40
11	2	11	1		10.35	-2.47	12	1	8	1		10.34	-10.12
12	2	0	1		53.67	-52.93	12	2	8	1		20.48	-20.78
12	4	0	1		55.04	-55.60	12	4	8	1	L	3.21	3.30
12	6	0	1		8.61	6.17	12	6	8	1		8.57	7.71
12	8	0	1		52.19	-44.50	12	8	8	1	L	3.77	-5.93
12	10	0	1		22.68	-23.38	12	10	8	1	L	1.46	2.99
12	12	0	1		73.90	70.99	12	1	9	1	L	.81	4.16

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  H    K    L  G C   F OBS  F CALC      H    K    L  G C   F OBS  F CALC
 12    5    9  1 L    6.36    6.66     13    4    9  1     14.64  -13.09
 12    7    9  1 L    1.99   -1.79     13    6    9  1     33.06   35.46
 12    9    9  1     21.20  -19.74     13    8    9  1 L    2.47    2.49
 12    2   10  1 L    7.29    8.26     13    1   10  1 L    5.87    6.31
 12    4   10  1     18.10   22.77     13    3   10  1     10.93   10.85
 12    6   10  1 L    6.96   -2.76     14    2    0  1     28.04  -24.08
 13    1    1  1      7.51    7.28     14    4    0  1     32.46  -33.11
 13    2    1  1     45.53  -44.03     14    6    0  1     18.27   19.42
 13    4    1  1     28.71  -27.22     14    8    0  1     18.24   24.71
 13    6    1  1     59.13   57.55     14   10    0  1     31.40  -27.20
 13    7    1  1      8.92   -9.11     14   12    0  1 L    5.05   -4.22
 13    8    1  1     30.62   26.86     14   14    0  1 L    3.01    7.93
 13    9    1  1      8.96   -9.52     14    1    1  1     22.49   19.87
 13   10    1  1 L    1.77    3.38     14    3    1  1 L    3.87   -1.03
 13   12    1  1 L    7.19   -2.73     14    4    1  1      8.35    7.55
 13   14    1  1 L    4.57    2.11     14    5    1  1     24.97   26.89
 13   16    1  1 L    4.14   -8.03     14    6    1  1     14.95   14.06
 13    1    2  1     67.39   71.93     14    7    1  1     24.20   25.95
 13    3    2  1     42.48   36.44     14    9    1  1     12.00  -13.90
 13    5    2  1     24.14   19.25     14   10    1  1     16.07  -16.05
 13    7    2  1     37.99   35.55     14   11    1  1     11.24    3.33
 13    9    2  1     32.71  -29.75     14   13    1  1     21.78   20.09
 13   11    2  1     28.84  -29.44     14   15    1  1     27.69  -23.25
 13   13    2  1     24.89   19.95     14    2    2  1     23.00  -21.74
 13   15    2  1     15.10   13.31     14    4    2  1     74.73  -69.69
 13    2    3  1     36.27  -36.46     14    6    2  1 L    4.52   -5.13
 13    4    3  1     12.24   10.86     14    8    2  1     90.57   87.53
 13    6    3  1 L    4.33    5.74     14   10    2  1     12.90  -16.13
 13    7    3  1      9.76   -9.63     14   12    2  1     45.57  -41.36
 13    8    3  1 L    5.85   -5.46     14   14    2  1     11.13   -7.78
 13   10    3  1     18.36   13.16     14    1    3  1     46.73   46.61
 13   12    3  1 L    2.56   -3.96     14    3    3  1     44.10  -42.20
 13   14    3  1     30.96  -28.57     14    5    3  1     55.50  -56.59
 13    1    4  1     29.96  -27.05     14    7    3  1      9.17   -9.86
 13    3    4  1     34.01  -33.95     14    9    3  1      7.60    7.15
 13    4    4  1     12.82   11.59     14   11    3  1     20.98   26.11
 13    5    4  1     15.25   14.55     14   13    3  1     13.72  -10.33
 13    7    4  1     21.49   23.13     14    1    4  1     11.98  -11.39
 13    9    4  1     31.64  -30.57     14    2    4  1 L    5.58    4.66
 13   11    4  1     17.07  -13.56     14    3    4  1     12.14  -11.87
 13   13    4  1 L    3.94    5.35     14    4    4  1 L    5.81    2.54
 13   15    4  1 L    3.86    4.91     14    6    4  1     14.46   12.66
 13    1    5  1     11.70   12.93     14    7    4  1     12.75   12.18
 13    2    5  1     86.33  -82.99     14    8    4  1      9.36   -1.80
 13    4    5  1     31.21  -27.92     14   10    4  1 L    3.39   -1.66
 13    6    5  1     84.38   79.77     14   12    4  1     17.79   14.25
 13    8    5  1     24.36   21.50     14   14    4  1 L    7.33    5.06
 13   10    5  1 L    3.32    7.64     14    1    5  1     44.44   44.97
 13   12    5  1      9.72   -6.85     14    2    5  1 L    8.05    8.84
 13   14    5  1     12.69  -18.43     14    3    5  1     32.02  -29.21
 13    1    6  1     24.54   28.00     14    5    5  1 L    4.88    4.73
 13    2    6  1      9.66  -10.22     14    7    5  1     22.18   24.43
 13    3    6  1     18.70   20.28     14    9    5  1     17.79  -20.28
 13    4    6  1      9.51    8.77     14   11    5  1     24.36   23.40
 13    5    6  1     17.63  -19.35     14   13    5  1     28.81   28.11
 13    7    6  1     17.00  -17.81     14    1    6  1     10.04  -10.48
 13    9    6  1      9.73    9.17     14    2    6  1      8.87    7.23
 13   11    6  1 L    7.73    3.90     14    4    6  1     12.89  -11.59
 13   13    6  1 L    3.92   -4.14     14    6    6  1      9.30   -9.90
 13    2    7  1     44.67  -40.48     14    8    6  1     34.40   31.35
 13    4    7  1     12.84   14.66     14   10    6  1     15.02   11.18
 13    6    7  1     17.98   13.22     14   12    6  1 L    8.87   -9.57
 13    8    7  1 L    9.48  -13.61     14    1    7  1     30.78   31.92
 13   10    7  1 L    6.57    4.55     14    3    7  1     33.33  -32.49
 13   12    7  1 L    3.71   -4.76     14    5    7  1     39.05  -41.57
 13    1    8  1     33.08  -36.89     14    7    7  1     11.33  -12.29
 13    3    8  1     22.19  -21.06     14    9    7  1 L    1.01    -.78
 13    5    8  1 L    5.45   -2.09     14   11    7  1     27.98   32.70
 13    7    8  1     13.13  -12.16     14    2    8  1     13.18   13.41
 13    9    8  1     10.97    7.46     14    4    8  1     28.92   32.10
 13    2    9  1     37.36  -38.86     14    6    8  1 L    0.00    1.80
```

H	K	L	G	C	F OBS	F CALC
14	8	8	1		38.29	-40.73
14	3	9	1		13.28	-11.71
14	5	9	1	L	8.25	8.96
15	2	1	1	L	5.45	4.35
15	3	1	1		13.26	-12.91
15	4	1	1	L	3.84	-.39
15	6	1	1		15.75	14.84
15	7	1	1		13.41	10.90
15	8	1	1		24.03	-25.44
15	10	1	1		20.17	-21.20
15	12	1	1		22.25	24.93
15	14	1	1	L	7.01	8.31
15	1	2	1		47.85	47.66
15	3	2	1		41.10	35.00
15	5	2	1		27.40	-29.97
15	7	2	1	L	1.05	-2.67
15	9	2	1		26.03	-22.18
15	11	2	1		22.96	-21.79
15	13	2	1		31.62	27.44
15	2	3	1	L	6.24	4.58
15	4	3	1		10.18	-10.37
15	6	3	1		11.00	-8.27
15	7	3	1		10.81	9.34
15	8	3	1	L	1.07	6.78
15	10	3	1		17.48	-18.05
15	12	3	1		12.93	-15.63
15	1	4	1		19.60	22.19
15	3	4	1		19.05	-20.84
15	5	4	1		32.76	-29.59
15	7	4	1		25.36	-19.56
15	9	4	1		45.99	42.62
15	11	4	1		29.75	25.31
15	13	4	1	L	7.78	-6.12
15	2	5	1		14.93	16.14
15	4	5	1	L	2.55	4.25
15	6	5	1		19.86	17.97
15	8	5	1		31.97	-34.29
15	10	5	1		39.41	-40.06
15	12	5	1		31.23	31.77
15	1	6	1		11.52	10.22
15	3	6	1		26.66	22.96
15	5	6	1	L	3.84	.40
15	7	6	1	L	2.27	-.09
15	9	6	1		34.15	-31.09
15	11	6	1		22.80	-20.01
15	2	7	1		13.32	14.11
15	4	7	1	L	9.65	10.10
15	6	7	1	L	7.11	4.11
15	8	7	1	L	3.11	1.66
15	1	8	1		17.55	-17.26
15	5	8	1	L	4.84	10.06
15	7	8	1		9.12	-6.13
16	2	0	1		27.66	29.05
16	4	0	1		66.23	61.54
16	6	0	1		11.38	10.18
16	8	0	1		16.98	20.52
16	10	0	1		35.40	-33.70
16	12	0	1		31.58	-33.94
16	1	1	1	L	4.82	1.05
16	3	1	1		7.99	-13.88
16	4	1	1		11.43	-9.86
16	5	1	1		15.37	13.05
16	7	1	1		13.69	16.33
16	9	1	1	L	3.38	1.52
16	11	1	1		12.66	6.78
16	13	1	1	L	7.40	-9.75
16	2	2	1		55.07	52.18
16	4	2	1		9.74	-9.11
16	6	2	1		24.51	20.47
16	8	2	1		10.06	-8.04
16	10	2	1		9.89	-15.22
16	12	2	1	L	.75	-.96
16	1	3	1		15.18	16.42
16	3	3	1		14.52	-15.49
16	5	3	1	L	5.16	-5.44
16	7	3	1		45.91	44.84
16	9	3	1	L	6.27	5.55
16	11	3	1		26.43	-23.82
16	2	4	1	L	5.73	7.70
16	4	4	1		41.66	36.00
16	6	4	1	L	5.58	4.63
16	8	4	1		9.90	15.74
16	10	4	1		21.54	-12.35
16	12	4	1		18.38	-19.21
16	1	5	1	L	2.95	3.27
16	3	5	1		29.70	-33.34
16	5	5	1		17.91	12.82
16	7	5	1		44.89	44.67
16	9	5	1	L	2.33	-.50
16	11	5	1	L	5.34	-6.48
16	6	6	1		13.14	-13.89
16	8	6	1		10.02	-10.05
16	1	7	1	L	0.00	7.22
16	3	7	1		15.62	-14.25
16	5	7	1	L	4.15	-5.03
16	7	7	1		32.05	30.55
16	2	8	1		23.52	-22.62
17	2	1	1		19.08	-17.71
17	4	1	1		9.52	-8.27
17	6	1	1		17.71	16.04
17	8	1	1	L	3.22	.65
17	10	1	1		11.87	-13.87
17	12	1	1		20.20	-13.44
17	1	2	1		59.48	-56.49
17	3	2	1		35.62	-32.93
17	5	2	1	L	5.46	-4.36
17	7	2	1	L	5.43	5.13
17	9	2	1		14.60	22.51
17	11	2	1		18.70	-14.57
17	2	3	1		35.31	35.91
17	4	3	1		36.76	-37.73
17	6	3	1		40.26	-39.46
17	8	3	1		18.98	25.13
17	10	3	1	L	0.00	1.93
17	1	4	1	L	1.86	4.65
17	3	4	1		41.18	36.02
17	5	4	1	L	1.24	-2.39
17	7	4	1	L	9.71	-9.37
17	9	4	1		23.82	23.10
17	2	5	1	L	4.54	.11
17	6	5	1	L	3.84	-.54
17	8	5	1		16.36	16.13
17	3	6	1		17.96	-19.02
17	5	6	1	L	0.00	.33
17	7	6	1	L	8.28	8.60
17	2	7	1		29.39	33.70
18	2	0	1		24.15	23.25
18	4	0	1		15.49	10.66
18	6	0	1		25.88	-31.07
18	8	0	1	L	2.82	-.29
18	10	0	1		30.65	32.57
18	1	1	1	L	6.55	4.95
18	3	1	1		17.37	12.42
18	5	1	1	L	7.01	5.08
18	7	1	1		40.42	-34.56
18	9	1	1		15.95	-11.85
18	2	2	1	L	2.20	2.20
18	4	2	1		18.01	18.24
18	6	2	1	L	6.13	-1.39
18	8	2	1		22.80	-24.11
18	10	2	1		11.29	8.56
18	1	3	1	L	4.37	5.61

```
  H     K     L    G  C  F  OBS    F  CALC    H     K     L    G  C  F  OBS    F  CALC
 18     3     3    1  L      6.15      1.04   19     7     2    1        13.85   -15.62
 18     5     3    1        16.68    -12.82   19     2     3    1        19.27    19.77
 18     7     3    1        40.60     35.56   19     4     3    1  L      5.37     -.59
 18     9     3    1        19.94     14.58   19     6     3    1        16.19    14.61
 18     4     4    1  L      0.00     -5.10   19     3     4    1        23.33    20.66
 18     6     4    1        25.77    -28.45   19     5     4    1  L      9.23     -.55
 18     8     4    1  L      3.64      3.45   19     2     5    1        10.77    -9.77
 18     3     5    1        26.53     24.78   19     4     5    1        12.24    -9.29
 18     5     5    1  L      3.19      1.50   20     2     0    1        34.34   -34.74
 18     2     6    1  L      9.05     -6.84   20     4     0    1  L      8.40    -6.45
 18     4     6    1  L      9.65     -1.30   20     6     0    1  L      7.42     4.87
 19     6     1    1        14.99    -11.20   20     3     1    1        11.34    10.78
 19     8     1    1        25.98     24.36   20     4     2    1  L      5.64     6.86
 19     3     2    1  L      2.37      7.64   20     3     3    1        11.02    -6.33
 19     5     2    1        33.31     33.32
```