FURTHER SULPHUR ISOTOPE STUDIES
OF THE
TAOLIN LEAD-ZINC ORE DEPOSIT

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By

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Submitted to the Department of Geology
in Partial Fulfilment of the Requirements
for the Degree
Bachelor of Science

McMaster University
May 1984

BACHELOR OF SCIENCE (1984)
(Geology)

McMASTER UNIVERSITY
Hamilton, Ontario

TITLE: Further Sulphur Isotope Studies of the Taolin Lead-Zinc Ore Deposit

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NUMBER OF PAGES: 88

ACKNOWLEDGEMENT

The author wishes to express her sincere thanks to Dr. C. E. Rees for his encouragement, directorship, financial assistance, patience, friendship and Hyperion in the course of this investigation. Andy Fyon and Dr. H. P. Schwarcz are gratefully acknowledged for their helpful discussions as are Catherina, Barb and Lincoln for their technical assistance. Thanks also go to Dave for lending his drafting expertise to the project.

This study was made possible by Ding Tiping who supplied all of the samples. His assistance is sincerely appreciated.

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ABSTRACT

Sulphur isotope data from coexisting sulphides and sulphates from the 120 m level of the Shangtancen ore body of the Taolin Pb-Zn ore deposit have been used to estimate the temperatures of sulphur mineral precipitation. The data indicate that sulphide was the dominant species in solution at both high and low temperatures. The data also show that the $\delta^{34}S$ value of total sulphur in solution was close to zero at high temperatures, but had low negative values (about -6.7°/₀₀) at low temperatures. This is interpreted in terms of the effects of mineral precipitation on the isotopic composition of the solution. The decrease of the $\delta^{34}S$ value of the total sulphur with decreasing temperature was brought about because the removal from the system, by precipitation, of isotopically heavy sulphate exceeded the removal from the system, by precipitation, of isotopically light sulphide.

I. INTRODUCTION

Ohmoto (1972), systematically expounded the effects of the changes in physico-chemical conditions on the compositions of precipitating minerals in hydrothermal systems. At the same time he pointed out that the effects of precipitation of different mineral phases on the isotopic composition of the hydrothermal fluid also had to be considered. Although since 1972 there have been many studies of sulphur isotopes in hydrothermal ore deposits (see, for example, Ohomoto and Rye (1979) and references therein) Ding and Rees (1984) were the first to illustrate an example of this effect in samples from the Taolin Pb-Zn ore deposit.

This work represents the second study of sulphur isotopes in the Taolin Pb-Zn ore deposit. This medium size deposit which is situated in the South of Lingjiang county, Hunan province, China is not of importance ecnomically but it is genetically significant. It is considered in China to be representative of mesothermal vein filling ore deposits because of its geological setting, mineral composition, alteration of country rocks and multiple stages of mineral deposition.

The purpose of this second examination of stable isotopes of the Taolin ore deposit was to determine the temperatures of mineral formation and the source of sulphur in the deposit. As well, the results were examined using the Ding and Rees model equations that were developed to explain the sulphur isotope systematics that were observed during the first study of Taolin.

Complete details of the analytical methods used have been included in this thesis as have the details of the Ding and Rees model. These equations describe the changes of the physico-chemical conditions with temperature in the ore forming fluid and show how these changes give rise to the observed pattern of sulphur isotope abundance variations.

II. SULPHUR ISOTOPE GEOCHEMISTRY

2.1 General Theory

Sulphur istope abundance variations are widely used in studies of sulphur sources and geochemical cycling of the element. Samples studied include meteorites, returned lunar rocks and soil plus various types of crustal sulphur.

The Type I carbonaceous chondrite meteorites containing about 2% sulphur are generally believed to represent unfractionated samples of the non volatile component of primordial matter from which the solar system was formed (see Henderson, 1982 and references therein). The average sulphur concentration in the crust of the earth has been estimated to be roughly 260 ppm (Henderson, 1982). The amount of sulphur present in the crust then represents only about 10^{-3} of its cosmic abundance. This low sulphur abundance may be due to a combination of the loss of volatile sulphur from the earth and the concentration of sulphur in the earths core. From geophysical evidence the core of the earth is not the exclusively Ni-Fe alloy that was once postulated because a lighter element is needed to correct for the measured density. Both oxygen and sulphur had been postulated for this role although at present there are more proponents for sulphur. It is estimated that 10% sulphur by weight is required to give the correct geophysical results and there is sufficient sulphur in C1 chondrites to make this postulate feasible.

In terrestrial, meteoritic and lunar materials the four naturally occurring sulphur isotopes are found with the following approximate relative abundances: ^{32}S (95.02%), ^{33}S (0.75%), ^{34}S (4.2%) and ^{36}S (0.017%) (Macnamara and Thode, 1950). Variations of these relative abundances occur because of the slight differences in the physical and chemical properties of the isotopes. These variations are usually expressed in terms of variations in the isotope ratio $^{34}S/^{32}S$ because ^{34}S and ^{32}S are the most convenient isotopes on which to perform measurements.

Sulphur isotope data are generally presented using the "del" notation:

$$\delta^{34}S, \text{°/}_{\circ\circ} = [(^{34}S/^{32}S)_{sample} / (^{34}S/^{32}S)_{standard} - 1] \times 1000$$

The standard used is the troilite phase (FeS) of the Canyon Diablo meteorite. The $^{34}S/^{32}S$ ratio for Canyon Diablo troilite is assigned, by convention, a value of 0.040045 (Ault and Jensen, 1963).

Some details of the chemical behavior of sulphur under the conditions in the upper most levels of the earths crust have been summarised by Neilsen (1979):

1. Under varying redox conditions the valence of the sulphur atom can change from S^2 via S^0 to S^{4+}. Metastable complexes with intermediate valences such as S_2^{2-}, S_3^{2-}, S_4^{2-}, S_5^{2-}, S_6^{2-}, $S_2O_3^{2-}$, can appear during the gentle oxidation of dissolved H_2S. The S^{2-} or (S^{1-}) group, however, forms the stable mineral pyrite (FeS_2) and this is by far the most abundant sulphide mineral in sedimentary rocks.

2. Inorganic reduction of sulphate needs such a high activation energy that the reaction with naturally available reductants is confined to temperatures probably above 250°C, i.e., to environments deep in the crust. Enzymatic complexing of the sulphate ion lowers this threshold and enables the reduction by living cells. This is the entry step into the "biological cycle" and the mechanism responsible for most of the global variation in S isotope composition.

3. In cold water metal sulphides are practically insoluble, while the solubility of sulphates (even that of $BaSO_4$) is high enough to make sulphate the mobile sulphur phase on the Earth's surface. When a rock unit contains sulphide and sulphate under equilibrium conditions, any circulation of groundwater will extract dissolved sulphate from the system. Generally this involves also a spatial separation between isotopically "light" and "heavy" sulphur.

4. This geochemical behavior favors the formation of local accumulations of sulphur minerals, either sulphides or sulphates, in an environment with consistently lower background concentration of sulphur. Once consolidated, such local "pools" withstand the attack of geologic processes for geologic times, and they will also preserve their natural S isotope record.

2.2 Sulphur Isotope Variations in Nature

The variability in nature of $^{34}S/^{32}S$ was first demonstrated by Thode (1949) and Trofimov (1949). Since then increasing use has been made of $\delta^{34}S$ variations in geochemical studies of terrestrial, meteoritic and lunar processes. The ranges of $\delta^{34}S$ values found in various types of samples are shown in Fig. 1.

Studies of meteorites have shown that the iron bearing species have a very narrow range of $\delta^{34}S$ values with a mean value of +0.13%. Chondrites show a wider spread with $\delta^{34}S$ values from 0°/oo to +4°/oo. Returned lunar samples show a narrow range (0°/oo to 1°/oo) of $\delta^{34}S$ values for rocks and a greater range (5°/oo to 13°/oo) for soils (Rees and Thode, 1981, and references therein).

The overall mean $\delta^{34}S$ of terrestrial sulphur agrees well with that of troilite sulphur. The $\delta^{34}S$ values of individual samples can be interpreted directly in terms of the net isotope fractionation which the materials have undergone (Neilson, 1979). For terrestrial samples there is a range of $\delta^{34}S$ values from about -65°/oo to +95°/oo although the majority of samples have $\delta^{34}S$ values between -40°/oo and +40°/oo. Igneous rocks tend to be isotopically similar to the meteorites suggesting the earth and meteorites have a common origin. Sedimentary sulphides on the other hand vary dramatically from +70°/oo to -70°/oo. Sedimentary sulphates are enriched in the heavy isotope by roughly 10°/oo to 30°/oo while modern sea water has a geographically constant value of +21°/oo (Rees, 1978). Volcanic

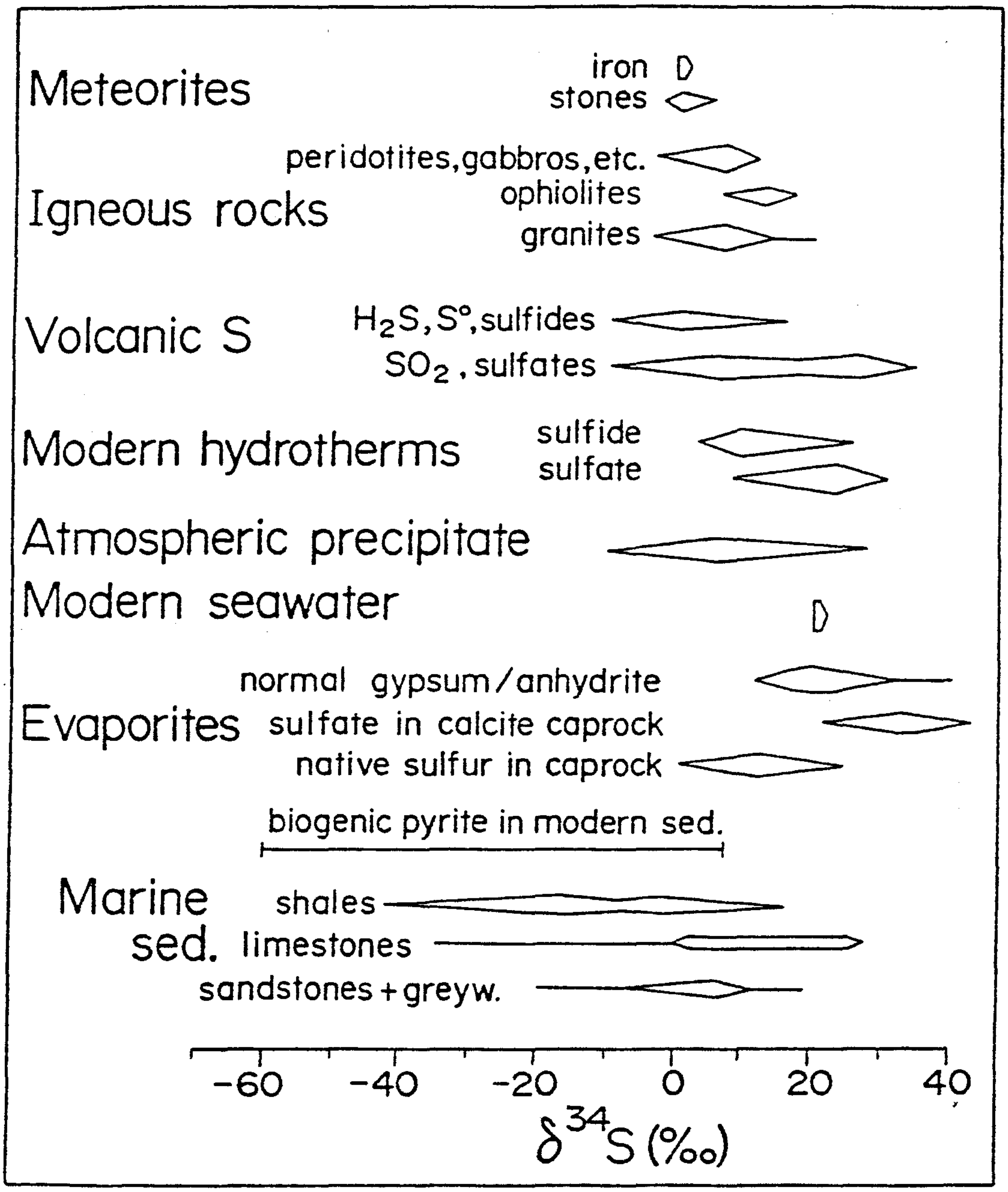


Fig. No. 1 Natural Variations in $\delta^{34}S$ Values sulphur has $\delta^{34}S$ values in the range -20°/∘∘ to +40°/∘∘ while hydrothermal sulphur shows variations from about 0°/∘∘ to roughly +30°/∘∘.

2.3 The Biological Sulphur Cycle

Since the sedimentary shell harbours ~50% of all crustal sulphur it plays a significant role in the average crustal $\delta^{34}S$ value (Neilson, 1979). Bacterial sulphate reduction on the sea floor splits up the dissolved marine sulphate into a reduced light fraction entering the sediment as pyrite, and a heavy fraction remaining as unreduced sulphate (Nielsen, 1979). This sulphur, through time, is uplifted, eroded, and finally precipitated again keeping a varied isotope population circulating through the environment.

Todays evaporites, which are deposited with negligable S isotope fractionation have a $\delta^{34}S$ value of 21°/∘∘ (Neilsen, 1979), that of today's ocean water. By examining evaporites from other periods it is found that the $\delta^{34}S$ value for ocean water has changed significantly. These changes correspond well with paleoclimatic change. For example, periods of high biological activity such as the Cambrian and Devonian show increased marine $\delta^{34}S$ values while periods of extended weathering such as the Permian show depleted values.

The large spread in $\delta^{34}S$ values in sulphides is primarily due to the isotope fractionation produced during the bacterial reduction of sulphate to sulphide. Dissimilatory sulphate reduction by the bacterium *Desulfovibrio desulfuricans* can be represented by the reaction scheme shown in Fig. 2 (Rees, 1973). The availability of nutrients, sulphate concentration and temperature all play a role in the overall isotope fractionation produced by the bacterium. Different environmental conditions therefore give different isotopic shifts between the $\delta^{34}S$ value of the source sulphate and that of the hydrogen sulphide produced.

Laboratory experiments on bacterial sulphate reduction have yielded product hydrogen sulphide with $\delta^{34}S$ values from about 2°/oo heavier to roughly 30°/oo lighter than that of the source sulphate. It is common in nature to find sulphide produced with $\delta^{34}S$ values up to 60°/oo lighter than that of the source sulphur.

The isotope fractionation in the inorganic chemical reduction of sulphate can be represented as a one step first order reaction which can be written as

$$^{32}SO_4^{=} \xrightarrow{k_2} H_2{}^{34}S$$
$$^{32}SO_4^{=} \xrightarrow{k_1} H_2{}^{32}S$$

where the rate constants for $^{32}SO_4^{=}$ and $^{34}SO_4^{=}$ reduction are written as k_1 and k_2 respectively. The experimentally determined value of k_1/k_2 is 1.025 at 25°C (Harrison and

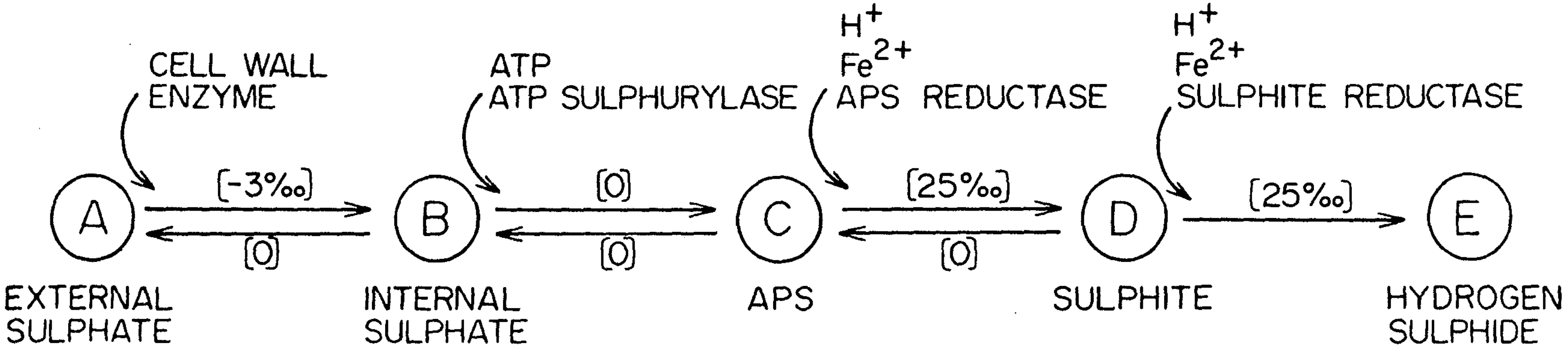


Fig. No. 2 Dissimilatory Sulphate Reduction by the Bacterium *Desulfovibrio Desulfuricans*

Thode, 1958) indicating that the light isotopic species reacts 2.5°% faster than the heavier one. This result is consistant with the theoretical isotope effect predicted for the breaking of a sulphur oxygen bond in sulphate.

In order to explain the isotope fractionation produced during the bacterial reduction of sulphate both in the laboratory and in nature it is necessary to take into account the complex reaction pathway. The overall isotope fractionation depends on the relative rates of the forward and backward reaction steps and the kinetic isotope effects associated with them. Rees (1973) and Burnie and Schwarcz (1972) have discussed the origins of observed isotope distributions in sedimentary sulphides.

2.4 Inorganic Fractionation of Sulphur Isotopes

Sulphur isotope fractionation in nature also takes place in inorganic reactions. Typical systems with isotope exchange under (approached) equilibrium fractionation are:

1) Sulphide and sulphate in the magmatic environment and in hydrothermal fluids at temperatures above 250°C
2) H_2S and SO_2 in volcanic vents
3) Dissolved sulphide and precipitating sulphide minerals in hydrothermal fluids (Ohmoto and Rye, 1979).

In certain cases variation of equilibrium fractionation with temperature allows observed values to be used to infer temperatures of equilibration, a procedure called sulphur isotope geothermometry.

Inorganic fractionation processes account for the spread around $\delta = 0$ found for volcanic sulphur and the isotope patterns found in hydrothermal sulphur deposits. In this latter case sulphur isotopes can be used to provide information on

1) temperatures of mineralization
2) the chemical conditions and mechanisms of ore deposition and
3) the sources of sulphur in the ore forming fluid (Neilsen, 1979).

This is discussed in detail in a later section.

2.5 Sulphur Ores

Sulphur is found in association with base metals such as iron, lead and nickel in certain environments in concentrations that have economic significance. Such ore bodies can be either primary (magmatic), sedimentary or hydrothermal in nature. A brief description is given for each of these ore types.

2.5.1 Sudbury Type Ores

The Sudbury Ni-Cu sulphide deposit represents an igneous intrusion, possibly of mantle origin. The ore sublayer intrudes between the Sudbury irruptive and the Archean/Proterozoic host rock footwall. The whole sequence is considered by many to represent an intruded astrobleme (Schwarcz, 1973 and references therein).

The formation of the very concentrated ore bodies has been described in terms of an immiscible fluid model. Irvine (1975) has demonstrated that silification of a mafic magma can lower the solubility of sulphur, resulting in the magma becoming sulphur saturated so that sulphides segregate from it. Sudbury has a structural and compositional environment conducive to this type of ore formation. Naldrett (1981) suggests that contamination with quartz rich material caused supersaturation of a mafic igneous intrusion. The footwall environment was such that the sulphide settled and crystallized undiluted by silicates which were also accumulating as the magma crystallized.

Isotope studies performed by Schwarcz (1973) show the $\delta^{34}S$ values for the nickel sulphide ore have a narrow range between 0.2°/₀₀ and 2.5°/₀₀ with a weighted average of 1.3°/₀₀. These results were interpreted by Schwarcz (1973) as representing "juvenile sulphur introduced from a deep source (presumably the mantle), and little fractionated with the respect to primordial, meteoric sulphur".

2.5.2 Sedimentary Type Ores

The Kuperschiefer Cu deposit of Mansfield Germany is a classic and well studied example of a sedimentary hosted sulphide deposit. The hosting tectono-sedimentary environment is a euxinic, intracratonic basin. The $\delta^{34}S$ values for the Kuperschiefer deposit form a skewed distribution but are generally very light ranging from -2°/₀₀ to -44°/₀₀. The large variation supports the opinion that biological activity played an important role in sulphate reduction in a reducing environment (Jensen, 1967; Schwarcz and Burnie, 1972). The black shales present also indicate an anerobic system (Jensen, 1967). Williams (1978) describes the framboidal habit of sulphides and the positive correlations between sulphide sulphur and organic carbon (features produced in modern sediments by bacterial sulphate reduction) as proof of biological activity. Evidence showing sulphide formation during very early diagenesis and sulphide formation at less than 100°C lends independent and supporting evidence to this view. Finally, Williams (1978) cites the fact that the $\delta^{34}S$ of the Kuperschiefer is 30 to 43 per mil lighter than coeval sea-water sulphate. Experimentally, bacterial sulphate reduction is the only fractionation process effective enough to cause the cited spread.

2.5.3 Hydrothermal Ores

In 1968 Sakai suggested that the sulphur iosotope composition of minerals could be controlled by the chemistry of ore forming solutions. This marked a turning point in sulphur isotope geochemistry. Ohmoto has extended these ideas and developed sophisticated models of isotopic behavior in hydrothermal systems (Ohmoto, 1972). Ohmoto, Rye and others (Ohmoto and Rye, 1978 and references therein) subsequently discussed these effects in natural systems. It was the classical view that $\delta^{34}S$ values close to zero represented primordial or magmatic sulphur but Ohmoto has demonstrated that sulphides precipitating from magmatic sulphur can exhibit a wide range of $\delta^{34}S$ values. He has also shown that sulphides which have precipitated from sea water whose $\delta^{34}S$ values equal 20°/₀₀ can have $\delta^{34}S$ values near 0°/₀₀ as in the Kuroko deposit.

Ohmoto (1970) studied $\delta^{34}S$, $\delta^{18}O$, and fluid inclusion data from the stratabound Cu-Pb-Zn Kuroko deposit of northern Japan. The $\delta^{34}S$ values for pyrite, galena, sphalerite and chalcopyrite all show a gradual decrease towards the top of the sequence. The temperatures given by the $\delta^{34}S$ differences between co-existing sulphides are from 200-300°C, while those from fluid inclusion data range from 100 to 265°C (Ohmoto, 1970). The oxygen data give $\delta^{18}O$ values for fluid inclusions slightly less than SMOW (-1.6°/₀₀ to .1°/₀₀) Ohmoto's conclusion is that the $\delta^{34}S$ values of the sulphides, the chemistry of the ores, and the mineralogy present in the deposit are best explained if the original sulphur in solution had the present day $\delta^{34}S$ value of 20°₀₀.

Kajiwara (1973) has simulated Kuroko type mineralization in the laboratory. This was "based on a model chloride-complex solution with the same metallic abundances as present day ocean water" (Kajiwara, 1973, p. 194). His results suggest that the shallow Kuroko hydrothermal system was the result of mineralization due to the reduction of the incorporated sea water. Together, Kajiwara's and Ohmoto's results strongly suggest that most of the sulphur in the Kuroko deposit is of sea water origin.

Since this time Ohmoto has carried out extensive research on the chemical nature of the ore forming fluids and the resulting sulphur isotope signature of various hydrothermal minerals. The major contribution of his studies has been "the recognition of large isotope fractionations among various sulphur species, particularly between oxidized and reduced forms of sulphur" (Ohmoto, 1970, p. 829). Factors that control this fractionation in hydrothermal minerals include 1) temperature, 2) $\delta^{34}S_{\Sigma S}$ and 3) the proportions of oxidized and reduced sulphur in solution (Ohmoto and Rye, 1974). Temperature controls the fractionation between the sulphur species while $\delta^{34}S_{\Sigma S}$ is a function of the sulphur source. T, pH, and fO_2 all play a role in the proportion of oxidized to reduced sulphur so these factors can be used to evaluate $\delta^{34}S$ values.

Ding and Rees (1984) have extended Ohmoto's ideas. In their study of the Taolin Pb-Zn mine of China they have examined the change in the bulk composition of a hydrothermal fluid as various sulphur species precipitated. Sulphur and oxygen isotope studies plus fluid inclusion data have been assembled to help unravel the isotope evolution of the mine. Like Ohmoto, Ding and Rees support the idea that the temperature of equilibrium fractionation and the solubility of the precipitating minerals play a role in the isotope pattern. They point out however that if precipitation of any one sulphur species is appreciable, the bulk isotopic composition of the fluid will change.

For example, in the 80 m level of the Shangtancen district of the Taolin deposit significant sulphide precipitation occurred relatively early in the evolution of the hydrothermal system. This depleted the fluid of light sulphur isotopes so that when the sulphates precipitated later in the deposit's history the total sulphur remaining in solution was enriched in heavy sulphur isotopes. Although oxygen isotope studies (Ding and Schwarcz, 1984) suggest a mixing of magmatic and meteoric water later in the system's history, no sulphur source other than a magmatic one has been found. This led to the conclusion that under certain circumstances it is necessary to take into account the effects of mineral deposition on the isotopic composition of sulphur remaining in solution.

III. GEOLOGY AND MINERALOGY OF THE TAOLIN Pb-Zn ORE DEPOSIT AND SUMMARY OF TAOLIN A

3.1 Geological Setting

The Taolin Pb-Zn ore deposit lies in a faulted zone between the Mofushan granite batholith and metamorphic arenaceous and argillaceous rocks of the Proterozoic Lingjiaxi system (Wang, 1958; referred to in Ding and Rees, 1984). About 10 kilometers north of the mining zone are minor exposures of shale and limestone of Upper Proterozoic and lower Paleozoic age. Tertiary red sandstones and conglomerate strata and Quaternary alluvium are the only other units exposed in the area.

The Mofushan granite batholith, occurring in the southern part of the mining area has an exposed area of 3,000 square kilometers. It intrudes the Lengjiaxi system and is covered by the Tertiary red sandstone. K-Ar dating of biotite in the granite suggests a date of 136 MY for the emplacement of the batholith (Li et al., 1964; referred to in Ding and Rees, 1984). From the centre to the margin the rock type changes gradually from medium grained biotite rich granite through porphyritic granite to migmitite. Extending for 20-30 km along a NEE trend is the 200-300 m wide mineralized faulted zone which contains the Taolin ore bodies (Fig. 3). These ore bodies, composed of mineral veins and brecciated ore masses occur as discontinuous lenses that extend for 7-8 km. They range in size from 500 to greater than 1000 m in length, 200-400 m in depth and several tens of meters thick (Ding and Rees, 1984).

The mineralized veins, ranging from tiny veinlets a few milimeters in thickness to major veins a few meters thick contain minerals whose shape and trend are highly variable.

The mining area itself is divided into 6 districts; Duashan, Guanshan, Shangtancen, Yinkongshan, Doujiachong and Qiupiao with Shangtancen and Yingonshan the major producing districts (Ding and Rees, 1984).

The mineralogy varies with district. At the centre of the mineralized zone (Shangtancen and Yinkongshan districts) sulphide rich mineralization dominates while at the ends of the mineralized zone (Duashan, Guanshan, Doujiachong and Quipiao districts) sulphate rich mineralization is dominant (Ding and Rees, 1984).

This study deals with samples from the Shangtancen district.

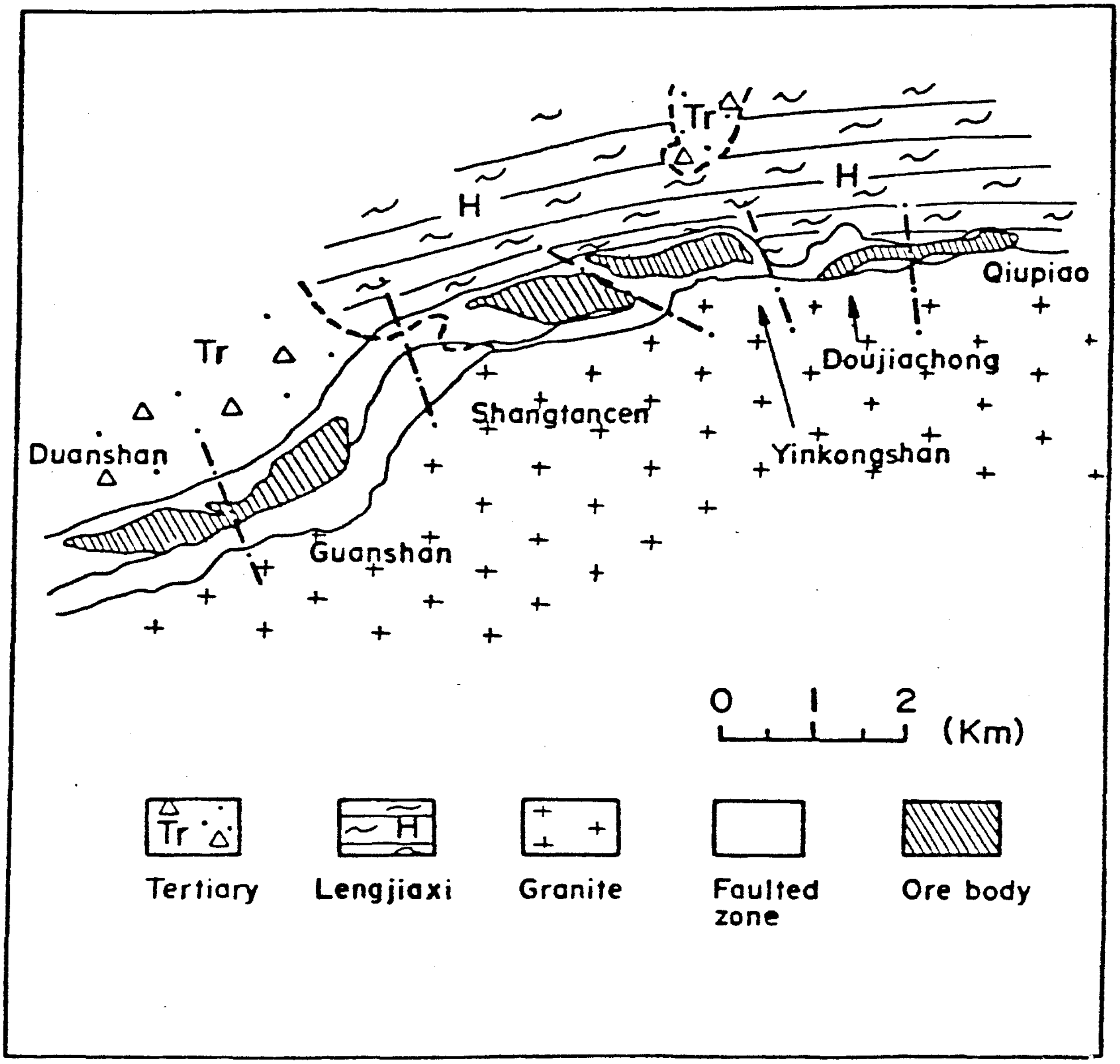


Fig. No. 3 Geological Setting of the Taolin Lead-Zinc Ore Deposit

3.2 Mineralogy

The minerals of major economic interest in the Taolin deposit are coarse grained galena (PbS) and sphalerite ((Zn,Fe)S). Chalcopyrite ($CuFeS_2$) and pyrite (FeS_2) also occur in minor amounts. Quartz, fluorite, barite and trace calcite make up the bulk of the gangue mineralogy. The grain size for the major sulphides is several millimeters for galena and chalcopyrite to cm size for the sphalerite.

The sample locations for Taolin B are shown in Fig. 4.

The most prominent wall rock alterations are silification, chloritization, and sericitization. The ore itself occurs in both zonal and brecciated structures.

Ding Tiping of the Institute of Mineral Deposits in Beijing, China has performed extensive sulphur, oxygen and Pb isotope studies of the 80 m level of the Shangtacen Mine (Ding and Rees, 1984). This work will hence forth be referred to as Taolin A.

3.3 Summary of Taolin A

Sulphur isotope data was obtained for coexisting sulphates and sulphides from Taolin A, the 80 m level of the Shangtancen Lead Zinc mine. The study indicates that at high temperatures sulphide was the dominant species in solution while at low temperatures sulphate dominated. Examination of

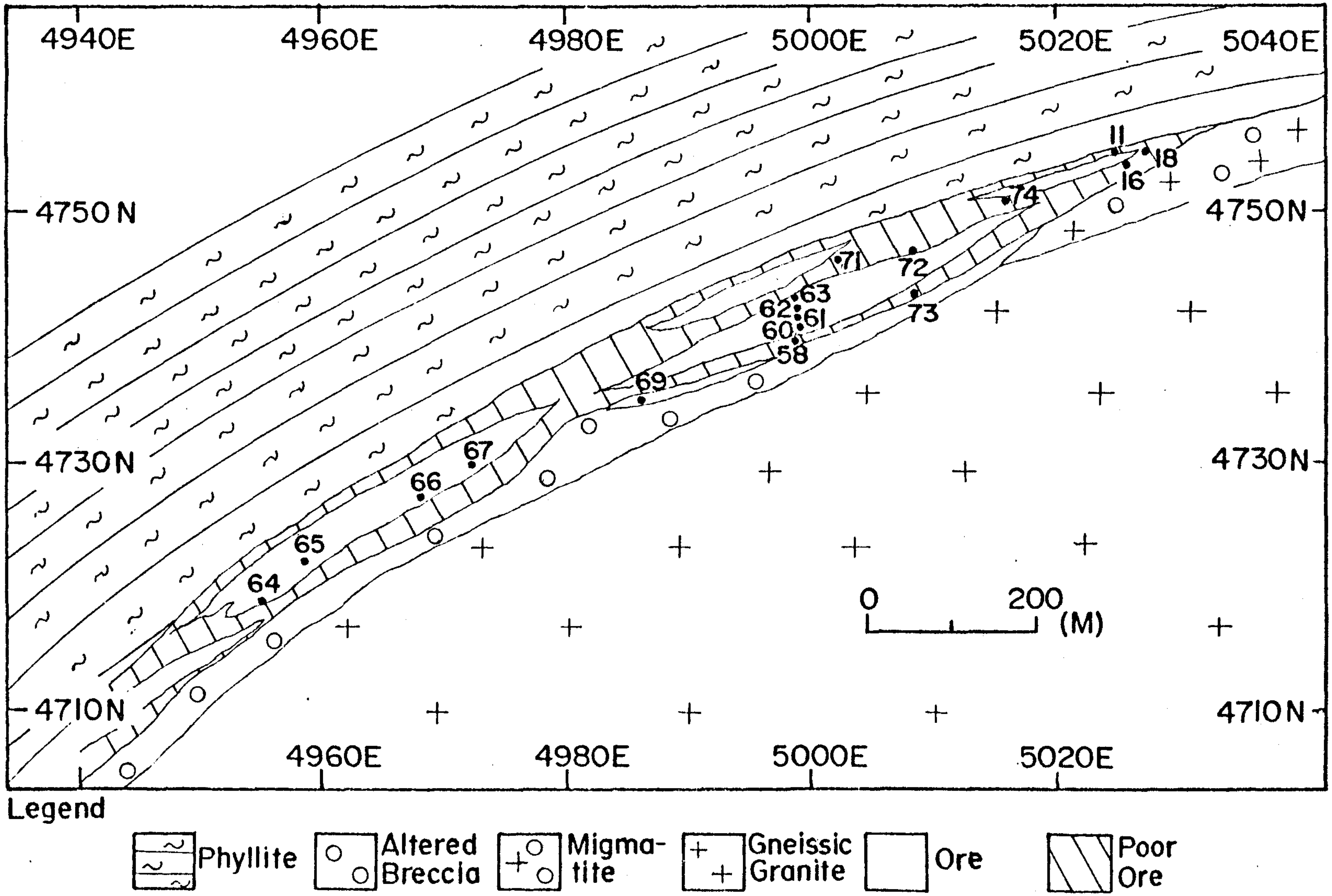


Fig. No. 4 Sample Locations for the 120 m Level in the Shangtancen District of the Taolin Pb-Zn Deposit the mine gives supporting structural evidence for two stages of crystallization. Stage I contains galena, dark brown sphalerite, chalcopyrite, quartz and fluorite. Stage II, which cross cuts Stage I, contains large amounts of barite with minor galena, light sphalerite, and traces of quartz, calcite and chalcedony.

The sulphur isotope data was used to show that the $\delta^{34}S_{\Sigma S}$, or total sulphur in solution, changed from close to 0°/₀₀ at high temperatures to high positive values of greater than 15°/₀₀ at low temperatures.

> "The increase in the $\delta^{34}S$ value of total sulphur was brought about by the removal from the system, by precipitation, of isotopically light sulphides (Ding and Rees, 1984)."

Using the "classical" Pickney and Rafter (1972) method to interpret the results Ding and Rees show that

for Taolin A Stage I $\delta^{34}S_{\Sigma S} = 0°/_{\circ\circ}$

and

for Taolin A Stage II $\delta^{34}S_{\Sigma S} = 15°/_{\circ\circ}$,

as shown in to Fig. 5. Stage I can be interpreted as having a lower crust or upper mantle source since this value resembles the ^{34}S of meteorites. Independent oxygen isotope

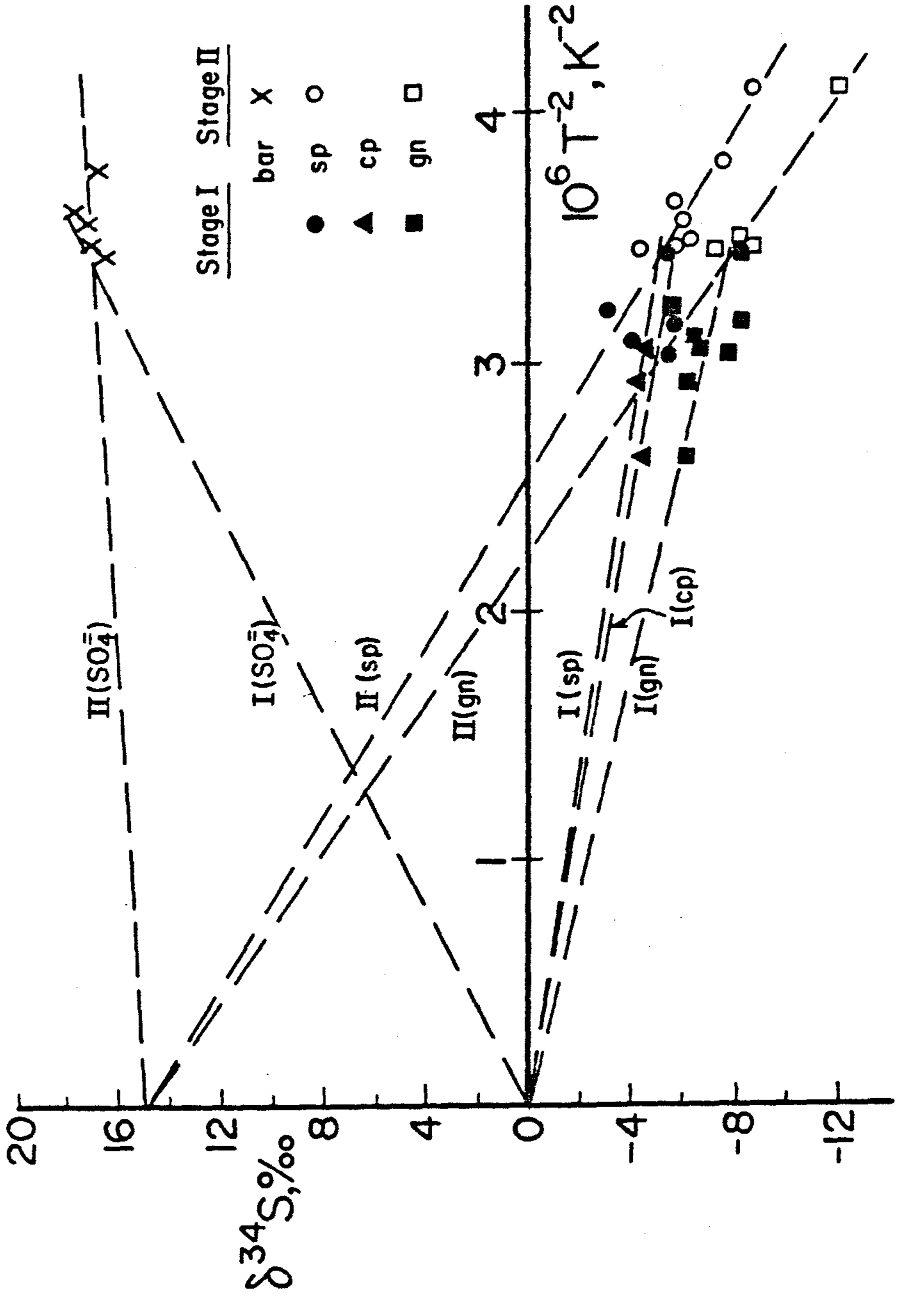


Fig. No. 5 Determination of $\delta^{34}S_{\Sigma S}$ Values for Stages 1 and II of Taolin A According to the Method of Pinckney and Rafter studies of the mine show the hydrothermal fluid was initially of magmatic composition which supports this view (Ding and Schwarcz, 1984). It is very difficult however to invent a sulphur source for Stage II with such a high $\delta^{34}S$. Ding and Rees interpret this as an example of mineral precipitation changing the bulk isotopic composition of a hydrothermal fluid.

The Ding and Rees approach to this problem is based on the assumption that the sulphate/sulphide ratio varies with T in response to changes in fO_2 and relative rates of precipitation of sulfate and sulphide. In Taolin A they suggest predominantly reducing conditions prevailed when sulphide was the main precipitate. However they suggest a change to oxidizing conditions occurred as the temperature dropped resulting in a sulphate rich precipitate. This is shown in Fig. 6 and Fig. 7. The study by Ding and Schwarcz (1984) of the oxygen systematics of the Taolin ore deposit indicate that as the hydrothermal fluid cooled it mixed with meteoric water, the probable source of the oxygen.

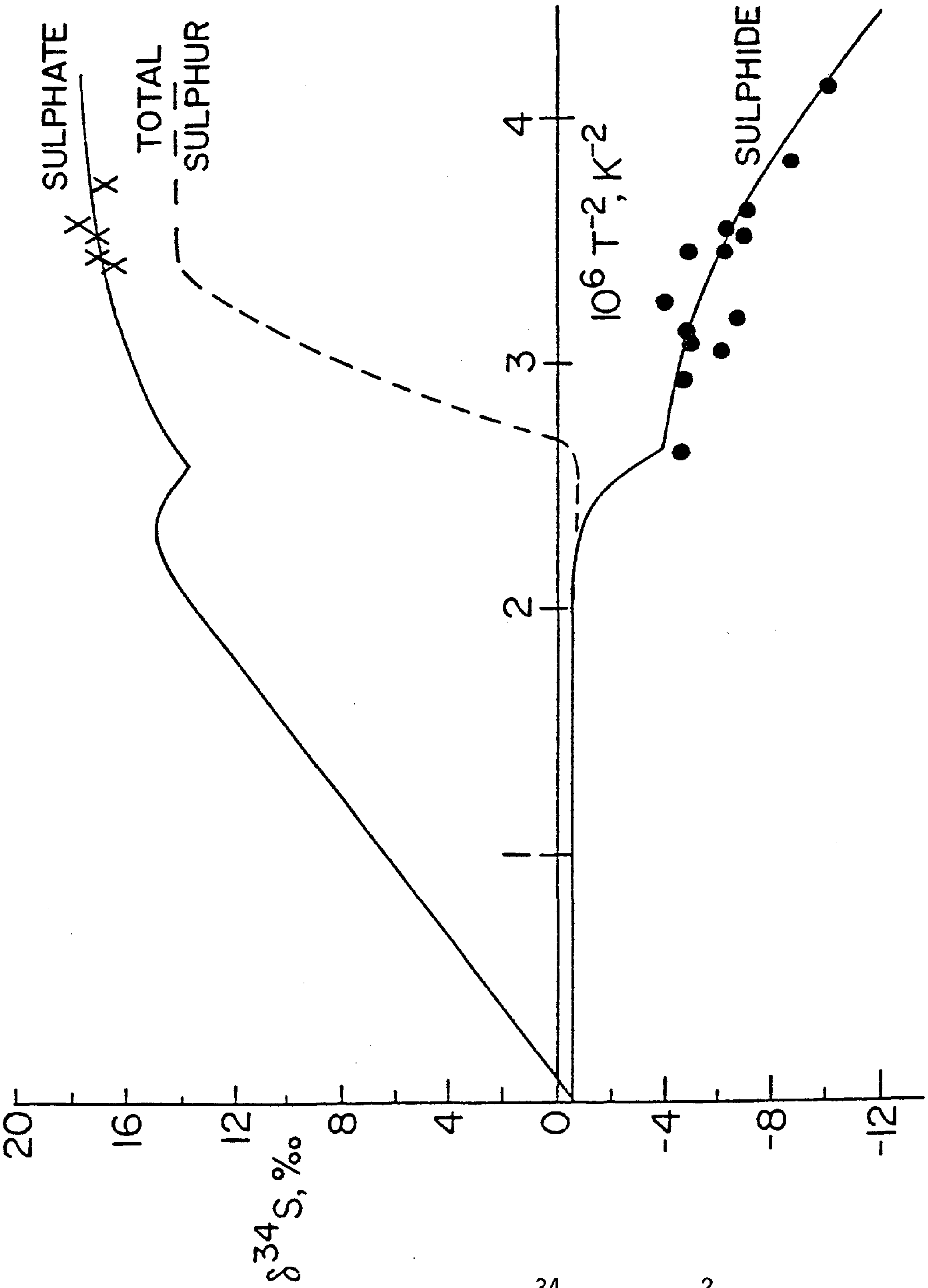


Fig. No. 6 Calculated Variations of $\delta^{34}S$ with $1/T^2$ for Taolin A Using the Ding and Rees (1984) Model Equations (see Appendix for details). The Data Points are for Sulphate (Barite) and "Weighted Average Sulphide" (see text)

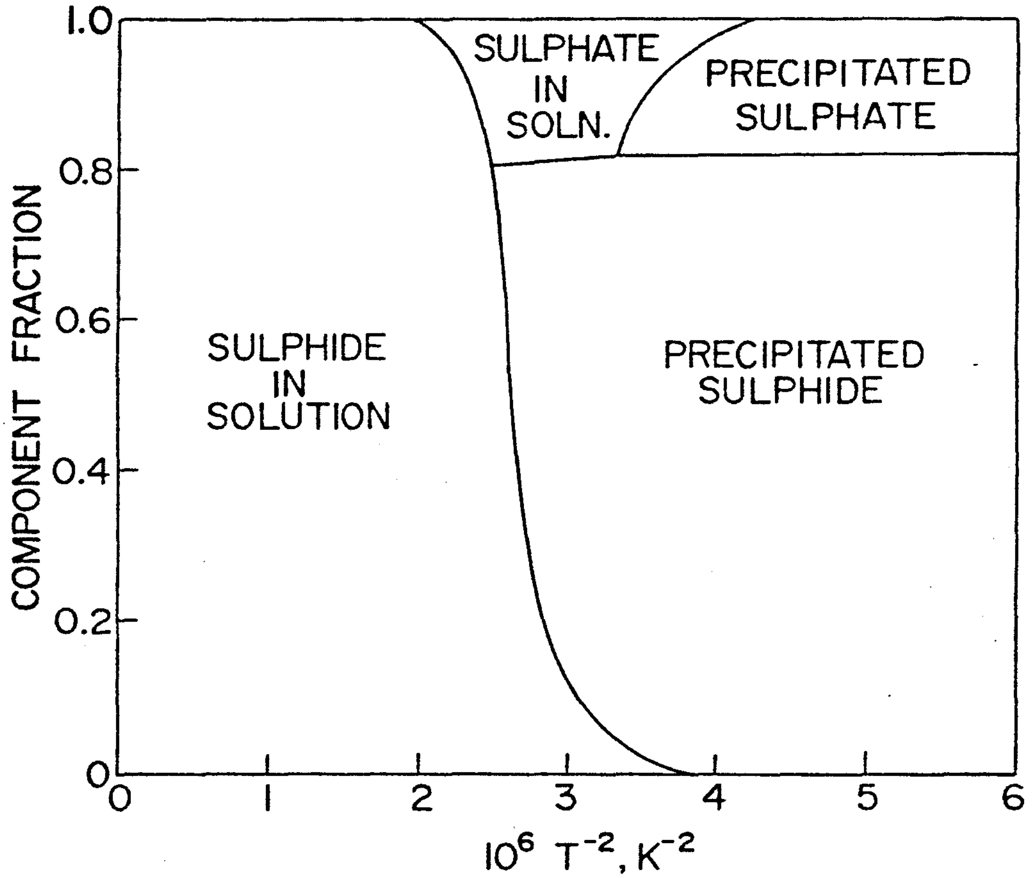


Fig. No. 7 Calculated Variations with $1/T^2$ of Sulphide in Solution, Sulphate in Solution, Precipitated Sulphide and Precipitated Sulphate for Taolin A.

IV. SAMPLES AND ANALYTICAL METHODS

4.1 Samples

All of the samples for this study were collected by Ding from the Shangtacen district. Of those collected most represent sulphide-sulphate or sulphide-sulphide pairs. No sulphur from the granite has been analysed successfully because the sulphur content is below the limit to be extracted using conventional mineral separation and chemical techniques. No primary sulphur bearing minerals have been recognized in the phyllite and schists of the Lengjiaxi system.

All of the minerals separated by Ding were hand-picked under the microscope. Grain pairs which shared a common interface were selected to help maximize the probability that the minerals were in chemical equilibrium when they crystallized. The sulphur in each of the samples was converted to silver sulphide, burned to form SO_2, and then examined isotopically using the mass spectrometer.

4.2 Analytical Methods

There are two methods presently used for the conversion of sulphide and sulphate samples to SO_2. The first method is direct burning of the sample. The second is chemical conversion of the mineral to silver sulphide (Ag_2S) followed by a solid donor, vacuum line burning process. Robinson and Kusakabe (1975) as well as Fritz et al. (1974) have noted that the direct burning method is often difficult. Converting the sulphur phases to silver sulphide avoids problems and removes silicates and other impurities from the minerals as well. Rees (personal communication) and others at McMaster University have found this to be the most satisfactory method. Consequently all samples analysed in this study were chemically converted to silver sulphide prior to production of sulphur dioxide.

Pyrite and chalcopyrite samples were oxidised to sulphate prior to conversion to silver sulphide. Barite samples and sulphate produced by the oxidation of pyrite and chalcopyrite were reduced to silver sulphide using so called "reducing mixture" while galena and sphalerite samples were converted to silver sulphide using hydrochloric acid. Details of these various methods are given below.

4.2.1 Conversion of Chalcopyrite and Pyrite to Form Barium Sulphate

50 mg of the sample is placed into a 600 ml pyrex beaker followed by 15 ml of concentrated nitric acid (HNO_3) and 2-3 ml of bromine. The mixture is left to stand covered for 12 hours allowing the sulphide to oxidize to sulphate. The solution is then heated on a steam bath to remove any remaining bromine. After evaporation to dryness 10 ml of concentrated HCl is added and evaporation to dryness is repeated.

The next step is to add 25 ml of H_2O and 2 ml of concentrated HCl and to let the solution stand for 5 minutes before bringing it to a boil. 20 ml of ammonium hydroxide is then added to the beaker and boiling is continued for an additional 30 seconds. This procedure precipitates iron as iron hydroxide. If the iron were left it would interfere with the production of a pure sulphate phase from the mineral sample. The solution is passed through a Whatman 541 filter paper to remove the iron hydroxide and the filter is washed with 400 ml of hot distilled water which ensures that sulphate is not trapped as well.

3 drops of methyl orange are added to the filtered solution followed by enough HCl to turn the solution slightly acidic. The solution is then brought to a boil in preparation for barium sulphate precipitation which is brought about by the addition of 10 ml of boiling 10% barium chloride and

the boiling of the resultant liquid until the precipitate floculates and settles to the bottom. The filtering procedure is repeated to trap the barium sulphate. Filtration is performed using Whatman #40 paper following which the paper is ignited in a porcelain crucible leaving only the barium sulphate precipitate which is now ready for reduction to silver sulphide.

4.2.2 Conversion of Barium Sulphate, Sphalerite and Galena to Silver Sulphide

Conversion of barium sulphate to silver sulphide is carried out with "Thode's mixture" which consists of 500 ml HI, 816 ml of concentrated HCl and 245 ml of 50% H_3PO_2 and which reduces sulphate to hydrogen sulphide. In the case of sphalerite and galena treatment with 8M HCl suffices to produce hydrogen sulphide.

The apparatus used is shown in Fig. 8. A 50 ml centrifuge tube, clearly marked for each sample is filled to the three quarters mark with cadmium acetate ($Cd(CH_3COO)_2$) and attached at point A. The pure barite or sulphide sample is added to the reaction vessel together with 50 ml of Thode's mixture or HCl, as appropriate. The reaction vessel is attached at point B and the pathway between the sample and the acetate test tube is flushed with a stream of nitrogen in order to carry hydrogen sulphide through to the cadium acetate. The reaction vessel is gently heated with a bunsen

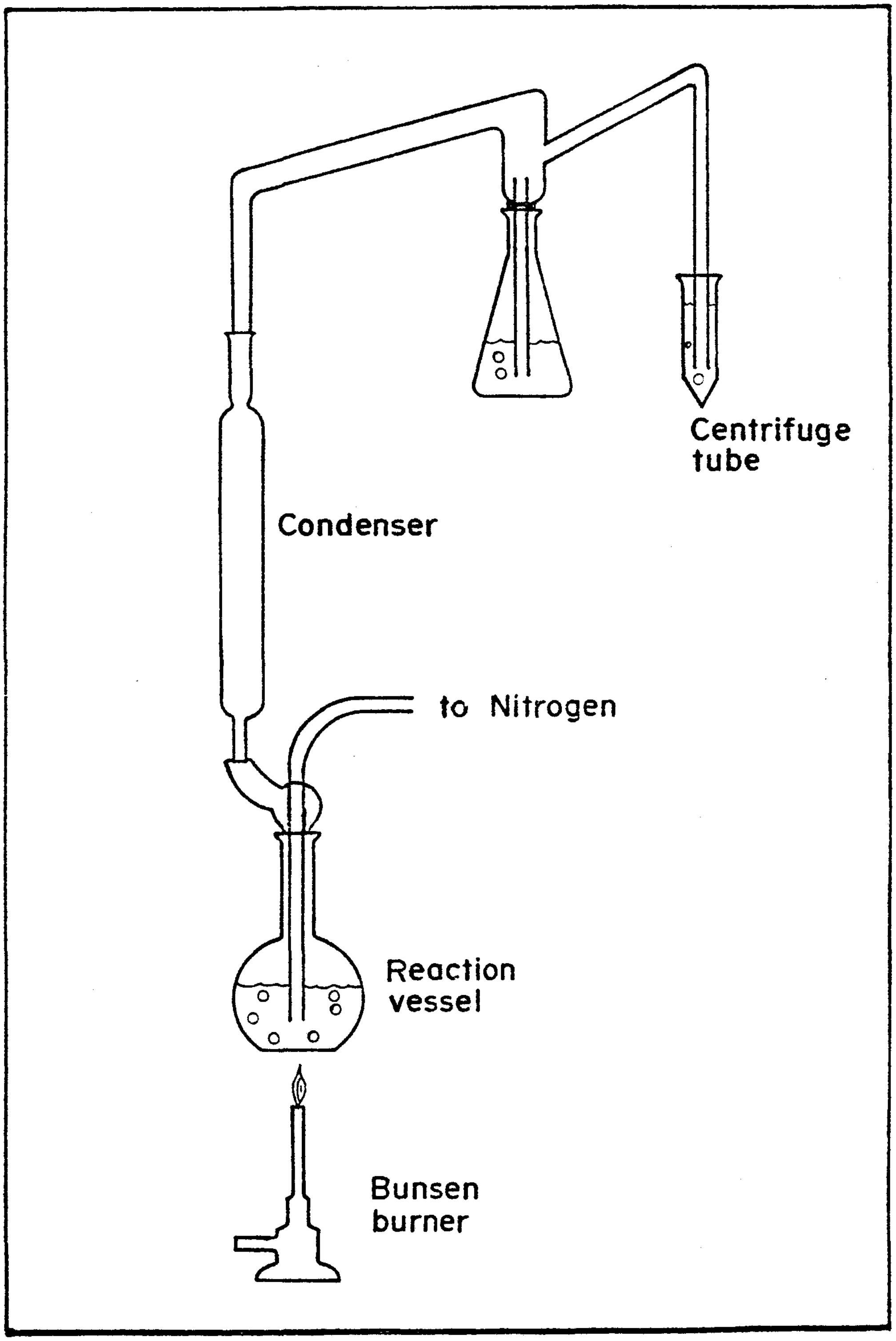


Fig. No. 8 Apparatus for Chemical Conversion of Sulphates and Sulphides to Silver Sulphide flame and the reaction solution brought to a boil in order to accelerate the production of hydrogen sulphide.

After 1 hour the reaction is complete and the centrifuge tube containing the cadmium sulphide produced by the reaction of hydrogen sulphide with cadmium acetate is removed from the line and its contents transferred to a 500 ml beaker. Silver nitrate ($AgNO_3$) is added to form silver sulphide (Ag_2S) and the mixture is boiled to aid in forming a good precipitate.

A water aspirator is used to achieve rapid filtration of the silver sulphide into a 15 ml type M Gooch crucible. The filtrate is washed with 15 ml ammonium hydroxide ($NH_4(OH)$) followed by 60 ml distilled water. The pyrex filter with its silver sulphide contents is dried overnight before the sample is placed into a container for storage prior to the production of sulphur dioxide.

4.3 Production of Sulphur Dioxide

Silver sulphide is most conveniently converted to sulphur dioxide using high temperature combustion under vacuum with a solid oxygen donor. Two different solid oxygen donors have been reported in the literature. Grinenko (1962) and Kaplan et al. (1970) reported the use of CuO for sulphide oxidation. Monster (1973) and Fritz et al. (1974) performed oxidation with both CuO and Cu_2O and recommended the use of

CuO because of better yields at lower temperatures and because CuO is more easily stored since it is stable in atmospheric oxygen. CuO is the solid oxygen donor used at McMaster University.

The apparatus used is shown in Fig. 9. 15 mg of silver sulphide and 23 mg of cupric oxide (CuO) are placed on a quartz boat and mixed. The procedure begins by evacuating the vacuum line, by closing valves 1, 2, 3, 5 and opening 4 and 6. The sample followed by a magnetic pusher, is placed into a quartz tube with a sealed end. The tube is secured to the vacuum line as shown and valve #1 is opened very slowly (so that the sample is not evacuated with the air) and the quartz tube evacuated. Pumping is continued until a pressure of 50 milliTorr is achieve after which valve #1 is closed. Then valves #2 and #3 are opened and #4 is closed.

The first two U traps are cooled to liquid nitrogen temperature in order to freeze CO_2, H_2O and SO_2 produced during the reaction and the sample boat is pushed into the oven using the magnetic pusher. Reaction proceeds at 1225°C for 10 minutes. This temperature is high enough to obtain 99 to 100% of the theoretical yield of SO_2 from silver sulphide in 10 minutes yet low enough to enhance the life of the furnace windings. The gases produced during the reaction are collected in the first U trap. The second trap is employed as a precautionary measure in case any sample gets past the first.

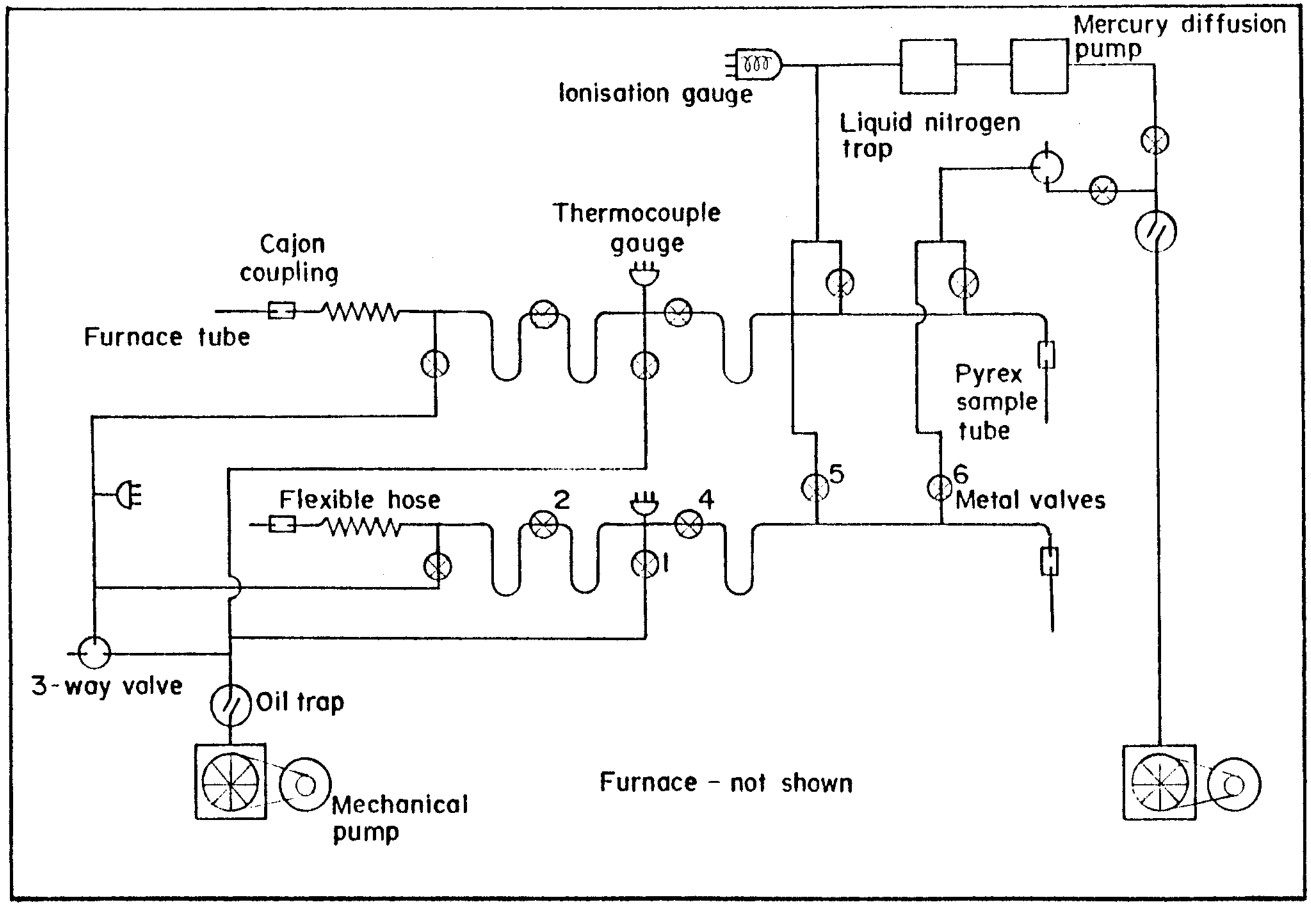


Fig. No. 9 Vacuum Line System for Burning Silver Sulphide to Form SO_2

In the next step the liquid nitrogen from the first U trap is transferred to the third allowing SO_2, CO_2, and H_2O to be vacuum transferred from the first U trap to the second while any nitrogen and oxygen are pumped away. Valve #2 is then closed separating the oven section from the rest of the system. H_2O is retained in the second U trap by replacing the liquid nitrogen with a dry ice acetone slush at -80°C. The CO_2 and SO_2, which are gaseous phases at this temperature, are vacuum transfered to the third U trap. Now valve #3 is opened and the third U trap is warmed to -131°C using a freezing n-pentane slush. The vacuum gauge must be observed carefully at this point. The CO_2 will be quickly released and evacuated from the system as evidenced by a jump in the line pressure (usually to > 200 mTorr). The pressure then falls to roughly 50 mTorr and begins a second rise, indicating the release of SO_2 from the trap. At this point valves #4 and #6 must be closed immediately so that the SO_2 sample stays in the vacuum line system and can be frozen down in a sample collecting tube which is cooled to liquid nitrogen temperature.

When the sample is frozen down in the collecting tube the tube is sealed at a point just below where it is attached to the vacuum line by fusing with a gas-oxygen flame. The sealed sample collection tube can then be labelled and stored for later mass spectrometry.

It is customary at McMaster to burn 2 known standard samples for every 8 unknowns. By comparing the standards to known results one can periodically check the accuracy of the burning process and of the mass spectrometer performance.

4.4 Mass Spectrometry

The mass spectrometer used is a 6" radius magnetic sector instrument with two faraday cups for simultaneous collection (Thode and Rees, 1971). The sample tube containing the sample of interest is attached to the inlet line of the mass spectrometer and the sample is vacuum transferred to the unknown sample reservoir. The sample of interest and a standard reference gas are then admitted alternately to the spectrometer. This procedure eliminates many instrumental biases by determining isotopic differences under constant instrumental conditions.

It is necessary to consider corrections for peak tailing and inlet leak offsets, and for background peaks in the mass spectrum (Rees, 1978 and authors therein). As well, with SO_2, one must take into account the interference in the SO^+ or SO^{2+} mass spectrum by ions containing O^{17} and O^{18}. Rees, and many others have developed corrections that may be applied to raw mass spectrometric data which take into account oxygen isotope interference. Rees (1978) has pointed out that sulphur dioxide gives rise to a mass spectrometer memory effect. It is caused by the slow flushing of unknown samples and the standard reference gas from the mass spectrometer inlet line. The result is that isotopic differences between samples are underestimated (Rees, 1978).

The possible combinations of isotopes to give SO_2 are listed below.

	Mass	
SO^{2+}	64	$^{32}S^{16}O^{16}O^+$
	65	$^{33}S^{16}O^{16}O^+$, $^{32}S^{16}O^{17}O^+$
	66	$^{34}S^{16}O^{16}O^+$, $^{33}S^{16}O^{17}O^+$, $^{32}S^{16}O^{18}O^+$, $^{32}S^{17}O^{17}O^+$

The mass spectrometer compares the ion currents at mass 66 with the sum of the ion currents at masses 64 and 65. This gives

$$R(66) = \frac{V(66)}{V(65+64)} = \frac{I(66)r1}{(I64+I65)r2}$$

where r1 and r2 are values that the grid leak resistors. The raw data is then in the form of $\delta(66)$, °/oo and is given by

$$\delta(66),\ {}^{\circ}/_{\circ\circ} = \left[\frac{R(66)_{\text{unknown}}}{R(66)_{\text{standard}}} - 1\right] \times 1000$$

where the standard is the reference SO_2 sample used for all analyses.

The $\delta^{34}S$ value relative to Canyon Diablo Troilite must be calculated from the $\delta(66)$ values. The procedure to do this is given in detail in Rees (1978); however a brief description is warranted here. The calibration involves the equation

$$\delta^{34}S = A + B\ \delta(66)$$

where A and B are constants that take into account:

1. Oxygen isotope interference.
2. The ^{33}S contribution at the ^{32}S faraday cup.
3. The isotope effects in sample admission, ionisation, transmission, and detection.
4. Memory effects that are produced in switching the sample to unknown in the machine with only a 1 minute delay rather than the 5 minutes that is needed to flush the line and eliminate this effect.

To determine A and B repeated analyses are performed on two silver sulphide samples whose $\delta^{34}S$ values have been accurately and precisely determined using SF_6 analysis (Rees, 1978). These measurements are taken regularly during the course of mass spectrometer operation, at McMaster about every 4 runs. The two reference samples are SL-277-1 and SL-277-6 with $\delta^{34}S$ values of +2.5°/₀₀ and +23.01°/₀₀ respectively.

During the period when the Taolin samples were analysed these reference materials gave δ(66) values of

0.23°/₀₀, 0.10°/₀₀, and 0.06°/₀₀

and

17.91°/₀₀, 17.78°/₀₀, 18.02°/₀₀, and 18.01°/₀₀

respectively, with mean values of 0.13°/₀₀ and 17.93°/₀₀. Using the equation above, the constants A and B are determined as follows:

$$23.01 = A + B\ (17.93)$$

and

$$2.52 = A + B\ (0.13)$$

so that

$$A = 2.37 \text{ and } B = 1.1511.$$

V. RESULTS

The isotopic results are listed in Table 1 as $\delta^{34}S$ values relative to Canyon Diablo troilite, where

$$\delta^{34}S, °/_{oo} = \frac{(^{34}S/^{32}S)_{sample} - (^{34}S/^{32}S)_{CDT}}{(^{34}S/^{32}S)_{CDT}} \times 1000.$$

$\delta^{34}S$ determinations have uncertainties of ±0.10% associated with them.

5.1 General

The data show the following:

1. Barite has a wide range of positive $\delta^{34}S$ values, from +4.3°/₀₀ to +17.6°/₀₀.
2. All sulphides have negative $\delta^{34}S$ values, from -3.2°/₀₀ to -11.9°/₀₀.

For individual minerals the ranges are:

galena: $-6.7°/_{oo}$ to $-11.9°/_{oo}$

spahlerite: $-3.2°/_{oo}$ to $-9.0°/_{oo}$

For chalcopyrite only one value, $-3.5°/_{oo}$, was determined.

5.2 Sulphur Isotope Thermometry

Although there are several calibration sets available for the calculation of temperatures from $\delta^{34}S$ data this study has adopted the group of equations given by Kajiwara and Krouse (1971). The relevant equations are

$$\Delta^{34}S_{sp-gn} = 0.8 \times 10^6 T^{-2}$$

and

$$\Delta^{34}S_{sp-cp} = 0.15 \times 10^6 T^{-2}.$$

For sulphide-barite pairs the equations that have been used for this study are the experimental results of Sakai and Dickson (1978) although the only data available is at 300°C. Assuming a linear variation with T^{-2} and using their datum of $\Delta^{34}S_{ba-sp}$ at 300°C the equation becomes

$$\Delta^{34}S_{ba-sp} = 6.44 \times 10^6 T^{-2}$$

Combining this equation with the equation for $\Delta^{34}S_{sp-gn}$ the following relation is generated

$$\Delta^{34}S_{ba-gn} = 7.24 \times 10^{6}T^{-2}$$

The temperatures calculated using these equations are shown in Table 1. The following observations can be made, assuming isotopic equilibrium between the pairs.

1. The spahlerite-galena pairs yield a wide temperature range of 90°C. The temperatures for these pairs fall between 293°C and 203°C. This spread is consistent with the minerals being precipitated over a long period. Samples 060, 069 and 073 give unacceptably high temperatures and are assumed to represent pairs which are not in isotopic equilibrium as in the case for the pairs 062, 063 and 067 which give negative temperature values. Although pair 074 was not used for fitting purposes and is not shown in the graph, its low temperature value of 128°C is very close to the predicted sulphide value at that temperature.
2. Barite appears to have precipitated over a wide range of temperatures ranging from 235°C to 526°C.
3. Chalcopyrite appears to have precipitated at high temperatures. The value calculated for Taolin B is 435°C.

Table 1. Sulphur isotope data for the 120 m level in the Shangtancen district of the Taolin Pb-Zn ore deposit.

	$\delta^{34}S$, °/oo					
Sample	sp	gn	cp	ba	$10^6(T°k)^{-2}$	T°C
058	-9.0	-11.8			3.6	257
060	-10.0	-10.4			0.4	1394
061	-5.4	-9.0			4.4	203
062	-8.3	-7.8			-	-
063		-4.4	-5.8		-	-
064	-5.4	-7.9			3.1	293
065	-4.0	-6.7			3.4	267
066	-3.2		-3.5		2.0	434
067	-7.0	-5.9			-	-
069	-3.3	-3.4			0.1	3455
071	-7.9			+12.3	3.1	291
072		-10.8		+6.4	2.4	375
073	-6.8	-7.7			1.1	665
074	-4.2	-9.2			6.2	128
076	-5.6	-8.6			3.8	237
077	-5.8			+4.3	1.6	526
078	-7.2			+17.6	3.9	236

VI. DISCUSSION

6.1 The Source of Sulphur in Taolin B

The "classical" method of Pinckney and Rafter (1972) was used to determine the $\delta^{34}S_{\Sigma S}$ for the sulphur deposition in Taolin B. This approach assumes implicitly that $\delta^{34}S_{\Sigma S}$ is constant over the range of temperatures encompassing the samples considered. This in turn implies that the quantities of sulphate and sulphide precipitated were negligibly small compared to the total quantity of sulphur in solution. Also, the partitioning between sulphate and sulphide in solution had to have remained constant.

Unlike Taolin A there is no isotopic evidence for 2 stages of mineralization and at this point there is no structural geological evidence either. For this reason all data points were used in the determination of the $\delta^{34}S_{\Sigma S}$ of the hydrothermal fluid. According to this method $\delta^{34}S_i$, the isotopic composition of mineral i, can be written as

$$\begin{aligned}\delta^{34}S_i &= \delta^{34}S_{\Sigma S} + \Delta^{34}S_{i-\Sigma S}\\ &= \delta^{34}S_{\Sigma S} + A_{i-\Sigma S}\,10^6 T^{-2}\end{aligned}$$

(Ding and Rees, 1984) where $A_{i-\Sigma S}$ is the coefficient representing the relationship between $\Delta^{34}S_{i-\Sigma S}$ and T and where $\delta^{34}S_{i-\Sigma S}$ is the relative isotope enrichment factor between mineral i and total sulphur.

The fit of the curve was estimated using a "best fit by eye" approach. The results are indicated in Fig. 10. Using this method $\delta^{34}S_{\Sigma S}$ for Taolin B is -6.7°/₀₀.

The initial sulphur isotope composition of the ore forming fluid of Taolin B determined by the Pinckney and Rafter approach is very different from the $\delta^{34}S_{\Sigma S}$ of either Stage I or Stage II of Taolin A. In Stage II of Taolin A a sulphur source with an initial isotope value of +15.0°/₀₀ had to be invoked to explain the observed value. Now in Taolin B a sulphur source with an initial $\delta^{34}S_{\Sigma S}$ of -6.7°/₀₀ must be sought. Because of the anomalously large spread in the $\delta^{34}S_{\Sigma S}$ values of Taolin A and Taolin B which are separated by only 40 m of Pb-Zn ore it appears then, that the "classical" Pinckney and Rafter straight line approach to finding the initial $\delta^{34}S_{\Sigma S}$ of an ore forming fluid is not an effective approach to explain the observed isotope trends of Taolin.

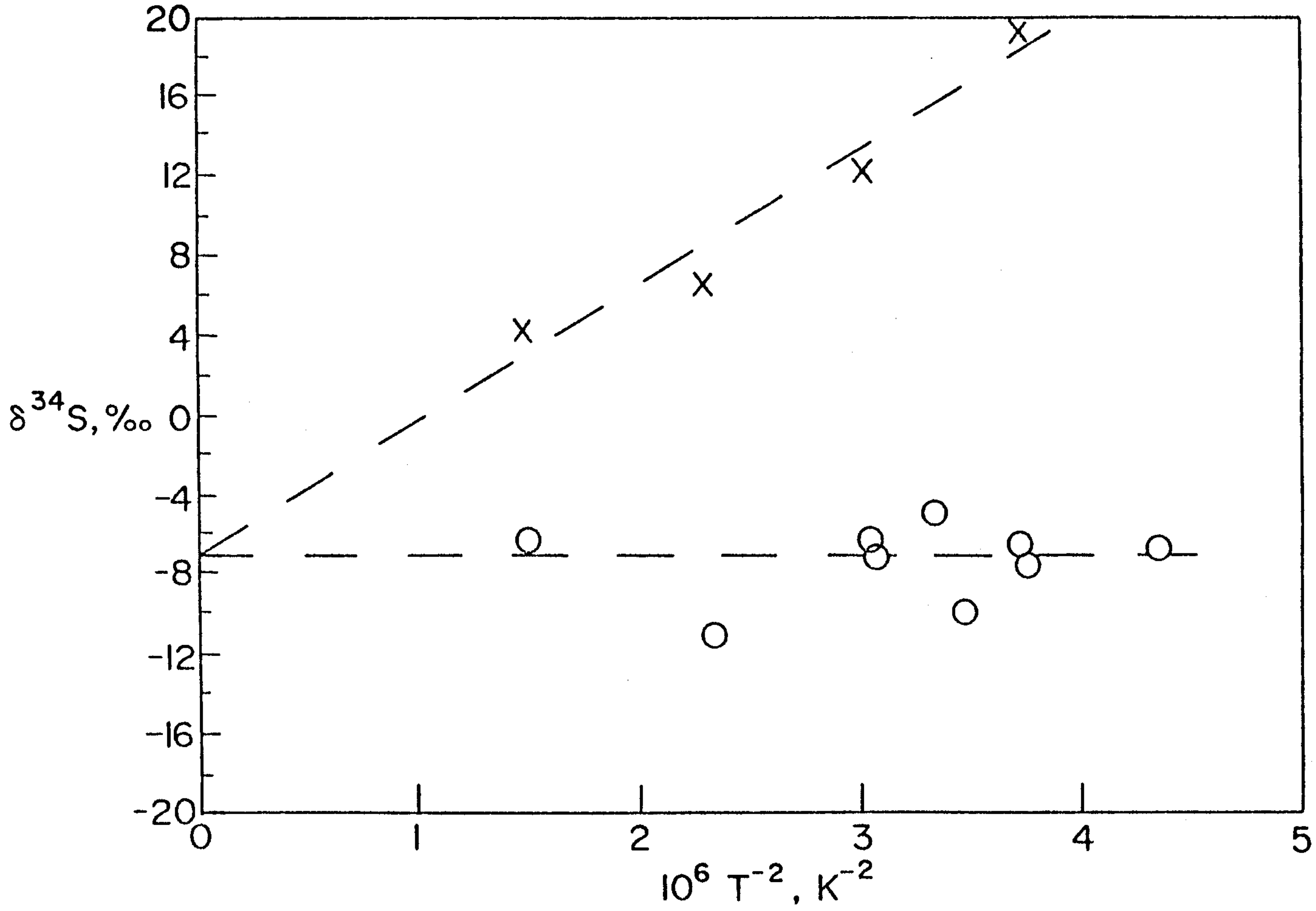


Fig. No. 10 Determination of $\delta^{34}S_{\Sigma S}$ values for Taolin B According to the Method of Pinckney and Rafter (1972)

The isotopic systematics of Taolin have been modelled using the Ding and Rees model equations which assume that the $\delta^{34}S$ of the total sulphur value changed continuously from the beginning of mineral precipitation until the end of mineral precipitation under the influence of the precipitation of isotopically light sulphides and isotopically heavy sulphates.

6.2 Ding and Rees Model for Taolin B

6.2.1 Qualitative

1. The precipitation of sulphur minerals was a batch process. That is, the precipitation took place from sulphur in solution which was not replenished by recharge or continuous input.
2. At temperatures above 530°C both sulphate and sulphide were precipitated because their concentrations in solution were limited by their solubility. The logarithm of the solubility of the sulphide and of the sulphate were assumed to vary linearly with temperature at all temperatures so that

$$\ln [\text{sulphide}] = \ln N + nT$$

and

$$\ln [\text{sulphate}] = \ln M + mT$$

where N, n, M, and m are constants.

3. As the temperature of the fluid decreased the partitioning between sulphate and sulphide in solution was maintained as a preponderance of sulphide. The logarithm of the ratio of dissolved sulphate to dissolved sulphide was assumed to vary linearly with temperature so that

$$\ln ([SO_4^{=}]/[H_2S]) = \ln L + lT$$

where L and l are constants.

4. The isotopic fractionation between sulphate and sulphide in solution decreased as $1/T^2$ with decreasing temperature assuming that isotopic equilibrium was maintained at all temperatures.
5. The precipitation of sulphate and sulphide involved no isotopic fractionation so that at any temperature the isotopic compositions of sulphate and sulphide in solution were the same as those of the sulphate and sulphide precipitated.
6. At very high temperatures, when no precipitation was taking place, $\delta^{34}S_{\Sigma S}$ remained constant at its initial value. An intermediate temperature range where only sulphide precipitation takes place was not observed in Taolin B. However in the computer modelling of the 120 m level of the mine the intermediate temperature range was squeezed to a width of 0.1°C so that in Taolin

B sulphate and sulphide precipitation would begin instanteously. At lower temperatures in Taolin B a decrease of the $\delta^{34}S_{\Sigma S}$ was observed.

The equations which govern the variations with temperature of the isotopic composition of total sulphur in solution, the isotope composition of precipitating sulphate and sulphide in solution, the concentrations of sulphide and sulphate in solution and the quantities of sulphate and sulphide precipitated are developed in the appendix.

6.2.2 Descriptive

Refer to Fig. 11 and 12.

According to the Ding and Rees model equations, at high temperatures the sulphur in solution was predominantly sulphide. This meant the $\delta^{34}S$ value of sulphide in solution was essentially the same as that of total sulphur, with a $\delta^{34}S$ value ~0.4°/₀₀. Sulphate in solution was only a minor component in the ore forming fluid at high temperatures. Its $\delta^{34}S$ value was displaced from that of total sulphur (and $\delta^{34}S$ of sulphide) by an amount proportional to $1/T^2$ and it increased linearly with $1/T^2$. Partitioning between sulphate and sulphide began at a very high temperature and the $\delta^{34}S$ of sulphide became steadily depressed with respect to the constant total sulphur value while the $\delta^{34}S$ of

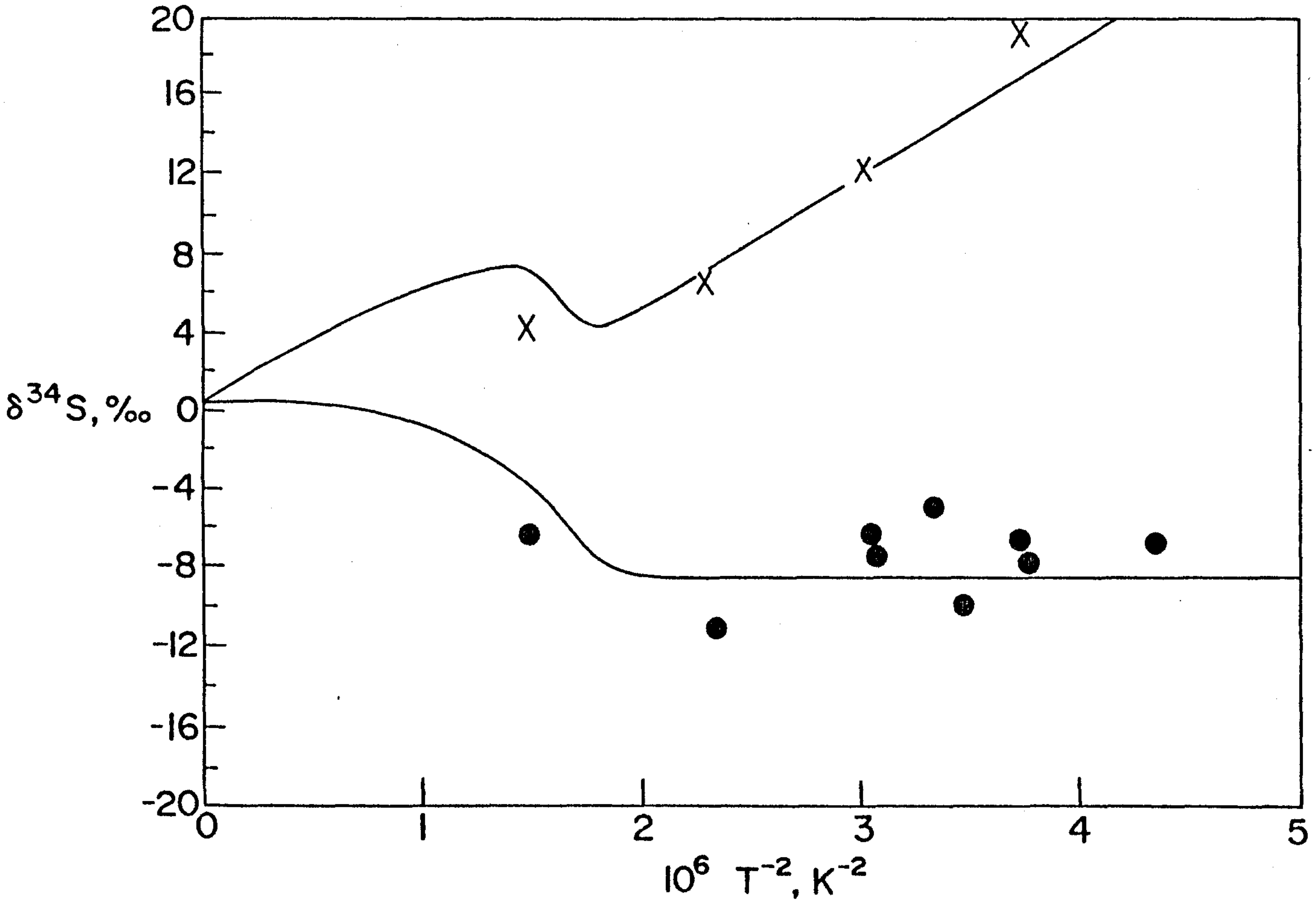


Fig. No. 11 Caluclated Variations of $\delta^{34}S$ with $1/T^2$ for Taolin B Using the Ding and Rees (1984) Model Equations (see Appendix)

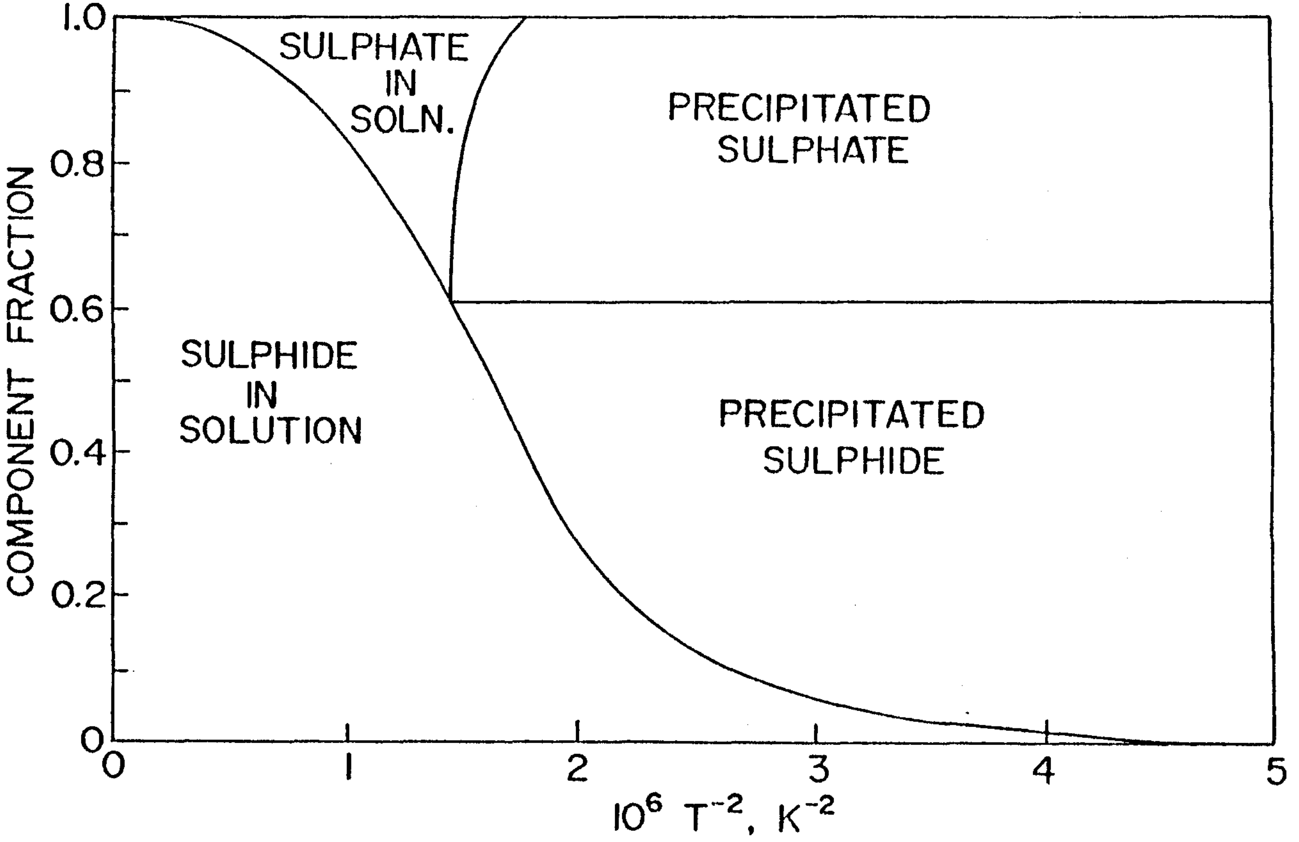


Fig. No. 12 Calculated Variations with $1/T^2$ of Sulphide in Solution, Sulphate in Solution, Precipitated Sulphide and Precipitated Sulfate for Taolin B sulphate increased. The value $\delta^{34}S_{\Sigma S}$ remained constant because there was no precipitation taking place.

As the temperature dropped to roughly 600°C the conditions in the ore forming fluid became more oxidising and appreciable amounts of sulphate in solution were formed. The increase in the $\delta^{34}S$ value of the sulphate in solution was arrested because as the amount of sulphate increased its isotopic value began to approach that of the total sulphur in solution. At the same time the $\delta^{34}S$ value of the sulphide in solution continued to fall. Eventually the dominating species in solution shifted to sulphate which caused $\delta^{34}S$ sulphate to drop sharply towards that of the total sulphur while pushing the $\delta^{34}S$ of the sulphide steadily below that of total sulphur. Since there was still an absence of precipitation, the $\delta^{34}S_{\Sigma S}$ remained at its initial value of +0.4°/₀₀.

When the temperature dropped to 530°C (X = 1.6) the concentration of both sulphide and sulphate in solution exceeded their solubilities and precipitation of sulphide and sulphate began. The precipitation of sulphate caused the removal from the fluid of significant amounts of isotopically heavy sulphur, and lead to a sharp decrease in the $\delta^{34}S$ value of the total sulphur remaining in solution.

This drop in $\delta^{34}S_{\Sigma S}$ leveled off at about 435°C (X = 2). At temperatures lower than this, the $\delta^{34}S$ of sulphate began to climb again by an amount proportional to

$1/T^2$ since it was no longer an appreciable species in solution. The $\delta^{34}S$ of sulphide dominated the solution so that the total sulphur of the hydrothermal fluid remained constant and equivalent to $\delta^{34}S$ sulphide which was also precipitating. Because the solubility of sulphate was low it was continuously being precipitated, therefore its $\delta^{34}S$ had little effect on the $\delta^{34}S$ of the total fluid at temperatures below 435°C.

The values for the Ding and Rees parameters that best fit the experimentally determined curve (using the best fit by eye approach) are:

BX = 2
BY = 4
LN = 10
LM = 60
DCI = 0.25

These parameters are clearly defined in the appendix.

6.3 Ding and Rees Model for Taolin A

Refer to Fig. 6.

For Taolin A the Ding and Rees model predicted different sulphate and sulphide behavior. At high temperatures sulphide was the dominant sulphur species in solution so that the $\delta^{34}S$ of the total fluid was identical to that of the $\delta^{34}S$ of sulphide of -0.5°/₀₀. Sulphate was a minor component at high temperatures. Its $\delta^{34}S$ increased linearly with $1/T^2$.

With a drop in temperature to 430°C (X = 2) changes were observed in the ore forming fluid. The hydrothermal fluid became more oxidizing and sulphate became an appreciable component of the solution arresting the increase in the $\delta^{34}S$ value of the sulphate, and actually driving it down towards the $\delta^{34}S$ of the total fluid. Because of the shift in $\delta^{34}S$ of sulphate the $\delta^{34}S$ value of the sulphide began to drop below that of the total sulphur remaining in solution, in the absence of any precipitation, at its initial value of -0.5°/oo.

When the temperature dropped below 344°C (X = 2.63) the precipitation of sulphide began because its concentration exceeded its solubility. Because the proportion of sulphide and sulphate in solution shifted from a preponderance of sulphide to a preponderance of sulphate the sulphides which precipitated at 344°C and lower temperatures had $\delta^{34}S$ values appreciably lower than the $\delta^{34}S$ of the total sulphur in solution. This removal from the fluid of light sulphur in the form of sulphide precipitate caused a marked increase in $\delta^{34}S$ of the total fluid as heavy sulphur tended to remain in solution as sulphate. This led to an increase in $\delta^{34}S$ of sulphate in solution, though the displacement between the increased $\delta^{34}S$ of total sulphur and sulphate continued to decrease as sulphate came to be the dominant sulphur species in solution.

When the temperature reached 265°C ($X = 3.45$) sulphate began to precipitate because it had exceeded its solubility in solution. This removal from solution of isotopically heavy sulphur arrested the continuing increase in the $\delta^{34}S$ of total sulphur.

Since the solution had shifted from a sulphide dominated fluid at high temperatures to a sulphate dominated fluid at 265°C and less, the $\delta^{34}S$ value of the sulphate increased only slightly while the $\delta^{34}S$ value of sulphide decreased markedly.

6.4 Comparison of the Ding and Rees Models of Taolin A and Taolin B

At high temperatures, the $\delta^{34}S_{\Sigma S}$ of both ore forming fluids were assumed to be equal to the $\delta^{34}S$ of sulphide in solution because this is thought to be the dominant sulphur species in solution. The total sulphur value for Taolin A was estimated to be -0.5°/∘∘ ± 1.0°/∘∘ while for Taolin B it was estimated to be +0.4°/∘∘ ± 1.0°/∘∘. In both models as temperatures dropped the fluid is thought to have become more oxidizing resulting in a partitioning of the $\delta^{34}S$ of the sulphate which increased linearly with $1/T^2$ while the $\delta^{34}S$ of total sulphur remained constant.

In Taolin A this partitioning continued linearly without precipitation to a temperature of 344°C ($X = 2.63$).

In Taolin B however, both sulphate and sulphide began precipitating at high temperatures. The $\delta^{34}S$ of the sulphate increased linearly with $1/T^2$ with respect to total sulphur, as in Taolin A, while the $\delta^{34}S$ of sulphide decreased steadily with respect to the $\delta^{34}S$ of the total sulphur in the fluid.

In both Taolin A and Taolin B there was a point at which sulphate became an appreciable species in solution. In Taolin A this occurred at about 290°C ($X = 2.3$), in Taolin B at a much higher temperature of about 530°C. In both cases this caused the $\delta^{34}S$ value of sulphate to move towards that of total sulphur in solution. At this point the $\delta^{34}S$ value of sulphide in Taolin A began falling below that of total sulphur, while the $\delta^{34}S$ value of sulphide Taolin B maintained its decline.

The increase of sulphate in solution had markedly different effects in Taolin A and Taolin B. In Taolin A the solubility of sulphide dropped past the critical point at 344°C ($X = 2.63$) and sulphide began to precipitate, causing a sharp $\delta^{34}S$ increase in the total sulphur as sulphate became the dominant species in solution. In Taolin B, the solubility of both sulphate and sulphide was exceeded and both began to precipitate at ~530°C. The solubility of sulphate was much less than that of sulphide which quickly drove the $\delta^{34}S$ of the total sulphur towards that of sulphide, the dominant species in solution.

Finally, at 265°C, sulphate began to precipitate in Taolin A, having exceeded its solubility in solution. This arrested the climb in $\delta^{34}S$ of total sulphur through the $\delta^{34}S$ of sulphide dropped steadily as sulphate was precipitated. Once the $\delta^{34}S$ of the total fluid shifted towards that of sulphide in Taolin B, the steady removal of sulphate from the system resulted in an increase of $\delta^{34}S$ of sulphate proportional to $1/T^2$. However, since the sulphate species was not appreciable in solution, the $\delta^{34}S$ of sulphide and sulphate remained constant from a temperature of 435°C and less in Taolin B.

6.5 Explanation of Differences Between Taolin A and Taolin B in a Geological Context

Ding and Rees developed their model for a solution that was predominately sulphide rich at high temperatures because evidence from the Pinckney and Rafter type examination of Stage I and Stage II of Taolin A suggested an increase in sulphate in solution with a decrease in temperature (Ding and Rees, personal communication). Geologically this seems a very viable assumption. It is well documented that an ore forming fluid which carries both sulphur and base metals such as zinc and lead must be both hot and acidic (see for example, Rose and Burt, 1979) which would tend to reduce elements such as sulphur, resulting in a sulphide species in solution. Wall rock alteration consisting of sericitization, chloritization and silicification also supports an acidic hydrothermal fluid (Rose and Burt and authors therein, 1979). As well fluorite, which is a major gangue mineral in the ore rich veins, suggest an acidic fluid source.

The increase of sulphate in solution at relatively high temperatures in both Taolin A and Taolin B could be due to wallrock -- hydrothermal fluid reduction -- oxidation reactions taking place as the fluid alters the surrounding mineral assemblages.

In both Taolin A and Taolin B sulphate in solution began a second climb at moderate temperatures. This could be interpreted as the effect of mixing oxygenated, cool meteoric water with the hydrothermal fluid. Oxygen isotope studies on Taolin A by Ding and Schwarcz (1984) indicate that a second fluid, probably meteoric water, affected the oxygen isotope signatures of the Taolin mineral assemblage. In Taolin A the change from oxidizing to reducing conditions was observed at the beginning of sulphate precipitation. The low temperature might have been due in part to the cooling of the hydrothermal fluid by the meteoric water. In Taolin B there was a less dramatic change over from predominately reducing to oxidizing conditions. This could have been the result of de-oxygenating the meteoric water at higher levels in the mine thus resulting in there being less oxygen to oxygenate the hydrothermal fluid. Also the influxing meteoric water would have warmed significantly as it passed to lower levels in the mine perhaps explaining the constant precipitation of sulphate from high temperatures for Taolin B.

The original $\delta^{34}S_{\Sigma S}$ for found Taolin A and Taolin B are very close using the Ding and Rees model equations unlike the anomalously different values found using the Pinckney and Rafter approach. The difference between the two was only 0.9°/oo which is a relatively insignificant spread in a geological context. It appears that the sulphur source for Taolin was juvenile sulphur derived from the upper mantle or from partial melting of pre-existing crust giving a total sulphur isotope signature of around 0.0% ± 1.0°/oo. This is supported by independent oxygen isotope evidence gathered by Ding and Schwarcz (1984) which suggests an original oxygen source for the hydrothermal fluid of magmatic or metamorphic origin.

VII. CONCLUSIONS

The sulphur isotope fractionation between coexisting sulphur minerals indicates that at the 120 m level of the Shangtancen mining district of the Taolin Pb-Zn ore deposit both sulphide and sulphate precipitation took place at temperatures between 530°C and 200°C.

The conventional, straight line extrapolation of data points to find the original $\delta^{34}S$ value of the hydrothermal fluid was rejected because 3 markedly different values were found within a 40 m depth. The spread in the original $\delta^{34}S$ between stage II of Taolin A and and the $\delta^{34}S$ of Taolin B was 26.7°/oo an anomalously large discrepancy in a geological context.

When the effects of precipitation of mineral phases on the isotopic composition of the sulphur bearing fluid were taken into account it was possible to model the ore forming fluid of Taolin B as having an initial $\delta^{34}S_{\Sigma S}$ of 0°/oo ± 1.0°/oo. The change with decreasing temperature of the partitioning between sulphide and sulphate in the ore forming fluid together with the precipitation of isotopically heavy sulphate and isotopically light sulphide influenced the isotopic composition of the total sulphur in solution and leads to good agreement between the predicted and observed isotopic compositions of sulphides and sulphates precipitated at various temperatures.

The difference between the initial $\delta^{34}S_{\Sigma S}$ of Taolin A and Taolin B determined using the Ding and Rees model equations was only 0.9°/₀₀ which was relatively insignificant geologically speaking, suggesting a common source of sulphur in both levels of the mine. The data presented for Taolin I correlates well with the data collected by Ding and Rees (1984) for Taolin A and is consistent with the behaviour of an ore forming fluid which initially contained juvenile sulphur in solution and which subsequently lost sulphur by precipitation. The Ding and Rees model equations developed in the appendix are for a system from which there is no loss of sulphur except by precipitation and for which there is no input of sulphur from other sources than the initial one.

VIII. SUGGESTIONS FOR FURTHER RESEARCH

Examining the mineralization of the whole Taolin ore zone one is impressed by the symmetry of mineral distribution. The central ore bodies (Shangtancen and Yinkongshan districts) (see Fig. 2) are rich in the sulphides sphalerite and galena while low in barite. At the ends of the mineralized zone (Duashan, Guanshan, Guipiao, and Doujiachong districts) this abundance pattern is reversed. The symmetry of the mineralization invites further research of the Taolin ore body.

To increase the understanding of the origin of the sulphur in the ore forming fluid the $\delta^{34}S_{\Sigma S}$ of each of the ore bodies should be examined. If all of the values are close to those found at Shangtancen the assumption that there is only one sulphur source for the deposit would be validated.

The oxygen isotope signature of each of the ore bodies should also be examined. As stated previously there is good evidence that the sulphur and base metals were carried together in a hot, acidic solution. By examining, the oxygen isotope signatures of the ore bodies rich in sulphate, it could be proven whether or not a large flux of meteoric water caused oxidation of the ore forming fluid resulting in barite production.

Provided a single sulphur source is validated for Taolin, oxygen isotope studies will support one of 2 models proposed here.

8.1.a Model I (see Fig. 13a)

If each ore body had received an identical amount of hydrothermal fluid as its neighbour (assuming identical composition) then influxing meteoric water would have caused the observed sulphate/sulphide ratios of the ore bodies. That is to say, the ore bodies on the ends would have received more meteoric water which would have caused significant oxidizing of the sulphur in solution, and thus significant sulphate precipitation. The middle ore bodies on the other hand would have received little meteoric water making sulphide the dominant precipitate. Oxygen isotope studies would indicate if the Duashan, Guanshan, Quipiao and Doiyiachang districts had large influxes of meteoric water. Mineralization temperatures of these districts might help explain whether influxing meteoric water was cool or warm.

8.1.b Model II (see Fig. 13b)

If each ore body received the same amount of influxing meteoric water (which oxygen isotope studies would reveal) then one might suggest that the amount of hydrothermal fluid in each ore body was different. It would appear that the central ore bodies received more hydrothermal fluid than the end members. Examining temperatures of crystallization of the ore zones would reveal if the Shangtancen and Yinkonghsan district ore bodies are close to the main hydrothermal water conduit as implied above.

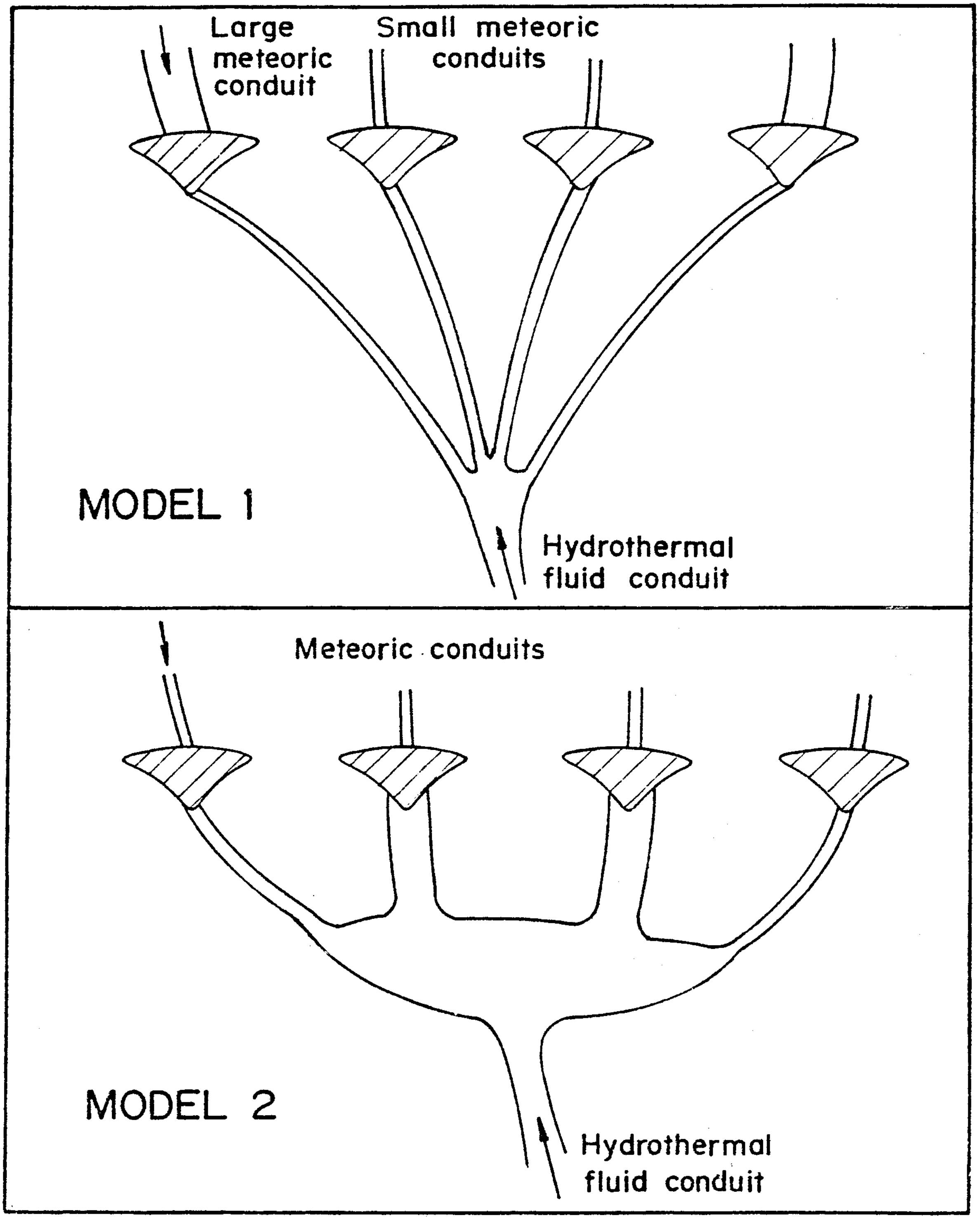


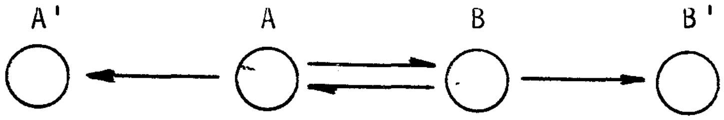
Fig. No. 13 Cartoon Model for the Taolin Ore Bodies

IX. APPENDIX

(Note: This appendix is adopted from Ding and Rees, 1984)

9.1 Introduction

The equations that were developed by Ding and Rees for the isotope systematics of sulphide and sulphate precipitation from solution as a function of temperature can be represented schematically as



A and B represent dissolved sulphate and dissolved sulphide while A' and B' represent precipitated sulphate and precipitated sulphide. A and B are always in isotopic equilibrium because the forward and backward steps between A and B are assumed to be rapid compared to the time of sulphur mineralization. This assumption is valid for Taolin because the large grain size of the mineral constituents indicate slow crystallization.

The partitioning between A and B is assumed to be a function of temperature.

The reaction rates between sulphide and sulphate in solution and precipitated sulphate and sulphide (from A to A' and B to B') are assumed to be controlled by the solubilities of sulphate and sulphide in solution at any given temperature. It is also assumed that no isotopic fractionation is involved in precipitation so that the sulphate and sulphide remaining in solution have the same isotopic composition of the sulphate and sulphide precipitate at that temperature (Ding and Rees, 1984).

As stated previously the equations that have been developed assume that the system is closed and that there is no recharge of the system and no loss of sulphate or sulphide.

9.2 Notes on Scales of Measurements

1. The model was developed relating isotopic composition to temperature with del values written as fractional differences in isotopic composition and not in permil units.
2. The variable X which varies as $1/T^2$ was introduced. For a convenient value of X temperatures were indicated in units of 1000 K.

3. The variation of the equilibrium fractionation between sulphate and sulphide was written as $\varepsilon = \varepsilon_0 x$. ε_0 was then the fractional difference from unity of the isotope equilibrium constant between sulphate and sulphide at 1000 K.
4. These scales were adopted because there was no need to introduce factors of 10^3 or 10^6 in the mathematical equations as would be necessary in conventional measurements.
5. The model was developed for the precipitation of a single sulphide species. In Taolin A sphalerite, galena and chalcopyrite were found in the approximate proportions 2:1:0. The fractionation between sulphate and sulphide was represented as

$$\varepsilon_{sp} = 0.00644 \times 10^6/T^2;$$
$$\varepsilon_{gn} = 0.00724 \times 10^6/T^2;$$
$$\varepsilon_{cp} = 0.00659 \times 10^6/T^2;$$

leading to

$$\varepsilon = 0.00671 \times 10^6/T^2$$

a weighted average equation that was convenient for model calculations.

9.3 Chemical Behaviour

9.3.1. High Temperature Regime

At high temperatures (> 530°C) it was assumed that the partitioning between sulphate and sulphide in solution changed in such a way that the natural logarithm of the sulphate/sulphide ratio varied linearly with absolute temperature so that

$$\ln(A/B) = \ln L - \ell T$$

where A is sulphate concentration, B is sulphide concentration, T is the absolute temperature and ln L and ℓ are constants. For convenience variations with $1/T^2$ were considered as opposed to T therefore

$$1/T^2 = x, \ T = 1/\sqrt{x}$$

resulting in

$$\ln(A/B) = \ln L - \ell \sqrt{x}.$$

A/B was represented as s giving

$$A/B = s = Le^{-\ell/\sqrt{x}}$$

C_0 which was defined as the initial total sulphur concentration in solution (and considered in this temperature regime to be constant) was represented as

$$C_0 = A + B$$

The following relations then followed:

$$A = \frac{s}{1 + s} C_0,$$

$$B = \frac{1}{1 + s} C_0.$$

When s equals unity A and B are equal indicating equal partitioning between sulphate and sulphide. Letting X represent the temperature at which this phenomenon occurs Ding and Rees complete the high temperature equations in the following manner.

$$1 = Le^{-\ell/\sqrt{x}}$$

so that

$$\ell = \sqrt{x}\ \ell nL.$$

writing

$$L = e^{Y}$$

gives

$$\ell = Y\sqrt{x}.$$

The parameters X and Y were chosen because of their convenience in fitting. X represents the value of $1/T^2$ at unity and Y is related to the steepness with which s changes with x in the vicinity of X.

To write the total quantities of sulphate and sulphide precipitated as A' and B' respectively in a differential form in this temperature regime

$$A' = 0$$

$$B' = 0$$

and

$$\frac{dA'}{dx} = 0; \quad \frac{dB'}{dx} = 0$$

leaving

$$\frac{dA}{dx} = -\frac{dB}{dx} .$$

9.3.2. Intermediate Temperature Regime

Note: for Taolin B there was no temperature observed at which sulphide was the only precipitate. For computer modelling purposes the intermediate temperature range was squeezed to be only 0.1°C wide, so that sulphate and sulphide precipitation began instantaneously.

At intermediate temperatures the concentration of sulphide in solution was limited by its solubility. There was no sulphate precipitation.

It was assumed that the logarithm of the solubility of sulphide varied linearly with temperature, at all temperatures so that in the intermediate and low temperature regimes the sulphide concentration in solution was controlled by

$$\ln B = \ln N + nT$$

where N and n were constants. Then

$$B = Ne^{n/\sqrt{x}}.$$

It was assumed that as in the high temperature regime

$$A/B = s = Le^{-\ell/\sqrt{x}}$$

so that

$$A = sNe^{n/\sqrt{x}}.$$

V was written as the total volume of the hydrothermal solution so that the total quantity of sulphide precipitated, B', was given by

$$\begin{aligned} B' &= V[C_0-(A+B)] \\ &= V[C_0-B(1+s)]. \end{aligned}$$

Again

$$A' = 0.$$

Differential equations for this temperature regime were then

$$\frac{dA}{dx} = s\frac{dB}{dx} + B\frac{ds}{dx};$$

$$\frac{dB'}{dx} = -VB\frac{ds}{dx} - V(1+s)\frac{dB}{dx};$$

and

$$\frac{dA'}{dx} = 0.$$

It was noted that the value of N could be determined. When x = x_1, which corresponded to the transition between the high and intermediate temperature regimes it was shown that,

$$B(x_1) = \frac{1}{1+s(x_1)}C_0 = Ne^{n/\sqrt{x_1}}$$

which meant that at x1, the high and intermediate temperature relations for B had to match giving

$$N = \frac{C_0}{[1+s(x_1)]e^{n/\sqrt{x_1}}}.$$

9.3.3. Low Temperature Regime

In Taolin B at temperatures below 530°C the concentration of both sulphate and sulphide in solution exceeded their solubility and precipitation of both took place. It was assumed that the logarithm of the solubility of sulphate varied linearly with temperature, at all temperatures. In the low temperature regime the sulphate concentration in solution was controlled by this relation so that

$$\ln A = \ln M + mT$$

where M and m were constants. This was written as

$$A = Me^{m/\sqrt{x}} \quad \text{and} \quad B = Ne^{n/\sqrt{x}}$$

as in the intermediate temperature regime so that the partitioning between sulphate and sulphide in solution was controlled by their respective solubilities. The total quantity of sulphate precipitated, A', was given by

$$A' = V[A(x_2)-A]$$

and the total quantity of sulphide precipitated was given by

$$B' = V[C_0-A-B-A'] = V[C_0-B-A(x_2)].$$

In differential equation form this became

$$\frac{dA'}{dx} = -V\frac{dA}{dx};\ \frac{dB'}{dx} = -V\frac{dB}{dx}\ .$$

The value of the constant M was determined. When $x = x_2$, which corresponded to the transition between the intermediate and low temperature regimes, then

$$A(x_2) = S(x_2)\ Ne^{n/\sqrt{x}} = Me^{m/\sqrt{x_2}}$$

which meant that at x_2 the intermediate and low temperature relations for A matched. This gave

$$M = \frac{s(x_2)Ne^{n/\sqrt{x_2}}}{e^{m/\sqrt{x_2}}} = \frac{s(x_2)}{1 + s(x_1)} \cdot \frac{e^{n/\sqrt{x_2}}}{e^{n/\sqrt{x_1}}} \cdot \frac{1}{e^{m/\sqrt{x_2}}} \cdot C_0.$$

This model was adapted to a Basic computer program by C. E. Rees in 1984 and was used to model Taolin B.

9.4 Isotopic Behaviour

9.4.1 General

The total concentration of sulphate plus sulphide in solution is given by

$$A + B = C.$$

By isotopic mass balance

$$A\delta_A + B\delta_B = C\delta_C = (A+B)\delta C.$$

δ_A, δ_B and δ_C are del values representing the fractional differences between the $^{34}S/^{32}S$ values in A, B and C and the $^{34}S/^{32}S$ value of the total sulphur in the standard reference material.

It is assumed that, at all temperatures, sulphate and sulphide in solution are in isotopic equilibrium, and that the isotope equilibrium fractionation varies linearly with $1/T^2$, so that

$$\delta_A - \delta_B = \varepsilon_o x$$

where ε_o is a constant. This relation is combined with the statement of isotopic mass balance to express δ_A and δ_B in terms of δ_C -- the isotopic composition of the total sulphur in solution:

$$\delta_A = \delta_C + \frac{B}{A + B}\varepsilon_o x; \quad \frac{\delta_A}{\varepsilon_o} = \frac{\delta_C}{\varepsilon_o} + \frac{B}{A + B}x$$

and

$$\delta_B = \delta_C - \frac{B}{A + B}\varepsilon_o x; \quad \frac{\delta_B}{\varepsilon_o} = \frac{\delta_C}{\varepsilon_o} - \frac{A}{A + B}x$$

Now consider the variation of δ_C with x. When

$$x \text{ changes from } x \text{ to } x + \Delta x$$

$$C \text{ changes from } C \text{ to } C + \Delta C$$

where

$$\Delta C = \frac{dC}{dx}\Delta x = \left(\frac{dA}{dx} + \frac{dB}{dx}\right)\Delta x$$

and δ_C changes from δ_C to $\delta_C + \Delta\delta_C$.

Assume that there is no isotope effect in either the precipitation of sulphate or of sulphide so that the isotopic composition of a precipitating species is the same as that of that species in solution.

$$\Delta A' = \frac{dA'}{dx}\Delta x.$$

This material has an isotopic composition equal to δ_A. The amount of sulphur lost by sulphide precipitation is

$$\Delta B' = \frac{dB'}{dx}\Delta x.$$

This material has an isotopic composition equal to δ_B.

Isotopic mass balance gives

$$V(C+\Delta C)\ (\delta_C+\Delta\delta_C) + \Delta A'\delta_A + \Delta B'\delta_B = VC\delta_C.$$

Expanding, and ignoring the second order term, gives

$$VC\delta_C + VC\Delta\delta_C + V\Delta C\delta_C + \Delta A'\delta_A + \Delta B'\delta_B = VC\delta_C$$

$$VC\Delta\delta_C + V\Delta C\delta_C + \Delta A'\delta_A + \Delta B'\delta_B = 0.$$

Substitute for ΔC, ΔA' and ΔB':

$$VC\Delta\delta_C + V[\frac{dA}{dx} + \frac{dB}{dx}]\Delta x\,\delta_C + \frac{dA'}{dx}\Delta x\,\delta_A + \frac{dB'}{dx}\Delta x\,\delta_B = 0$$

Write

$$C = A + B;\ \delta_A = \delta_C + \frac{B}{A+B}\varepsilon_o x;\ \delta_B = \delta_C - \frac{A}{A+B}\varepsilon_o x:$$

$$V(A+B)\Delta\delta_C + V[\frac{dA}{dx} + \frac{dB}{dx}]\delta_C\Delta x + \frac{dA'}{dx}[\delta_C + \frac{B}{A+B}\varepsilon_o x]\Delta x$$

$$+ \frac{dB'}{dx}[\delta_C - \frac{A}{A+B}\varepsilon_o x]\Delta x = 0.$$

Or, rearranging:

$$V(A+B)\Delta\delta_C + [V\frac{dA}{dx} + V\frac{dB}{dx} + \frac{dA'}{dx} + \frac{dB'}{dx}]\delta_C\Delta x$$

$$+ \frac{B}{A+B}\frac{dA'}{dx}\varepsilon_o x\Delta x - \frac{A}{A+B}\frac{dB'}{dx}\varepsilon_o x\Delta x = 0.$$

Dividing throughout by $(A+B)\varepsilon_0 \Delta x$ and writing, in the limit, for infinitesimal values of Δx,

$$\frac{\Delta\delta_C}{\Delta x} = \frac{d\delta_C}{dx}$$

and rearranging

$$V\frac{1}{\varepsilon_0}\frac{d\delta_C}{dx} = \frac{1}{A+B}\left[V\frac{dA}{dx} + V\frac{dB}{dx} + \frac{dA'}{dx} + \frac{dB'}{dx}\right]\frac{\delta_C}{\varepsilon_0}$$

$$- \frac{1}{(A+B)^2}\left[B\frac{dA'}{dx} - A\frac{dB'}{dx}\right]x.$$

9.4.2 High Temperatures (T > 530°C)

From section 9.3.1, at high temperatures,

$$\frac{dA}{dx} = -\frac{dB}{dx};\ \frac{dA'}{dx} = 0;\ \frac{dB'}{dx} = 0.$$

Substituting these values in the equation for $d\delta_C/dx$ gives

$$\frac{V}{\varepsilon_0}\frac{d\delta_C}{dx} = 0$$

so that δ_C is constant. Write this constant as $\delta_C(i)$ representing the initial isotopic composition of the total sulphur in solution. Using the equations relating δ_A and δ_B to δ_C, developed in section 9.4.1, and writing A/B as s, gives

$$\frac{\delta_A}{\varepsilon_o} = \frac{\delta_C(i)}{\varepsilon_o} + \frac{1}{1 + s}x$$

and

$$\frac{\delta_B}{\varepsilon_o} = \frac{\delta_A}{\varepsilon_o} - x$$

where

$$s = Le^{-\ell/\sqrt{x}}.$$

9.4.3 Intermediate Temperatures (squeezed to 0.1°C width in Taolin B because sulphide and sulphate precipitation occur simultaneously)

From section 9.3.2, at intermediate temperatures

$$\frac{dA}{dx} = s\frac{dB}{dx} + B\frac{ds}{dx};\ \frac{dA'}{dx} = 0;\ \frac{dB'}{dx} = -VB\frac{ds}{dx} - V(1+s)\frac{dB}{dx}.$$

Substituting these values in the equation for $d\delta_C/dx$ gives

$$\frac{V}{\varepsilon_o}\frac{d\delta_C}{dx} = -\frac{A}{(A+B)^2}\left[VB\frac{ds}{dx} + V(1+s)\frac{dB}{dx}\right]x.$$

Writing A/B as s gives

$$\frac{A}{(A+B)^2} = \frac{A}{(1+s)^2}\cdot\frac{1}{B^2} = \frac{s}{(1+s)^2}\cdot\frac{1}{B}$$

so that, cancelling V,

$$\frac{1}{\varepsilon_o}\frac{d\delta_C}{dx} = -\frac{s}{(1+s)^2}\frac{1}{B}\left[B\frac{ds}{dx} + (1+s)\frac{dB}{dx}\right]x.$$

Now,

$$s = Le^{-\ell/\sqrt{x}};\ B = Ne^{n/\sqrt{x}}$$

so that

$$\frac{ds}{dx} = \frac{\ell}{2x\sqrt{x}}s;\ \frac{dB}{dx} = -\frac{n}{2x\sqrt{x}}B$$

and

$$\frac{1}{\varepsilon_o}\frac{d\delta_C}{dx} = -\frac{1}{2}\frac{s}{(1+s)^2}\left[\ell s - n(1+s)\right]\frac{1}{\sqrt{x}}.$$

Thus, in the intermediate temperature regime,

$$\frac{\delta_C}{\varepsilon_o} = \frac{\delta_C(x_1)}{\varepsilon_o} - \int_{x_1}^{x}\frac{1}{2}\frac{s}{(1+s)^2}\left[\ell s - n(1+s)\right]\frac{1}{\sqrt{x}}dx$$

and, as in the previous section

$$\frac{\delta_A}{\varepsilon_o} = \frac{\delta_C}{\varepsilon_o} + \frac{1}{1+s}x$$

and

$$\frac{\delta_B}{\varepsilon_o} = \frac{\delta_A}{\varepsilon_o} - x.$$

9.4.4 Low Temperatures (T < 530°C)

From section 9.3.3, at low temperatures

$$\frac{dA'}{dx} = -V\frac{dA}{dx};\ \frac{dB'}{dx} = -V\frac{dB}{dx}.$$

Substituting these values in the equation for $d\delta_C/dx$ gives

$$\frac{V}{\varepsilon_o}\frac{d\delta_C}{dx} = -\frac{1}{(A+B)^2}\left[VA\frac{dB}{dx} - VB\frac{dA}{dx}\right]x.$$

Now

$$A = Me^{m/\sqrt{x}};\ B = Ne^{n/\sqrt{x}}$$

$$\frac{dA}{dx} = -\frac{m}{2x\sqrt{x}}A;\ \frac{dB}{dx} = -\frac{n}{2x\sqrt{x}}B$$

so that

$$\frac{1}{\varepsilon_o}\frac{d\delta_C}{dx} = -\frac{1}{2}\frac{1}{(A+B)^2}[BAm - Ban]\frac{1}{\sqrt{x}}$$

$$= \frac{1}{2}\frac{AB}{(A+B)^2}[m-n]\frac{1}{\sqrt{x}}.$$

This expression can be simplifed somewhat for purposes of calculation. Note that

$$\frac{A}{B} = \frac{M}{N}e\ (m-n)/\sqrt{x}.$$

Writing M/N as p and (m-n) as q gives

$$\frac{(A+B)^2}{AB} = \frac{A^2 + 2AB + B^2}{AB} = \frac{A}{B} + 2 + \frac{B}{A} = pe^{q/\sqrt{x}} + 2 + \frac{1}{p}e^{-q/\sqrt{x}}.$$

Note that from section 9.3.3

$$p = \frac{M}{N} = s(x_2)e^{-q/\sqrt{x_2}}.$$

Thus, for values of x greater than x_2

$$\frac{\delta_C}{\varepsilon_o} = \frac{\delta_C(x_2)}{\varepsilon_o} - \int_{x_2}^{x} \frac{1}{2} \frac{1}{pe^{q/\sqrt{x}} + 2 + \frac{1}{p}e^{-q/\sqrt{x}}} q \frac{1}{\sqrt{x}} dx.$$

From section 9.4.1

$$\frac{\delta_A}{\varepsilon_o} = \frac{\delta_C}{\varepsilon_o} + \frac{B}{A+B}x.$$

$$= \frac{\delta_C}{\varepsilon_o} + \frac{1}{1 + A/B}x$$

Thus

$$\frac{\delta_A}{\varepsilon_o} = \frac{\delta_C}{\varepsilon_o} + \frac{1}{1 + pe^{q/\sqrt{x}}}x$$

and

$$\frac{\delta_B}{\varepsilon_o} = \frac{\delta_A}{\varepsilon_o} - x.$$

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