DETERMINATION OF METAMORPHIC GRADE FOR TWO FORMATIONS OF THE HURONIAN SUPERGROUP: WHITEFISH FALLS AREA, ONTARIO

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DETERMINATION OF METAMORPHIC GRADE FOR TWO FORMATIONS OF THE HURONIAN SUPERGROUP: WHITEFISH FALLS AREA, ONTARIO

by

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Scope and Contents:

Samples from the Whitefish Falls Area were examined petrographically and chemically to determine the regional grade of metamorphism. Mineralogy from the Lorrain formation (quartzities) and Gowganda Formation (argillites) were apparently incongrous. The resolution of this problem formed the major part of the study.

Mineralogically the quartzites contained a kyanitequartz paragenesis with a subordinate kyanite-chloritoidquartz paragenesis. The argillites showed a chlorite-biotite -plagioclase-calcite-quartz paragenesis with only minor epidote present. From textural evidence possible reactions were deduced which were used to set the upper and lower limits for pressure and temperature. These boundaries were $470^{\circ}C$ and 3.9 kb., lower limit and $550^{\circ}C$ with a variable pressure for the upper limit.

II

Chemically, whole rock analysis was used to determine the parameters for various chemographic diagrams. AFM, ACF and AKF plots for the argillites showed a very restrictive composition which excluded the almandine field and promoted the biotite field. The bulk composition of the argillites was cited as the main reason for the inhibition of high grade index minerals, thus appearing to be lower grade than their quartzite counterparts. AFM and AKF diagrams for the quartzites verified their mineralogy and proved their high grade nature.

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INTRODUCTION

The rocks of the Whitefish Falls-Willisville, Ontario area consist of a thick metasedimentary sequence known as the H uronian Supergroup. The mineralogical and compositional variations between two of its members; the Lorrain formation and Gowganda formation were studied with regard to their metamorphism.

The two members lie adjacent to each other in the field with a conformable contact. Although both have undergone a similar metamorphic history the mineral assemblages in each appear to be incongruous. High grade aluminous minerals are present in the quarzites which have no apparent counterpart in the argillites. This paradox was the subject of the present study.

As Winkler (1967) and Hyndman (1972) stated, the bulk composition of a rock determines to a great extent the metamorphic mineral assemblages. It was for this reason that X-ray spectrographic analyses were conducted to determine major element concentrations. The resultant data coupled with petrographic observations were combined to give ACFK diagrams. These diagrams along with the petrographic work provided the major sources for the study.

FIG.1



LOCATION MAP

MODIFIED AFTER CASSHYAP (1969)



GEOLOGIC MAP

ESPANOLA

2 KM

FIG. 2

Ν

46.15

General Geological Setting

The Lorrain and Gowganda formations are members of the Huronian Supergroup which lie in the Southern tectonic province of the Canadian Shield. The rocks are around 1.9 billion years old in the study area (Fairbairn et al 1969).

The geology of the area is outlined by F.W. Chandler in his thesis. (1969)

In general the area is composed of three major sedimentary cycles. The bottom member of each cycle is marked by impure quartzites which grade vertically into a conglomeratic-argillitic member. Each cycle is capped by an orthoquartzite. The Penokean orogeny (Card et al 1972) has affected the area by tightly folding, faulting and metamorphosing the strats. The main trend of the folds is east-west. Open to subisoclinal folds have contorted the area into synclinal and anticlinal structures. In particular the La Cloche Syncline is located in the study area. These flexural slip features have been moderately affected by a secondary deformation represented by minor folds and crenulation cleavages. The general axial trend has also been in an east-west direction. A third period of non-penetrative strain-slip cleavages and kink bands intersect the area in a northwesterly to north-easterly trend.

A large number of fault sets has transected the entire Sudbury-Espanola area. Although repeated movement on most is evident the initial movement appears to have been down faulting to the south. Nipissing diabase and later mafic dikes have followed these weakness planes cutting across the entire region.

Within the study area intrusive activity has been minimal. Except for mafic dikes and sills there have been no other intrusions. This has simplified the problem by eliminating the effects of the contact metamorphism.

Background

Important variables that should have some bearing on the final answer are the conditions of metamorphism and the provenance of the two formations.

According to Card et al (1972) the Sudbury-Espanola region has undergone metamorphism of the low pressure intermediate facies. This facies as defined by Miyashiro (1961) is characterized by the coexistence of andalusite and staurolite. The coexistence of andalusite, staurolite and kyanite also indicates a low pressure intermediate group. In the study area the metamorphic determination has been confused by the incongruous mineralogy of the tillites and quartzites. The quartzites contain kyanite and quartz as coexisting minerals with subordinate kyanite-chloritoid-quartz assemblages.

The tillites; however, show an apparently lower grade mineralogy with biotite-chlorite-calcite-plagioclase-quartz assemblages being the most common.

Although many explanations could account for such a discrepancy it is probable that no relationship other than differences in rock composition controlled the differences in development of the metamorphic minerals. With this possibility in mind the compositional variations and their significance were explored.

The two members had a different sedimentary mode of formation. The different modes of formation would account for the variation in bulk composition. Accordingly a brief review of the depositional regime and provenance of the two members is necessary.

The Gowganda formation lies stratigraphically beneath the Lorrain. Casshyap (1969) recognized four mappable units in the study area; these being in ascending order: a lower diamictic conglomerate, a laminated argillite, an upper diamictic conglomerate and an intercalated zone of sandstone, argillite and conglomerate. The Gowganda has long been thought to be glacial in origin. Lindsey (1970) has presented the most convincing evidence for its glacial origin. Wet-based glaciers and their associated processes were responsible for the build up of the sediments in the Gowganda. The glacial processes did not remove from the sediments the clays or other

FIG. 3



MODIFIED AFTER CASSHYAP (1969) AND

YOUNG (1973)

easily weathered components. Therefore the sediments would be expected to reflect this by way of their mineralogy and chemical composition.

The Lorrain formation can be divided into three broad units as defined by Young (1973). The lower unit is a vari-coloured feldspathic argillite-quartzite; the middle unit a quartz-jasper congiomerate and an upper unit of pure to aluminous orthoquartzites. The upper unit has been considered by Chandler (1969) to have undergone tropical leaching similar to bauxitisitation. This leaching combined with the lack of clay-forming ions has been thought to give rise to authigenic kaolinite which upon metamorphism gave rise to kyanite.

The general transport direction as indicated by crossbedding suggests a northerly source for the Lorrain sediments. Extensive reworking and removal of easily weathered mineral constituents is indicated by the silica rich sediments of the sequences.

The drastic change from glacial to tropical climate constitutes drastically different conditions of formation for each member. The differences in chemical and mechanical weathering were partly responsible for producing two different bulk compositional regimes. One would therefore expect to find difference in the consequent mineral assemblages.

PETROGRAPHICAL ANALYSIS

Thirty thin sections, fifteen quartzites and fifteen argillites were studied. Samples taken by Dr. H.P. Schwarcz in Curtin Township were supplemented with samples taken by the Ontario Department of Mines in the same area. The mineralogy of each slide was determined and textural features were noted.

Argillites

The argillites are comprised mainly of quartz, chlorite and biotite. Commonly associated with these minerals are calcite, plagioclase, muscovite and pyrite. Rarely the minerals epidote and hematite are found in the thin sections.

Quartz was present in all the slides observed. Typically it occurred as anhedral grains. Where the proportion of quartz was low with respect to the rest of the minerals the grains were usually small and showed straight extinction. Where the proportion of quartz was higher the grains on the average were larger and showed more signs of stress. (i.e. undulose extinction.)

Chlorite was identified in all the slides as well. The grains were pale green in normal light with anomalous

brown interference colours. Birefringence estimates were low for all the chlorites; generally near 0.002. Numerous samples were tested for their refractive indices. In all cases the chlorites had an R.I. greater than 1.57 and less than 1.66. Most of the chlorites had an R.I. of around 1.61 with a few at 1.60. Combining the R.I. with the birefringence an estimate of the Fe/Fe + Mg ratio can be made. Using the graph given by Deer, Howie and Zussman (1966) a Fe/Fe + Mg ratio of between 0.35 and 0.45 was determined. Physically the lower iron content is reflected by the anemalous brown interference colours. (Albee 1962) Deer, Howie and Zussman call these chlorites unoxdized. In one slide, 68-Kc-24; however, chlorites had blue interference colours which indicated a more oxidized condition. This was reflected by the higher proportion of hematite in the slide. The chlorites were usually parallel to the foliation or to bedding planes. In the sandy slides chlorite occurred as aggregates or small euhedral to anhedral flakes. In many of the slides chlorite was closely associated with either biotite or calcite or both.

Biotite was present in the majority of thin sections of argillaceous nature. Biotite was either subordinate to • or equal to the amount of chlorite but rarely was it more abundant. Where this occurred epidote was present and the biotite crystals were more euhedral and well formed. The biotite was usually pleochroic brown to light brown but in

some slides the grains were identified on the basis of their biaxially negative figures with low 2V. The biotite was parallel to the bedding in some cases but grains aligned parallel to foliations cross-cutting the beds were not uncommon. In some slides biotite was the main mineral in filling cracks and fissures. The close association of biotite with chlorite was in the form of coexisting phases in a single crystal or contact between two adjacent grains with diffuse interfaces.

Calcite was one of the major accessories in the slides. The mineral was abundant in only slide, 68-KC-24. In this slide calcite grains formed discrete layers between chlorite and biotite rich layers. In the other slides calcite occurred as isolated grains or clusters. Where present, the grains were usually associated with chlorite or pyrite. In both cases the calcite formed distinct boundaries between the other mineral grains and themselves. In these slides calcite was always subordinate to chlorite and biotite.

Plagioclase crystals were present in many but not all of the argillites. It was always in some stage of alteration involving formation of a micaceous phase. The compositions of the laths were determined using the Michel-Levy twin test. Values thus determined ranged from An_2 to An_{13} . These values are accurate to the limits of the statistical average taken for each determination. As many crystals as possible were

tested to obtain a maximum spread in values. In all cases no less than five crystals in each slide were tested, in some cases as many as fifteen. Thus the values obtained are thought to reflect accurately the An contents in the plagioclases.

The muscovite was always fine grained in the thin sections. It occurred as small highly birefringent flakes in the matrix or as inclusions in other minerals. Under high power the flakes were anheral. Frequently muscovite occurred as inclusions within the plagioclase crystals. Elsewhere muscovite and quartz were closely associated although no reactions between the two were noted.

Epidote and hematite were rare accessories seen in a few slides. The epidote was a pale green colour with moderate birefringence. It was closely associated with chlorite, biotite andquartz in slide C-72-99, and with chlorite, plagioclase and quartz in slide S-72-68. The textures suggest reactions involving these phases. The presence of hematite was restricted to a few slides. In slide 68-KC-24 it formed highly incised and variable shaped porphryoblasts. In other slides it occurred as anhedral aggregates. Usually the hematite stained the silicate minerals but it was observed forming around such minerals as chlorite andmore rarely biotite. Pyrite was the major opaque mineral observed. Euhedral cubes to anhedral grains were scattered throughout many of the slides. Chlorite and calcite were preferentially associated with the pyrite. In some slides calcite occurred in stress shadows, in other slides chlorite rimmed the pyrite grains. Magnetite was seen in only one slide, NC-22.

Quartzites

The samples from the Lorrain formation were comprised mainly of quartz, kyanite and a micaceous phase. Minor but important accessories were chlortoid, rutile, magnetite and hematite.

Quartz was by far the most ubiquitous mineral in all the thin sections. The grains varied from slide to slide. In some, the grains assumed a polygonal appearance typical of fusion and overgrowth. In other thin sections the quartz grains have been elongated from stress. The edges were serrated and distinct from adjacent grains. Yet in other thin sections the quartz grains were anhedral showing little sign of stress. Quartz grains contacted all other grains in the thin sections due to its great abundance.

The recognition of kyanite in the thin sections involved the use of detailed optical properties. In the thin sections the orientation of the kyanite crystals varied. The 010 plane had very low birefringence with no cleavage traces.

TABLE 1

Model Percentages of Minerals in Thin Section (Estimated)

•

| Argillites | Qtz. | Mica. | Chl. | Cal. | Bio. | Plag. | Epi. | Py. | Mag. | Hem. | Ky. | Chd. | Rutile |
|------------|------|-------|------|------|------|-------|------|-----|------|------|----------|-----------------------|--------|
| 68-KC-08 | 40 | 10 | 25 | 2 | 15 | - | - | 10 | _ | - | - | - | - |
| 68-KC-09 | 40 | 10 | 20 | 2 | 25 | - | - | 3 | - | - | - | - | - |
| 68-KC-07 | 45 | 5 | · 5 | - | 25 | 10 | - | 5 | - | - | - | - [·] | tr. |
| 68-KC-19 | 60 | 30 | - | - | - | - | - | tr. | - | 10 | - | - | - |
| 68-NC-22 | 40 | 5 | 35 | - | 10 | | - | tr. | 10 | - | - | - | |
| 68-KC-24 | 20 | tr. | 40 | 25 | - | tr. | - | 5 | - | 10 | | - | - |
| 68-NC-25 | 35 | 5 | 45 | - | 5 | _ | _ | - | - | 10 | - | - | - |
| C-72-37 | 50 | 35 | tr. | - | - | 15 | - | - | - | - | - | - | tr. |
| C-72-68 | 50 | 4 | 2 | 2 | 7 | 35 . | - | | - | - | _ | - | - |
| C-72-85 | 50 | 25 | tr. | - | - | 20 | - | — | - | - | _ | - | tr. |
| C-72-99 | 40 | 20 | 3 | 2 | 10 | 15 | 10 | - | - | - | - | - | _ |
| S-72-113 | 60 | tr. | tr. | 3 | tr. | 35 | _ | - | ~ | tr. | - | _ | 1 |

TABLE 1 (Cont'd) Argillites Chl. Cal. Bio. Plag. Py. Mag. Hem. Ky. Chd. Qtz. Mica. Epi. . S-72-115 5 5 30 15 10 1 20 15 _ -~ S-72-163 6 5 2 25 15 45 ----------68-KC-02 20 70 10 -----------------_ 68-KC-03 70 10 20 ---------------------68-KC-05 75 20 2 _ ------------------------68-KC-11A 40 58 -----_ -_ ----------68-NC-12 75 20 5 --------_ -----_ 68-KC-13 25 75 tr. -_ ---~ ---68-KC-18 75 15 10 -— ----------------------68-KC-21 43 15 40 ------

| | | | • | | | | | | | | | | |
|----------|----|----|---|---|---|---|---|---|----|-----|----|----|-----|
| S-72-76 | 65 | 10 | - | - | - | - | - | _ | 3 | 2 | 10 | 10 | tr. |
| C-72-83 | 85 | 4 | - | - | - | - | - | - | - | - | 10 | 1 | tr. |
| S-72-124 | 75 | 22 | - | - | - | - | - | - | - | - | 3 | | tr. |
| S-72-173 | 60 | 10 | - | - | - | - | - | - | 10 | tr. | 15 | 5 | - |
| S-72-174 | 50 | 27 | - | - | - | - | _ | - | - | - | 20 | 1 | 2 |

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Rutile

-

2

tr.

tr.

3

2

tr.

tr.

tr.

The best interference figures were obtained from such sections; they gave biaxial negative figures with moderate to large 2V's. The 100 plane showed higher birefringence and one cleavage parallel to the elongation of the crystal. Parallel extinction was common on this plane. Interference figures were harder to obtain and more difficult to interpret. The 001 plane, showed good cleavage in two directions at roughly 90° to each other. Flash figures were all that was obtained from this plane. Crushed crystals from several samples were tested for their refractive indices. In all instances crystals with high relief had a refractive index of 1.71 or greater which corresponds to that of kyanite.

Kyanite was restricted to the interstices of quartz crystals. Generally they showed no alignment with the stress field. In many of the thin sections the kyanite was rimmed by mica which was most likely muscovite as determined by X-ray. There was always a close relationship between the two minerals. Two or more crystals of different crystallographic orientations often shared common grain boundaries in many of the thin sections. The crystals for the most part were subhedral in shape and distinctly lacking abundant inclusions. In slide S-72-174, however, kyanite occurred as large pervasive porphyroblasts with numerous anhedral quartz inclusions.

The micaceous phase in the quartzites was very difficult to identify optically. Consequently X-ray diffraction

techniques were used to determine the major component of this phase. From three samples deemed representative of the quartzites X-ray patterns were obtained. In two, muscovite and paragonite were the phases present. In the other muscovite was the major phase. Muscovite was identified by strong reflections at 3.38 Å and at 4.99 Å. Paragonite was identified by a reflection at 3.20 Å and one at 4.27 Å. Pyrophyllite was absent from all the samples tested.

In the thin sections the white mica was typically fine grained, consisting of needles or very thin laths. They were generally situated between the quartz grains' often following the crystal boundaries. In all the slides the muscovite was observed in contact with the kyanite. Seldom included in the kyanite, it was more readily found around the edges of the crystals. In some cases the white mica followed foliation planes and in one slide it was observed to be separated by two foliations at 90°. More often, though, the crystals were randomly orientated in the slides with the major control being the inter-quartz grain spaces.

One sample containing paragonite was a very fine grained mass of highly birefringent material in thin section. It was highly foliated and no aluminous minerals were visible in the thin section.

Chloritold was the most important accessory mineral identified in the thin sections. The crystals displayed

blue-green to grey pleochroism in plane light. Under crossed nichols they had high relief and moderate birefringence. In many instances the crystals were zoned. It was not present in all the thin sections.

Chloritoid was always found to coexist with kyanite. Although chloritoid occurred as separate euhedral grains it was often bordered by kyanite crystals. In fact in slide 72-124 chloritoid was observed enclosed within a kyanite porphroblast. Such features strongly suggest conversion of one mineral to the other.

Chloritoid was also associated with magnetite and hematite. In one slide the chloritoid was seen oxidizing to hematite while in another slide it was seen adjacent to a magnetite grain.

Magnetite and hematite occurred as anhedral grains. As will be shown later there appears to be reaction involving the conversion of chloritoid to kyanite with magnetite and hematite as products.

Rutile was present as a trace component in many slides. It was identified by its extremely high relief, high birefringence and uniaxial positive interference figure. It always occurred as anhedral grains. There was no special association with any other mineral and the grains were randomly oriented.

Reactions between phases

The textural configurations and associations of the minerals in the thin sections should lead to a consistent interpretation of possible reactions. According to Carmicheal (1969) each thin section can be considered as a chemical system. The textural features seen within each section can be used to determine the metamorphic reactions most probable. The system is closed with respect to aluminium due to the low mobility of its ion. The ions K^+ , Na⁺, Fe⁺², and Ca⁺² are more mobile and able to migrate further distances in the thin section.

The close association of chlorite with biotite in the argillites is suggestive of one reaction. There appears to be direct conversion within the same crystal from chlorite to biotite. This suggests a simple reaction:

Chlorite - Biotite

However this is not possible since the chemical compositions of the two minerals are different. Migration of potassium from muscovite is required to balance the reaction. The Mg-rich chlorite present suggests that iron from the chlorite was being re-located in the biotite. Thus rewriting the reaction including muscovite:

(Fe,Mg)-Chlorite+Muscovite == Biotite + Mg-Chlorite+Quartz + H₀0

(1)

The formation of biotite in many of the rocks, as stated by Winkler (1967) is indicative of prograde metamorphism in the greenschist facies. The intimate association of biotite with chlorite suggests that the metamorphism is in the Quartz-Albite-Epidote-Biotite subfacies or higher. Since the coexistence of biotite-chlorite-muscovite is stable from this point through the rest of the greenschist facies the above argument represents the minimum conditions of metamorphism of the argillites.

Although epidote is not present in many of the slides its formation is useful to some extent. It and biotite form under similar conditions. Therefore it is also useful in setting the lower limit of metamorphism for the study area.

In order to achieve a more accurate determination of metamorphism, other indicators are needed. The variation of the chemical properties of chlorite with increasing metamorphic grade has been examined by Albee (1962). According to him chlorite becomes more magnesium rich in the higher grades of metamorphism. As noted previously there is a relative enrichment of Mg over Fe in the chlorites of these argillites as indicated by the Fe/Fe + Mg ratio. From Winkler's (1967) work Mg-chlorite is formed by prograde reaction in the upper greenschist facies corresponding to the Quartz-Albite-Epidote-Almandine surfaces. Albee (1965) has described a paragenesis similar to that observed here, from Lincoln Mtn., Vermont.

His attempts to prove that the coexisting minerals were prograde showed that the chlorites were very similar to those from the present study. Albee concluded that Mg/Fe ratios were highest in the garnet-chlortoid assemblages. He also showed that any enrichment of Mg in the chlorites was accompanied by a decrease of Fe. The iron was preferentially relocated in the biotite according to the equation:

3Fe-chlorite + 5Mg-biotite == 3Mg-chlorite + 5Fe-biotite

Other phases which could accomodate iron in the study area are pyrite and hematite. The sympathetic relationship between the chlorite and pyrite is one line of evidence for this latter suggestion.

The plagioclase in the thin sections was determined by Michel-Levy twin tests to be albite with compositions An_2 to An_{13} . Wenk (1962) has shown that as metamorphism proceeds the amount of anorthite in the plagioclases increases if calcite is present in the assemblage. Deer, Howie and Zussman (1966) as well as Winkler (1967) document the absence of plagioclase with An_7 in the low grade chlorite and biotite zones of the greenschist facies. Wenk distinguishes between two subfacies, The Albite-Epidote-Amphibolite facies and the Oligioclase-Epidote-Amphibolite faceis which signify the 21

(2)

transition from An less 7 per cent to An greater than 7 percent. This transition roughly corresponds to the upper greenschist facies. Plagioclase with An_7 or greater is generally regarded as signifying conditions indicative of the onset of the amphibolite facies. The fact that plagioclase with An less than 7 percent and An greater than 7 percent are present in the same thin section suggests conditions of the upper greenschist facies transitional to the amphibolite facies. Winkler and Deer, Howie and Zussman are in agreement in stating that the plagioclase conversion to An_7 occurs between the almandine and staurolite isograds or in the upper greenschist facies. A possible reaction which might apply in this situation is:

> Chlorite + Muscovite + Quartz + Calcite + Albite = Plagioclase + Biotite + $H_20 + C0_2$ (3)

By this reaction biotite is also formed and calcite is destroyed. The reaction is problematic in these argillites due to the low calcium content. It is probable though in light of the fact that all the solid phases of the equation were present in the slides.

It would appear, then, that the argillites have been metamorphosed to a higher grade than previous sources have suggested.

If the determined metamorphism of the argillites is correct it should be compatible with metamorphism of the quartzites. The textures and mineralogy of the quartzites should indicate a similar metamorphic grade.

Kyanite is a key index mineral in the quartzites. Much work has been done on the stabilites of the aluminosilicates polymorphs and the locations of their invariant curves and triple point. One of the more recent studies by Holdaway (1971) fixes the triple point at 501^OC and 3.76kb. This is lower than previous studies but as Holdaway points out these earlier studies failed to account for free energy differences between kyanite and sillimanite in the crushed state.

The kyanite in the thin sections is closely associated with a micaceous phase. This phase is determined by X-ray diffraction proved to be largely muscovite with some paragonite. The relationship between the two phases appears to be stable with no reactions indicated. If as suggested by Chandler (1969) the original minerals in the quartzites were a mixture of pyrophyllite, kaolinite and potassium feldspar than a possible reaction is:

Kaolinite + Pyrophyllite + K-feldspar == Muscovite + Kyanite + Quartz + H_2^0 (4)

If any amount of sodium was present, as is likely, then paragonite might also appear.

The breakdown of pyrophyllite occurs at 470° C and 3.9 kb. according to Kerrick (1968). See Fig. 4. Its absence in the quartzites as indicated by the X-ray analysis suggests that the upper stability of the mineral was exceeded. This defines the lower limit of metamorphism for the study area.

Chloritoid is an excellent indicator of metamorphism. Together with its coexistence with kyanite a very good determination of metamorphic conditions is possible. Much work has been done on the upper stability limit of chloritoid (Ganguly, 1968, 1969 ; Ganguly and Newton 1968; Richardson 1968; and Halferdahl 1961). Various breakdown reactions for a wide variety of starting components have been investigated by the previous authors. In general it is believed that the variables controlling the stability of chloritoid are temperature, pressure and oxygen fugacity.

In many experiments involving high oxygen fugacity the breakdown products of chloritoid are staurolite, magnetite, quartz and vapour (Ganguly and Newton 1968). This may proceed:

Chloritoid + $0_2 =$ Staurolite + Magnetite + Quartz + H_2^0 (5)

FIG. 4





The fact that Staurolite does not appear in any of the slides strongly suggests that the field area was not metamorphosed to the staurolite isograd, see Fig. 4. The observed mineral phases in the quartzites consists of chloritoid, kyanite, quartz, magnetite and muscovite. In most of the cases the chloritoid appears to be stable but in a few slides it is converting to kyanite. The possible reaction for this breakdown as suggested by Ganguly and Newton is:

Chloritoid +
$$0_2 = Kyanite + Magnetite + H_20$$
 (6)

This equation is dependent upon a relatively high pressure of 0_2 . The temperature range suggested for this breakdown is from $530-570^{\circ}$ C and 550° C being most often quoted. The coexistence of chloritoid and kyanite suggests fairly high pressures. Considering the aluminosilicates' relationships and work by the above mentioned authors the pressure for this breakdown seems likely to lie above 5 kb.

In light of the fact that staurolite is absent from the rocks and only a few samples showed conversion to kyanite the inferred temperature for the study area is in the range 470-550°C. Thus a consistent metamorphic history is compatible for both the argillites and quartzites. Winkler (1967) notes that in the highest temperature part of the Greenschist facies a characteristic assemblage is kyanite + chloritoid + chlorite + quartz + muscovite + paragonite + rutile. With the exception of chlorite, which would not be expected in an orthoquartzite all the minerals of this assemblage were observed. This lends added support to the observation that the staurolite isograd has not been reached in this area.

Further support for the pressure and temperature regime comes from the muscovite-paragonite coexistence. Albee (1965) cites the relationship of Ca-free muscovite with paragonite corresponds to temperatures in the range of 500-550°C with pressures in the range of 5-7 kb. From the chemical analysis the quartzites are devoid of calcium which indicates the muscovite is indeed Ca-free.

The muscovite and paragonite in the quartzites can be used to determine a relative metamorphic grade. Zen and Albee (1964) showed how the basal spacings of muscovite and paragonite were related to metamorphic grade. According to the equation:

$$y = 12.250 - 0.2634x \pm .006A$$
(7)

where $y = d(002)_{2m}$ paragonite and $x = d(002)_{2m}$ muscovite, the difference between x and y can be calculated. This corresponds to predetermined samples from known metamorphic grades. From the X-ray diffraction patterns a spacing of 9.97 Å was determined for muscovite on one pattern. Using $\mathbf{27}$

this figure in the equation a y-value of 9.63 Å was obtained for the paragonite. This corresponds to a difference of 0.34 Å. From Zen and Albee's work, differences of 0.318-0.364 Å were obtained for chloritoid and quartz assemblages in the almandine isograd. from various regions throughout the world. The muscovite-paragonite relationships for the Mt. Lincoln area Vermont as noted by Albee (1965) are almost identical in basal spacings to those from the study area.

CHEMICAL ANALYSIS

Having shown that the argillites and the quartzites are compatible petrographically the question remains as to why the argillites do not show development of high grade minerals such as almandine and chloritoid. In addition it would be useful to see if the quartzites' chemistry verifies its petrology.

To accomplish this, whole rock X-ray fluorescence was carried out on a number of samples: The samples included some from thin section work while the remainder were not studied petrographically. In all, fourteen samples, seven argillites and seven quartzites were prepared. The samples were prepared following the procedure outlined by Marchand (1973) so that pressed discs of boric acid and sample were formed. These discs were then analysed on a Philips automatic

sequential spectrometer, model PW 1450, at McMaster University. The spectrometer analysed four different samples for ten major elements on each run which took from 10 to 15 minutes. The major elements analysed included Si, Al, total Fe, Mg, Ca, Na, K, Ti, Mn, and P. A tungsten discharge tube was used throughout the entire analysis.

Twenty-five standards were run against the prepared samples with one remaining in the spectrometer to act as a drift monitor.

The plotting of the various ternary chemographic diagrams was achieved through computer techniques. The program, Trimod, was modified by J.M. Wolff after B.M. Gunn's original Triang program. The Trimod program plots a variety of binary and ternary chemographic diagrams. The ones used by the author were the AFM projection through muscovite, the ACF plot and the AKF plot. The program Trimod is presented in Wolff's Thesis (1974).

The AFM plot shown in Fig. 5 demonstrates the phases that should coexist in the argillites. The composition of the argillites falls into a narrow range so that only chlorite and biotite would be expected to be present in the thin sections. The argillite composition is exclusive of the almandine field so that it would not develop at this grade of metamorphism. The diagram shows the relative enrichment of iron and magnesium with respect to aluminum.



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FIG. 5

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TABLE 2

WHOLE ROCK ANALYSIS IN WEIGHT % OXIDES (UNNORMALIZED)

| SAMPLES | ${\tt Si0}_2$ | ^{A1} 2 ⁰ 3 | Fe (total) | MgO | Ca0 | Na0 | ^K 2 ⁰ | $^{\text{TiO}}2$ | MnO | ^P 2 ⁰ 5 | Total |
|------------|---------------|--------------------------------|---------------|------|------|------|-----------------------------|------------------|-----|-------------------------------|---------------|
| Argillites | | | | | | | | | | | |
| 72-162 | 60.30 | 15.65 | 8.24 | 5.75 | .97 | 4.08 | 2.94 | .76 | .06 | .12 | 98 .88 |
| -032 | 72.34 | 12.76 | 2.87 | 1.67 | .94 | 5.03 | 2.48 | .38 | .03 | .07 | 98.57 |
| -024 | 58.31 | 15.13 | 9.65 | 9.14 | .71 | 2.87 | 2.69 | •.50 | .09 | .11 | 99.20 |
| -163 | 67.89 | 13.69 | 5.07 | 3.24 | .60 | 3.96 | 3.28 | .63 | .04 | .11 | 98.51 |
| KC-22 | 58.04 | 16.32 | 11.16 | 4.53 | 1.31 | 3.95 | 2.74 | .74 | .16 | .18 | 99.13 |
| -07 | 64.61 | 14.31 | 6.29 | 3.54 | 1.83 | 4.38 | 2.64 | .67 | .12 | .10 | 98.49 |
| -24 | 44.80 | 12.77 | 19.62 | 6.79 | 7.88 | 1.87 | 2.96 | 3.20 | .15 | . 25 | 100.28 |
| Quartzites | | | | | | | | | | | |
| KC-03* | 92.91 | 8,69 | 0.0 | .16 | 0.0 | 1.17 | .60 | .15 | 0.0 | .02 | 103.63 |
| -12* | 94.52 | 8,65 | , 01 | .20 | 0.0 | 1.37 | .55 | .09 | 0.0 | .03 | 105.36 |
| 72-83* | 96.69 | 8.84 | 0.0 | .17 | 0.0 | 1.26 | .15 | .12 | 0.0 | .03 | 107.13 |
| -49* | 87.65 | 9,59 | .01 | .22 | 0.0 | 1,26 | 2.10 | .14 | 0.0 | .03 | 100.95 |
| -36 | 81.46 | 10.52 | 1.21 | .56 | 0.0 | 1.13 | 4.62 | .14 | 0.0 | .03 | 99.63 |
| 122 | 84.68 | 9.91 | .70 | .37 | 0.0 | 1.14 | 3.43 | .13 | 0.0 | .02 | 100.32 |
| -174 | 77.20 | 17.06 | .17 | .20 | 0.0 | 1.39 | 3.18 | .42 | 0.0 | .04 | 99.61 |
| | | | | | | | | | | | |

* No standards with SiO_2 greater than 85%, samples are in error

| | WHOLE RC | CK ANALYS | IS IN WEI | GHT % OX | IDES | (NORMAL | IZED) | | |
|--------------|--------------------------------|---------------|-----------|----------|------|------------------|-------|-----|-------------------------------|
| SAMPLES Si02 | ^{A1} 2 ⁰ 3 | Fe (total) | MgO | Ca0 | Na0 | к ₂ 0 | Ti02 | MnO | ^P 2 ⁰ 5 |
| Argillites | | | | | | | | | |
| 72-162 60.92 | 2 16.04 | 8.33 | 5.81 | .98 | 4.12 | 2.97 | .77 | .06 | .12 |
| -032 73.39 | 9 12.94 | 2.91 | 1.69 | .95 | 5.10 | 2.50 | .38 | .03 | .07 |
| -024 58.78 | 8 15.25 | 9.72 | 9.20 | . 72 | 2.89 | 2.71 | .51 | .09 | .11 |
| -063 68.89 | 9 13.89 | 5.16 | 3.29 | .61 | 4.03 | 3.34 | .64 | .04 | .11 |
| KC-22 58.5 | 5 16.46 | 11.26 | 4.57 | 1.33 | 3.98 | 2.76 | .75 | .16 | .18 |
| -07 65.00 |) 14.53 | 6.38 | 3.60 | 1.86 | 4.45 | 2.68 | .68 | .12 | .10 |
| -24 44.76 | 5 12.72 | 19.56 | 6,76 | 7.85 | 1.86 | 2,95 | 3.19 | .15 | .25 |
| Quartzites | | | | | | | | | |
| KC-03* 89.62 | 2 8.37 | 0.0 | ,15 | 0.0 | 1.12 | .58 | .14 | 0.0 | .02 |
| -12* 89.73 | 1 8,21 | .01 | .19 | 0.0 | 1.30 | . 47 | .08 | 0.0 | .03 |
| 72-83* 90.15 | 5 8.24 | 0.0 | .16 | 0.0 | 1.17 | .14 | .11 | 0.0 | .03 |
| -49* 86.80 | 9.48 | .01 | .22 | 0.0 | 1.24 | 2.08 | .14 | 0.0 | .03 |
| -36 81.7 | 1 10.57 | 1.21 | .56 | 0.0 | 1.13 | 4.65 | ,14 | 0.0 | .03 |
| -122 84.47 | 7 9.86 | .70 | .37 | 0.0 | 1.13 | 3.41 | .13 | 0.0 | .02 |
| -174 77.50 | 0 17.08 | .17 | .20 | 0.0 | 1.40 | 3.19 | .42 | 0.0 | .04 |

TABLE 3

*Standards with SiO_2 greater than 85% were not available

Thus the development of Al-rich minerals is also excluded. The AFM plot compares favourably with one drawn by Albee (1965) for an assemblage of argillites in Vermount. The trend of negatively sloping tie lines between chlorite and biotite are present in the same area as those drawn for the study area (see Fig. 6). There is, however, a slightly greater enrichment of Mg in the Vermont chlorites which suggests that the Whitefish Falls rocks are slightly lower grade than Albee's. This is represented by the extent of the chlorite field in figure 5. Fox (1971) studied the Agnew Lake area with respect to mineral assemblages. Although he had no actual mineral data he drew an AFM plot for the area. It is shown in figure 6b merely to give an idea of the chlorite-biotite tie lines as inferred for this area. The Agnew Lake area has been metamorphosed above the staurolite isograd. (Card 1964)

The ACF plot in figure 7 shows a compatible paragenesis for the argillites. The compositions fall into a very restrictive field. All the compositions fall below the almandine field so that it is excluded from the paragenesis. The presence of calcite, epidote and anorthite in plagioclase are suggested by the compositions. The proportion of FeO + MgO in the argillites explains why the relative abundances of epidote and calcite are low.

The AFK plot, figure 8, complements the ACF plot. Once again the almandine field is excluded from the para-



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genesis. The high FeO + MgO content results in biotite being a prominent phase in these rocks. The restricted composition of the argillites has inhibited the development of high grade index minerals.

Similar plots were made for the quartzites. The raw data for four of the samples are dubious due to the fact that no standard was available covering the SiO₂ range of greater than eighty-five percent. This resulted in false readings for these samples. With this in mind the following results are presented for the remaining three samples.

The AFM plot, figure 9, shows the paragenesis for the quartzites is compatible with that observed. The tie lines connecting kyanite with chloritoid enclose the quartzites' compositions and effectively inhibit the development of other minerals. The compositions indicate that staurolite could form if the metamorphic grade was high enough. There is no chemical restriction upon its formation. This lends added strength to the conclusion that the metamorphism was upper greenschist facies. The tie lines also suggest that much more chloritoid should be present than actually exists. From modal estimates of the quartzites, \cdot Table 1, there is always some iron tied up in phases like magnetite and hematite, where chloritoid is abundant. This tends to distort the analysis to show more chloritoid than there actually is present. The close association of chloritoid with magnetite and hematite in the thin sections makes

the distinction between the phases very difficult on the AFM plot.

The composition of the quartzites was not suitable for an ACF plot. This is to be expected in light of the fact that there was no calcium reported in any of the samples.

The AFK plot, figure 10, shows a mineral paragenesis of kyanite-chloritoid-muscovite-K-feldspar. This is acceptable since K-feldspar often is indicated by such plots when in fact there is none present. For the same reasons as mentioned above the amount of chloritoid indicated is greater than actually is present.





CONCLUSIONS:

. The above study has shown that the paradox between the high grade quartzite mineralogy and the apparently low grade mineralogy of the argillites can be explained by their bulk compositions. Chemical data supports the petrographic observations which determine the metamorphic grade. In the Whitefish Falls area the previous confusion surrounding the conditions of metamorphism can now be removed. The absence of pyrophyllite in the quartzites and the presence of kyanite sets a lower limit of 470°C and 3.9 kb. as outlined by Kerrick (1968). The presence of chloritoid in the quartzites coupled with the absence of staurolite indicates that the breakdown temperature of 550°C has not been reached, setting an upper limit on the temperature. The coexistence of kyanite with chlortoid indicates high pressure. The stability field of kyanite is certainly greater than 3.9kb and other studies from areas of similar mineralogy (Albee 1965) suggest that 10 kb. is not unreasonable as an upper pressure limit on the kyonite stability field.

There are certain chemical factors not previously discussed which have a bearing on the metamorphism. One such factor is oxygen fugacity. There is strong evidence that the quartzites were subjected to high oxygen fugacities whereas the argillites underwent low oxygen fugacity. In the quartzites the presence of magnetite and hematite indicate high f0₂ conditions. The effect of such high f0₂ promotes the thermal stability of chloritoid by 50-60°C. (Ganguly and Newton 1968). Thus it would have been possible for the temperatures to have entered the amphibolite facies without the breakdown of chloritoid. However to quote from Ganguly (1968): "Nevertheless, kyanites are found to be restricted to the highly oxidized rocks whereas the staurolites are mainly confined to the relatively less oxidized ones..... Thus we see that the isograds defined by the minerals above lose significance, in the sense that isograds are commonly understood, in the relatively oxidized paragenesis".

In the argillites pyrite is the stable opaque, which indicates a reducing environment. The presence of hematite in certain slides appears to be later oxidation associated with weathering. The low oxygen fugacity would inhibit the development of chloritoid and kyanite in the argillites. Also iron would remain in the silicate phase or combine with sulphur rather than form oxides.

Another chemical component not investigated was the partial pressure of water. As the grade of metamorphism proceeds, water is released and presumably moves out of the chemical system. A high pH_20 would generally lower the

temperature of reaction. There is little evidence; however, that such a high pH_2^0 existed in the quartzites. The presence of hydrated minerals such as muscovite is normal for the mineral paragenesis and metamorphic conditions. Likewise the argillites show little evidence for high pH_2^0 . The hydrated minerals, chlorite, biotite and muscovite are all stable under variable pH_2^0 conditions.

Kyanite is widespread throughout the Lorrain formation. It has been reported in many localites along the north shore of Lake Huron. (Chandler 1969). Its spatial distribution has not been studied with respect to metamorphic isograds in this area. Consequently there has been little work done on the drawing of isograds. The coexistence of kyanite and chloritoid is a rare assemblage as Albee (1965) noted. Its significance as an isograd has not been accurately ascertained. In light of Ganguly's statement regarding the effect of oxygen fugacity on these minerals it is doubtful that an isograd for the study area could be drawn.

The inhibition of "high grade" minerals in the argillites is a function of the bulk composition. All available aluminum in the rocks was combined in the plagioclase, muscovite, chlorite and biotite, which excluded the development of kyanite and chloritoid. The low calcium in all the samples indicates Ca minerals such as epidote would not develop extensively. In fact, as shown by the ACF plot

for the argillites the almandine field is excluded from the mineral paragenesis. This suggests that low-grade calcium minerals such as calcite would exist metastably in these assemblages.

Therefore, the study shows that the apparent incongruous mineral parageneses of the quartzites and argillites are in fact compatible within a single set of metamorphic conditions. In addition these conditions are comparable with the upper greenschist facies which match the metamorphic regimes determined in surrounding areas.

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