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Fractures and Fracture Fillings in the Guelph Formation, Steetley Quarry Flamborough, Ontario. Fractures and Fracture Filling

in the Guelph Formation,

Flamborough

by

Ian T. Campbell

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То

Janette

Abstract

The North Quarry (north of Ontario Highway 4) is located in Flamborough Ontario. In it, rocks of the Guelph formation are well exposed. The Guelph formation consists of dolomite and at the North Quarry has an average thickness of 30m. These rocks are cut by three predominant joint sets which have no indication of shear motion. The 030° set was formed as a result of compaction and loading; It appears to represent an upward joint propagation mirroring the Algonquin Arch trend. Joint sets 120° and 160° are a north western analogue to the conjugate pair described by Nickelson and Hough (1967) in the north eastern United States.

Vein data and sampled minerals, using techniques such as cathodoluminescence, photoluminescence, and isotope analysis enable paragenesis of joint propagation and crystallization relationships to be inferred. Possible stress field configurations have been deduced from these data. The joint set 030° was the first to open. Next, a minor east-west trending set opened. Joint sets 120° and 160° are the last to open. The joints were infilled by cement in the order of Organics > Calcite > Sulphides > Iron Oxides. Buckle heaves in the quarry were unreliable indicators of neotectonic stress.

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To Sensei Henry De Lima, who taught me 3 simple rules that helped me achieve my goals.

- 1. Always listen to and obey your Sensei.
- 2. Always do your best.
- 3. <u>Never, ever, give up</u>.

Table of Contents

Page

Abstract	iv
Acknowledgements	v
Table of Contents	vi
Background	1
Introduction	4
Fractures	9
Proposed Stress Configuration	13
Neotectonic Stress	17
Vein Fill	23
Cathodoluminescence	28
UV Photoluminescence	38
Isotopic Data	40
Conclusion	45
Appendix	49

Background

The geology of the north eastern United States and southern Ontario has been a point of interest for geologists for many years. Its complexity and mineral and petroleum potential has been the subject of many discussions, and has entertained geologists for over a hundred years. Besides academic interest in the regional geology, there have also been significant economic contributions. For example, some of the earliest oil was discovered at Petrolia. Also the large evaporite deposits have supported the chemical industry at Sarnia. The stratigraphy of the region is well documented but still can be a topic of argument. Structural geologists have noticed that folding and jointing (fabric) in the rock units changes as one travels from the Appalachians towards the Michigan basin. In the south east portions of New York, and Pensilvania, the rocks are folded and are extensively jointed. In north western New York state and southern western Ontario the joints are not as extensive, and there is no indication of folding. With the aid of Plate Tectonics the paragenesis of the regional fabric may be explained by the building of the Appalachian mountains.

A joint is a fracture in a body of rock for which there is little or relatively no movement along strike. Structural geologists use three mutually perpendicular stresses, σ_i (i=1,2,3), to account for the joint propagation. Conventionally $\sigma_1 > \sigma_2 > \sigma_3$, with compression being positive. Thus a purely dilational joint will have σ_3 perpendicular to the strike of the joint. In the purely dilational situation, σ_1 would then be along the strike of the joint while σ_2 would

1

be perpendicular to σ 1. Had the fracture not been dilational, but instead a compressional feature, stress in the same directional stress would possibly be represented by σ 1.

A joint interfering topographic feature in southern Ontario and north west portions of New York State is the Niagara Escarpment. It runs from Niagara northwest to Tobermory, with numerous embayments. In Ontario, one such embayment is the Dundas Valley. Joints and lineaments were found to increase in density closer to the Escarpment, and also changed orientation, (Gross, and Engelder, 1991).

For the purposes of this study, joints are any dilational fracture in a rock. Veins are mineral filled joints, and are a subset of joints.

Variables controlling the orientations of fractures are: Mechanical properties of the rock (competency), zones of weaknesses, and the stresses applied. Depth of burial, and bedding thickness have shown to control the orientation of the joints (Nickelson and Hough, 1967).

Several structural geologists have noted that there are more than one set of joints. Defining these sets and suggesting possible mechanisms of cause has been a concern of people such as Nickelson, Hough, Parker, Engelder, and Sandford. The strike of the joint sets is summarized in diagram 1.

2

Plotted Rose diagrams, for which the long axes represent the most predominant joint orientation, Display the regional joint trends. Data taken from: Parker(1942), Gross and Engelder (1986) and Daniel (1990).



Introduction

This study focuses on a quarry in Flamborough, Ontario (diagram 2). The site is quarry called North Quarry and is owned and operated by Steetley Quarry Products Inc. It is located north of Ontario highway 4. The closest site of published data is Dundas, which is a neighbouring town. The local stratigraphy is Lower to Middle Silurian (diagram 3). The unit from which all data were taken is the Guelph Formation. The Guelph formation is composed of dolomite and at the quarry, it has an average thickness of 30m.

At the time of data collection the quarry was active; As a result only a limited number of stations (5) was established (diagram 4). All sites were located above the quarry floor and as far as possible from the faces so that blasting, and truck induced fracture noise would be minimal.

Sites 2 and 3 were located along faces at which active mining was occurring. Due to slight ground cover at stations 1, 2, and 3, measurements had to be taken close to the rock face and some traverses extended 20m away from the wall. Each station had little or no overburden and could be seen easily.

Measurements of azimuths, and joint spacing were taken by traversing across the outcrop. Using a tape laid perpendicular to the average strike of the joint set of interest, intersecting joints were measured. Also, whenever possible vein-filling materials were noted. In total 438 joints were measured.

The goal of this work is to add data to the regional joint picture, to suggest stress field configurations, and to discuss qualitatively the joint set propagation and vein-

<u>4</u>

filling historical relationships.

Road Map describing the site location.



The local Stratigraphy (Lower-Middle Silurian)

Gueiph ERAMOSA VINEMOUNT MIDDLE SILURIAN GOAT ISLAND GASPORT ROCHESTER IRONDEQUOIT REYNALES THOROLD --GRIMSBY LOWER SILURIAN CABOT HEAD MANITOULIN WHIRLPOOL QUEENSTON ORD E



Map of the North Quarry (not to scale), with the station locations.



Fractures

Measured data are presented in the form of rose diagrams for each station. A class interval of 5 degrees (diagram 5) has been used throughout. Individual station joint populations were also noted.

Expected increases of variations in joint azimuths due to blasting procedures has not been seen. Only in the immediate vicinity (radius of 2m) of the centers where charges had been set off are there visible arcuate joint patterns.

Throughout the entire study area vertical stylolites were not seen; Thus there is no evidence of horizontal directed compression.

3 joint sets (A,B,C) have been recognised. The strike of set A ranges from 025° to 040°, and has a mean orientation of 030°. While a second set, B, the strike ranges from 110° to 125°, and has a mean orientation of 120°. The third joint set, C, the strike ranges from 155° to 165° and has a mean orientation of 160°. There are minor areal variations of orientations of 5° for these sets. In addition stations 3 and 4, have minor east-west trending joint sets.

There may be some bias in the observations/measurements of joint sets very close to the quarry walls. Joint sets sub-parallel to a wall tend to be more obvious, and to be preferentially noted; Joint sets (and veins) at high angles to the local wall are less obvious, even suppressed. For example, along the face for which site 1 was measured, joint sets A and C, the most North South orientated joint sets are clearly predominant; the quarry wall runs north-south. Only in thin section were other joint and vein sets visible (<u>Cathodoluminescence</u>). Along the

<u>9</u>

south wall near site 5, joint set B, the most east-west joint set, is predominant; the south wall runs east-west. While sampling vein fill minerals from the base and top of the quarry faces, the joint bias was also noticeable. It was only after the samples had been cut one could see other joints and vein filling minerals.

The correlation of sets A and B is very consistent from station to station. This enabled the drawing of a grid like map representing the predominant joints across the entire quarry (diagram 6); note spacing is not representative of actual joint spacing.

The geometry of the quarry, and its somewhat rectangular shape suggests that the rocks have broken along each face in a manner such that the two predominant joint sets (A, and C) would yield the maximum stone quantity per blast. Note the most western quarry wall varies where there are measurable variations and additional east-west trending joint sets (primarily the south west wall).

Rose diagrams plotted for each station measured. Each petal is a percentage of the population.



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A grid representing the two most consistent joint trends. The map (not to scale) does not infer any joint spacing.



Proposed Stress Configuration

A compilation of all joint and vein data has been represented in a single rose diagram, (diagram 7). The minor variations noted previously in the individual stations are now very small. Also the mean of the three joint sets A, B, and C, can now be better resolved as 030°, 125°, and 154°.

Since all 3 joints sets are purely dilational in nature, there can be no single mechanism responsible for their origin. Instead, it is proposed that set A was formed at a completely different time than sets B and C.

Joint set A does not conform to any joint trend of the region in the literature. Therefore one must consider other possible explanations for joint propagation. It is possible that, during the loading and lithification processes, joints of set A were formed as a result of mirroring the Precambrian basement rock. This implies that the initiation of joint set A predates joint sets B and C. Also, joint set A may have grown over time as more sediments were deposited.

The Algonquin Arch (diagram 8), can be described roughly, as having an axis orientation of 30°, which matches the strike of set A. It is reasonable to assume that after the sedimentation and during lithification and dewatering stages, joints would have propagated upwards that mirrored the Algonquin Arch orientation simply by "draping" and compacting the sediment over the Arch, thus overloading and causing failure. Hydrostatic forces from dewatering of the sediments could have aided in the joint formation by acting to reduce the effective stress.

A wide ranging survey by Parker (1942) of joints in coal, shale, and

<u>13</u>

sandstone, in the north eastern United States led to his recognition of three primary joint sets (I,II,III). He labelled joint set II as systematic, and joint set I as nonsystematic, both of which had been described previously as wrench faults (Ashley, 1928), sinistral (II) or dextral (I). The "dextral" set has an orientation of N68°W (112°), while the "sinistral" set has an orientation of N34°W (146°). Together they have been seen as a conjugate pair, implying a σ 1 orientation of N50°W (130°). Nickelson and Hough (1967) reported the two joint sets as rotating about the fold axes at the Alleghanian Front; as the fold axes changed orientation, set II maintained a roughly perpendicular orientation to those fold axes. These faults have been interpreted Early Pennsylvanian in age, and are the result of the late stage Appalachian mountain building (Nickleson, and Hough, 1967).

Joint sets B and C can be seen as an south western Ontario "analog" of the conjugate fault set described by Nickelson and Hough (1967). Invoking the same mechanism as that described for the conjugate pair of faults, the propagation of joint sets B and C can be rationalised. The distance from the Houtzdale quadrangle (approximately 100 Km N.E of Pitsburgh) to the North Quarry is well over 600 Km. Over such a distance the principle force must have attenuated significantly such that only a dilation was possible, without any movement along strike.

<u>14</u>

Rose diagram for all fractures in the North Quarry. Each petal is a percentage of the total population.



NORTH QUARRY

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A map of the Precambrian basement rock. Note the trend of the Algonquin Arch (30°). The * represents the site location.

Precambrian Basement



Neotectonic Stress

Neotectonic stress is a term structural geologists use to describe modern (post Miocene) stress. Overcoring and strain gauge measurements are commonly used to determine the azimuth of neotectonic stress. Buckle releases, here termed popups, have also been used as a natural indicator of recent stress release. Popups are formed when removal of overlying material allows the elastic strain energy, stored in the rock, either from neotectonic or a residual source to be released in a vertical fashion. Likewise, true popups that are formed during ice removal (glacial rebound) have been used to indicate recent stress (diagram 9). The stored elastic energy also may be responsible for the "pushing" of blocks from the face of the wall and into the quarry (Gross, and Engelder, 1991).

Popup remnants were found in the northern most parts of the quarry (Plates 1,2). Because the quarry is presently active most of these were found crushed (Plate 2). However, along the northeastern portion of the North Quarry, relatively untouched (virgin) popups (Plate 1) were measured. The azimuth of each section of popup was measured (diagram 10) along with lengths. The average orientation is roughly 30°. This implies a σ 1 orientation of 120°. The azimuths of different sections seem to have been controlled by the position of the popups relative to the quarry wall. The closer the buckles are to the walls the more azimuths seem to vary. The southern most portion of the popups continued for 80m in the 30° orientation before it deviated significantly. One section of the major popup noticed was found in a seemingly virgin form (Plate 3). Three

<u>17</u>

traverses (diagram 10), were taken across the popups. The calculated average maximum shortening was 1.36% over the measured length. However this value is a gross overestimate for the quarry by a factor of 40, since the lengths measured were no more than 10m, while the buckles probably represent a shortening across the entire quarry (approximately 400Km). Thus the percentage shortening is 0.03% or less.

Comparing North Quarry values of azimuths for the popups to those reported in Port Colborne (Williams, Corkey, and Lorek, 1984), there is a 90° difference. The buckles reported by those authors, were characteristically long with little variation in azimuth, and had an average orientation of 140°. This implies a σ 1 orientation of 050°. They also reported a buckle set that had an én echelon form. Other measurements of neotectonic stress have been synthesized and recorded by Engelder (1982) in New York and N.E. parts of Pennsylvania. These measurements were derived from overcoring. The data presented show a very strong argument for a σ 1 orientation of 068°.

The data in the North Quarry was taken primarily from one popup and the majority of line elements were not measurable due to quarry operations. The variations between the data found at the North Quarry, and data from Port Colborne (Williams, Corkey, and Lorek, 1984) and New York (Engelder, 1982) and from other glacial popup and buckle heaves reported by Daniel (1990) in southern Ontario, cannot be explained (diagram 9). This may suggest that the buckle releases may in fact not be a reasonable indicator of regional neotectonic stress.

<u>18</u>

Lines representing the strike of σ 1 (Neotectonic stress). The data was taken from Parker (1942), Gross and Engelder (1991), and Daniel (1990).


Long and relatively untouched popups in the north eastern portion of the quarry.

Plate 2

A popup that has been crushed by quarry practises.





A virgin popup, for which percentage shortening was calculated.

Plate 9

An east-west fracture, for which 20° fractures can be seen abutting against, and not cross cutting. Therefore the 90° fracture must predate the 20° set.





diagram 10

A map of the popups found in the north eastern portion of the quarry. The lines represent measured lengths and strike. Vertical cross sections of traverses a, b, and c. Collected data was used to calculate the percentage shortening.



Vein Fill

The majority of joints noted in the field were not filled with any cement. Only a very small proportion of those that were recorded as containing vein fill were completely filled. Quite often a only smear of minerals were noticed along the joint surfaces. In all cases cited the cements grew inwards to fill the joints.

Only four mineral fill types (organics (Bitumen), calcite, galena (sulphides), and iron oxides) were seen. Composite rose diagrams were also made for veins of specific minerals for the entire quarry (diagrams 11,12,13,14). There respective populations and class intervals were also reported.

Assuming an open plumbing system at the time of vein filling it is possible to infer a vein filling history.

The organic rose diagram (diagram 11), when compared to the others, has the largest percentage of fill for any one particular joint set, namely the 160° joint set (36%). Calcite mineral fill (diagram 12) has a very wide range of orientations which clearly show that calcite exploited all possible joints. The 160° calcite vein set is 15% smaller in proportion than that represented by the organics. Also the 160° vein set is 5% smaller in the galena (sulphides) (diagram 13) cement, and even smaller in the iron oxides (diagram 14) (4% smaller, an almost negligible amount (6%)).

The strike of 20° calcite vein set is very poorly defined. However the rose diagrams representing galena (sulphides), and iron oxides, have very well defined strikes of all veins. The strike of the iron oxides vein sets are very well defined.

<u>23</u>

The 20° vein set is the most predominant set in all the rose diagrams. This might suggest that the 20° joint set is the most consistent joint set throughout the entire quarry (Fractures).

Trends such as the reduction in the percentage of mineral fill in vein sets (ie 160°), and the increasing strike definition of the 20° vein set, as one proceeds from the organics precipitation to the iron oxides, suggest a distinguishable loss of joint space, due to vein filling. Therefore a possible vein filling order can be interpreted: Organics>calcite>galena (sulphides)>iron oxides.

A 90° vein set is seen in the organics, and calcite rose diagram. However it is absent in the galena rose diagram, but crops up again in the iron oxide diagram. This trend can not be accounted for on the basis of the data set collected. However it is possible that crystal forming fluids could have had different temperatures for different joint sets, and thus the kinetics would have prohibited the sulphide ore deposition. It is also possible that the minor joint set trending east-west during the time of crystallization was preferentially exposed to the atmosphere or oxidizing meteoric waters such that the sulphides would not have crystallized from solution.

Chemically speaking, a vein filling paragenesis presented above is also reasonable since organics, and sulphides such as sphalerite, and galena would need a reduced environment to precipitate (Mason, and Moore, 1966), while the iron oxides would need an oxygenating environment to precipitate.

Reduced connate water carrying organics (petroleum) (Mostaghel, 1983)

<u>24</u>

and metal chloride complexes rose to the surface and filled veins below the water table before all other vein filling activity (for a more detail discussion see <u>Cathodoluminescence</u> and <u>Isotopic Data</u>). This seems plausible since petroleum would separate from the water column while migrating outward and upward from the Appalachian basin (Mostaghel,1983) and be deposited first since it is less dense than other substances.

diagram 14

Rose diagram (percentage values) of <u>Iron Oxide</u> Precipitation. Note the well defined strikes when compared to calcite (diagram 12).

diagram 11

Rose diagram (percentage values) representing the trends of <u>Organic</u>, precipitation. Note the very large (36%) 160° precipitated trend.



Class Interval	 5	Degrees
Population	 -5	2

Class Ir	nterval	. 10 Degrees
Populati	on	. 14

diagram 13

Rose diagram representing the <u>Sulphide</u> mineral (primarily Galena) precipitation (each petal is a percentage value).

diagram 12

Rose diagram representing <u>Calcite</u> precipitation. Note all possible directions were exploited. Also the strikes of the veins are highly variable and not well defined. (each petal plotted is a percentage value).



Calcite



Population	45	
Class Interval	10	Degrees

Cathodoluminescence

Cathodoluminescence is a multipurpose technique. Some of its common uses include guick identification of minerals and vein fill purposes. In addition, cement paragenetic chemistry changes can be seen and some of their trace elements identified. In basic theory an electron beam passes through a vacuum chamber and is then redirected 90° and focused to a spot on the surface of the specimen. The electrons then are either absorbed or promote luminesce. When a mineral luminesces, it is quite often identifiable by its characteristic glow intensity and color. For example, calcite, CaCO₃, will luminesce a bright yellow, while dolomite, (Ca,Mg)CO₃, will luminesce a dull red. It is the minor constituents in crystal lattice that are often responsible for the intensity of the luminescence. Cations known as 'quenchers', such as Fe⁺², Mg⁺², Pb⁺², and Ni⁺², absorb the electrons. Others such as Mn⁺² are known to be responsible for a specific luminescence; these are called 'activators'. The ratio of activators/guenchers, such as Mn⁺²/Fe⁺² in dolomite and calcite, determines the intensity (diagram 15). Some authors have reported relative compositions of Mn⁺², and Fe⁺² based on intensity values (diagram 16).

For the purpose of this study, cathodoluminescence has been used as a simple petrological tool. Its main function was to aid in distinguishing between calcite and dolomite. Coupled with regular optical methods, it has enabled the identification of microfractures not seen in the face sampled (Plate 4). Cathodoluminescence also has enabled the identification of vein fill material.

<u>28</u>

A paragenetic interpretation that might otherwise have been misinterpreted was clearly seen properly using cathodoluminescence. A hand specimen containing the 90° vein set appears to show two different generations of vein crystal growth (cementation). A rusty iron stained mass appears to have been the first generation of vein crystal growth since it is the closest one to the host rock. The second layer of crystal growth appears to be calcite (perfect crystals) (Plate 5), since it is seen as the closest of the two growing towards the center of the joint. In thin section, this appears to be the case also, and one might conclude that the calcite layer was the later of the two cements. However, the cathodoluminescence shows that a darker (quenched) layer (Plate 6), composed of iron oxides surrounds many calcite crystals. This implies that the iron oxide vein fill was younger than the calcite.

In all three vein sets sampled (20°,90°,120°), the calcite of the vein fill, and the vugs displays a bright outer luminescent overgrowth (Plates 7,8). This suggests a change in the pore fluid chemistry. Because the 3 vein sets have similar changes luminescent characteristics, differences in pore fluid chemistry between the veins cannot be inferred. Therefore a joint hierarchy can not be interpreted.

In hand specimen, it is clear that galena was precipitated along each of the major joint sets. As mentioned previously, Pb^{+2} is a quencher, and the substitution for Ca⁺² in the calcite lattice would inhibit the luminescence of the calcite. Reduction of the pore fluids perhaps by addition of H₂S to them would have

<u>29</u>

removed the Pb⁺² from the pre calcite fluids and reprecipitated it as galena in the following manner.

$$SO_4^{-2}$$
+ $CH_4 \rightarrow H_2S + CO_2$
 H_2S + MeCI(complexes) \rightarrow PbS (galena) + H_2CI
 CO_2 + CaO \rightarrow CaCO₃ (calcite)

Thus with the addition of H_2S the removal of ferrous Fe⁺², and Pb⁺² from the pore fluid permits the luminescence of the crystals. This argument suggests that the sulphides were precipitated before the calcite. However if the kinetics of the pore fluids were favourable before the introduction of the connate water, calcite would have precipitated (Vein Fill).

It has been argued (Mostaghel, 1983) that the connate water carried petroleum products. He suggests that the depth of burial, 2.4 km, for the source rocks in the Appalachian basin, was not deep enough for the leaching of heavy metals to contribute to the formation of the sulphides. However it can be shown that 2.4 km is certainly deep enough to remove the metals (Kennedy, and Newton, 1963).

There must have been two fluids mixing, since one would have to be reducing (ie connate water carrying CH_4 or CHO_2) and the of atmospheric origin carrying SO_4^{-2} . Of course it is possible that sulfur reducing bacteria were abundant in the pore fluids, so that when the deep water carrying petroleum and metal chloride (Mostaghel, 1983) complexes met sulfur was abundant.

Simple wet chemical tests were completed, for mineral identification. Hand

specimens representing the three joint sets $(20^\circ, 90^\circ, 120^\circ)$ were crushed and digested in nitric acid. A yellow precipitate indicative of sulfur was found at the bottom of each rock sample after the acid digestion. The solutions were decanted and then were treated with Na₂S to precipitate characteristic colours indicative certain ions. Each specimen tested had the same results.

HNO₃ + Na₂S + sample:
$$\rightarrow$$
 Rusty Red (Fe⁺²)
 \rightarrow Cloudy white (Zn⁺²)
 \rightarrow Black (Pb⁺²)

Together these aid in the identification of the sulphides (sphalerite and galena) as well as iron oxides.

diagram 15

The relationship between the Mn and Fe contents and the luminescence intensity of dolomites. Borrowed from SEPM Short Course No.10. (Originally from Fairchild 1983.)

diagram 16

The relationship between Mn and Fe percentages accounting for the dull luminescence resulting from inhomogeneous chemistry.







4A was taken under cross polars (20X). Using cathodoluminescence, 4B, the micro vein fill (a) can be identified as calcite, while the majority of the matrix can be identified as dolomite.



A

B

5A and 5B show perfect calcite rhombohedrons, which show no evidence of shear. 5A was collected in the North Quarry. 5B was collected in a Quarry south of Ontario highway 5 (donated by Steetley Quarry). Both samples represent the east-west (90°) trending vein.



5A



5B

6A shows a thin section, under cathodoluminescence (20X) that was cut perpendicular to an east-west trending vein. The darker (a) portion is the matrix (dolomite). The lighter (more luminescent) portions are calcite (b, and d). The dark vein running through the center (c) is iron oxide.

6B was taken under normal light (50X). The areas marked (b) are calcite, while (a) is dolomite. The large crystal marked (b) can be immediately seen below (d) in 6A.

6C shows a close up view (100X) of the crystal marked (b) in 6B. It is surrounded by iron oxide. Therefore the iron oxide post dates the calcite in this particular case.



6A



7A shows a thin section primarily composed of matrix dolomite, taken under cross polars (20X). There are a few euhedral crystals (ie a). However the majority of the matrix is indistinguishable.

7B was taken using cathodoluminescence. Vug lined crystals (ie a) have a bright luminescent syntaxial overgrowths (calcite). Although it is difficult to see in black and white photography, the cements luminesce brighter towards the center of the vugs (b). This represents a mineralogical change, either due to the loss of quenching metals or the accumulation of Mn.



7A

7B

Photographs 8A and 8B, show a thin section cut perpendicular to the intersection of a 20° vein marked (a) in 8A and a 120° vein marked (b) in 8A. The magnification was 20x. Using cathodoluminescence (8B), both vein cements were seen as identical in composition. The luminescence of the cement increases towards the fracture. This represents a change in mineralogy towards the latest cementation event.



8A

8B

UV Photoluminescence

Steetley Quarry donated a very large mass of well formed calcite crystals, reported to have been from the 90° vein set, sampled from a Quarry south of highway 5. Their large size (approximately 7 cm) and transparency enabled testing by photoluminescence.

Using an ordinary UV source and a transparent crystal, one can use photoluminescence to aid in the identification of minerals and their trace elements in a very manner similar to <u>cathodoluminescence</u>. Instead of exciting the crystal surface the UV radiation passes through the entire crystal and produces a characteristic glow. With the help and expertise of D. Shopov, I conducted a simple flash test. A single crystal of calcite was placed on top of a flash, in a dark room, and the flash was then set off. The color and glow was then noted. The crystal glowed a bright red and then a moderate green. According to Shopov, the red glow is due to Mn⁺². According to theoretical studies, Mn⁺² does not luminescence on its own, but it does luminescence in the presence of Pb^{+2} . The Pb⁺² is a strong absorber of UV radiation; it also donates electrons when in the presence of UV. The Pb⁺² ions are responsible for excitement of the Mn⁺², indicated by the bright red glow, by donation of electrons since both of these ions would occupy the similar lattice positions. The moderate green glow, (according to Shopov), is the result of the presence of residual organic materials. Thus the pore water temperature could not have been any greater than 200°; otherwise the organics would have decomposed. Based on the crystal morphology and

<u>38</u>

photoluminescence intensity, the pore forming water could not have been less than 60° [Shopov, p.c.]. Dr. Shopov estimated the pore water temperature, based on this evidence, was approximately 150°.

Isotopic Data

Calcite was taken from 2 hand specimens representing the three vein sets previously discussed. Carbon and oxygen isotope ratios were calculated on the PDP scale. In theory one should be able to infer a temperature or chemical difference in the pore forming fluids if one joint set has larger or smaller values of δO^{18} and δC^{13} than another. With the addition of data from outcrop, handspecimens, and petrographic evidence one may be able to reconstruct the historical relationships of the joint/vein sets. Assuming a constant pore fluid bulk chemistry of different fluids, different δO^{18} values indicate a temperature difference between fluids. Relatively high values of δO^{18} are a result of isotopic fractionation, and loss of O¹⁶ relative to O¹⁸ due to cooling, since it is kinetically favourable to incorporate the less vibrational isotope into the lattice positions which is the heavier of the two (SEPM Short Course No.10, 1983). On the other hand, differences in δC^{13} values indicate a chemical difference if the temperatures are assumed constant. For example, large positive values of δC^{13} (2 PDP) are characteristic of atmospheric carbon due to loss of C¹².

The three joint/vein sets clearly are not uniform in isotopic composition (diagram 17). Joint sets (A and B) 20°, and 120° have very similar ratios for oxygen and carbon and thus no distinction can be made between these two on that basis. This suggests that these joints formed in a connected plumbing system. However, the 90° joint set has very much lower δC^{13} values when compared to the other two. In addition, the δO^{18} values are <u>slightly</u> lower than

<u>40</u>

those of the other two joint sets. The different oxygen isotope values indicate a slightly lower pore fluid temperature of no greater than 8° (SEPM Short Course No.10,1983). However the δC^{13} values of the 90° set are sharply different from those of the 20°, and 120° vein sets. The large negative values, (-25 PDP) indicate a methane source. The large positive δC^{13} values (0.5 PDP) of joint sets 20°, and 120° are likely the result of atmospheric carbon in the fluids. Gross, Engelder, Gross, and Poulson (1992) have reported values of δO^{18} (diagram 17) that spanned the range at Steetley Quarry. They found large negative values of δC^{13} (ie -16 PDP), along the north eastern United States (southern portions of Lake Ontario) and one in Dundas (see diagram).

Methane can not form in the presence of oxygen and it needs relatively high temperatures to form. Thus, the non-oxygenated (connate) waters that carried the methane must have come from a fairly deep source. This water would have risen to the near-surface and there, in contact with atmospheric waters, precipitated calcite.

 $CH_4 + O_2 \rightarrow CO_2 + H_2O$ $CO_2 + H_2O \rightarrow H^+ + HCO_3^ OH^- + HCO_3^- + Ca \rightarrow CaCO_3 + H_2O$

This would account for the extremely low δO^{18} values found in the 90° vein set.

As noted before, the bulk pore fluid chemistry for the three veins sets is identical and can not be differentiated using cathodoluminescence or wet chemistry techniques. However the isotopic values of carbon and oxygen can readily distinguish the 90° vein set from the 20°, and 120° vein set. These data, in combination with other observations, enable a possible paragenesis to be discussed.

Initially the rock units in the region were primarily $(CaCO_3)$ limestone. Then a massive flooding occurred to dolomitize the limestone by removing some of the Ca^{+2} and replacing it with Mg^{+2} . Sometime later a tensional stress regime succeeded in forming the 90° joint set. Next a deep water possibly carrying methane (reducing environment) rose to the surface and met with meteoric water (previously discussed) to precipitate calcite cement. The later pore fluids could have been from the same source, or could have migrated from a different source a latter time. If the fluids responsible for the hematite and galena were of the same source then H₂S could have been introduced to the system to preferentially remove the iron and lead out of solution to produce galena, and sphalerite, and through later oxidization processes, iron oxides. The evidence supporting the iron oxide postdating the calcite vein fill was seen in thin section (Vein Fill, Cathodoluminescence). Next the predominant joint sets 20° and 120° could have opened synchronously or at different times. Evidence supporting the proposition that the joint set 20° is younger than 90° can be seen in the outcrop (Plate 9). The 20° joints are seen abutting against the 90° joint and are not seen to have continued across it. Along the 90° set there is no evidence for shearing in thin section or in hand specimen. In fact, the dilation for some fractures was so large

<u>42</u>

it permitted the growth of perfect, non-directional calcite crystals (Plate 5). Since the chemical, petrological, and isotope data suggest the possibility of the same fluid migrating through the joint sets 20° and 120° it is likely that an open plumbing system existed after the vein crystallization of the joint set 90°. The sulphides (galena, sphalerite), are likely to have formed in a similar manner to those of the 90° vein set. That is, they could have arrived from the same pore fluid as the calcite, but at a later stage through the introduction of a reducing fluid to precipitate the mineral sulphides. Evidence for galena being a late stage mineral comes from hand specimen and thin section where it was found overlying the calcite.
diagram 17

Delta carbon 13, and oxygen 18, values are plotted against their respective orientations.

Note the joined circles (Gross, and Engelder, 1992) the large represents the span of carbon values previously reported, and the smaller represents the span of oxygen values previously reported.

22° and 120° veins have similar values, and thus can be considered the result of the same fluids.

However the 90° vein has very low carbon values, which are characteristic of methane carrying waters. This implies the 90° vein filling may have occured at a different time than the other two.





Conclusion

Using a Precambrian basement map of the region, the propagation of the 30° joint set can be related to the Algonquin Arch. The 30° joint set was the first to open, and continued to open as more sediment were deposited. A minor 90° joint set (Vein Fill, Isotopic Data) which does not appear in the composite joint rose diagram, was the next to propagate. Isotopic data of the 90° vein fill material distinguish it from the 120° and 160° veins. Thus suggesting that there may not have been an open pluming system at the time of crystallization. The isotopic data also show δC^{13} values that are characteristic of methane carrying fluids. Gross,Engelder, and Poulson (1992) also report very light δC^{13} values but failed to mention that they are a result of methane. The discovery of the characteristic signature of methane in the calcite crystals, can enable one to date the methane in the Silurian of the region using U/Pb ratio methods (Smith, Farquhar, and Hancock, 1991).

The joints, 120°, and 160°, can be related to the late stages of Appalachia mountain building, and are "analogous" to the conjugate fault set reported by Nickelson, and Hough (1967).

It is important to note that the observations and conclusions drawn may only be reliable for the Silurian units found in North Quarry, since with depth the strikes of the joints may differ (Nickelson, and Hough , 1967).

To properly define the strike of the neotectonic stress a reliable method such as overcoring should be employed.

<u>45</u>

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Appendix

Field Data

1			5	;			4				3	3			2		
EW			SSW11el				SSW2tel				NNW1			NWW2			
dist 0 59	orie 121.5 124.5	Lor Min 35 2	dist 0 203	orie 118.5 118.5	Lor 31	Min	dist 0 77	orie 29.5 34.5	Lor 116	Min	dist 0 5	orie 35.1 39.1	Lor Min 1172	dist 0 815	orie 114.5 98.5	Lor 25	Min 3
152 329 0	123.5 336.5 213.5	2,3 124	215 485 570	139.5 114.5 110.5		2	126 223 300	28.5 34.5 23.5		1 1	9 26 33	36.1 28.1 163.1		1095 1250 0	119.5 117.5 113.5	26	2,3 3
55 83 173	208.5 35.5 36.5	2	610 740 791	121.5 122.5 123.5		2	363 426 458	31 26.5 36.5		1	41 45 58	22.1 155.1 153.1	1,2	49 79 82	114.5 118.5 138.5		3
0 98 155 279	33.5 31.5 34.5 29.5	122	825 875 935 972	120.5 121.5 114.5 121.5		2	470 560 685 748	23.5 24.5 28.5 33.5		,	64 75 79 86	150.1 20.1 162.1 35.1	1	85 94 105 119	121.5 120.5 119.5 123.5		2,3 2,3 3
375 482 560	32.5 39.5 32.5		990 1025 1090	123.5 128.5 110.5			777 802 861	31.5 31.5 163.5		1	86.1 96 103	34.1 38.1 155.1	1 2 1	129 139 151	111.5 101.5 139.5		
673 703 0	31.5 31.5 133.5	42	1162 1232 1330	111.5 122.5 94.5		1 1,2	868 920 931	29.5 29.5 23.5		1	125 155 169	98.1 44,1 34.1	1,3	275 300 310	116.5 109.5 119.5		3 2,3
295 450 0	141.5 119.5 124.5 36.5	3 126	1420 1480 1561 1605	118.5 129.5 63.5			963 1011 1002	27.5 28.5 36.5 154.5			181 202 210	35.1 34.1 169.1		335 410 436	125.5 118.5 128.5		2 3
62 120 245	35.5 31.5 28.5		1625 1701 1749	96.5 99.5 125.5		1,2 1	1036 1047 1068	28.5 34.5 29.5			226 231 237	33.1 29.1 54.1	1	0 60 110	22.5 28.5 41.5	113	3 2,3
355 392 502 643	33.5 33.5 29.5 31.5		1780 1815 1847 1875	43.5 42.5 101.5 109.5			1084 1147 1217 1212	27.5 24 21.5 23.5			249 254 256 274	30.1 39.1 32.1 33.1		135 138 142 154	53.5 28.5 26.5 28.5		3 3
323 0 200	29.5 135.5 126.5	47	2027 2056 2090	110.5 97.5 105.5		1	1245 1310 1317 1349	134.5 18.5 28.5			278 290 325	36.1 23.1 34.1		168 170 181	39.5 60.5 29.5		2,3
0 100 220	36.5 35.5 37.5	123 3	2179 2202 2260	107.5 139.5 109.5		2	1355 1358 0	31.5 27.5 128.5	39		360 369 382	29.1 12.1 37.1	١	200 201 210	53.5 23.5 33.5		2,3
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161 180 244 378	114.5 148.5 149.5	3	2566 2595 0 35	108.5 116.5 29.5	119	1	340 343 352 365	110.5 31.5 33.5 27.5			472 495 504 521	25.5 178.5 148.5 33.5		298 300 309 315	425 27.5 166 325		2,3 2,3
445 520 630	152.5 151.5 183.5		60 80 129	30.5 358.5 32.5		., <u>د</u> ۱	370 382 443	25.5 127.5 102.5			535 545 564	140.5 162.5 43.5		320 324 337	51.5 28.5 23.5		
0 92 190	132.5 127.5 143.5	45 3	166 200 219	31.5 33.5 32.5		1	470 488 512	112.5 153.5 133.5		2	567 590 615	168.5 33.5 35.5	12	344 356 0	31.5 28.5 66.5	121	3 3
290 418	126.5	3	2/6 340	23.5		1	531	29.5 121.5			631	25.5	2	254	29.5		

EW					SSW1tel				SSW2tei				NNW1				NWW2			
	dist	orie	Lot	Min	dist	orie	Lor	Min	dist	orie	Lor	Min	dist	orie	Lor	Min	dist	orie	Lor	Min
					381	26.5			561	116.5			644	156.5		1,2	353	33.5		
					429	30.5		1	586	34.5			655	13.5			383	58.5		
					470	26.5			598	34.5			670	31.5			488	43.5		
					489	29.5			630	117.5			702	28.5			670	27.5		
					588	29.5		1,2	636	28.5			724	25.5			1098	29.5		
					609	25.5			642	118.5			770	38.5						
					635	31.5		1	658	95.5			799	43.5			179	19.5	103	
					685	33.5			657	28.5			800	29.5			91	23.5		
					731	24.5			689	36.5			840	45.5			325	34.5		
					778	19.5			710	121.5			860	24.5			249	34.5		
					799	42.5			696	153.5			923	28.5			430	27.5		
					877	27.5			721	33.5			945	29.5			487	38.5		
					898	29.5			742	155.5			0	129.5	34		537	24.5		
					921	28.5			769	151.5			30	130.5		2	1241	27.5		
					979	32.5			858	117.5			100	127.5			1590	29.5		
					990	31.5		1	930	22.5			121	133.5						
					1055	28.5			956	21.5			207	123.5						
					1116	30.5			960	21.5			222	108.5						
					1177	32.5			970	24.5			229	142.5						
					1255	31.5			0	29.5	111		250	141.5						
					1304	32.5			81	29.5			280	123.5		1,2				
					1355	30.5		1	92	37.5			291	161.5						
					1401	29.5			107	39.5		3	328	156.5						
					1442	31.5		1	114	36.5			340	124.5		2				
					1483	35.5			131	35.5			362	159.5						
					1496	32.5			197	37.5			381	157.5						
					1576	27.5			207	33.5		1,4	525	119.5						
					1594	31.5		2	228	31.5		1,4	540	125.5						
					1637	38.5			237	29.5		1,4	575	118.5						
					1720	32.5			247	27.5		1,4	596	156.5		2				
					1933	25.5			302	23.5			646	100.5						
					1951	25.5			331	29.5			706	112.5						
					1978	33.5			356	151.5			770	106.5						
					2028	29.5		1	365	154.5		4	779	124.5		1,2				
					2036	35.5			405	148.5		4	791	129.5						
					2066	29.5			427	22.5		1	795	132.5						
					2080	30.5			431	32.5		4	815	123.5						
					2092	38.5			443	150.5		1,4								
					2114	28.5			0	121.5	30									
					2138	38.5			35	106.5										
					2165	29.5			50	99.5		1,4								
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					530	1125			210	141.2		•								
					1100	112.0														
					2315	115.5	124	1,2												
					422	36.3	124	•												
					420	20.0														
					1000	33.5														
					2010	28.5		•												
					2080	19.0														
					2200	31.5														
					1615	29.0														

Isotope Data

Vein	(dC13	dO18	
2	3	0.994	-5.681	+/- 0.1 PDP
2	3	1.128	-5.837	+/- 0.1 PDP
2	3	1.058	-5.978	+/- 0.1 PDP
9	0	-13.715	-7.166	+/- 0.1 PDP
9	0	-15.216	-7.283	+/- 0.1 PDP
9	0	-14.458	-7.292	+/- 0.1 PDP
12	0	0.815	-5.955	+/- 0.1 PDP
12	0	0.392	-5.768	+/- 0.1 PDP
12	0	0.072	-6.713	+/- 0.1 PDP
9	5	-25.184	-7.262	+/- 0.1 PDP
9	5	-21.295	-7.128	+/- 0.1 PDP
9	5	-24.847	-7.307	+/- 0.1 PDP