Geochemistry of Garnet Xenocrysts and Garnet-bearing Xenoliths in Ordovician Bentonites

Abstract of
a thesis presented to the Faculty
of the State University of New York
at Albany
in partial fulfillment of the requirements
for the degree of
Master of Science
School of Science and Mathematics
Department of Geological Sciences

Barbara Bock

1990

Abstract

Within outcrops of the black Utica shales south of the Mohawk Valley narrow reentrants parallel with stratification are visible, often accompanied by a marked orange-staining of the underlying strata. These rentrant features indicate the presence of bentonites weathered back faster then the enclosing shales. These bentonites are presumably magmatic ashes related to extensive volcanism when an island arc collided with the North American continent in the late Ordovician about 450 million years ago (Taconic orogeny).

Bentonites are good stratigraphic markers because of the short time-interval they represent and the large area they cover. Therefore they are commonly used as correlation tools. In this study an attempt was made to use the minerals (i.e. garnets) as a correlation tool in contrast to earlier attempts to correlate bentonites by chemical fingerprinting using bulk chemistry (Huff, 1986; Kolata et al., 1986, 1987).

The mineral content of these bentonites was separated and analyzed. In this study special attention was paid to the garnets and garnet-bearing rock fragments. The garnets were analyzed using an electron microprobe for major elements and trace elements, i.e. Ti, Sc, Zn and Y. In the single crystals as well as in the rock fragments two groups of garnets are observed: (1) pink grains containing 0.4-5 mol.% grossular, 56-79 mol.% almandine, 12-40 mol.% pyrope, 1-5 mol.% spessartine, and <2.2 mol.% andradite; and (2) dark grains containing 14-24 mol.% grossular, 48-76 mol.% almandine, 2-35 mol.% pyrope, 1-9 mol.% spessartine, and <7 mol.% andradite.

For the trace elements some general trends are observed, especially a positive correlation of TiO_2 with CaO, with up to 1150 ppm TiO_2 in the CaO-rich garnets. A negative correlation of Sc and CaO is observed, leading to higher amounts of Sc (100-200 ppm) in the CaO-poor garnets compared to the CaO-rich garnets which contain generally less than 100 ppm Sc. Yttrium does not show a distinct behavior with

changing CaO content, but it appears to favor slightly garnets with higher CaO content.

Geothermobarometry calculations (Berman and Perkins, 1987; Lindsley and Anderson, 1983; Ellis and Green, 1979; Fuhrman and Lindsley, 1988; Ghent, 1976; Kohn and Spears, 1990) were attempted on rock fragments with suitable mineral assemblages. Calculated temperatures and pressures included: (1) 600°C on pyroxene pairs; (2) 605-625°C and 6.5-7.5 kbar on a rock fragment containing garnet-hornblende-quartz-plagioclase; (3) 450-550°C on feldspars; (4) 600-650°C on clinopyroxene-garnet pairs; and (5) pressures of 4.5 kbar at 600°C for the assemblage garnet-plagioclase-aluminosilicate and quartz, which support the view that the garnets and rock fragments are derived from a metamorphic source of about granulite-facies grade.

The incorporation of xenocrysts and xenoliths into the bentonites can be explained by the disruption and integration of Grenville-like crust into the ash during eruption. This explanation is consistent with the ages derived from a K-feldspar aliquot of one of the bentonites using the Ar/Ar method of dating, which shows a thermal history similar to Grenville crust K-feldspars and an age of 550-750 million years. This is too old to be derived from metamorphism during the Taconic event, nor can these feldspars be explained as authigenic phases; therefore, the best explanation is a different source than the volcanism at 450 million years, and a minimum age for this source of 750 million years, and probably older.

The subject of this investigation is split into two parts: (1) Garnets as means of correlation and (2) garnets as indicators for the source of the magmas creating the bentonites. Both lines of investigation were unsuccessful. The xenocrystic garnets in the bentonites cannot be used for correlation purposes and are also of very limited use to define a source area because of their metamorphic character.

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Acknowledgements

First of all I thank all the people that made it possible for me to come to Albany and enter the Master's program, without their support many experiences I gathered would not have been possible.

Thanks to my committee members Stephen DeLong, Bill Kidd and George Putman for reading my thesis and making helpful suggestions to improve it. Bill Kidd and George Putman helped during the field work with their knowledge of the area and discussions.

Special thanks to John Delano for all of the support and advise he gave me over the past three years.

Carsten S. earns all my gratitude for putting up with my moods, questions and counterarguments; his computer was a great help to evaluate data and design diagrams.

Dave Wark introduced me to the use of the microprobe and helped me to set up a trace element schedule making the analyses possible.

Thanks to all my friends in the Department of Geological Sciences and outside who helped me in various ways with their friendship, advise and discussions.

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1. Introduction

The term "bentonite" was introduced by Knight (1898) for clay mineral seams with soapy properties in the Fort Benton unit of Cretaceous age in Wyoming. At that time Knight was not aware of their volcanic origin and described only their appearance. This created some controversy about the term bentonite. Today, one group of authors (Grim and Güven, 1978; Hosterman and Roen, 1984; Roen and Hosterman, 1982, 1983) define a bentonite to be a clay-rich, smectite-dominated, strongly water-absorbent layer regardless of its origin. The other group (Forsman, 1984; Huff, 1983; Person, 1982) call every layer that consists of altered volcanic ash a bentonite even when the clay component is mainly illite and hence the ability of the layer to absorb water is lost (in most Paleozoic bentonites). I have chosen to follow the usage given by Person (1982) who proposed two stages of genesis for a bentonite: firstly, aerial transport and deposition of volcanic ash, and secondly, alteration processes which break down the volcanic glass and pumice to form clay minerals.

Such altered ashes represent a short time interval - one volcanic eruption might last from several hours to up to four days - and they are widespread, for example ash deposits from the Toba eruption in Indonesia covered an area of at least 5 x 10^6 km^2 (Ninkovich et al., 1978). For these reasons - short duration, and large areal extent - bentonites are widely used as a tool for correlation.

Kay (1931) was among the first to use bentonites as correlation tools on the North American craton. By looking at the lithology and paleontology of the under- and overlying strata, he was able to correlate an Ordovician bentonite (Hounsfield bentonite) from New York State over to Kentucky and Tennessee to the Mississippi Valley. Kolata et al. (1986, 1987) correlated bentonites in the Mississippi Valley by chemical fingerprinting based on their bulk chemistry and estimated that they covered an area of at least 1.3 x 10^6 km^2. The explosive volcanism that produced all these bentonites is related to the collision of an island arc with eastern North America (Taconic Orogeny) during the late Ordovician (Rowley and Kidd, 1981; Cisne et al. 1982; Cisne et al. 1984; Hay and Cisne, 1988). A modern example for such a tectonic setting is the Timor Trough where the volcanic Banda arc is colliding at present with the passive margin of northwestern Australia.

The approach of Kolata et al. (1986, 1987) to correlate bentonites by chemical fingerprinting has also been used by Huff (1983) and Cullen-Lollis and Huff (1986). Samson et al. (1988, 1989) have attempted similar correlation studying primary igneous phenocrysts (apatites and zircons). Isotopic analyses of such zircons has allowed Samson et al. (1989) to obtain precise dates of some bentonites.

This study of late Ordovician bentonites from the Mohawk Valley is focused on an abundant heavy mineral component of garnets, hornblendes and pyroxenes. The clay minerals which are the major component of the bentonites were not investigated. The purpose of my study was to examine possible methods of correlation using the garnets and to attempt to find more information about the volcanism that created the bentonites. The specific question addressed here is whether trace elements in garnets are superior to major elements in correlating or ascribing a source area to the garnets. The discovery of small rock fragments (up to 600 microns) of variable mineral assemblages also allowed some applications of geothermobarometry.

In the beginning of this investigation the origin of the garnets, pyroxenes, hornblendes and rock fragments was not clear. Thus, phenocrystic versus xenocrystic and magmatic versus metamorphic origins had to be decided.

2. Geologic Setting

The bentonites from New York State that are the focus of this study are interbedded in autochthonous Ordovician sediments deposited during a continent - arc collision. In these sediments the facies changes upwards from carbonate to shale to flysch deposition. This sequence of different facies types is typical for passive margin shelf-slope-active trench settings. The change in the sediments is a reaction to the changing depositional environment (i.e. increasing water depth and orogenic sediment input).

The Trenton limestone is the lowest unit from which a bentonite was collected and is named after Trenton Falls gorge of West Canada Creek (Kay, 1953). This thin (5-100 meters) formation consists of stable platform and shelf sediments deposited in shallow water. The sedimentation rate for the Trenton Formation is about 20-30 meters per million years (Hay and Cisne, 1988). Above the Trenton Formation, there is a transitional facies belt, the Dolgeville Formation, which consists of thin (5-20 cm) layers of micritic limestone (calciturbidites) interbedded with shale. This facies interfingers with the shales of the overlying Utica Formation in one location in the lower part of Canajoharie Creek (above bentonite 103), but it is not present at Flat Creek. The best outcrop (about 15 meters in height) of the Dolgeville Formation is found along I-90 about 25 kilometers east of Utica (Fisher, 1976).

The Utica shale is a time transgressive unit that replaces the Trenton limestone and Dolgeville Formation. It is deposited from within the Appalachian orogen, in the east or southeast, progressively westwards, being younger to the west. It reaches and overlaps (Lake St. John area in Quebec) the Precambrian shield in late medial-Ordovician time, when it had its maximum propagation from the orogen (Riva, 1969). The formation consists of grey-black, finely-laminated, calcareous shales and contains a very small portion, but at all levels, of thin interbedded limestones (calciturbidites). In one locality phosphatic nodules have been observed within the shale, along the roadcut of exit 29A of I-90. The fauna of the Utica consists of widely distributed brachiopods, trilobites, cephalopods, and graptolites, all making a detailed biostratigraphical framework possible (Cisne et al., 1982).

Rowley et al. (1979), Cisne et al. (1982, 1984), Hiscott (1984) and Hay and Cisne (1988) suggest that the Utica shale was deposited in the Taconic Foreland basin which formed by subsidence of the margin of the North American continent due to tectonic loading in the east. Bradley and Kusky (1986) give a description of the tectonic setting of the sedimentary sequences in the Taconic Foreland Basin. The thickness of the shales varies from the east to the west, becoming thinner to the west, and reaches a maximum thickness of about 300 meters in the Mohawk Valley. The sedimentation rate was circa 50-100 meters per million years (Hay and Cisne, 1988), so that the entire unit represents a record of no more than about 10 million years.

The Schenectady Formation, and its equivalent farther to the west, the Frankfort Formation, overlie the Utica shales. These formations consist of coarse-grained sandstones, graywacke turbidites, and grey shales, derived from the south. The sedimentation rate for this period was high with rates of 200-250 meters per million years suggested by Hay and Cisne (1988), and the unit reaches a maximum thickness of about 500 meters in the Mohawk Valley.

The source area for the bentonites found in all these sediments of the Mohawk Valley is not definitely known. The Ammonoosuc Volcanics which represent an island arc accreted to the North American continent during the Taconic orogeny, are a possible source, although the mineralogy of these volcanics (Schumacher, 1983) and isotopic data do not favor them as a source area for the bentonites (Delano et al., 1990).

Similarly, the source area of the bentonites in the Mississippi Valley is unknown. Samson et al. (1989) considered as possible source areas of those bentonites New Brunswick, and/or the British Isles allowing for much subsequent and hypothetical strike - slip translation along the Appalachian - Caledonian orogen. Paleogeographic data are contradictory, and it is unclear where those provinces were located in the Ordovician. Kolata et al. (1986, p. 1) suggested a source for the K-bentonites of the Mississippi Valley in the Appalachians, because bentonites are "more numerous, thicker and coarser, in or adjacent to the Appalachians than in areas further west". Sloan (1987) observed (as Kolata et al., 1986, p. 18 and 21) a southward thickening of the lower bentonites in the Mississippi Valley and drew a map showing the "Deike volcano", which he located in Alabama as the possible source area.

With the help of the heavy mineral xenocryst and rock fragment content (i.e. the garnets) a petrologic description and definition of the P-T conditions of a possible source area can be obtained; this may help to constrain the location and nature of the source region better then it is at present.

The New York State medial Ordovician bentonites are extraordinarily rich in their content of heavy minerals. Similar enrichment of the heavy mineral assemblage in bentonites is seldom reported for other ashes. For example the deep sea ashes of the Quaternary Toba or Santorini eruptions do not contain such a variety of heavy minerals. This richness might be an indicator of special circumstances under which the eruptions that created the bentonites of the Mohawk Valley occurred.

3. Field Area

The majority of samples for this study of bentonites was taken in two creeks approximately 5 km apart (Figure 1 and 2). They are Canajoharie Creek and Flat Creek which are located about 80 km west of Albany just south of the Mohawk Valley. These two creeks were extensively sampled and mapped (Figure 2 and 3). Since the outcrop is almost continuous, they are used for a test of correlation. Some bentonite material was also obtained from Yatesville Creek approximately 6-7 km east of Flat Creek. A complete stratigraphic column is not made from this creek because glacial debris obscures the outcrop and makes measuring a complete section impossible.

One bentonite within the Trenton limestone was collected in an old quarry along U.S. Highway 169 (coordinates: 74° 57.6'W, 43° 54.3'N), about one kilometer south of Middleville (Kay, 1931).

Another, extremely clean bentonite (89-050) was recovered from behind a large waterfall in a creek described by Kay (1953), page 24-25: ". . . a half mile above the road (U.S. Highway 28) along the second stream south of County Home." This locality is about 2 km southwest of Middleville (74° 59'W, 43° 07'N).

The northernmost material comes from northwest of Copenhagen about 10 km south of Watertown (88-048 resampled as 89-048). The latitude and longitude of the quarry in which the sample was collected are: 43° 54.3'N, 75° 42.6'W. The overlying glacial sediment was also sampled and the minerals analyzed.

One bentonite sample (Hounsfield bentonite) was collected in an old, abandoned quarry outside Dexter, NY. This sample was of special interest to us because Kay (1931) correlated this metabentonite of Black Riverian age (on top of the Leary limestone below the Watertown limestone) with a bentonite that is also observed in Ontario, Kentucky, Tennessee, Missouri and Iowa (Figure 4). Kolata et al. (1986) state that the Hounsfield metabentonite described by Kay (1931) is equivalent to the Millbrig

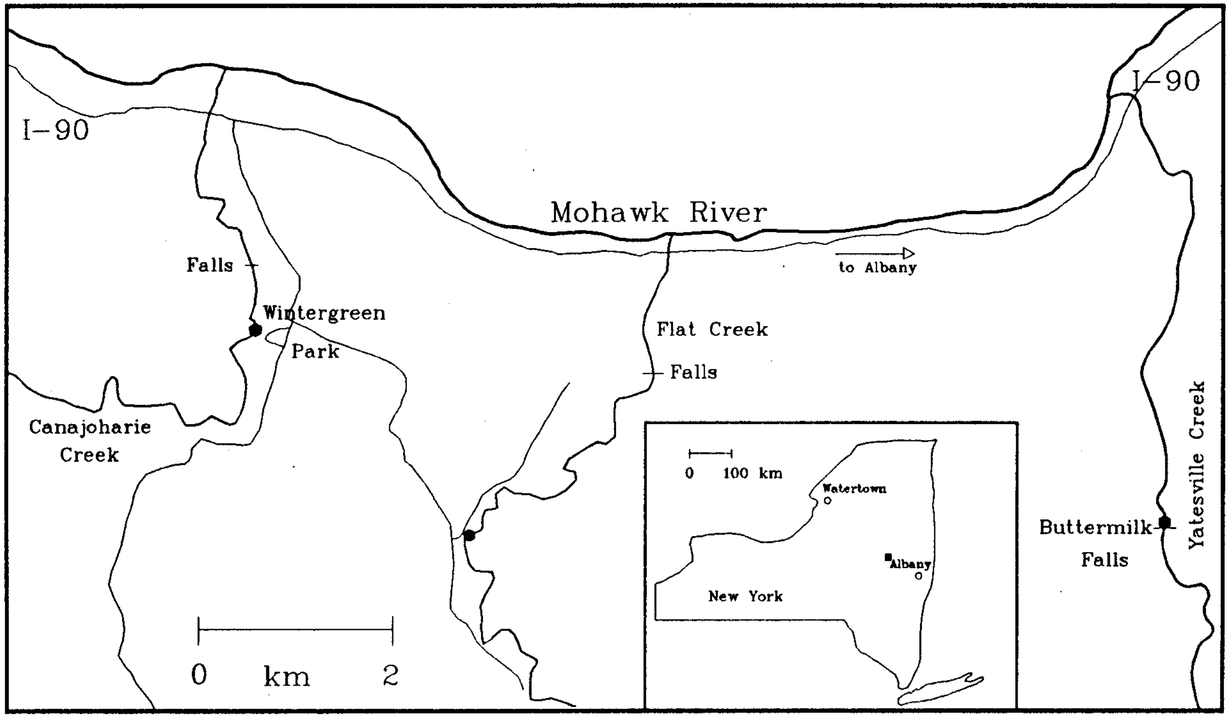


Figure 1: Generalized map showing sample localities in the Mohawk Valley (pentagons: entrance to the creeks). The insert shows outlines of New York State indicating the area of sample locations from the Mohawk Valley (black square) to about 10 km southeast of Watertown.

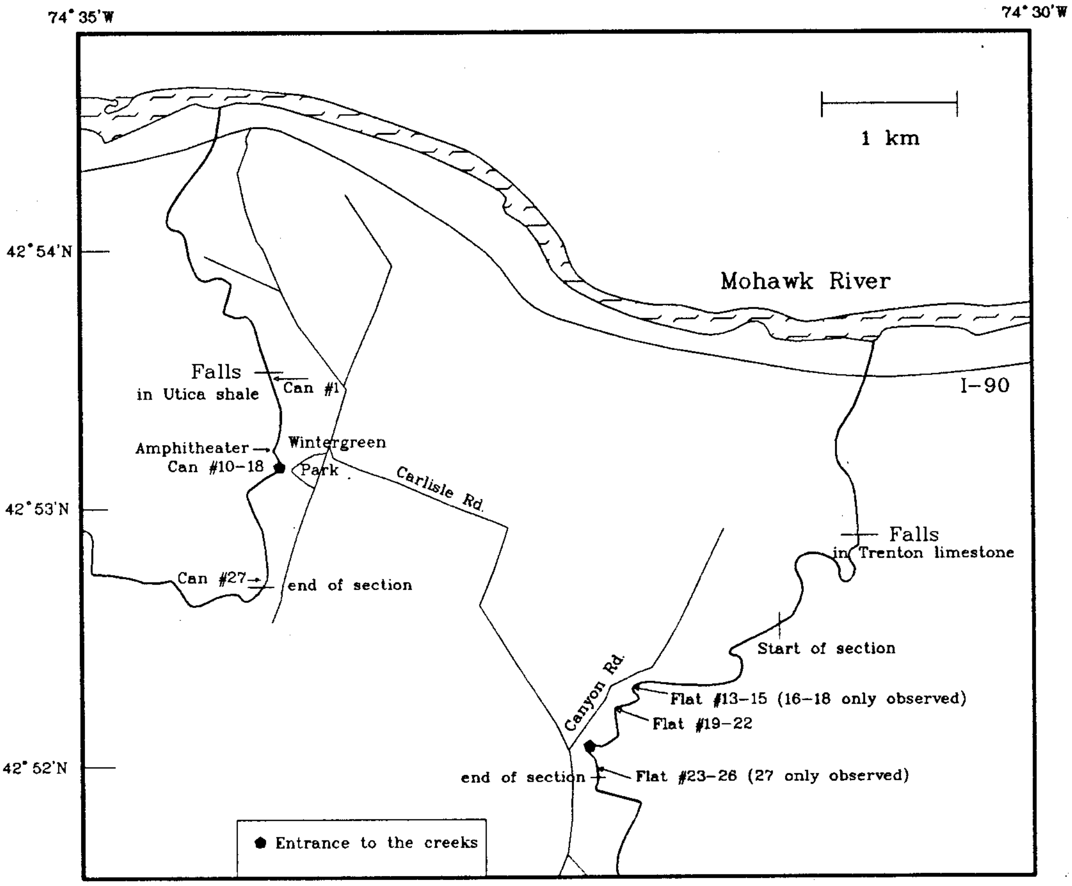


Figure 2: Closeup of Canajoharie and Flat Creeks

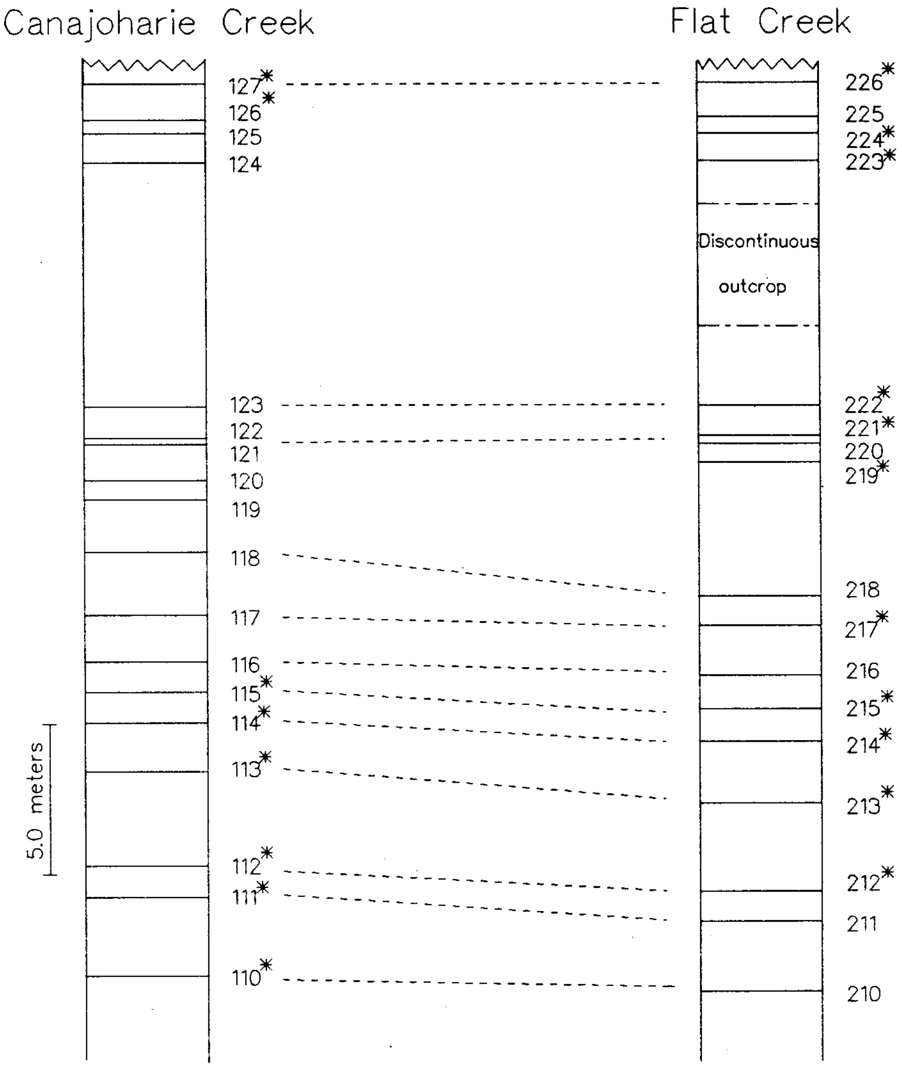


Figure 3: Stratigraphic columns measured for Canajoharie and Flat Creeks showing the correlation of the bentonites based on stratigraphy (*sampled).

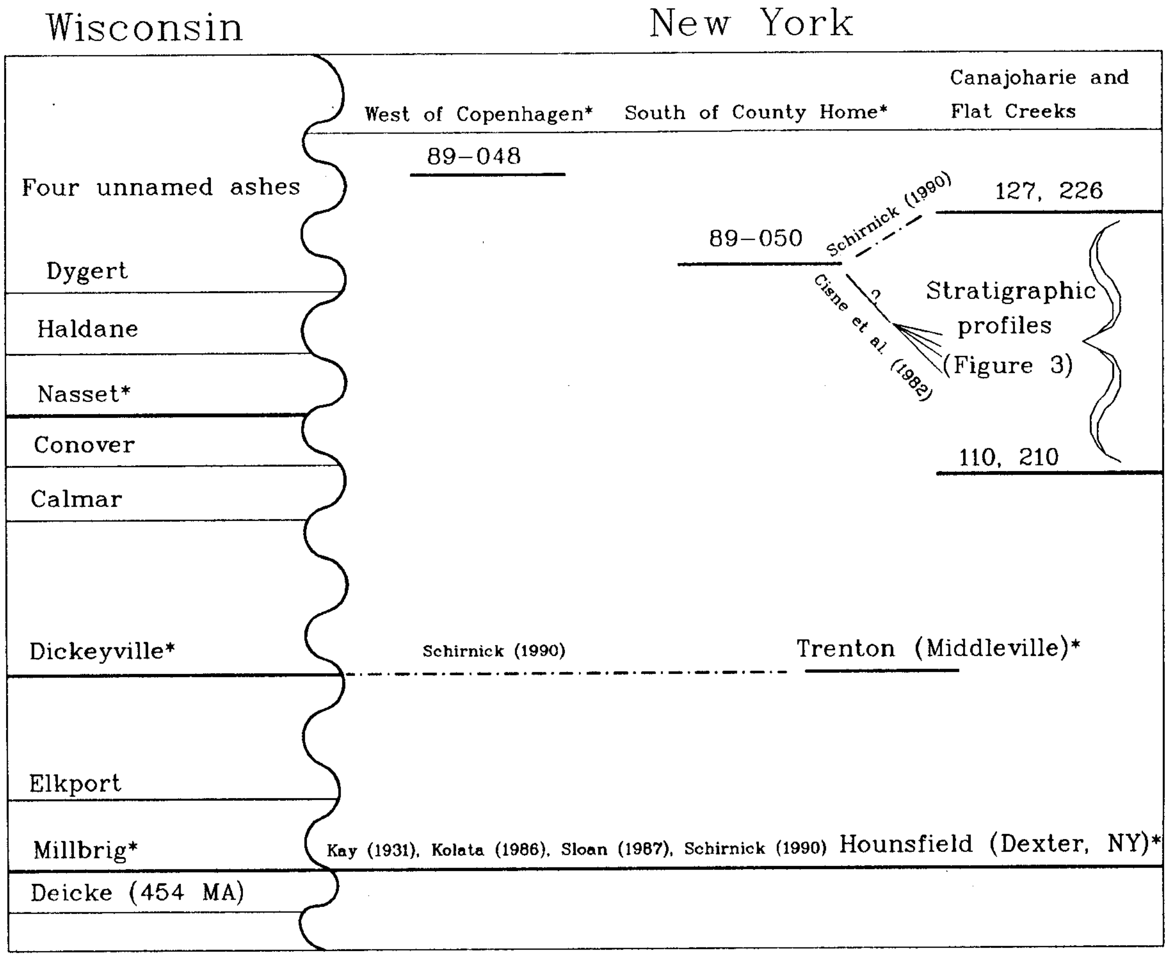


Figure 4: Correlation of New York and Wisconsin bentonites (Wisconsin profile after Sloan, 1987). Discrepancy between Cisne's et al. (1982) bentonite swarm and Schirnick's correlation shown.
* for exact location of outcrop see text page 6

K-bentonite in the Mississippi Valley (Figure 4).

The samples furthest away from Albany were recovered in Wisconsin. The Millbrig and Dickeyville bentonites were collected along U.S. Highway 61, about 6.4 kilometers northwest of Dickeyville (42^o 37'N, 90^o 37'W), and at a roadcut of U.S. Highway 52, just north of Guttenberg (42^o 48'N, 91^o 6'W) the Nasset bentonite was collected (Figure 4 for stratigraphic position). These bentonites are described by Kolata et al. (1986), and were used for correlation over the Midwest by chemical fingerprinting. We were able to locate exactly the outcrop sampled by Kolata et al., since a picture of the outcrop is used as coverpage by Kolata et al. (1986). The collection of this material should solve several questions: (a) Are the same minerals present in the bentonites of the Mississippi Valley that are observed in the bentonites of the Mohawk Valley?, (b) is correlation based on mineral content possible? and (c) are differences present in grain sizes of the minerals indicating sorting effects?

The bentonites collected within the black shales and argillaceous parts of the flysch reach a maximum thickness of about 10 cm (generally about 1-2 cm). They exhibit sharp lower and upper contacts with the shale. Commonly a 'mixed layer' can be observed on top of the bentonites (Figure 5, 5.1, chapter 6.1). This layer contains a large amount of igneous and/or high-grade metamorphic minerals (i.e. quartz, feldspars, hornblendes, garnets and pyroxenes) compared to the normal Utica shale (Delano, 1990). These minerals are thought to have migrated out of the bentonite into the shale, most likely through bioturbation.

As the bentonites are not lithified, they weather easily and are identified in outcrop as reentrants. Often containing large amounts of diagenetic pyrite, the bentonites stain the underlying rocks with a bright yellow-orange color. Through weathering the bentonites themselves are likely to change color, but after digging about 5 cm into a layer, the fresh material is light grey and feels greasy or soapy. Usually no grading was observed; only sample 89-048 showed an unusual sort of grain size distribution (for

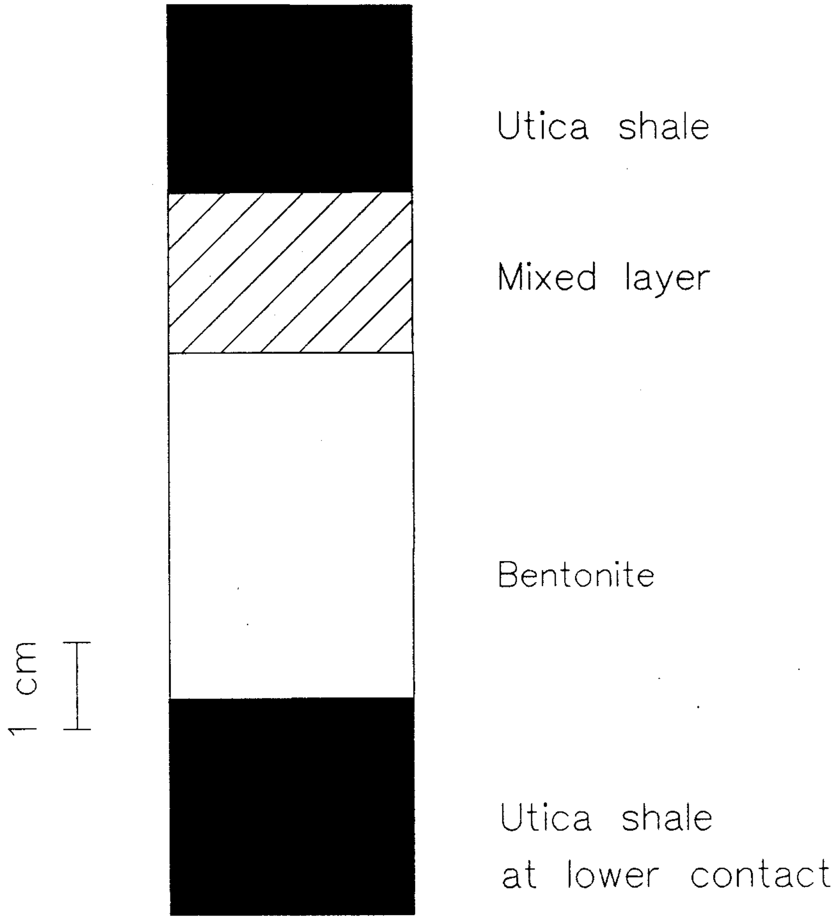


Figure 5: Stratigraphic zones commonly observed across bentonites in the Utica Formation, scale approximate (after Delano et al., 1990).

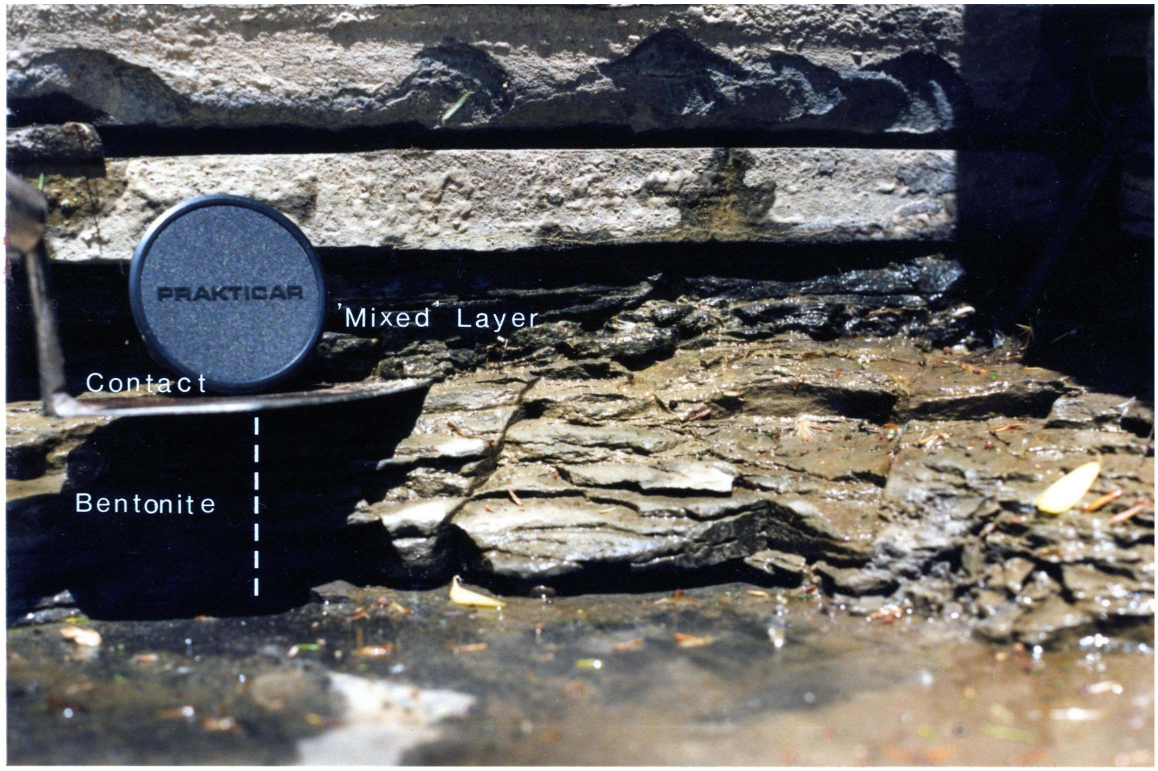


Figure 5.1: Bentonite 127 and 'mixed' layer on top.

detail see 6.4).

The question of lateral continuity was not addressed because of the difficulties in collecting these bentonites. Often, the outcrop is not large, a few meters long, and the layer itself thin, and the overlying shale is thick and not easily removed.
To follow one layer over a long distance in these creeks is virtually impossible, because normally a bentonite is only exposed on one side of the creek. Even though the shales are flat lying, it is hard or impossible to unambiguously identify one bentonite - observed high in a cliff - further upstream in the same creek again.

For the correlation work, matching the stratigraphic columns of Canajoharie Creek and Flat Creek (Figure 3) was very helpful. Based on the stratigraphic correlation, the bentonites were chosen for further petrological work.

A comparison of our measured sections with Professor Cisne's stratigraphic profiles of these creeks showed that the stratigraphic profiles of Canajoharie match perfectly, and also the ones of Flat Creek fit well. The stratigraphic columns disagree only in one part (Figure 4). This disagreement is the "bentonite swarm", where one thick bentonite (observed in localities 1, 4, 6, 7, 9, 10 and 15, in Cisne et al., 1982) splits up into four thinner ones in Canajoharie Creek and Flat Creek (equivalents to bentonites #14, #15, #16 and #17 in Figure 3). During our investigation we went farther upstream in Canajoharie Creek and found another very thick bentonite, Can #27 that appears to be correlatable to the thick bentonite observed in the roadcut of exit 29A along I-90 (profile 13) by Cisne et al. (1982).

3.1. Description of Canajoharie Creek

Canajoharie Creek can be entered (pentagon in Figure 1 and 2) through Wintergreen Park, approximately at the level of bentonite #18 (Figure 1 and 2). The latitude and longitude coordinates for this part of the creek are: 42^{0} 53.3'N, 74^{0} 33.9'W.

In Canajoharie Creek we observed 29 bentonites, of which 11 could be collected. In this creek going downstream one finds the contact of the Utica shale with the underlying Trenton Group limestone which crops out in the village of Canajoharie below the dam. Going upstream from the Trenton limestone, one arrives at a large waterfall (about 15 meters) in which the first two bentonites are visible. Taking the lower one as point zero there are about twelve meters of Utica shale below that bentonite, followed downwards by a transitional zone of about 3 meters that consists of limestone and thin shale bands that have the appearance of megaripples (Riva, 1969). This phenomenon might be caused by compaction and/or slumping. It does not seem reasonable that it indicates a tectonic event, since the overlying as well as the underlying units do not expose similar features.

The black Utica shales are flat lying, and the two bentonites exposed in the waterfall can be followed a long distance downstream, but high in the cliff, and were therefore not collected. In the cliff above these two bentonites two other bentonites are visible, that are exposed in the section above the falls and labeled there as bentonite #1 and #2.

The collection of bentonites starts on top of the waterfall with sample #1 and numbers in increasing order were given upstream. For analyses the samples are labeled either as Can and the associated number of the bentonite, or they were given a three digit number starting with 1 (Can #1 = 101).

The best exposure of the bentonites in Canajoharie Creek is given in the 'amphitheater' (Figure 2, 5.2). Bentonites 110 through 118 are visible in this high cliff

Figure 5.2: Bentonites 110-118 in amphitheater (Figure 2) of Canajoharie Creek. Length of the measuring stick is two meters.

on the west side of the creek. Only the lowest bentonite (110) can be collected there. Samples of 112, 113, 114 and 115 were collected a short distance upstream along the east-facing cliff shown in Figure 5.3.

As will be documented in Chapter 6.5, Can #14 (or 114) is a remarkable xenocryst- and xenolith-rich bentonite. To get some control whether these minerals and rock fragments could have just been deposited by the present stream in the reentrant at the outside of this layer several samples were taken at different heights relative to the stream. An attempt to drill horizontally into the bentonite (penetration of about 10-15 cm) was made to get fresh bentonite material that cannot be contaminated by stream ediment. The result was as before: this layer is xenocryst- and xenolith-rich.

Near the top of the section a complicated feature (Figure 5.4, 5.4.1, 5.5 and 5.5.1) is found. Either one bentonite (Can #27) is duplicated and disrupted, or more bentonites were deposited and subsequently in part eroded, so that now only lenses of bentonitic material are left. Looking at the sediment between the different pieces of the bentonitic material, it appears to be in a tongue like shape which gives the impression of a rollover. Since Cisne et al. (1982), described slumping in an extremely thick bentonite at I-90 (exit 29A, profile 13), I think it is possible to explain this feature also as slumping of the unconsolidated material, and the 'two' bentontites are the result of sliding of one thick bentonite layer that is now underlying itself, and also to correlate the two bentonites tentatively.

The stratigraphic column (Figure 3) ends when the outcrop becomes obscured by glacial debris after about 88 meters of outcrop. There may be more bentonites within this section of Canajoharie Creek, but if there are, they are so thin that it is impossible to sample this material (indents of less than one millimeter).

In the shales variable amounts of fossils are observed, with an especially rich zone on top of sample 114. On the level of Can #18 a few corals were found within the shale, both upside down and in apparent life position.

Figure 5.3: This cliff - a short distance upstream from the amphitheater - is the sample location for 112, 113, 114 and 115.

Figure 5.4: Sample location of bentonite 127, showing the feature that is believed to be slumping.

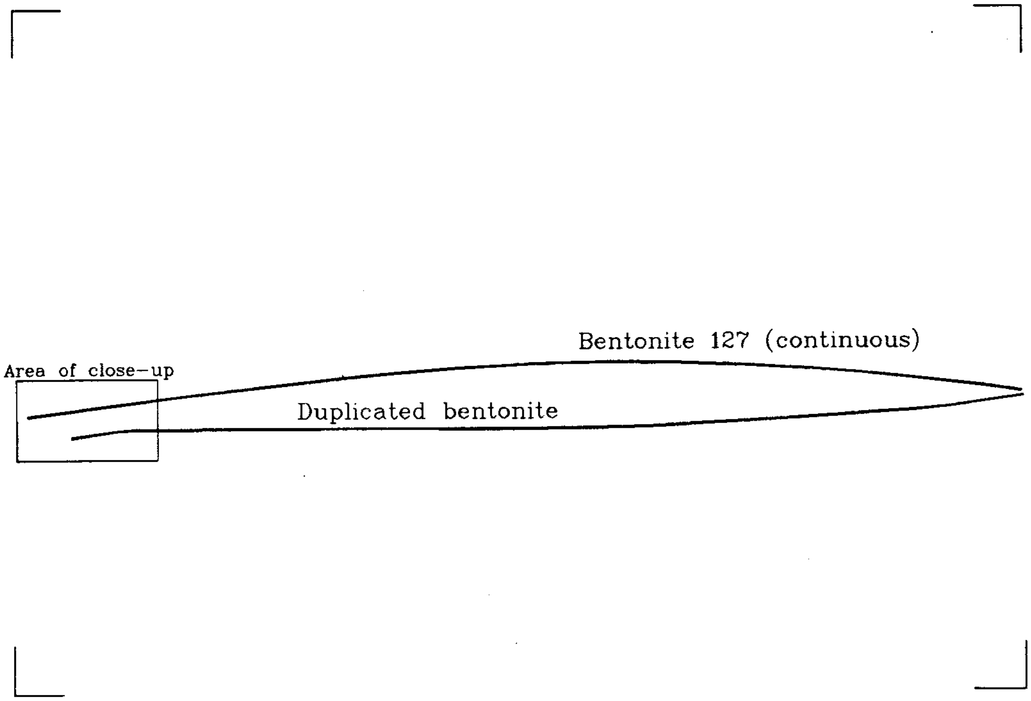


Figure 5.4.1: Sketch of bentonite in the picture above.

Figure 5.5: Close-up, showing that the bentonite, which is continuous to the left, is suddenly underlain by a 'second' bentonite layer.

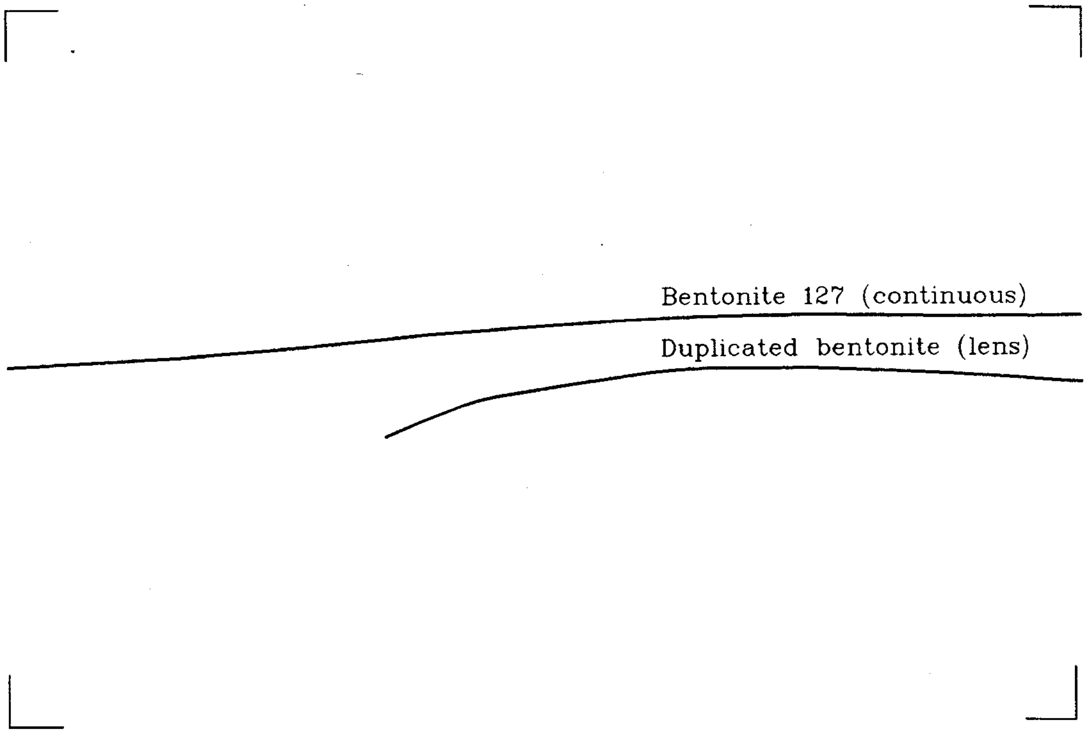


Figure 5.5.1: Sketch of bentonite in the picture above.

Also veins filled with calcite and pyrite, striking about 100-134^{o} were observed upstream from the parking lot entrance. On the calcite - shale contact a slickenside is exposed indicating that the shale must have been consolidated when the displacement occurred.

On top of the measured section lie about five meters of yellowish weathering, probably dolomitic calciturbidites and shale. These strata are observed in the cliff across the creek, when entering at the parking area level. Calciturbidites also occur further downstream (level of bentonite 103) as part of the Dolgeville Formation.

The stratigraphic columns do not show the whole measured section, since correlation between bentonites from Canajoharie and Flat Creeks is only possibly from bentonite #10 upwards and also all the discussed samples are collected in the shown interval (Figure 3).

3.2. Description of Flat Creek

Flat Creek is about 5 km east of Canajoharie Creek and was also extensively mapped (Figure 1, 2 and 3). The latitude and longitude for this creek are: 42^{0} 52.5'N, 74^{0} 31.5'W. This creek is entered at the beginning of Canyon Road (pentagon in Figure 1 and 2). The symbols for samples of this creek are either Flat and the assigned bentonite number, or 2 for the creek plus the bentonite number.

The strata above the Trenton limestone are far more disturbed than in Canajoharie Creek. Because of this the stratigraphic column was chosen to begin with bentonite (205) from which point on the geology allows accurate measurements. Below that point four more bentonites were observed, but were neither taken into the stratigraphic column nor analyzed.

As in Canajoharie Creek there is above the Trenton limestone a wavy zone of interlayered limestone and shale. The limestone is fossil-rich, as in Canajoharie Creek. The most striking difference with Canajoharie Creek is a large waterfall in the limestone (about 15 meters).

In Flat Creek 27 K-bentonites were observed of which 16 were sampled. The fossils found in Canajoharie Creek were also seen in Flat Creek with the exception of the corals. Thin calcite veins run in 110^{0} direction through the shales. At the bottom of the cliff (west side) where bentonites 113-117 are visible calcite veins, with angular pieces of shale within them, are exposed striking approximately 140^{0}. A slickenside is observed in this cliff running approximately parallel to these veins into the cliff with a direction of $140\text{-}150^{0}$. These two directions 110 and $140\text{-}150^{0}$ are the only ones observed.

Bentonite Flat #14 that corresponds, according to the stratigraphic sections, to Can #14, is depleted in xenocrystic minerals. First, a sampling bias was suspected to be the reason for this difference between the two #14's, but after most careful resampling of

Flat #14 it became clear that the mineral contents of these two bentonites are different.

At the top of Flat Creek section there is also a thick bentonite, 226, that is correlatable to Canajoharie Creek (127) based on the measured stratigraphic columns (Figure 3). This bentonite however shows no sign of slumping and supports Cisne's et al. (1982) view that slumping is only a local phenomenon due to slope failure.

Above the measured section there is similarly as in Canajoharie Creek some meters of yellowish weathering material observed in a cliff. The stratigraphic column ends when the outcrop becomes obscured by glacial debris.

The total height of this section is only 51 meters, but since the measurements do not start at the contact with the Trenton limestone, this does not indicate that the height of the section is in fact changed this much over such a short distance.

3.3. Description of Yatesville Creek

In Yatesville Creek the outcrop is much more obscured by glacial deposits than in Canajoharie Creek or Flat Creek. Yatesville Creek is the locality furthest east, which means closest to the Ordovician arc. Latitude and longitude of this creek are 42^{o} 52.2'N, 74^{o} 27.0'W. The parking lot at the level of the falls (pentagon in Figure 1) was used as entrance into the creek. No complete stratigraphic column was measured, since glacial debris deposited in the middle of the creek obscures the outcrop.

Remarkably, flysch is exposed in this creek on top of the section and a bentonite in the Schenectady Formation could be sampled. The sample locality is about eleven meters upstream from top of the fall (Figure 1). This bentonite contains also a large heavy mineral component, and is indistinguishable from the bentonites collected in the Utica Formation.

A total of ten bentonites was collected in this creek and the number assigned to the creek for analyses is 3.

There were relatively many fossils observed within this creek. About in the middle of the creek there was a sealily found, and further above, at about 32 meters downstream from top of Buttermilk Falls, a cephalopod of about 20 cm length: Another feature, observed nowhere else, is a sandstone dike that cross cuts the creek at about 16.5 meters below the top of the falls. In the Schenectady Formation there is a graptolite-rich bed seen circa 25 meters above the top of Buttermilk Falls.

4. Analytical Procedures

4.1. Sieving of Bentonites and Cleaning of Mineral Content

About one kilogram of each of the collected bentonites was sieved with water, through sieve sizes of 1000 microns, 500 microns, 250 microns, 125 microns, 63 microns, and 45 microns. The water and clay mixture that ran through the sieves was collected in buckets, allowed to settle, and then was dried and weighed.

The settling times of the <45-microns fractions of the bentonites were variable, ranging from as little as one hour to more than twelve hours. Also, the color of the <45-microns water-clay mixture was not uniform. Colors ranged from cloudy-white to grayish to orange.

The >45-microns material collected in the sieves was cleaned in the ultrasonic cleaner with water and acetone for up to 10 hours. If coating on the minerals was observed, the samples were treated with hydrochloric acid (a process that unfortunately destroys not only calcite, but also apatite), nitric acid (which destroys pyrite when brought to a boil), and sulfuric acid (to remove barite). The reactions of the mineral component of the bentonites to these acids were also variable, ranging from sluggish reactions, often connected with color changes, to violent foaming reactions. The agents that led to the different reactions are unknown. After the treatment with acids, the minerals were cleaned in acetone, dried under an infra-red light, and weighed.

For X-ray fluorescence and instrumental neutron activation analyses bulk samples of 101, 114, 127 (several times), 214, Millbrig, and 89-048 and different fractions of 114 and 214 (<250 microns, <125 microns, <63 microns and <45 microns) were sent out to laboratories located at McGill University, University of Michigan and Cornell University (Table I).

Table I: X-ray fluorescence analyses of Ordovician bentonites

Descript.	Can #1	Can #14 bulk	Can #14 <45	Can #27	Can #27
(wt.%)					
SiO2	40.47	51.40	45.76	49.93	51.58
TiO2	0.55	0.34	0.41	0.61	0.52
Al2O3	23.75	23.17	24.28	30.59	28.96
Fe2O3	16.36	2.34	3.47	2.21	2.36
MnO	0.01	0.03	0.04	0.01	0.00
MgO	1.52	1.51	1.78	2.00	2.05
CaO	0.43	4.30	6.16	0.62	0.94
Na2O	0.27	0.67	0.01	0.19	0.21
K2O	4.53	4.17	4.56	6.34	5.93
P2O5	0.22	0.07	0.09	0.20	0.20
LOI	13.10	9.84	11.79	7.05	7.23
Total	101.21	97.84	98.35	99.75	99.98
(ppm)					
BaO	335	15400	6974	208	154
V	66	39	50	54	48
Cr2O3	23	0	16	19	15
Ni	122	46	91	13	21
Nb	6	0	5	19	19
Zr	158	158	126	233	250
Y	6	7	7	24	30
Sr	115	1095	1250	148	264
Rb	141	116	121	152	153
Pb	163	18	36	27	19
Th	34	15	18	53	53

Table I: (continued)

Descript.	Flat #14 bulk	Flat #14 <45	Millbrig bulk	89-048
(wt.%)				
SiO2	52.23	47.80	56.50	57.36
TiO2	0.33	0.38	0.30	0.33
Al2O3	26.21	26.69	19.70	8.74
Fe2O3	5.43	7.11	1.97	2.47
MnO	0.02	0.02	0.03	0.06
MgO	1.77	1.83	2.09	1.51
CaO	0.38	0.53	7.76	13.01
Na2O	0.07	0.00	0.00	1.50
K2O	5.64	5.78	10.22	2.65
P2O5	0.05	0.06	0.08	0.13
LOI	8.23	10.53	0.57	11.98
Total	100.36	100.73	99.22	99.74
(ppm)				
BaO	301	356	250	520
V	17	30	26	25
Cr2O3	49	101	0	0
Ni	72	48	32	14
Nb	6	7	15	7
Zr	138	86	165	182
Y	<5	<5	15	24
Sr	205	181	79	283
Rb	136	133	92	74
Pb	59	87	26	7
Th	15	15	22	0

4.2. Mineral Separation

The first step of mineral separation was performed with bromoform having a density of 2.87 to 2.90. The separate that sank in bromoform was then put through methylene iodide (density of 3.32 to 3.38) for further separation.

The next step was putting the separate that sank in bromoform and/or methylene iodide through a Frantz isodynamic magnetic separator, Model L-1. Slope and tilt for best separation are 20^{0} and 15^{0} respectively. The first run was performed to remove the magnetite. For this purpose, a funnel of paper was first attached to the outside of the magnetic separator, and then the material was put through the funnel and caught in a small bucket. Only the strongly magnetic magnetite was caught by the magnet and could easily be recovered. The remaining minerals were put through the magnetic separator at settings of 0.25, 0.45, 0.75, 1.0, and 1.7 amperes. These different currents split the minerals into (a) Fe-Ti oxides, (b) garnets, hornblendes, and pyroxenes, (c) pyroxenes, hornblendes, and garnets, and (d) the slightly to wholly non-magnetic minerals (i.e. barite and pyrite, if not previously removed, and zircons, apatite and unrecognized phases).

After this, the minerals of interest were handpicked. Since two groups of garnets were always observed within the different grain sizes, the analyses on the microprobe were done on the +250 and +125 microns fractions (because the coarser grains are easier to handle). Analyses of garnets from the Nasset bentonite, which lacked coarser grains, were performed on the +125 and +63 microns fractions.

The hand-picked garnets were epoxied onto a slide in lines according to their color. To make them stay in line during the hardening of the epoxy, it is necessary to prepare a thin line of epoxy, put the minerals into it, and then harden the epoxy. One can then fill up a larger area of the slide with epoxy and harden it again to make polishing easier. This procedure made it possible to find the garnets easily through the microprobe's optics, and, more importantly, to remain organized during and after a microprobe session, thereby making it possible to find the grains again in another session (e.g. to reanalyze the same garnet as second standard).

4.3. Microprobe Setup

The microprobe analyses on the minerals were performed with the Jeol Superprobe 733 at the Department of Geology at Rensselaer Polytechnic Institute. Major elements were analyzed with an accelerating voltage of 15 kV with a sample current of 20 nanoamperes and counting time of 40 seconds. Trace elements were analyzed at an accelerating voltage of 20 kV, instead of 15 kV, and trace element analyses were performed with column automation with a current of 400 nanoamperes, and the counting time was increased to 100 seconds.

The JEOL superprobe has five wavelength dispersive spectrometers with two different crystals each. The spectrometers were set to use the following crystals for analyses:

Spectrometer 1: TAP for Al and Mg
Spectrometer 2: PET for Ca and Ti
Spectrometer 3: TAP for Si and Y
Spectrometer 4: LIF for Mn and Sc
Spectrometer 5: LIF for Fe and Zn

The data obtained by column automation were reduced by ZAF (atomic number {Z}, absorption {A}, fluorescence {F} matrix correction), while in cases where only major elements were analyzed, the Bence-Albee matrix correction (Bence and Albee, 1968) was used. The Robert Victor garnet was used to calibrate Al, Mg, Ca, Si, and Fe; rutile for

Ti; tephroite for Mn; pure metal foil for Sc (low current for calibration); Drake and Weill glass #3 (rare earth element- and yttrium-rich glass) for Y; and a ZnO for Zn.

The calibration was checked on the Dutsen garnet and on one garnet from Flat #17 with high Y abundance to ensure that the data from different sessions are comparable. The detection limits (MDL) for the trace elements are: Y, 26 ppm; Sc, 24 ppm; Ti, 14 ppm; and Zn, 31 ppm at 400 nanoamperes and 100 seconds counting time.

The analytical error for Si, Al and Fe is for all analyses ±0.5 %, for Mn and Mg it ranges from ±2.0-4.4 % and ±0.6-1.5 % respectively, depending on the abundance of MnO and MgO. For Ca the error is ranging from ±0.6-0.8 % (CaO above 5 wt.%) to ±1.0-1.8 % (CaO below 5 wt.%).

To obtain reliable data, abundances with a relative error of less than ±25.5 % have to be present (all errors higher than 25.5% will be given as 25.5%). Therefore, 80 ppm of Y, 49 ppm of Sc, 45 ppm of Ti, and 78 ppm of Zn are required to reach a relative error smaller than 25.5%. Ti was abundant enough in all garnets to get valid data. Sc and Y often occurred in amounts too low to give reliable values, but are still recorded (Table I).

To ensure that the long counting times would not cause element mobility (volatilization), a spot on one grain was analyzed for 31 minutes. The variations observed after 400, 800, 1040 and 1840 seconds are minimal for the major elements (circa one percent). For the trace elements the mobility is higher, but not significant because the analytical error is larger for these elements.

4.4. Shale Treatment

To prepare the shales for chemical analyses, they were first scrubbed under running water with a toothbrush to remove soil and plant material. After drying, they were crushed in a Denver Fire Clay jaw crusher, broken down into smaller pieces in a C. W. Cook roller mill, and finally pulverized in a Spex tungsten-carbide shatterbox. About one kilogram per sample was processed in the above described way, and 20-30 grams of this pulverized material was filled into vials and sent out for analyses.

A different treatment was applied to shales for checking their mineral content. These shales were cautiously crushed in the roller mill (i.e. the gap between the rolls was wider than for a shale processed for chemical analyses), sieved - dry and wet - through the 1000 microns sieve, and, if necessary, crushed again. The material <1000 microns was dried for an hour at 120°C, then treated with acids (HCl and HNO_3) in an attempt to dissolve the shale matrix and separate a possible xenocrystic component. After the acid treatment the material was washed with water, dried again, and put through bromoform for separation of heavy minerals, but no appreciable amount of minerals (i.e. garnets) was recovered from the shales collected some distance away from the bentonites.

This test seemed necessary to ensure that the mineral component of the shale was small, and that the bentonites were not contaminated by minerals (i.e. garnets) of the shale.

5. Shale Geochemistry

The shales are a time-transgressive unit. They plot (Figure 6) on a line connecting the Trenton limestone (platform) with the flysch data (orogenic material). This trend reflects that they are truly transitional.

The shales, which appear monotonous in outcrop, show time-related changes in their compositions (Delano et al., in prep.). The best example of a systematic change with time is the carbonate content of the shales, which decreases with stratigraphic height (= time). The FeO abundances in the shales are negatively correlated with the carbonate content. This trend is also evident in the calciturbidites. While the stratigraphically lower calciturbidites are CaO-rich (~ 50 wt.%) and FeO- and MgO-poor (~ 2 wt.%), the higher ones are CaO-poor (~ 25 wt.%) and enriched in FeO and MgO (~ 10 wt.%). These changes may be due to either a change of provenance (island arc) or diagenetic processes (or both).

A difference in the chemistry of the sediments at different stratigraphic levels becomes visible when looking at the relative phyllosilicate and tectosilicate components expressed as (Al*2)/[Si+(Al*2)] of the Trenton limestone and the Utica shales. While the Trenton limestone contains a high phyllosilicate component, the stratigraphically low shales contain a higher tectosilicate component (lower (Al*2)/[Si+(Al*2)]). The transition appears to be a jump from relatively high ratios (0.46-0.49) to low ratios of 0.38-0.39. With increasing height in the section the shales become first more enriched in silica ((Al*2)/[Si+(Al*2)] down to 0.36), a change that can indicate a higher modal amount of quartz, a change in the illite/smectite ratio of the shales or a different source area. Higher in the Utica section this trend turns around and the (Al*2)/[Si+(Al*2)] ratios increase again. This increase of the aluminum content of the shales toward the top of the section is not understood, and since the overlying sediments are flysch this deflection of the trend is unexpected. Further, it is observed that the (Al*2)/[Si+(Al*2)] ratios vary

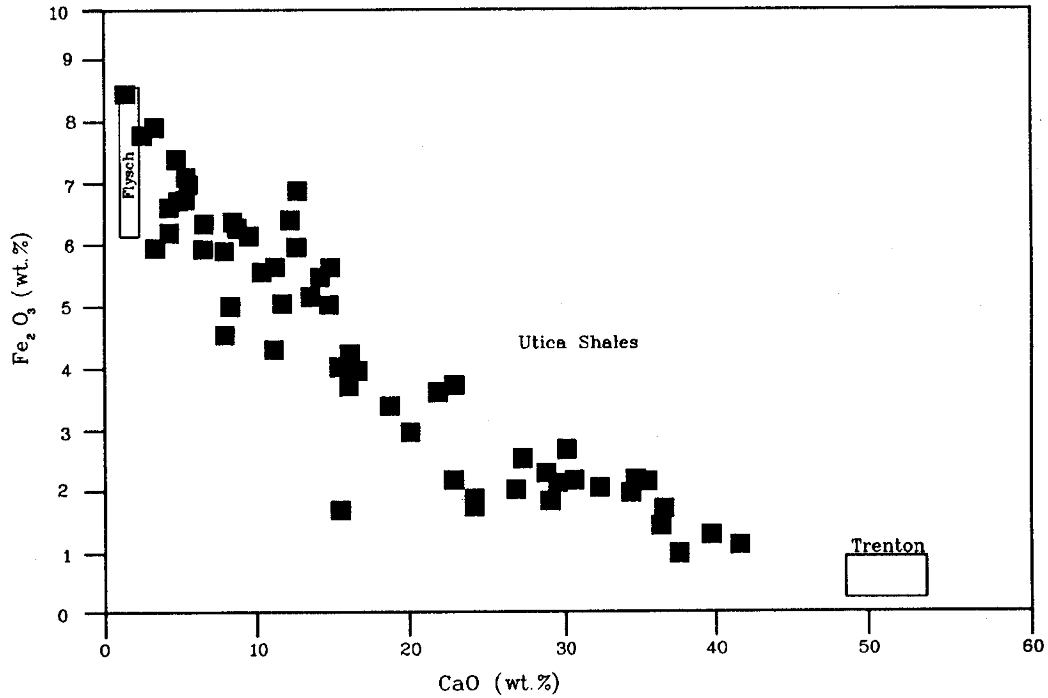


Figure 6: The Utica shale is truly a time-transgressive unit connecting the Trenton Group limestones (older) and the flysch of the Schenectady Formation (younger) after Delano et al., in prep..

in different creeks but they appear to be converging towards a common value of about 0.42 on the top of the shales. The trends in different creeks appear subparallel. Further research is required to explain this behavior and to determine the variability of the shale composition within a stratigraphic level.

Sr-isotopic data from shale samples are a further indicator of sedimentary environment changes during the time of shale deposition. Isotope analyses on shales were performed at the University of Michigan by Matthias Ohr, on the carbonate fraction of Utica shale samples, whose stratigraphic positions are accurately known. Time-corrected $^{87}Sr/^{86}Sr$ ratios (440 million years) increase from 0.708125 to 0.711977 with stratigraphic height. Therefore, the changes of the isotopic ratios are related to changes in the CaO and MgO abundances - increase of the isotopic ratio while the Ca/Mg ratio is decreasing - this trend might indicate diagenetic processes after deposition.

Also, changes in the sedimentary basin are a possible factor for the increasing Sr ratios. The Taconic Foreland basin appeared to be always connected to the open ocean (Hay and Cisne, 1989), but restricted inflow of ocean water (due to collision) seems possible. Tectonic development of a 'barrier' might restrict the exchange of water so that the mixing time of the two water bodies might become too long compared to the residence time of the elements in seawater. This view is similar to the observation of Keto and Jacobson (1987) who found isotopic variations and proposed a physical boundary to inhibit mixing of the two separate water bodies of the Iapetus and Panthalassa oceans.

6. Bentonites

6.1. Bentonite Geochemistry

The character of the volcanism that created the bentonites was probably silicic, since it is unrealistic to expect explosive volcanism from low viscosity basic lavas (Fisher and Schmincke, 1984).

A more quantitative estimate of the melt composition can be made from a plot of the analyses from the bentonites in a Winchester and Floyd diagram (Figure 7). K-bentonites along the Cincinnati Arch plot in this diagram fairly close to the field of the bentonites from the Utica Formation (Huff and Türkmenoglu, 1981). Since most of the major elements (e.g. Na, K, Si, Mg) are mobile in bentonites during diagenesis, these elements cannot define the composition of the former glass. Instead, the elements used in the Winchester and Floyd diagram (Zr, Ti, Nb and Y) are believed to be immobile during diagenesis (Staudigel and Hart, 1983; Spears and Kanaris-Sotiriou, 1979; Teale and Spears, 1986; Roberts and Merriman, 1990). Furthermore, the use of element ratios instead of single element abundances is an advantage, since ratios of immobile elements are not affected by mobility of other elements, while absolute abundances might show relative enrichment or depletion due to hydration. Within the diagram of Winchester and Floyd most of the bentonites plot in the vicinity of the trachyandesitic to rhyodacitic field. This suggests that the volcanism represented by the bentonites is rhyolitic to dacitic (Delano et al., 1990).

Further investigations revealed that TiO_2 might have been mobile in the bentonites. When looking at the composition of the 'mixed layer' this mobility seems to be apparent in a plot of TiO_2 against Al_2O_3 (Figure 8.5). Plotting different elements (Figure 8.1-8.4) against Al_2O_3, the validity of the description as a mixed layer becomes clear. The'mixed' layer plots on the mixing line between shale and bentonite composition. This interpretation is only of limited value as shown by the behavior of TiO_2 (Figure 8.5).

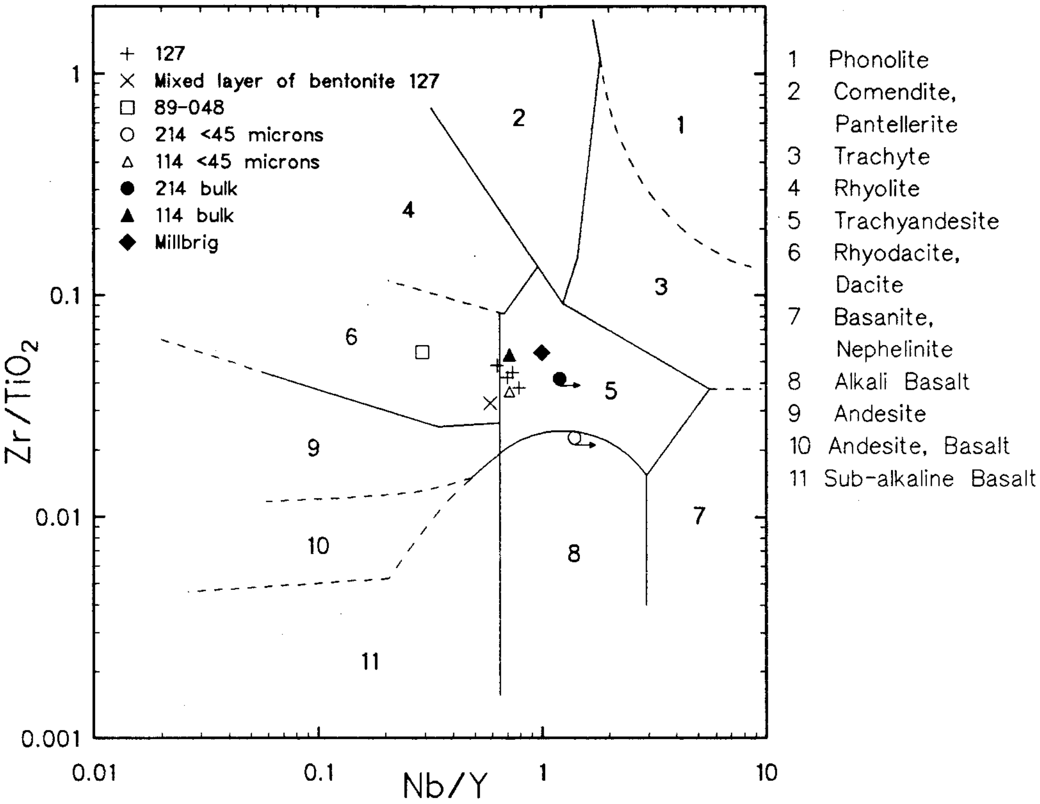


Figure 7: Modified diagram after Winchester and Floyd (1977). Symbols show the probable original rock type for the bentonites. Symbols with arrows indicate minimum ratios due to small abundance of Nb.

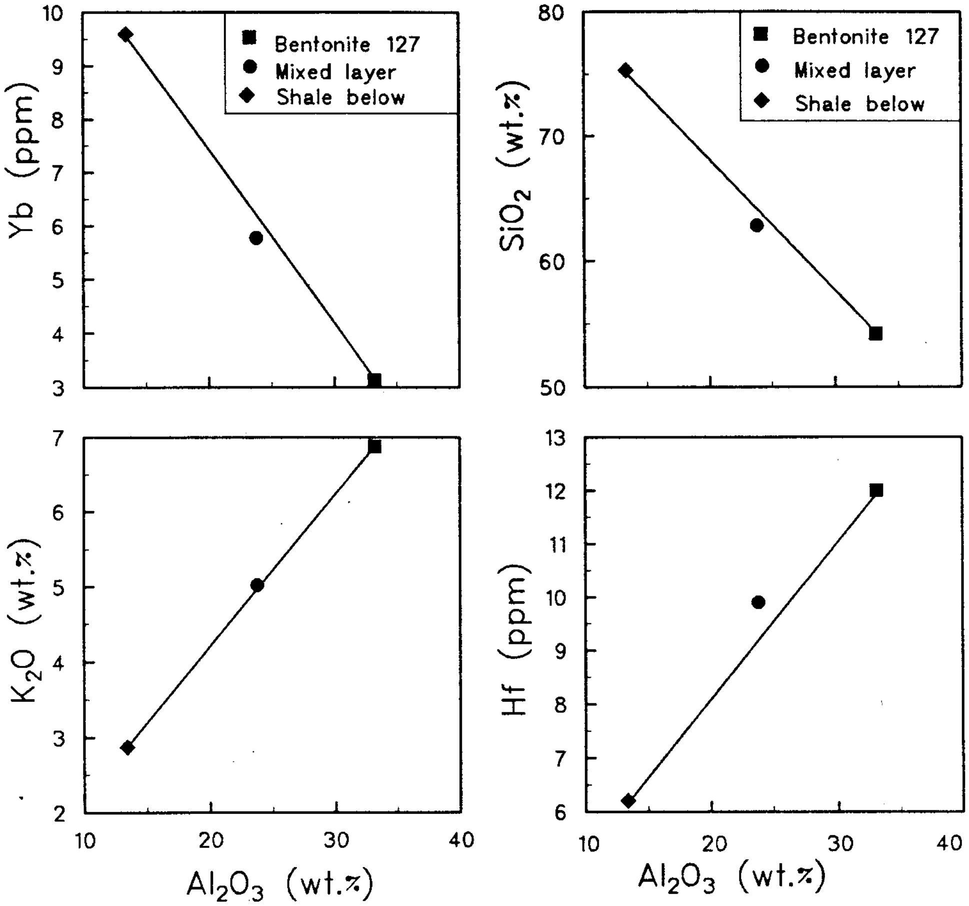


Figure 8.1-8.4: Different elements plotted against Al_2O_3 show that the 'mixed layer' can be explained for some elements as a feature of pure two component mixing.

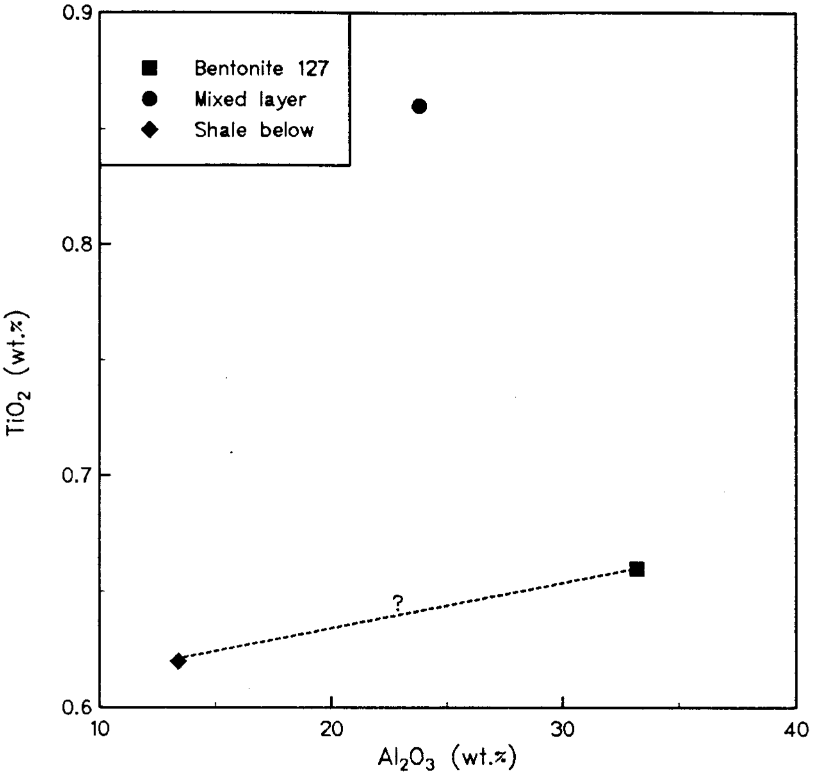


Figure 8.5: The behavior of TiO_2 shows that diagenetic mobility is required besides pure mixing to explain the feature of the 'mixed' layer.

Al_2O_3 on the x-axis was chosen because of its immobility during diagenesis. The same immobility can be assessed for TiO_2. Astonishingly, the TiO_2 abundances do not define a line plotted against Al_2O_3 (Figure 8.5). This behavior indicates mobility of TiO_2 (also observed by Huff and Türkmenoglu, 1981). The abundance of Sc (Table II) shows that this "misbehavior" of TiO_2 is not due to an analytical error or induced by analytical uncertainty. Sc is geochemically similar to TiO_2, and the fact that both elements are too abundant in the mixed layer is indicative of some other process (i.e. diagenetic mobility) besides pure mixing (Delano et al., 1990).

Nb (not analyzed in Table II) is geochemically similar to TiO_2 and hence might have been mobile. Thus, the element combination of the Winchester and Floyd diagram might not be suitable to represent the true composition of the original parent rock.

Also, variations in Zr content in the different size fractions might lead to a shift of the data points (Table I, Figure 7). Whether the bulk sample or the <45-microns fraction is closer to the real liquid composition is determined by the mineral component removed during the sieving process, either phenocrysts or xenocrysts.

The mixed layer plots slightly differently than the bentonite in Figure 7, and might be closer to the true magma composition, when elements migrated out of the bentonite into the mixed layer. Such mobility can be observed in the rare earth element pattern. The rare earth elements that are generally immobile during diagenesis show mobility when the chondrite normalized rare earth element abundances of (a) the shale at the lower contact with the bentonite, (b) the bentonite itself, (c) the overlying mixed layer, and (d) an average Utica shale are plotted on CaO- and LOI-free basis (Figure 9). The underlying shale and the 'mixed' layer show a strong enrichment in rare earth elements compared to the bentonite and normal (without/undetected bentonite component) Utica shale in the higher part of Canajoharie Creek (average of four shale samples from Canajoharie Creek). This enrichment of the 'mixed' layer and the directly underlying shale can be explained by rare earth mobility. The bentonite rare earth element pattern

Table II: Chemical composition of a bentonite (127), the underlying shale, the 'mixed layer' (on top), and Utica shale (ave. of 4) on a CaO- and LOI-free basis

weight%	Shale below	Bentonite	Mixed layer	Utica shale
SiO2	75.3	54.2	62.8	68.0
TiO2	0.62	0.66	0.86	0.77
Al2O3	13.4	33.2	23.8	15.2
Fe2O3	3.64	2.40	3.48	5.68
MnO	0.06	0.02	0.05	0.09
MgO	2.83	2.17	2.52	5.19
CaO	--	--	--	--
Na2O	1.02	0.30	1.10	0.99
K2O	2.87	6.88	5.02	3.29
P2O5	0.23	0.22	0.27	0.41
(ppm)				
Sc	18	15	23	15
V	90	59	90	99
Cr	76	14	64	95
Co	11	11	22	19
Ni	30	2	29	61
Rb	n.a.	165	164	148
Y	n.a.	26	41	43
Zr	n.a.	253	280	274
Nb	n.a.	21	24	23
Cs	7	13	9.2	8.8
Ba	452	228	321	433
La	121	21.6	102	49.5
Ce	278	74.1	209	97.6
Nd	125	32.9	76	46.2
Sm	24.2	8.83	13.3	9.16
Eu	2.01	0.14	0.92	1.45
Tb	2.84	0.74	1.51	1.16
Yb	9.59	3.13	5.77	3.89
Lu	1.44	0.44	0.79	0.53
Hf	6.2	12	9.9	5.6
Th	15	63	34	14
U	12	20	14	7.6

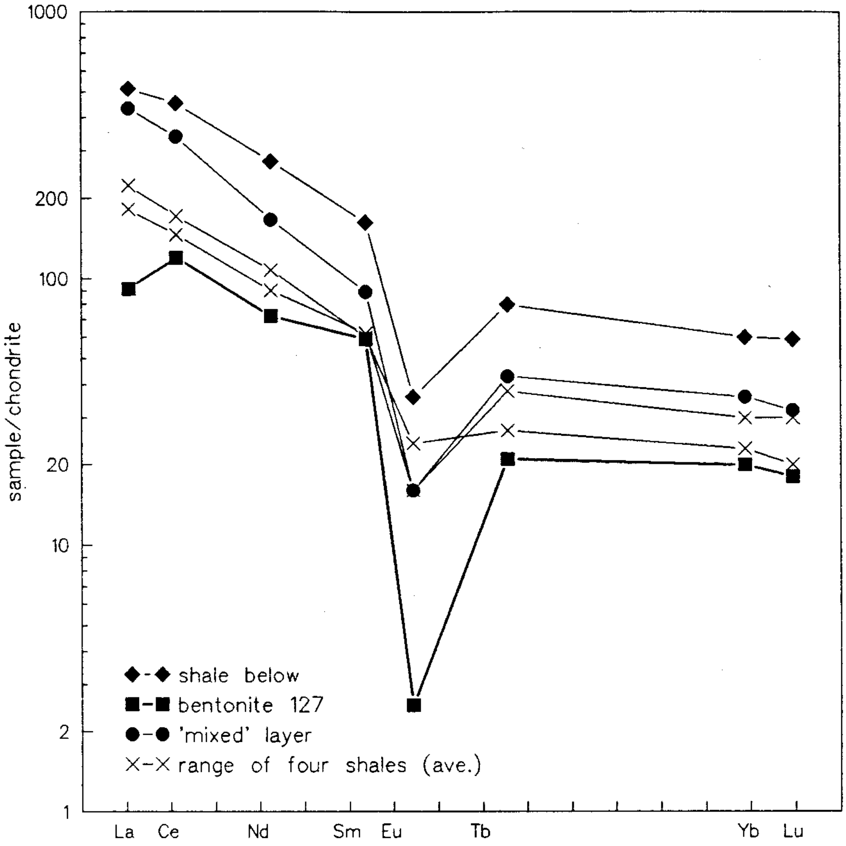


Figure 9: Chondrite-normalized (Anders & Ebihara, 1982) abundances of rare earth elements of bentonite 127, the 'mixed' layer on top, the underlying shale and the range of four bentonites collected away some distance away from bentonites in the higher section of Canajoharie Creek (after Delano et al., 1990).

shows a very strong negative Eu-anomaly, and a positive Ce-anomaly. The light and heavy rare earth elements do not form a continuous line.

Another indicator for silicic volcanism might be the low TiO_2/Al_2O_3 ratio of about 0.02 (Spears and Kanaris-Sotiriou, 1979; Teale and Spears, 1986). However, bearing in mind the unusual behavior of TiO_2 in Figure 8.5, the validity of this ratio appears questionable.

The most convincing evidence for the original melt composition is melt inclusions within zircons and quartz (Schirnick, 1990) that are thought to represent trapped liquid. The SiO_2 and K_2O abundances - after recalculation on volatile-free basis - of the inclusions are high (about 77.5 wt.% and 4.5-6 wt.% respectively), and the CaO and MgO contents are low with 0.7 and 0.02 wt.% respectively (also volatile-free). Not only the melt composition could be derived with confidence, but also diagenetic changes of the glass could be better understood. Finding melt inclusions with connections to the bentonite (through cracks in the zircon) made this possible. The composition of these altered inclusions was not only similar to the <45-microns fraction of 214, but also to the until then unidentified brown phase of the bentonites 127, 214, 306, 308.

For a long time, the composition of the glass (now altered to bentonite) was unknown in this study. The processes known were enrichment of the original glass with FeO, CaO, K_2O and MgO, and loss of SiO_2 and Na_2O. The leaching of SiO_2 leads to an increase of the Al_2O_3 abundance. FeO enrichment appears as pyrite in the bentonites. This enrichment can be explained by FeO mobility in a reducing environment, where FeO becomes trapped in the even more reducing environment of the bentonite. The environment of deposition, seawater and calcareous shales, can account for the CaO enrichment.

The loss of Na_2O and SiO_2, and the enrichment of MgO, CaO, and K_2O is typical for the process of devitrification (Altaner et al., 1984; Fisher and Schmincke, 1984; Scheidegger et al., 1978).

6.2. Bentonite Mineralogy

The bentonites collected in the Mohawk Valley are generally about 2 cm (up to 10 cm) thick, which is thin compared to the thicknesses (i.e. 1-40 cm) reported from the bentonites in the Mississippi Valley (Kolata et al., 1986). The bentonites in the Mississippi Valley are classified in three different groups (Sloan, 1987). The stratigraphically lowest group (Deicke, Millbrig, Elkport, and Dickeyville bentonites) is of Rocklandian to early Kirkfieldian age (Kolata et al., 1986; Sloan, 1987). Of this group the Deicke bentonite is especially important, since it marks the Black River - Trenton boundary (Sloan, 1987). The Deicke bentonite is dated to be 454±3 million years by Kunk and Sutter (1984) using Ar/Ar abundances in biotites. This lowest group of bentonites thickens towards the south, indicating that their source area was located in that direction (Kay, 1931; Kolata et al., 1986; Samson et al. 1989; Sloan, 1887). The bentonites of the lowest group contain only apatites, zircons, and rare biotites (Kolata et al., 1986; Samson et al., 1988; samples from Millbrig and Dikeyville).

The middle group consists of the Calmar, Canover, Nasset, Haldane, and Dygerts bentonites that are late Shermanian age.

The only bentonite from the middle group studied by Samson et al. (1988) was the Nasset bentonite. They found that, while the lower bentonites (i.e. Deicke and Millbrig) have only primary zircons, apatites, and rare biotite, the Nasset bentonite also contains hornblende, almandine-rich garnet, and pyroxene (also observed in our sample of the Nasset). Samson et al. (1989) reported, without explanation, that hornblende and garnet were primary phases. This inference can be of importance.

Samson et al. (1988) stated that Kolata et al. (1986) were not able to classify bentonites on the basis of whole-rock chemistry because of contamination by shale and limestone, and also because of element mobility. For these reasons, Samson et al. (1988, 1989) studied "phenocryst" composition to avoid the difficulties of contamination and element mobility. They chose apatites (1988), and zircons and apatites (1989) for their work. These minerals are doubtless phenocrysts, thus making it possible to achieve valid results, even with a possibly erroneous interpretation of garnets and hornblendes.

Little work has been done on the highest group of four unnamed ashes (Sloan, 1987).

The mineral content of the bentonites from the Mohawk Valley consists of two groups of garnets (see Chapter 7.2.1.), plagioclase feldspar, alkali feldspar, clinopyroxenes, orthopyroxenes, hornblendes, aluminosilicates, quartz, Fe-Ti oxides and rare sphene and tourmaline, and zircon and apatite which are concentrated in the +63 micron and +45 micron size fractions. A brown phase found in 306, 308, 214 and 127 was analyzed with the microprobe, but could not be identified as a mineral. Melt inclusions in zircons and quartz (Schirnick, 1990) connected to the bentonite by cracks in the zircon crystal have the same chemical composition as this brown phase and the analyzed <45-microns fractions. Thus, the brown phase is believed to be an alteration product of the former glass.

Assuming that garnets, hornblendes, and pyroxenes are xenocrysts, the <45-microns fractions should be closest to the true liquid composition. According to Fisher and Schmincke (1984) minerals in ashes are most abundant in the 2000-62.5-microns fractions and therefore the <45-microns fractions should have a small mineral component. Our results indicate that there is not much of a chemical difference between the analyses of a bulk bentonite sample and material <45-microns (Table I). This means that either the minerals do not contribute enough to have a major influence on the bulk chemistry, or that their influence is still present in the <45-microns fraction. Only the Zr abundances show a difference. In the case of the zircons the minerals are phenocrysts (no inherited cores observed, Schirnick, 1990) and the <45-microns fraction should be therefore farther away from the true magma composition than the bulk value in Figure 7, since the zircons are a phenocrystic phase that was extracted (besides xenocrysts). Variable element abundances in different size fractions are important since the minerals are possibly no phenocrysts and a bulk analysis does not represent the magma composition (influence of xenocrysts).

Because of all the possibilities of contamination, the correlation by fingerprinting using bulk chemistry does not seem to be the most reliable method. Over- or underestimates of element abundances will occur, when the mineral component is disregarded. Immobile element abundances especially (for example, heavy rare earth elements) that are concentrated in minerals (possible xenocrysts) might lead to wrong conclusions.

Changes of the ash composition occurring downwind from the volcano are another obstacle for correlation by bulk chemistry. Fisher and Schmincke (1984) describe a gain of SiO_2 and K_2O accompanied with a loss of Al_2O_3, CaO and TiO_2 inferred by different transport distances of phases (glass versus minerals) with variable densities (eolian fractionation after Lirer et al., 1973).

This method of correlation by fingerprinting is not applicable when the stratigraphic relations of the bentonite are unclear. Kolata et al. (1986) state that an unknown bentonite layer cannot be correlated. One needs a firm biostratigraphic framework to undertake the correlation ("an unknown K-bentonite bed must be precisely placed in its chronostratigraphic and lithostratigraphic context", Kolata et al., 1986). Hence, the result of the correlation must be at least partly known before one can use this method. This study attempts to correlate different bentonite layers using their mineral content and establish a method that can correlate single bentonite beds. An earlier attempt to correlate strata with the help of bentonites did not work: "Clay and heavy mineralogy of K-bentonite beds were not useful for stratigraphic correlation because the samples exhibited no systematic variations in clay and heavy mineral content between beds." (Trippi, 1986).

If Person (1982) is right and the depositional environment is the main determinant of the bentonite formation, then the method of correlation by fingerprinting using bulk samples finds its limits with changing basin conditions.

For correlation purposes, the discovery that the bentonite collected in the Trenton Formation does not contain any garnets, pyroxenes, or hornblendes is of major importance. The Wisconsin bentonites (Millbrig, Dickeyville, and the unnamed bentonite), which belong to the lowest group, are time equivalent to the bentonite in the Trenton Formation (Kay, 1931; Kolata et al., 1986; Schirnick, 1990, correlate the Millbrig with the Hounsfield bentonite; Schirnick, 1990 correlates the Trenton bentonite and the Dickeyville bentonite). These older bentonites are non-garnet, non-pyroxene, and non-hornblende bearing. The younger Nasset bentonite, like the bentonites of the Utica Formation, contains garnets, pyroxenes, and hornblendes. All younger bentonites seem to have been erupted under conditions that enabled them to carry garnets and other (xenocrystic and phenocrystic) heavy minerals.

Two different source volcanoes or volcanic systems might have created the observed sequence of bentonites. For the lower bentonites in the Midwest that contain no garnets, hornblendes, pyroxenes and Fe-Ti oxides, the Deike volcano (Sloan, 1987) or a similar volcanic system might be the source shared with the bentonite from the Trenton limestone, while the higher group might share their mineral-rich source with the northeastern bentonites of the Utica Formation.

6.3. Grain-size Distribution Curve

We washed material of 27 bentonites to see whether the bentonites that are stratigraphically correlatable show corresponding grain size distributions. We also wanted to see whether the Wisconsin bentonites would show effects of sorting (i.e. would be finer grained). For this purpose, approximately 0.5 kilogram of bentonite material was washed. The <45-microns fractions (water-clay mixture) were collected with care. The fine material removed from the coarser fractions during the ultrasonic cleaning was added to the run-off. After settling, the water was decanted and the <45-micron fraction was dried and weighed. The cleaned minerals were also dried and weighed.

A cumulative weight percent curve (Figure 10) shows a broad envelope in which most of the bentonites are enclosed. Stratigraphically correlatable layers cannot be recognized, with the exception of the layers 114 and 214, and are therefore not shown. 114 and 214 are both coarser than all other bentonites. Also, their curves are less steep than the curves of the other bentonites. The only samples that were coarser than these two bentonites are the sample of stream sediment from Canajoharie Creek and the glacial sand collected in the same quarry as the bentonite 89-048.

The bentonite of the Trenton Formation is the finest sample and does not come close to the envelope defined by the bentonites of the Utica Formation. It contained an unusually large amount of pyrite (about 90% in the >45-microns fraction) and fossils.

The samples of Millbrig, Dickeyville, and the unnamed Wisconsin bentonite fall within the envelope defined by the bentonites of the Utica Formation (Figure 10). This should not be the case if the bentonites are time equivalent to the Trenton bentonite and have the same source. These Wisconsin bentonites were expected to be finer grained than the Trenton bentonite because they were supposedly further away from the source. The coarser grain size of the Wisconsin bentonites is thought to be related to contamination for two reasons. First, the contamination with shale and calcite is

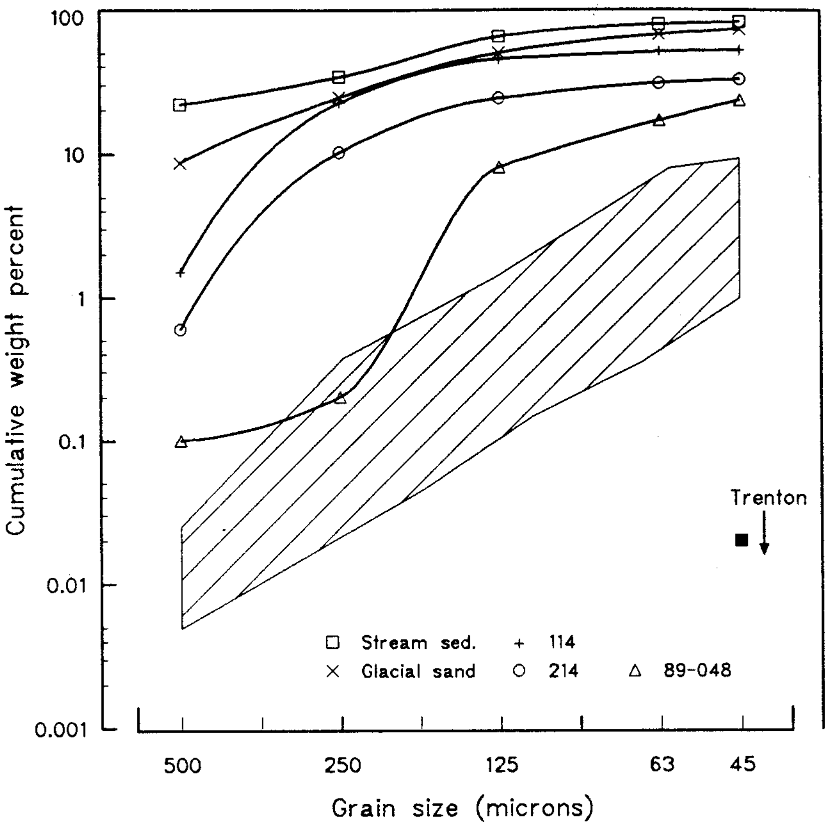


Figure 10: Grain-size distribution curve for the analyzed bentonites. Most of the bentonites fall within the hatched area. The finest sample collected is the one from the Trenton Limestone shown as the black square reaches the limits of this drawing only in the 45 micron fraction (after Delano et al., 1990).

stronger in these samples (Kolata et al. 1986; Samson et al., 1988). Second, the presence of authigenic minerals (i.e. feldspars) might lead to a coarser appearance of bentonites. The Millbrig contains authigenic feldspars (Kolata et al., 1986). This became apparent in two ways: First, dating an aliquot of K-feldspars with the Ar/Ar method gave apparent ages of about 450 million years with a drop of the plateau to younger ages (350 million years), which can be produced by authigenic feldspars. The drop of the plateau cannot be explained with the loss of argon, since feldspars have a closure temperature of about 200°C. The feldspars should cool quickly below this temperature being deposited on a water surface and having not experienced metamorphism after deposition. Second, feldspar analyses on the microprobe indicate the presence of authigenic feldspars in the Millbrig bentonite. This authigenic feldspar population is identified as being high in potassium and low in barium. It is present in the Millbrig bentonite, but missing in the bentonite of 214. An aliquot of K-feldspars from 214 gave an age of 550-750 million years and did not show a drop to younger ages indicating the absence of an authigenic feldspar population.

Overall, the cumulative grain-size distribution curve is not helpful, since it does not reveal any systematic changes between the different bentonite layers in time. For correlation purposes it is not useful because the stratigraphically correlatable bentonites cannot be recognized as identical or distinguished from others (Figure 10). Comparison with similar plots for volcanic eruptions in the literature is impossible, since grain sizes larger than 500 microns are not present. Another difference is that the plotted curves might not resemble the grain size of the volcanic minerals alone, but rather a combination of volcanic minerals, xenocrysts and authigenic phases.

6.4. The "Bentonite" 89-048

This 'bentonite' layer was mineral-rich (i.e. rich in pyroxenes and garnets). After the mineral separation, one could recognize a third group of garnets by its blood-red to brownish color, only by microscopic examination. The composition of these garnets is andraditic with high Ti contents (3000-4000 ppm) and virtually no Zn, Sc, and Y. The chemical analyses of this bentonite turned out to be zirconium-rich and aluminum-poor (Table I), which is atypical for a bentonite.

Seven single K-feldspars were analyzed in several steps with the method of $^{40}Ar/^{39}Ar$ dating. All grains gave total gas ages between 715 and 1018 million years. This is too old to be related to the volcanism that created the bentonites. Therefore, these K-feldspars must be contaminants of older material predating the volcanic events in the late Ordovician. These older ages appear not to be due to excess argon because the difference of about 300 million years would require an unreasonably large amount of excess argon. The low Al_2O_3 content and the presence of a third group of garnets were unusual for the studied bentonites, indicating either a different volcanic source of this bentonite or evidence that this layer is not a bentonite. Because of these facts, we went back to resample that layer. A large plate of overlying shale was removed, and the upper contact of the bentonite became visible, exhibiting a wavy pattern. Ripples of coarser and finer material, which did not seem to resemble grading, and did not parallel the crack pattern of the overlying shale, were visible. Therefore, the idea of the ripples representing overlying glacial sediment that migrated downward into the bentonite had to be rejected. Another possible explanation for this grain size distribution is that recent bioturbation might have caused the pattern within the bentonite. Because of the andradites, the unusual chemical composition (Table I) this layer may not be a bentonite. On the other hand the fact that this layer is not lithified, would be hard to explain in case the layer is not a bentonite. Since this bentonite might be stratigraphically even higher than the bentonite from the Schenectady Formation (collected in Yatesville Creek), the changes observed might be indicators for a change in the crustal component captured during eruption. This example shows that it is not always easy to identify a bentonite in the field, especially when the layer is dry and exposed in a different environment from all the other samples.

6.5. The Problem of Canajoharie and Flat #14

In general, the mineral content of the treated bentonites is very similar, with the exception of 114, 115 and 214, 215. While 114 is extremely mineral-rich, 214 is lacking heavy minerals like garnets, hornblende and pyroxenes, but carries Fe-Ti-oxides and a well developed zircon population (Schirnick, 1990). Instead of minerals, yellow-orange aggregates are found which might be alteration products of minerals. No core of original material is left in these aggregates, and determining what they replace was impossible.

This difference in the two samples is startling, especially since they are the same layer according to the stratigraphic columns (Figure 3). The mystery of where the minerals of 214 have gone to or what made them disappear could not be resolved. A scenario of another source of 214 and 114, for example explaining the layer as a result of unusual Ordovician detrital or glacial (Pleistocene) sedimentation, does not appear reasonable.

The chemical analyses of the two samples are very similar to all the other bentonites, with the exception that 114 is strongly enriched in barium, a mobile element. 114 and 214 plot in the Winchester and Floyd diagram (Figure 7) together with all the other bentonites. The chemical analysis of 114 has low totals (97.84 and 98.35 for the bulk and <45-microns fraction respectively) indicating that one element is present outside the analysis. The analyzing laboratory suggested lithium as the missing element. The only minerals that have, to my knowledge, Li in their structure would be the mica lepidolite and zeolites, but no micas or zeolites were observed in the bentonites.

The grain-size distribution curves of these two bentonites are totally different from all other bentonites but very similar to each other - they are much coarser and comparatively flat - a point that supports the correlation. In both creeks the #15 bentonites have no heavy minerals, and are therefore similar to 214. The #16 layers are unaccessible in both creeks and only in Flat Creek was #17 collectable. In this sample the "normal" mineral content was observed. An explanation for the missing minerals could be some dissolving agent, perhaps acidic. This agent would have to dissolve a part of the heavy minerals, leaving the zircons unattacked. The disappearance of the minerals in both creeks at the level of #15, might show that the agent was migrating from east to west, which would mean, it could be subduction related. The scenario seems unrealistic, since the feldspars, which are less stable than garnets, pyroxenes and hornblendes, apparently survived such a hypothetical attack.

7. Garnets

7.1. Literature Review

Finding garnets in these bentonites was surprising, since garnets are most commonly found in metamorphic rocks. They are not unknown in igneous rocks, however, and have been described in granites, rhyolites and other siliceous rocks (Abbott, 1981; Allan and Clarke, 1981; Bacon and Duffield, 1981; Barley, 1987; Birch and Gleadow, 1974; Clemens and Wall, 1984; Du Bray, 1988; Fitton, 1972; Fitton et al., 1982; Gilbert and Rogers, 1989; Green, 1977; Green and Ringwood, 1968; Harrison, 1988; Irving and Frey, 1978; Jaffe, 1951; Kistler et al., 1981; Miller and Stoddard, 1981; Oliver, 1956; Stone, 1988; Thirwall and Fitton, 1983; Wood, 1974). Garnet-bearing magmas are commonly peraluminous, calcalkaline and corundum-normative (Cawthorn and Brown, 1976; Miller and Stoddard, 1981).

The garnets - observed in the bentonites - could be incorporated into these Ordovician ashes in three ways: (a) as igneous phenocrysts, (b) as pieces of igneous or metamorphic wall rock incorporated during the ascent of the magma or (c) as residue of a partially molten source rock (Fitton, 1972; Harrison, 1988; Stone, 1988; Vennum and Meyer, 1979; Wood, 1974).

Miller and Stoddard (1981) observed that typical garnets from granitoids contain more than 10 mol.% spessartine, while garnets with less than 10 mol.% spessartine are evidence for elevated pressures. Green (1977) showed that the typical garnet from silicic igneous rocks contains about 2-6 mol.% grossular and 2-10 mol.% spessartine when formed at pressures of about 5-7 kbar. These molar proportions are very similar to the ones found by Oliver (1956) in Lake District phenocrystic garnets: Almandine 67-79 mol.%, spessartine 4-13 mol.%, pyrope 6-21 mol.%, and grossular and andradite together 4-11 mol.%.

Garnets from Precambrian granulite terrains are characterized by Deer et al. (1982) as having almandine 60-70 mol.%, spessartine 1-5 mol.%, pyrope 30-5 mol.%, and grossular plus andradite 5-20 mol.%.

Birch and Gleadow (1974) wrote after their investigation on Australian garnets: "Comparison of Types 1 (igneous), 2 (metamorphic), 3 (igneous) and 4 (only one grain) garnets with garnets from granulite facies terrains and other acid volcanic rocks, shows there is no obvious chemical distinction between garnets from these sources". Garnet analyses of phenocrysts in silicic rocks reveal that almost no chemical restrictions exist for these garnets. Even though many igneous garnets are enriched in FeO and MnO, a distinction cannot be made between igneous and metamorphic compositions (Birch and Gleadow, 1974; Stone, 1988).

Mantle garnets show a strong enrichment in magnesium compared to crustal garnets (Wimmenauer, 1985), while extremely high manganese content stabilizes garnets at very low pressures (lower than 3 kbar, Green, 1977; Miller and Stoddard, 1981; Stone, 1988). These two criteria are not met by the garnets of the bentonites, so that a mantle origin as well as a very low pressure environment can be excluded as a source for them.

The CaO contents reported seem to suggest that phenocrystic garnets have low CaO contents (Bacon and Duffield, 1981; Fitton, 1972; Harrison, 1988; Kistler et al., 1981). Gilbert and Rogers (1989), however, described Permian phenocrystic garnets from the Pyrenees with 14-19 mol.% grossular (the highest grossular content in phenocrystic garnets reported in the literature). They suggested that the high CaO content is related to high pressures in the source area of the garnets. Fitton (1972) observed in the Borrowdale Volcanics that CaO abundances in garnets decreased going from andesites to dacites.

Perkins et al. (1982) described metamorphic garnets of granulite facies, in a sampling area of only 40 km x 80 km, with low (below 5 wt.%) and high (above 5 wt.%) CaO abundances. The CaO content increases with higher pressure (Ellis and Green, 1979; Green and Ringwood, 1968 - experimental work; Green, 1977 - for igneous garnets; Kepezhinskas, 1973 - for metamorphic garnets); the highest CaO content is found at the lowest grade of metamorphism, similar to MnO (Miyashiro, 1953; Miyashiro and Shido, 1973; Nandi, 1967; Sturt, 1962 - all worked on metamorphic garnets). The CaO content decreases irregularly with increasing temperature (Nicholls and Harris, 1980 - experimental work). At the same time the CaO content of the host will have a major influence on the amount of this element incorporated into a garnet (Fitton, 1972; Green, 1977). Therefore, the CaO content might not be the most useful discriminator to describe P-T conditions of garnet formation.

Green and Ringwood (1968) demonstrated experimentally that garnet can be a liquidus phase in rhyodacitic liquids at pressures of 9-18 kbar. They found further that the water pressure of the magma has major influence on the stabilization of garnet. In wet magma garnets might crystallize at lower pressures than 9 kbar (also Harrison, 1988). Having in mind that the volcanism is related to a subduction zone - with the possibility to remelt water-rich sediments - it seems possible to reach high enough pressures to crystallize garnets.

Generally two source areas are viable for phenocrystic garnets: (1) dry, high-pressure environments or (2) highly evolved, shallower and more water-rich peraluminous magmas (Harrison, 1988; Stone, 1988). Wood (1974) suggested as source area for the garnets developed in rhyolites (New Zealand) the lower crust or upper mantle region (33-55 km). At high pressures the crust - consisting of high-grade amphibolite and granulite facies metamorphic rocks - would start to melt and the products (rhyolites) are thought to be equivalents to charnockites, probably erupted because of high water contents.

Cawthorn and Brown (1976) reported that garnets crystallizing from highly differentiated magmas under crustal pressures exclude other ferromagnesian phases. This observation is in unison with the observations on the Borrowdale Volcanics: augites cease to crystallize when garnet crystallization starts (Fitton, 1972).

Metamorphic garnets are sensitive to changes in P-T conditions. Miyashiro (1953) observed in garnets of increasing metamorphic grades a tendency to regular substitutions. These trends observed for the cations in the eight-fold position are believed to be a feature related to crystal structure. Mn^{2+} (0.91Å) has the ideal size to fill the eight-fold position (cubic distorted) in the garnet structure, and therefore easily enters this crystallographic site. At elevated pressures first Fe^{2+} (0.83Å) and then Mg^{2+} (0.78Å), which are both smaller than Mn^{2+}, can substitute more easily for Mn. Ca^{2+} (1.06Å), the largest of the cations is believed to be favored in igneous garnets at higher pressures in any liquid at a fixed CaO content (Green, 1977).

Increasing CaO abundances in garnets of higher metamorphic grades may be due to the breakdown of less stable minerals like epidote and plagioclase. These minerals might become unstable, break down and thereby release CaO, which could enter the garnet structure.

Reactions that may occur: plagioclase + pyroxene = garnet + quartz
plagioclase = garnet + aluminum-silicate + quartz

Miyashiro (1953) found in his study of CaO-poor garnets from different metamorphic grades that the MnO content of garnets decreases with increasing metamorphism, while FeO and at higher grades of metamorphism MgO are the favored cations. Miyashiro and Shido (1973) explain the loss of MnO with increasing metamorphism by an increasing population of garnets and therefore, less available MnO in the host rock distributed between more garnets. On the other hand, Müller and Schneider (1971) found by comparison of Miyashiro's (1953), Engel and Engel's (1960), and their own metamorphic garnets from three different host rocks, that simple relationships between metamorphic grade and MnO content do not hold. They observed in arkosic and pyroclastic host rocks that with increasing metamorphic grade the MnO content is unaffected or even rises. However, for pelitic rocks the general relationship of lower MnO content with increasing metamorphism was confirmed.

Similar trends to the ones observed by Miyashiro (1953) were found by Engel and Engel (1960) (Figure 11). They observed in garnets from the Adirondacks that with increasing metamorphism certain elements (Zn, Ti, and Mg) are favored in the garnet structure, while others (Fe_2O_3, Y, and Sc) leave the garnet. Sturt (1962) gave a summary of the work by Miyashiro (1953) and the Engels (1960), and reported additional data on garnets of pelitic schists. He observed in CaO-poor garnets a regular trend plotting (CaO+MnO) versus (MgO+FeO). The garnets fall on a line with a negative slope recording the grade of metamorphism. The lowest metamorphic conditions are reported by garnets with high (CaO+MnO) and low (MgO+FeO). This trend is confirmed by Nandi (1967) who also measured the unit cell edges of the garnets.

On the other hand, differences in the host rock composition can override P-T information retained by garnets. The lack of knowledge about the host rock composition makes deduction of the source area by garnet chemistry a difficult task. Garnets crystallized under the same P-T conditions will look different, when they are developed in different rock types (Müller and Schneider, 1971).

In the literature phenocrysts and xenocrysts are often distinguished on the basis of the abundance of inclusions: inclusion-rich indicates more likely metamorphic origin, inclusion-free magmatic origin (Clemens and Wall, 1984; Stone, 1988). Also, to infer from the presence of other intergrown phenocrystic minerals the character of the garnets seems to be common practice (Wood, 1974). This procedure is not helpful with the garnets in the bentonites, because some are inclusion-rich, others clear and free of inclusions. A clear relationship as in the garnets of Clemens and Wall (1984) could not be observed. Among their garnets they detected a group (D) in which the cores of the garnets were inclusion-rich bearing quartz and sillimanite (=metamorphic), while the rims were inclusion-free (magmatic). Hence, the conclusion can be drawn that the cores are older metamorphic garnets overgrown by magmatic rims. The compositions of all

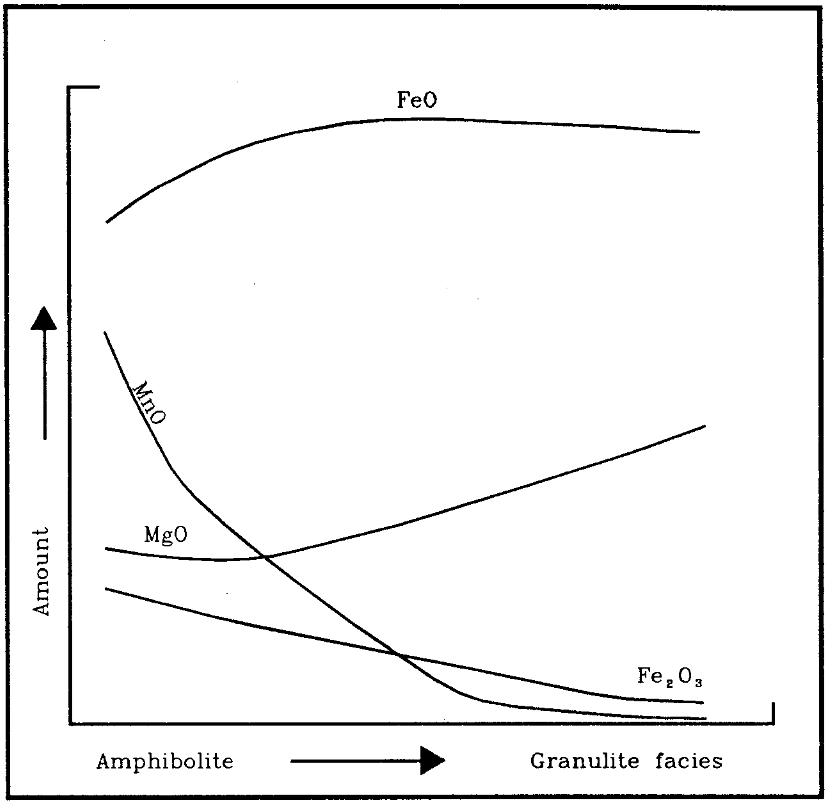


Figure 11: Varying element abundances in garnets of different metamorphic grades (after Engel and Engel, 1960)

the observed garnet groups (A, C, D) are not very distinct, so that by compositional differences a distinction of the groups seems impossible. A similar feature of overgrowth is observed by Rumble and Finnerty (1974), where garnets of Ordovician age were overgrown by rims in the Devonian. In this case, the composition of the garnet cores and the rims are completely different.

Another way to decide the question whether the garnets are phenocrysts or xenocrysts is the observation of the occurrence within different hosts (Birch and Gleadow, 1974; Fitton, 1972; Gilbert and Rogers, 1989). Fitton (1972) observed different garnet compositions depending on the character (andesite or dacite) of the host volcanics. This coupled occurrence of garnet and host is a safe indicator of phenocrystic minerals. In the case where the minerals are contamination, the occurrence of minerals (garnets) with the same composition(s) in every host would be more reasonable. This is observed in the Utica bentonites.

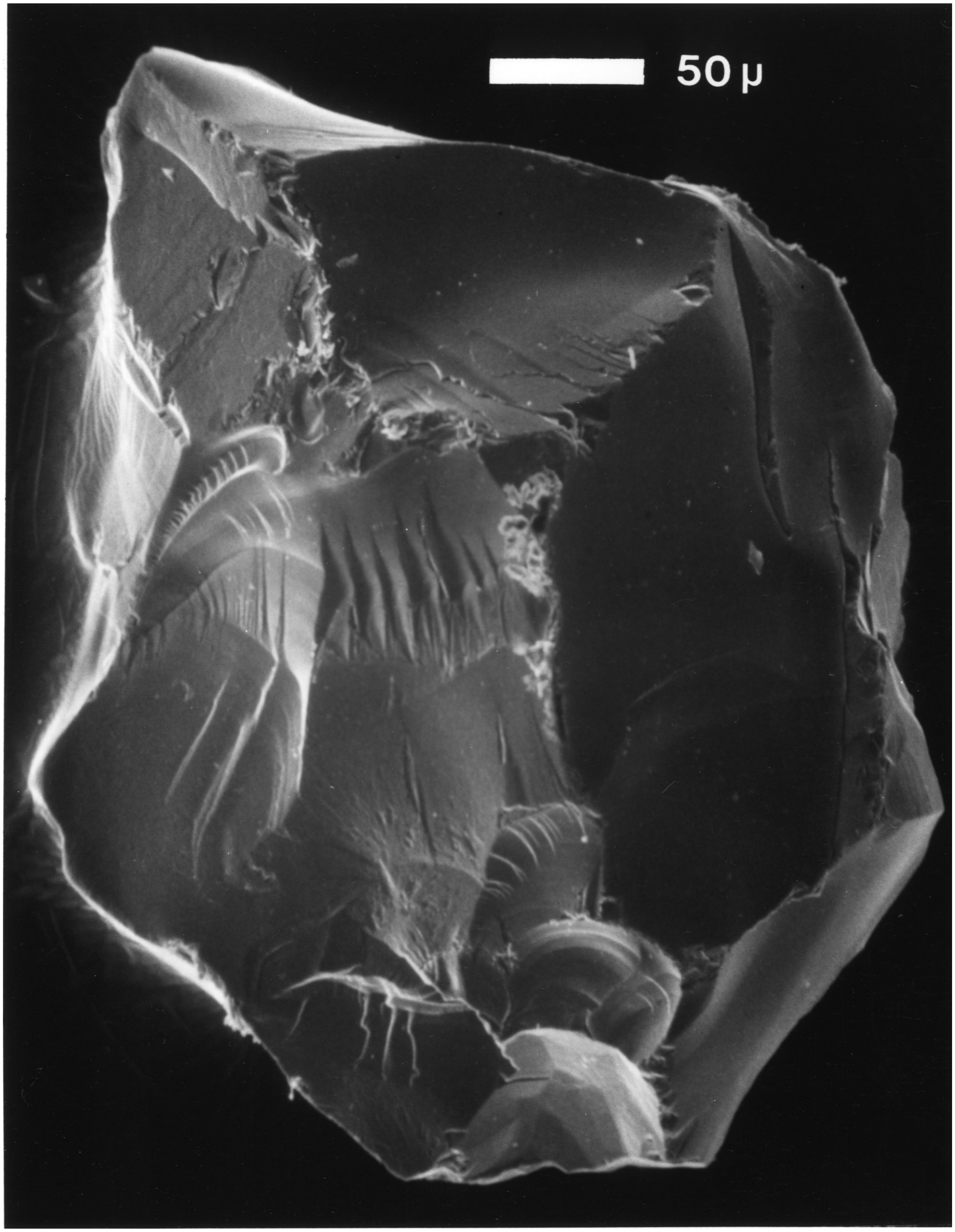
After the literature research one has to come to the conclusion: Garnets of different environments can hardly be recognized by major element chemistry. Only the very extreme cases of mantle origin or very low pressure origin might be deduced from major element chemistry. The trace elements might be more diagnostic for variable source compositions, and be able to reveal subtler differences. For example, the K_D-values between garnet and melt for rare earth elements are believed to change with the silicon content of the melt, but also with temperature of the system and the CaO content of the garnet (Nicholls and Harris, 1980). Knowing that the magma was of rhyolitic composition (melt inclusions from Schirnick, 1990), some constraints can be placed on abundances of trace elements in phenocrystic garnets.

The ultimate difficulty is that the original igneous mineral assemblage of the magma that produced the bentonites is unknown. Therefore, partition coefficients that compare for example the Mg-Fe exchanges between ferromagnesian minerals like garnet and pyroxene, hornblende or biotite are not necessarily applicable (Birch and Gleadow, 1974;

Wood, 1974). These circumstances make the rock fragments valuable because they are the first indicators of the mineral assemblages, true grain sizes, and equilibrium conditions between phases. They are relicts of the garnet's source area.

The only possibility that the garnets are totally unrelated to the genesis of the bentonites would be that the garnets are detrital. This could be possible, since the bentonites crop out in creeks and the stream sediment is garnet-bearing. Garnet contamination by the stream sediment can be excluded because of the sampling methods. The garnets could also be a contamination by garnet-bearing shales soon after the ash deposition. The sparseness of garnets in the shales contradicts this theory. Furthermore, examination of some garnets with the scanning electron microscope in the Biology Department at SUNYA makes a detrital origin implausible. The garnets are unrounded, showing conchoidal fractures and V-shaped pits (Figure 12). It is hard to believe they were transported as detrital grains, when compared to rounded to subrounded alluvial garnets (Albanese and Kelley, 1990; Simpson, 1976).

Figure 12: SEM photograph showing a representative garnet exhibiting sharp edges and conchoidal fractures.


50 μ

7.2. Microprobe Results on Garnets

7.2.1. Major Elements

Three hundred and fifteen major-element analyses were done on two hundred twenty-five individual garnet grains. No evidence for zoning was found in the duplicate analyses. The diagrams presented show one hundred twenty-six data points and contain no double analyses. Representative garnet analyses are given in Tables III.I and III.II.

Interestingly, the garnets found within the bentonites show two distinct colors: A pink group and a dark red group. An hypothesis was that one of these groups represents a magmatic population, while the other one a metamorphic population. These two groups of different colored garnets are readily distinguished by their CaO content (Table III.I and III.II). While the light colored garnets contain generally less than 5 wt.% CaO (= 0.4 up to 10 mol.% grossular), the dark colored garnets contain more than 5 and up to 8.7 wt.% CaO (= 15-22 mol.% grossular) (Figure 13).

Quartz is the most common inclusion within the garnets of the bentonites, but apatite, ilmenite, hornblende, feldspar, and zircon are also observed. The problem with analyzing these inclusions is that they are often very small, and therefore, the garnet composition blends in the analysis.

Zoning could not be observed in either group of the garnets. The absence of zoning in the garnets of the rock fragments, where the garnets still show crystal faces and their original size (Figure 14), supports the view that there is no zoning present.

The dark garnets have a lower sum of FeO and MnO content than the pink garnets and also show a maximum of analyses with low MgO contents (around 3 wt.%). The pink garnets have MgO contents of 5-11 wt.%. The MnO content of the garnets of both groups is low, below 3 wt.%, indicating after Miller and Stoddard (1981) elevated pressures (also Green, 1977; Stone, 1988).

Table III.I: Representative microprobe analyses of dark (CaO-rich) garnets (Major elements in weight percent, trace elements in ppm; recalculation in mol percent after Rickwood (1968), Fe2O3 recalculation (see appendix B))

SiO2	37.65	38.16	36.81	37.14	37.53	37.36	38.37	37.12	37.57
TiO2	0.03	0.10	0.05	0.03	0.04	0.04	0.04	0.06	0.04
Al2O3	20.00	20.08	20.65	20.36	20.51	21.89	22.07	20.16	20.63
Fe2O3	1.60	2.20	0.80	1.10	0.50	0.00	0.00	1.60	0.50
FeO	32.81	26.89	32.68	31.83	32.58	32.75	29.03	31.62	31.57
MnO	1.21	3.83	1.61	2.20	1.31	1.22	1.83	1.71	1.45
MgO	1.00	1.83	0.60	0.72	0.79	0.96	4.26	0.72	0.89
CaO	6.78	8.93	7.21	7.15	7.02	7.73	6.38	7.84	7.58
Total	101.08	102.02	100.41	100.54	100.28	101.94	101.98	100.83	100.23
Ti	157	621	314	152	251	258	223	368	220
Zn	103	98	66	83	132	107	99	35	172
Y	1977	1482	1026	962	870	848	709	670	656
Sc	32	59	0	25	49	38	173	70	29
Andr.	4.89	6.50	2.45	3.34	1.50	0.00	0.59	4.90	1.52
Pyr.	4.02	7.20	2.41	2.90	3.20	3.82	16.54	2.90	3.58
Spess.	2.80	8.50	3.71	5.02	3.01	2.76	4.04	3.90	3.32
Gross.	14.70	18.70	18.52	17.30	18.90	22.20	17.20	17.80	20.41
Alm.	73.70	59.10	73.00	71.43	73.40	71.30	61.60	70.60	71.17

Table III.I: (continued)

SiO2	38.07	37.09	37.27	36.62	36.94	38.22	38.63	38.02	38.76
TiO2	0.04	0.04	0.08	0.06	0.06	0.03	0.04	0.03	0.12
Al2O3	20.67	20.46	20.21	20.76	20.72	20.32	22.42	21.10	22.00
Fe2O3	1.10	1.60	1.30	0.80	1.00	1.40	0.00	0.70	0.60
FeO	32.39	27.64	32.46	31.17	31.65	28.52	26.89	30.74	25.83
MnO	1.19	1.65	1.43	1.12	0.75	2.66	2.58	1.01	0.91
MgO	1.01	3.48	0.56	1.22	1.13	3.04	5.26	2.69	6.09
CaO	7.77	7.54	7.55	8.28	8.21	6.55	5.93	7.10	7.47
Total	102.23	99.50	100.85	100.03	100.46	100.75	101.75	101.38	101.78
Ti	215	219	456	355	364	181	239	166	691
Zn	101	10	122	110	190	43	80	0	51
Y	534	495	484	476	279	201	160	149	0
Sc	11	108	1	48	32	82	248	26	79
Andr.	3.33	4.87	3.94	2.47	3.06	4.21	0.00	2.10	1.75
Pyr.	4.00	13.98	2.24	5.00	4.56	12.07	20.30	10.54	23.41
Spess.	2.67	3.77	3.26	2.60	1.70	6.01	5.65	2.24	1.98
Gross.	18.74	16.92	17.79	21.75	20.80	14.51	16.44	17.92	18.90
Alm.	71.30	60.46	72.77	68.22	69.90	63.20	57.60	67.22	53.96

Table III.II: Representantive microprobe analyses of light (CaO-poor) garnets (Major elements in weight percent, trace elements in ppm; recalculation in mole percent after Rickwood (1968), Fe2O3 recalculation (see appendix B))

SiO2	37.59	38.29	38.33	38.70	38.53	39.35	37.66	38.67	37.58
TiO2	0.00	0.01	0.00	0.02	0.01	0.02	0.01	0.01	0.01
Al2O3	22.36	21.83	22.21	22.22	21.67	21.94	21.13	22.27	21.35
Fe2O3	0.00	0.10	0.00	0.10	0.60	0.10	0.70	0.00	0.70
FeO	32.90	32.44	31.22	28.90	28.84	28.00	34.66	29.45	32.81
MnO	0.74	0.63	0.57	0.46	0.53	0.63	0.68	0.49	0.70
MgO	5.47	6.06	6.84	8.78	8.08	9.05	4.91	8.26	6.33
CaO	1.36	1.87	1.74	1.56	2.12	1.42	1.11	1.60	0.89
Total	100.43	101.25	100.92	100.74	100.40	100.50	100.85	100.77	100.38
Ti	26	68	16	143	86	146	43	79	66
Zn	89	137	61	213	105	137	87	161	105
Y	1496	1062	463	439	282	260	186	180	180
Sc	111	128	134	110	190	169	141	127	170
Andr.	0.00	0.29	0.00	0.30	1.74	0.30	2.10	0.00	2.10
Pyr.	21.70	23.60	26.60	33.79	31.30	34.66	19.42	31.84	25.10
Spess.	1.66	1.40	1.30	1.00	1.20	1.37	1.54	1.08	1.57
Gross.	3.89	4.90	4.90	4.03	4.15	3.60	1.05	4.44	0.44
Alm.	72.76	69.80	67.30	60.90	61.67	60.10	75.90	62.60	70.80

Table III.II: (continued)

SiO2	39.19	38.56	38.23	39.20	38.48	38.46	39.40	38.91	38.16
TiO2	0.01	0.02	0.00	0.02	0.01	0.01	0.02	0.01	0.02
Al2O3	22.11	22.11	22.87	22.96	21.90	21.89	22.76	22.45	21.80
Fe2O3	0.20	0.00	0.00	0.00	0.30	0.60	0.00	0.30	0.00
FeO	30.53	31.45	32.81	29.37	31.48	27.20	28.57	27.23	32.88
MnO	0.60	0.41	1.27	0.63	1.02	0.51	0.43	0.30	0.52
MgO	7.72	7.25	5.76	8.26	6.83	9.67	9.50	10.43	5.36
CaO	1.19	1.28	1.23	1.24	1.50	1.47	1.53	1.19	2.20
Total	101.55	101.07	102.17	101.67	101.52	99.81	102.20	100.82	100.93
Ti	79	102	29	97	38	65	107	76	92
Zn	107	160	67	94	136	186	154	206	151
Y	170	167	135	91	89	86	67	0	0
Sc	163	146	185	154	159	163	147	81	87
Andr.	0.60	0.00	0.00	0.00	0.90	1.76	0.00	0.90	0.00
Pyr.	29.63	28.03	22.50	31.79	26.45	37.48	35.93	39.95	20.90
Spess.	1.23	0.89	2.80	1.40	2.24	1.13	0.93	0.66	1.15
Gross.	2.71	3.56	3.70	3.40	3.30	2.35	4.20	2.40	6.16
Alm.	65.78	67.52	71.30	63.40	67.13	57.29	58.98	56.12	71.77

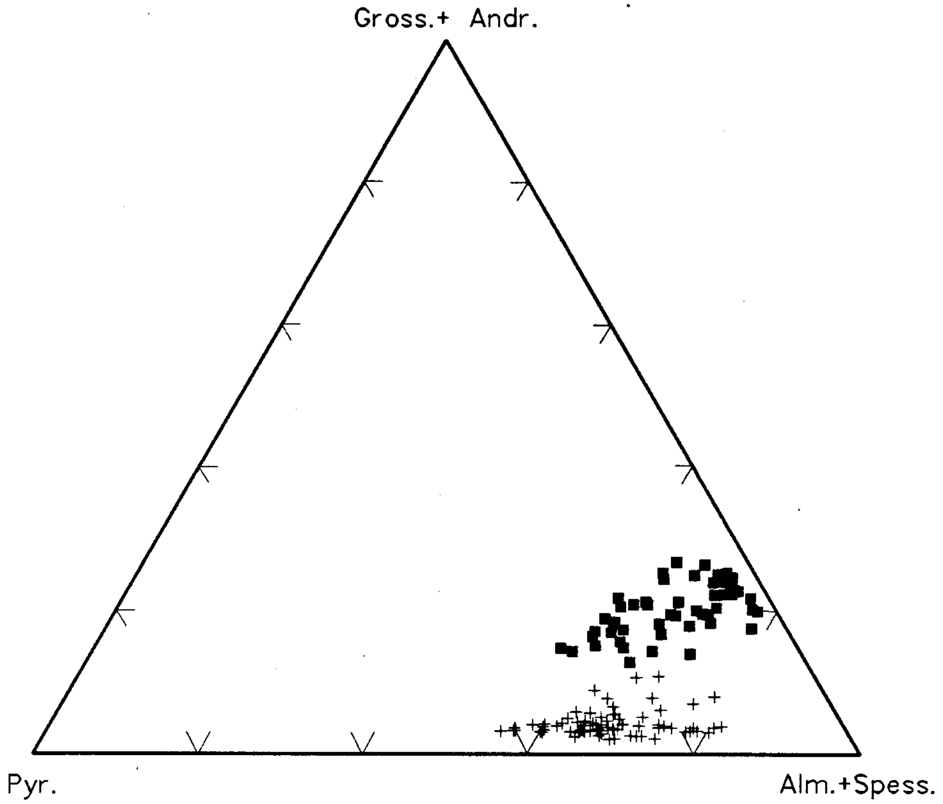
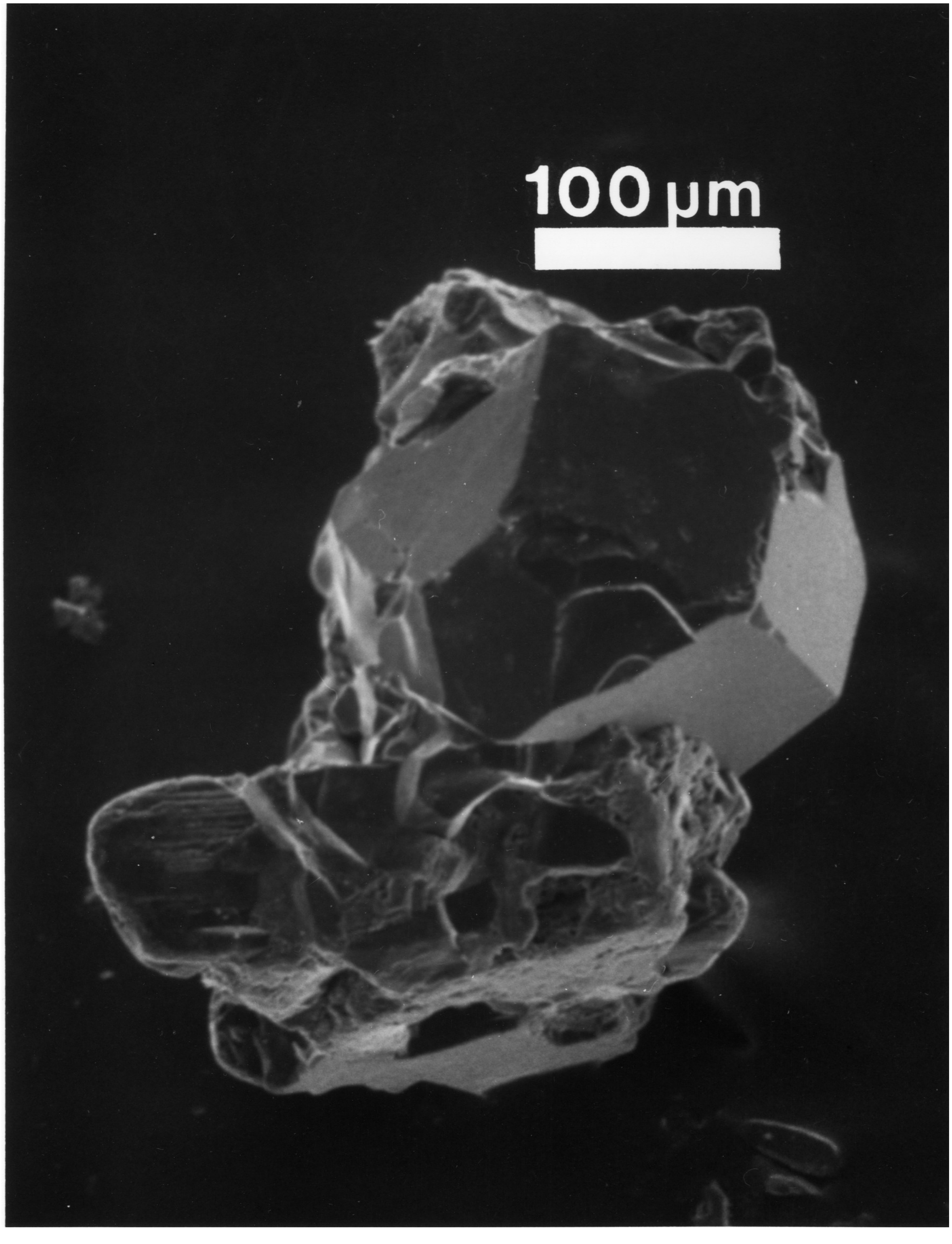


Figure 13: Ternary diagram showing the two different groups of single grain garnets (■ dark=ca. 20 mol.% grossular, + pink=ca. 4 mol.% grossular).

Figure 14: SEM picture of rock fragment 307-1 showing crystal faces.


100 µm

Stone (1988) showed in a ternary diagram with the components almandine-spessartine-pyrope the compositions of garnets from volcanic rocks. Many garnets of the bentonites plot within the outlined field for volcanic garnets, and hence, could be of volcanic origin. The disadvantage of this diagram is that the garnets are expressed with only three components (almandine, spessartine and pyrope) omitting the grossular component.

Unfortunately, for correlation purposes, the garnets of all bentonites plot within the same field (Figure 13), and it is impossible to trace one bentonite layer by its garnet content. Only the sample 89-048 from Copenhagen could be identified as different from a normal Utica bentonite with the help of the garnets. This layer contained, besides the usual two groups of garnets, a third major group of garnets of andraditic composition. They show a high CaO and high TiO_2 content which might be the cause for their very dark color. Dowty (1971) attributes the dark brown color of andradites to charge-transfer absorptions.

7.2.2. Trace Elements

One hundred fifty-seven garnet analyses including trace elements were performed on one hundred twenty-six individual grains. Trace elements that seemed worth an attempt to analyze were: Ti, Sc, Y, Zn, Yb, Ce, Zr and Cr. After 30 analyses of 20 individual grains with counting times up to 1000 seconds and a sample current of 100 nanoampere, Ce, Zr, Yb and Cr were taken out of the analyses. No measurable amounts of Ce, Yb and Zr could be detected. Remarkable about the abundances of Cr is that none of the dark garnets contained Cr, not even when containing high abundances of TiO_2. Instead, from 12 light garnets analyzed, 6 contained measurable amounts of Cr

(100-190 ppm). Cr was not correlated with any other trace element, but seems to be positively correlated with MgO. Garnets with more than 8 wt.% MgO carried measurable amounts of Cr indicating that the Cr-bearing endmember is not in the CaO series (Uvarovite), but might be the endmember knorringite $(Mg,Cr)_3Al_2Si_3O_{12}$.

The difficulty in evaluating the results on the trace elements was the sparseness of data in literature. I completely agree with Harrison (1988): "Yttrium analyses are rarely presented for garnets, and the study by Jaffe (1951) is by far the most extensive work on this subject".

The amount of TiO_2 is positively correlated with the CaO content, so that the dark garnets contain more TiO_2 than the light garnets (Figure 15). While the TiO_2 distribution appears to be positively correlated with the CaO abundance within the dark garnets, in the light garnets no correlation of these two elements can be recognized. Sc shows for the two groups a negative correlation with CaO and is therefore enriched in the light garnets (Figure 16). Within the single groups no correlation of CaO and Sc abundances is visible. Y is not enriched in either of the two groups, but seems to favor slightly the dark garnets. As in the major elements no zoning could be observed in the trace elements. However, in garnets with high Y abundances, Y might vary considerably (variations of about 200 ppm). In general, the garnets of the bentonites are Y-poor. Compared to the limited data in the literature, they contain too little Y to be crystallized in a rhyolitic or dacitic magma. Jaffe (1951) describes the garnets of schists as MgO-rich and Y-poor. Many of the pink garnets would fit very well to these characteristics. High pyrope content (40-70 mol.%) is stated by Deer et al. (1985) to be typical for garnets from granulite-facies.

The garnets from the Lake District (Oliver, 1956) contain 2000-3000 ppm Y, which are typical amounts of this element for garnets of granitic and pegmatitic origin (Fitton, 1972: Y in garnets of dacites about 1700 ppm; Harrison, 1988: Y up to 1.67 wt.%; Du Bray, 1988: Y of 300-3000 ppm).

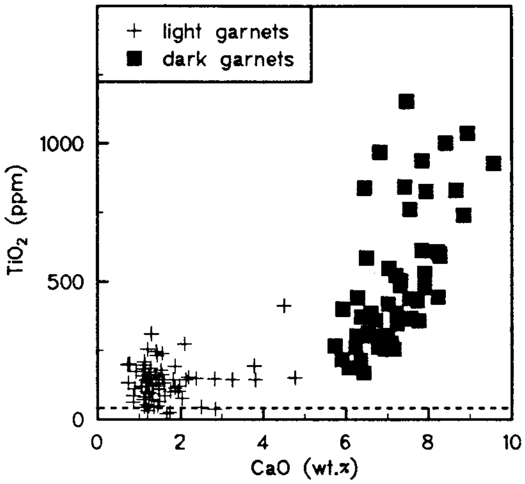


Figure 15: TiO_2 plotted against the CaO content showing the positive correlation between the two elements in the garnets of the Utica Formation.

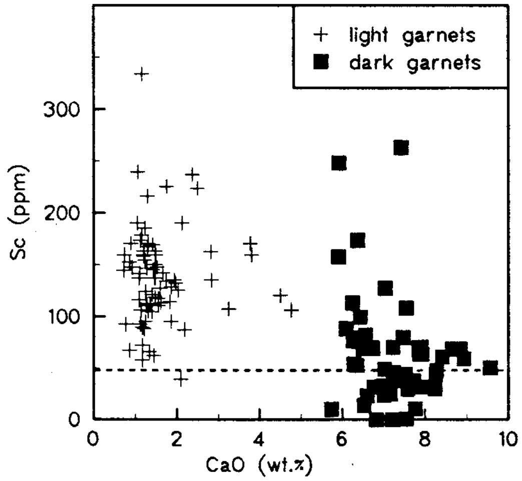


Figure 16: Systematic variations of Sc with CaO abundances in the garnets of the Utica Formation. Dashed lines in Figures 15 and 16 indicate abundances of trace elements above which the analytical errors are smaller than 25.5%.

Jaffe (1951) derived the following rules of element distribution in garnets: (a) Sc is generally highest in pyrope-rich garnets, (b) spessartine garnets contain the highest amount of Y (the proposed substitution is Y+Al = Mn+Si), and (c) high amounts of Y are less common in pyrope and uncommon in CaO-rich garnets. In his analyses of thirteen CaO-rich garnets from different localities, only one garnet showed traces of Y (less than 0.5 wt.%). This garnet sample was taken from the western Adirondacks, NY.

The garnets of the bentonites do not follow these proposed trends: Sc is enriched in the pink garnets which generally have higher MgO contents than the dark garnets, but within the pink garnet Sc does not vary regularly with the MgO content. The MnO content of both groups of garnets is very low, therefore high amounts of Y cannot be expected. The dark garnets are very slightly more MnO-rich than the pink garnets, and again a trace of a trend might be present, but it is not a strong and consistent tendency. As to (c), the observations on the garnets of the bentonites are contradictory to Jaffe's, since the dark (= CaO-rich) garnets are slightly enriched in Y.

The dark garnets of the bentonites define a trend such, that MgO-poor, FeO-rich garnets are enriched in Y compared to MgO-rich, FeO-poor garnets. This trend becomes visible in a diagram plotting FeO against MgO, marking garnets with high and low Y abundances with different symbols (Figure 17.1). FeO and MgO are strongly negatively correlated, and Y is most enriched in garnets with high FeO and low MgO abundances.

The few garnets recovered from the Nasset bentonite (only two dark and 22 pink garnets) were not analyzed for trace elements. The two dark garnets recovered from this bentonite plot at the lower and upper end of the trend defined by the dark garnets of the bentonites in Figure 17.1 (Figure 17.2). The pink ones fit the trend of the pink garnets of the Utica Formation with the exception of three strongly MnO enriched (around 10 wt.%) pink garnets (Figure 17.2).

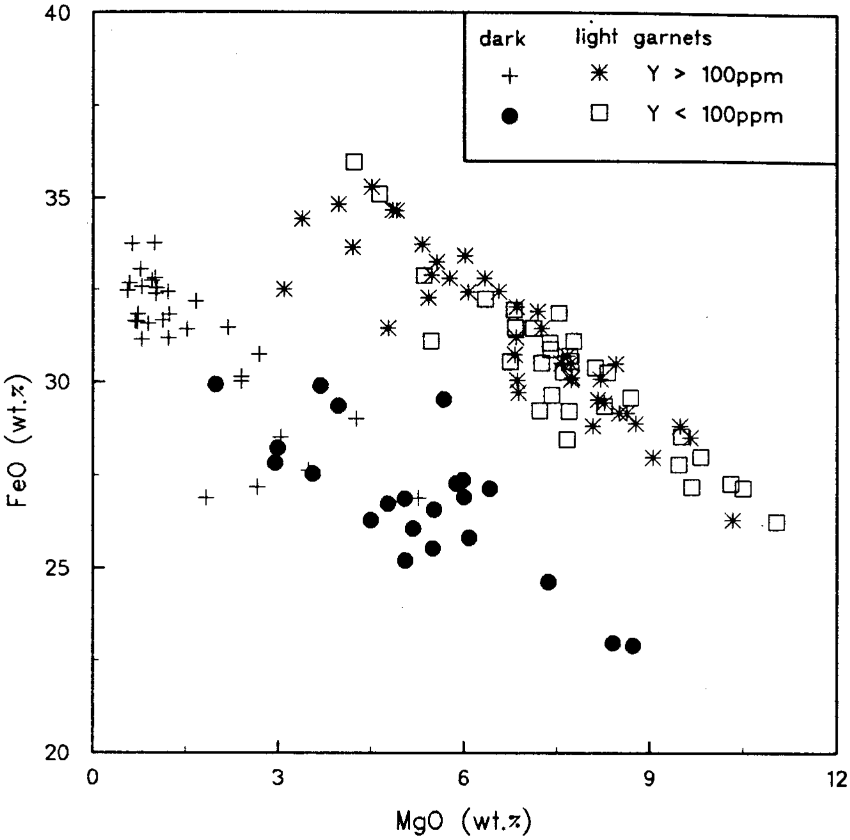


Figure 17.1: Besides the negative correlation of FeO and MgO abundances of the single garnets a negative (positive) correlation of Y and MgO (FeO) abundances can be observed. In the light garnets this correlation of the Y abundance and the MgO or FeO content is missing.

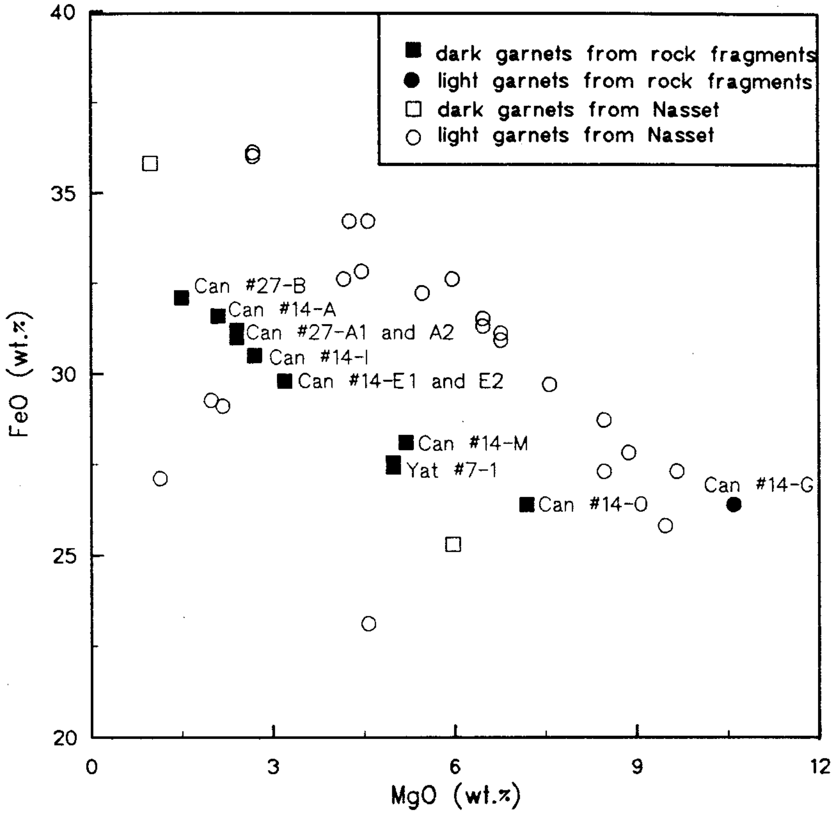


Figure 17.2: FeO plotted against MgO for individual garnets from the Nasset bentonite and the garnets of the rockfragments. The same trends as for the single garnets from the bentonites of the Utica Formation are visible. The light garnets from the Nasset deviating from the trend contain high abundances of MnO.

Engel and Engel (1960) showed that garnets from the Adirondacks (between Emeryville and Colton) have almost constant ratios of Y/Sc (3-4). The Mn/Sc ratio ranges from about 80 in their garnets of lower metamorphic grade to 20-23 in the higher-grade metamorphic garnets. Looking for similar trends in the garnets of the bentonites is a failure. The Y/Sc ratio varies from 0.0 up to 484. The ratio of the dark, Y-rich garnets range from 484 to 0.7, the ones of the dark, Y-poor garnets from 1.0 to 0.0. The ranges for the pink Y-rich garnets go from 13.5 to 0.7 and for the pink Y-poor ones from 0.8 to 0.0.

Also, the Mn/Sc ratio varies over a much larger range of values, from 14 to about 500. The range becomes a bit closer (14-110) looking only at the light garnets, but there is still not a small range defined as in the garnets from Engel and Engel (1960).

7.3. Results on Rock Fragments

A total of only 21 rock fragments was found, which is an average of fewer than one fragment per kilogram of bentonite. The microliths have a size of up to 600 microns. It is astonishing that they survived an eruption 450 million years ago, burial within the shales, and diagenesis, and still look so fragile (Figure 14). Ten of these rock fragments had an assemblage that included garnets (Garnet analyses in Table IV and V). Besides garnets there are hornblendes, pyroxenes, feldspars, quartz, Fe-Ti oxides and apatite present in the rock fragments (Table VI).

While the pink garnets are the dominant group in the single crystals (about twice to three times as abundant as the dark ones) they are more rare in rock fragments than the dark garnets (1:9). Among the nine dark garnets in the fragments was one andradite (Can #14-L). While the pink garnets seem to be under-represented in the microliths,

Table IV: Microprobe analyses of garnets from rock fragments

(Major elements in weight percent, trace elements in ppm; recalculation in mole percent after Rickwood (1968); recalculation of Fe2O3 see appendix B; analyses of fragments from 114 performed by J.W. Delano)

Frg.	114-A	114-G	114-I	114-L	114-M	114-O	307-1	127-B
SiO2	37.34	39.17	37.20	36.54	37.84	38.30	38.50	38.00
Al2O3	20.54	22.81	21.21	14.68	22.26	22.48	21.20	20.35
Fe2O3	1.30	0.00	0.50	11.20	1.20	0.30	0.90	0.80
FeO	30.45	26.37	30.10	7.10	26.91	26.14	26.50	31.41
MnO	1.27	0.31	1.11	0.12	0.81	0.94	1.77	0.98
MgO	2.09	10.60	2.72	0.16	5.13	7.16	4.98	1.52
CaO	7.57	1.62	7.14	29.75	7.08	5.97	7.04	7.22
Total	100.56	100.88	99.98	99.55	101.23	101.29	100.89	100.28
Ti	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	232
Zn	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	126
Y	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	319
Sc	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	70
Andr.	3.9	0.0	1.5	34.6	3.6	0.9	2.6	2.5
Pyr.	8.3	40.3	10.9	0.7	20.2	27.9	19.3	6.1
Spess.	2.9	0.7	2.5	0.3	1.8	2.1	3.9	2.3
Gross.	17.8	4.4	19.0	52.6	16.5	15.8	17.0	18.5
Alm.	67.1	54.6	66.0	11.8	57.9	53.4	57.2	70.6

Table V: Microprobe analyses of garnets occurring within the same rock fragment

Frg.	114-E2	114-E1	127-A2	127-A1
SiO2	37.37	37.09	37.59	37.76
Al2O3	21.64	21.60	20.50	20.41
Fe2O3	0.30	0.60	1.20	1.10
FeO	29.47	29.38	30.15	30.03
MnO	1.64	1.64	1.52	1.47
MgO	3.14	3.23	2.40	2.40
CaO	7.13	7.28	6.97	7.01
Total	100.69	100.82	100.33	100.18
Ti	n.a.	n.a.	153	183
Zn	n.a.	n.a.	57	109
Y	n.a.	n.a.	697	901
Sc	n.a.	n.a.	33	24
Andr.	0.9	1.8	3.6	3.3
Pyr.	13.0	13.0	9.5	9.6
Spess.	3.4	3.8	3.4	3.3
Gross.	19.5	19.2	16.3	16.8
Alm.	63.3	62.2	67.2	67.0

Table VI: Mineral assemblages of garnet-bearing rock fragments

	Garnet	Hornbl.	Plag.	K-spar	Quartz	Opx	Cpx	Apatite	Fe-Ti oxide
Can #14-A	dark	-	-	-	*	*	*	*	*
Can #14-E	dark	*	*	-	-	*	-	-	-
Can #14-G	light	-	*	-	*	-	-	-	-
Can #14-I	dark	*	*	*	*	-	-	-	*
Can #14-L	andr.	-	-	mix	-	-	-	-	-
Can #14-M	dark	-	*	-	trace	*	*	-	-
Can #14-O	dark	*	*	-	-	-	-	-	-
Can #27-A	dark	-	*	*	*	-	-	-	*
Can #27-B	dark	-	*	*	*	-	-	-	*
Yat. #7-1	dark	*							

* present - absent

the andradites are over-represented. In the bentonites of the Utica Formation andradites are uncommon. Only two single garnets of andraditic composition were observed in the layer 217. This reversed distribution of light to dark garnets might be an indication of different grain sizes of the garnets in their host rocks, suggesting that the pink garnets were larger than the dark ones - in fact too large to be incorporated into rock fragments of only 600 or less microns. If this explanation is correct, then this could be evidence that the light garnets are from a higher grade metamorphic terrain then the dark ones, since generally grain size increases with metamorphic grade.

Another possible reason for the rareness of rock fragments containing pink garnets could be a different, less stable mineral assemblage, which was destroyed during assimilation, eruption, or diagenesis.

Garnet-bearing rock fragments were recovered only from bentonite Can #14 (seven), Can #27 (two) and from bentonite #7 in Yatesville Creek (one). In this respect 114 is again remarkable. Unfortunately, the rock fragment of the bentonite 307 was lost after the analyses for major elements on the garnet and therefore, no more information could be obtained.

In these three units, the garnets of the rock fragments are identical to the single grains (Figure 18, Table VI). In two rock fragments (Can #14-E, Can #27-A) two separate garnet grains could be analyzed (Table V). The major elements of the garnets of one rock fragment are very similar, suggesting equilibrium conditions, at least on this scale. The Y content of the two garnets in rock fragment 127-A, however, are quite different (Table V). This might be due to the fact that the garnets are metamorphic and the abundance of Y was fluctuating over very small distances. In a magma, even when the magma chamber is zoned, such high variations would not be expected within one microlith.

The rock fragment bearing the pink garnet (Can #14-G) carried, besides the pink garnet, quartz, plagioclase and an aluminum-silicate phase, a mineral assemblage that is

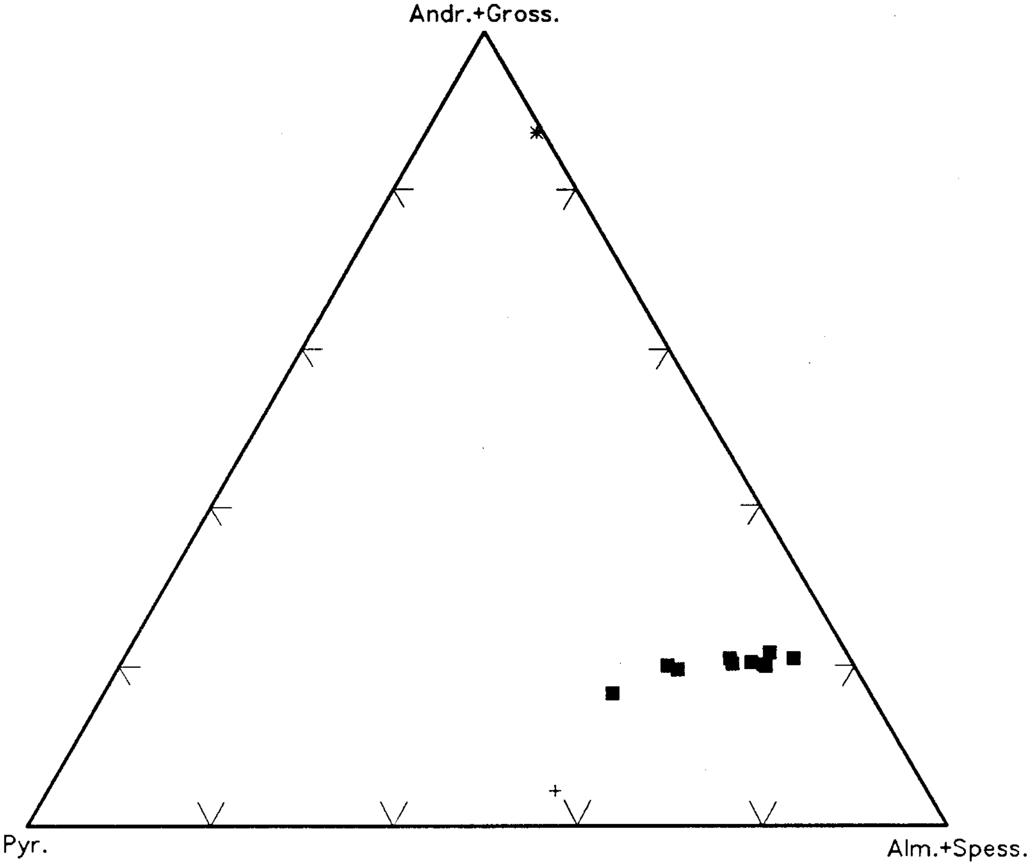


Figure 18: Compositions of garnets found in microliths. These garnets show the same compositional groups as the single grains (■ dark, + light, ⁎ andradite).

typical for metapelites (Ghent, 1976; Kepezhinskas, 1973).

Geothermobarometry was applied to rock fragments (Chapter 7.4) to get information about the crystallization conditions. Signs of retrograde changes could not be detected on the minerals of the microliths, suggesting that the thermobarometry may give valuable results. But since the rock fragments are very small and the mineral assemblage might be only fragmental, results must be handled with caution.

The appearance of the rock fragments is already a strong indicator that they are of metamorphic and not of magmatic origin. The minerals of the rock fragments show a preferred orientation, and the grain boundaries form triple junctions with 120° angles as often observed in metamorphic rocks (Figure 19). The garnets that occur as single crystals have exactly the same composition in their major-element chemistry as the garnets of the rock fragments. Few analyses of trace-elements were done on the garnets of the rock fragments. As in the major-elements, the garnets of the rock fragments show for the trace-elements approximately the same range of compositions as the single grains.

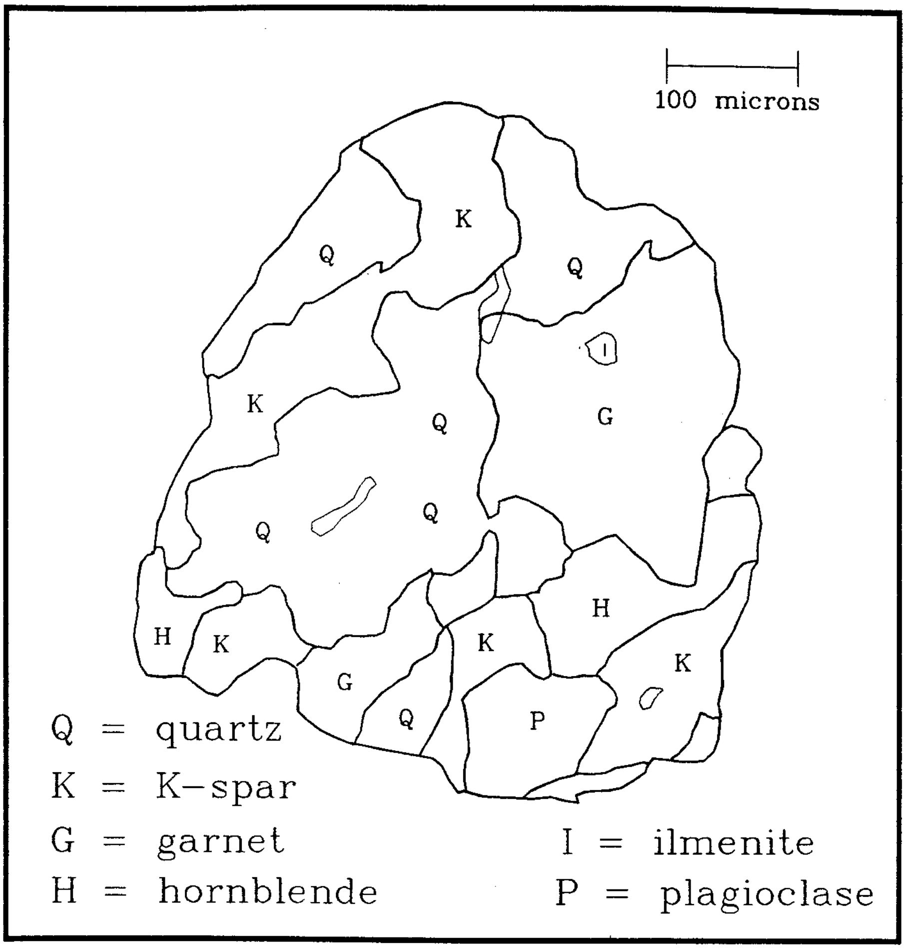


Figure 20: Map of rock fragment 114–I showing mineral assemblage and metamorphic textures.

7.4. Geothermobarometry

Three orthopyroxene - clinopyroxene pairs (Can #14-A, Can #14-H (not garnet-bearing), and Can #14-M) indicate temperatures of about 600°C using the graphical two-pyroxene thermometer of Lindsley and Anderson (1982) (Delano et al., 1990). This temperature is calculated for pressures of one kilobar. For every kilobar increase in pressure 2-4°C must be added. The two-pyroxene thermometer is based on the phase equilibria of diopside - enstatite and hedenbergite - ferrosilite and can be used directly on pyroxenes that have low contents of Al and other minor components.

The thermometer of Ellis and Green (1979) uses the empirical relation:

$$T(^{o}K) = \{3104X_{Ca}^{Gt} + 3030 + 10.86P\ (kbar)\}/\{\ln K_D + 1.9034\}$$

to calculate temperatures on garnet - clinopyroxene pairs. The garnet - clinopyroxene pair of Can #14-A gives a slightly higher temperature of 620-650°C than 600°C from the pyroxenes, while Can #14-M with temperatures of 594-605°C is in good agreement with the temperatures calculated with those calculated with the two-pyroxene thermometer. These temperatures on the garnet - clinopyroxene pairs are calculated for assumed pressures of 4-8 kbar respectively, and it can be seen that the temperatures are not very sensitive to changes in pressure.

The rock fragments (114-I, 114-E and 114-O) plot in this order toward the FeO-poor, MgO-rich end of Figure 17.2, and might show the effects of increasing pressure because the Y content is decreasing towards this end (interpretation following Engel and Engel, 1960: higher metamorphic grade in this direction).

Using the Al_T-barometer of Hollister et al. (1987) on the hornblendes of Can #14-I, Can #14-E and Can #14-O, where

$$P\ [\pm 1\ kbar] = -4.76+5.03*Al_T$$ (with Al_T equal to the total number of Al cations based on 23 oxygens),

the pressure is observed to increase from 6.8 to 8.8±1 kbar in these three rock fragments.

This barometer was developed for calcalkaline plutons with the mineral assemblage quartz, plagioclase, orthoclase, biotite, hornblende, sphene and epidote (which is not entirely present in these rock fragments) and therefore might not be applicable. Since the rock fragment Can #14-I gives a pressure range from 6.8-7.4±1 kbar, however, the result is at least plausible (see below).

The TiO_2 abundances in these hornblendes increases in the same order. The hornblende of Can #14-O contains the highest amount of TiO_2 (4.36 wt.%), Can #14-E has a lower abundance (3.0 wt.%) and Can #14-I contains the smallest amount of TiO_2 with 1.77 wt.%. Raase (1974) attributed the increasing TiO_2 content of metamorphic hornblendes to higher temperatures after plotting a histogram of the observed Ti contents of hornblendes (on basis of 23 oxygens) of different metamorphic grades. Increasing temperature is contradictory to the calculated temperatures on the pyroxene pairs (Can #14-A, Can #14-M), garnet - clinopyroxene (Can #14-A, Can #14-M) and garnet - hornblende (Can #14-I).

The garnet + hornblende + plagioclase + quartz geothermobarometer of Kohn and Spear (1990), which is based on the equilibrium: 6 Anorthite + 3 Tremolite (Fe-Actinolite) = 2 Grossular + 1 Pyrope (Almandine) + 3 Tschermakite (Fe-Tschermakite) + 6 Quartz, and their Fe end-member equivalents in brackets applied to Can #14-I (the only rock fragment with the required mineral assemblage), gave a pressure range from 6.5-7.5 kbar and a temperature range of 605-625°C (Figure 20, 21). With this temperature information the trend of increasing metamorphism in the direction MgO-rich, FeO-poor end of Figure 17.1 and 17.2 does not seem to be followed. However, increasing grade of metamorphism might imply not a temperature change, but increasing pressure.

The calculated P-T conditions for Can #14-I plot in the kyanite field according to the phase diagram of Holdaway (1971). The triple point of the three aluminum-silicate phases (andalusite - sillimanite - kyanite) lies at 501°C and 3.76 kbar (Figure 20).

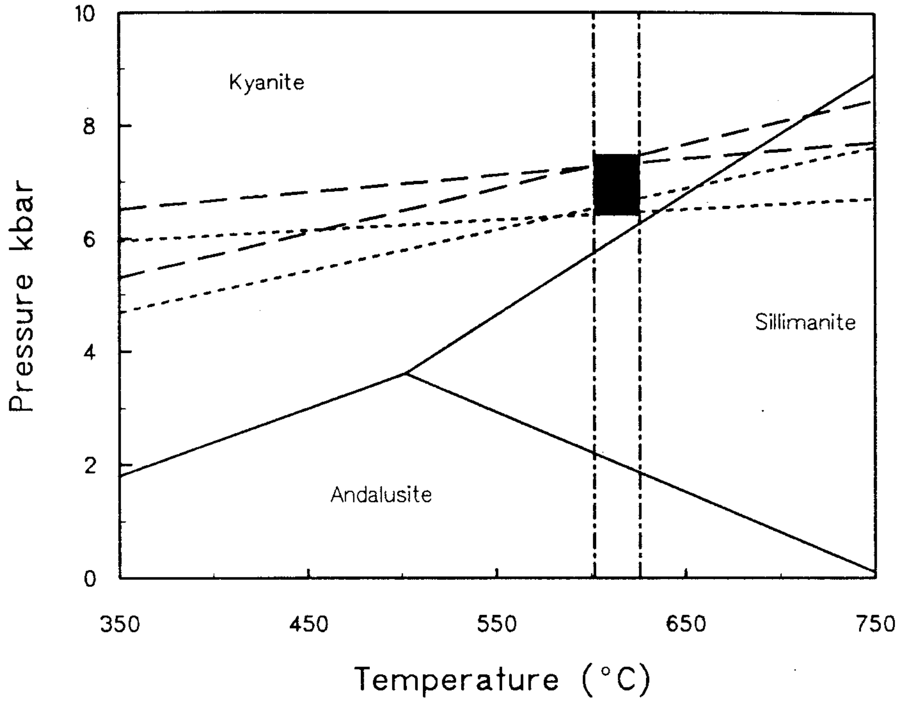


Figure 20: The black square shows the pressure and temperature range calculated for the rock fragment Can #14-I with the geothermobarometer of Kohn and Spear (1990).

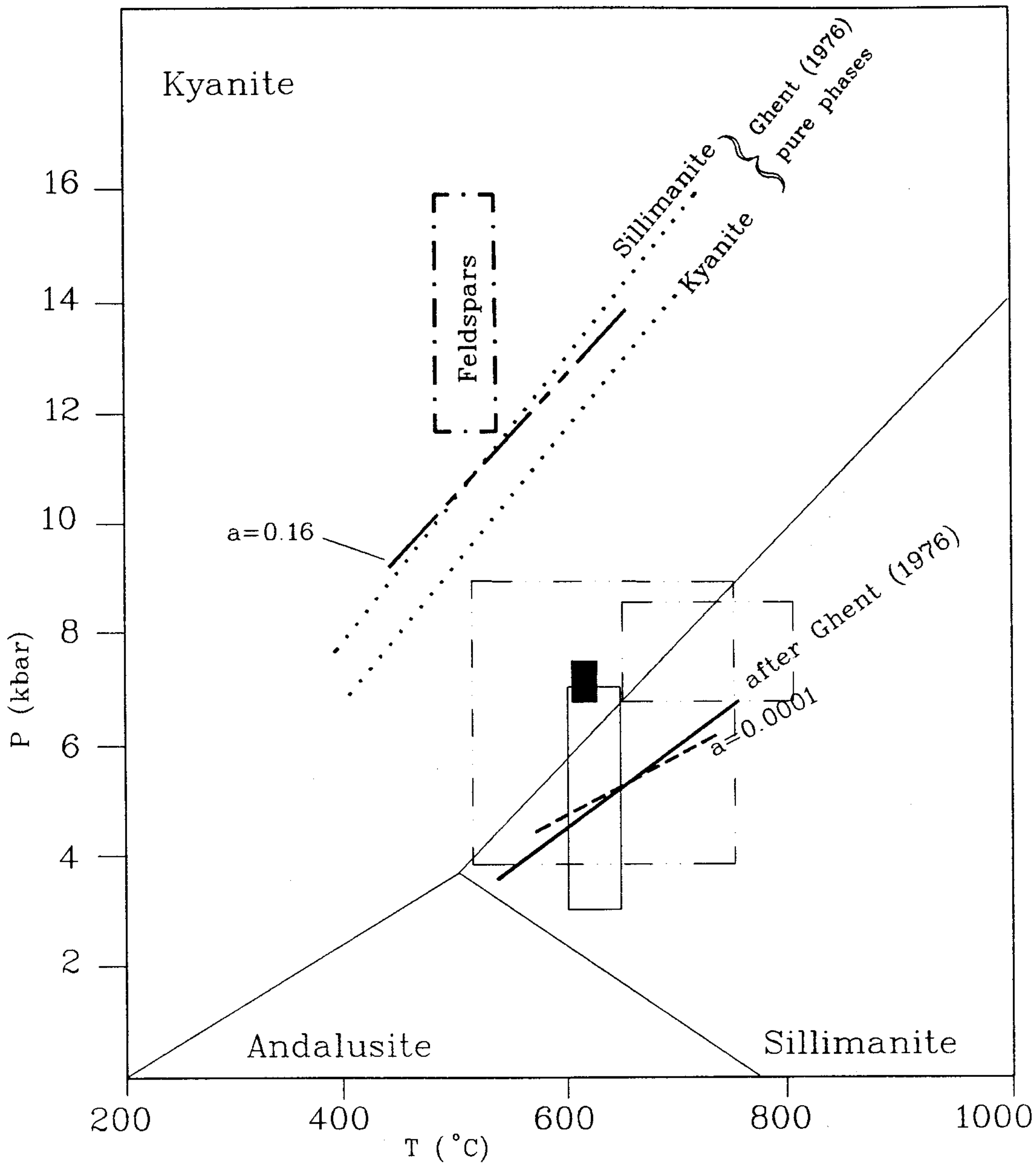


Figure 21: Summary of P-T information calculated with different thermobarometers. The black box marks the conditions from Can #14-I, the solid line represents the estimate derived from Can #14-G (after Ghent, 1976). The box with the solid line shows 'reasonable' P-T conditions by comparison to high-grade metamorphic terrains in the literature. The dash-dot-dot boxes show P-T conditions from literature for a) the smaller box - Adirondacks after Bohlen et al. (1985) and (1989), b) granulite terrains in Canada after Newton and Haselton (1981).

The rock fragment containing the light garnet (Can #14-G) bears plagioclase, an aluminum silicate phase and quartz besides the garnet. For this rock fragment the barometer of Ghent (1976) is applicable to determine the equilibrium pressure. The reaction on which the barometer is based is:

3 Anorthite = Grossular + 2 Al_2SiO_5 + Quartz

The disadvantages of this barometer are that it requires a low variance mineral assemblage (which must be assumed in absence of a larger sample) and an independent temperature estimate. A source of an under- or overestimate of the pressure is that the activities of the grossular and anorthite can be determined only with large uncertainties. Ghent (1976) assumed that the activities are approximately equal to the mole fractions of grossular and anorthite respectively (ideal solid solutions). Calculating the log K_D (using Ghent's equation: $\log K_D = 3 \log X_{Gr} - 3 \log X_{An}$) gives the value of -2.77 which is, after Ghent, typical for the sillimanite zone. Also, plotting three times the grossular molar fraction against three times the anorthite molar fraction, the rock fragment Can #14-G falls in the sillimanite zone outlined by Ghent (1976). A pressure of 4.5 kbar results from using the log K_D-value of -2.77 and the formula ($0 = \{-2817.2/T\} + 7.4351 - \{0.2678(P-1)/T\}$ for sillimanite) assuming a temperature of 600°C (Figure 21).

A similar pressure estimate can be derived from the relationship of CaO content in garnet and anorthite content in plagioclase, which was investigated by Kepezhinskas (1973) based on the same equation as Ghent (1976). He plotted the anorthite content of the plagioclase versus CaO (wt.%) of the garnet for meta-pelites of medium temperature metamorphism. Can #14-G falls in the field of the amphibolite facies. Unfortunately, the diagram ends at CaO equal to 5 wt.%. Therefore, the high CaO contents of the dark garnets are not represented in this diagram and its use is restricted to the one rock fragment. This relationship is not a linear trend and the different zones are not well defined, so that extrapolation towards higher CaO contents in garnets is impossible.

The thermobarometer of Berman and Perkins (1987), also applicable to the rock fragment Can #14-G, is based on a large self-consistent database using the relationship 3 Anorthite = 2 Sillimanite + Quartz + Grossular. The advantage of this program is that it allows changes in the activities. Running the program for pure phases the stability field of sillimanite is above the stability field of kyanite. Since this result was startling a recalculation of the equivalent equations by Ghent (1976) was done with a very similar result (Figure 21). Calculation of P-T conditions in Berman and Perkin's (1987) program - using molar fractions (0.044 and 0.37 for grossular and anorthite respectively) as approximate activities - led to unexpectedly high pressures. For a temperature of 600°C a pressure of about 12.8 kbars was calculated. The shift from the pure phase case to the one with the molar fractions as activities is almost negligible. Therefore, the activities were determined using the equations given by Haselton and Newton (1981). The result (0.16 and 0.61 for grossular and anorthite respectively) fed into the program of Berman and Perkins (1987) gave again unreasonably high pressure (for 600°C about 12.6 kbar). Leaving the activity of the anorthite untouched the activity of the grossular component must drop down to 0.0001 in order to calculate reasonable pressures (Figure 21).

The conclusion of this is that either the minerals of the rock fragment are in disequilibrium - caused by retrograde changes of the minerals - or that the garnet composition (almandine-pyrope) does not allow the use of this program because the grossular component is too small.

Slightly lower temperatures than 600-650°C were calculated on feldspar pairs of the bentonites using the thermometer of Fuhrman and Lindsley (1988). The temperatures calculated range from 474-550°C. The pressures calculated by this program are not very reliable, and with 16-11 kbars probably too high (Figure 21). Other mineral combinations from the same rock fragments as the feldspars gave 600°C and showed no indication of extremely high pressures (i.e. garnet have high Y contents in rock fragment Can #27-A and B, Figure 17.2).

Through comparison to data in the literature (Anovitz and Essene, 1990; Bohlen et al. 1985, 1989; Newton and Haselton, 1981; Newton and Perkins, 1982) the improbability of the calculated data from the feldspars and the program by Berman and Perkins becomes clear (Figure 21). A summary of all different geothermobarometers used on the microliths and the results derived is given in Table VII. From these data it seems possible to deduce that the metamorphism of the source rocks must have reached conditions of the upper amphibolite- to granulite-facies.

All these thermobarometric data must be viewed with caution. Firstly because the rock fragments are very small and might not represent the whole rock. Secondly because under granulite conditions the peak metamorphism might be lost due to high diffusion rates in minerals at the high temperatures of granulite metamorphism. The closure temperatures for feldspars are at about 200°C the lowest and therefore it is least likely that feldspars record peak metamorphic conditions, but also the temperatures reported by the garnets and pyroxenes might not be the peak temperatures reached during metamorphism (Anovitz and Chase, 1990; Frost and Chacko, 1989; Selverstone and Chamberlain, 1990).

Table VII: Summary of applied geothermobarometers

Rock fragment	Mineral (pairs)	Author	Result
Can #14-A	opx-cpx	Lindsley & Anderson (1983)	600°C
Can #14-A	gt-cpx	Ellis & Green (1979)	620 - 650°C, 4 - 8 kbar
Can #14-E	hbl	Hollister et al. (1987)	7.2 - 7.7 kbar
Can #14-G	plag-gt-sill-qtz	Ghent (1976)	600°C, 4.5 kbar
Can #14-G	gt-plag	Kepezhinskas (1973)	amphibolite-facies
Can #14-G	plag-gt-sill-qtz	Berman & Perkins (1987)	600°C, 12 kbar
Can #14-I	hbl	Hollister et al. (1987)	6.8 - 7.4 kbar
Can #14-I	gt-hbl-plag-qtz	Kohn & Spear (1990)	610°C, 6.5 - 7.5 kbar
Can #14-M	opx-cpx	Lindsley & Anderson (1983)	600°C
Can #14-M	gt-cpx	Ellis & Green (1979)	594 - 605°C, 4 - 8 kbar
Can #14-O	hbl	Hollister et al. (1987)	8.8 kbar
Can #27-A	fsp	Fuhrman & Lindsley (1988)	500°C, 15 kbar
Can #27-B	fsp	Fuhrman & Lindsley (1988)	465°C, 10 kbar

8. Discussion

After all these analyses and observations on garnets, the decision must be made: What is the origin of the garnets? In case they are phenocrysts they might be able to point out the composition and P-T conditions of their host magma. Du Bray (1988) shares the opinion of Wood (1974) that garnets might be the carrier of important information on magma genesis and may be employed as indicators of the tectonic regime prevailing at the time of host granitoid genesis.

When they are metamorphic garnets, they might tell about the crust that was involved in the magma genesis.

Reasons for the decision that the dark garnets are of metamorphic origin include their high CaO content, which is unusual for magmatic garnets, and their low Y content.

The metamorphic, garnet-bearing rock fragments are the best evidence for the metamorphic origin of the garnets. Without them a decision would be harder to defend. In their presence, it appears necessary to conclude the absence of magmatic garnets. Furthermore, the garnets in the rock fragments contain high Y abundances indicating that metamorphism does not preclude high amounts of Y in the garnets.

Both dark and pink garnets with low Y abundances cannot have crystallized in a rhyolitic magma. The Y-rich group (Y higher than 800 ppm) contains only 8 dark and 4 pink garnets. Hence, the majority of garnets has to be excluded on the basis of too low Y abundances.

The Y content of a rhyolite is variable from 20-90 ppm depending on the melted source, the degree of differentiation and the temperature of the magma. The K_D-value for a garnet is dependent on magma composition, CaO content, and temperature of the magma (Irving and Frey, 1978; Nicholls and Harris, 1980), but a reasonable estimate might be 30-70, based on diagrams of rare earth element partition coefficients from different hosts (Irving, 1976; Irving and Frey, 1978; Nicholls and Harris, 1980). In general, a trend is observed that with increasing acidic character of the magma and lower temperatures the K_D-values increase. Strongest enrichment in Y would be expected of garnets crystallized in a highly differentiated magma (Nicholls and Harris, 1980). Therefore, an Y abundance of about 800 ppm must be required for any garnet crystallized from a rhyolitic liquid. Also, high TiO_2 contents (up to about 1000 ppm) in dark garnets, coupled with high Y abundances (1482 ppm) are not compatible with growth in a silicic magma.

The light garnets, the group suspected to contain phenocrysts because of their low CaO content, seem to be even less suited to bear phenocrysts. They were suspected to be similar to the garnets of the Borrowdale Volcanics. These volcanics are of the same age as the bentonites. However, the suite of the Borrowdale Volcanics shows a development of the magma from andesitic to dacitic composition accompanied by a change in garnet chemistry. The MgO content of these garnets decreases with increasing silica content of the host (andesite to dacite), while the FeO, Y and Sc content are increasing with increasing silica content (Fitton, 1972). The garnets of the dacite contain already higher Y and Sc abundances than the garnets of the bentonites. Since the magma of the volcanism that created the bentonites was rhyolitic (Schirnick, 1990), the Y and Sc abundances of the garnets are too low to be derived from a rhyolitic magma.

Also, the high MgO content of the pink garnets would be strong evidence for a more basic source. The garnets in the Borrowdale group - developed in dacitic melt - have MgO contents of about 3.4 wt.% (Fitton, 1972), while the garnets derived from andesites have higher MgO contents. Assuming that the pink garnets crystallized from a rhyolitic magma, they should contain less than 3.4 wt.% MgO. In Figure 17.1 it can be seen that all pink garnets contain more than 3 wt.% MgO. Therefore, a source of rhyolitic character can be excluded.

This view is supported by a parallel investigation on zircons of these bentonites by

Schirnick (1990). Melt inclusions within the zircons suggest that the magma from which they developed was only slightly peraluminous and was probably not able to produce garnets (Schirnick, 1990).

Garnets that contain 40-70 mol% pyrope are according to Deer, Howie and Zussman (1985) an indicator for granulite facies metamorphism. This range of values comes close to the observed abundances of the pink garnets. The differences in MgO contents of the pink garnets can be most easily explained by different MgO contents of the host rocks, disregarding the argument of increasing metamorphism with higher MgO content.

Applying Sturt's (1962) diagram ({MgO+FeO} versus {CaO+MnO}) to the pink garnets results in a cluster of points. This indicates that the garnets experienced the same P-T conditions and differences within the group of the pink garnets might be derived from different host rock compositions (differences in Y, MgO, FeO, MnO), since different metamorphic conditions should produce a trend with a negative slope for increasing metamorphic conditions in garnets of the same parent rock.

MnO abundances are observed to be lower when a large amount of garnets is developed and the same amount of MnO was partitioned into many garnets (Miyashiro and Shido, 1976). Elevated pressure promotes the crystallization of garnets and more garnets share the present MnO of the source rock, so that the pressure itself does not govern the MnO abundances in the garnets, but the amount of crystallizing garnet. This reasoning would be consistent with the higher abundance of pink garnets in the bentonites having a generally lower MnO abundances than the dark garnets.

The dark garnets on the other hand might be showing a trend of increasing metamorphism by their different abundances of MgO and FeO which are contrary to the pink garnets following a regular trend in the Y abundances (Figure 17.1).

Comparison of the garnets to garnets of metapelites and metabasites from the Adirondacks (Ree, pers. comm.) shows that the pink garnets are identical with the garnets of the metapelites, while the dark garnets fit within the garnets found in the metabasites. The only difference between these garnets from a known source and the garnets found in the bentonites is the absence of zoning in the garnets of the bentonites. High-grade metamorphism could account for the absence of zoning, as Woodsworth (1977) stated that zoning of minerals in high-grade metamorphic rocks is generally weak. Garnets become homogenized at temperatures above 650°C. (Woodsworth, 1977; Yardley, 1977).

P-T estimates for the metabasites investigated by Ree are about 650°C and around 6 kbar. The metapelites are strongly retrograded and P-T calculations are not reliable. From the spatial closeness of the samples the assumption of the same P-T conditions for both groups of rocks seems reasonable (Ree, pers. comm.). This occurrence shows that it is possible that depending on the parent rock metamorphic garnets of the same metamorphic grade can show very different compositions.

To be able to define the source area more closely with the help of the garnets is not possible, since the compositions of garnets are dependent on too many factors and do not vary enough or are not extreme enough to closely define a source area. For example deciding whether observed compositional differences are due to different source compositions or metamorphic grades or a combination of these two factors is crucial. This study can give no answer to this question. Brown and Earle (1983) observed in Timor that volcanoes erupt through a sequence rocks of different metamorphic grades. If the same is true for the volcanic events in the Ordovician then the garnets could be not only from different horizontal locations but also a mixture of garnets from different vertical levels.

The age of the crust blasted up during the Ordovician eruptions was about 600 million years at the time of the eruption (age data from feldspars). Its thickness and metamorphic grade, could have provided a very special environment (high pressure) able to produce mineral-rich ashes. To find an adequate example at the present, one might look to the South American continental margin. Its rhyolitic volcanism erupting through continental crust might be a comparable geologic setting.

The attempt of correlation using garnet compositions fails because the garnets do not change their compositions with stratigraphic height (=time) and the abundances of the individual grains within the two groups also remain the same. During handpicking of the garnets for microprobe analyses light garnets appeared always to be more abundant than dark garnets. A count of light and dark garnet grains recovered from bentonite 114 showed that the light garnets are two- to three times as abundant as the dark garnets. As Morton (1985) found: "The overlap in garnet composition in rocks of differing parageneses makes it unlikely that detrital garnet associations could actually fingerprint rocks in the hinterland." Even though the garnets of the bentonites are not detrital in a strict sense, the problem is the same. Too many unknowns (host rock composition, mineral assemblage, P-T conditions) influence the garnet composition to allow a close determination of a source for the garnets. There are, however, constraints that can be placed on the source. The age of the xenocrystic component in the bentonites is well constrained by Ar/Ar dating of K-feldspars of Flat #14. The apparent age spectrum indicates a minimum age of 550-750 million years. High grade metamorphic terrain of about Grenville age must have been involved in some way in the genesis of the magma or been encountered on the way of the magma to the surface by the evidence of the rock fragments. How the garnets were incorporated into the ash is not known. If this problem could be solved, the magma genesis could be better understood. Since the country rock is garnet-bearing I favor the thought of the garnets being picked up by the magma during ascent and eruption.

Where the source was located is still not known. In Sweden bentonites of Ordovician age are also observed with unclear origin (Samson et al., 1989). A common source for the Swedish and North American bentonites may be feasible The questions to investigate are the configuration of the continents during Ordovician time, how high the volcanic cloud could have risen, and which winds would have been the transporting agent for the ashes. For instance, the stratosphere wind directions in the Ordovician might have changed with the seasons, as they do today, summer winds blowing from east to west, winter winds blowing from west to east (Person, 1982; Delano et al., 1990). These changing wind directions would cause a distribution of the bentonites to different continents (America during the summer, Scandinavia during the winter).

With the help of isopach maps over an extensive area Elder (1988) was able to conclude that the Cretaceous bentonites observed through large parts of the western interior of the United States are derived from two different volcanic source areas. The continent of North America (Laurentia) was rotated during Ordovician time about 45^{0} counterclockwise compared with its present position (Van der Voo, 1988). An unresolved question is the position of the parts of the Appalachian mobile belt, Baltica and southern Great Britain at that time. To be a common source area for Swedish and North American bentonites, a source would have to be fairly close to both continents. An exact correlation combined with an isopach map might be the best approach towards the location of the source area. The mineral assemblages found in the bentonites are just not unique enough to identify a source area.

9. Conclusions

The garnets are not useful as tools for correlation purposes, since all bentonites show the same garnet populations. This ubiquitous occurrence of the garnets is already evidence for their xenocrystic character.

No phenocrysts are distributed among the garnets by evidence of the rock fragments and low Y abundances.

Trace elements help to discriminate between different garnet populations, but too little is known about the distribution coefficients to model accurate source conditions. For correlation purposes the trace elements give no advantage to the major elements, since different groups of garnets are not discernible.

The island arc that collided with North America was built on continental crust of granulite metamorphic grade, containing garnets, pyroxenes, hornblendes, and feldspars with an age of at least 550-700 million years formed at pressures and temperatures of about 7 kbar and $600^{o}C$ respectively. Further evidence that the volcanism involved a microcontinent and not an island-arc are the high $^{87}Sr/^{86}Sr$ ratios observed in bentonites and inherited zircon cores reported by Samson (1990).

Garnets might be able to define their source area better, if more material derived from the source region than the microliths can be recovered. In the present samples, there are too many unknowns to get further information from the garnets.

Trace and rare earth element contents of the garnets might be superior compared to major elements to derive more information about their source area, but it is not clear whether they would ever be useful for correlation purposes. The garnets are just too well mixed from an unknown number of sources and vary not at all over the investigated stratigraphic levels.

U/Pb dating of the garnets (as done by Mezger et al., 1988) might lead to a clearer definition of the source areas and conceivably to a correlation tool.

Probing the garnets by SIMS or FTMS for relative rare earth element spectra might give a better resolution to find more discriminating criteria.

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Appendix A

This Master's thesis began as part of a project on the sedimentary aspects of the Taconic Foreland basin in New York State undertaken by J.W. Delano.
The samples in Wisconsin (Dickeyville, Millbrig and one unnamed ash from the same outcorp) were collected by C. Schirnick and myself in the spring of 1989; the sample of the Nasset bentonite was collected by C. Schirnick in the summer of 1988. The bentonite samples, and many shale and calciturbidite samples from the State New York were collected by C. Schirnick, J.W. Delano and myself. The shale samples (85-008, 87-037, 87-039, and 87-123) used as average Utica shale were collected by J.W. Delano before the start of my participation in this project.

The profiles of Canajoharie and Flat Creeks were measured by C. Schirnick and myself during the fall of 1988 and spring 1989. Additional stratigraphic sections were measured in Yatesville and Harter Hill Creeks by J.W. Delano, W.S.F. Kidd, C. Schirnick and myself.

The processing of the shale samples for geochemical analyses and mineral separation (i.e. cleaning, crushing, shattering, etc.) was done jointly by J.W. Delano, C. Schirnick and myself.

The bentonites were sieved by J.W. Delano, C. Schirnick and myself, since handling a stack of five sieves and a water bucket is facilitated by the presence of a second person.

The necessary mineral separations (i.e. heavy liquids and magnetic separation) were performed by C. Schirnick and myself under the supervision of J.W. Delano.

I performed the handpicking, polishing, mounting and analyses on the microprobe of the garnet grains used in the diagrams of this thesis.

The rock fragments from Can #14 discussed in this thesis were mounted, polished and analyzed by J.W. Delano.

First results of the ongoing resaerch were published in the article: Petrology and geochemistry of Ordovician K-bentonites in New York state: Constraints on the nature of a volcanic arc (Journal of Geology, 1990) by J.W. Delano, C. Schirnick, B. Bock, W.S.F. Kidd, M.T. Heizler, G.W. Putman, S.E. DeLong and M. Ohr. Another paper (Geochemistry of Ordovician flysch, black shales, and calciturbidites from New York State (USA) and Quebec (Canada): Tectonic Implications by J.W. Delano et al. is in preparation.

Appendix B

Since the microprobe is only able to analyse for total iron as FeO, the amount of Fe_2O_3 present in the garnets must be calculated from stoichiometry in order to estimate the andradite component. The steps of the recalculation are as follows:

(a) Divide the analyzed weight percent by the molecular weight of each oxide; for the iron oxides express the weight percentage of Fe_2O_3 as x and FeO as y.

(b) By multiplication of the results of step (a) with the number of cations, the cation proportions can be calculated.

(c) By multiplication of the results of step (b) with the number of oxygens, the oxygen proportions are determined. Therefore, the oxygen proportions of Fe_2O_3 are 3*x divided by 159.7 or x/53.23 (1), while the oxygen proportions of FeO are y/71.85 (2). As an example assume that the analyzed FeO^{tot} = 30 wt.%, so that $FeO + (0.9*Fe_2O_3) = 30$ wt.% FeO^{tot}, or expressed with the introduced symbols: $y + 0.9*x = 30$. Solving this equation for y and substituting the resulting formula in equation (2) gives: $(30 - 0.9*x)/71.85$ for the oxygen proportion of FeO leaving only one unknown.

(d) Sum up the oxygen proportions. The observation in this step will be that the sum of the oxygen proportions equals the sum of the oxygen proportions given by the microprobe plus a small factor times x (=Fe_2O_3), since the oxygen proportions will increase through the recalculation of Fe_2O_3.

The task is now to select a value for x. The possible range of values for x is from 0 to 1.11134*FeO, thus, in the example x can range from 0 to 33.34. From the garnet formula $X_3Y_2Z_3O_{12}$ it is known that the ideal garnet contains 12 oxygens. Therefore, after the recalculation of the oxygen proportions to 12, the cations must sum up to 8 in an ideal garnet. This value x fits best whose square of the sum of the deviations shows the smallest difference to 8. It was determined by iterative calculations with changing x values using a computer program written by S.E. DeLong.