

PETROLOGY AND GEOCHEMISTRY OF ORDOVICIAN K-BENTONITES IN NEW YORK STATE: CONSTRAINTS ON THE NATURE OF A VOLCANIC ARC¹

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ABSTRACT

Altered volcanic ashes (K-bentonites) in the late Ordovician (Caradocian) Utica shale of New York State are the product of explosive arc volcanism. Most of the 30 K-bentonites examined in this investigation contain fragmental crystals and rock fragments (microliths) up to 600 μm in diameter that generally are neither detrital contamination from the surrounding black shale nor igneous phenocrysts. The dominant phases are garnet (two groups; $\text{Gr}_{15-20} \text{Alm}_{45-75} \text{Py}_{35-0} \text{Sp}_{2-5}$; $\text{Gr}_{2-5} \text{Alm}_{55-85} \text{Py}_{10-40} \text{Sp}_1$), plagioclase feldspar (An_{80-10}), alkali feldspar (Or_{99-0}), clinopyroxene ($\text{Wo}_{50-40} \text{En}_{50-30} \text{Fs}_{0-30}$), and orthopyroxene ($\text{Wo}_{1-2} \text{En}_{77-32} \text{Fs}_{32-66}$), accompanied by lesser quantities of hornblende, aluminosilicate, quartz, sphene, Fe-Ti oxides, apatite, and zircon. Most of the fragmental crystals appear to be derived from the same source as the metamorphic microliths, which possess minerals with similar compositions. Both crystals and microliths are interpreted as xenocrysts and xenoliths from the ancient continental crust on which the Ordovician arc was constructed. They became entrained in the volcanic plume during explosive eruptions. A Precambrian age acquired on K-feldspars from one K-bentonite using the $^{40}\text{Ar}/^{39}\text{Ar}$ method shows that these xenocrysts were derived from depths of less than 5–10 km in the microcontinent at the time of late Ordovician volcanism. The occurrence of xenocrysts and xenoliths in these K-bentonites underscores the importance of performing detailed petrology on ash layers prior to the onset of more sophisticated tasks (e.g., isotopic age determinations; regional stratigraphic correlations of K-bentonites based upon chemical compositions).

INTRODUCTION

Late Ordovician K-bentonites are regionally extensive throughout the eastern half of North America (e.g., Brun and Chagnon 1979; Cullen-Lollis and Huff 1986; Fox and Grant 1944; Huff and Turkmenoglu 1981; Huff 1983; Kay 1931, 1935; Kolata et al. 1987; Mossler and Hayes 1966; Nelson 1922; Ross 1928; Samson et al. 1988; Weaver 1953, 1963). This widespread distribution is thought to have been caused by explosive silicic volcanism erupting from an arc that converged on the eastern margin of North America. During this time, sea level was high (e.g., Cisne et al. 1984), and much of the North American continent was the site of limestone and shale deposition which allowed for the preservation of these extensive ash falls.

This study into the petrology and geochemistry of late Ordovician K-bentonites in the Utica shale and Trenton limestone was initiated to: (a) explore the record of explosive silicic volcanism associated with subduction and collision during the Taconic Orogeny; (b) develop and test criteria that could prove helpful in using these volcanic ash horizons for regional stratigraphic correlations; and (c) provide additional isotopic ages to define better the Ordovician time scale. Although these tasks have been made more complicated by our discovery, in most sampled K-bentonites, of a dominant population of crystals and rock fragments that are not crystallization products of subduction zone magmatism, the non-magmatic components provide constraints on the nature of the arc. Furthermore, this report is a cautionary note to on-going studies of K-bentonites where petrology and mineralogy have not been integrated into the scientific strategy.

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GEOLOGIC AND TECTONIC SETTING

K-bentonites occur as ≤ 10 cm thick layers in Ordovician black shales (Utica Fm.) and argillaceous parts of flysch (Schenectady Fm.) of New York State. The 30 K-bentonite layers sampled in this study were collected

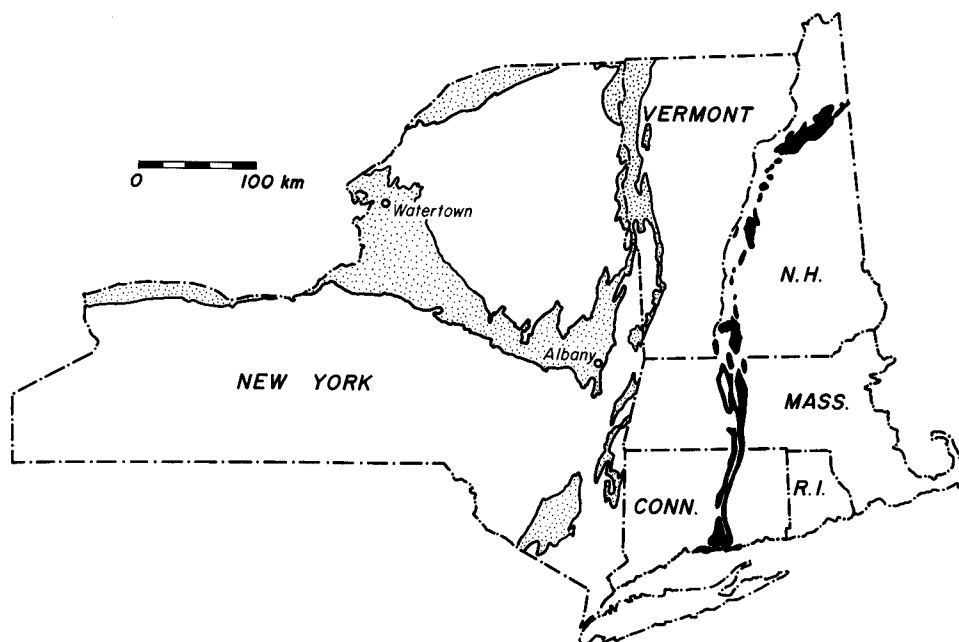


FIG. 1.—Generalized geologic map of New York State and western New England showing the distribution of (a) Ordovician sedimentary rocks of platform and flysch facies in New York and Vermont (stippled area) and (b) the Ordovician arc (black area; modified after Field 1975; K. Hollocher pers. comm. 1989) consisting of metavolcanic and metaplutonic rocks (Ammonoosuc Volcanics; and related gneisses in the cores of gneiss domes in the Bronson Hill anticlinorium) that was accreted onto the North American margin. Samples analyzed in the present study were collected in Ordovician strata cropping out from about 50 km west of Albany, N.Y. to about 10 km southeast of Watertown, N.Y.

(table Z) in strata that crop out from about 50 km west of Albany, NY to about 10 km southeast of Watertown, NY (fig. 1; Note: tables X–Z are available from *The Journal of Geology* Data Depository free of charge upon request and also from the first author upon request). These K-bentonites are easy to recognize in outcrop. First, because they are unlithified, they erode faster than the surrounding black shales (Utica Fm.) causing a pronounced reentrant along that particular stratigraphic horizon. Second, weathering of ash layers enriched in authigenic sulfides commonly produces a prominent orange staining. Third, fresh samples of K-bentonites obtained by excavating several centimeters into the layer are usually light gray with a soapy feel characteristic of montmorillonitic clay, in contrast to the surrounding black shales.

The Utica Fm. consists of about 300 m of flat-lying black, often calcareous, shales. It generally overlies thin (5–100 m) limestones, also of late Ordovician (Caradocian) age

(Trenton Group), and is itself overlain by a hundreds to thousands of meters thick sequence of late Ordovician graywacke turbidites and gray shales (flysch), normally referred to as either the Schenectady Fm. or the Frankfort Fm. The passage upward from shallow-water limestones (Trenton) to deeper-water shales (Utica) is thought to represent an increase in subsidence rate of the shallow-water carbonate platform that occupied parts of eastern North America since the early Cambrian. The age of the rocks (from graptolite fossils; Ruedemann and Chadwick 1935) shows that this change from limestone to shale is diachronous, being younger toward the west; similarly, the change upward from shales to flysch is also diachronous in the same sense (data summarized in Fisher 1977; see also Rowley and Kidd 1981; Bradley and Kusky 1986). At any point in time, three facies belts existed with (a) shallow-water carbonate platform in the west, (b) passing east to deeper-water shales, and then (c) to flysch with the quartzo-

feldspathic turbidites constrained to flow in a deep trough. This trough (or trench) was bounded to the east by an active accretionary thrust stack (the Taconic Allochthon and related structures; Chapple 1973, 1979; Rowley and Kidd 1981). The subsidence recorded by the change from Trenton limestone to Utica shale deposition was probably due to lithospheric flexure caused by loading of the North American continent by the Taconic thrust stack (Cisne et al. 1982). The westward migration with time of this thrust stack is believed to have driven the migration of the diachronous facies (Rowley and Kidd 1981; Bradley and Kusky 1986). Eastward-dipping subduction of lithosphere created a volcanic arc (fig. 1) in conjunction with the accretionary thrust stack on its leading edge. Although the ~25 bentonites found in the Utica shale (e.g., Cisne et al. 1982; Rowley and Kidd 1981; Trippi 1986) are probably the product of explosive arc volcanism, present geochemical and isotopic evidence does not favor the arc segment now exposed to the east in New Hampshire, Massachusetts, and Connecticut (fig. 1) as the eruptive source; consequently the volcanic source of these bentonites is not known as yet. A section across the present northwestern continental margin of Australia, the Timor Trough, Timor, and the Banda arc is an analog for the late Ordovician tectonic setting described above, with the Utica Fm. equivalent to muds deposited on the deep-water outer-trench slope of the Timor Trough (e.g., Zen 1967; Rowley and Kidd 1981; Cisne et al. 1982; Shanmugam and Lash 1982; Karig et al. 1987).

ANALYTICAL PROCEDURES

The K-bentonites were separated into size-fractions by washing through sieves (600 μm , 500 μm , 250 μm , 125 μm , 63 μm , 45 μm). Due to the non-lithified nature of the K-bentonites, samples were not crushed prior to sieving. To remove the small quantities of clay adhering to grain surfaces, each size-fraction was submerged in an ultrasonic cleaner for up to 10 hrs in various solutions: water; water + acetone; dilute nitric acid; dilute hydrochloric acid. Heavy liquids (bromoform; methylene iodide) and a Frantz isodynamic magnetic separator were used to concentrate the minerals according to their

density and magnetic susceptibility, respectively.

Grain mounts made from the resulting concentrates were ground and polished for microscopic inspection and chemical analysis by electron microprobe. Minerals and rock fragments (i.e., microliths) were chemically analyzed using a JEOL 733 Superprobe located in the Department of Geology at the Rensselaer Polytechnic Institute. This instrument has five wavelength dispersive spectrometers with on-line data reduction. The microprobe analysis was performed with an accelerating potential of 15 KeV and a sample current of 12 nanoamps. Backscattered electron imaging of the microliths was carried out with a 15 KeV electron beam and 1.5 nanoamp sample current.

The analytical procedures for $^{40}\text{Ar}/^{39}\text{Ar}$ data acquisition for the bulk alkali-feldspar aliquots are described in Harrison and Fitz Gerald (1986). In addition, single crystals of alkali feldspar were analyzed on a VG 1200S mass spectrometer and argon extraction was accomplished using an argon-ion continuous laser. Individual crystals weighed <100 μg . Typical extraction blanks comprised less than 1% of the total ^{40}Ar signal.

Bulk samples of K-bentonite were analyzed by X-ray fluorescence and instrumental neutron activation at laboratories located at McGill University, University of Michigan, and Cornell University.

MINERALOGY AND PETROLOGY

Garnets.—Two compositional groups of almandine-rich garnet are a common occurrence in the K-bentonites of the Utica Fm., both populations occurring in individual K-bentonites. The garnets are angular fragments up to 300 μm in maximum dimension. These two groups (fig. 2) are distinguished on the basis of their grossular abundance (5 mole % and 20 mole %). In grain mounts, the high-grossular garnets are deep red, whereas the low-grossular garnets are pale pink.

The occurrence of garnets in silicic igneous rocks has been observed and discussed by numerous authors (e.g., Abbott 1981; Allan and Clarke 1981; Barley 1987; Birch and Gleadow 1974; Bryant 1975; Clemens and Wall 1981, 1984; du Bray 1988; Fitton 1972; Fitton et al. 1982; Green and Ringwood 1972; Green 1977, 1978; Hall 1965; Kistler et al.

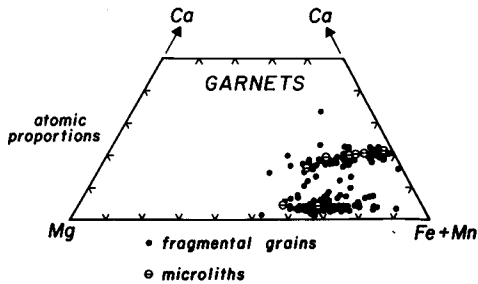


FIG. 2.—Molar proportions of pyrope ($Mg_6Al_4Si_6O_{24}$), almandine ($Fe_6Al_4Si_6O_{24}$), spessartine ($Mn_6Al_4Si_6O_{24}$), and grossular ($Ca_6Al_4Si_6O_{24}$) in garnets that occur in the K-bentonites as fragmental grains and in microliths. The garnets appear to form two compositionally distinct groups at ~5 mole % and ~20 mole % grossular.

1981; Leake 1967; Miller and Stoddard 1981; Oliver 1956, 1961; Searle and Fryer 1986; Vennum 1979; Warren 1970; Wood 1974; Wybron et al. 1981). A review of this subject by Miller and Stoddard (1981) showed that almandine-rich garnets in silicic magmatic rocks had a large compositional range with respect to the abundance of the Mn component, spessartine (fig. 3). Since experiments (Green 1977, 1978) have shown that Mn-enrichment stabilizes garnets in silicic magmas to pressures of <3 kbar, only low-Mn garnets are thought to be indicative of high (>7 kbar) pressures (e.g., Miller and Stoddard 1981). The two groups of garnets (fig. 2) observed in individual Ordovician K-bentonites have comparably low Mn abundances (fig. 3) and therefore appear to be high-pressure phases.

The presence of two compositionally distinct groups of garnet (fig. 2) within many of the Ordovician K-bentonites sampled in this study was a dilemma until rock fragments (i.e., microliths) up to 600 μm in diameter were observed and analyzed by electron microprobe. Microliths (fig. 4) have garnets that are compositionally similar to the fragmental garnets (figs. 2, 3). These fine-grained microliths have metamorphic textures and appear to have been derived from the same source as the fragmental garnet grains.

Pyroxenes.—Pyroxenes are a common mineral in some of the Ordovician K-bentonites of eastern New York State. Electron microprobe analyses of fragmental pyroxenes extracted from a single K-bentonite have been projected onto the quadrilateral

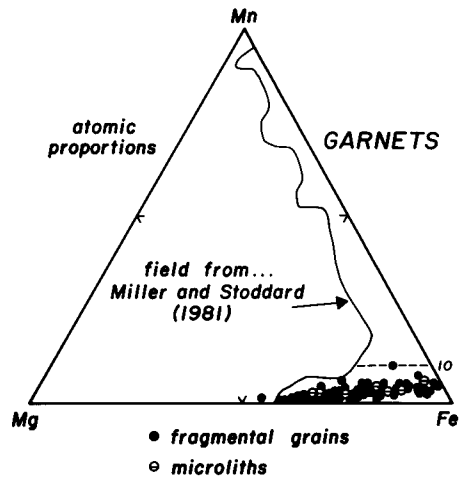
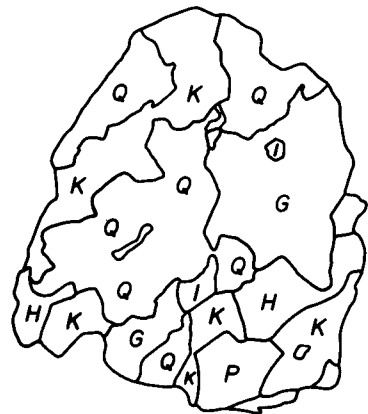


FIG. 3.—Atomic proportions of Mg, Fe, and Mn in garnets that occur in the K-bentonites as fragmental grains and in microliths. Compositions of garnets known to occur in silicic igneous rocks plot within the field defined by Miller and Stoddard (1981). The dashed horizontal line is at 10 atomic % Mn. Garnets having <10 atomic % Mn are considered likely candidates for high-pressure (>7 kbar) crystals (e.g., Green 1977).



G GARNET
H HORNBLENDE
I ILMENITE
K K-FELDSPAR
P PLAGIOCLASE
Q QUARTZ

FIG. 4.—Map of a rock fragment (microlith) that is representative of a suite that occurs in the K-bentonites of New York State. This map is based upon a backscattered electron image obtained using an electron microprobe.

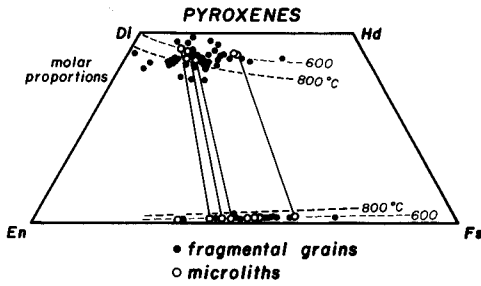


FIG. 5.—Molar proportions of enstatite (En; $Mg_2Si_2O_6$), ferrosilite (Fs; $Fe_2Si_2O_6$), diopside (Di; $CaMgSi_2O_6$), and hedenbergite (Hd; $FeCaSi_2O_6$) in pyroxenes that occur in the K-bentonites as fragmental grains and in microliths. The pyroxene compositions have been projected onto the quadrilateral using the method of Lindsley and Andersen (1983). The temperature contours are from Lindsley and Andersen (1983). Coexisting augites and orthopyroxenes in microliths are connected by tie-lines.

(fig. 5) using the molar recalculation program of Lindsley and Andersen (1983). No pigeonites have yet been observed. The observed compositional range of fragmental pyroxenes is more diverse than usually found in silicic arc volcanics (e.g., Camus et al. 1987; Kittleman 1973; Self et al. 1984; Westgate et al. 1987).

Pyroxenes within microliths have also been analyzed by electron microprobe. Coexisting pairs of orthopyroxene and augite in these microliths are connected by tie-lines in figure 5. Most of the pyroxenes observed in the microliths contain <10 mole % non-quadrilateral components and are therefore suitable for thermometry. Tie-lines in figure 5 indicate equilibration temperatures in the vicinity of $600 \pm 50^\circ C$ for the pyroxenes.

Feldspars.—Microliths (fig. 4) occurring in the K-bentonites commonly contain two feldspars. Tie-lines in figure 6 connect coexisting pairs of alkali and plagioclase feldspars occurring in those rock fragments. Equilibration temperatures have been estimated using the thermometer of Fuhrman and Lindsley (1988) and range from $425^\circ C$ to $525^\circ C$, i.e., metamorphic, not magmatic, temperatures.

An aliquot of alkali feldspars (fig. 7) in the 125–250 μm size-fraction of Flat Creek bentonite #14 (“Flat 14”: $42^\circ 53' N$; $74^\circ 32' W$) was analyzed by electron microprobe and by the $^{40}Ar/^{39}Ar$ method. This aliquot contained some perthitic grains indicative of meta-

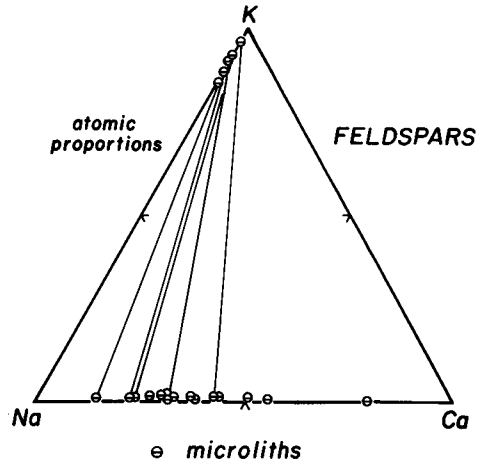


FIG. 6.—Ternary diagram showing the compositions of feldspars that occur in microliths in the K-bentonites. Coexisting alkali feldspars and plagioclase feldspars in any one microlith are connected by tie-lines.

morphic, not igneous, processes. Since the K-bentonite from which these crystals were extracted is late Ordovician (e.g., Cisne et al. 1982), a Proterozoic age (fig. 7) for these feldspars is considered diagnostic of their origin. In addition, $^{40}Ar/^{39}Ar$ ages acquired on seven single crystals of alkali feldspar separated from another Utica shale K-bentonite (near Copenhagen, N.Y., $43^\circ 54.3' N$; $75^\circ 42.6' W$) had apparent ages between 715 Ma and 1018 Ma (table X).

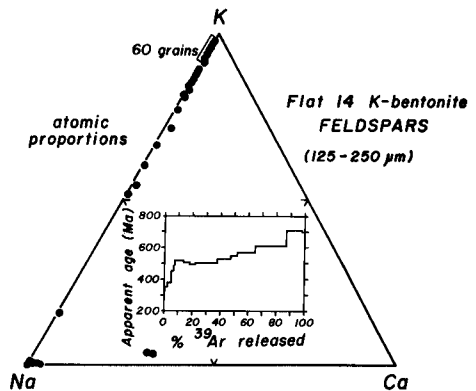


FIG. 7.— $^{39}Ar/^{40}Ar$ incremental heating and electron microprobe results from a 125 to 250 μm aliquot of feldspars separated from an Ordovician K-bentonite (#14 from Flat Creek) in New York State. The apparent age of 525–700 Ma demonstrates that most of the K-feldspars in this aliquot were xenocrysts, rather than either volcanic phenocrysts or authigenic phases.

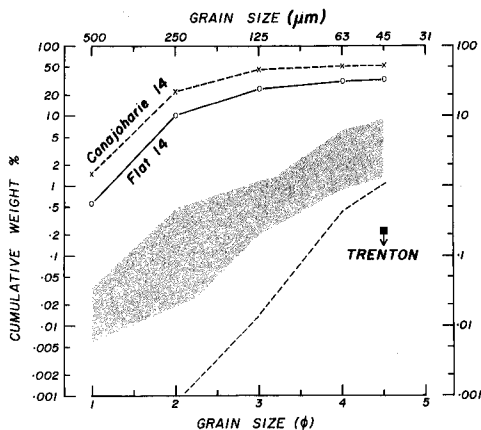


FIG. 8.—Summary of 45 μm and coarser portion of grain-size distributions observed in K-bentonites from New York State. The stippled area includes about half of the K-bentonites examined for grain-size distribution (table Z) from the Utica Fm. The coarsest K-bentonites (Canajoharie 14 and Flat 14) are mentioned explicitly in the text. The finest-grained K-bentonite in the Utica shale is shown by the dashed line below the stippled area. Grain-size is shown in μm and in phi units, where $\text{phi} = -\log_2(\text{mm})$. The vertical axis is a logarithmic scale. The black square labeled "Trenton" is an upper limit for a K-bentonite collected (table Z) from the Ordovician Trenton Fm. (platform carbonate).

Grain-Size Distribution.—Figure 8 summarizes the coarser portion of grain-size distributions observed in 21 Ordovician K-bentonites. With one exception ("Trenton"), all samples were collected from the Utica Fm. About half of the K-bentonites have grain-size distributions that fall within the stippled band in figure 8. The bentonite labeled Canajoharie 14 ($42^{\circ}53'N$; $74^{\circ}34'W$) is the coarsest specimen and contains the richest collection of xenocrysts and microliths. The Flat 14 bentonite had its alkali feldspars analyzed by electron microprobe and by $^{40}\text{Ar}/^{39}\text{Ar}$ thermochronology (fig. 7). Chemical analyses of these two K-bentonites are included in table Y. The bentonite with the finest grain-size distribution in the Utica Fm. is indicated by the dashed line in figure 8. The Trenton bentonite (fig. 8) was collected in the Ordovician carbonates (Trenton Fm.) underlying the Utica Fm. and $<0.2\%$ of its mass has grain sizes $>45 \mu\text{m}$.

DISCUSSION

Source of Crystals and Microliths.—The microliths, and majority of the feldspars, py-

roxenes, and garnets, that occur as $>45 \mu\text{m}$ fragments in most of these late Ordovician K-bentonites appear to be high-grade metamorphic components from Proterozoic continental crust. This conclusion is based on: (a) the compositional diversity of minerals in individual K-bentonites, which is far beyond that expected for magmatic phenocrysts in silicic volcanics; (b) $^{40}\text{Ar}/^{39}\text{Ar}$ thermochronology on aliquots of coarse K-feldspars that yield Proterozoic ages; (c) metamorphic textures of microliths having well-developed 120° triple junctions among adjacent mineral phases; and (d) high-grade metamorphic temperatures at 400° – 600°C , indicated by geothermometry of coexisting pyroxenes and feldspars in microlithic fragments.

The non-magmatic components that frequently occur in the K-bentonites can be interpreted as either (a) xenocrysts and xenoliths ejected during explosive volcanism or (b) detrital sedimentary contamination in secondary bentonites formed from reworked ash (e.g., Weaver 1963). We believe that a "xenolithic" scenario better fits the following constraints and has sufficient precedent (Druitt et al. 1989; Eichelberger and Koch 1979). First, the overwhelming proportion of garnets, pyroxenes, and feldspars are angular fragmental crystals with no evidence of the rounding that should be expected in a "sedimentary contamination" scenario. Explosive disruption of continental basement during volcanism would produce these angular broken crystals, as is readily observed in crystal and lithic tuffs. Second, the black shales of the Utica Formation are characteristically fine-grained, and our preliminary studies show they contain only a tiny proportion of detrital grains $>45 \mu\text{m}$ across ($\leq 1 \text{ mg}$ of crystals per 1 kg of shale), which is below the limit of abundance shown in figure 8. This paucity of large crystals of appropriate mineral composition in the shales makes these Ordovician muds an unlikely source for the crystalline and lithic components in the K-bentonites via sedimentary contamination. The minute quantities of $>45 \mu\text{m}$ detritus in the black shales may have resulted from currents that occasionally scoured the bottom, causing local erosion and deposition of K-bentonite components into the surrounding muds.

The presence of continental-derived xenocrysts and microliths in these Ordovician K-

bentonites indicates to us that the silicic magmas ascended through continental crust. This crust may have formed the basement on which the volcanic arc was constructed. Explosive, Plinian-style eruptions disrupted this crust causing crystal and rock fragments to become entrained in the volcanic plume. Additional evidence in support of continental crust involvement is (a) the high $^{87}\text{Sr}/^{86}\text{Sr}$ initial ratios of Ordovician K-bentonites (Samson et al. 1989; Williams et al. 1982) and (b) the presence of old, inherited Pb in zircons contained within the K-bentonites (Samson et al. 1989).

The significant occurrence of non-magmatic components in most of the K-bentonites of the Utica Fm. appears to contrast with their low abundance in K-bentonites of comparable age in the Mississippi Valley and Pennsylvania (e.g., Allen 1929; Cullen-Lollis and Huff 1986; Huff 1983; Kolata et al. 1987; Samson 1986; Samson et al. 1988). However, Samson et al. (1989) have recently reported almandine-rich garnets in an Ordovician K-bentonite (Nasset) from the Mississippi Valley. In fact, although no electron microprobe data are yet available, there are two populations of garnet based on color (i.e., pink and red; S. Samson pers. comm. 1989) that may be similar to those discussed in this study from New York State (fig. 2.).

Although it is tempting to link genetically the distinctive occurrences of garnets in Ordovician silicic volcanics of England (i.e., Borrowdale Volcanics in the Lake District) and eastern North America, the petrogenesis of the garnets is not related. For instance, the Borrowdale garnets are compositionally distinct and appear to be high-pressure magmatic phenocrysts (e.g., Fitton 1972; Fitton et al. 1982; Oliver 1956, 1961; Thirlwall and Fitton 1983), whereas the garnets occurring in some North American K-bentonites are xenocrysts, as shown in the present study.

$^{40}\text{Ar}/^{39}\text{Ar}$ Chronology.—The crystals and microliths in the Ordovician K-bentonites of New York State appear to be disrupted pieces of continental crust, which presumably formed the basement of the volcanic arc. Since the closure temperature for Ar diffusion in these K-feldspars is between 150°–350°C, the apparent age (525–700 Ma; fig. 7) of the feldspars in the size range 125–250 μm indicates that the xenocrysts likely resided at depths of <5–10 km in the continental base-

ment for >75 Ma prior to their disruption during explosive Ordovician volcanism. The remarkable Ar-isotopic similarity between these K-bentonite feldspars and Adirondack feldspars (Heizler and Harrison 1987) suggests that the crustal uplift histories of the microcontinent on which the arc was built and the crystalline basement of northeastern New York State were nearly identical.

The age spectrum in figure 7 is clearly dominated by apparent ages older than the stratigraphic age of the bentonite (~450 Ma). Since the sample aliquot (fig. 7) probably consists of three generic components (i.e., late Proterozoic xenocrysts + Ordovician phenocrysts + younger authigenic feldspars), the age spectrum (fig. 7) indicates that the late Proterozoic xenocrysts dominate. This is supported by single crystal analyses from another K-bentonite (Table X) in which all seven crystals yielded late Proterozoic ages. Although we realize that seven crystals are probably too few to be a true representation of the bulk feldspar population, these results strongly suggest a dominance of xenocrysts.

The apparent ages of <450 Ma in the initial 5% of the gas released (fig. 7) are related to partial loss of argon by the older crystals due to burial and reheating (Heizler and Harrison 1987) of the Utica Fm. and/or authigenic growth at <350 Ma.

Geochemistry of K-bentonites.—These K-bentonites, which have sharp lower contacts with the Utica shale (fig. 9), are generally light gray, either non-lithified or become so upon soaking in water, and have a soapy feel. A dark gray, lithified layer occurs above and in sharp contact with the bentonite. We interpret this upper zone as being a "mixed layer" (e.g., bioturbation; reworking by bottom currents) of Utica shale and K-bentonite \pm xenocrysts (fig. 9), in agreement with studies of other bentonite occurrences (e.g., Cameron and Anderson 1980; Fisher and Schmincke 1984; Ninkovich et al. 1978; Watkins et al. 1978). Although this view is generally supported by (a) chemical analyses (table 1) and by (b) elevated concentrations of angular fragmental crystals (i.e., xenocrysts) compared to normal Utica shale, figure 10 indicates that the composition of this "mixed layer" cannot be a simple blend of Utica shale + bentonite \pm xenocrysts. Note that the bentonite has a peculiar rare earth element (REE) pattern characterized by: (a) a

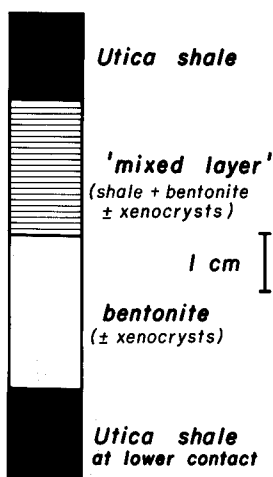


FIG. 9.—Schematic illustration of the stratigraphic zones commonly exhibited by K-bentonites in the Utica Fm. of New York State.

strongly negative Eu-anomaly; (b) a positive Ce anomaly; and (c) a decoupling of light- and heavy-REE such that the pattern is discontinuous. Due to the diagenetic mobility of these rare earth elements (e.g., Zielinski 1982) out of the K-bentonite into the upper mixed layer and the lower contact shale, we believe that the bentonite itself conveys little information about the REE pattern of the original ash.

Bulk chemical analyses of the K-bentonites have been made by X-ray fluorescence techniques (Table Y) to provide some constraints on the compositional nature of the original volcanic ash. Since it is well established that major fluxes of mobile elements into and out of volcanic ashes occur during diagenetic processes (e.g., Altaner et al. 1984; Brusewitz 1986; Noble 1967; Zielinski 1982), a reliance on immobile elements is required. For example, Winchester and Floyd (1977) devised a method for distinguishing igneous compositions by using diagnostic ratios among immobile elements (fig. 11). Based on the compositions of the mixed zones (black circles in fig. 11) and bentonites (open hexagons in fig. 11), the original bulk compositions of K-bentonites are estimated to have been trachyandesite to rhyodacite and chemically distinct from felsic volcanics (shaded area in fig. 11) located in the Ordovician arc of Connecticut, Massachusetts, and New Hampshire (fig. 1; Schumacher 1983). The

compositional effect the xenocryst components have on these K-bentonites is most evident by the sample (Canajoharie 12; Table Y) that plots within the alkali basalt field in figure 11; in most samples the effect is small.

Although the designation of "trachyandesite to rhyodacite" covers a wide range of volcanic compositions and is not particularly surprising, the chondrite-normalized REE abundances in the upper mixed layer and lower contact shale (fig. 9), are quantitatively dominated by REE that migrated from the adjacent K-bentonite (fig. 10), and these patterns, including the magnitude of the Eu anomaly, are comparable to continental rhyolites and rhyodacites (e.g., Izett 1981; Musselwhite et al. 1989).

Stratigraphy and Time.—Due to their widespread occurrence, Ordovician K-bentonites have great potential as stratigraphic marker-horizons (e.g., Brun and Chagnon 1979; Kay 1935; Huff 1983). However, this task is predicated on successful correlation of individual horizons on a regional scale. Correlation efforts have relied principally on paleontology/stratigraphy (e.g., Cisne et al. 1982), "chemical fingerprinting" from bulk chemical analyses (e.g., Kolata et al. 1987; Sarna-Wojcicki et al. 1985), mineral chemistry of phenocrysts (e.g., Kittleman 1973; Samson 1986; Smith and Leeman 1982), or combinations thereof. It is readily apparent that the occurrence of xenocrysts and xenoliths in K-bentonites adds yet another complicating factor to the already challenging task of correlation. For example, "chemical fingerprinting" of K-bentonites from eastern New York State to the Mississippi Valley (assuming that some of the units are in fact correlative) would be a potentially risky operation without taking into account any chemical effects of the xenocryst-xenolith components in the eastern localities (Walker 1972). This problem might be surmounted by analyzing fractions (e.g., $<45 \mu\text{m}$) of the eastern K-bentonites that contained a high proportion of the altered pumice relative to the non-magmatic constituents. Similarly, K-bentonite correlation through bulk chemical analysis of mineral concentrates (e.g., Samson 1986) with the implied assumption of a phenocryst origin for that particular mineral (e.g., apatite; zircon) could be jeopardized if the crystals were derived from more than one source

TABLE 1

CHEMICAL COMPOSITIONS OF A STRATIFIED K-BENTONITE (CANAJOHARIE 27) AND AVERAGE UTICA SHALE (ON A CAO-* AND LOI-FREE BASIS)

(wt %)	Shale at lower contact	K-bentonite	"Mixed layer"	Utica shale (4 samples) (average)
SiO ₂	75.3	54.2	62.8	68.0
TiO ₂	.62	.66	.86	.77
Al ₂ O ₃	13.4	33.2	23.8	15.2
Fe ₂ O ₃	3.64	2.40	3.48	5.68
MnO	.06	.02	.05	.09
MgO	2.83	2.17	2.52	5.19
CaO
Na ₂ O	1.02	.30	1.10	.99
K ₂ O	2.87	6.88	5.02	3.29
P ₂ O ₅	.23	.22	.27	.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. ^a	165	164	148
Y	n.a. ^a	26	41	43
Zr	n.a. ^a	253	280	274
Nb	n.a. ^a	21	24	23
Cs	7.0	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	76.0	46.2
Sm	24.2	8.83	13.3	9.16
Eu	2.01	.14	.92	1.45
Tb	2.84	.74	1.51	1.16
Yb	9.59	3.13	5.77	3.89
Lu	1.44	.44	.79	.53
Hf	6.2	12	9.9	5.6
Th	15	63	34	14
U	12	20	14	7.6

NOTE.—Refer to figure 9 for the relative stratigraphic position of the units listed. USGS SCo - 1 standard used; analysis of this standard available on request to the first author.

^a n.a. = not analyzed.

(e.g., phenocrysts + xenocrysts). In addition, diagenetic mobility of the REE (e.g., fig. 9) would also complicate matters for correlations using chemical fingerprinting, in which the REE are important discriminators (e.g., Kolata et al. 1987), unless the same exact alteration has occurred everywhere to all sampled bentonites.

The occurrence of non-magmatic components in these K-bentonites also aggravates the task of determining their eruption ages using conventional isotopic methods. For instance, ages of K-bentonites based on ⁴⁰Ar/³⁹Ar analysis of a polygrain aliquot should be viewed with caution until detailed petrologic examination can demonstrate that xenocrysts

and authigenic phases are not a significant component in the analyzed aliquot. Complications arising from the occurrence of volcanically blasted country rock in K-bentonites for isotopically determining the eruption age have also been discussed by Hills and Baadsgaard (1967) and Baadsgaard and Lerbekmo (1982). However, ⁴⁰Ar/³⁹Ar data acquired on individual crystals of feldspars (table 1) and hornblendes, as well as U-Pb ages on individual zircons by ion microprobe (e.g., Harrison et al. 1987), should be capable of identifying phenocrysts for which the eruption age could be confidently known.

Atmospheric Dispersal of Ordovician Vol-

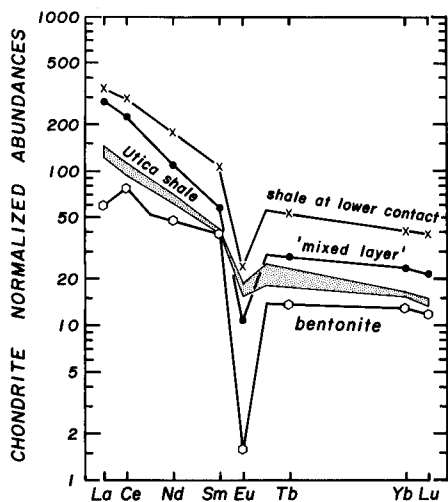


FIG. 10.—Chondrite-normalized abundances of rare earth elements indicate that the "mixed layer" (solid circles) is not a simple blend of average Utica shale (shaded) + bentonite (open hexagons). Diagenetic mobility of the REE out of the bentonite into the "mixed layer" and shale at lower contact (x's) is required. Refer to figure 9 for the relative stratigraphic position of these layers. Elemental abundances are recalculated on a CaO- and LOI-free basis.

canic Ash.—During Plinian-style volcanic eruptions, the ash can ascend to 30 to 40 km (e.g., Jakosky 1986; Sparks and Wilson 1976; Walker 1981) where its dispersal is controlled by winds in the stratosphere, rather than by low-altitude trade winds (e.g., Hildebrand 1988; Sigurdsson and Carey 1981). At present the stratospheric winds, which have speeds of 20 to 50 m/sec, change direction as a function of season—in the summer they blow from the east, but in the winter they blow from the west (Holton 1979; p. 297; Person 1982).

If the stratospheric winds during the Ordovician behaved in a similar fashion, then the consequences for ash dispersal could have been intriguing. For example, if the volcanic arc that generated the Ordovician K-bentonites now observed in the eastern half of North America and in portions of Scandinavia was located in the Appalachian-Caledonian ocean (Iapetus) at approximately 30°S latitude (e.g., Faller et al. 1977; Samson et al. 1989; Van der Voo 1988), then ash erupted during the summer months would have been transported westward toward the North America craton. In contrast, K-bentonites in Europe and Scandinavia may be

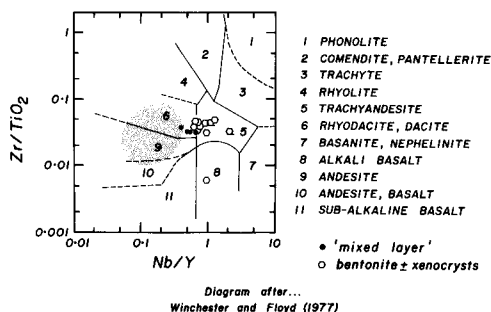


FIG. 11.—Ratios of four relatively immobile elements suggest that these Ordovician K-bentonites were composed of volcanic ash having compositions of trachyandesite to rhyodacite. The open hexagons show bulk compositions of K-bentonites having substantial proportions of the non-magmatic components (i.e., xenocrysts; xenoliths). The black circles are the "mixed layers" at the upper contacts of four bentonites. The tails on two of the open hexagons indicate that their Nb/Y ratios are minimum values. The stippled field contains analyses of felsic Ammonoosuc volcanics (Schumacher 1983) from the middle Ordovician arc located to the east (fig. 1). This discriminant diagram is modified after Winchester and Floyd (1977). Average Utica shale (table 1) plots near the solid circles representing "mixed layers."

products of major eruptions that occurred during the winter when the ash was dispersed eastward. If this view has merit, it may be unrealistic to expect that individual Ordovician K-bentonites could be correlated between, for example, North America and Scandinavia, even though these ash layers may all be derived from the same volcanic arc. However, the detailed geologic implications of ash dispersal by stratospheric winds depend in large part on continued improvement of paleogeographic reconstructions for the Ordovician (e.g., Cocks and Fortey 1982; Faller et al. 1977; Scotese 1984; Van der Voo 1983; Wilde et al. 1989; Ziegler et al. 1979).

CONCLUSIONS

The data collected during this investigation support the following conclusions:

(a) Many of the Ordovician K-bentonites in the Utica shale of New York State contain a rich and varied assemblage of crystals and microliths in the >45 μm size-fraction. A dominant portion of this component is non-magmatic (i.e., xenocrysts; xenoliths).

(b) Many of the crystals and microliths were apparently derived from shallow (<5–10 km depth) levels of Proterozoic continental crust

on which a volcanic arc was constructed. Explosive disruption of this crust during silicic arc volcanism may have caused these crustal fragments to become part of the K-bentonites.

c) The crystals and microliths that are so abundant in the New York State K-bentonites also appear to be present, albeit in smaller quantities, in a K-bentonite of comparable age in the Mississippi Valley (Samson et al. 1989).

d) The presence of non-magmatic components in K-bentonites of New York State makes the task of stratigraphic correlation throughout the eastern half of North America by chemical, petrologic, and isotopic methods a more challenging task than previously thought.

e) Detailed petrology can be a useful pre-

cursor to any geochemical or isotopic investigation of K-bentonites.

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