

THE SIGNIFICANCE OF SULFATES AND SULFIDES IN SILURIAN BENTONITES AT ARISAIG, NOVA SCOTIA

EMILY SEIDER

Whitman College

Research Advisor: Kirsten Nicolaysen

INTRODUCTION

The Northumberland coast at Arisaig, Nova Scotia hosts North America's largest known series of Silurian K-bentonites. Over 40 separate ash beds have been identified in the Beechhill Cove, Ross Brook, and McAdam Brook Formations of the Arisaig Group (Fig. 1) (Bergstrom, 1997). Previous trace element analyses conducted by Bergstrom et al. (1997) suggested that most Arisaig bentonites came from a subalkaline, silicic magma series of dacitic composition, though a few of the more alkaline layers could be classified as andesitic. Furthermore, Bergstrom et al. (1997) interpreted the ash beds as originating from subduction-related plate margin volcanism due to partial melting of hydrous crustal rocks. However, the location of source volcanoes for these bentonites is unclear. The relatively small size of primary crystal grains does imply that the Arisaig ash probably traveled tens to hundreds of kilometers from its vent before being deposited in an intercontinental basin.

The purpose of further studying the geochemistry of these bentonite beds is to verify the results found by Bergstrom about the general composition of the ash, attempt to correlate apparently stratigraphically equivalent beds, and to explain the origin of previously undescribed sulfate and sulfide minerals extracted from the ash.



Figure 1. Photograph of a bentonite bed at the Beechhill Cove West locality.

METHODS

Sample Collection and Preparation

Twenty two bulk samples were located and extracted along the shore between Arisaig Harbor and Moydart Point (see Figure 1 of Sanders-Lackey et al., this volume). In the lab, 6 representative samples were chosen for processing based on their degree of induration and stratigraphic position. After soaking in water and sodium pyrophosphate they were disaggregated in a household drink mixer (after Emerson, 2004). Indurated samples from Beechhill Cove East were gently ground by hand in a mortar and pestle. Samples were then wet-sieved with nylon mesh to remove clay portions and dried at 110° C. The 74 μ m – 295 μ m size fraction was sorted by density

with heavy liquids. Magnetic particles were also removed. Nonmagnetic mineral grains with a density greater than 2.85 g/mL minerals were hand picked and, after preliminary investigations with a scanning electron microscope, mounted for electron microprobe analyses.

Bulk samples from all 22 bentonite beds were also prepared for X-ray Fluorescence spectroscopy (XRF) at Whitman College. Bentonites were dried in an air-drying oven for 24 hours at 110° C. Material was then ground in an aluminum mortar and pestle until uniform in grain size. Approximately 12 mL of each homogenized sample was prepared for analysis.

Electron Microprobe Analyses

Under 1-4x stereoscopic magnification, hand picking from the sieved and sorted samples recovered sulfates and sulfides from the bentonites. These minerals were mounted and polished for analysis in an electron microprobe. Electron Microprobe analyses were conducted at the University of Oregon on a Cameca SX100 electron probe microanalyzer.

overlapping elements, corrections were applied to Na for Zn interference, Ba for Cu interference, and to Ti for Cu interference (Donovan, 1993). Formulas were made with oxygen calculated from cation stoichiometry. These were incorporated into the matrix corrections as well.

X-Ray Fluorescence Spectroscopy

Bulk samples were analyzed for major and trace element oxides using an Innov-X Alpha series portable X-ray fluorescence spectrometer in a lab test stand. All analyses were run for 180 seconds. After calibration on a steel alloy, four repeated standardizations of the instrument showed a peak resolution of 230. NIST Standard Reference Material 2710, Montana Soil was used as the analytical standard. Ten replicate analyses of NIST 2710 yielded average percent relative deviations typically between 0.7% and 3%, though sulfur was considerably higher at ~15% (Table 1) Elements of particular interest included Fe, Zr, and Ti because they are high field strength trace elements (HFSE) and have been demonstrated to be relatively immobile in bentonites (Bergstrom, 1997).

TABLE 1. ERROR IN XRF BULK SAMPLE ANALYSES

Element	S	Ti	Zr	Fe	Mn	K	Ca
Average (ppm)	8919.71	3229.21	120.52	37041.34	10275.19	22207.66	13101.30
Standard Deviation	1361.05	68.88	3.13	287.47	81.27	227.40	232.77
% Relative Deviation	15.26	2.13	2.59	0.78	0.79	1.02	1.78
Element	Cu	Zn	Mo	Ba	Pb	Rb	Sr
Average (ppm)	3043.68	7163.48	17.31	784.02	5745.27	128.08	337.96
Standard Deviation	42.56	70.19	2.13	54.73	51.48	2.43	2.65
% Relative Deviation	1.40	0.98	12.32	6.98	0.90	1.90	0.79

Table 1. Deviation of the XRF bulk sample analyses. Values are based on ten replicate analyses of NIST Standard Reference Material 2710, Montana Soil.

The instrument was equipped with four tunable wavelength dispersive spectrometers and run with Probwin NT/2000/XP, version 7.06 software. Unknown and standard intensities were corrected for deadtime, while standard intensities were also corrected for standard drift over time. In case of interference from

Another reason for using these elements is that none of them are major constituents of seawater or brines. Sulfur was also a focus of the XRF analysis because of the above mentioned sulfate and sulfide minerals. The XRF analysis was also used to test stratigraphic relationships between the Beechhill East locality and the Beechhill

West locality, two sample sites separated by a cove and frequent faulting. K-bentonites from Beechhill Cove East have been speculated to be the same as K-bentonites from Beechhill West (Bergstrom, 1997). If this is the case, a close match between the chemistry of the two sets of samples would be expected.

the bentonite beds was compared to relative stratigraphy (Fig. 2) Some of the samples that contain barite and sphalerite are from the samples found to have high bulk sulfur content, but some are from relatively low sulfur samples.

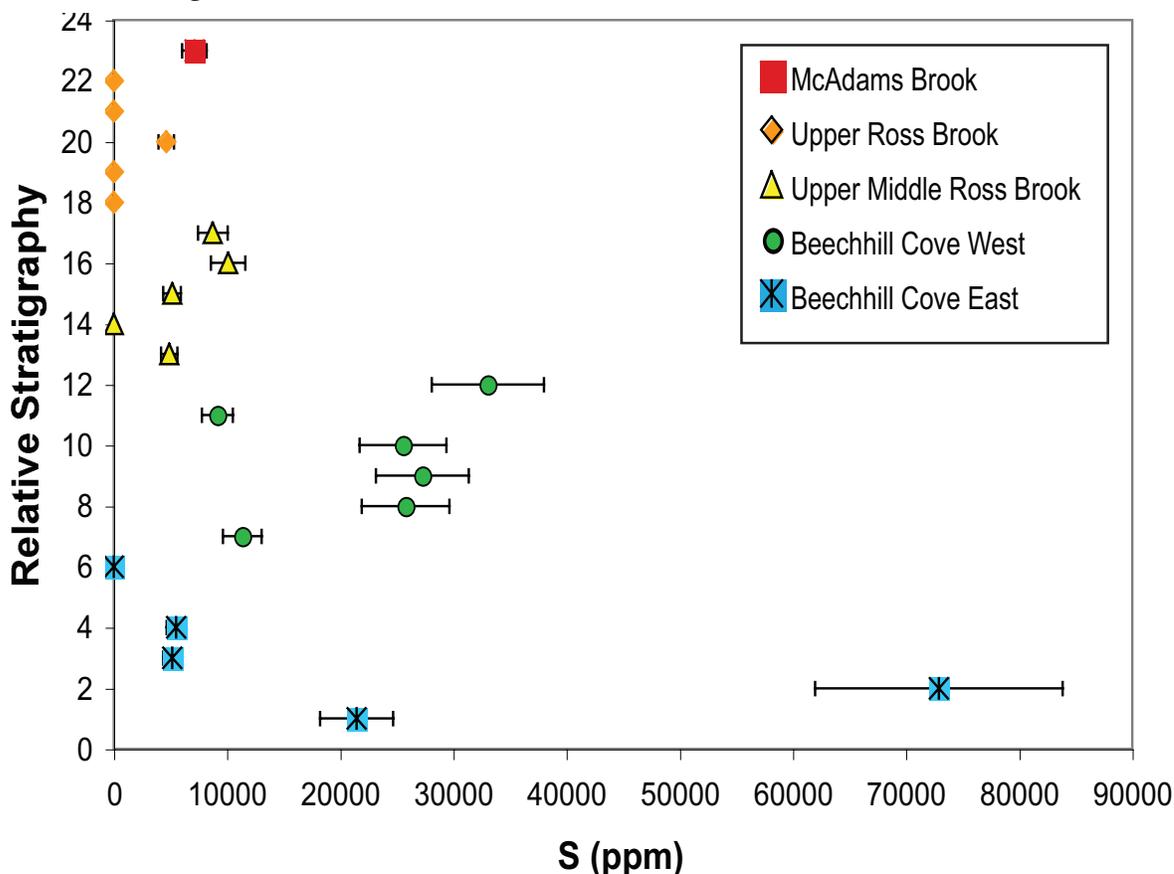


Figure 2. Sulfur content of each bulk sample in relative stratigraphic order, as measured by XRF spectroscopy. Percent errors are calculated from variation in the repeated standard analyses shown in Table 1. Values shown as zero are below the detectable limit.

RESULTS

Preliminary scanning electron microprobe analyses of the high density minerals retrieved from the bentonites revealed barite (BaSO_4) and sphalerite ($[\text{Zn},\text{Fe}]\text{S}$) crystals. Further analysis using the electron microprobe revealed stoichiometric compositions of $\text{Ba}_{-1}\text{S}_{1.01}\text{O}_{4.05}$ and $(\text{Zn}_{1.01},\text{Fe}_{0.001})\text{S}_{.969}$. Using the concentrations of trace elements obtained from the XRF, sulfur content across the stratigraphy of all

There also appears to be a significant separation between the low sulfur (less than 1200 ppm) and high sulfur concentrations (greater than 20,000 ppm), though high sulfur samples occur lower stratigraphically. Figure 3 shows the relationships between HFSE from various ash beds. Significant grouping of compositions between different bentonites can be seen in these plots; notably Zr was remarkably consistent and high for Beechhill Cove East and West samples though Fe contents varied considerably.

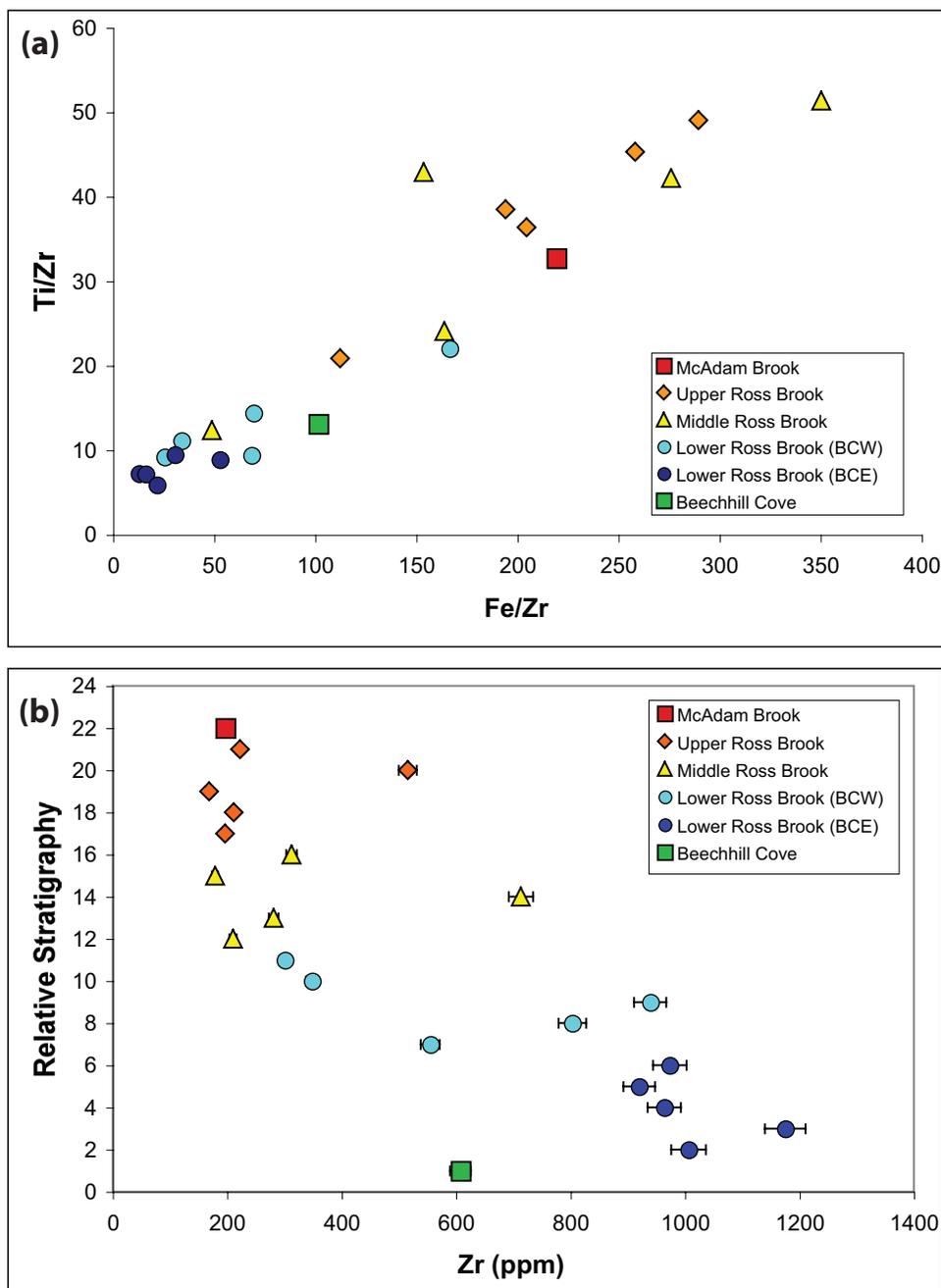


Figure 3. Relationships in concentrations of elements from bulk bentonite samples, as measured by XRF spectroscopy. a) Zircon is a fluid immobile element and is in low abundance in seawater. The decreasing amount of Zr in younger bentonites may indicate variation in original ash composition. Percent errors are calculated from variations in ten repeated standard analyses. b) Iron and Ti concentrations are compared because they are both HFSEs. They should be fluid immobile and thus represent concentrations of the original ash. The elements are normalized to Zr, a conserved element, to elucidate the effects of a primary magmatic signature. The trend implies fractional crystallization or possibly magma mixing.

DISCUSSION

Sulfates and Sulfides

The presence of sulfates and sulfides was unexpected as these minerals were not described in Bergstrom's study of these bentonites, nor

do other bentonite studies particularly mention these minerals. The deposition of the Arisaig bentonites in a marine basin may explain the origin of these minerals. Barite is a common trace mineral of many deep-sea sediments (Berner, 1998) and may have simply been

precipitating out of the water at the same time as the volcanic eruptions. Sphalerite has been observed to form from microbial reduction of sulfates in anoxic environments (Labrenz, 2000). Such formation of sulfides is the most prominent mechanism for sulfur removal from seawater, as the formation of barite is limited by the low concentration of Ba in the ocean (Holland, 1965). Barite is a reliable source of paleo $^{34}\text{S}/^{32}\text{S}$ ratios (Berner, 1998). Further investigations into the isotopic ratios of the sulfur in barite found in the bentonites could provide a record of changes in the Iapetus Ocean's sulfur cycles and possibly a history of the biological processes that cause this isotope fractionation.

Implications of Bulk Sample Geochemistry

The biostratigraphy and lithologic facies of shales of the Beechhill Cove Formation surrounding the Beechhill Cove East and West bentonites indicate that the beds in both locations were deposited during the same time interval (Melchin, 2005). It would be reasonable to expect that the same bentonite beds would be present in both localities, and these beds would cluster in the trace element plots in figure 3. Two Beechhill Cove West samples show similarly high Zr abundances as the Beechhill Cove East samples (Fig. 2a). This is probably the most reliable indication of a stratigraphic correlation because Fe, which varies considerably, could be mobilized post-deposition depending on local oxidation conditions and fluid movement through the unit. These same samples also have similar Ti values (Fig. 2b), but they are not as close as the Zr values. Both of these HFSE, which should be characteristically immobile in fluids, vary outside of analytical precision for this group, so it cannot be stated for sure that these are the same bentonites outcropping at the East and West localities. However, this variation may be due to local concentrations of heavy accessory minerals such as zircon, rutile or titanomagnetite in the ash beds, and thus the bulk samples, so

correlation is still a possibility.

The trend apparent in Figure 3a supports that chemically related ash beds throughout the Arisaig Group originated from genetically related volcanic eruptions. Figure 3b shows that S does not show a primary igneous signature. Bergstrom speculated that there were at least two volcanic sources for the ash beds, based on their range of chemical compositions. The data obtained from this study (Fig. 3) suggests that this interpretation is reasonable.

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