STRONTIUM ISOTOPIC ANALYSIS OF TEPHRA: A CASE STUDY FROM THE WESTERN INTERIOR SEAWAY

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Introduction

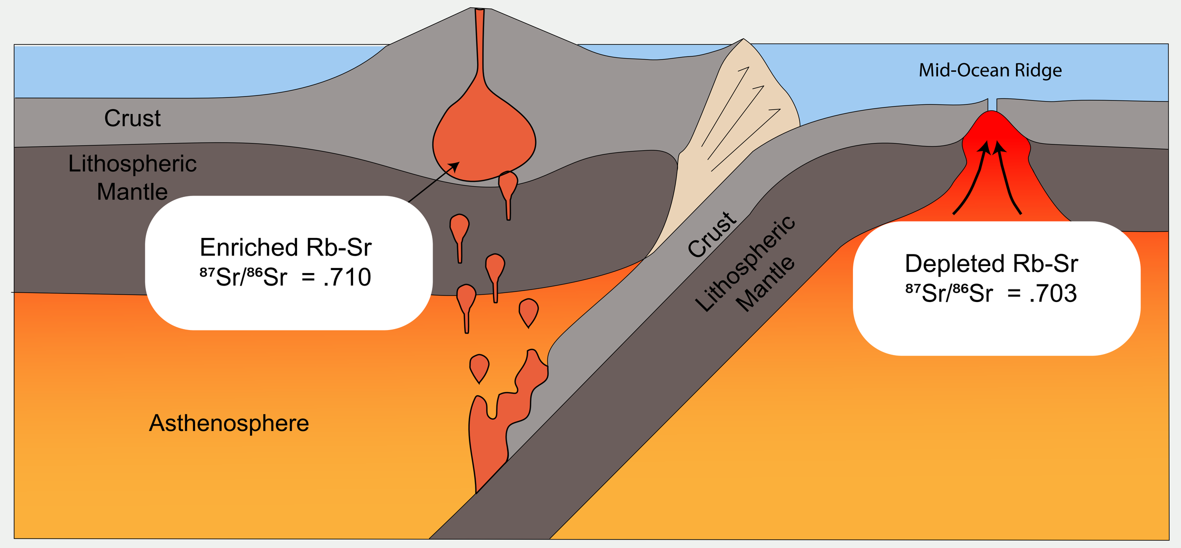
Ash and oceans: A comparative study of isotopic chemistry

The Western Interior Seaway (WIS), the epicontinental sea stretching across North America during the Late Cretaceous, is home to a myriad of bentonite layers found amid typical marine stratigraphic sequences. Apart from being a highly economic resource, bentonites are renowned for their correlative utility, providing geologists with a powerful stratigraphic tool. During the Late Cretaceous, active volcanism was responsible for the ubiquitous bentonites found within the WIS.

Bentonites are a claystone, authigenically formed from devitrified volcanic glass. Even though bentonites consist almost entirely of authigenic smectitic clay, primary volcanic minerals (zircon, apatite, feldspar, etc.) are commonly preserved, revealing the clay's explosive origin. The two-sided nature of bentonites- a sedimentary rock made entirely of clay, but born from magma- reveals an interesting issue about how to classify these ubiquitous geologic anomalies. What source does the chemistry reflect? Has the chemistry been altered to reflect the original preserved volcanic signature or a diagenetic signature of the preservational environment. Is a bentonite more "pyro" (igneous) or more "clast" (sedimentary)?

Strontium Isotopic System

Every strontium bearing rock and mineral on the planet has a preserved isotopic signature that can be analyzed using mass spectrometry. The ratio of ^{87}Sr to ^{86}Sr is commonly used for determining the provenance and fractionation history of mineral phases, and can also be used for isochron-based radiometric dating. Rubidium 87 decays to strontium 87 with a half-life of 48.8 Ga. Therefore, rock systems with higher rubidium concentrations have, over time, produced more radiogenic strontium 87. This leads to higher ratios of $^{87}Sr/^{86}Sr$, and because rubidium is an incompatible element with respect to most mafic mineral phases, felsic rocks tend to have higher $^{87}Sr/^{86}Sr$ ratios. For example, mid-ocean ridge basalts have an average $^{87}Sr/^{86}Sr$ = 0.703 (depleted), while average continental crust $^{87}Sr/^{86}Sr$ = 0.710 (enriched). Most rocks fall in between these values, due to assimilation of various rock types.

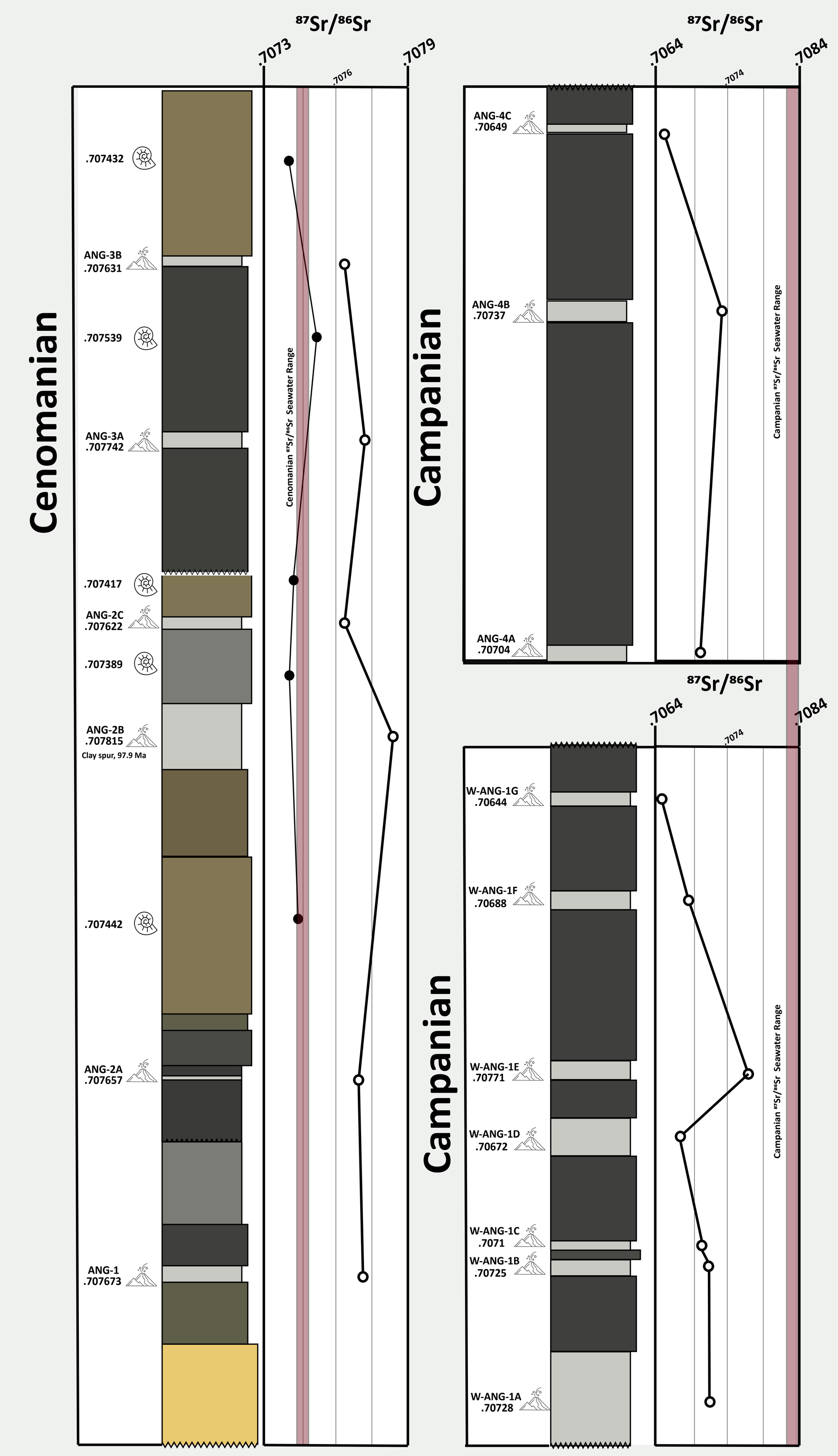


Mid-ocean ridge basalts have a much lower radiogenic strontium signature from Rb depletion in the mantle. Subduction zone melts have fractionated high concentrations of Rb, resulting in increased amounts of ^{87}Sr from radiogenic decay.

One of the most common uses for strontium isotopes is strontium stratigraphy. The strontium signature of seawater, which is consistent world-wide at any given moment, is preserved in shelly organisms as a substitution of calcium. Due to the diagenetic nature of bentonite clay, the nature of strontium associated with devitrified ash is not certain. Is the strontium ratio of bentonites diagenetically preserved from the seawater in which the clay formed, or is the original magmatic signature preferentially biased? Bentonites are a powerful tool in stratigraphic correlations, and utilizing strontium isotopes from such event horizons would be a highly precise and relatively cost-effective tool for various geological applications.

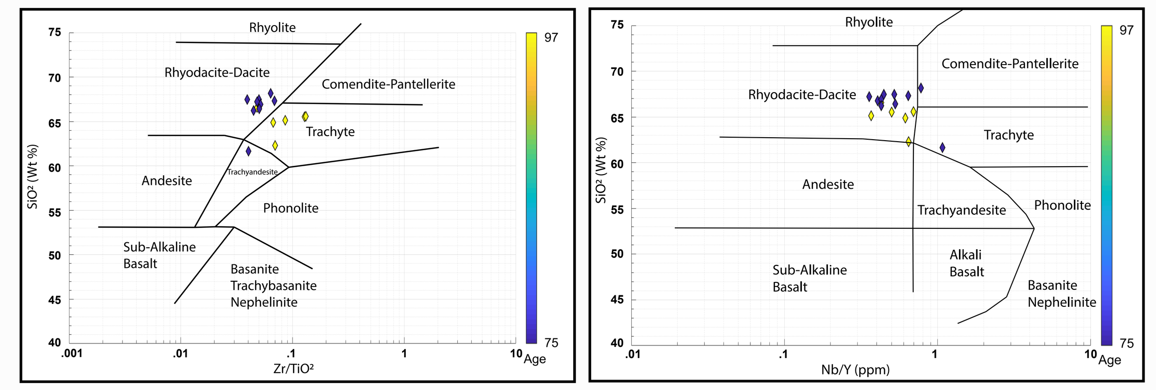
Results

Strontium Isotopes

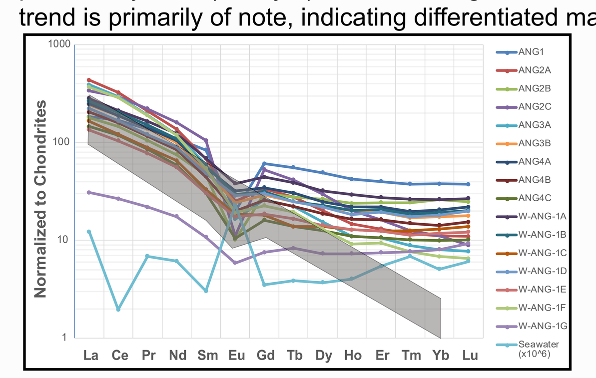


Stratigraphic columns plotted against $^{87}Sr/^{86}Sr$ values for bentonites. Sample localities Ang-1,2,3 are approximately 97 Ma (Cenomanian) and demonstrate a strontium trend higher than Cenomanian seawater (range highlighted in red). Interspersed fossil specimens were tested as well and approximately match the documented strontium range at that time. Sample localities Ang-4 and W-Ang-1 are approximately 75 Ma (Campanian) and have a large range of strontium values, possibly due to increased incorporation of exotic terrane into volcanic melt. The seawater strontium composition at this time was approximately .708, significantly higher than all bentonites tested.

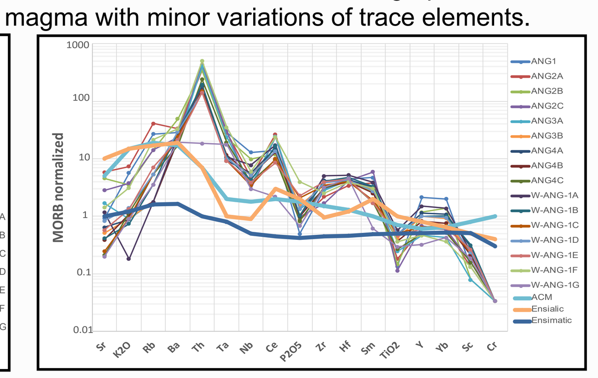
Geochemical Discrimination Diagrams



Various discrimination diagrams can be utilized to determine rock type within the calc-alkaline igneous sequence. Color is separated by age; yellow is Cenomanian (dated to 97 Ma), blue is Campanian (approximately 75 Ma). Plotting the bentonites on Winchester & Floyd (1977) plots of SiO2 vs. Zr/TiO2 and Nb/Y shows a clear felsic igneous affinity to the calc-alkaline series of dacite/rhyodacite, with possible syenitic (trachyte) source. Though there is some variation between the two graphs, the felsic trend is primarily of note, indicating differentiated magma with minor variations of trace elements.

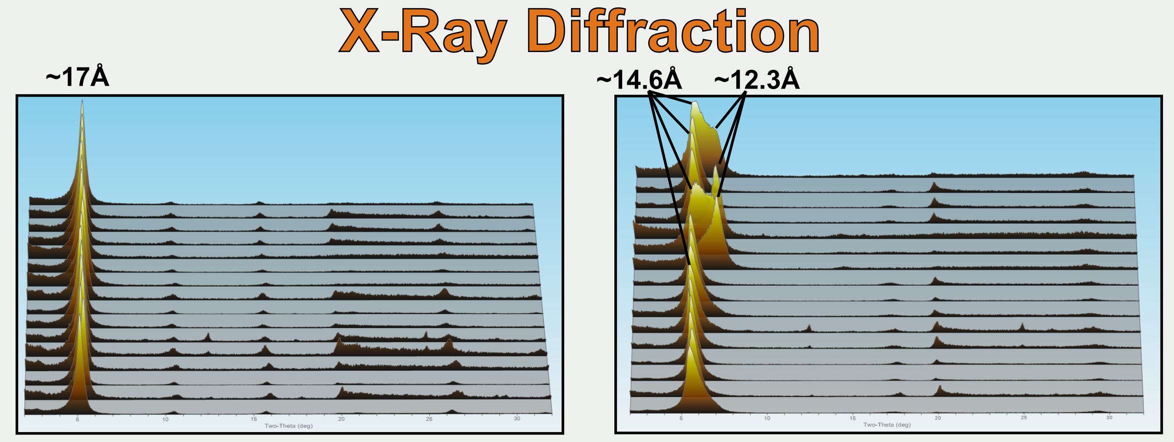


The bentonite rare earth element data, normalized to chondrites. The shaded region is the range of values for a region in the Idaho batholith, a probable source of most Cretaceous ash beds. The irregular light blue curve represents present day seawater values (x10^6). It is clear that the bentonite REE trends are not influenced by seawater, but very closely match the Idaho batholith values, including sharing a strong Europium anomaly. Bentonite trends higher concentrations of heavy REE (Gd - Lu), probably due to accumulation from incompatibility.



A series of trace elements, normalized to MORB values, for the series of bentonites. The weighted trends represent average data from active continental margins (ACM), ensialic convergent margins, and ensimatic convergent margins. The bentonite trend follows the ACM/Ensialic data more closely, though peaks and troughs vary throughout. This is most likely due to the chemical nature of the liquidus, concentrated with incompatible elements (such as Ba, Th, and Ta), REE elements (represented by Ce), and depleted in alkali/alkalines from feldspar accumulation in the pluton.

X-Ray Diffraction



Ethylene Glycolated **Air-Dried**

Diagenesis is a key concern when documenting geochemical trends of clay, so X-Ray Diffraction provided a means for determining if consideration should be taken for thermal maturation or enhanced burial. Unadulterated bentonites are primarily composed of smectite (montmorillonite), as can be seen in the diffractograms above. If smectite is subjected to thermal influences, enhanced dissolution from pore waters, or pressure from tectonically induced burial, it diagenetically alters to mixed-layer illite/smectite, as the interlayer Ca + Na is replaced by K. As can be seen in the glycol expanded material, every sample tested is pure montmorillonite, with the dominate 001 peak at 17Å. This indicates that the material has not undergone any diagenetic alteration and can be used for geochemical classifications. Also of note, the air-dried material shows two distinct peaks, one at ~14.6Å, and one at ~12.3Å. a different in air-dried d-spacing arises from variations in interlayer cations. In this case, the larger spacing is an abundance of Ca, while the smaller is primarily Na.

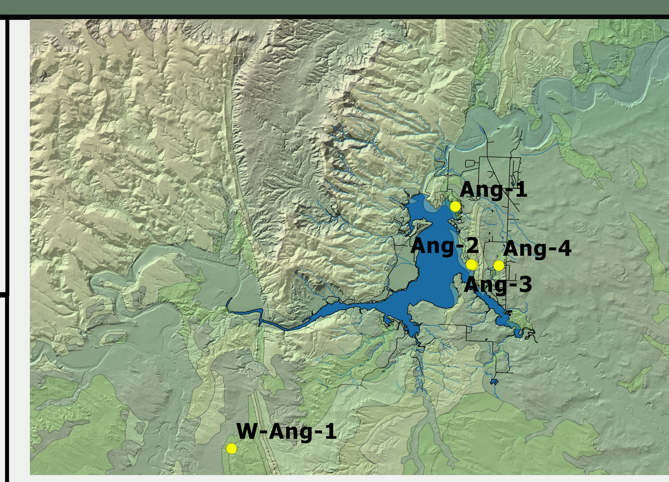
Methods

$^{87}_{37}Rb \rightarrow ^{87}_{36}Sr + ^{0}_{-1}\beta$

- Strontium isotopic signatures of alternating bentonite and fossil horizons have been compared, determining whether bentonite chemistry has been influenced by diagenetic processes or if the original magmatic signature is preserved through the devitrification process. (Analysis performed at the University of Illinois)

ICP-MS/OE

- Element abundance quantification was calculated for each bulk bentonite sample. Data is normalized to mid-ocean ridge basalt and compared to existing datasets for magmatic comparisons. (Analysis performed by ActLabs Ltd)

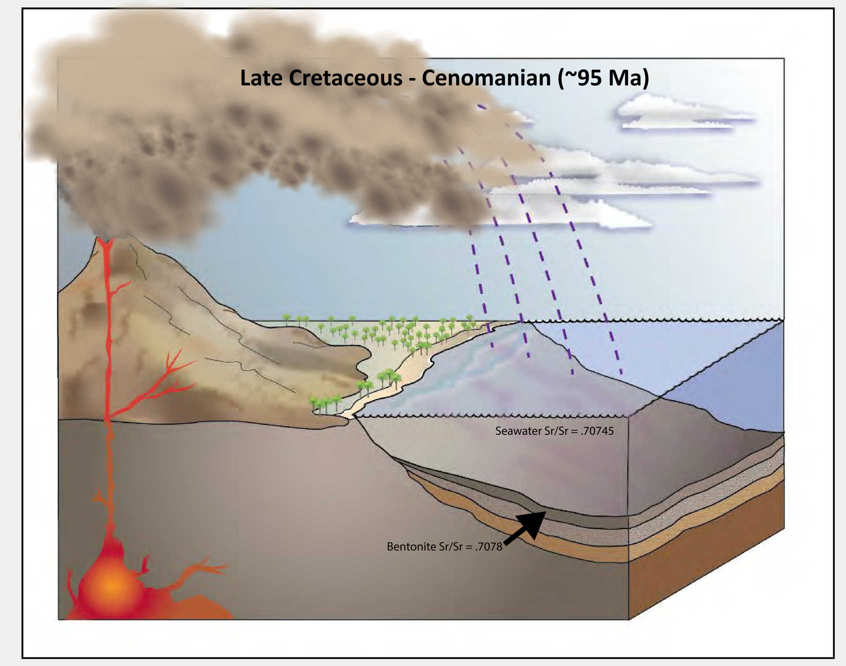


Bulk bentonite samples were collected from the southern rim of the Black Hills, near the Angostura Reservoir in South Dakota

X-Ray Diffraction

- Mineralogical data was quantified for bulk bentonite and isolated clay speciation. Variations in smectite structure were determined to provide evidence of post-burial diagenesis or thermal maturation. (Analysis performed at the University of Cincinnati)

Discussion

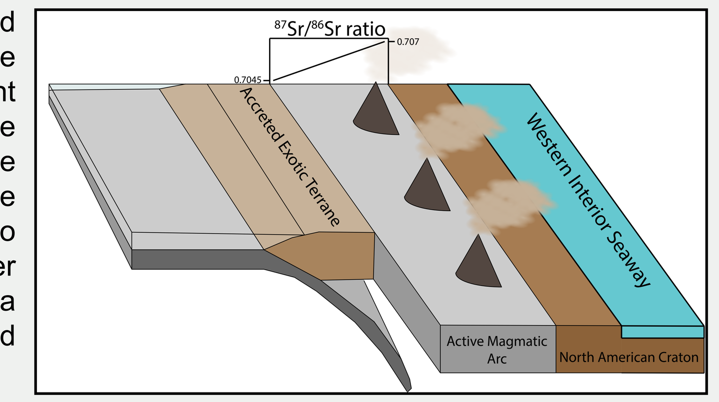


Model of bentonite formation. Volcanic ash is deposited in adjacent basins and rapidly devitrified into pure clay. Strontium ratios are distinctly different from seawater. Adapted from WSGS summary report, 2014.

Several discrete datasets have been compiled in an effort to understand the geochemical affinities of bentonites, and how to classify them with respect to their igneous and sedimentary origins. When volcanic ash is deposited into a marine sedimentary basin, it undergoes rapid devitrification, a chemical dissolution of volcanic glass into a stable clay phase. This diagenetic alteration of glass to clay could mean significant changes in the geochemical makeup of the preserved ash layer, but evidence appears to prove otherwise.

The initial hypothesis for bentonite $^{87}Sr/^{86}Sr$ speculated that the interlayer cations of the diagenetic smectite retain seawater strontium through cationic replacement of calcium with strontium. This is a common process in carbonate material, as strontium is a significant substitution element for calcium, due to the similar ionic radii and charge. By testing the $^{87}Sr/^{86}Sr$ ratio of alternating carbonate fossils and bentonites, this hypothesis was determined to be false. Cenomanian (~97 Ma) global strontium composition are approximately 0.7074, and Campanian (~75 Ma) values are approximately 0.7078. Throughout the stratigraphic sections, fossils maintained values very close to Cenomanian global strontium levels whereas bentonites had values significantly higher than this, ranging from 0.70762 to 0.70782. Campanian fossil samples have not been tested, but the bentonite strontium values range from 0.7064 to 0.7077, averaging lower than accepted Campanian seawater values (0.7078).

The bentonite strontium values uphold a process that occurred due to the onset of the Idaho batholith magmatism: as the subduction of the Farallon Plate incorporated ancient continental crust into the liquidus, the strontium ratio became more radiogenic from the felsic country rock. The well-documented Salmon River .706 isopleth runs through the batholith, marking the transition from ensimatic arc magma to the widespread initiation of an active continental margin over the distance of a few kilometers. The suture zone follows a W-E trend of 0.704 to 0.707, a range of which all tested bentonites fall. Campanian samples have a increased instance of lower radiogenic ratios, following the tectonic trend of exotic terrane incorporation into the melt, assimilating lower strontium ratio compositions on the North American cordillera.



Accretion of exotic terranes has created a distinct strontium range in the Idaho batholith; less radiogenic in the west, more radiogenic in the east. Adapted from Giorgis et al., 2005.

Conclusions & Future Directions

This study has provided evidence that whole rock bentonites may be used, under conditions of minimal diagenetic alteration, as a geochemical proxy for the magmatic source of which the ash originated. Magmatic trends can be tracked through time in regions where abundant bentonites are preserved, and may be used to reconstruct magmatic regimes in ancient subduction zones. Stratigraphic applications will be tested in future work.

- Strontium isotopic ratios ($^{87}Sr/^{86}Sr$) of altered tephra deposits (bentonites) is representative of the original magmatic source from which the ash was ejected.
- Cenomanian volcanism had a higher strontium ratio than seawater, a reflection of the magmatic nature of the isotopic composition.
- Geochemical discrimination plots indicate a distinct calc-alkaline influence on all bentonites tested. All samples fall primarily within dacite/rhyodacite geochemical boundaries with respect to Zr/TiO_2 and Nb/Y vs SiO_2.
- Rare earth element and trace element trends closely follow igneous counterparts, including data plotted from the Idaho batholith. Many incompatible elements are enriched in the liquidus, which is translated to the preserved ash.