

BORON ISOTOPE COMPOSITION OF SMECTITE IN SUEVITES AT THE RIES CRATER, GERMANY.

Nele Muttik^{1,2}, Kalle Kirsimäe¹, Horton E. Newsom² and Lynda B. Williams³, ¹Department of Geology, University of Tartu, Ravila 14a, 50411 Tartu, Estonia (nele.muttik@ut.ee, kalle.kirsimae@ut.ee), ² Department of Earth and Planetary science, Institute of Meteoritics, University of New Mexico, Albuquerque, NM 87131, USA (newsom@unm.edu), ³School of Earth and Space Exploration, Arizona State University, Tempe, AZ 85287-1404, USA (lynda.williams@asu.edu)

Introduction: The temperature and evolution of fluid compositions in hydrothermal systems is important for understanding the resulting mineral assemblage. Mixed layer phyllosilicates have been identified in CRISM data in many martian settings [1, 2]. Because mixed layer phyllosilicates are considered to represent higher temperatures than ambient, this could suggest an origin by an early high temperature phase of a hydrothermal system. However, the phyllosilicates in many terrestrial hydrothermal settings can be recrystallized by diagenesis and later fluids to reflect lower temperature conditions.

Hydrothermal alteration of impactites at the 24 km diameter Ries Crater in Germany has been proposed in the past [3, 4], however recent work by Muttik et al. [5, 6] find $\delta^{18}\text{O}$ and δD isotope evidence for relatively low temperature alteration. These studies show, that clay minerals are ubiquitous throughout the studied surficial and crater-fill suevite sequences. Smectite is the most abundant clay mineral in surficial suevites and smectite and mixed-layer illite-smectite were found to be dominant in crater-fill suevites. Using $\delta^{18}\text{O}$ and δD isotope analysis of secondary smectitic clay fractions, the estimated fluid temperatures suggest smectite precipitation in surficial suevites in equilibrium with meteoric fluids at temperatures 16 ± 5 °C in agreement with the long-term variation of modern precipitation in the area. The stable isotope composition of smectite in crater-fill suevite, however, suggests a trend of monotonously increasing temperatures from 43 to 112 °C, with increasing depth through the breccia sequence. This demonstrates a different origin of alteration and temperature distribution for the surficial and crater filling melt-bearing impact breccias in the Ries crater [6].

Here we present preliminary data that examines the $\delta^{11}\text{B}$ ratio of the secondary clay minerals separated from the alteration zones of the surficial and crater-fill suevites in the Ries crater to determine the temperature and fluid composition during initial phyllosilicate formation in suevite from the Nördlingen 1973 drill core and surficial deposits to see if they have been subject to retrograde diagenesis.

Material and methods: Studied material represents surficial suevites, collected from 4 outcrops within and around the Ries impact structure, and drill core material from the Nördlingen 1973 drill core at the suevite sequence 340 m to 525 m interval.

B-isotopes and B-content of the <2 μm clays were measured using a Cameca 3f secondary ion mass spectrometer (SIMS) following Hervig [7] at the Arizona State University. B-isotope values were corrected for instrumental mass fractionation (IMF) by comparison with SIMS analyses of a reference material, Silver Hill Illite (Clay Minerals Society Source Clay, IMt-1).

Results: The average $\delta^{11}\text{B}$ values measured in secondary clay minerals of the Ries surficial suevites, before the NH_4Cl exchange treatment, ranged from -26.3‰ to -22.7‰ and B concentrations ranged from ~8 to ~58 ppm. After the exchangeable B was removed, the B concentrations were about higher (≥ 3 ppm) and the average $\delta^{11}\text{B}$ value were -29.2‰ to -29.5‰, which can be due to the larger errors. Nevertheless, the average $\delta^{11}\text{B}$ values of smectite in surficial suevites before ($-24.55 \pm 1.8\%$) and after ($-29.35 \pm 0.2\%$) the NH_4Cl exchange process were identical within error ($\pm 1\sigma$ mean).

The average $\delta^{11}\text{B}$ values before the NH_4Cl exchange treatment for secondary clays in crater-fill suevites ranged from -8.9‰ to -1.2‰, except sample R09 from depth at 525m with average $\delta^{11}\text{B}$ value -21.9‰. B concentrations ranged from ~10 to ~37 ppm. The average $\delta^{11}\text{B}$ value in smectite from crater-fill suevite after the NH_4Cl exchange process stayed within the error and had values similar to the values measured before exchange treatment.

Discussion: There is a significant difference between the boron isotopic composition of the secondary clay minerals of the surficial and crater filling suevite samples. The surficial suevite samples show strongly depleted $\delta^{11}\text{B}$ composition ($-24.55 \pm 1.8\%$) compared to samples from the crater filling sequence that have in average $\delta^{11}\text{B}$ 4.07‰, except the deepest sample R09, which also indicates depleted boron isotopic composition (-21.8%).

Secondary smectite in altered suevites originates mostly from devitrification/recrystallisation of impact glass. Chaussidon and Koeberl [8] have shown that the boron isotopic composition of tektites and impact glasses have a rather limited range of $\delta^{11}\text{B}$, with an average of $2.7\% \pm 1.5\%$ and are similar to those of surface continental source rocks. Typically the smectite from altered volcanic ash or weathered continental sources is expected to have an initial B-isotopic composition of B around 0‰ [9, 10], whereas the B iso-

tope fractionation becomes important during boron coordination change by the illitization of smectite when B is fixed into lattice structure tetrahedral sites [11]. The coordination change from trigonal to tetrahedral bonds and large fractionation can occur also by adsorption of B onto mineral surfaces/interlayers [e.g., 12]. However, this adsorbed and/or interlayer B should have been removed by cation exchange meaning that depleted $\delta^{11}\text{B}$ in smectite in surficial samples was incorporated by replacing Si in tetrahedral positions during the growth of the authigenic smectite.

Interestingly, the δD and $\delta^{11}\text{B}$ composition of studied surficial smectites plots a line (Fig.1) parallel to Boron Meteoric Line (BML) [13], with nearly the same slope (2.8 vs 2.6 in BML). This would indicate that the smectite in surficial suevites precipitated in equilibrium with the boron composition in precipitation water that dominated in an open (surficial weathering) system. Moreover, if we adopt the empirical B isotope fractionation equation of Williams et al. [14] and use the fluid temperatures calculated for smectite precipitation by a single mineral geothermometry equation [15] then the $\delta^{11}\text{B}$ composition of the fluids would have been $7.5 \pm 1.6\text{‰}$. This value agrees with the composition of continental rains at distance from sea and/or high latitudes/altitudes [e.g., 13].

In contrast, the smectite separated from the crater-fill suevites shows more variable and more positive (not fractionated) boron isotopic composition, though the smectite δD and $\delta^{18}\text{O}$ geothermometry suggest paleo-temperatures above the onset of illitization ($>60\text{--}70^\circ\text{C}$). Indeed some random mixed layering ($<5\%$ of illitic layers) has been indicated by X-ray diffraction characteristics [6]. The lack of isotopic fractionation between interlayer and tetrahedrally bound B could be the result of B existing in similar coordination environments (i.e., both tetrahedral) in the secondary clay minerals in the crater-fill suevite and in the fluid from which it precipitated. The coordination of dissolved B is pH dependent, with predominately trigonal coordination at neutral to low pH and tetrahedral coordination at higher pH [10]. This suggests that the fluid from which secondary clay phases formed have been somewhat alkaline, thereby limiting isotopic fractionation by lack of coordination change. Limited B isotope fractionation between smectite and the fluid from which it precipitated could also occur if the alteration took place at high (i.e., close to magmatic) temperatures. However, previous studies indicate that this is unlikely and that smectite in crater fill suevites formed at relatively low temperatures ($<100\text{--}150^\circ\text{C}$) [6].

By applying the boron fractionation equation the alteration fluid in crater filling sequence would have had a $\delta^{11}\text{B}$ value $22.77 \pm 3.42\text{‰}$, except the deepest

sample that suggests isotopic composition of the fluid of about 1.9‰ . This enriched B composition of the water implies to input/mixing of positive $\delta^{11}\text{B}$ water (saline brines, seawater) or dissolution of boron rich mineral phases (borates) with positive isotopic composition. Sedimentological data indicate that the Ries crater was filled by a alkaline-evaporative (meso- to hyperhaline) saline shallow-water lake that probably existed for 0.3 to 2 million years after the impact. It is possible that the impact-induced hydrothermal system was fed by waters draining from lake, though the oxygen isotope composition fluids calculated from the $\delta^{18}\text{O}$ values of the authigenic smectites suggest meteoric origin of the hydrothermal fluids.

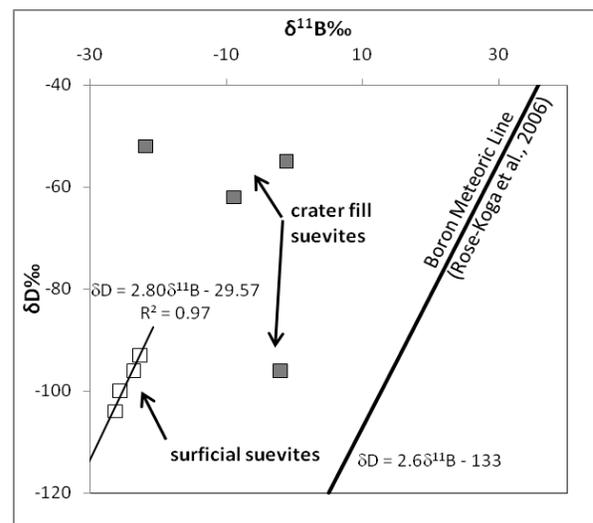


Fig. 1. B and D isotopic composition of smectites in Ries crater. δD data from Muttik et al. [6].

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