Intracrystalline boron isotope partitioning in illite-smectite: Testing the geothermometer

LYNDA B. WILLIAMS,* AMANDA TURNER, AND RICHARD L. HERVIG

School of Earth and Space Exploration, Arizona State University, Tempe, Arizona 85287-1404 U.S.A.

ABSTRACT

Intracrystalline B-isotope differences of ~40‰, are observed between the interlayer and tetrahedral crystallographic sites of interstratified illite-smectite (I-S). We tested the hypothesis that partitioning of B-isotopes between these sites could provide a low-temperature, single-mineral geothermometer. Samples studied include a metabentonite transected by a dike in the Cretaceous Pierre Shale (200–500 °C), buried mudstones from the Eocene Wilcox Formation (60–125 °C), and I-S products from hydrothermal experiments (300–350 °C). Different reaction kinetics are represented by these different sample sets, therefore results test the equilibrium partitioning of B in the interlayer vs. tetrahedral sites.

In all samples, interlayer $\delta^{11}B$ values are isotopically heavier than the tetrahedral $\delta^{11}B$. Because $^{11}B$ prefers trigonal coordination, we infer that B(OH)$_3$ dominates the interlayer sites. Within each sample set, the intracrystalline differences are greatest (20–40‰) in the most expanded I-S (i.e., smectite-rich), and approach 0 as illitization increases. There is good correlation ($R^2 = 0.84$) between the interlayer $\delta^{11}B$ (calculated by mass balance) and water $\delta^{11}B$ indicated by the established maximum temperature of each sample. These results suggest that the interlayer sites of I-S preserve the B isotopic composition of water at the temperature that produced the authigenic illite. Direct measurements of interlayer $\delta^{11}B$ equilibrated with water of known $\delta^{11}B$ are needed to refine the relationship with temperature, but the existing data indicate the following temperature dependent relationship: $T$ (°C) = ($\delta^{11}B_{tetrahedral} - \delta^{11}B_{interlayer} + 30)/0.05$.

Keywords: Boron isotopes, illite-smectite, isotope equilibrium, intracrystalline geothermometer

INTRODUCTION

Boron has two isotopes, $^{11}B$ (~80% abundance) and $^{10}B$ (~20% abundance) that primarily bond to oxygen in minerals and water but can also bond to C, N, S, and P in organic compounds (Flores-Parra and Contreras 2000; Dembitsky et al. 2002). The B-coordination is variable, with $^{11}B$ showing a preference for trigonal coordination, whereas $^{10}B$ is concentrated in tetrahedral sites (e.g., Palmer and Swihart 1996). Partitioning of boron between compounds with trigonal versus tetrahedral coordination produces large isotope fractionations at diagenetic temperatures (Sanyal et al. 2000; Hervig et al. 2002; Sanchez-Valle et al. 2005). For simplicity this text refers to these species as “trigonal B” and “tetrahedral B” indicating their coordination.

In water, the predominant B species are boric acid [B(OH)$_3$] and borate anion [B(OH)$_4$], with relative abundances determined primarily by the pH of the fluid (Dickson 1990; Hemming and Hanson 1992). Boric acid dominates at pH values below the pKa (9.2 for pure water; 8.6 for saline water; Hershey et al. 1986). As temperature increases, the pKa shifts to higher values, thus a majority of natural waters associated with organic-rich diagenetic sediments are dominated by trigonal boron.

Seawater has a pH near the equivalence point (at 25 °C) allowing the use of boron isotopes for investigating paleo-pH variations ratios recorded by authigenic carbonates (Spivack et al. 1993; Sanyal et al. 1995; Palmer et al. 1998). Boron can therefore be useful in two different ways. If the pH is fixed, B-isotopes can be used to determine temperature and where the temperature is fixed (e.g., seawater), it may be a useful pH monitor (Hemming and Hanson 1992; Spivack et al. 1993).

For the common case of equilibrium between trigonal coordination [B(OH)$_3$] in solution (acidic pore fluid) and tetrahedral coordination in silicate minerals (or melts), B isotope fractionation can be approximated by a linear function of reciprocal absolute temperature (Williams et al. 2001a; Hervig et al. 2002). As more experimental data have become available (Wunder et al. 2005; Klotchco et al. 2006; Tossel 2006), the slope of the regression curve has changed only minimally (Fig. 1) producing the following empirical equation (for water with low ionic strength):  

$$1000 \ln \alpha_{tetrahedral-water} = -10350/T (K) + 3.28 \tag{1}$$

where $\alpha$ is ($^{11}B/^{10}B$)$_{tetrahedral}/(^{11}B/^{10}B)_{water}$. Where there is no coordination change between water and minerals, the isotope fractionation is minimal (Schwarz et al. 1969; Palmer et al. 1987; Hervig et al. 2002).

Models for the incorporation of B into clay minerals first focused on B-adsorption because large quantities (>100 ppm) of B are commonly adsorbed on marine clays (Spivack et al. 1987; Palmer et al. 1987; Leeman and Sisson 1996). Because the

* E-mail: Lynda.Williams@asu.edu