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THE CALCULATION OF WATER-ROCK RATIOS USING TRACE ELEMENT (Li, B) STABLE ISOTOPES

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ABSTRACT

The amount of aqueous fluids circulating into the oceanic crust can be estimated using mass balance equations based on stable isotope exchange between rock and water. Unlike oxygen and strontium, isotopic exchange of trace elements (such as B or Li) between fluids and rocks, operates along with a chemical evolution of the rocks (e.g. a large enrichment of B or Li) that must be integrated into any model of water-rock interaction. We propose a general dimensionless mass balance equation for single-pass open systems that describes the equilibrium elemental distribution and the isotopic composition of reacting rocks as a function of the amount of circulating water. Water-rock ratios calculated from B compositions of hydrothermally-altered basalts range from 8 to 100. They are lower than those previously published (most W/R > 300) but comparable to those inferred from Sr isotope ratios measured in the same samples (3 < W/R < 30). Similar low water-rock ratios from 2 to 20 are calculated from Li isotope compositions of altered basalts and serpentinized peridotites.

Keywords: water-rock ratio, oceanic crust, stable isotope, boron, lithium.

1. INTRODUCTION

The interactions between fluids and rocks in geological settings are commonly quantified using the principle of stable isotope exchange at equilibrium for calculating water-rock ratios (W/R). Mass balance equations have been proposed to calculate water-rock ratios in closed and open systems. The main applications have involved the $^{18}O/^{16}O$ (Taylor, 1977; Gregory and Taylor, 1981), D/H (Taylor, 1978; Sakai et al., 1991) and $^{87}Sr/^{86}Sr$ ratios measured in altered and fresh rocks (Albarède et al., 1981; 1995). Such techniques provide minimal values of water-rock ratios depending on both isotope partitioning and kinetics of exchange between rock and water. More recently, attempts have been made to extend the modeling of water-rock interactions between the oceanic crust and seawater by using the B and Li stable isotope compositions of altered basalts and peridotites (Spivack and Edmond, 1987; Chan et al., 1993, 1994; Smith et al, 1995). The use of stable isotope ratios of trace elements needs to take into account the variation of the elemental ratio between fresh and altered rocks as a function of the amount of water reacting with rocks. This parameter may be neglected when modeling water-rock interactions with oxygen and strontium since their concentrations in rocks and reacting water remain quite constant as reactions progress. However, high variations are reported for boron (~ 0.5 ppm in fresh MORB, and up to 100 ppm for altered oceanic basalts; Smith et al., 1995) and for lithium (~ 4 ppm in fresh MORB and up to 75 ppm for low temperature altered basalts; Chan et al., 1992) with increasing rates of alteration of the oceanic crust. Moreover, mass balance equations proposed for O, Sr or H isotopic ratios are formulated with the relevant approximation that the minor isotope is present in trace abundance (see Albarède, 1995; Criss, 1999). This approximation is not necessary valid when considering elements such as Li and B (the relative isotopic abundance is about 0.075 for ^{6}Li and 0.2 for ^{10}B). Therefore, we propose to formulate a mass balance equation for open systems that could be applied to trace element stable isotope ratios.

2. FORMULATION OF THE MASS-BALANCE EQUATION

The isotopic ratio k_2/k_1 of the altered rocks is calculated considering a dynamic single-pass open system where infinitesimal amounts of water dW, of fixed elemental concentration C_w^i and isotopic ratio R_w^i, react completely with the rock, then leaves the system. The mass fraction of water (f_w) and rock (f_r) in the bulk system are assumed to be constant. Unlike Taylor (1977; 1978) or Albarède (1995), we consider that the bulk concentration of the element k may vary during the interaction process.

We assume that the atomic weight of the element k is identical in both rock and water. Except for unrealistic differences in isotopic ratios, this approximation is generally valid. For example, if we consider boron for which the isotopic abundance of the minor isotope (^{10}B) is nearly 20%, the difference in the atomic weight is less than 0.2% for δ^{11}B values of –40 and +60‰. The evolution of the ratio of k_2 over k_1 is thus described by the following first-order differential equation:

$$d\left[M_T\left(f_w \cdot C_w^{k_1} \cdot R_w + f_r \cdot C_r^{k_1} \cdot R_r\right)\right] = \left(C_w^{k_1}\right)^i \cdot R_w^i \cdot dW - C_w^{k_1} \cdot R_W \cdot dW, \qquad (1)$$

where $C_w^{k_1}$ and $C_r^{k_1}$ are the concentrations of isotope k_1, k_2, R_w and R_r the isotopic ratio k_2/k_1, in water and rock, respectively. The i exponent notes initial values, and M_T is the total mass of the system with $f_r + f_w = 1$.

At equilibrium, K^{k_1}, the partition coefficient of isotope k_1 between rock and water is expressed as $C_r^{k_1}/C_w^{k_1}$ and the isotopic fractionation factor is defined as $\alpha = R_r/R_w$. Substituting $C_w^{k_1}$ and R_w into equation (1) gives:

$$f_w \cdot \frac{1}{K^{k_1} \cdot \alpha} \frac{d\left(C_r^{k_1} \cdot R_r\right)}{dQ} + (1 - f_w) \cdot \frac{d\left(C_r^{k_1} \cdot R_r\right)}{dQ} = \left(C_w^{k_1}\right)^i \cdot R_w^i - \frac{C_r^{k_i} \cdot R_r}{K^{k_1 \cdot \alpha}}, \qquad (2)$$

where $dQ = dW / M_T$ is the incremental water-rock ratio in mass unit as defined in Albarède (1). Rearranging the terms leads to the following equation:

$$\frac{d\left(C_r^{k_1} \cdot R_r\right)}{C_r^{k_1} \cdot R_r - K^{k_1} \cdot \alpha \cdot \left(C_w^{k_1}\right)^i \cdot R_w^i} = -\frac{dQ}{f_w(1 - K^{k_1} \cdot \alpha) + K^{k_1} \cdot \alpha} \qquad (3)$$

When Q is expressed as a function of the mass unit water-rock ratio W/R

$$Q = \frac{W}{M_T} = \frac{W}{R}(1 - f_w)$$

the equation (3) has the solution:

$$C_r^{k_1} \cdot R_r = K^{k_1} \cdot \alpha \cdot \left(C_w^{k_1}\right)^i \cdot R_w^i + \left[\left(C_r^{k_1}\right)^i \cdot R_r^i - K^{k_i} \cdot \alpha \cdot \left(C_w^{k_i}\right)^i \cdot R_w^i\right] \cdot \exp\left(-\frac{W/R \cdot (1 - f_w)}{f_w(1 - K^{k_1} \cdot \alpha) + K^{k_1} \cdot \alpha}\right. \qquad (4)$$

Using the same notations and approximation as above, the concentration $C_r^{k_1}$ in altered rocks is calculated using a mass balance equation that describes the equilibrium distribution of a single isotope between fluids and rocks in an open-system (1):

$$d\left[M_T\left(f_w \cdot C_w^{k_1} + f_r \cdot C_r^{k_1}\right)\right] = \left(C_w^{k_1}\right)^i \cdot dW - C_w^{k_1} \cdot dW \tag{5}$$

which has the solution

$$C_r^{k_1} = K^{k_1} \cdot \left(C_w^{k_1}\right)^i + [\left(C_r^{k_1}\right)^i - K^{k_1} \cdot \left(C_w^{k_1}\right)^i] \exp\left(-\frac{\frac{W}{R} \cdot (1 - f_w)}{f_w(1 - K^{k_1}) + K^{k_1}}\right) \tag{6}$$

Then, substituting $C_r^{k_1}$ in equation (4), a general formula is obtained that links the isotopic composition of an altered rock to the water-rock ratio in mass unit. Considering that no assumption on the isotopic abundance of the minor isotope nor on elemental concentrations in rock and water is made, these mass balance equations (4, 6) describing isotopic exchange in open system constitute an adequate formulation to calculate water-rock ratios from trace element stable isotopes.

Assuming that the element k is mainly constituted by the two isotopes k_1 and k_2, the partition coefficient of isotope k_1 between rock and water, K^{k_1}, can be expressed as a function of the bulk distribution coefficient, D:

$$K^{k_1} = D \cdot \frac{1 + R_w}{1 + R_r} = \frac{D}{\alpha} \cdot \frac{\alpha + R_r}{1 + R_r} \tag{7}$$

As α is generally close to 1, K^{k_1} can be safely approximated to D except if huge isotopic fractionation occurs between rocks and water. For example, considering again the case of boron isotopes, a α value of 1.1 and an unrealistic high $^{10}B/^{11}B$ of 0.3 result in a difference between K^{k_1} and D of about 2 %, which is significantly lower that the uncertainties on the experimental determination of the distribution coefficient of boron between rocks and water.

If the rock porosity can be neglected (i.e. $f_w = 0$) and assuming that the concentration of the element k is proportional to that of the major isotope k_1, equation (6) reduces to the following mass balance relation (e.g. Spivack and Edmond, 1987):

$$C_r = D \cdot (C_r^i - D \cdot C_w^i) \exp\left(-\frac{W/R}{D}\right) \tag{8}$$

where D is the distribution coefficient of the element between rock and water, and the isotopic ratio of the altered rock becomes:

$$R_r = \frac{1}{C_r}\left[D \cdot \alpha \cdot C_w^i \cdot R_w^i + (C_r^i \cdot R_r^i - D \cdot \alpha \cdot C_w^i \cdot R_w^i) \times \exp\left(-\frac{W/R}{D \cdot \alpha}\right)\right] \tag{9}$$

If equation (9) is applied to an isotopic system in which only one isotope is widely exchanged such as $^{18}O/^{16}O$ or $^{87}Sr/^{86}Sr$ when Sr abundance does not vary during water-rock interactions, this formulation reduces to the previously published material balance equations using the δ notation (Gregory and Taylor, 1981; Albarède, 1981; 1995) or the isotopic ratio notation with W/R in atomic units (Criss, 1999).

3. WATER-ROCK RATIOS CALCULATED FROM B AND Li

Because of its high mobility to aqueous fluids, boron isotopes have been widely used to estimate fluid transfers between solid and fluid Earth envelopes (e.g. Palmer and Swihart, 1996), in particular during the alteration of the oceanic crust (Spivack and Edmond, 1987; Smith et al., 1995). Spivack and Edmond (1987) designed a model of boron isotopic exchange between the oceanic crust and seawater in which the isotopic evolution of hydrothermal fluids follows a Rayleigh-type distillation. The mainstay of this model is a negative exponential dependence of the $\delta^{11}B$ of altered basalts on the water-rock ratio, which leads to compute unexpected high $\delta^{11}B$ (higher than 100‰) for water-rock ratios lower than 20. Consequently, measured $\delta^{11}B$ values of oceanic basalts, which do not exceed 25‰, are interpreted as resulting from alteration by very large amounts of seawater-derived fluids ($W/R > 300$). Such water-rock ratios are not in agreement with those deduced from Sr isotope measurements of low-temperature altered basalts. For example, calculating water-rock ratios from $^{87}Sr/^{86}Sr$ of altered oceanic rocks of ODP 417/418 site (Staudigel et al., 1995) leads to values lower than 30 even though a mean water-rock ratio of about 400 is estimated in the same location, based on B isotopes (Smith et al., 1995). Moreover, off-axis low temperature alteration is characterized by water-rock ratio lower than about 50 deduced from Sr isotope composition of altered basalts (Elderfield et al., 1999).

Calculations of W/R using B are illustrated in Figure 1 that shows $\delta^{11}B$ variations of altered rocks versus W/R using equations (4, 6), assuming that K^{k_1} is equal to D. The distribution coefficient D between rock and water depends on the temperature of alteration, which can be itself estimated by using the relationship between the $\delta^{18}O$ of smectite in equilibrium with seawater and B concentration (Spivack and Edmond, 1987). The considered D range of values corresponds to alteration temperatures from 1°C to 100°C. The computed curves reveal that $\delta^{11}B$ values of

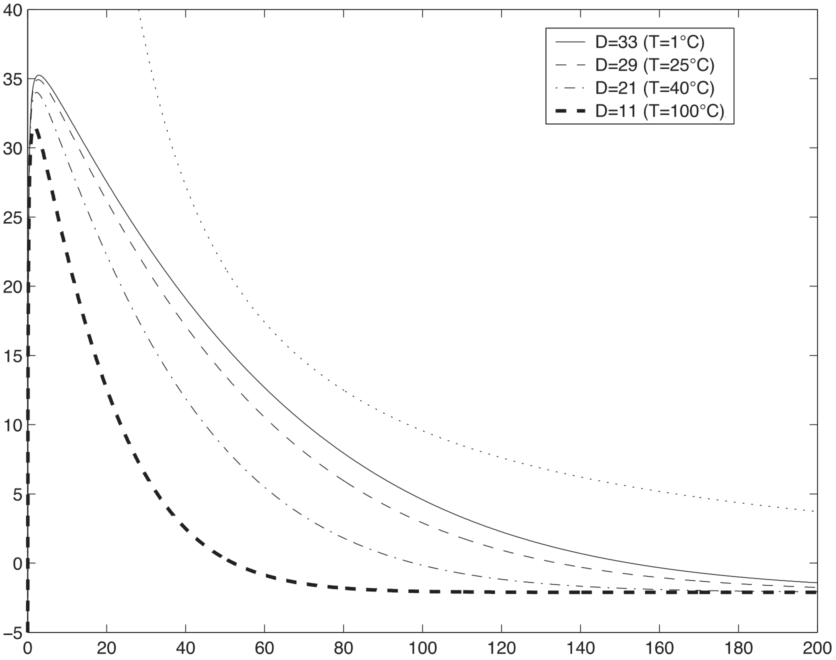

Figure 1: Calculated $\delta^{11}B$ of altered oceanic rocks as a function of the water-rock ratio ($\alpha = 0.960$ and D = 11 to 33). Since only negligible differences are obtained for porosity between 0 and 40%, f_w is approximated to 0. The dotted curve corresponds to the $\delta^{11}B$ calculated with the equation given by Spivack and Edmond (1987). The grey area delimits the field of boron isotope compositions prevailing into the oceanic crust (Smith et al., 1995).

altered rocks are strongly dependent on *W/R* up to values of 100. Nevertheless, calculated water-rock ratios highly depend on both the choice of the distribution coefficient D and fractionation factor α, which remain to be experimentally determined for chlorite, amphibole and serpentine. These minerals are indeed the most common produced during the hydrothermal alteration of the oceanic crust. The equation obtained by combining (4) and (6) has no analytical solution but water-rock ratios can be calculated using either a numerical or a graphical (Fig.1) resolution method. For example, considering the mean $\delta^{11}B$ of 0.8‰ obtained by combining sample measurements from DSDP Holes 417 and 418 (Smith et al., 1995), *W/R* are calculated between 45 (for D = 11) and 135 (for D = 33). These values are significantly lower than those previously proposed (*W/R* about 400), and are in agreement with the range (20–160) estimated from heat flux measurements (Elderfield and Schultz, 1996), even though such a comparison remains difficult because of the highly uncertainty associated with off-axis hydrothermal heat and water fluxes.

Since D values are still poorly known, calculating water-rock ratios for individual samples with varying B concentrations require to use equation (4) in which $C_r^{k_1}$ is approximated to the ^{11}B content of the altered sample. In this case, *W/R* in mass unit can be expressed as:

$$W\Big/R = -\left(\alpha \cdot K^{k_1} + \frac{f_w}{1-f_w}\right)\ln\frac{\left(C_w^{k_1}\right)^i \cdot R_w^i \cdot \alpha \cdot K^{k_1} - R_r \cdot C_r^{k_1}}{\left(C_w^{k_1}\right)^i \cdot R_w^i \cdot \alpha \cdot K^{k_1} - R_r^i \cdot \left(C_r^{k_1}\right)^i} \qquad (10)$$

Water-rock ratios in open system are calculated using equation (10) in which f_w is assumed to be negligible (Table 1) for a set of hydrothermally-altered basalts for which both Sr and B elemental and isotopic compositions are available (Smith et al.,1995; Staudigel et al., 1995). Similar ranges of *W/R* values are obtained for B and Sr isotopes, that are 1.5–50 and 3–31, respectively.

Table 1: Calculated W/R ratios from equation 4 ($(W/R)_B$), equation 9 ($(W/R)_{Sr}$) and equation 8 ($(W/R)_B^{\alpha}$), using abundance and isotope ratios of B (Smith et al., 1995) and Sr (Staudigel et al., 1995) of samples from DSDP/ODP sites 417/418.

Sample	B (ppm)	δ^{11}B (‰)	$(W/R)_B$	$(W/R)_B^{\alpha}$	Sr (ppm)	^{87}Sr/^{86}Sr	$(W/R)_{Sr}$
417A-24	104	1.6	48.0	46.1	192	0.707212	30.4
417A-32	52	0.6	15.1	14.6	202	0.705879	18.5
417A-44/46	69	2.4	22.4	21.7	200	0.705793	17.7
417D-22/27	26	–1.7	6.6	6.3	165	0.704697	8.7
417D-39	40	3.1	10.8	10.5	143	0.705058	9.0
417D59/60	25	–2.5	6.3	6.1	158	0.704689	8.3
418A-15	30	2.3	7.7	7.5	153	0.704359	6.6
418A-40	23	3.8	5.7	5.5	221	0.705554	17.6
418A-73/75	11.8	1.2	2.7	2.6	140	0.703987	4.7
418A-86	7.2	0.4	1.6	1.5	132	0.703744	3.7

A simple analytical calculation of the water-rock ratio can also be made by using B concentrations alone, according to equation (8). Theoretically, such a method should provide minimum estimates of *W/R* since this equation only describes B elemental exchange between rocks and water and ignores any isotopic exchange. Results given in Table 1 reveal surprisingly that the differences between the two methods are negligible. Consequently, it appears that the boron content of rocks could provide a good quantification of the extent of fluid exchange with rocks, as also suggested by the correlation of boron concentration with water content (Donnelly et al., 1979), and also with K contents or $\delta^{18}O$ (Smith et al., 1995).

The geochemistry of lithium has been recently applied to the study of oceanic hydrothermal activity, and water-rock ratios can be similarly calculated using equations (4, 6). The concentration of lithium is close to 5 ppm in MORB, reaches 40 ppm in low-temperature altered basalts (Chan et al., 1992) and is of 0.19 ppm in seawater. The δ^6Li values of altered basalts commonly lie between –14 and –6 ‰, lower than the mean value of –4 ‰ of fresh MOR basalts (Chan et al., 1992; 1993; You and Chan, 1996). The isotopic fractionation between basalts and seawater has been estimated to 1.019 for an alteration temperature of 2°C and 1.009 at 160°C (Chan and Edmond, 1988; Chan et al., 1992; 1993). As no distribution coefficient between minerals and water was determined so far, we used an empirical bulk distribution coefficient D between 50 and 500. These values represent fractionations leading to altered rocks with Li concentrations between 10 and 100 ppm at equilibrium with unevolved seawater (Fig. 2). The Li content of altered rocks cannot constrain the value of the water-rock ratio because of the lack of knowledge of the distribution coefficient. For example, a Li concentration of 15 ppm in an altered basalt can be explained by a water-rock ratio of 50 if $D \sim 500$, and nearly 150 when $D \sim 100$.

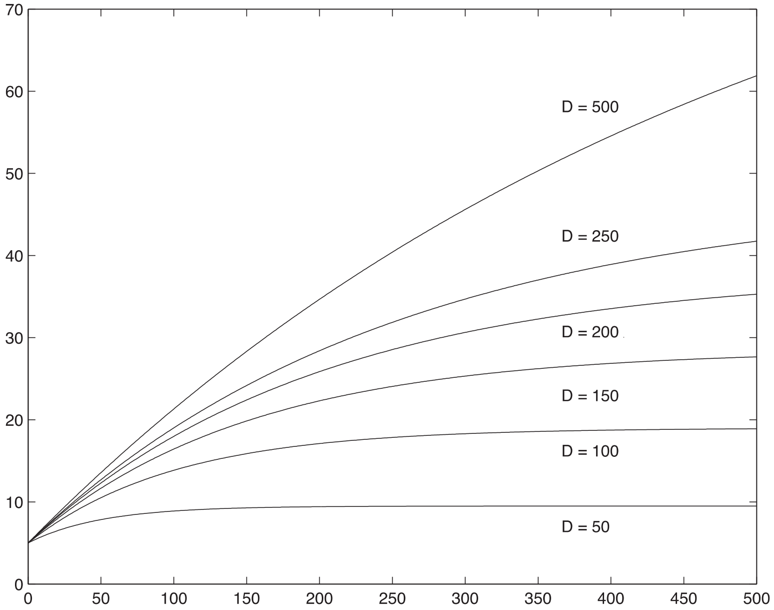

Figure 2: Calculated lithium concentrations of altered basalts as a function of water-rock ratios, with $D = 50$ to 500. Fresh MORB Li content is 5 ppm and ranges from 5 to 40 ppm in altered oceanic basalts (Chan et al., 1992).

The calculated curves of isotopic evolution as a function of W/R (Fig. 3) show that the δ^6Li of exchanging rocks with seawater can provide water-rock ratios with an accurate resolution when remaining lower than 100. If the distribution coefficient is not lower than 100 and if the water-rock ratio does not exceed 40, the differences between the curves are small and a precise knowledge of *D* is therefore not crucial. Using a graphical resolution of the system of equations (4, 6), the δ^6Li (–14 to –6‰) of the altered basalts correspond to water-rock ratios ranging from 1 to 25 (given *D* higher than 100). Water-rock ratios calculated from Li and Sr analyses of serpentinized peridotites (Decitre et al., 2002) display similar ranges of values, 2 to 40 and 1 to 18, respectively.

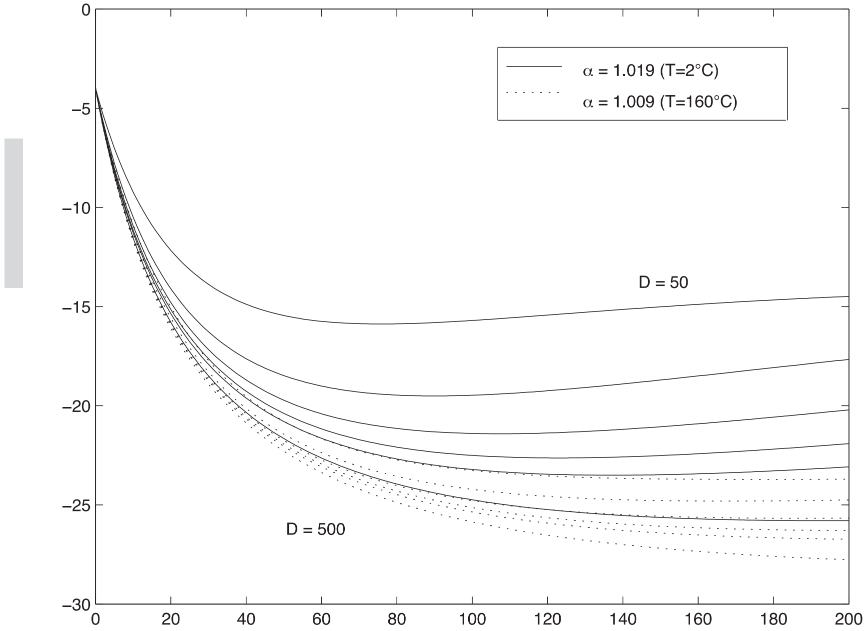

Figure 3: Calculated δ^6Li of altered basalts as a function of water-rock ratios, with *D* = 50 to 500 and α = 1.009 to 1.019. Gray area corresponds to the range of δ^6Li measured in low temperature altered oceanic basalts and peridotites (see text for references).

4. CONCLUSION

The quantification of fluid-rock interactions with the stable isotopes of trace elements requires the use of a general mass balance equation modeling both chemical and isotopic exchange at equilibrium. Calculated water-rock ratios using boron or lithium elemental and isotopic compositions of oceanic rocks are consistent with those deduced from Sr isotope ratios. When considering any element whose concentration does not widely change with the water-rock ratio (e.g. oxygen, strontium), our general equation is reduced to the previously published material balance equations (Taylor, 1977; Gregory and Taylor, 1981; Albarède, 1981; 1995; Criss, 1999).

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