



Unbiased isotope equilibrium factors from partial isotope exchange experiments in 3-exchange site systems

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Abstract

Two methods are available in order to evaluate the equilibrium isotope fractionation factors between exchange sites or phases from partial isotope exchange experiments. The first one developed by Northrop and Clayton (1966) is designed for isotope exchanges between two exchange sites (hereafter, the N&C method), the second one from Zheng et al. (1994) is a refinement of the first one to account for a third isotope exchanging site (hereafter, the Z method).

In this paper, we use a simple model of isotope kinetic exchange for a 3-exchange site system (such as hydroxysilicates where oxygen occurs as OH and non-OH groups like in muscovite, chlorite, serpentine, or water or calcite) to explore the behavior of the N&C and Z methods. We show that these two methods lead to significant biases that cannot be detected with the usual graphical tests proposed by the authors.

Our model shows that biases originate because isotopes are fractionated between all these exchanging sites. Actually, we point out that the variable mobility (or exchangeability) of isotopes in and between the exchange sites only controls the amplitude of the bias, but is not essential to the production of this bias as previously suggested. Setting a priori two of the three exchange sites at isotopic equilibrium remove the bias and thus is required for future partial exchange experiments to produce accurate and unbiased extrapolated equilibrium fractionation factors.

Our modeling applied to published partial oxygen isotope exchange experiments for 3-exchange site systems (the muscovite–calcite (Chacko et al., 1996), the chlorite–water (Cole and Ripley, 1998) and the serpentine–water (Saccocia et al., 2009)) shows that the extrapolated equilibrium fractionation factors (reported as $1000\ln(\alpha)$) using either the N&C or the Z methods lead to bias that may reach several δ per mil in a few cases. These problematic cases, may be because experiments were conducted at low temperature and did not reach high exchange percentages (<50%) such as the chlorite–water and the serpentine–water experiments.

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1. INTRODUCTION

Oxygen isotope geothermometry is one of the most important parts of stable isotope geochemistry. To use it demands first a precise knowledge of the temperature

dependence of isotope fractionation factors between phases (calibration) and secondly proofs that isotope equilibrium occurred and is preserved in geological systems (rocks). Both are important issues in the use of oxygen isotope geothermometry.

Temperature dependence of fractionation factors have been studied using both theoretical and experimental approaches:

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- (i) Theoretical calculations (Urey, 1947; Bigeleisen and Mayer, 1947; Bottinga and Javoy 1973, 1975; Javoy, 1977; Criss, 1991) have explained the decrease of the fractionation amplitude with $1/T^2$ at high temperatures (≈ 500 – 1000 °C) for the common mineral pairs. This was investigated further by Kieffer (1982), Clayton and Kieffer (1991) and Criss (1991), who computed the partition function ratios for isotopes in compounds and derived temperature calibrations of isotope fractionation factors at thermodynamic equilibrium. The precision of these computed calibrations is generally not good enough to be applied in all cases because the frequency shifts of the vibrational modes resulting from isotope substitutions are not precisely determined. Using the empirical additivity principle of Schütze (1980), Zheng (1993) calculated a set of calibrations, which is in agreement with that derived from the partition function computations for anhydrous silicate minerals. In additions, recent efforts based on ab initio calculation have led to very significant improvements of these calculations (Meheut et al., 2007).
- (ii) Isotope exchange experiments have also been run to provide strong constraints on equilibrium fractionation factors. But due to slowness of atom exchanges between minerals and other phases at moderate and low temperatures (<700 °C), isotopic equilibrium is rarely reached and models of isotope exchange must be used to extrapolate equilibrium factors from partial isotope exchange experiments. The most popular extrapolation method is that of Northrop and Clayton (1966) corrected later by Criss (1999). For a set of companion experiments run in the same conditions, displaying the change of the isotopic contrast ($\Delta_f - \Delta_i$) vs. the initial isotopic contrast, Δ_i , yields a line whose value of the intercept is the equilibrium fractionation factor, and whose slope is related to the inverse of the exchange fraction. This relationship derives from the assumption that isotope exchanges between the exchanging sites follow first-order kinetic law. Although this extrapolation method was designed for 2-exchange site systems (the dolomite-water system), it is widely used for 3-exchange site systems for which it has not been designed (O'Neil and Taylor, 1969; Sakai and Tsutsumi, 1978; Fortier et al., 1994; Chacko et al. 1996; Cole and Ripley, 1998; Fayek and Kyser, 2000; Saccocia et al. 2009; ...). Generally, this misuse is not considered as a problem for partial exchange experiments which reach large degrees of isotope exchange ($>\approx 75\%$) although it has raised some concerns (O'Neil and Taylor, 1969; Sheppard, 1980, 2004; Sheppard and Gilg, 1996; Cole and Ripley, 1998). Recognizing this problem, Zheng et al. (1994), have proposed a refinement of the N&C method to make it suitable for 3-exchange site systems. However, this approach demands a priori knowledge of the equilibrium fractionation factor between two of the three exchange sites. Such knowledge is generally not available except in very particular cases (e.g. when

the two of the three exchanging sites are water and calcite for example as in Zheng et al. 1994).

The aim of this paper is to explore these extrapolation methods and to explain when and why in some cases they failed to yield correct extrapolated equilibrium fractionation factors. We will confirm that using 2-exchange site methods for 3-exchange site systems may lead to erroneous extrapolated equilibrium values even in the case of large isotopic exchange fractions among the three exchange sites. We will explain why this problem exists and show how it might be corrected in order to get true, unbiased, equilibrium fractionation factors. This will help for the future design of reliable isotope exchange experiments.

2. MATHEMATICAL MODEL OF ISOTOPIC EXCHANGE IN A 3-EXCHANGE SITE SYSTEM

For the purpose of our assessment, we develop a mathematical model for the isotopic exchange in a 3-exchange site system as described below. It will be used to explore the sensitivity of the N&C and Z extrapolation methods and describe the conditions under which these methods produce biased results. It will also be used to explore the parameter space (proportions of the exchange site, rates of exchange, and initial isotopic disequilibrium between exchange sites) of isotope exchange experiments, and determine the conditions for which these extrapolation methods yield correct, i.e. non-biased, results.

The mathematical model is described below:

Let three exchange sites {I, II, III}, containing oxygen atoms, with respective molar fractions: X_I , X_{II} , X_{III} , be at thermodynamic equilibrium except for their isotopic ratios ($^{18}\text{O}/^{16}\text{O}$) (respectively R_I , R_{II} , R_{III}). Let us suppose the oxygen atoms are exchanged between the 3 exchange sites at constant exchange rates (respectively k_{I-II} , k_{II-III} and k_{I-III}); the case for non-constant k 's will be explored later in this paper (Section 6).

For experiments of infinite duration ($t = \infty$) the isotopic ratios of the three exchange sites attain their equilibrium fractionation values:

$$\alpha_{I-II} = \frac{R_{I,t=\infty}}{R_{II,t=\infty}}, \quad \alpha_{I-III} = \frac{R_{I,t=\infty}}{R_{III,t=\infty}}, \quad \alpha_{II-III} = \frac{R_{II,t=\infty}}{R_{III,t=\infty}}$$

whereas during the course of the exchange, at any time t , apparent non-equilibrium fractionations occur.

$$\alpha_{I-II,t} = \frac{R_{I,t}}{R_{II,t}}, \quad \alpha_{I-III,t} = \frac{R_{I,t}}{R_{III,t}}, \quad \alpha_{II-III,t} = \frac{R_{II,t}}{R_{III,t}}$$

Specifically, the exchange sites evolve towards their equilibrium isotopic compositions as oxygen exchange proceeds with time.

The changes of the isotopic ratios versus time (t) are given by the equations of Abell et al. (1957), McKay (1938), Northrop and Clayton (1966), Criss et al. (1987), Criss (1999).

For exchange sites I, II and III, respectively, the equations are:

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