



The confines of triple oxygen isotope exponents in elemental and complex mass-dependent processes

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Abstract

Small differences in triple isotope relationships, or $\Delta^{17}\text{O}$ in the case of oxygen, have been increasingly used to study a range of problems including hydrological cycles, stratosphere-troposphere exchange, biogeochemical pathways and fluxes, and the Moon's origin in the geochemical and cosmochemical communities. A $\Delta^{17}\text{O}$ value depends on the triple isotope exponent θ of involved reaction steps. However, the probabilistic distribution of the intrinsic and apparent θ values has not been examined for elemental processes and for processes that are out of equilibrium or bearing reservoir-transport complexities. A lack of knowledge on the confines of θ may hamper our understanding of the subtle differences among mass-dependent processes and may result in mischaracterization of a set of mass-dependent processes as being in violation of mass-dependent rules. Here we advocate a reductionist approach and explore θ confines starting from kinetic isotope effects (*KIEs*) within the framework of transition state theory (TST). The advantage of our *KIE* approach is that any elemental or composite, equilibrium or non-equilibrium process can be reduced to a set of *KIEs* with corresponding θ_{KIE} .

We establish that the *KIE* between a reactant and a transition state (TS) is intrinsic. Given a range of *KIEs* known for Earth processes involving oxygen, we use a Monte Carlo calculation method and a range of oxygen-bonded molecular masses to obtain a distribution of θ_{KIE} values and subsequently that of θ_{eq} . Next, complexities are examined by looking into expected effects due to reaction progress, unbalanced fluxes, and reference frame. Finally, compounded reservoir-transport effects are examined using two simple processes – Rayleigh Distillation (RD) and Fractional Distillation (FD). Our results show that the apparent θ values between two species or two states of the same evolving species have much broader confines than the commonly used “canonical” confines of 0.51–0.53, particularly when the overall fractionation factors are close to 1.000. Equilibrium processes exhibit the narrowest α - θ value distribution. More complex processes or non-equilibrium further broaden the confines of the apparent θ values for reaction systems. The compounded reservoir-transport effects of RD and FD demonstrate that non-canonical apparent θ and large non-zero $\Delta^{17}\text{O}$ values are achievable even when all involved elemental steps are strictly mass-dependent. This study calls for a research effort to determine *KIE* and θ_{KIE} for important natural processes, and for cautions in interpreting a slope value drawn in a $\delta^{17}\text{O}$ – $\delta^{18}\text{O}$ space, as the slope is only a superficial manifestation of a set of complex reaction pathways and dynamics.

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1. INTRODUCTION

In a physical, chemical, or biological process, oxygen-bearing species go through a re-distribution of $^{18}\text{O}/^{16}\text{O}$ as well as $^{17}\text{O}/^{16}\text{O}$ ratios, which are expressed correspondingly as isotope fractionation factors α^{18} and

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α^{17} ($\alpha \equiv R_A/R_B$; $R = {}^{18}\text{O}/{}^{16}\text{O}$ or ${}^{17}\text{O}/{}^{16}\text{O}$; and A and B can be two species or the same species at two different times). At high temperatures, the logarithm of the equilibrium isotope effect $\ln\alpha$ is proportional to the product of $F * \Delta m / (m_1 * m_2)$, in which F is the force constant of O bond and m_1 and m_2 are two of the oxygen isotopes, say, ${}^{16}\text{O}$ and ${}^{18}\text{O}$, or ${}^{16}\text{O}$ and ${}^{17}\text{O}$ (Bigeleisen, 1949, 1965). Because F is the same for isotopologues, the ratio of $\ln\alpha^{17}/\ln\alpha^{18}$ is then related simply to isotope masses. If we denote θ for this ratio, θ assumes a value of 0.5305 for the triple oxygen isotope system.

The θ values for equilibrium processes at $-50\text{ }^\circ\text{C}$ to $1000\text{ }^\circ\text{C}$ have been explored theoretically by Cao and Liu (2011), in which an equilibrium θ between any oxygen-bearing species A and B is obtained by calculating α_A , β_A , α_B , and β_B using quantum chemistry methods based on the Bigeleisen–Mayer equation. The introduction of a new concept κ , defined as $\ln\beta^{17}/\ln\beta^{18}$, which is the equilibrium θ value for an isotope exchange reaction between an O-bearing species and the ideal gaseous monatomic O, simplified the θ_{eq} calculation. It is found that at temperatures from $-50\text{ }^\circ\text{C}$ to $1000\text{ }^\circ\text{C}$, κ has a rather narrow range varying from 0.5275 to 0.5303 for all β or reduced partition function ratios (*RPF*Rs). Here the lower value 0.5275 is calculated based on one of the strongest bound oxygen species CO_2 . Given the corresponding κ s, the θ was then found to vary from 0.523 to 0.526 for examined mineral–water equilibrium exchange cases, with an approx. 0.001 increase per $100\text{ }^\circ\text{C}$ temperature increase. The apparent narrow θ range is based on a few pairs and is not the general picture. The full confines of the θ_{eq} need to be explored.

An overall restricted range of θ_{eq} would produce a tight linear correlation between $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$, defined as $\ln(R_{\text{sample}}/R_{\text{reference}})$, among oxygen-bearing species on Earth, which is indeed manifested as the terrestrial fractionation line (Clayton et al., 1973; Rumble et al., 2007). Recently, thanks to the increasing resolving power of analytical tools, smaller and smaller differences in the relationship between $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$, or $\Delta^{17}\text{O}$ differences ($\Delta^{17}\text{O} \equiv \delta^{17}\text{O} - C * \delta^{18}\text{O}$, and C is an assigned straight-line slope value in a $\delta^{18}\text{O}$ – $\delta^{17}\text{O}$ space), have been measured and interpreted in geochemical literature. Small mass-dependent deviations in the ${}^{17}\text{O}$ content in water have become an added dimension to understanding the kinetics of hydrological cycles (Angert et al., 2004; Barkan and Luz, 2005, 2007; Luz and Barkan, 2005; Landais et al., 2006, 2012). Approx. 0.2‰ $\Delta^{17}\text{O}$ differences are also reported among seawater, sedimentary rocks, and mantle rocks (Levin et al., 2014; Pack and Herwartz, 2014; Passey et al., 2014; Herwartz et al., 2015). Small non-mass-dependent ${}^{17}\text{O}$ anomalies in modern atmospheric O_2 was recognized earlier (Luz et al., 1999) and applied to quantify biogeochemical cycling (Blunier et al., 2002; Angert et al., 2003; Hendricks et al., 2005), while questions remain on the exact magnitude of those ${}^{17}\text{O}$ anomalies (Young et al., 2002, 2014; Bao et al., 2008). The small ${}^{17}\text{O}$ anomalies in air O_2 have inspired an effort to explore its utility in animal physiology, diagenesis, and the geological O_2 record in phosphate minerals (Gehler et al., 2011; Pack et al., 2013). Small $\Delta^{17}\text{O}$ differences have also been

predicted (Hoag et al., 2005) and reported (Thiemens et al., 2014) for tropospheric CO_2 . The improved analytical capacity has resulted in a further survey of terrestrial (e.g. Rumble et al., 2007) and lunar (Herwartz et al., 2014) triple oxygen isotope compositions. Concepts and the underlying mechanisms for the observed small mass-dependent $\Delta^{17}\text{O}$ differences have been explored (Miller, 2002; Young et al., 2002). There are also phenomena displaying non-canonical triple oxygen or triple sulfur isotope relationships that should otherwise be purely mass-dependent. For example, SF_6 ice–vapor equilibrium at low T (137–173 K) has a ${}^{33}\theta$ value of ca. 0.55, significantly beyond the cononical value of ca. 0.52 (Eiler et al., 2013). A slow thermal decomposition of carbonate minerals by laser heating can generate CO_2 that is ca. 0.20‰ higher than the residue CaO in $\Delta^{17}\text{O}$ (Miller et al., 2002). A modeling study on microbial sulfate uptake also demonstrates that when the overall degree of sulfur isotope fractionation $\Delta\delta^{34}\text{S}$ is small, e.g. less than 15‰, the apparent ${}^{33}\theta$ would deviate from the equilibrium value of 0.515 and become as low as 0.508 (Wing and Halevy, 2014). In addition, Sun and Bao (2011a,b) reported up to 1‰ difference in $\Delta^{17}\text{O}$ between O_2 gases at the two temperature ends of a thermal gradient. The current rapidly increased geochemical literature on small $\Delta^{17}\text{O}$ and similarly on small $\Delta^{33}\text{S}$ is in need of a critical evaluation. While it is important to examine individual cases reported in literature, we first address a question that is at the very foundation of the $\Delta^{17}\text{O}$ value differences or deviations: What are the confines of θ for mass-dependent processes? Or can an apparent non-canonical θ value or a distinct non-zero $\Delta^{17}\text{O}$ value be expected for a process in which each of its elemental steps is strictly mass-dependent? In this study, a “canonical” θ value is loosely placed in the range of 0.51–0.53.

As illustrated above, the confines of θ are not fully known even for equilibrium processes, let alone for non-equilibrium processes in nature. Note that an equilibrium process refers to a process in which forward and backward reactions go through the same transition state (TS) with the same fluxes. Thus, non-equilibrium process refers to any process that does not have equal backward and forward fluxes or in which the backward and forward reactions link to different TSs. In that sense, steady-states with equal backward and forward reaction fluxes with respect to a species of interest but which link to different TSs are also non-equilibrium processes. To explore both equilibrium and non-equilibrium processes, we start from the transition state theory (TST) or the Absolute Rate Theory (Eyring, 1935). TST states that there is a barrier between a reactant and a product along its reaction coordinate, and the TS is on the top of the barrier and it is at quasi-equilibrium with the reactant (Eyring, 1935; Felipe et al., 2001). In other words, we shall derive the triple oxygen isotope relationships for equilibrium and non-equilibrium processes starting from the kinetic isotope effect (*KIE*), i.e. θ_{KIE} for the reactant-TS step.

Unfortunately, research efforts in calibrating *KIE* or θ_{KIE} for the many important natural processes is embarrassingly sparse at this moment. Therefore, in this paper, we will first model the confines of θ_{KIE} for the fundamental

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