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Density functional theory calculations of equilibrium oxygen isotope fractionation between borate minerals and aqueous fluids

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Abstract: Borax, ulexite, and colemanite minerals are by far the most important economic source of boron and occur almost exclusively in nonmarine evaporite deposits. While much is known about the geological setting in which they are found, surprisingly little is known about the chemical and physical properties of the brines from which they are formed. Oxygen isotope studies have the potential to reveal important new information regarding borate formation, but unlike most other common oxygen-bearing salts precipitated from brines, there are no experimental data regarding the oxygen isotope fractionation factors between borates and brines. As a first attempt to address this gap in our understanding we have determined $\Delta^{18}O_{borate\text{-}water}$ values between 0 and 100 °C using density functional theory calculations (DFT). These results predicted $\Delta^{18}O_{borate\text{-}water}$ values of 12.87, 22.32, and 17.5‰ at 25 °C for borax, colemanite and ulexite, respectively.

Key words: Oxygen isotopes, nonmarine evaporites, borax, ulexite, colemanite, borate deposits

1. Introduction

Borates are the most important economic source of boron (Kistler and Helvaci, 1994; Helvaci and Palmer, 2017), with Türkiye hosting approximately two-thirds of the global economic reserve. Most of the world's major borate deposits are found in nonmarine evaporate deposits formed by the evaporation of boron-rich fluids in enclosed basins in collisional tectonic settings (Helvaci, 2005). Although approximately 20 borate minerals are extracted commercially, worldwide (Garrett, 1998), the most economically important minerals are borax ($Na_2[B_4O_5(OH)_4]\cdot 8H_2O$), ulexite ($NaCa[B_5O_6(OH)_6]\cdot 5H_2O$) and colemanite ($Ca[B_3O_4(OH)_3]\cdot H_2O$) (Helvaci and Palmer, 2017). Because of its global prominence, much of our understanding of the formation of borate minerals has come from studies of deposits within Türkiye. These studies have revealed that the boron-rich fluids most likely derive from pooled geothermal fluids that leached boron from nearby ultrapotassic volcanic rocks and alteration of tuff layers deposited in extensional basins (Helvaci, 2005; Palmer et al., 2019). The pooled fluids likely formed playa lakes that underwent evaporation and precipitation of the borate minerals in the sustained arid climate prevalent during the Miocene in the eastern Mediterranean region (Rouchy et al., 2006; Helvaci, 2015). Similar processes were also likely responsible for the formation of other large borate deposits in South America and China (Helvaci and Palmer, 2017).

While this general model of borate mineral formation is widely accepted, we still do not understand much about the physical and chemical conditions present in the Turkish Miocene playa lakes. For example, we do not know the temperature of the formation of the borate minerals. This is important for several reasons. For example, Palmer and Helvaci (1995; 1997) used the boron isotope compositions of colemanite, ulexite and borax to infer the pH values of the brines that precipitated these borate minerals, but in the absence of paleotemperature data they were forced to

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assume a uniform average temperature of 25 °C. While we lack quantitative paleotemperature data for the borate deposits, palynology studies suggest that the climate of the eastern Mediterranean was seasonal during the Miocene (Kayseri-Özer, 2013). As with other stable isotopes, boron isotope fractionation factors are temperature dependent; hence, this uncertainty in the paleotemperature means that the calculated pH values can only be treated as approximate at this stage.

For many minerals, the most reliable means of reconstructing their formation temperatures come from oxygen isotope studies. For example, diagenetic clay minerals (that are intercalated in many borate deposits (Helvaci, 2015)) have well-calibrated oxygen and hydrogen isotope factors (Savin and Epstein, 1970). However, no published data are available for oxygen isotope fractionation between borates and water that would allow the $\delta^{18}O$ values of the borate minerals to be used as paleothermometers. As a first step towards addressing this knowledge gap, we have calculated oxygen isotope fractionation factors between borates and water using density functional theory calculations.

2. Computational methods

2.1 Calculation of equilibrium boron and oxygen isotope fractionation

The theories of Bigeleisen and Mayer (1947) and Urey (1947) indicate that the equilibrium isotopic fractionation due to changes in vibrational frequencies caused by the isotopic substitution in a given system can be estimated using standard thermodynamic and quantum mechanical approaches. The reduced partition function ratio (i.e. RPFR) of isotopes of element X between phase A and monatomic ideal gas can be calculated by the harmonic approximation as follows:

$$RPFR(X) = \frac{Z^*}{Z} = \prod_i^N \frac{u_i^*}{u_i} \frac{\exp\left(-\frac{u_i^*}{2}\right)}{1-\exp(-u_i^*)} \frac{1-\exp(-u_i)}{\exp\left(-\frac{u_i}{2}\right)}, \quad \text{(Eq. 1)}$$

where Z^* and Z refer to the vibrational partition function for the heavy and light isotopes respectively; N is the total number of vibrational modes; the subscript i is the vibrational mode order number. For convenience, the reduced isotopic partition function ratio (*RPFR*) was converted to the b factor using the relationship $\beta = RPFR^{1/n}$. The exponent of $1/n$ is a normalization factor to account for multiple substitutions in substance A containing more than one atom of X. The term of $u_i (u^*_i)$ was calculated from the relationship:

$$u_i = \frac{hc \times v_i}{kT}, \quad \text{(Eq. 2)}$$

where h is Plank's constant, c is the speed of light, v_i is the vibrational frequency in cm^{-1}, k is Boltzmann's constant, and T is the temperature in degrees Kelvin. The isotope fractionation at equilibrium between phases A and B can be expressed as

$$\Delta_{A-B} \sim 1000 ln\alpha_{A-B} = 1000 ln\beta_A - 1000 ln\beta_B \ . \quad \text{(Eq. 3)}$$

All calculations were carried out using the Cambridge Serial Total Energy Software Package (CASTEP) (Clark et al., 2005). The generalized-gradient approximation (GGA) method, together with the exchange-correlation functional of Perdew-Burke-Ernzerhof (PBE) (Perdew et al., 1996), and norm-conserving pseudopotentials were used for both the geometric optimizations and phonon frequency calculations for the PBC model of the minerals. The lattice parameters and calculation sets for borate minerals, including the output parameters of k-points, cut-off energy, and q-points for "fine" quality are listed in Table 1.

2.2. Models for minerals

2.2.1. Models for borate minerals

In theoretical calculations it is important to create models to represent minerals and fluids because minerals have discrete compositions, but fluids have a continuum of compositions. For minerals, the periodic boundary conditions method is generally used to produce accurate theoretical isotope fractionations between minerals. This method has been refined within the local atomic structure of minerals and fluids to carry out electronic structure calculations of the equilibrium isotope fractionations between different minerals and aqueous solutions (Rustad et al., 2010). To calculate the stable oxygen isotope fractionation factors among colemanite, ulexite, borax and fluid, we obtained the initial crystal structure data from the American Mineralogist Crystal Structure Database (AMCSD) (http://rruff.geo.arizona.edu/AMS/amcsd.php). The structures of borax, colemanite and ulexite were taken from Levy and Lisensky (1978), Burns and Hawthorne (1993), and Ghose et al. (1978), respectively (Figure 1).

All initial structures were optimized using variable cell-shape molecular dynamics (Wentzcovitch, 1991) and the configurations with the lowest total energy were then selected for the vibrational frequency calculation. The results of the DFT calculation were compared with the available experimental data to examine the accuracy of the calculated phonon frequency. We also compared vibrational calculations using 23 q-points in borax, which gives consistent results to those obtained using the gamma-point only in both boron and oxygen isotope fractionation.

2.2.2. Computational error estimation

PBE calculations generally overestimate the experimental lattice parameters of minerals. This systematic error is typical of the PBE approximation and is usually associated

Table 1. The computational parameters of lattice constant, *k*-points, cut-off energy, *q*4 points and quality for frequency calculations of borate minerals.

Minerals	***Borax***	***Colemanite***	***Ulexite***
a (Å)	8.081	8.879	8.887
b (Å)	8.081	11.329	12.949
c (Å)	12.216	6.147	6.701
a (°)	102.802	90	90.193
β (°)	102.802	112.103	109.715
γ (°)	84.248	90	104.821
Volume (Å³)	757.356	572.857	698.407
N_{atoms}	86	68	80
K-point grid			
cut-off energy (eV)	750	800	800
Quality	Fine	Fine	Fine
Formula	$Na_2B_4O_5(OH)_4{\cdot}8H_2O$	$Ca_2[B_3O_4(OH)_3]_2{\cdot}2H_2O$	$NaCaB_5O_6(OH)_6{\cdot}5H_2O$

with a systematic underestimation of the phonon frequencies (Méheut et al., 2007). Comparisons between the calculated phonon frequencies of borate minerals from this study and experimental results show that PBE calculations generally reproduce the frequencies with a systematic underestimation of up to 4%, which is in good agreement with the study by Méheut et al. (2007). According to the error analyses of Méheut et al. (2009), a relative uncertainty of the calculated frequencies of *n*% results in an uncertainty on 1000lnβ of *n*% (at low temperature) and 2*n*% (at high temperature).

According to the error estimation scheme proposed by Kowalski et al. (2013), the overall absolute errors for 1000lnβ and 1000lna in ‰ can be estimated from $\frac{1000ln\beta \times 5\%}{2}$ and $\frac{(1000ln\beta_A + 1000ln\beta_B) \times 5\%}{2}$, respectively.

3. Results

3.1. Calculation of RPFRs of oxygen isotopes for borate minerals

The calculated vibrational frequencies of borate agree well with the available experimental data (Figure 2), with the slope between calculated frequencies and measured frequencies being 0.9988 ± 0.011 (1σ, R^2 = 0.9997). The computed temperature dependences of the equilibrium oxygen isotope fractionation are shown in Figures 3a and 3b and their polynomial fitting parameters of the RPFR as a function of temperature are reported in Table 2. A measure of the accuracy of vibrational calculations for borax is provided by comparing the results obtained using 23 *q*-points and the gamma-point only. The variance is <0.36‰ at 298 K (Figure 3a), which is comparable with typical given analytical precisions for oxygen isotope values ($\delta^{18}O$) of ±0.5‰.

The calculated results show that colemanite is enriched in heavy oxygen isotopes ($10^3 ln\beta$ of 96.56‰, 298 K) and borax is enriched in ^{11}B ($10^3 ln\beta$ of 181.93‰, 298 K) among the three borate minerals investigated. The $10^3 ln\beta$ values decrease in the sequence of colemanite > ulexite > borax (Figures 3a and 3b). The equilibrium oxygen isotope fractionation range is 4.68‰ ($\Delta^{18}O_{colemanite\text{-}ulexite}$, 298 K) and 9.46‰ ($\Delta^{18}O_{colemanite\text{-}borax}$, 298 K), respectively.

In addition to the boron-oxygen tetrahedron, the oxygen atoms are also distributed in crystalline water groups in the borate minerals (Figure 1). Due to the difference of the force field for oxygen atoms in the various oxygen-containing groups, the ratio of boron-oxygen groups/H_2O groups in the borate minerals influences the equilibrium oxygen isotope fractionation (Figure 4).

Compared to the $10^3 ln\beta$ of oxygen isotope in aqueous H_2O (He et al., 2022), all the borate minerals are seen to be enriched in heavy oxygen isotopes relative to aqueous H_2O. Hence the precipitating borate has a heavier $\delta^{18}O$ value than the brine. From the calculated results, the $\Delta^{18}O_{borate\text{-}water}$, is 22.36‰ for colemanite, 17.68‰ for ulexite and 12.90‰ for borax at a temperature of 298 K (Figure 3b).

4. Discussion and wider implications

This study has produced the first borate mineral-water oxygen isotope fractionation factors. Still, it is essential to note that they are the results of theoretical calculations and that experimental studies would be advisable to confirm

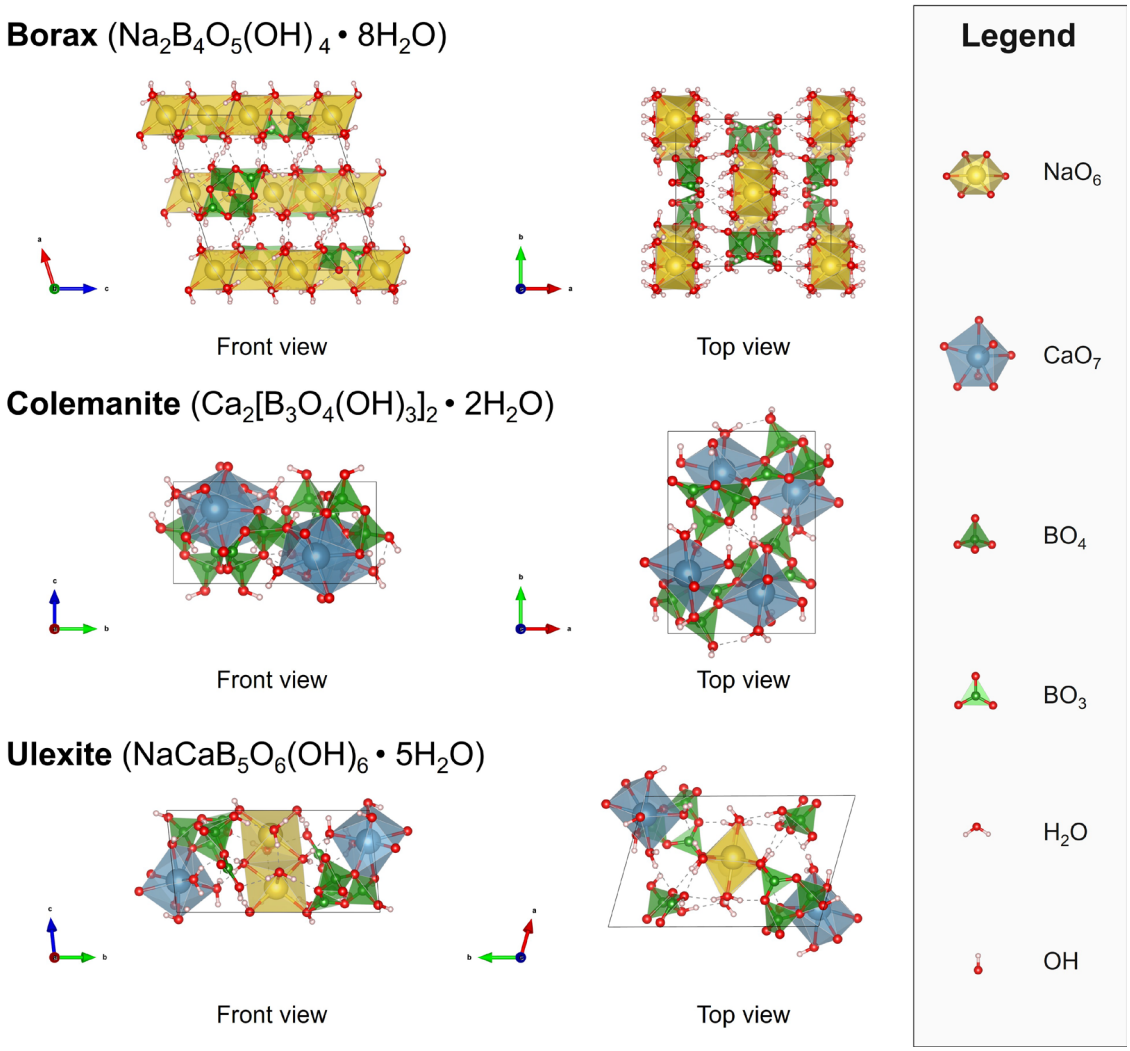

Figure. 1. A series of periodic boundary cell (PBC) models for borate minerals used for the phonon frequency calculations.

the results obtained here. However, it is nontrivial to carry out such experiments under equilibrium conditions. In addition, the methods employed in this study have been successfully used to calculate a wide range of isotope fractionation factors for different elements (e.g., B, C, Mg, Ca, Fe, Ag) from Earth's surface to deep mantle conditions that show close agreement with the results of experimental studies (e.g., Rudstad et al., 2008, 2010; Rudstad and Yin, 2009; Li et al., 2020, 2021, 2022; Wang et al., 2022). Hence, the results presented here provide a sound basis for exploring the potential utility of oxygen isotope studies of borate deposits.

An additional complication to applying the theoretical oxygen isotope fractions factors (and one that would also impact experimental studies) is that the calculated $10^3 \ln\beta$ values are the bulk values including all the oxygen atoms in the structural formulae given above. In addition to the boron-oxygen tetrahedron, the oxygen atoms are also distributed in crystalline water groups in the borate minerals (Figure 1). Due to the difference of the force field for oxygen atoms in the various oxygen-containing groups, the ratio of boron-oxygen groups/crystalline water groups in the borate minerals influences the equilibrium oxygen isotope fractionation (Figure 4). This observation will have implications for $\delta^{18}O$ values obtained from analyses of borate minerals. If the sample was heated before analysis, causing the water groups to be driven off, the resultant $\delta^{18}O$ values would increase above those of the pristine, hydrated mineral. This would be a particular problem for borax, which commonly loses five crystalline water

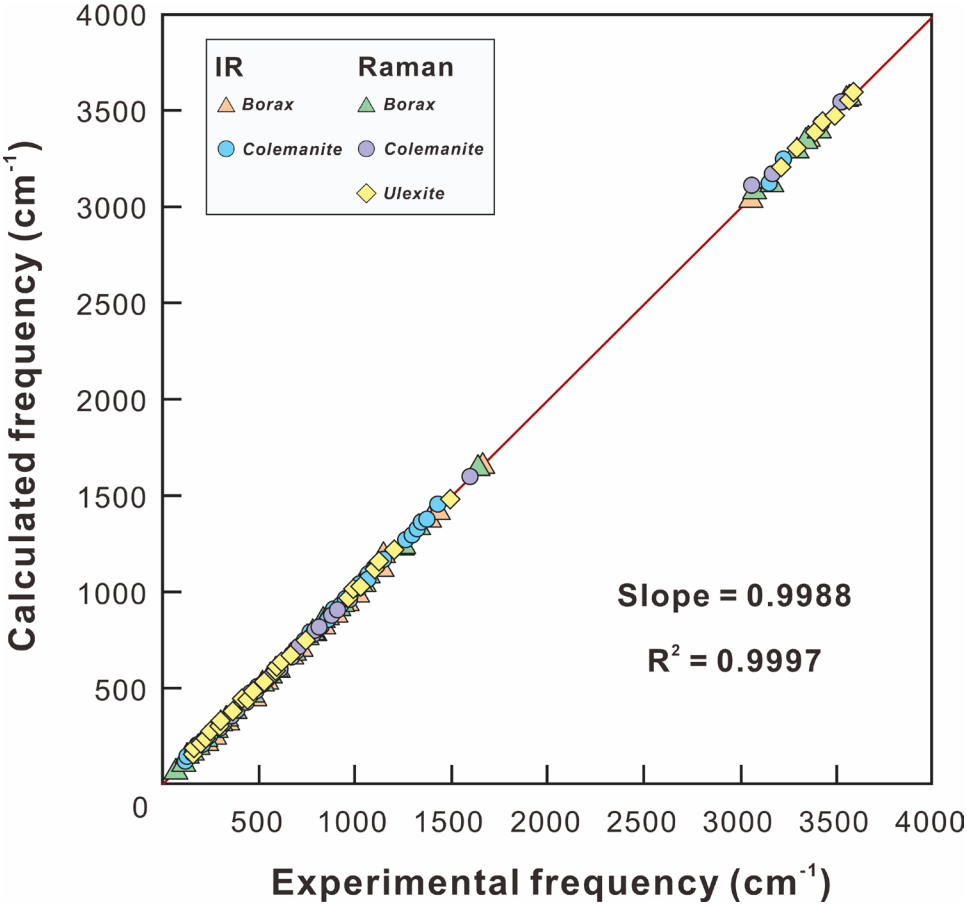

Figure 2. Comparison of calculated vibrational frequencies of minerals with the experimental Raman and IR data. IR data: Devi et al. (1994) for borax; Frost et al. (2013) for colemanite. Raman data: Devi et al. (1994) for borax; Frost et al. (2013) for colemanite; Kloprogge and Frost (1999) and Hurai et al. (2015) for ulexite.

groups immediately after sampling, to form tincalconite, $Na_2B_4O_5(OH)_4{\cdot}3H_2O$. It would therefore be important that any reported $\delta^{18}O$ data for borates contains details of whether the crystalline water groups were included in the analyses.

The primary purpose of this study is to provide an important framework for future oxygen isotope studies of borate deposits that involve analyses of borate and associated minerals. Nevertheless, it is worth noting how such studies may reveal important new information concerning borate deposit formation. The most obvious application would be determining the temperature at which the different borate minerals precipitated in a particular deposit. This would require assumptions regarding the water's oxygen isotope composition from the precipitated minerals. Still, the composition of meteoric and geothermal waters has long been well-constrained as a function of latitude and local geology (e.g., Craig, 1963). Different borate minerals are commonly interbedded in both Turkish and South American borate deposits (Helvaci and Alonso, 2000); hence, oxygen isotope analyses of closely coexisting borate minerals may aid in determining the extent to which changes in borate mineralogy reflect changing chemical and physical conditions. Oxygen isotope analyses may also help distinguish between borate minerals in deposits that were precipitated directly from lake waters versus those that precipitated within sediments (e.g., Helvaci, 1995) as the latter would be expected to record diagenetically altered porewater oxygen isotope compositions.

5. Conclusion

Measurements of the oxygen isotope composition of borax, ulexite and colemanite in borate deposits can reveal important information concerning the chemical and

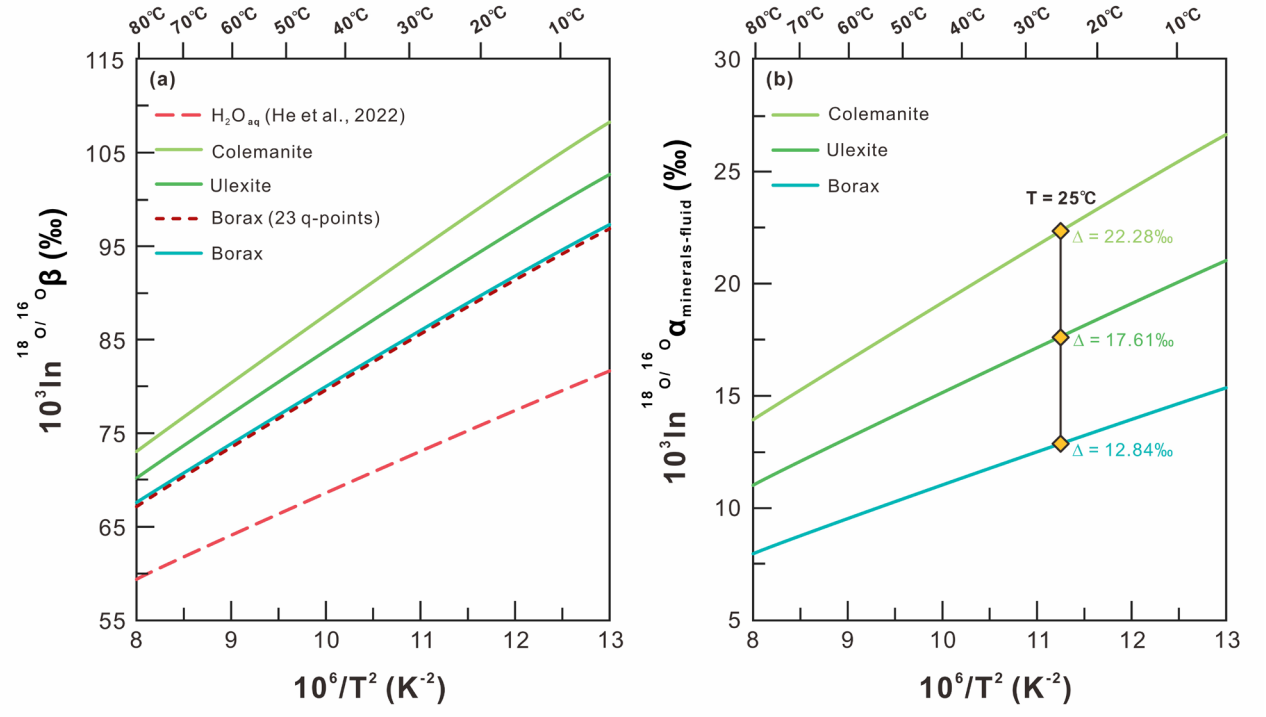

Figure 3. (a) The reduced partition function ratios ($10^3 \ln\beta$) of $^{18}O/^{16}O$ for borate minerals and fluid as a function of temperature ($10^6/T^2$). (b) The equilibrium oxygen isotope fractionation ($10^3 \ln b_{mineral\text{-}fluid} = \Delta^{18}O_{mineral\text{-}fluid}$) between borate minerals and fluid as a function of temperature ($10^6/T^2$).

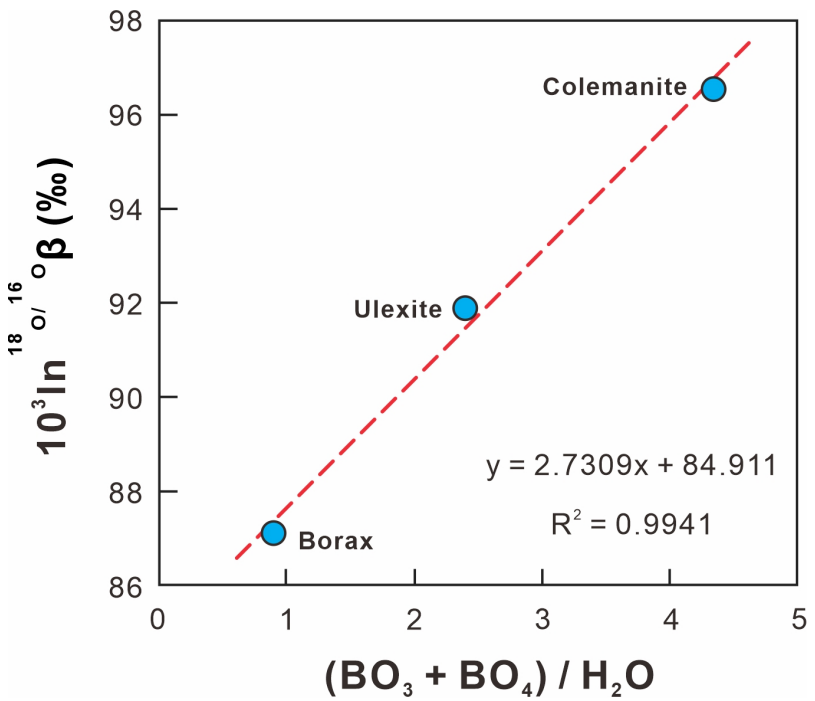

Figure 4. Relationship between ($10^3 \ln\beta$) of $^{18}O/^{16}O$ with ratios of B-O groups/H_2O groups in borate minerals, illustrating the influence of the force field for oxygen atoms in the various oxygen-containing groups.

Table 2. Polynomial fitting parameters for the relationship of ($10^3 ln\beta$) vs. $10^6/T^2$ for borate minerals and H_2O.

Mineral	***a***	***b***	***c***	***d***
Borax	0	–0.0939	7.9036	1.0280
Colemanite	0	–0.0971	9.0366	7.1285
Ulexite	0	–0.0953	8.4619	8.6972
H_2O	0.0082	–0.3326	8.6720	7.0634

Note: Polynomial fitting equation: $10^3 ln\beta = a\,x^3 + b\,x^2 + c\,x + d$, where $x = 10^6/T^2$ and T is temperature in Kelvin. All polynomial fittings are performed between 273 K and 373 K. Values for H_2O from He and Li (2022).

physical processes that led to their formation. Without experimental data for oxygen isotope fractionation factors between these borate minerals and water, we have calculated these values using density functional theory calculations. These calculations yield the following relationships for the $\Delta^{18}O_{borate\text{-}water}$ values in per mil units between 0 and 100 °C, where T is measured in °C:

$\Delta^{18}O_{borax\text{-}water} = 0.0004\ T^2 - 0.1305\ T + 15.869$

$\Delta^{18}O_{colemanite\text{-}water} = 0.0007\ T^2 - 0.2253\ T + 27.542$

$\Delta^{18}O_{ulexite\text{-}water} = 0.0005\ T^2 - 0.1776\ T + 21.750.$

While confirmation of these theoretical oxygen isotope fractionation factors by experimental studies would be preferable, these results demonstrate that there are significant and distinct temperature-dependent oxygen isotope fractionation factors between water and different borate minerals. Applying these results to analyses of borate minerals themselves may have important implications for furthering our understanding of the formation of borate deposits.

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