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2 **Equilibria, kinetics, and boron isotope partitioning in the aqueous boric acid –**
3 **hydrofluoric acid system**

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Abstract. The aqueous boric, hydrofluoric, and fluoroboric acid systems are key to a variety of applications, including boron measurements in marine carbonates for CO₂ system reconstructions, chemical analysis and synthesis, polymer science, sandstone acidizing, and more. Here we present a comprehensive study of chemical equilibria and boron isotope partitioning in the aqueous boric acid – hydrofluoric acid system. We work out the chemical speciation of the various dissolved compounds over a wide range of *pH*, total fluorine (F_T), and total boron (B_T) concentrations. We show that at low *pH* ($0 \leq pH \leq 4$) and $F_T \gg B_T$, the dominant aqueous species is BF_4^- , a result relevant to recent advances in high precision measurements of boron concentration and isotopic composition. Using experimental data on kinetic rate constants, we provide estimates for the equilibration time of the slowest reaction in the system as a function of *pH* and $[HF]$, assuming $F_T \gg B_T$. Furthermore, we present the first quantum-chemical (QC) computations to determine boron isotope fractionation in the fluoroboric acid system. Our calculations suggest that the equilibrium boron isotope fractionation between BF_3 and BF_4^- is slightly smaller than that calculated between $B(OH)_3$ and $B(OH)_4^-$. Based on the QC methods X3LYP/6-311+G(d,p) (X3LYP+) and MP2/aug-cc-pVTZ (MP2TZ), $\alpha_{(BF_3-BF_4^-)} \simeq 1.030$ and 1.025 , respectively. However, BF_4^- is enriched in ¹¹B relative to $B(OH)_4^-$, i.e., $\alpha_{(BF_4^- - B(OH)_4^-)} \simeq 1.010$ (X3LYP+) and 1.020 (MP2TZ), respectively. Selection of the QC method (level of theory and basis set) represents the largest uncertainty in the calculations. The effect of hydration on the calculated boron isotope fractionation turned out to be minor in most cases, except for BF_4^- and $B(OH)_3$. Finally, we provide suggestions on best practice for boric acid – hydrofluoric acid applications in geochemical boron analyses.

1 Introduction

Fluoroboron compounds have a wide variety of uses. A recent geochemical application is in the high precision analysis of boron concentration and isotopic composition (Misra et al., 2014b; Rae et al., 2018; He et al., 2019). These boron measurements have application in marine carbonates as tracers of the CO₂ system (e.g., Branson, 2018; Rae, 2018; Hönisch et al., 2019), in silicates as tracers of seawater exchange with oceanic crust (Marschall, 2018) and subduction (De Hoog and Savov, 2018), and various other fundamental and environmental uses (e.g., Rosner et al., 2011; Penman et al., 2013; Guoinseau et al., 2018). Boron trifluoride (BF₃) and fluoroboric acid (HBF₄) also have a wide range of applications in chemical analysis and synthesis. BF₃ is used in various organic synthesis reactions, such as the reduction of aldehydes and ketones to alcohols and hydrocarbons (Fry et al., 1978), due to its properties as a Lewis acid. HBF₄ is also used as a catalyst in organic synthesis and in the electroplating of tin and tin alloys, alongside various applications in polymer science, sandstone acidizing, manufacturing of fluoroborate salts, and more (e.g., Palaniappan and Devi, 2008; Leong and Ben Mahmud, 2019).

CITE ABOVE? (Wei et al., 2013; Li et al., 2019)

While the chemical and isotopic equilibrium in the boric acid system in aqueous solution is relatively well understood, including $\alpha_{\text{B(OH)}_3\text{-B(OH)}_4^-}$ (e.g. Zeebe, 2005; Liu and Tossell, 2005; Klochko et al., 2006; Nir et al., 2015), the partitioning of boron and its isotopes in the aqueous boric acid – hydrofluoric acid system has not been investigated in detail. This leads to uncertainties on how best to apply this method in laboratory procedures and potential pitfalls associated with isotope fractionation between B-F species. Here we work out the equilibria and kinetics of boron species in the presence of hydrofluoric acid, provide the first

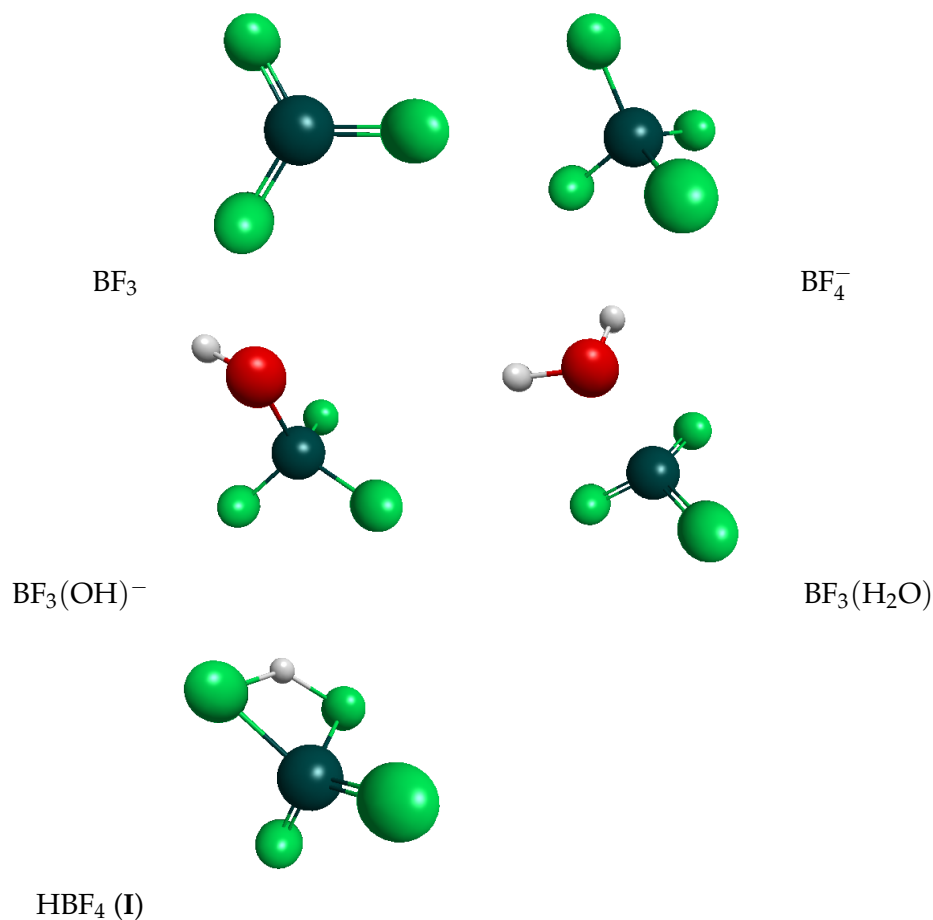
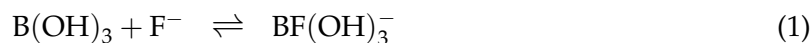


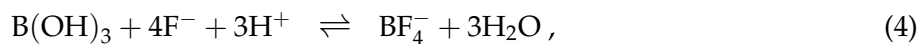
Figure 1. Geometries of several key compounds examined in this study. Structures shown were optimized using quantum-chemical calculations for isolated (“gas-phase”) molecules. Dark-green: boron, light-green: fluorine, red: oxygen, white: hydrogen. The notations $\text{BF}_3(\text{H}_2\text{O})$ and $\text{HBF}_3(\text{OH})$ will be used synonymously here for structures similar to the $\text{BF}_3(\text{H}_2\text{O})$ geometry shown (for details, see Section 4.1). (I) indicates geometrically unstable (one calculated frequency is imaginary).

59 quantum-chemical calculations for isotopic fractionation factors in this system, and comment
 60 on best practice in the practical application of HF in boron analyses.

61 2 Chemical Equilibrium

62 The reactions that link the boric acid – hydrofluoric acid system (involving B-F
 63 compounds, see Fig. 1) may be written as (Wamser, 1951; Mesmer et al., 1973):



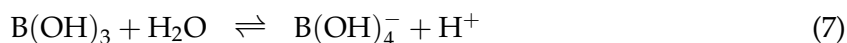


64 with

$$K_1 = \frac{[\text{BF(OH)}_3^-]}{[\text{B(OH)}_3][\text{F}^-]} \quad ; \quad K_2 = \frac{[\text{BF}_2(\text{OH})_2^-]}{[\text{B(OH)}_3][\text{F}^-]^2[\text{H}^+]} \quad (5)$$

$$K_3 = \frac{[\text{BF}_3(\text{OH})^-]}{[\text{B(OH)}_3][\text{F}^-]^3[\text{H}^+]^2} \quad ; \quad K_4 = \frac{[\text{BF}_4^-]}{[\text{B(OH)}_3][\text{F}^-]^4[\text{H}^+]^3}. \quad (6)$$

65 In addition, we take into account the relatively well known dissociation reactions:



66 with

$$K_B = \frac{[\text{B(OH)}_4^-][\text{H}^+]}{[\text{B(OH)}_3]} ; K_F = \frac{[\text{F}^-][\text{H}^+]}{[\text{HF}]} ; K_w = [\text{H}^+][\text{OH}^-]. \quad (10)$$

67 Furthermore, equilibrium between the four $\text{BF}_i(\text{OH})_{4-i}^-$ ions ($i = 1, \dots, 4$) in reactions (1)-(4)

68 and their protonated forms $\text{HBF}(\text{OH})_3$, $\text{HBF}_2(\text{OH})_2$, $\text{HBF}_3(\text{OH})$, and HBF_4 need to be

69 considered. For example,



70 and so forth.

71 Given the immediate reaction of BF_3 with water, gaseous BF_3 can likely be neglected for
 72 dilute solutions at room temperature. For example, complete absorption of 1.17 mol BF_3 per
 73 kg H_2O has been reported at 25°C with no BF_3 observed by infrared analysis in the vapor
 74 phase (Scarpiello and Cooper, 1964). Some gas manufacturers state BF_3 "solubilities" of ~ 3.2 g
 75 per g H_2O at 0°C (47 mol BF_3 /kg H_2O), yet the origin and method for obtaining this value is

76 difficult to track down. Also, “solubility” appears misleading here as hydrates are instantly
 77 formed, rather than dissolved BF_3 . Raman spectra of a $\text{BF}_3\text{-H}_2\text{O}$ mix (ratio 1:2) showed three
 78 of the four fundamentals of a tetrahedral molecule (not of a trigonal molecule like BF_3), almost
 79 identical to those of an aqueous $\text{NaBF}_3(\text{OH})$ solution (Maya, 1977). These observations are
 80 consistent with Anbar and Guttman (1960)’s estimate of $[\text{HBF}_3(\text{OH})]/[\text{BF}_3] \simeq 5 \times 10^6$ based
 81 on free energies.

82 The equilibrium constants K_i have been determined in 1 M NaNO_3 and 1 M NaCl
 83 solutions (Grassino and Hume, 1971; Mesmer et al., 1973); K_B , K_F , and K_w are relatively well
 84 known, also at different ionic strengths. In this study, we use the set of constants given by
 85 Mesmer et al. (1973) in 1 M NaCl (see Table 1). The acid dissociation constants K'_i are less
 86 well known. For instance, the acid strength of HBF_4 has been estimated to be similar to HCl
 87 and H_2SO_4 in aqueous solution (Wamser, 1951; Fărcasiu and Hâncu, 1997). Thus, we assign
 88 the value $pK'_4 = -3.0$ (actual value is of minor importance as long as $\lesssim -2.0$). The acid
 89 strength of $\text{HBF}_3(\text{OH})$ and $\text{HBF}_2(\text{OH})_2$ was deemed similar to CCl_3COOH and CHCl_2COOH ,
 90 respectively (Wamser, 1951), broadly consistent with estimates based on $\text{HBF}_3(\text{OH})$ and
 91 $\text{HBF}_2(\text{OH})_2$ concentrations in solution (Mesmer et al., 1973). Hence we use $pK'_3 = 0.66$ and
 92 $pK'_2 = 1.35$ (Lide, 2004). For the weakest of the four acids, $\text{HBF}(\text{OH})_3$, we assign $pK'_1 = 2.0$
 93 (actual value is of minor importance as long as $\lesssim 5.0$) (Table 1).

94 To link equilibrium and kinetics, the equilibrium constant for the hydrolysis of fluoboric
 95 acid will also be required (see reaction (13), Section 3 below):

$$K_h = \frac{[\text{BF}_3(\text{OH})^-][\text{HF}]}{[\text{BF}_4^-]}, \quad (12)$$

96 which we set to $K_h = 2.3 \times 10^{-3}$ M ($pK_h = 2.64$, Wamser, 1948) at 25°C for consistency with
 97 Wamser’s kinetic data used in Section 3. Compatibility between K_h and the set of K ’s from

Table 1. Equilibrium constants at 25°C used in this study ($pK = -\log K$).

pK	pK_1	pK_2	pK_3	pK_4	pK_B	pK_F	pK_w	pK'_1	pK'_2	pK'_3	pK'_4	pK_h
Note	<i>a</i>	<i>a</i>	<i>a</i>	<i>b</i>	<i>a</i>	<i>a</i>	<i>a</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>c</i>
Value	0.36	-7.06	-13.69	-19.21	8.81	2.89	13.73	2.00	1.35	0.66	-3.00	2.64

^a Mesmer et al. (1973), 1 M NaCl.

^b See text.

^c Wamser (1948).

98 Mesmer et al. (1973) (Table 1), then determines $pK_4 = -19.21$, because $K_4 = K_3/K_F/K_h$.

99 Note that Mesmer et al. (1973) did not measure K_4 but determined its value using the same
100 reasoning as applied here.

101 Given equilibrium constants, pH , total boron and total fluorine, the speciation in the boric
102 acid – hydrofluoric acid system can be calculated (Appendix A). At low pH ($0 \leq pH \leq 4$) and
103 $F_T \gg B_T$, the dominant aqueous species is BF_4^- , followed by $BF_3(OH)^-$ (Fig. 2). Also, under
104 most of those conditions, the protonated forms $[HBF_i(OH)_{4-i}]$ make up a small fraction
105 of B_T and F_T (not shown). One exception is $HBF_3(OH)$ with significant concentrations at
106 very low pH (Fig. 2). However, note that there is considerable uncertainty in the calculated
107 $[HBF_3(OH)]$, as only estimated values for pK'_3 are available (see above). Our speciation results
108 (Fig. 2) are similar to, but different from, those of Katagiri et al. (2006), who used a different
109 set of constants and did not take into account the protonated forms $[HBF_i(OH)_{4-i}]$.

110 The rising concentration of $HBF_3(OH)$ at $[H^+] > 10^0$ (negative pH) can be understood
111 considering the relevant equilibria and their pK values (Table 1). At very high $[H^+]$, the most
112 abundant species are BF_4^- , $BF_3(OH)^-$, HBF_4 , and $HBF_3(OH)$. As one might expect, at low pH ,
113 $[BF_4^-] > [BF_3(OH)^-]$. However, the balance between these species is additionally controlled

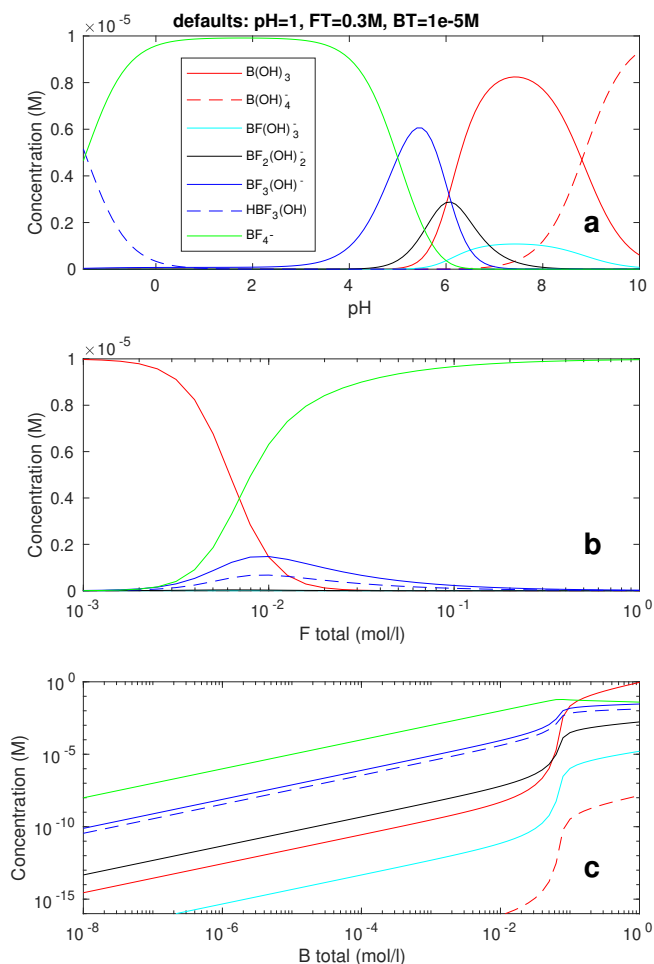


Figure 2. Speciation in the boric acid – hydrofluoric acid system at 25°C as a function of (a) pH , (b) F_T , and (c) B_T . Default parameter values (when not varied) are $pH = 1.0$, $F_T = 0.3$ M, and $B_T = 1 \times 10^{-5}$ M. Note that $[HBF_3(OH)]$ is uncertain as only estimated values for pK'_3 are available.

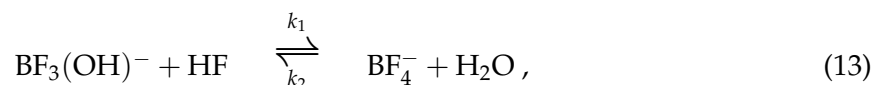
114 by the acid strengths of the protonated forms, HBF_4 and $HBF_3(OH)$, of which HBF_4 is the
 115 stronger acid (pK 's of -3.00 vs. $+0.66$, see Table 1). It turns out that for the pK set used
 116 here, the difference in acid strength between HBF_4 and $HBF_3(OH)$ dominates that between
 117 BF_4^- and $BF_3(OH)^-$, leading to high $[HBF_3(OH)]$ at very low pH . In fact, using equilibrium
 118 relations such as Eqs. (6), (10), and (11), and $F_T \gg B_T$, the hydrogen ion concentration $[H^+]$ ^{*}
 119 at which $[HBF_3(OH)] = [BF_4^-]$ can be estimated as $[H^+]$ ^{*} $\simeq K'_3 K_4 K_F F_T / K_3$, or $pH^* \simeq -1.5$, in
 120 agreement with the complete speciation calculation (Fig. 2).

121 2.1 Note of caution

122 For the present study, we opted for the set of equilibrium constants (K 's) from [Mesmer](#)
 123 [et al. \(1973\)](#) (Table 1), as the set appears internally consistent. However, these K 's apply to
 124 1 M NaCl solutions and not to solutions of different ionic strengths in general. Unfortunately,
 125 the dependence on ionic strength is unknown at present. [Mesmer et al. \(1973\)](#) noted that their
 126 equilibrium constant for the hydrolysis of $\text{BF}_3(\text{OH})^-$ to produce $\text{BF}_2(\text{OH})_2^-$ and undissociated
 127 HF (1.8×10^{-4}) is considerably lower than the value 0.011 estimated by [Wamser \(1951\)](#).
 128 Furthermore, the acid dissociation constants K'_i have only been estimated, not measured, at
 129 this point. As a result, our equilibrium calculations (Fig. 2) should be taken as a basic guide to
 130 the speciation in the system. However, that speciation only applies to a single ionic strength
 131 and may also change in the future as new or improved data for equilibrium constants become
 132 available. Caution seems also warranted regarding the available kinetic data for the system,
 133 as values reported by two different studies for one particular rate constant differ by a factor
 134 of ~ 2 -3 (see Section 3).

135 3 Kinetics

136 Among the reactions in the fluoroboric acid system, only the following is considered
 137 slow ([Wamser, 1948, 1951](#); [Anbar and Guttmann, 1960](#)):



138 which will be assumed the slowest reaction in the system and examined in the following.

139 Reaction (13) leads to the rate law:

$$\frac{d[\text{BF}_4^-]}{dt} = k_1[\text{BF}_3(\text{OH})^-][\text{HF}] - k_2[\text{BF}_4^-]. \quad (14)$$

140 Wamser (1951) found the forward reaction ((13) left to right) to be acid-catalyzed, with:

$$k_1 = k_1^0 + k_1^H[H^+], \quad (15)$$

141 where $k_1^0 = 0.064 \text{ l mol}^{-1} \text{ min}^{-1}$ and $k_1^H = 7.35$ at 25°C . The measured values in Table II of
 142 Wamser (1951) at $\text{pH} = 1.65$ and 1.36 (0.244 and $0.387 \text{ l mol}^{-1} \text{ min}^{-1}$) are consistent with
 143 those in Table IV of Wamser (1948) (0.244 and $0.392 \text{ l mol}^{-1} \text{ min}^{-1}$) at 25°C . We are unaware
 144 of any other studies that determined k_1 experimentally.

145 Wamser (1948) also studied the BF_4^- hydrolysis, i.e., the backward reaction of (13) and
 146 provided values for k_2 (his Table IV), which varied with the initial concentration of BF_4^- .
 147 Wamser (1948) stated that the observed variation of k_2 may be in part a result of $[\text{H}^+]$ changes,
 148 which varied simultaneously with initial concentrations. In fact, Anbar and Guttmann (1960)
 149 found the BF_4^- hydrolysis to be first order in $[\text{BF}_4^-]$ and $[\text{H}^+]$ and suggested the rate law
 150 $R = k'_2[\text{H}^+][\text{BF}_4^-]$. Assuming also the BF_4^- hydrolysis to be acid-catalyzed and assuming
 151 pH values of 1.65 and 1.36 for initial concentrations of 0.0561 M and 0.1105 M in Table IV
 152 of Wamser (1948) (cf. Table II, Wamser (1951)), we can calculate a catalyzed hydrolysis rate
 153 constant from:

$$k_2 = k_2^0 + k_2^H[\text{H}^+], \quad (16)$$

154 by fitting Eq. (16) to Wamser's k_2 values, which yields $k_2^0 = 1.47 \times 10^{-4} \text{ min}^{-1}$ and
 155 $k_2^H = 1.69 \times 10^{-2} \text{ l mol}^{-1} \text{ min}^{-1}$. The latter may be compared to $k'_2 \simeq 7 \times 10^{-3} \text{ l mol}^{-1} \text{ min}^{-1}$
 156 given by Anbar and Guttmann (1960), which is less than half the k_2^H value as derived
 157 from Wamser (1948). The reason for the discrepancy is unclear at this point. However,
 158 note that the ratio of Wamser's $k_2/k_1 \simeq 2.3 \times 10^{-3} \text{ M}$ (Table IV, Wamser (1948)), i.e., the
 159 equilibrium constant (K_h) of reaction (13), was consistent with his value derived from

160 titration data ($K_h = 2.04 \times 10^{-3}$ M). This lends confidence to the kinetic data of [Wamser](#)
 161 (1948, 1951), which we use in the following. Also, for internal consistency between k_1 and
 162 k_2 as implemented here (Eqs. (15) and (16)), we made sure that the ratios of individual
 163 k_i^j 's that are dominant at low vs. high pH, respectively, yield the desired K_h value, i.e.,
 164 $k_2^0/k_1^0 = 1.47 \times 10^{-4}/0.064 = k_2^H/k_1^H = 1.69 \times 10^{-2}/7.35 = 2.3 \times 10^{-3}$.

165 Given k_1 and k_2 , the rate law (Eq. (14)) can be solved analytically with some critical
 166 assumptions (Appendix B). First, our solution is only valid at low pH, where $[\text{BF}_3(\text{OH})^-]$ and
 167 $[\text{BF}_4^-]$ are the dominant B-F species and other compounds such as $\text{BF}_2(\text{OH})_2^-$ and $\text{BF}(\text{OH})_3^-$
 168 can be ignored. Second, $[\text{H}^+]$ and $[\text{HF}]$ are assumed to remain constant during the reaction. If
 169 $[\text{H}^+]$ varies, our acid-catalyzed rates cannot be treated using constant k_1 and k_2 (Eqs. (15) and
 170 (16)). Importantly, constant $[\text{HF}]$ during the reaction usually requires the hydrofluoric acid
 171 concentration to be much greater than the total boron concentration B_T . The condition "much
 172 greater" is critical, as even for initial molar ratios $[\text{HF}] : B_T = 4 : 1$, nearly 4 moles of fluorine
 173 per mole of boron may be consumed, if a large fraction of BF_4^- is formed during the reaction
 174 (see discussion in [Wamser, 1948, 1951](#)). Hence without a substantial $[\text{HF}]$ excess over B_T , the
 175 rate may slow down significantly in the course of the reaction as $[\text{HF}]$ drops. Note that in
 176 such cases, the final equilibrium extent of hydrolysis and product/reactant ratio (Eq. (12)) is
 177 given by the final, not initial, $[\text{HF}]$ (cf. Table V, [Wamser, 1948](#)).

178 With the above assumptions, the characteristic (e-folding) time τ for the reaction may be
 179 calculated as (Appendix B):

$$\tau = (k_1[\text{HF}] + k_2)^{-1}. \quad (17)$$

180 Using k_1 and k_2 values derived from [Wamser \(1948, 1951\)](#) (Eqs. (15) and (16)), the calculated
 181 time for 99% equilibration ($t_{99\%} = -\ln(0.01) \times \tau$) is less than ~ 1 min for $[\text{HF}] > 0.01$ M

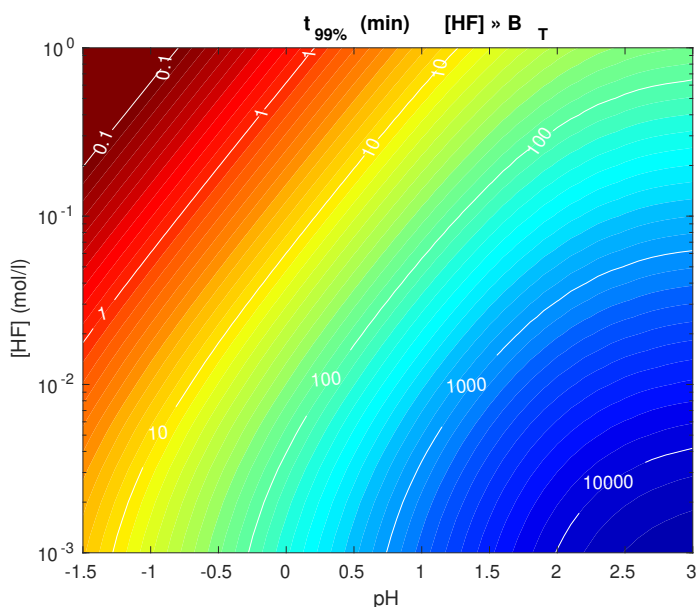


Figure 3. Calculated time for 99% equilibration of reaction (13) at 25°C, assuming [HF] to be much greater than the total boron concentration B_T (see text).

182 and $[H^+] > 1$ M due to acid catalysis (Fig. 3). However, $t_{99\%}$ increases dramatically to over
 183 10,000 min (167 h) at low [HF] and $pH > 2$. Thus, the equilibration time is very sensitive
 184 to [HF] and pH . We note, however, that the specific numbers presented here should be
 185 taken with caution due to the limited available experimental studies on the subject and the
 186 disagreement between them (discussed above).

187 4 Isotopic Equilibrium: Theory

188 Isotopic fractionation factors in thermodynamic equilibrium are calculated from first
 189 principles based on differences in the vibrational energy of molecules. In this study, we
 190 determine fundamental frequencies and molecular forces using quantum-chemical (QC)
 191 computations (e.g. Jensen, 2004; Schauble, 2004; Zeebe, 2005; Guo et al., 2009; Rustad et al.,
 192 2010; Zeebe, 2014). Fractionation factors were calculated from reduced partition function

193 ratios (Urey, 1947):

$$\left(\frac{Q'}{Q}\right)_r = \frac{s}{s'} \prod_i \frac{u'_i}{u_i} \frac{\exp(-u'_i/2)}{\exp(-u_i/2)} \frac{1 - \exp(-u_i)}{1 - \exp(-u'_i)}, \quad (18)$$

194 with s and s' being symmetry numbers, $u_i = hc\omega_i/kT$ and $u'_i = hc\omega'_i/kT$ where h is Planck's
 195 constant, c is the speed of light, k is Boltzmann's constant, T is temperature in Kelvin, and ω_i
 196 and ω'_i are the frequencies of the isotopic molecules or the solute-water clusters. Note that
 197 Eq. (18) is based on the harmonic approximation and hence requires harmonic ω 's as input
 198 (see discussion in Zeebe (2005)), which we calculate here using QC calculations. In contrast,
 199 observed ω 's include anharmonicity but will nevertheless be compared to harmonic ω 's (see
 200 Section 5.1). In the present case, errors introduced by anharmonicity (e.g., Zeebe, 2005) are
 201 likely much smaller than those due to different QC methods (see below). The theoretical
 202 calculations yield β -factors, which, for a compound A is given by:

$$\beta_A = \left(\frac{Q'_A}{Q_A}\right)^{\frac{1}{k}}, \quad (19)$$

203 where k is the number of atoms being exchanged ($k = 1$ for boron in the compounds
 204 considered here). Finally, the fractionation factor α between two compounds A and B is given
 205 by:

$$\alpha_{(A-B)} = \frac{\beta_A}{\beta_B}.$$

206 4.1 Quantum-chemical computations

207 We used the quantum-chemical software package GAMESS, Sep-2018-R3 (Gordon and
 208 Schmidt, 2005) and different computational methods (differing in level of theory, LoT, and
 209 basis sets) to determine geometries and frequencies of key compounds in the boric acid
 210 – hydrofluoric acid system (Fig. 1). A very basic but fast method (HF/6-31G(d), HFb for

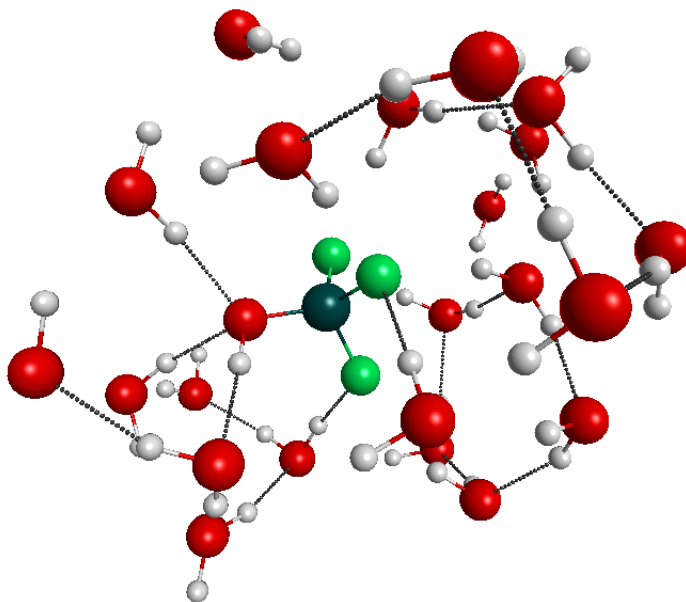


Figure 4. Solute-water cluster example. Optimized geometry of a hydrated $\text{BF}_3(\text{OH})^-$ ion including 22 water molecules (C_1 symmetry) based on X3LYP/6-311+G(d,p) calculated with GAMESS (Gordon and Schmidt, 2005). Dark-green: boron, light-green: fluorine, red: oxygen, white: hydrogen. Dotted lines indicate hydrogen bonds.

211 short) was used for initial guesses and pre-optimization (for methods, see e.g., Jensen, 2004;
212 Gordon and Schmidt, 2005). However, α 's and β -factors obtained with HFb should be taken
213 with caution because the method has limited accuracy. The density functional theory (DFT)
214 method X3LYP/6-311+G(d,p) (X3LYP+) was employed for higher level optimizations and large
215 solute-water clusters with up to $n = 22$ water molecules (Fig. 4). Computations with the most
216 complete basis sets tested here were performed with MP2/aug-cc-pVDZ and MP2/aug-cc-pVTZ
217 (MP2DZ, MP2TZ), which are however computationally expensive and mostly impractical for
218 large solute-water clusters.

219 We selected the methods HFb, X3LYP+, and MP2TZ because they are frequently used
220 in QC computations and similar LoT and basis sets have been applied to boron isotope
221 calculations previously (e.g. Oi, 2000; Zeebe, 2005; Liu and Tossell, 2005; Rustad et al., 2010).

222 Also, X3LYP+ and MP2TZ yield values for $\alpha_{(\text{B}(\text{OH})_3-\text{B}(\text{OH})_4^-)}$ that cluster around the upper and
223 lower end of the spectrum (Rustad et al., 2010). However, even for isolated (“gas-phase”)
224 molecules (see below), the higher-level DFT and MP2 methods differed by up to 5‰ in
225 α 's (Table 2). Given these differences, we refrain from testing further QC methods, which
226 will unlikely narrow down the range of α values. The selected LoT and basis set therefore
227 represents the largest uncertainty in our calculations, whereas the effect of hydration on the
228 calculated boron isotope fractionation turned out to be less significant in most cases (see
229 below).

230 For HFb and MP2DZ frequencies, scale factors of $s = 0.92$ and 1.03 were applied, whereas
231 unscaled frequencies were used from X3LYP+ and MP2TZ computations. The scale factors
232 applied here are close to those obtained from general low-frequency fits to >1,000 observed
233 frequencies and are consistent with scale factors from our previous work on boron, carbon,
234 and oxygen isotopes (Scott and Radom, 1996; Merrick et al., 2007; Zeebe, 2005, 2014). For all
235 molecules and solute-water clusters studied here (see Figs. 1 and 4), geometry optimizations
236 were followed by full Hessian (force-constant matrix) runs to determine frequencies and to
237 ensure that none of the calculated frequencies was imaginary (geometrically unstable, e.g.,
238 HBF_4 at C_{2v} symmetry, see Fig. 1).

239 As mentioned above, the notations $\text{BF}_3(\text{H}_2\text{O})$ and $\text{HBF}_3(\text{OH})$ are used synonymously
240 here (see Fig. 1). Note that initial geometries in which one hydrogen was positioned near any
241 of the three F atoms quickly evolved into separate $\text{BF}_2(\text{OH})^-$ and HF structures. This was the
242 case for the isolated $\text{HBF}_3(\text{OH})$ molecule, as well as for a hydrated unit including $n = 6$ water
243 molecules. The B-O distance, which is large in $\text{BF}_3(\text{H}_2\text{O})$ (~ 1.84 Å, Fig. 1), is substantially
244 smaller in the $\text{BF}_3(\text{H}_2\text{O}) \cdot (\text{H}_2\text{O})_6$ cluster (~ 1.54 Å) (both at X3LYP/6-311+G(d,p) level).

245

246 4.2 Uncertainties in computed α 's

247 The range in the computed fractionation factors from the higher-level DFT and MP2
248 methods is reported here as an uncertainty estimate, as different QC methods yield
249 significantly different values for α (see below). Other approaches have been used in the
250 literature. For instance, propagated uncertainties in the computed frequencies derived for
251 well-studied small molecules have been used as an error estimate for a single QC method
252 (e.g., [Kowalski et al., 2013](#)). This approach is based on the well known tendency of certain
253 methods to systematically under- or overestimate frequencies. However, this is a systematic,
254 not random error (commonly corrected for by a scale factor, see Section 4.1), which says little
255 about the QC method's accuracy when applied to a specific system for which experimental
256 frequencies and α 's are yet lacking. (Note that a QC method's precision for a fixed geometry is
257 undefined as one method yields exactly one set of frequencies and one α value for that case.)
258 Furthermore, it is not uncommon that certain QC methods give large errors in only a few
259 (but critical) frequencies that deviate substantially from errors accounted for by an average
260 frequency scaling. Also, the computed α value and its error for a given method is sensitive to
261 the calculated frequency *shift* upon isotopic substitution, which is not necessarily related to
262 the average error in absolute frequency for that method.

263 Alternatively, by averaging results from different QC methods, a "theoretical mean" α has
264 been calculated to report its $\pm 1\sigma$ standard deviation as error (e.g., [Li et al., 2020](#)). However, it
265 is important to realize that selected QC methods and their numerical results do not represent
266 a set whose statistical sample mean approaches "a true mean value" for large N . Rather,
267 the set of QC methods included in the analysis is an often arbitrary selection made by the

investigator, which inevitably leads to bias (some studies, for example, only include density functional theory methods). Furthermore, it is not clear whether results from methods with known limited accuracy such as HF/6-31G(d) should be included or not, which may be highly problematic in some cases, but inconsequential in others (HF/6-31G(d) fortuitously yields acceptable α values in several cases). For the various reasons outlined above, the uncertainty estimate reported here is given as the range in the computed α from different methods. We include results from the higher-level DFT and MP2 methods and exclude results from HF/6-31G(d).

5 Boron Isotope Partitioning

Given the dominant aqueous species discussed in Section 2, our calculations of boron isotope fractionation factors (α 's) will mainly focus on $\text{B}(\text{OH})_3$, $\text{B}(\text{OH})_4^-$, BF_4^- , and $\text{BF}_3(\text{OH})^-$. Of those compounds, the fractionation between $\text{B}(\text{OH})_3$ and $\text{B}(\text{OH})_4^-$ in aqueous solution has been established theoretically and experimentally and is described elsewhere (e.g. Zeebe, 2005; Liu and Tossell, 2005; Klochko et al., 2006; Rustad et al., 2010; Nir et al., 2015). To provide insight into the systematics of boron fractionation, we also include BF_3 for comparison between $\alpha_{(\text{BF}_3-\text{BF}_4^-)}$ and $\alpha_{(\text{B}(\text{OH})_3-\text{B}(\text{OH})_4^-)}$ (α_{BF34} and α_{34} for short), and HBF_4 and $\text{HBF}_3(\text{OH})$ to assess the effect of protonation on α 's.

5.1 Gas phase estimates

It is instructive to consider first quantum-chemical calculations for isolated (“gas-phase”) molecules to gain an overview of α 's in the boric–hydrofluoric acid system and to examine differences between levels of theory. It turned out that isolated HBF_4 was geometrically unstable at all LoT tested here, i.e., either one calculated frequency was imaginary (C_{2v}

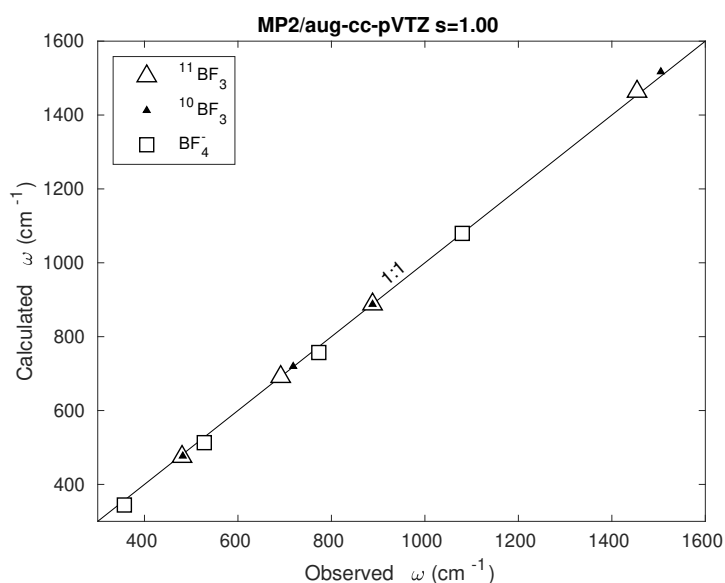


Figure 5. Calculated vs. observed fundamental frequencies of BF_3 and BF_4^- (Vanderryn, 1959; Nakane and Ōyama, 1966; Bates et al., 1971). Calculated ω 's obtained at MP2/aug-cc-pVTZ level are unscaled ($s = 1.0$).

290 symmetry, Fig. 1), or the geometry optimization led to $\text{BF}_3 + \text{HF}$, suggesting that HBF_4
 291 should not exist in the gas phase (Fărcasiu and Hâncu, 1997; Otto, 1999). Starting with
 292 HBF_4 in C_{2v} symmetry, adding two H_2O molecules ($\text{HBF}_4 \cdot (\text{H}_2\text{O})_2$), and then removing all
 293 symmetry restrictions in the calculation (C_1), led to disintegration into a $\text{BF}_3 - \text{FH} - (\text{H}_2\text{O})_2$
 294 configuration, in which BF_3 was slightly non-planar (tested with HF/6-31G(d)). An alternative
 295 configuration (C_1) that resembled $\text{BF}_4^- - \text{H}_3\text{O}^+ - \text{H}_2\text{O}$ was geometrically stable at all LoT
 296 tested here.

297 The calculated fundamental molecular frequencies (ω 's) and their shift upon isotopic
 298 substitution are key to evaluate Eq. (18). Measured ω 's are available, e.g., for BF_3 (Vanderryn,
 299 1959; Nakane and Ōyama, 1966) and BF_4^- from NaBF_4 in aqueous solution (Bates et al., 1971)
 300 and can be compared to calculated frequencies from our quantum-chemical computations
 301 (Fig. 5). The match is quite good at the highest LoT tested here (MP2/aug-cc-pVTZ) — the

302 calculated ω 's line up close to the 1:1 line without scaling (scale factor $s = 1$). At a basic
303 LoT (HF/6-31G(d)) the asymmetric stretch in BF_3 at $\sim 1450 \text{ cm}^{-1}$ falls slightly below the 1:1
304 line, while the asymmetric stretch in BF_4^- at $\sim 1100 \text{ cm}^{-1}$ falls above the 1:1 line ($s = 0.92$,
305 not shown). As a result, the β -factors of BF_3 and BF_4^- are probably too small and too large,
306 respectively, and hence $\alpha_{\text{BF}_3\text{F}_4}$ at HF/6-31G(d) is likely underestimated (Fig. 6, Table 2, see
307 [Electronic Annex](#)).

308 Despite differences between LoT and basis sets, a few patterns emerge from our
309 calculations that appear robust. First, all B-F compounds considered are enriched in ^{11}B
310 relative to $\text{B}(\text{OH})_4^-$ (Fig. 6). Second, BF_3 and BF_4^- are isotopically heavier than $\text{B}(\text{OH})_3$ and
311 $\text{B}(\text{OH})_4^-$, respectively, indicating that boron is more strongly bound in the B-F than the B-OH
312 compounds, given the pairwise similar molecular geometries (D_{3h} vs. C_{3h} and T_d vs. S_4
313 symmetry). The order of ^{11}B enrichment may have been expected from bond strength and
314 bond length (d) of B-F vs. B-O in these compounds (e.g., $d_{\text{B-F}} \simeq 1.31 \text{ \AA}$ in BF_3 , $d_{\text{B-O}} \simeq 1.37 \text{ \AA}$
315 in $\text{B}(\text{OH})_3$). Furthermore, the β -factor of $\text{BF}_3(\text{OH})^-$ falls below or close to that of BF_4^- and the
316 effect of protonation is small (compare, e.g., fractionation between $\text{BF}_3(\text{OH})^-$ and $\text{HBF}_3(\text{OH})$,
317 see Fig. 6).

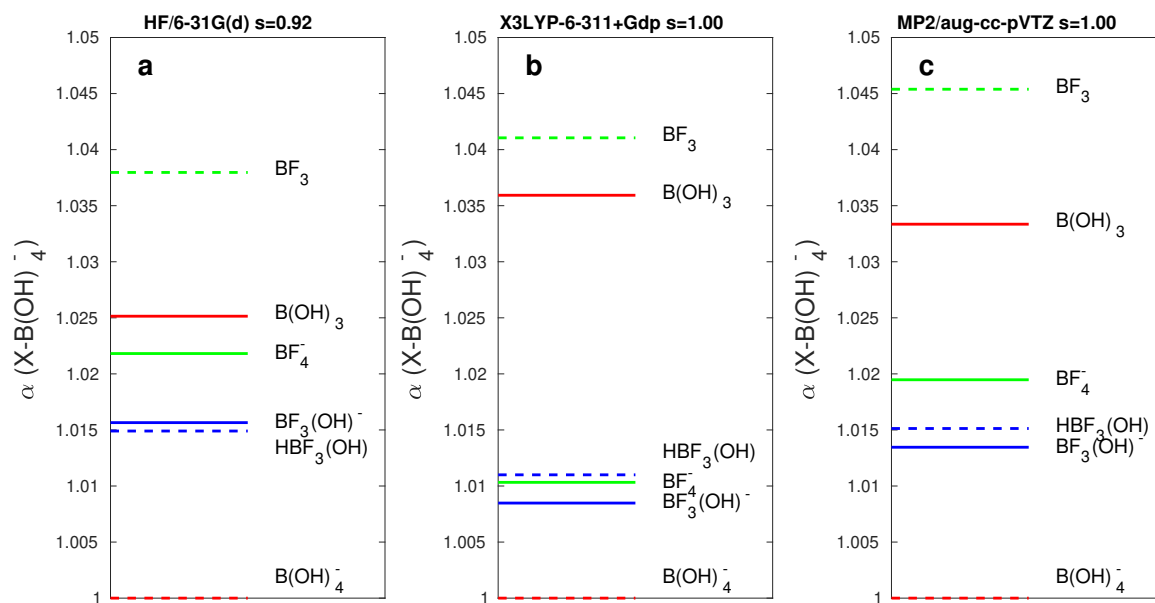


Figure 6. Calculated stable boron isotope fractionation of selected compounds in the boric acid – hydrofluoric acid system at 25°C relative to B(OH)_4^- . The level of theory and size of the basis set increase from a to c.

Table 2. Calculated gas phase β -factors and α 's at 25°C (see [Electronic Annex](#)). ^a

	HFb	X3LYP+	MP2TZ
	β		
B(OH) ₃	1.2313	1.2340	1.2363
B(OH) ₄ ⁻	1.2011	1.1913	1.1964
BF ₃	1.2467	1.2401	1.2507
BF ₄ ⁻	1.2273	1.2035	1.2197
BF ₃ (OH) ⁻	1.2199	1.2013	1.2125
HBF ₃ (OH) ^b	1.2190	1.2043	1.2145
HBF ₄	I^c	I	I
BF(OH) ₃ ⁻			1.2002
BF ₂ (OH) ₂ ⁻			1.2057
	α		
α_{34}	1.0252	1.0358	1.0333
α_{BF34}	1.0158	1.0304	1.0254

^aHFb = HF/6-31G(d), X3LYP+ = X3LYP/6-311+G(d,p), MP2TZ = MP2/aug-cc-pVTZ with scale factors $s = [0.92 \ 1.00 \ 1.00]$.

^bHBF₃(OH) = BF₃(H₂O).

^c**I** = one ω imaginary (geometrically unstable, see text).

318 The details of the calculated β -factors and α 's depend, however, on the LoT and basis
319 sets used (see Fig. 6 and Table 2). For instance, the order of boron isotope enrichment in
320 $\text{HBF}_3(\text{OH})$ vs. $\text{BF}_3(\text{OH})^-$ is reversed for HFb, compared to X3LYP+ and MP2TZ (Fig. 6).
321 Considering only the higher-level DFT and MP2 methods, BF_4^- is enriched in ^{11}B relative to
322 $\text{B}(\text{OH})_4^-$ by $\sim 10\%$ for X3LYP+ but by $\sim 20\%$ for MP2TZ, respectively. The two methods differ
323 by 5% in $\alpha_{(\text{BF}_3-\text{BF}_4^-)}$ (see Table 2). Selection of the QC method (level of theory and basis set)
324 thus represents the largest uncertainty in our isotope calculations for most compounds (cf.
325 Section 5.2).

326 5.2 Solute-water clusters

327 We also performed geometry optimizations and Hessian (force-constant matrix) runs for
328 large solute-water clusters with up to $n = 22$ water molecules using the density functional
329 theory (DFT) method X3LYP/6-311+G(d,p) (X3LYP+) (cf. Fig. 4). MP2/aug-cc-pVDZ and
330 MP2/aug-cc-pVTZ (MP2DZ and MP2TZ) are computationally too expensive and mostly
331 impractical for large solute-water clusters (we tested MP2DZ for $n \leq 6$). It turned out that
332 the effect of hydration on the calculated β -factors for boron isotope exchange is minor in
333 most cases, except for BF_4^- and $\text{B}(\text{OH})_3$ (Fig. 7). For instance, the hydration effect reduces
334 $\alpha_{(\text{B}(\text{OH})_3-\text{B}(\text{OH})_4^-)}$ by $\sim 6\%$ at 25°C as n increases from 0 to 20 for X3LYP+ (included in our
335 calculations on temperature dependence, see Section 5.4). However, the effect of hydration
336 is much smaller in most other cases and, importantly, less significant for MP2DZ than for
337 X3LYP+ (Fig. 7), suggesting that our "gas-phase" estimates from MP2TZ are reasonable
338 approximations to boron isotope fractionation in aqueous solution in most cases (Table 2).
339 Clearly, the overall uncertainties introduced by different QC methods (Fig. 6) are substantially
340 larger than those resulting from hydration, except for BF_4^- and $\text{B}(\text{OH})_3$ at X3LYP+ (Fig. 7).

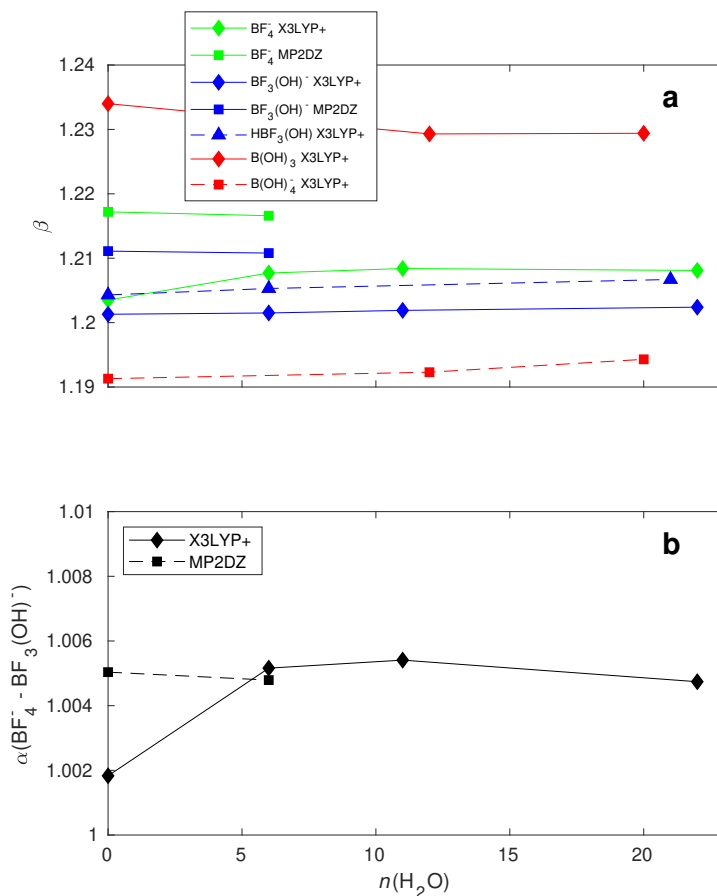


Figure 7. Selected β -factors and $\alpha_{(\text{BF}_4^- - \text{BF}_3(\text{OH})^-)}$ from computations including solute-water clusters with up to $n = 22$ water molecules.

341 5.3 Boron isotope partitioning vs. pH

342 Given the calculated fractionation factors (α 's) between the various compounds (e.g.,
 343 Table 2) and the speciation vs. $p\text{H}$ (Fig. 2), the boron isotope partitioning in the boric acid
 344 – hydrofluoric acid system as a function of $p\text{H}$ can be calculated. The correct mass balance
 345 calculation uses fractional abundances rather than isotope ratios, R 's (e.g., Hayes, 1982).
 346 However, the difference is at most 0.15‰ in the present case (see Appendix C). Using R 's, a

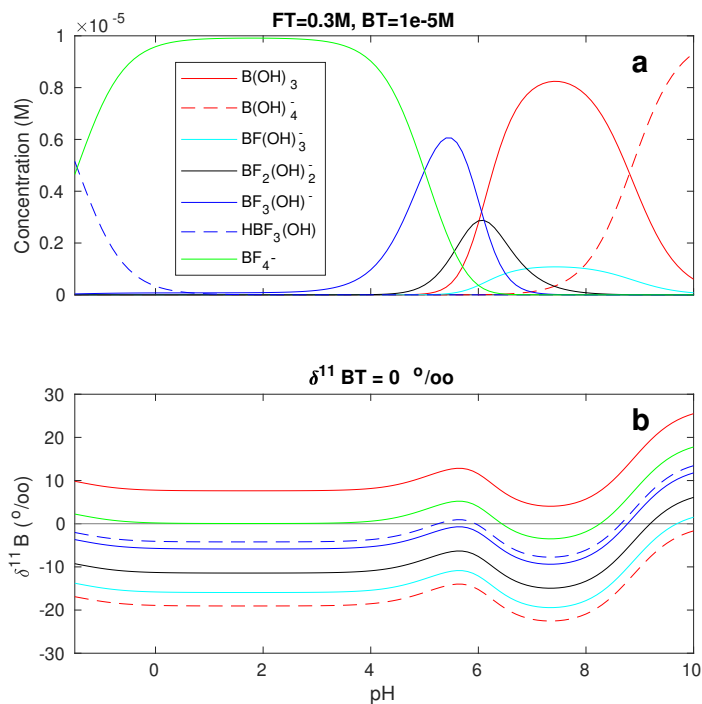


Figure 8. Speciation and boron isotope partitioning in the boric acid – hydrofluoric acid system at 25°C. (a) Note that [HBF₃(OH)] is uncertain as only estimated values for pK'_3 are available. (b) The boron isotope composition of total boron (B_T) in the system was set to $\delta^{11}\text{B}_T = 0\text{‰}$.

347 general isotope mass balance at any given pH may be written as:

$$R_T X_T = \sum R_i c_i, \quad (20)$$

348 where index T refers to 'Total', and X_T and c_i are the total inventory and individual

349 concentrations of compounds containing element X , respectively. If we express all α 's relative

350 to a single compound A , we can write $R_i = \alpha_i R_A$. Then,

$$R_T X_T = R_A \sum \alpha_i c_i, \quad (21)$$

351 which can be solved for R_A :

$$R_A = R_T X_T / \sum \alpha_i c_i. \quad (22)$$

352 All remaining R 's are calculated from $R_i = \alpha_i R_A$. These expressions were evaluated at 25°C
 353 using MP2TZ-calculated values for most α 's (Table 2), the experimental α_{34} (Klochko et al.,
 354 2006), and $\delta^{11}\text{B}_T = 0\text{‰}$ (Fig. 8). The β -factors of $\text{BF}(\text{OH})_3^-$ and $\text{BF}_2(\text{OH})_2^-$ at MP2TZ level
 355 were calculated as 1.2002 and 1.2057 (Table 2). The concentrations of the protonated forms
 356 $\text{HBF}(\text{OH})_3$, etc., are very small and make virtually no difference, except for $\text{HBF}_3(\text{OH})$ at
 357 very low $p\text{H}$. The β -factors of the protonated forms were taken equal to the corresponding
 358 non-protonated forms. As expected, over the $p\text{H}$ range where BF_4^- dominates, the $\delta^{11}\text{B}$ of BF_4^-
 359 is close to $\delta^{11}\text{B}_T = 0\text{‰}$. The boron isotope partitioning only shifts above $p\text{H} \simeq 4$, first towards
 360 $\text{BF}_3(\text{OH})^-$, then $\text{B}(\text{OH})_3$, and finally $\text{B}(\text{OH})_4^-$, having respective $\delta^{11}\text{B}$ values close to $\delta^{11}\text{B}_T$
 361 (Fig. 8).

362 5.4 Effect of temperature

363 Given that the effect of hydration on boron fractionation for most B-F compounds is
 364 small relative to the effect of different LoT (Fig. 7), we calculated the temperature dependence
 365 of $\alpha_{(\text{BF}_3-\text{BF}_4^-)}$ based on isolated molecules at the highest LoT tested here (MP2/aug-cc-pVTZ,
 366 Fig. 9). For $\alpha_{(\text{B}(\text{OH})_3-\text{B}(\text{OH})_4^-)} = \alpha_{34}$ we use results from our X3LYP/6-311+G(d,p) calculations
 367 of solute-water clusters with $n = 20$. We also include an α_{34}^* , which uses the measured α_{34}
 368 seawater value at 25°C (Klochko et al., 2006) and an estimated temperature dependence based
 369 on the slope of our calculated α_{34} scaled by the ratio $\alpha_{34}^*/\alpha_{34}$ at 25°C (Fig. 7). From 0 to 40°C,
 370 the calculated α 's are very nearly linear vs. temperature for which we provide a fit of the form:

$$\varepsilon = (\alpha - 1)10^3 = \varepsilon_{25} + \lambda \cdot (T_C - 25), \quad (23)$$

371 where T_C is temperature in °C. From 0 to 300°C, we use a fit of the form:

$$\varepsilon = a + b/T + c/T^2, \quad (24)$$

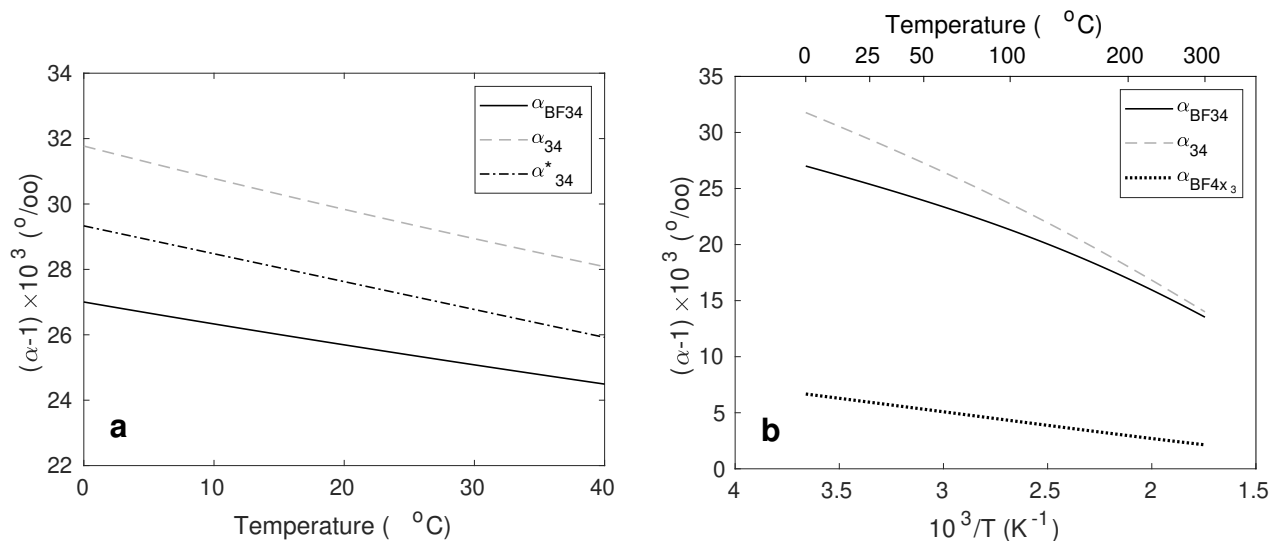


Figure 9. Temperature dependence of α 's. $\alpha_{\text{BF}_3\text{4}} = \alpha_{(\text{BF}_3-\text{BF}_4^-)}$ at MP2/aug-cc-pVTZ level; $\alpha_{34} = \alpha_{(\text{B}(\text{OH})_3-\text{B}(\text{OH})_4^-)}$ from X3LYP/6-311+G(d,p) calculations of solute-water clusters with $n = 20$. (a) α_{34}^* uses the measured α_{34} seawater value at 25°C (Klochko et al., 2006) and the slope of the calculated α_{34} (dashed line) scaled by the ratio $\alpha_{34}^*/\alpha_{34}$ at 25°C. (b) $\alpha_{\text{BF}_4\text{x}_3} = \alpha_{(\text{BF}_4^--\text{BF}_3(\text{OH})^-)}$.

372 where T is temperature in Kelvin (for fit coefficients, see Table 3). The maximum errors of our
 373 fits are less than $\sim 0.15\%$.

Table 3. Coefficients for temperature fits Eqs. (23) and (24).

	ε_{25}	λ	a	$b \times 10^{-3}$	$c \times 10^{-6}$	Notes
$\alpha_{(\text{BF}_3-\text{BF}_4^-)}$	25.4	-0.0627	-7.3143	14.3867	-1.3806	‡
$\alpha_{(\text{B}(\text{OH})_3-\text{B}(\text{OH})_4^-)}$	29.4	-0.0921	-8.9720	15.0475	-1.0757	#
$\alpha_{(\text{B}(\text{OH})_3-\text{B}(\text{OH})_4^-)}^*$	27.2	-0.0852				&

‡MP2/aug-cc-pVTZ.

#X3LYP/6-311+G(d,p), $n = 20$.

&See text.

374 6 Best Practice in Boron Analyses with HF Addition

375 Recently, it has been shown that addition of hydrofluoric acid can improve washout
376 times of boron in the introduction systems of (MC-)ICPMS instruments (Misra et al., 2014b;
377 Rae et al., 2018; He et al., 2019). Slow washout of boron results from the volatility of $B(OH)_3$
378 (Brenner and Cheatham, 1998), which can be entrained from droplets coating the walls of
379 ICPMS spray chambers (Al-Ammar et al., 1999), leading to persistence of up to 50% of the
380 initial signal after ~ 5 min of wash, and associated memory effects between samples and
381 standards.

382 Previously, addition of ammonia gas to the spray chamber has been used to help
383 combat this issue, leading to improved signal memory of 2% after ~ 3 min wash (Al-Ammar
384 et al., 2000; Foster, 2008). This result can be explained by conversion of volatile boric acid
385 to non-volatile borate ion at elevated pH. Notably, as samples, standards, and blanks are
386 introduced in 0.5 M HNO_3 , and as the ~ 3 ml min^{-1} NH_3 gas flux is diluted in the spray
387 chamber by ~ 1 l min^{-1} Ar, the bulk solution in the spray chamber remains acidic ($pH < 1$
388 when tested). We therefore suggest that the suppression of boron volatility caused by NH_3
389 addition results from pronounced elevation of pH (to greater than the boric acid $pK \simeq 9$) on
390 the surface layer (and perhaps in the aqueous diffusion boundary layer) of otherwise acidic
391 droplets.

392 Addition of HF offers an alternative method of improving boron washout. This was
393 first noted by Makishima et al. (1997) and studied in more detail by Misra et al. (2014b,a);
394 Rae et al. (2018); He et al. (2019). The examination of boron partitioning here allows us to
395 provide further insights into best practice in boron analysis in an HF matrix. Avoiding the
396 presence of volatile $B(OH)_3$ requires that all boric acid is converted to fluoroboric species.

397 This requires an excess of F^- ions over total boron, which is found with a combination of low
398 pH, high total fluorine, and low total boron (Fig. 2). Boron is typically analyzed at sub-ppm
399 concentrations in geochemistry, so overly high boron concentrations are unlikely to present
400 an issue (cf. Fig. 2c). However, relatively high total concentrations of HF are needed to ensure
401 complete consumption of $B(OH)_3$ (Fig. 2b). This is a function of HF's pK (~ 3), which means
402 that at $pH = 1$, only $\sim 1\%$ of total fluorine is present as free F^- (Eq. (10)). Low pH (< 5) is also
403 required (Fig. 2a), which is typical in geochemical analyses, and cautions against attempting
404 to use HF and NH_3 in combination to reduce boron washout.

405 The kinetics of $B(OH)_3$ reaction with HF are generally fast, except for the formation of the
406 final product, BF_4^- (reaction (13)). As a result, volatile $B(OH)_3$ may still be present in solutions
407 to which HF has recently been added. As well as reducing the efficiency of the washout,
408 this has the potential to impart isotopic fractionation, via preferential loss of the isotopically
409 heavy trigonal $B(OH)_3$. To avoid this, solutions should have HF added in advance of analysis
410 depending on pH and $[HF]$ (see Fig. 3). Slow conversion to BF_4^- may also limit the efficiency
411 of washout if HF is used only as a rinse solution rather than being added to the analytes.

412 The current procedure in the STAiG laboratory at the University of St Andrews is to run
413 MC-ICPMS boron isotope analyses in 0.5 M HNO_3 + 0.3 M HF (see Rae et al., 2018). This
414 matrix is used for all solutions — standards, samples, and blanks — and results in washout
415 to $\sim 0.5\%$ in 3 minutes (cf. $\sim 3\%$ when using NH_3 gas). Samples, initially in 0.5 M HNO_3
416 following chemical purification, are “spiked” with a small volume of concentrated HF (to
417 avoid dilution) about 1/2 hour prior to analysis (the estimated 99% equilibration time at
418 this pH and HF content is ~ 10 minutes, see Fig. 3). Maintaining a constant matrix for all
419 solutions in the run is generally desirable to avoid differences in mass bias or background

420 contamination, though we note that solutions of the standard NIST 951 run as test samples
421 with HF concentrations ranging from 0 to 0.5 M show no systematic differences. For analysis
422 of trace boron concentrations, however, we use HF only in the wash solution. We do
423 not add HF to our trace element samples, despite the potential further improvement in
424 washout, due to the lower overall boron concentrations, higher throughput of samples, risk
425 of contamination of other elements, and reduced contribution of boron washout to precision.
426 Also note that HF should not be added to samples that are to be separated by ion exchange
427 chromatography with Amberlite 743, as BF_4^- does not interact well with this resin.

428 Alongside the improved washout, use of HF also has advantages over NH_3 in terms of
429 machine sensitivity, avoiding a signal decrease of $\sim 10\text{-}20\%$ with NH_3 , and stability and run
430 times, avoiding build-up of ammonium nitrate salts in the injector. The main drawback of HF
431 use is the safety hazard, requiring careful operating procedures (for instance use of neoprene
432 rather than nitrile gloves), though note that a 0.3 M solution is equivalent to a $\sim 1\%$ dilution,
433 considerably less hazardous than fully concentrated HF (29 M). Hydrofluoric acid use also
434 requires an “inert” sample introduction kit, including self-aspirating Teflon nebulizers, Teflon
435 spray chambers, and sapphire injectors.

436 7 Summary and Conclusions

437 In the present study, we have examined the equilibria and kinetics in the aqueous
438 boric acid – hydrofluoric acid system using available experimental data. We have presented
439 the first quantum-chemical computations to determine boron isotope fractionation in the
440 fluoroboric acid system and have provided suggestions on best practice in the application of
441 HF in experimental boron analyses. Our results show that at low $p\text{H}$ ($0 \leq p\text{H} \leq 4$) and for
442 total fluorine (F_T) much greater than total boron (B_T), the dominant aqueous species is BF_4^- .

443 Our estimated time for 99% equilibration ($t_{99\%}$) of the slowest reaction in the system (forming
444 BF_4^-) is less than ~ 1 min at constant $[\text{HF}] > 0.01$ M and $[\text{H}^+] > 1$ M, assuming $F_T \gg B_T$.
445 However, $t_{99\%}$ increases dramatically to over 167 h at low $[\text{HF}]$ and $p\text{H} > 2$, suggesting
446 that the equilibration time is very sensitive to $[\text{HF}]$ and $p\text{H}$. Our quantum-chemical (QC)
447 computations suggest that the equilibrium boron isotope fractionation between BF_3 and BF_4^-
448 is slightly smaller than that calculated between $\text{B}(\text{OH})_3$ and $\text{B}(\text{OH})_4^-$. Yet, BF_4^- is enriched
449 in ^{11}B relative to $\text{B}(\text{OH})_4^-$ in all our calculations ($\alpha_{(\text{BF}_4^- - \text{B}(\text{OH})_4^-)} > 1.0$), regardless of the QC
450 method tested. Unfortunately, even considering only the higher-level QC methods tested, the
451 calculated α values differ by $\sim 10\%$ in $\alpha_{(\text{BF}_4^- - \text{B}(\text{OH})_4^-)}$ and by $\sim 5\%$ in $\alpha_{(\text{BF}_3 - \text{BF}_4^-)}$. Selection of
452 the QC method (level of theory and basis set) thus represents the largest uncertainty in our
453 isotope calculations for most compounds. The effect of hydration on the calculated boron
454 isotope fractionation is much smaller in most cases, except for BF_4^- and $\text{B}(\text{OH})_3$ computed
455 with the density functional theory method X3LYP/6-311+G(d,p).

456
457 The results of our study should be helpful for implementing and advancing geochemical
458 applications in high precision analyses of boron concentration and isotopic composition. One
459 specific application is the addition of hydrofluoric acid to boron samples, which has recently
460 been shown to improve washout times of boron in the introduction systems of (MC-)ICPMS
461 instruments. However, beyond geochemical applications, our study should serve as a
462 general resource for a variety of studies dealing with equilibria, kinetics, and boron isotope
463 fractionation in the aqueous boric acid – hydrofluoric acid system, including applications in
464 physical chemistry, polymer science, sandstone acidizing, and more.

465 **Acknowledgments.** To be added.

466 **Appendix A: Equilibrium speciation**

467 To simplify the calculations, we use in the following $x_i = [\text{BF}_i(\text{OH})_{4-i}^-]$,
 468 $y_i = [\text{HBF}_i(\text{OH})_{4-i}]$ ($i = 1, \dots, 4$), $b_3 = [\text{B}(\text{OH})_3]$, $b_4 = [\text{B}(\text{OH})_4^-]$, $f = [\text{F}^-]$, $g = [\text{HF}]$,
 469 $h = [\text{H}^+]$, and $L_i = 1/K_i'$. Using equilibrium relationships (see Section 2), we can thus write:
 470 $y_i = x_i h L_i$, $g = f h L_F$, and $b_4 = b_3 K_B/h$. Given pH, total boron (B_T) and total fluorine (F_T), the
 471 mass balance equations read:

$$B_T = b_3(1 + K_B/h) + \sum x_i(1 + hL_i) \quad (\text{A1})$$

$$F_T = f(1 + hL_F) + \sum i x_i(1 + hL_i), \quad (\text{A2})$$

472 in which we substitute x_i 's using K_i 's (Eqs. (5) and (6)):

$$B_T = b_3 [1 + K_B/h + \sum a_i(1 + hL_i)f^i] \quad (\text{A3})$$

$$F_T = f(1 + hL_F) + b_3 \sum i a_i(1 + hL_i)f^i, \quad (\text{A4})$$

473 with $a_1 = K_1$, $a_2 = K_2 h$, $a_3 = K_3 h^2$, $a_4 = K_4 h^3$, and eliminate b_3 :

$$B_T \sum i a_i(1 + hL_i)f^i = [F_T - f(1 + hL_F)][1 + K_B/h + \sum a_i(1 + hL_i)f^i]. \quad (\text{A5})$$

474 This expression can be solved numerically for f at given pH. b_3 can now be obtained from

475 Eq. (A3), all x_i determined from Eqs. (5) and (6), and all y_i from $y_i = x_i h L_i$.

476 **Appendix B: Analytical solution of kinetic rate equation**

477 The kinetic rate equation (14):

$$\frac{d[\text{BF}_4^-]}{dt} = k_1[\text{BF}_3(\text{OH})^-][\text{HF}] - k_2[\text{BF}_4^-] \quad (\text{B6})$$

478 can be solved analytically with some critical assumptions. We assume low pH where

479 $[\text{BF}_3(\text{OH})^-]$ and $[\text{BF}_4^-]$ are the dominant B-F species, hence we set $B_T = [\text{BF}_3(\text{OH})^-] + [\text{BF}_4^-]$.

480 Furthermore, we assume constant $[\text{H}^+]$ and $[\text{HF}]$ during the reaction, which should hold

481 approximately for $F_T \gg B_T$. Then:

$$\frac{d[\text{BF}_4^-]}{dt} = k_1(B_T - [\text{BF}_4^-])[\text{HF}] - k_2[\text{BF}_4^-] \quad (\text{B7})$$

$$= -(k_1[\text{HF}] + k_2)[\text{BF}_4^-] + k_1 B_T [\text{HF}] = -k[\text{BF}_4^-] + \gamma, \quad (\text{B8})$$

482 where $k = (k_1[\text{HF}] + k_2) = \tau^{-1}$ is the overall rate constant (inverse characteristic time scale)

483 and $\gamma = k_1 B_T [\text{HF}]$ is a constant. The solution is:

$$[\text{BF}_4^-](t) = ([\text{BF}_4^-]_0 - \gamma/k) \exp(-kt) + \gamma/k, \quad (\text{B9})$$

484 where index '0' indicates initial $[\text{BF}_4^-]$ at $t = 0$ and $\gamma/k = (k_1 B_T [\text{HF}]) / (k_1 [\text{HF}] + k_2)$ equals

485 $[\text{BF}_4^-]$ in equilibrium, which can be shown using $k_2/k_1 = K_h = [\text{BF}_3(\text{OH})^-]_{eq} [\text{HF}] / [\text{BF}_4^-]_{eq}$,

486 as it should be. Our solution (Eq. (B9)) is similar to Eq. (4) of [Fucskó et al. \(1993\)](#), except

487 that our solution allows for explicitly specifying $[\text{BF}_4^-]_0$. The time evolution is given by the

488 exponential term and hence the characteristic (e-folding) time $\tau = (k_1[\text{HF}] + k_2)^{-1}$.

489 **Appendix C: Isotope mass balance using fractional abundance**

490 The correct isotope mass balance using fractional abundances (r 's) reads (e.g., [Hayes,](#)
491 [1982](#)):

$$r_T X_T = \sum r_i c_i , \quad (\text{C10})$$

492 where index T refers to 'Total', and X_T and c_i are the total inventory and individual
493 concentrations of compounds containing element X , respectively. Using $r_i = R_i / (1 + R_i)$ and
494 expressing all α 's relative to a single compound A , we can write $R_i = \alpha_i R_A$ and thus:

$$r_T X_T = \sum c_i R_i / (1 + R_i) = \sum c_i \alpha_i R_A / (1 + \alpha_i R_A) , \quad (\text{C11})$$

495 which can be solved numerically for R_A . All remaining R 's are calculated from $R_i = \alpha_i R_A$.
496 In the present case, the result only differs from a mass balance using R 's (Eq. [22](#)) by at most
497 0.15‰.

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