Simultaneous Calculation of Chemical and Isotope Equilibria Using the GEOCHEQ_Isotope Software: Oxygen Isotopes

V. B. Polyakov^{a, b, *}, M. V. Mironenko^{a, **, *}, and M. V. Alenina^a

^a Vernadsky Institute of Geochemistry and Analytical Chemistry (GEOKhI), Russian Academy of Sciences, Moscow, 119991 Russia

^b Korzhinskii Institute of Experimental Mineralogy (IEM), Russian Academy of Sciences, Chernogolovka, Moscow oblast, 142432 Russia

*e-mail: vpolyakov@mail.ru

**e-mail: mironenko@geokhi.ru

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Abstract—The GEOCHEQ_Isotope software package, elaborated previously for modeling chemical and carbon isotope equilibria in hydrothermal and hydrogeochemical systems by minimizing the Gibbs energy, is extended to the simultaneous calculation of carbon and oxygen isotopic effects. Similar to what was done for carbon, the β -factor formalism was used to develop algorithms and a database for calculating the isotopic effects of oxygen. According to the developed algorithm, the Gibbs energy of formation of a rare isotopologue, $G^*(P, T)$, is calculated through the Gibbs energy of formation of the main isotopologue, the value of the $\beta^{18}\text{O}$ factor of this substance, and the mass ratio of the rare (^{18}O) and main (^{16}O) isotopes. The isotope mixture is assumed to be ideal. The temperature dependence of the β -factor is unified as a polynomial in reciprocal absolute temperature. Necessary information on oxygen isotope equilibria involving important geochemical compounds was critically analyzed, and the available data were reconciled and modified. The temperature dependences of the $\beta^{18}\text{O}$ -factors were correspondingly optimized. The thermodynamic database was updated by adding information on the temperature dependence of $\beta^{18}\text{O}$ -factors specified by polynomial coefficients for each substance. The usage of the GEOCHEQ_Isotope software package and the corresponding database is demonstrated by modeling the dependence of oxygen and carbon isotope fractionation factors on the acidity of the solution (pH) in a carbonate hydrothermal system. The simulation results are in a good agreement with experimental data available from the literature. The enrichment of dissolved carbonates in the ^{18}O heavy oxygen isotope relative to water decreases with increasing pH of the system. At the same time, a pH increase results in a decrease in the negative carbon isotope shift between calcite and dissolved carbonates. At high pH values (~ 11), the isotope shift inversion and the enrichment of the dissolved carbonate in the heavy carbon isotope relative to calcite are predicted.

Keywords: chemical and isotope equilibria, Gibbs free energy minimization, β -factor, oxygen isotope fractionation, carbon isotope fractionation

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INTRODUCTION

Studies of the isotopic effects of oxygen is of paramount importance in isotope geochemistry. The great majority of isotope geothermometers make use of oxygen isotopes. This paper is devoted to the simultaneous computation of chemical and oxygen isotope equilibria with the GEOCHEQ_Isotope software package. The principal approaches to and methods of calculating oxygen isotopic effects utilized in this study are generally analogous to those we have applied when studying carbon isotopic effects. The first ever simultaneous simulation of chemical and isotope equilibria by minimizing the Gibbs free energy (this method is referred to as the *method of isotope–chemical system*, and its idea was formulated by B.N. Ryzhenko)

was carried out for sulfur isotopes (Bannikova et al., 1987; Grichuk, 1987, 1988, 2000; Grichuk and Lein, 1991). The method enables calculating chemical and isotope equilibria simultaneously, in contrast to the usual approaches (Ohmoto, 1972), in which first chemical and then isotope equilibria are evaluated.

As was pointed out in (Mironenko et al., 2018), one of the main reasons why simultaneous simulations of chemical and isotope equilibria are still used inadequately little is the absence of internally consistent thermodynamic databases on rare isotopologues. One of the tasks of our study is to bridge this gap by developing a database for simulating geochemical processes with regard to oxygen isotopic effects, based on critical analysis of information on isotope equilibria.

APPROACHES AND METHODS

Similar to what has been done in studying carbon isotopic effects (Mironenko et al., 2018), the simulations used herein were conducted with a software package (Mironenko et al., 2020) that utilizes the SUPCRT92 database (Johnson et al., 1992), which has been later updated and corrected. The GEOCHEQ software package minimizes the Gibbs energy by the algorithm of the convex simplex (de Capitani and Brown, 1987). The isotopic effects of an element are calculated within the GEOCHEQ_Isotope extension of the GEOCHEQ software package by using isotopes of the element as independent components (instead of the chemical element as whole), and the list of substances is appended with the corresponding isotopologues (Mironenko et al., 2018). For oxygen, these are ^{16}O and ^{18}O and their isotopologues.

All isotopic effects are computed in GEOCHEQ_Isotope in the approximation of an ideal mixture of isotopes, in which isotope substitutions in different sites do not affect one another, and the isotopic effects are independent of the multiplicity of the isotope substitution. For molecules containing several atoms of a given element, this approximation is commonly formulated as the rule of geometric mean (Galimov, 1973, 1974). The approximation by an ideal mixture is valid for all elements except hydrogen at temperatures above 100 K (Polyakov, 1993). This approximation is deemed to be valid by default in the overwhelming majority of geochemical simulations, if no clumped isotopic effects are computed (Grichuk, 2000; Hill et al., 2014, 2020; Schauble and Young, 2020). Similar to carbon isotopic effects, the calculations in this study were carried out using the formalism of the β -factor. The concept of the β -factor was coined by Ya.M. Varshavskii and S.E. Vaisberg (1957) on the basis of the previously suggested (Bigeleisen and Mayer, 1947) reduced isotopic partition function ratio. However, it was E.M. Galimov (1973, 1974, 1982, 2006) who introduced the concept of the β -factor into the practice of geochemical research. It is convenient to express the β -factor of a substance that contains atoms of the chemical element of interest in equivalent settings in a logarithmic form, in terms of the Gibbs energy

$$\ln \beta = (G(P, T) - G^*(P, T))/zRT - 1.5(m^*/m), \quad (1)$$

where β is the β -factor, G is the Gibbs energy, P is the pressure, T is the temperature, R is the absolute gas constant, z is the multiplicity of the isotope substitution, m is the mass of the isotope, and the heavy isotopes are marked with *. According to this, the equilibrium isotope fractionation factor ($\alpha_{A/B}$) between two substances A and B is equal to the ratio of their β -factors

$$\alpha_{A/B} = \beta_A/\beta_B, \quad (2a)$$

or, in the logarithmic form for the isotope shift ($\Delta_{A/B}$)

$$\Delta_{A/B} \equiv \alpha_{A/B} - 1 \approx \ln \beta_A - \ln \beta_B. \quad (2b)$$

In (2b), $|\beta - 1| \ll 1$.

If atoms of an isotopically substituted element occur in nonequivalent settings, equations (1) and (2a) should be refined. Because natural isotope exchange processes involve all of the isotopologues, one should know how the β -factor of a compound as whole relates to the site-specific β -factors for isotope substitutions in certain nonequivalent positions. The theory of intermolecular isotopic effects developed by E.M. Galimov (1973, 1974, 1981, 1982, 2006) for carbon isotopes is universal and can be applied to the fractionation of oxygen isotopes, because geochemical studies often deal with substances containing several oxygen atoms and some of them are in nonequivalent positions¹. In particular, E.M. Galimov has demonstrated that, in the case of rare isotope substitutions, the β -factor of the compound is generally related to the β -factors of monosubstituted isotopologues (β_i) by the relation (Galimov, 1973, 1981, 1982):

$$\beta \approx \frac{1}{n} \sum_{i=1}^n \beta_i. \quad (3a)$$

Relation (3a) was referred to by E.M. Galimov as the first additivity law (Galimov, 1981; 1982).² It has been later demonstrated that relation (3a) is valid not only at rare isotope substitutions but also when β_i is insignificantly different from unity (Polyakov, 1987; Polyakov and Horita, 2021). Also, the logarithmic form is slightly more precise (Polyakov and Horita, 2021).

$$\ln \beta \approx \frac{1}{n} \sum_{i=1}^n \ln \beta_i; \quad |\ln \beta_i| \approx |\beta_i - 1| \ll 1. \quad (3b)$$

Because the intramolecular effects of oxygen are not computed in this GEOCHEQ_Isotope version, the use of the β -factor of the substance as a whole according to the Eq. (3b) makes it possible to minimize the increase in the database due to introduction of data on the isotopologues of various multiplicity and localization. Hence, in calculating an equilibrium fractionation of oxygen isotopes with the GEOCHEQ_Isotope complex, it is sufficient to consider the ^{18}O isotopologue along with the most abundant ^{16}O one, and a change in the Gibbs energy per one atom of this ^{18}O isotopologue calculated according to (1), analogously to what has been earlier done for the fractionation of $^{13}\text{C}/^{12}\text{C}$ carbon isotopes (Mironenko et al., 2018).

¹ The term *intrastructural isotopic effect* is sometimes used for intramolecular isotopic effects in solids (e.g., Ustinov et al., 1988).

² The second additivity law is the method of the isotopic bond numbers (Galimov, 1973, 1981, 1982).

The oxygen β -factors insignificantly depend on pressure (Polyakov and Kharlashina, 1994), and hence, only their temperature dependences are incorporated into the GEOCHEQ_Isotope software. The temperature dependences of the $\beta^{18}\text{O}$ -factors are presented in the form of polynomials in the reciprocal absolute temperatures, as has been done for the carbon β -factors (Mironenko et al., 2018)

$$10^3 \ln \beta = A_0 + A_1 x^1 + A_2 x^2 + A_3 x^3 + A_4 x^4 + A_5 x^5, \quad (4)$$

where $x = 10^6/T^2$, and A_i is the coefficients of polynomial (4), which are given in Table 1.

Another additions to the computation of chemical and isotope equilibria in system involving the ^{18}O isotope is the following modification of the formulas for the molalities of the solute components in view of the occurrence of the H_2^{18}O isotopologue

$$m_i = \frac{n_i \times 55.51}{(n_{\text{H}_2^{16}\text{O}} + n_{\text{H}_2^{18}\text{O}})}, \quad (5)$$

where m_i is the molality of component i , and n_i is the number of moles of component, and 55.51 is the number of moles corresponding to 1 kg of water.

β -FACTORS IN THE GEOCHEQ_ISOTOPE THERMODYNAMIC DATABASE

Similar to what pertains to the carbon isotopic factors (Mironenko et al., 2018), the accuracy and justification of the calculations of the oxygen isotope equilibria depend, first of all, on the accuracy of data on the β -factors utilized in the GEOCHEQ_Isotope software package. Equilibrium oxygen isotope fractionation factors can be evaluated experimentally and/or theoretically. Equilibrium oxygen isotope fractionation factors are experimentally determined using the Northrop–Clayton partial isotope exchange method (Northrop and Clayton, 1966) and the three-isotope method (Matsuhisa et al., 1978). Oxygen isotope geothermometers are also calibrated using empirical techniques (Clayton et al., 1968; Ustinov et al., 1978; Macey and Harris, 2006). A review of these techniques and their advantages and disadvantages can be found in (Chacko et al., 2001). The theoretical calculations are conducted based on model vibrational spectra (Urey, 1947; Bigeleisen and Mayer, 1947; Kieffer, 1982), the interatomic potential (Patel et al., 1991), and ab initio principles, based on the density functional method (Schauble, 2004; Blanchard et al., 2009; Hill et al., 2014; Krylov et al., 2017; Schauble and Young, 2021). Ab initio computations lately became the most widely used. The oxygen β -factors of many minerals were calculated with the application of the semiempirical method of increments (Schütze H., 1980; Zheng, 1991; 1999), which, in essence, is E.M. Galimov's method of isotopic bond numbers (Galimov, 1973, 1974) extended to crystalline bodies. The latter results

have, however, to be treated with care, because they often come in conflict with both experimental data and theoretical calculations (Horita and Clayton, 2007).

Oxygen Isotope Fractionation Factors in the System $\text{H}_2\text{O}-\text{CO}_2(\text{gas})$ —dissolved Inorganic Carbon

The great majority of experimental determinations of the equilibrium oxygen isotope fractionation factors were conducted with the involvement of H_2O and CO_2 (Chacko et al., 2001), and hence, an accurate choice between the $\beta^{18}\text{O}$ -factors of H_2O and CO_2 is of principal importance for the calibration of the entire set of data on oxygen isotope equilibria.

$\beta^{18}\text{O}$ -factors of H_2O . The oxygen β -factors of water vapor were calculated using various theoretical approaches. The computations on the basis of spectroscopic data and molecular constants were made with regard to the anharmonicity and interaction between oscillations and rotations (Bron et al., 1973; Richet et al., 1977). Recent ab initio computations were carried out based on the density functional (Hill et al., 2014, 2020; Guo and Zhou, 2019; Schauble and Young, 2021). These calculations were conducted using diverse techniques, and their results are in reasonably good mutual agreement. The coefficients of approximating polynomial (4) used in the GEOCHEQ_Isotope software are listed in Table 1. The $\beta^{18}\text{O}$ -factors for liquid H_2O were computed (Table 1) by adding the oxygen values of $\ln \beta$ for water vapor and experimentally determined $\ln \alpha$ values for equilibrium fractionation of oxygen isotopes between liquid H_2O and saturated vapor (Horita and Wesolowski, 1994)

$\beta^{18}\text{O}$ -factors of CO_2 and dissolved inorganic carbon.

The β -factors of CO_2 were computed by analogy with what has been done for water: from spectroscopic data and molecular constants (Richet et al., 1977) and ab initio principles (Hill et al., 2014, 2020; Guo and Zhou, 2019; Schauble and Young, 2021). The data were then used to calculate the coefficients of polynomial (4) for $\text{O}_{2(\text{gas})}$ (Table 1). Also, experimental data are available on the equilibrium oxygen isotope fractionation between $\text{CO}_{2(\text{gas})}$ and $\text{H}_2\text{O}_{(\text{liq})}$ at 25°C , because these values are used in determining water isotope composition. Numerous experiments (see references in Chacko et al., 2001) enabled the IAEA Consultants Group to recommend the value of 1.0412 at 25°C (Hoefs, 2018) as that of equilibrium fractionation coefficient in the system $\text{CO}_{2(\text{gas})}-\text{H}_2\text{O}_{(\text{liq})}$. Estimates are also now available for the temperature ranges of $5-100^\circ\text{C}$ (Brenninkmeijer et al., 1983) and $130-350^\circ\text{C}$ (Truesdell, 1974). Comparison of the equilibrium isotope fractionation factors in the system $\text{CO}_{2(\text{gas})}-\text{H}_2\text{O}_{(\text{liq})}$ calculated using GEOCHEQ_Isotope data (Table 1) and corresponding experimental values are exhibited in Fig. 1; the experimental and calculation data are obviously in reasonably good agreement.

Table 1. Coefficients of the polynomial $10^3 \ln \beta = A_0 + A_1x^1 + A_2x^2 + A_3x^3 + A_4x^4 + A_5x^5$ for the calculation of the temperature function of the carbon β -factors

Species	Coefficients of the polynomial (4) for calculating $\beta^{18}\text{O}$ -factors						References
	$A_5 \times 10^5$	$A_4 \times 10^3$	$A_3 \times 10^2$	A_2	A_1	A_0	
H ₂ O (vapor, supercritical fluid)	9.4061	-4.5191	9.0272	-1.0263	14.2552	0	Bron et al., 1973; Richet et al., 1977; Hill et al., 2014; 2020; Guo and Zhou, 2019; Schauble and Young, 2021
H ₂ O (liquid)	12.5205	-5.9793	11.7997	-1.2802	12.3064	-0.2719	Horita and Wesolowky, 1994
CO ₂ (gas)	12.5770	-5.7152	10.9758	-1.2875	16.6328	0	Richet et al., 1977; Hill et al., 2014, 2020; Guo and Zhou, 2019; Schauble and Young, 2021
HCO ₃ ⁻	7.1964	-3.2198	6.1426	-0.7597	13.3181	0	Guo and Zhou, 2019; Beck et al., 2005
CO ₃ ²⁻	2.3089	-1.1561	2.6730	-0.4529	11.5340	0	Guo and Zhou, 2019; Beck et al., 2006
H ₂ CO ₃	11.0249	-4.8602	8.9747	-1.0256	15.2492	0	Guo and Zhou, 2019; Beck et al., 2007
CO (ra3)	32.1713	-13.5446	23.0002	-2.1794	18.5424	0	Bron et al., 1973; Richet et al., 1977; Schauble and Young, 2021
Ca ₂ CO ₃ ²⁻ ·n(H ₂ O)	2.8385	-1.3560	2.9337	-0.4644	11.5005	0	Hill et al., 2020
Ca ₂ ⁺ HCO ₃ ⁻ ·n(H ₂ O)	12.3083	-5.1550	8.8026	-0.9209	13.7407	0	Hill et al., 2020
Calcite CaCO ₃	2.7471	-1.3188	2.9157	-0.4758	11.9672	0	Hill et al., 2014, 2020; Guo and Zhou, 2019; Schauble and Young, 2021; Cayton and Kieffer, 1991; Chacko and Deines, 2008; Chacko et al., 1991; Polyakov, 2008
Aragonite CaCO ₃	3.1991	-1.5106	3.2486	-0.5083	12.2459	0	Hill et al., 2014; 2020; Guo and Zhou, 2019; Schauble and Young, 2021; Chacko and Deines, 2008;
Vaterite CaCO ₃	3.1214	-1.4835	3.2296	-0.5156	12.5852	0	Chacko and Deines, 2008;
Magnesite MgCO ₃	3.1639	-1.5048	3.2836	-0.5313	13.4051	0	Chacko and Deines, 2008; Schauble and Young, 2021; Hill et al., 2020
Dolomite CaMg(CO ₃) ₂	2.8572	-1.3689	3.0184	-0.4929	12.5339	0	Chacko and Deines, 2008; Schauble and Young, 2021; Hill et al., 2020
Cerrusite PbCO ₃	2.5060	-1.2069	2.6803	-0.4396	11.0728	0	Chacko and Deines, 2008
Ottavite CdCO ₃	2.7787	-1.3355	2.9593	-0.4852	12.2691	0	Chacko and Deines, 2008
Rhodochrosite MnCO ₃	2.7141	-1.3070	2.9055	-0.4726	12.2243	0	Chacko and Deines, 2008
Siderite FeCO ₃	2.9128	-1.3926	3.0607	-0.4956	12.2988	0	Chacko and Deines, 2008
Ankerite CaFe(CO ₃) ₂	2.6661	-1.2873	2.8732	-0.4752	12.0625	0	Chacko and Deines, 2008
Smithsonite ZnCO ₃	2.7726	-1.3354	2.9707	-0.4903	12.4862	0	Chacko and Deines, 2008

Table 1. (Contd.)

Species	Coefficients of the polynomial (4) for calculating $\beta^{18}\text{O}$ -factors						References
	$A_5 \times 10^5$	$A_4 \times 10^3$	$A_3 \times 10^2$	A_2	A_1	A_0	
Strontianite SrCO_3	2.9762	-1.4135	3.0693	-0.4874	11.9085	0	Chacko and Deines, 2008
Witherite BaCO_3	2.7424	-1.3109	2.8769	-0.4638	11.4521	0	Chacko and Deines, 2008
Zabuyelite Li_2CO_3	2.7955	-1.3436	2.9781	-0.4908	12.6321	0	Chacko and Deines, 2008
Natrite Na_2CO_3	2.5863	-1.2479	2.7803	-0.4574	11.4606	0	Chacko and Deines, 2008
α -quartz (SiO_2)	1.7849	-0.9257	2.3197	-0.4453	12.7676	0	Schauble and Young, 2021; Chacko et al., 1996; Clayton and Kieffer, 1991
Albite NaSi_3O_8	1.1491	0.6176	1.6476	-0.3506	11.5927	0	Schauble and Young, 2021; Chacko et al., 1996; Clayton and Kieffer, 1991
Microcline KAlSi_3O_8	1.1595	-0.6234	1.6630	-0.3529	11.5774	0	Schauble and Young, 2021; Chacko et al., 1996; Clayton and Kieffer, 1991
Anorthite $\text{CaAl}_2\text{Si}_2\text{O}_8$	0.7420	-0.4139	1.1781	-0.2782	10.5704	0	Schauble and Young, 2021; Chacko et al., 1996; Clayton and Kieffer, 1991
Diopside $\text{CaMg}(\text{Si}_2\text{O}_6)$	0.5267	-0.3023	0.9010	-0.2289	9.8071	0	Schauble and Young, 2021; Chacko et al., 1996; Clayton and Kieffer, 1991
Jadeite $\text{NaAl}(\text{Si}_2\text{O}_6)$	0.6909	-0.3869	1.1094	-0.2669	10.7115	0	Schauble and Young, 2021
Forsterite Mg_2SiO_4	0.2832	-0.1702	0.5602	-0.1691	8.9993	0	Schauble and Young, 2021; Chacko et al., 1996; Clayton and Kieffer, 1991
Zircon ZrSiO_4	0.4345	-0.2561	0.7951	-0.2128	9.5926	0	Schauble and Young, 2021; Chacko et al., 1996; Clayton and Kieffer, 1991; Polyakov and Kuskov, 1994
Grossular $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_3$	0.2130	-0.1366	0.4841	-0.1581	9.0199	0	Schauble and Young, 2021; Krylov, 2019
Lizardite $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$	14.4778	-5.7486	8.9051	-0.7744	10.9752	0	Schauble and Young, 2021;
Kaolinite $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	14.4249	-5.7581	9.0446	-0.8215	12.3262	0	Schauble and Young, 2021;
Phlogopite $\text{KMg}_3(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2$	5.8428	-2.3759	3.9461	-0.4375	10.3503	0	Schauble and Young, 2021; Chacko et al., 1996; Clayton and Kieffer, 1991
Tremolite $\text{Ca}_2\text{Mg}_5(\text{OH})_2\text{Si}_8\text{O}_{22}$	3.3038	-1.4029	2.5845	-0.3607	10.5184	0	Schauble and Young, 2021; Chacko et al., 1996; Clayton and Kieffer, 1991
Glaucofanane $\text{Na}_2\text{Mg}_3\text{Al}_2(\text{OH})_2\text{Si}_8\text{O}_{22}$	3.4104	-1.4582	2.7186	-0.3837	10.9892	0	Schauble and Young, 2021
Spinel (ordinary) MgAl_2O_4	0.0495	-0.0422	0.2128	-0.1041	8.3127	0	Schauble and Young, 2021
Diaspore $\text{AlO}(\text{OH})$	9.2163	-3.7200	5.9344	-0.5584	10.6488	0	Schauble and Young, 2021
Xenotime YPO_4	0.6862	-0.3844	1.1007	-0.2629	10.3347	0	Schauble and Young, 2021
Xenotime LuPO_4	0.7250	-0.4042	1.1484	-0.2712	10.5328	0	Schauble and Young, 2021

Table 1. (Contd.)

Species	Coefficients of the polynomial (4) for calculating $\beta^{18}\text{O}$ -factors							References
	$A_5 \times 10^5$	$A_4 \times 10^3$	$A_3 \times 10^2$	A_2	A_1	A_0		
Mineralize LaPO_4	0.6350	0.3576	1.0324	-0.2491	9.8310	0	Schauble and Young, 2021	
Fluorapatite $\text{Ca}_5(\text{PO}_4)_3\text{F}$	0.6895	-0.3850	1.0965	-0.2595	9.9952	0	Schauble and Young, 2021; Chacko et al., 1996	
Anhydrite CaSO_4	1.1221	-0.5974	1.5739	-0.3324	11.0553	0	Schauble and Young, 2021	
Barite BaSO_4	0.9841	-0.5284	1.4137	-0.3065	10.5378	0	Schauble and Young, 2021	
Nahcolite NaHCO_3	8.3082	-3.5920	6.5731	-0.7858	13.7585	0	Schauble and Young, 2021	
Nitratite NaNO_3	2.4492	-1.1958	2.7249	-0.4648	11.7580	0	Schauble and Young, 2021	
Hematite Fe_2O_3	0	0	0.0524	-0.0520	5.9923	0	Blanchard et al., 2015; Polyakov et al., 2001	
Goethite FeOOH	0	0	0.5279	-0.1875	7.1664	0	Blanchard et al., 2015	
Muscovite $\text{KAl}_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2$	2.7471	-1.3188	3.4257	-0.3958	10.9522	0	Chacko et al., 1996	
Magnetite Fe_3O_4	69.7674	-21.3501	20.6729	-0.6777	7.0760	0	Cole et al., 2005; Blattner et al., 1999; Zhang et al., 1995; Mander-nack et al., 1999	
Rutile TiO_2	0	0	0.1160	-0.0816	6.9304	0	Clayton and Kieffer, 1991; Krylov and Kuznetsov, 2019	
Anatase TiO_2	0	0	0.1530	-0.0991	7.3428	0	Krylov and Kuznetsov, 2019	
Brookite TiO_2	0	0	0.1390	-0.0916	7.9088	0	Krylov and Kuznetsov, 2019	
Cassiterite SnO_2	0	0	0.0803	-0.0737	7.1760	0	Polyakov et al., 2005	
Corundum Al_2O_3	0	0	0.0360	-0.0891	9.0336	0	Krylov et al., 2017; Krylov and Evarestov, 2018	
Kyanite Al_2SiO_5	0	0	0.2820	-0.1933	10.6647	0	Krylov et al., 2020	
Sillimanite Al_2SiO_5	0	0	0.1406	-0.1749	10.5148	0	Krylov et al., 2020	
Andalusite Al_2SiO_5	0	0	0.5500	-0.0757	10.1402	0	Krylov et al., 2020	
Andradite $\text{Ca}_3\text{Fe}_2(\text{SiO}_4)_3$	0	0	0.4020	-0.1509	8.7247	0	Krylov and Glebovitsky, 2017	
Pyrope $\text{Mg}_3\text{Al}_2(\text{SiO}_4)_3$	0	0	0.56700	-0.92040	9.68511	0	Krylov and Glebovitsky, 2017	
Spessartine $\text{Mn}_3\text{Al}_2(\text{SiO}_4)_3$	0	0	0.49900	-0.17598	9.33600	0	Krylov and Glebovitsky, 2017	
Almandine $\text{Fe}_3\text{Al}_2(\text{SiO}_4)_3$	0	0	0.53900	-0.18465	9.45295	0	Krylov and Glebovitsky, 2017	
Uvarovite $\text{Ca}_3\text{Cr}_2(\text{SiO}_4)_3$	0	0	0.38500	-0.14749	8.71526	0	Krylov and Glebovitsky, 2017

Fig. 1. Comparison of GEOCHEQ_Isotope data on the equilibrium oxygen isotope fractionation factors in the H_2O – CO_2 –dissolved inorganic carbon system with experimentally determined values. The inaccuracy of the experimental equilibrium oxygen isotope fractionation factors is no larger than the size of the symbols.

Dissolved inorganic carbon is represented in GEOCHEQ_Isotope by solute carbonate species: CO_2 , H_2CO_3 , HCO_3^- , and CO_3^{2-} . The β -factors of these species were *ab initio* calculated using the density functional theory approach (Hill et al., 2014, 2020; Guo and Zhou, 2019; Schauble and Young, 2021). The GEOCHEQ_Isotope database (Table 1) incorporates computation results (Guo and Zhou, 2019), which are in the best agreement with experimental data (Beck et al., 2005). Experimental data on solute carbonate species (Beck et al., 2005) are in a good agreement with equilibrium isotope fractionation factors between these solute species and water that were calculated based on data from GEOCHEQ_Isotope database (Fig. 1). Note that the $\beta^{18}\text{O}$ -factors for the dissolved neutral CO_2 species were assumed to be equal to those in the gas phase. The calculated and experimental values for the equilibrium fractionation of oxygen isotopes differ by 0.1‰, i.e., their differences is smaller than the inaccuracies of both the measurements and the calculations (Fig. 1).

Oxygen β -Factors of Carbonate Minerals

Fractionation of oxygen isotopes in the system calcite– CO_2 . From the standpoint of isotope geochemistry, calcite seems to be the most important carbonate mineral. The reason for this is that the fractionation

coefficients of oxygen isotopes experimentally determined in the anhydrous system (i.e., without H_2O fluid) link to calcite (Chacko et al., 2001; Clayton and Kieffer, 1991). In view of this, it is very important to estimate equilibrium distribution in the system calcite– CO_2 because, as is demonstrated above, the $\beta^{18}\text{O}$ -factor of CO_2 has been reliably determined. For calcite, the *ab initio* calculations (Hill et al., 2014, 2020; Guo and Zhou, 2019; Schauble and Young, 2021) and those on the basis of the model oscillation spectra of the Kieffer type (Clayton and Kieffer, 1991; Chacko and Deines, 2008; Polyakov, 2008) agree well to each other. In GEOCHEQ_Isotope, the values of the $\beta^{18}\text{O}$ -factor are assumed equal to the *ab initio* computation results. At temperatures above 400 K, these data coincide with estimates in (Clayton and Kieffer, 1991). The difference between the values assumed for the $\beta^{18}\text{O}$ -factor of calcite in GEOCHEQ_Isotope and calculated based on the Kieffer spectrum model in a quasiharmonic approximation (Polyakov, 2008) are also much smaller than the scatter of the experimental data (Fig. 2). A somewhat greater difference was found between the $\text{CaCO}_3/\text{CO}_2$ fractionation curve (Chacko and Deines, 2008) and the fractionation curve calculated using the GEOCHEQ_Isotope database. This difference is explained by the underestimation of the Einstein oscillator fre-

Fig. 2. Comparison of various estimates of the equilibrium oxygen isotope fractionation factor in the calcite–CO₂ system.

quency $\nu_3 = 1460 \text{ cm}^{-1}$ (Mironenko et al., 2018), which leads to underestimated values of the calcite β -factor. This effect is smaller for the $\beta^{18}\text{O}$ -factor of calcite than for the $\beta^{13}\text{C}$ -factor. Equilibrium fractionation in the system calcite–CO₂ that was calculated using the values of the $\beta^{18}\text{O}$ -factor for calcite from the GEOCHEQ_Isotope database is generally in a good agreement with the experimentally measured equilibrium oxygen isotope fractionation factor for this system (Fig. 2).

Effects of oxygen isotope fractionation between carbonate minerals. The method applied to calculating the coefficients of polynomial (4) for carbonate minerals was analogous to the method used for their $\beta^{13}\text{C}$ -factors (Mironenko et al., 2018). Considering that the fractionation between carbonate minerals is well described by the model (Chacko and Deines, 2008) but the $\beta^{18}\text{O}$ -factors of calcite are underestimated compared to the values assumed in GEOCHEQ_Isotope (Fig. 2), the difference between the values of $10^3 \ln \beta$ of calcite accepted in the GEOCHEQ_Isotope database and those in the model (Chacko and Deines, 2008) was added to the values of $10^3 \ln \beta$ for carbonate minerals

$$\begin{aligned} \ln \beta_{\text{carb}} &= \ln \beta_{\text{calc}} + (\ln \beta_{\text{carb}}^{\text{CD}} - \ln \beta_{\text{calc}}^{\text{CD}}) \\ &= \ln \beta_{\text{carb}}^{\text{CD}} + (\ln \beta_{\text{calc}} - \ln \beta_{\text{calc}}^{\text{CD}}), \end{aligned} \quad (6)$$

where β_{carb} and β_{calc} are the $\beta^{18}\text{O}$ -factors for the carbonate mineral and calcite in the GEOCHEQ_Isotope database, and $\ln \beta_{\text{carb}}^{\text{CD}}$ and $\ln \beta_{\text{calc}}^{\text{CD}}$ are the same factors calculated by the model (Chacko and Deines, 2008). The coefficients of polynomial (4) for the $\beta^{18}\text{O}$ -factors of carbonates calculated according to (6) are given in Table 1.

Figure 3 makes it possible to compare the fractionation of oxygen isotopes in the system dolomite–water according to data in GEOCHEQ_Isotope and experimental calibrations of other authors. The experimental values of the oxygen equilibrium fractionation factors between dolomite and water and the calculation data found using the GEOCHEQ_Isotope database are obviously in a good agreement.

Oxygen β -Factors of Silicates and Oxides in the GEOCHEQ_Isotope Software Package

Many applications of the geochemistry of stable isotopes are related to the fractionation of oxygen iso-

Fig. 3. Fractionation of oxygen isotopes in the system dolomite–water.

topes in silicates and oxides. The coefficients of polynomial (4) for the calculation of the $\beta^{18}\text{O}$ -factors of these minerals, which were incorporated into GEOCHEQ_Isotope, are presented in Table 1. Most of these data were obtained by means of *ab initio* calculations. On the one hand, these results agree well with experimental and empirical data, and on the other hand, they enable extrapolations of the results to conditions inaccessible in the experiments. Some results obtained by various researchers with the use of different methods must be reconciled. An example of this is the calibrations of the $\beta^{18}\text{O}$ -factors of TiO_2 polymorphs: rutile, anatase, and brookite. The $\beta^{18}\text{O}$ -factors of these polymorphs computed *ab initio* with the application of the supercell method (Krylov and Kuznetsov, 2019) are in very good agreement with the empirical calibration of the geothermometers (Zack and Kooijman, 2017). However, the $\beta^{18}\text{O}$ -factors of rutile are in notably poorer agreement with experimental and theoretical estimates of the oxygen isotope fractionation factors between the rutile–quartz and rutile–calcite (Fig. 4) than the calibration for rutile calculated based on a Kieffer model spectrum (Clayton and Kieffer, 1991). We have reconciled the various calibrations using an approach analogous to that applied for carbonates. We estimated the difference

between the $\beta^{18}\text{O}$ -factors obtained for rutile by these two methods and then corrected the $\beta^{18}\text{O}$ -factors of the TiO_2 polymorphs for this value and thus retained the calibration of the geothermometers and ensured reasonably good agreement with experimental and empirical estimates for the rutile–quartz and rutile–calcite isotope fractionation coefficients.

When selecting the calibrations of the $\beta^{18}\text{O}$ -factors for the GEOCHEQ_Isotope database, we have paid much attention to the consistency of the data. It is the consistency of the estimates of the $\beta^{18}\text{O}$ -factors obtained by different techniques (or the possibility of making these data mutually consistent) that has been applied as the criterion of the reliability of the data.

The $\beta^{18}\text{O}$ -factors of oxides were determined, along with conventional techniques mentioned above, also by some new approaches. In this situation, it is particularly important to verify the results obtained by the new techniques by using conventional techniques, which have already proven to be reliable. For oxides whose cations possess a “Mössbauer” isotope, $\beta^{18}\text{O}$ -factors can be estimated from experimental data on the gamma-resonant scattering and heat capacity. This method was applied to measurements of the $\beta^{18}\text{O}$ -factor for hematite (Polyakov et al., 2001) and cassiterite (Polyakov et al., 2005). For cassiterite, this test has

Fig. 4. On the problem of reconciling the $\beta^{18}\text{O}$ -factors of rutile.

been done experimentally, using the Norton–Clayton method (Hu et al., 2005) and by the method of empirical calibration with the use of other isotope geothermometers and temperature estimation from data on gas–liquid inclusions (Macey and Harris, 2006). Similar to what has been done for hematite, the test can be conducted by comparing the $\beta^{18}\text{O}$ -factors of hematite calculated *ab initio* and derived from experimental data on the temperature shift in the Mössbauer spectra and heat capacity. These estimates for the $\beta^{18}\text{O}$ -factor of hematite practically exactly coincide: even at room temperature, the difference in $10^3 \ln \beta$ is ~ 0.3 (0.4% of the $10^3 \ln \beta$ value), and this difference further diminishes with increasing temperature.

Analogously, data can be made consistent for grossular, for which two calculations are available (Krylov and Glebovitsky, 2017; Schauble and Young, 2020), both based on the density of states functional approach but obtained using different methods. The consistency of these data is slightly poorer ($\sim 3.3\%$ of the $10^3 \ln \beta$ value) but is still acceptable (Fig. 5). Both computations are in a good agreement with the experimental fractionation coefficients for grossular–calcite (Rosenbaum and Mathey, 1995, 1996) and grossular–aqueous supercritical fluid. The values of the $\beta^{18}\text{O}$ -factor of grossular accepted in GEOCHEQ_Isotope obtained by averaging the two calibrations (Table 1).

The usage of β -factors in databases requires the values of these factors computed for broad tempera-

ture ranges. This is most commonly done in theoretical calculation studies, but sometimes no such calculation data are available. In such situations, data obtained by various authors can be made consistent. This situation occurs with the $\beta^{18}\text{O}$ -factors for magnetite. Reliable experimental data are available for the equilibrium fractionation of oxygen isotopes in the system magnetite– H_2O at temperatures higher than 300°C (Cole et al., 2004), and there are unsystematic scarce data on isotope fractionation in the system magnetite– H_2O at low temperatures (Blattner et al., 1999; Zhang et al., 1995; Mandernack et al., 1999). We used these experimental data to plot an interpolation polynomial of form (4) for the magnetite– H_2O fractionation curve (Fig. 6). To obtain a polynomial for the $\beta^{18}\text{O}$ -factor of magnetite, the coefficients of the polynomial for water (liquid or supercritical fluid, $T > 647 \text{ K}$) from Table 1 were added to the coefficients of the polynomial for the fractionation curve. The polynomials thus obtained were used to plot the temperature dependence of the $\beta^{18}\text{O}$ -factor of magnetite. This curve was smoothed by approximating it again using a polynomial of form (4). The results are summarized in Table 4.

Above, we described the main principles, methods, and techniques used to reconcile the data and compile a base of natural isotopic data in GEOCHEQ_Isotope. Detailed discussions of particulars of some related issues is beyond the scope of this paper and

Fig. 5. Comparison of the $\beta^{18}\text{O}$ -factor of grossular calculated by different techniques with experimental data.

shall be rather referred to a manual for the user of this software package.

SIMULTANEOUS COMPUTATIONS OF EQUILIBRIUM OXYGEN AND CARBON ISOTOPE EFFECTS AND CHEMICAL COMPOSITION IN A HYDROTHERMAL SYSTEM

The GEOCHEQ_Isotope software now enables one to simulate chemical processes with regard to oxygen and carbon isotope effects. As an illustrative example of this simulation, we chose a system, which is analogous to that described in (Mironenko et al., 2018). The calculation method of chemical equilibria with regard to both oxygen and carbon isotope equilibria is generally analogous to those applied to models that involved estimates only of equilibrium carbon isotopic effects (Mironenko et al., 2018, 2021; Sidkina et al., 2019). A natural change was the addition of the ^{18}O isotope as an independent component and ^{18}O isotopologues to the list of substances subject to Gibbs energy minimization. The molality of the components of aqueous solutions was calculated by formula (5).

As an example of the application of GEOCHEQ_Isotope, we have computed chemical and isotope equilibria in CO_2 -bearing hydrothermal system of the bulk composition 1 mole CO_2 + 1 kg H_2O + 1.4 moles CO_2 at 15, 25, and 40°C and a pressure of 40 bar, depending on pH. The $^{18}\text{O}/^{16}\text{O}$ and $^{13}\text{C}/^{12}\text{C}$ isotope ratios were specified in the system according to the natural abundances of these isotopes. We considered ^{16}O -, ^{18}O -, ^{12}C -, and ^{13}C -isotopologues of H_2O , $\text{CO}_2(\text{aq})$, HCO_3^- , CO_3^{2-} , $\text{CaCO}_3(\text{aq})$, CaHCO_3^+ , $\text{CO}_2(\text{gas})$, $\text{CH}_4(\text{gas})$, and $\text{H}_2\text{O}(\text{gas})$. For this system, the dependence of the composition of dissolved inorganic (carbonate) carbon on the equilibrium fractionation of oxygen isotopes between solute carbonate species and water depending on pH have been studied experimentally and theoretically (Beck et al., 2005). These experimental results only insignificantly different from the carbonate system discussed herein. In the GEOCHEQ_Isotope simulations, we analyzed the possibility of formation of the solute $\text{CaCO}_3(\text{aq})$ and CaHCO_3^- species, whereas these species were ignored in (Beck et al., 2005). At the same time, theoretical modeling in (Beck et al., 2005) involved the solute H_2CO_3 species. It should be stressed that the H_2CO_3 concentration was,

Fig. 6. Equilibrium fractionation of oxygen isotopes ($^{18}\text{O}/^{16}\text{O}$) in the magnetite– H_2O system.

according to the modeling results, close to 0.2–0.3% of the total concentration of dissolved carbonate carbon at $\text{pH} < 5$ and drastically decreased at increasing pH . The results obtained by GEOCHEQ_Isotope simulation of the composition of the carbonate species are shown in Fig. 7. Our simulation results agree well with earlier results in (Beck et al., 2005).

The dominance of one or another solute species of carbonate carbon depending on pH , with regard to the difference in the values of the $\beta^{18}\text{O}$ - and $\beta^{13}\text{C}$ -factors of the solute carbonate species (Table 1, Fig. 1), predetermines the dependence of the equilibrium fractionation coefficient of oxygen and carbon isotopes between total dissolved inorganic carbon and coexisting phases. Figure 8 shows examples of such dependences simulated with GEOCHEQ_Isotope. For oxygen isotopes, reliable experimental data (Beck et al., 2005) are currently available on the equilibrium fractionation of dissolved carbonate carbon and water at temperatures of 15–40°C. Our simulation results are in good agreement with these experimental data (Fig. 8). The decrease in dissolved carbonates in the heavy oxygen isotope relative to water at increasing pH (Fig. 8) is explained by the successive changes in the dominant carbonate species $\text{CO}_2(\text{aq}) \rightarrow \text{HCO}_3^- \rightarrow \text{CO}_3^{2-}$, along

with that the equilibrium fractionation factors between these carbonate species and water (and hence, their $\beta^{18}\text{O}$ -factors) decrease in the same sequence (Fig. 1). The situation with carbon isotopes is opposite: the $\beta^{13}\text{C}$ -factors of the aforementioned carbonate species occur in the opposite order (Mironenko et al., 2021), and hence, the depletion of dissolved carbonate carbon in the ^{13}C heavy isotope is reduced as pH is increased. The isotope shift for carbon between dissolved carbonate carbon and calcite at high pH shows an inversion, because the $\beta^{13}\text{C}$ -factor for the dominant carbonate species CO_3^{2-} is greater than that of calcite (Fig. 8).

CONCLUSIONS

We present an extension for the database of the GEOCHEQ_Isotope software package. This extension was designed to enable simultaneous simulations of chemical and isotope equilibria by means of minimizing the Gibbs free energy for the calculation of oxygen isotope equilibria. Similar to what has been done with carbon isotopes, this software version is underlain by the β -factor formalism in an approximation of an ideal mixture of isotopes.

Fig. 7. Dependence of the composition of dissolved carbon on pH: data of *GEOCHEQ_Isotope* simulations. Various species are dominant at different pH values. Calcium-bearing species only insignificantly contribute to the overall budget of carbonate carbon. The CaHCO_3^+ fraction reaches 7% only at low pH.

Fig. 8. Dependence of the equilibrium fractionation factors of oxygen isotopes (in the system dissolved inorganic carbon–water) and carbon isotopes (in the system dissolved inorganic carbon–calcite) on the pH of the solution.

The presented version of GEOCHEQ_Isotope uses the GEOCHEQ database (Mironenko et al., 2000) to describes nonisotope thermodynamic properties of substances. The Gibbs energy of the isotopologues is calculated using known values of the β -factors according to Eq. (1), with regard to additivity relations between the $\ln\beta$ of a compound as a whole and $\ln\beta_i$ of the monosubstituted isotopologues.

In this version, the computational algorithms are adapted to situations when oxygen isotopes are analyzed, and the accuracy of the computations is improved. In particular, the current equation for calculating the molality takes into account the presence of the H_2^{18}O isotopologue.

Available information on equilibrium fractionation factors of oxygen isotopes has been critically analyzed, and the data have been made mutually consistent. The temperature dependences of the oxygen β -factors are unified and written in the form of polynomials (4) in reciprocal absolute temperature.

The application of the GEOCHEQ_Isotope software package for simultaneous calculations of chemical, oxygen and carbon isotope equilibria was tested by simulating the dependence of the composition of solute carbonate species and the $^{18}\text{O}/^{16}\text{O}$ equilibrium fractionation coefficient between solute carbon and water, depending on the pH of the solution. The data are in a good agreement with experimental results (Beck et al., 2005). The enrichment of dissolved carbonate carbon in the ^{18}O heavy isotope decreases with increasing pH because of a systematic change of the dominant carbonate specie in the sequence $\text{CO}_2(\text{aq}) \rightarrow \text{HCO}_3^- \rightarrow \text{CO}_3^{2-}$, which is characterized by a decrease in the values of the $\beta^{18}\text{O}$ -factor ($\beta^{18}\text{O}_{\text{CO}_2} > \beta^{18}\text{O}_{\text{HCO}_3^-} > \beta^{18}\text{O}_{\text{CO}_3^{2-}}$). For carbon, a pH increase leads to an increase in the fractionation coefficient for dissolved carbonate carbon—calcite because $\beta^{13}\text{C}_{\text{CO}_2} < \beta^{13}\text{C}_{\text{HCO}_3^-} < \beta^{13}\text{C}_{\text{CO}_3^{2-}}$. At high pH (~ 11), the equilibrium isotope shift exhibits an inversion, and the dissolved inorganic carbon enriches in the ^{13}C isotope relative to calcite.

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