OXYGEN ISOTOPE FRACTIONATION IN URANIUM OXIDES*

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ABSTRACT

Thermodynamic oxygen isotope factors for uranium oxides have been calculated by means of the modified increment method. The sequence of ^{18}O-enrichment in the uranium oxides with respect to the common rock-forming minerals is predicted as follows: spinel < uraninite ≤ brannerite ≤ hematite < rutile < pitchblende < cassiterite ≤ uranium blacks ≤ coffinite < sedovite ≤ UO_3 < illite. Two sets of self-consistent fractionation factors between the uranium oxides and water and between the uranium oxides and the other minerals have been obtained for 0~ 1200°C. The theoretical results are applicable to the isotopic geothermometry of uranium ores when pairing with other gangue minerals in hydrothermal uranium deposits.

Keywords Oxygen isotopes, Fractionations, Theoretical calculations, Uranium oxides, Geothermometry

1 INTRODUCTION

Uranium oxides often occur either as uraninite in granites or as pitchblende in hydrothermal uranium deposits. Hattori *et al.*[1] observed very low $\delta^{18}O$ values of -20‰ to –30‰ (SMOW) in natural uraninites with respect to large $\delta^{18}O$ values of +10‰ in coexisting quartz. Weyer *et al.*[2] obtained that pitchblende and coffinite have $\delta^{18}O$ values of +0.8‰ to 3.4‰ while coexisting illites have $\delta^{18}O$ values of +5.6‰ to 13.1‰. The extreme ^{18}O depletion in uranium oxides requires a sufficient study on their equilibrium oxygen isotope properties. It is also essential to quantitative application of oxygen isotope data to geological thermometry and geochemical tracing.

So far neither experimental measurement nor empirical estimate has been reported for oxygen isotope fractionation in uranium minerals. Only available determination is the theoretical calculations of Hattori and Halas[3] on UO_2 and UO_3 using selected crystal field models for optical modes and Debye functions for acoustic modes. Their results appear not good enough to account for the known ^{18}O depletion in the uranium oxides.

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By means of the modified increment method Zheng[4] has systematically calculated oxygen isotope fractionation in metal oxides. The results obtained are in good agreement with known experimental and/or empirical data. The low-temperature validity of the theoretical calibrations has been confirmed by the synthetic experiments of Bird *et al.*[5]. The goal of this study is to extend the theoretical calculation to uranium oxides.

2 CALCULATION METHOD AND RESULTS

The statistical mechanical theory of isotopic fractionation is severely limited when applied to systems containing cindensed phases[3,4,6]. The modified increment method has been proven to be an accurate approach for calculating oxygen isotope fractionation in solid minerals as a function of statistical mechanical and crystal structural effects[4,7,8]. In principle, the degree of ^{18}O-enrichment in a given mineral can be quantitatively represented by the size of its oxygen isotope index ($I-^{18}$O). Quartz is taken as the reference mineral and thus its $I-^{18}$O index is defined as 1.0000. The greater the $I-^{18}$O index of a mineral, the more ^{18}O-enriched in it. The $I-^{18}$O value of the mineral is calculated by summing the normalized ^{18}O-increment ($i'_{\text{ct}-\text{o}}$) for different cation-oxygen bonds in its crystal structure. The ^{18}O-increment is determined by the effects of cation-oxygen bond strength ($C_{\text{ct}-\text{o}}$) and cation mass on isotopic substitution ($W_{\text{ct}-\text{o}}$). The cation-oxygen bond strength is defined as a function of cation oxidation state (V), coordination number (CN_{ct}) and corresponding ionic radii ($r_{\text{ct}} + r_{\text{o}}$). Substantially, the $I-^{18}$O index of a mineral results from a marriage of crystal chemistry with the relationship between vibrational frequency and reduced mass.

The method of calculating $I-^{18}$O indices for metal oxides has been describecd by Zheng[4] in detail and thus is not repeated here. The following uranium oxides are dealt with in this study: (1) uraninite UO_2, pitchblende $UO_2 \cdot 2UO_3$, and uranium blacks $UO_2 \cdot 6UO_3$; (2) brannerite UTi_2O_6, sedovite UMo_2O_8, and coffinite $USiO_4$. In these uranium oxides, except Si^{4+} which is in fourfold coordination with oxygen, the other cations are is in eightfold coordination while each oxygen is in fourfold or threefold coordination. The normalized ^{18}O-increments of the cation-oxygen bonds in the uranium oxides are calculated and presented in Table 1.

Table 1

Calculation of the normalized ^{18}O-increments for uranium oxides

Bond	CN_{ct}	CN_{o}	$r_{\text{ct}} + r_{\text{o}}$(nm)	m_{ct}	$W_{\text{ct}-\text{o}}$	$C_{\text{ct}-\text{o}}$	$i_{\text{ct}-\text{o}}$	$i'_{\text{ct}-\text{o}}$
$Si^{4+}-O$	4	2	0.161	28.09	1.03748	0.62112	0.02285	1.0000
$Si^{4+}-O$	4	3	0.162	28.09	1.03748	0.61728	0.02271	0.9939
$U^{4+}-O$	8	4	0.238	238.03	1.05665	0.21008	0.01158	0.5066
$U^{4+}-O$	8	3	0.236	238.03	1.05665	0.21186	0.01167	0.5109
$U^{6+}-O$	8	3	0.230	238.03	1.05665	0.32609	0.01797	0.7864
$Ti^{4+}-O$	8	4	0.193	47.90	1.04455	0.25907	0.01129	0.4942
$Mo^{6+}-O$	8	4	0.192	95.94	1.05131	0.39063	0.01954	0.8554

Applying th reduced partition function ratios of quartz calculated by Kieffer[6], the thermodynamic oxygen isotope factors for the uranium oxides are computed, as presented in Table 2 in the form of $10^3 \ln \beta$ equation. $(M_{16}/M_{18})^{3/2}$ stands for the mass normalization parameter[4]. By combining the thermodynamic oxygen isotope factors listed in Table 2, the algebraic expressions of the self-consistent fractionation factors in the form of $10^3 \ln \alpha$ equation can be obtained between mineral and mineral and between mineral and water by the relation:

Table 2

The thermodynamic oxygen isotope factors for uranium oxides

$(10^3 \ln \beta = A \times 10^6/T^2 + B \times 10^3/T + C)$

Minerals	$(M_{16}/M_{18})^{3/2}$	$I-^{18}O$	A	B	C
Uraninite	0.97818	0.4702	4.639	3.024	-1.61
Pitchblende	0.97216	0.6475	5.638	5.127	-2.56
U blacks	0.97053	0.6984	5.861	5.806	-2.85
UO_3	0.96934	0.7365	6.011	6.334	-3.08
Brannerite	0.95954	0.4715	4.648	3.037	-1.62
Sedovite	0.95847	0.7276	5.977	6.210	-3.02
Coffinite	0.96472	0.7083	5.901	5.939	-2.91
Quartz	0.90786	1.0000	6.673	10.398	-4.78
Illite	0.91407	0.8367	6.337	7.801	-3.70
Hematite	0.94618	0.4809	4.709	3.138	-1.67
Calcite	—	—	6.207	10.499	-4.78
Water	—	—	2.194	15.163	-4.72

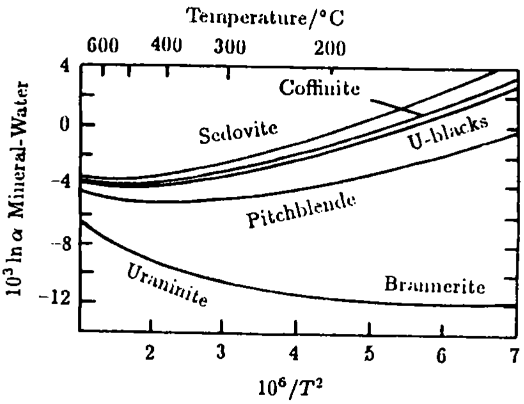

Fig.1 Calculated temperature dependence of oxygen isotope fractionations between uranium oxides and water

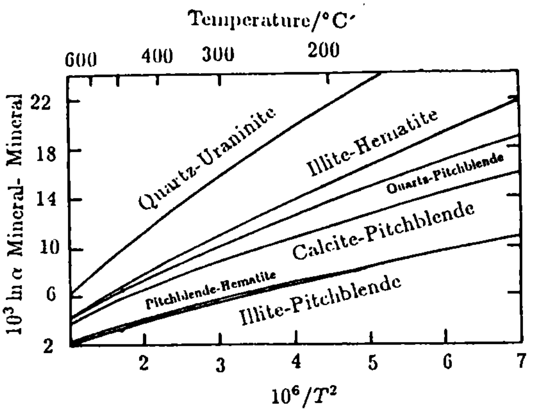

Fig.2 Calculated temperature dependence of oxygen isotope fractionations between the uranium oxides and the other minerals

The fractionations involving hematite and illite are after Zheng[4,9]

$$\ln \alpha_{x-y} = \ln \beta_x - \ln \beta_y \tag{1}$$

The valid temperature range for the theoretical calibrations is from 0 to 1200°C. Errors contributed to the fractionation factors by the modified increment method can be estimated within ±5% of the factor values[4,8,9]. Figs.1 and 2 illustrate temperature dependence of the calculated fractionations between the uranium oxides and water and between the uranium oxides and the other minerals, respectively.

3 DISCUSSION

According to the size of the $I-{}^{18}O$ indices in Table 2, the sequence of ^{18}O-enrichment in the uranium oxides is obtained as follows: uraninite $\leq$ brannerite $<$ pitchblende $<$ uranium blacks $\leq$ coffinite $<$ sedovite $<$ UO_3. Being the mixture of UO_2 with UO_3 in different proportions, oxygen isotope fractionations in pitchblende and uranium blacks are between those of UO_2 and UO_3.

As shown in Fig.1, the uranium oxides are depleted in ^{18}O relative to water at temperatures above 200°C. Like hematite, uraninite and brannerite are significantly depleted in ^{18}O (up to −12 ‰) with respect to water at hydrothermal temperatures. Precipitation of pitchblende from a hydrothermal fluid can result in rising of fluid $\delta^{18}O$ (+2‰ to +4‰).

Comparing with common metal oxide minerals[4], uraninite behaves like hematite isotopically and is thus enriched with ^{18}O relative to spinel. While pitchblende behaves like rutile and is thus depleted in ^{18}O relative to cassiterite. At 200°C, the oxygen isotope fractionation between quartz and uraninite is predicted to be 2.15 ‰ while that between quartz and pitchblende is 1.36 ‰. As depicted in Fig.2, oxygen isotope fractionations between uranium oxides and the other minerals are large enough to make them as good isotopic geothermometers.

Table 3 shows a case study of isotopic geothermometry based on the theoretical calibrations for the uranium oxides in this work and those for illite and hematite in Zheng[4,9]. The isotopic data are after Weyer *et al.*[1] who analysed the oxygen isotope compositions of illite, pitchblende and hematite samples from the Lone Gull unconformity related vein-like type uranium deposit in Canada. The ore zones consist of pitchblende and coffinite which are surrounded by illitic alteration halos. The following fractionation equations are applied to the geothermometry:

$$10^3 \ln \alpha_{\text{illite-pitchblende}} = 0.70 \times 10^6/T^2 + 2.67 \times 10^3/T - 1.14 \qquad (2)$$

$$10^3 \ln \alpha_{\text{pitchblende-hematite}} = 0.93 \times 10^6/T^2 + 1.99 \times 10^3/T - 0.89 \qquad (3)$$

$$10^3 \ln \alpha_{\text{illite-hematite}} = 1.63 \times 10^6/T^2 + 4.66 \times 10^3/T - 2.03 \qquad (4)$$

where T is the temperature in Kelvin.

The concordant temperatures are obtained for the sample Dh195 where the fractionation for the illite-pitchblende pair yields 195°C, the pitchblende-hematite pair 175°C, and illite-hematite pair 185°C. The other three sets of the illite-pitchblende pair yield the similar temperatures of 235 to 245°C. These temperatures can be reasonably interpreted to represent the formation temperature of the uranium ores in this deposit. Furthermore, the oxygen isotope composition of fluid from which the pitchblende precipitated can be estimated by the use of the isotopic temperatures in Table 3. The fluid $\delta^{18}O$ values obtained are from −5.8 ‰ to −6.5 ‰ (SMOW), which suggest an origin of meteoric water for the ore-forming fluid[10]. In this regard, this example demonstrates the applicability of the present theoretical calibrations for the uranium oxides to geochemical tracing and isotopic geothermometry in natural assemblages.

Table 3

Oxygen isotope geothermometry for Lone Gull hydrothermal uranium deposit

Sample No.	Minerals	$\delta^{18}O$ / ‰	Fractionation	t/°C
Dh191	Illite	7.8	6.8(ill-pit)	235
	Pitchblende	1.0	—	—
Dh195	Illite	11.1	7.8(ill-pit)	195
	Pitchblende	3.3	8.2(pit-hem)	175
	Hematite	−4.9	16.0(ill-hem)	185
Dh122	Illite	8.4	6.7(ill-pit)	240
	Pitchblende	1.7	—	—
Dh137	Illite	8.2	6.6(ill-pit)	245
	Pitchblende	1.6	—	—

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