Oxygen isotope fractionation in metal monoxides

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Introduction

Studies of the equilibrium oxygen isotope properties of solid minerals are essential to quantitative application of oxygen isotope data to geological thermometry and geochemical tracing. Metal monoxides appear to have been overlooked in this respect. Neither theoretical calculations nor experimental measurements nor empirical estimates have been reported for oxygen isotope fractionation in them. Oxygen isotope fractionation in metal multi-oxide minerals has been systematically calculated by Zheng (1991) using the modified increment method. 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.* (1993). The goal of this study is to extend the theoretical calculation to metal monoxides.

Calculation method and results

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 (Schütze, 1980; Zheng, 1991 and 1993). The method of calculating I-^{18}O indice for metal oxides has been described by Zheng (1991) in detail and is not repeated here. Three structural types of metal monoxides are dealt with in this study: (1) $M^{IV}O^{IV}$ type, which includes bromellite (BeO), montroydite (HgO), tenorite (CuO) and zincite (ZnO); (2) $M^{VI}O^{VI}O$ type, which includes bunsenite (NiO), lime (CaO), manganosite (MnO), periclase (MgO) and wuestite (FeO); and (3) $M_2^{II}O^{IV}$ type, which is represented by cuprite (CuO). Taking the Si–O bond in quartz as reference, the normalized ^{18}O-increments of the cation–oxygen bonds in the metal monoxides are calculated and presented in Table 1.

Applying the reduced partition function ratios of quartz calculated by Kieffer (1982), the thermodynamic oxygen isotope factors for the metal monoxides are computed, as presented in Table 2 in the form of $10^3 \ln\beta$ equation. By combining the thermodynamic oxygen isotope factors listed in Table 2, the algebraic expressions of the fractionation factors in the form of $10^3 \ln\alpha$ equation can be obtained among the minerals and fluids for the temperature range of 0 to 1200°C. The error contributed to the fractionation factors by the modified increment method can be estimated within ±5%.

Summary

Acccording to the size of the I-^{18}O indice in Table 2, the sequence of ^{18}O-enrichment in the metal monoxides is obtained as follows: bromellite > zincite > tenorite > montroydite > cuprite ≫ bunsenite > wuestite > manganosite > lime > periclase. Obviously, the oxides of the $M^{IV}O^{IV}$ structure is significantly enriched in ^{18}O relative to those of the $M^{VI}O^{VI}$ structure.

Zheng (1991) has calculated the I-^{18}O indice of

Table 1. Calculation of the normalized ^{18}O-increments for metal monoxides

Bond	CN_{ct}	CN_o	$r_{ct}+r_o$(Å)	m_{ct}	W_{ct-o}	C_{ct-o}	i_{ct-o}	i'_{ct-o}
Si–O	4	2	1.61	28.09	1.03748	0.62112	0.02285	1.0000
Be–O	4	4	1.65	9.01	1.02064	0.60606	0.01238	0.5419
Hg–O	4	4	2.34	200.59	1.05580	0.21368	0.01160	0.5078
Cu–O	4	4	2.00	63.54	1.04757	0.25000	0.01162	0.5085
Cu–O	2	4	2.32	63.54	1.04757	0.21552	0.01002	0.4383
Ni–O	6	6	2.09	58.71	1.04674	0.15949	0.00729	0.3188
Ca–O	6	6	2.40	40.08	1.04234	0.13889	0.00576	0.2521
Mn–O	6	6	2.15	54.94	1.04613	0.15504	0.00699	0.3060
Mg–O	6	6	2.12	24.31	1.03537	0.15723	0.00547	0.2392
Fe–O	6	6	2.10	55.85	1.04631	0.15873	0.00719	0.3145

Table 2. The thermodynamic oxygen isotope factors for metal monoxides

Mineral	$(M_{16}/M_{18})^{3/2}$	$(10^3 \ln\beta = A\times10^6/T^2 + B\times10^3/T + C)$ I-^{18}O	A	B	C
Bromellite	0.89101	0.5521	5.145	3.941	–2.03
Zincite	0.96423	0.4876	4.753	3.211	–1.70
Tenorite	0.96343	0.4792	4.698	3.120	–1.66
Montroydite	0.98631	0.4674	4.620	2.994	–1.60
Cuprite	0.94033	0.4232	4.312	2.542	–1.39
Bunsenite	0.96115	0.3011	3.331	1.459	–0.87
Wuestite	0.95965	0.2975	3.299	1.431	–0.85
Manganosite	0.95915	0.2896	3.228	1.371	–0.82
Lime	0.94879	0.2374	2.739	0.998	–0.63
Periclase	0.92994	0.2335	2.701	0.973	–0.62
Quartz	0.90786	1.0000	6.673	10.398	–4.78
Calcite			6.207	10.499	–4.78
Water			2.194	15.163	–4.72
Carbon dioxide			4.494	20.506	–8.23

the metal multi-oxide minerals. In comparison to the results from this study, the sequence of ^{18}O-enrichment in common metal oxides can be expected as follows: cassiterite > rutile > magnetite > ilmenite > zincite > hematite > uraninite > chromite > cuprite > corundum > spinel> wuestite > periclase. In this context, water is also significantly enriched in ^{18}O relative to the metal monoxides. The present calculations suggest that the metal monoxides of the $M^{VI}O^{VI}$ structure may be the most ^{18}O-depleted group in solid minerals.

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