

Oxygen isotope fractionation in magnetites: structural effect and oxygen inheritance

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Received 20 June 1994; revision accepted 16 November 1994

Abstract

The modified increment method is applied to the calculation of oxygen isotope fractionation in different structures of magnetite. The results show that, at isotopic equilibrium, the magnetite of a spinel-type structure has the very similar behavior of oxygen isotope partitioning to hematite, but it is considerably depleted in ^{18}O relative to the magnetite of an inverse spinel-type structure. This provides a resolution to the systematic discrepancy in the quartz–magnetite oxygen isotope fractionation between previous theoretical calculations of the author and the experimental determinations of H. Chiba and coworkers. An oxygen isotope inheritance is suggested in which the magnetites used in the experiments could have inherited the oxygen isotope feature of a precursor mineral hematite. The oxygen isotope inheritance may be common in the formation of secondary minerals in laboratory and nature. Most magnetite would be of the spinel-type structure in the infancy of its crystallization. The oxygen isotope study on magnetite may provide insight into the mechanism of mineralogical reactions during magnetite formation under laboratorial or natural conditions.

1. Introduction

Magnetite is of special interest in oxygen isotope geochemistry. It is one of the major phases in most crustal rocks and represents a wide range of temperatures and pressures of formation. In equilibrium mineral assemblages, it has a smaller $^{18}\text{O}/^{16}\text{O}$ ratio than the other common rock-forming minerals. The quartz–magnetite pair has a very large isotopic fractionation and hence provides the most sensitive isotopic geothermometer.

In the past three decades a large number of studies have been made calibrating mineral-pair isotopic fractionations for the purpose of geothermometry. Oxygen isotope fractionations involving magnetite have been determined by experimental measurements (O'Neil

and Clayton, 1964; Bertenrath et al., 1973; Matthews, 1976; Downs et al., 1981; Chiba et al., 1989), theoretical calculations (Becker and Clayton, 1976; Zheng, 1991), and empirical estimates (Bottinga and Javoy, 1973; Blattner et al., 1983). Unfortunately, these calibrations disagree significantly with each other. This hampers the quantitative interpretation of oxygen isotope data for magnetites from various rocks.

Zheng (1991) calculated oxygen isotope fractionation in magnetite by means of the modified increment method. An inverse spinel-type structure was used for the magnetite. As a result, the calculated fractionations between quartz and magnetite are systematically greater than those determined experimentally by Chiba et al. (1989) using the partial equilibrium approach of the calcite-exchange technique. Methodology for both theoretical calculation and experimental determination

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has proved sufficiently valid for the purpose of calibrating oxygen isotope fractionation in minerals (Chiba et al., 1989; Clayton et al., 1989; Zheng, 1991, 1992, 1993a, b; Bird et al., 1993). In this regard, it has been a puzzle why there exists the systematical discrepancy. The goal of this study is to provide a resolution to the discrepancy.

2. Calculation method and results

The present calculations follow the modified increment method employed by Zheng (1991, 1993a) for calculating oxygen isotope fractionation in metal oxides and anhydrous silicates. Primarily, the increment method was developed by Schütze (1980) and was brought to public attention by Richter and Hoernes (1988). In principle, the degree of ^{18}O enrichment of a mineral can be quantified by the oxygen isotope index of the mineral ($I\text{-}^{18}\text{O}$) relative to a reference mineral. The $I\text{-}^{18}\text{O}$ index is calculated by summing the normalized ^{18}O increments ($i'_{\text{ct-o}}$) for different cation–oxygen bonds in the mineral structure. The ^{18}O increment ($i_{\text{ct-o}}$) is determined by the effects of cation–oxygen bond strength ($C_{\text{ct-o}}$) and cation mass on isotopic substitution ($W_{\text{ct-o}}$). The cation–oxygen bond strength is defined as a function of cation oxidation state (V), coordination number (CN_{ct}) and corresponding ionic radii ($r_{\text{ct}} + r_{\text{o}}$). Essentially, the $I\text{-}^{18}\text{O}$ index of minerals results from a marriage of crystal chemistry with the relationship between vibrational frequency and reduced mass. In this context, the modified increment method does not follow the theory of stable isotope fractionation presented by Bigeleisen and Mayer (1947) and Urey (1947) based on the methods of statistical thermodynamics. But it has developed cer-

tain mathematical relationships concerning atoms in mineral crystals and captured the most important aspects involving vibrational frequencies and their isotopic shifts (Zheng, 1991, 1993a, b).

The two structures of magnetite are dealt with in this study. One is of an inverse spinel-type with the structural formula $\text{Fe}^{3+}[\text{Fe}^{2+}\text{Fe}^{3+}]\text{O}_4$. In the normal magnetite, Fe^{2+} cations are distributed in the octahedral sites, and one half of Fe^{3+} cations occupy the tetrahedral sites and the other half the octahedral sites. The other is of a spinel-type with the structural formula $\text{Fe}^{2+}[\text{Fe}^{3+}]_2\text{O}_4$. In the abnormal magnetite, Fe^{2+} cations are distributed in the tetrahedral sites, whereas Fe^{3+} cations occupy the octahedral sites. It is the structural difference that dictates the oxygen isotope partitioning in the two different structures of magnetite. It must be pointed out that magnetite is generally described to be of the inverse-spinel type structure (e.g., Berry et al., 1983). However, this does not preclude the possibility of the presence of the spinel-type magnetite in nature, because it is not easy to identify the structure of magnetite by the usual X-ray method.

The procedures of calculating the $I\text{-}^{18}\text{O}$ indices of iron oxides have been given in Zheng (1991) and are thus not repeated here. The Si–O bond in quartz is taken as reference. The parameters used are listed in Table 1, where the interatomic distances are after Muller and Roy (1974). Applying the reduced partition function ratios recommended by Zheng (1991, 1993a) for quartz, calcite and water, the oxygen isotope fractionations between quartz and magnetite, between calcite and magnetite and between magnetite and water, respectively, are calculated, as presented in Table 2. Errors contributed to the resulting fractionation factors by the method itself are estimated to be $\sim \pm 5\%$ of the factor values (Zheng, 1993b).

Table 1
Calculation of the normalized ^{18}O increments for magnetites

Bond	CN_{ct}	CN_{o}	$r_{\text{ct}} + r_{\text{o}}$	m_{ct}	$W_{\text{ct-o}}$	$C_{\text{ct-o}}$	$i_{\text{ct-o}}$	$i'_{\text{ct-o}}$
$\text{Si}^{4+}\text{-O}$	4	2	1.61	28.09	1.03748	0.62112	0.02285	1.0000
$\text{Fe}^{3+}\text{-O}$	4	4	1.87	55.85	1.04631	0.40107	0.01816	0.7946
$\text{Fe}^{3+}\text{-O}$	6	4	1.98	55.85	1.04631	0.25253	0.01146	0.5012
$\text{Fe}^{2+}\text{-O}$	4	4	2.01	55.85	1.04631	0.24876	0.01126	0.4928
$\text{Fe}^{2+}\text{-O}$	6	4	2.075	55.85	1.04631	0.16064	0.00728	0.3187

Mean ionic radii of Fe^{3+} or Fe^{2+} in high- and low-spin states are taken for the calculation.

Table 2

The calculated oxygen isotope fractionations in magnetites ($10^3 \ln \alpha = A \times 10^6/T^2 + B \times 10^3/T + C$)

Structure	$I-^{18}\text{O}$	Quartz–magnetite			Calcite–magnetite			Magnetite–water		
		A	B	C	A	B	C	A	B	C
Inverse spinel-type	0.5404	1.60	6.59	−2.81	1.13	6.70	−2.81	2.88	−11.36	2.89
Spinel-type	0.4768	1.99	7.30	−3.13	1.52	7.41	−3.13	2.49	−12.07	3.00

3. Discussion

Figs. 1 and 2 show comparisons of the fractionation factors for the quartz–magnetite and magnetite–water systems calculated in this study with those derived from the experimental and empirical calibrations. Apparently, the fractionations determined experimentally by Chiba et al. (1989) for the quartz–magnetite system and those by Bertenrath et al. (1973) for the magnetite–water system are in excellent agreement with the present calculations on the magnetite of the spinel-type structure. On the other hand, the fractionations for the magnetite–water system calculated in this study on the magnetite of the inverse spinel-type structure are very close to those calculated previously by Becker and

Clayton (1976) based on the experimental measurements of O'Neil and Clayton (1964).

Obviously, the systematic discrepancy in the quartz–magnetite oxygen isotope fractionation between the experimental calibration of Chiba et al. (1989) and the theoretical calculation of Zheng (1991) can be accounted for by assigning Fe^{2+} to the tetrahedral site, i.e. by dealing with a magnetite of the spinel-type structure in the calculation of ^{18}O increment. The calculated $I-^{18}\text{O}$ index is 0.4768 for this structure of magnetite. The magnetite of the spinel-type structure has the very similar behavior of oxygen isotope fractionation to hematite ($I-^{18}\text{O} = 0.4809$; Zheng, 1991), but it is significantly depleted in ^{18}O relative to the magnetite of the inverse spinel-type structure ($I-^{18}\text{O} = 0.5404$).

Fleet (1981) observed at room temperature that natural magnetite has a defect structure, with interstitial Fe^{3+} cations in the tetrahedral sites and corresponding vacancies in the octahedral sites. In regards to occupation of Fe^{2+} cations in the octahedral sites, works by Wu and Mason (1981) and Trestmann-Matts et al. (1984) show that in pure synthetic magnetite the occupation decreases from ~ 0.85 at 600°C to $\frac{2}{3}$ (random distribution) at 1450°C . These are potential causes for the complexity of oxygen isotope partitioning in magnetites. Possibly, the correct application of oxygen isotope geothermometry using the mineral pairs containing magnetite requires an exact analysis of the high-temperature crystal structure of magnetites in question.

The present calculations on magnetite of the inverse spinel-type structure provide a real calibration on oxygen isotope fractionation in the normal magnetite. In this context, the magnetites obtained in the hydrothermal experiments of Bertenrath et al. (1973) and those used in the calcite-exchange experiments of Chiba et al. (1989) are either of a spinel-type structure or formed from a hematite precursor. Unfortunately, the

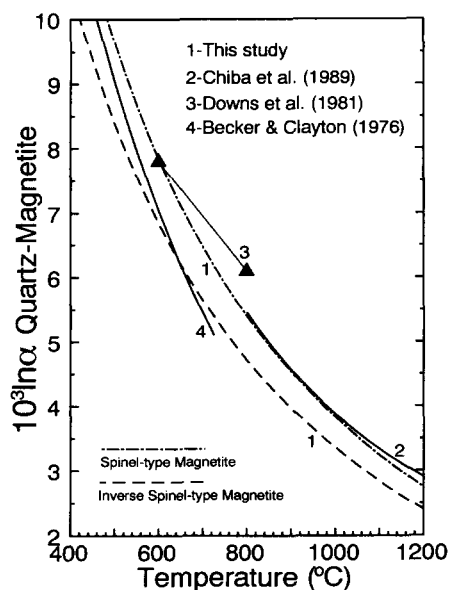


Fig. 1. Comparison of the quartz–magnetite oxygen isotope fractionations calculated in this study with those derived by Becker and Clayton (1976), Downs et al. (1981), and Chiba et al. (1989).

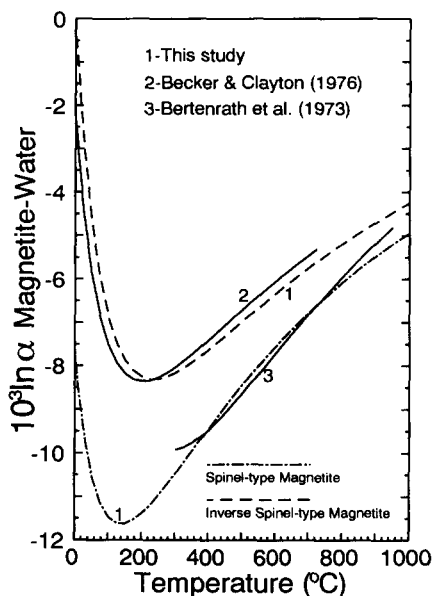


Fig. 2. Comparison of the magnetite–water oxygen isotope fractionations calculated in this study with those derived by Bertenrath et al. (1973) and Becker and Clayton (1976).

magnetites in the run products of the experiments were not studied by Bertenrath et al. (1973) and Chiba et al. (1989) in sufficient detail to indicate the structural type to which they belong at high temperatures. Nevertheless, it is known that in the experiments of Bertenrath et al. (1973) hematite was reduced to magnetite in the presence of water at Ni–NiO buffered oxygen fugacities. In the experiments of Chiba et al. (1989), the magnetite starting material was a natural one from the Brockman Iron Formation of the Hamersley Range in Western Australia, which could be also a product of reduction from hematite at low temperatures (Becker and Clayton, 1976).

In order to resolve the discrepancy a possible geochemical mechanism can be suggested as follows. The magnetites in the experiments are secondary and they were of the spinel-type structure in the infancy of its crystallization. The infant magnetite would have evolved from reduction of hematite and thus inherited the feature of crystal structure in the precursor mineral. Namely, all the Fe^{3+} were distributed in the octahedral sites and the Fe^{2+} newly formed by reduction of Fe^{3+} only took up the tetrahedral sites, resulting in the magnetites of the spinel-type structure. According to the principle of the increment method (Schütze, 1980;

Zheng, 1991), the oxygen isotope partitioning in solid minerals is principally determined by the crystal structure of the minerals. Consequently, the experimental calibrations involving the secondary magnetites yield the fractionations which correspond to those for the magnetite of the spinel-type structure rather than those for the magnetite of the inverse spinel-type structure. In this context, structural re-equilibration in magnetite crystals could be a rapid process, because it only involves electronic transfer from the tetrahedral sites to the octahedral sites.

In contrast, achieving oxygen isotope re-equilibrium in the magnetite crystals may be a much more sluggish process, if there was no recrystallization during the structural re-equilibration. For this reason, the secondary magnetites might have preserved the oxygen isotopic feature inherited from the magnetite of the spinel-type structure and thus from its precursor hematite. This could take place either under the experimental conditions or in the natural system. The primary feature of oxygen isotopes was not altered despite the structural re-equilibration in the magnetite crystals. In this regard, the oxygen isotope composition of magnetite may be influenced by starting materials and reaction paths. Therefore, the oxygen isotope fractionations calibrated by Bertenrath et al. (1973) and Chiba et al. (1989) do not represent those in the magnetite of the inverse spinel-type structure.

The oxygen isotope composition of magnetite and hematite has been determined for a number of metamorphic iron-formations (e.g., James and Clayton, 1962; Perry and Bonnicksen, 1966; Becker and Clayton, 1976; Hoefs et al., 1982; Sharp et al., 1988). It is commonly assumed that hematite behaves like magnetite isotopically (e.g., James and Clayton, 1962; Becker and Clayton, 1976; Hoefs et al., 1982). The assumption is valid theoretically, given that the hematite is a precursor for magnetite, because hematite is considerably depleted in ^{18}O relative to the normal magnetite at isotopic equilibrium (Zheng, 1991). By separating magnetite from the main constituent hematite in banded iron-formation samples from the Iron Quadrangle in Brazil, Hoefs et al. (1982) observed that there is no difference in the oxygen isotope composition between the two iron oxide minerals. This can be readily interpreted to indicate that the magnetite was formed by reducing hematite under the metamorphic conditions.

On the other hand, a considerable enrichment of ^{18}O in magnetite relative to hematite was observed by Becker and Clayton (1976) in coexisting magnetite and hematite samples from the Hamersley Range iron-formation. Siderite coexists with magnetite. The considerable fractionations between magnetite and hematite in the iron-formation may imply that the magnetite has formed from the reaction of FeCO_3 plus H_2O to produce Fe_3O_4 and HCO_3^- rather than from reduction of hematite. This reaction path is similar to that in the synthesis experiments of O'Neil and Clayton (1964).

Becker and Clayton (1976) calculated the oxygen isotope fractionation in magnetite in such a way that the upper and lower limits to the isotopic partition function ratios for magnetite were obtained, using the constraints set by the low-temperature heat capacity of magnetite (Dixon et al., 1965) and by the corrected high-temperature magnetite–water fractionations determined by O'Neil and Clayton (1964) at 700° and 800°C. The magnetite in the experiments of O'Neil and Clayton (1964) was a product of decomposing FeCO_3 . Figs. 1 and 2 show the fair agreement of the calculated results by Becker and Clayton (1976) with the present ones on the magnetite of the inverse spinel-type structure. This could imply that the oxygen isotope fractionations determined by O'Neil and Clayton (1964) represent the oxygen isotope partitioning in the magnetite of the inverse spinel-type structure. So do the fractionations calculated by Becker and Clayton (1976).

According to the calculations of Zheng (1991), ilmenite has the $I^{18}\text{O}$ index of 0.5132. At thermodynamic isotopic equilibrium, ilmenite is depleted in ^{18}O relative to the magnetite of the inverse spinel-type structure ($I^{18}\text{O} = 0.5404$), but it is enriched in ^{18}O relative to hematite ($I^{18}\text{O} = 0.4809$) and the magnetite of the spinel-type structure ($I^{18}\text{O} = 0.4768$). However, it was commonly observed in nature that ilmenite is enriched in ^{18}O relative to magnetite, with the relationship of $\Delta^{18}\text{O}_{\text{Quartz-Ilmenite}} = 0.95 \cdot \Delta^{18}\text{O}_{\text{Quartz-Magnetite}}$ (Bottinga and Javoy, 1975). This discrepancy can be resolved by assuming that the magnetite coexisting with the ilmenite in the natural assemblages would form by the reduction of a hematite, and therefore has preserved the oxygen isotope signature inherited from the precursor hematite.

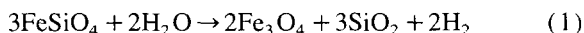
O'Neil (1977) suggested that the stable isotope technique can be well suited to the study of possible inheritance of structural units of precursor minerals during mineralogical reactions. In a series of experiments, O'Neil and Kharaka (1976) heated kaolinite in water at 350°C to produce pyrophyllite and diaspore. Hydrogen isotope exchange went essentially to completion during the profound change in mineralogy. However, only 33% of possible exchange of oxygen isotopes took place concomitantly. Because of chemical and structural similarities to kaolinite, the pyrophyllite could inherit the oxygen of intact units from the precursor, but the diaspore would undergo isotopic exchange with the water during its formation (O'Neil, 1977). Oxygen isotope inheritance of scheelite from wolframite under hydrothermal conditions has been suggested by Zheng (1992). Bird et al. (1993, 1994) noted the possibility of oxygen isotope inheritance for the TiO_2 system and aluminium hydroxides at low temperatures. The present study demonstrates that magnetite can inherit the oxygen isotope signature from its precursor hematite.

Sharp (1990) developed an empirical approach to determine the oxygen diffusion coefficients in minerals by correlating crystal grain size with the oxygen isotope composition of a silicate or oxide mineral hosted by a marble. In his study on magnetite, the calcite–magnetite fractionation equation determined by Chiba et al. (1989) was applied to calculation of isotopic temperatures. The isotopic fractionations of 6.8–9.7‰ between calcite and magnetite yielded isotopic temperatures ranging 655–505°C. The oxygen diffusion rates in magnetite thus obtained are significantly lower than those experimentally determined by Giletti and Hess (1988). However, the magnetites measured by Sharp (1990) formed at high temperatures and thus are different from those used by Chiba et al. (1989) in their experiments. If the calcite–magnetite fractionation equation calculated in this study for the magnetite of the inverse spinel-type structure is applied, the isotopic temperatures calculated are from 560° to 395°C, being systematically $\sim 100^\circ\text{C}$ lower than the previous ones. As a result, oxygen diffusion rates in magnetite estimated previously by Sharp (1990) could become much faster and thus are very close to those determined experimentally by Giletti and Hess (1988).

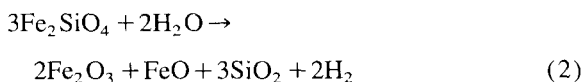
4. Implications for the mechanism of magnetite formation

The above discussion has demonstrated that the discrepancy in oxygen isotope fractionation involving magnetites between the theoretical calculations and the experimental determinations can be resolved by assuming the oxygen isotope inheritance of the magnetites from the precursor hematite. This can throw some light on the mechanism of mineralogical reactions during magnetite formation in nature or under laboratorial conditions.

Downs et al. (1981) directly measured oxygen isotope fractionation between quartz and magnetite at 700° and 800°C via the reaction:



under the conditions of controlled hydrogen fugacity. The run products were analysed by X-ray diffraction and examined under the microscope to ascertain that the reaction had gone to completion. As shown in Fig. 1, the quartz–magnetite fractionations obtained by Downs et al. (1981) are very close to the theoretical ones involving the magnetite of the spinel-type structure. If the results from both experimental measurement and theoretical calculation are correct, it may imply that the magnetite of the experimental product resulted from the combination of Fe_2O_3 with FeO via the two-step reactions:

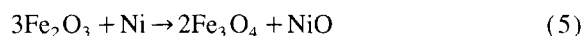


where Fe_2O_3 is hematite with Fe^{3+} occupying the octahedral sites. FeO is not wüstite (wüstite $I^{-18}\text{O}$ is 0.2975; Zheng, 1994) and thus its Fe^{2+} is distributed in the tetrahedral sites rather than in the octahedral sites. Following the procedures of calculating ^{18}O increment described by Zheng (1991), it is obtained that the FeO has the $I^{-18}\text{O}$ index of 0.4662. Theoretically, the FeO is slightly depleted in ^{18}O relative to hematite ($I^{-18}\text{O} = 0.4809$). When the Fe_2O_3 and FeO were combined to form magnetite (Fe_3O_4), the oxygen isotope signature of both Fe_2O_3 and FeO was conveyed to the magnetite through the simple relation:

$$I^{-18}\text{O}_{\text{Fe}_3\text{O}_4} = (2 \cdot I^{-18}\text{O}_{\text{Fe}_2\text{O}_3} + I^{-18}\text{O}_{\text{FeO}}) / 3 \quad (4)$$

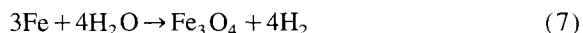
The newly formed magnetite would be of the spinel-type structure in the infancy of its crystallization. As a result, the oxygen isotope fractionation in magnetite determined by Downs et al. (1981) has inherited this structure from the precursors hematite and FeO. Therefore, it is responsible for fractionations involving the magnetite of the spinel-type structure, though structural re-equilibrium may have been achieved by the electronic transfer within the magnetite crystals.

In the experiments of Bertenrath et al. (1973), the following reaction would have taken place:



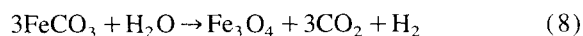
Like the case of the experiments of Downs et al. (1981), the newly formed magnetite would be of the spinel-type structure in the infancy of its crystallization after reduction from hematite. As a consequence, the magnetite–water fractionations measured by Bertenrath et al. (1973) are like those calculated theoretically for the hematite–water system (Zheng, 1991), and therefore they are responsible for the fractionations involving the magnetite of the spinel-type structure.

Matthews (1976) synthesized magnetites under hydrothermal conditions by the following reactions:



Oxygen isotope fractionations between the synthesized magnetites and water were measured by the author, who obtained a value of -7.83% for reaction (6) at 565°C and a value of -7.20% for reaction (7) at 560°C. Both reactions involve magnetite formation by solution and precipitation, with the inherent possibility of establishing isotopic equilibrium between the product phases. Specifically, hematite has been involved in the formation of magnetite via reaction (6). The experimental value of Matthews (1976) at 565°C agrees well with the theoretical value of -7.86% at the same temperature calculated for the magnetite of the spinel-type structure in this study. This agreement may also imply that the magnetites synthesized by Matthews (1976) via reaction (6) would have the spinel-type structure in the infancy of its crystallization.

However, hematite could be not involved in the experiments of O'Neil and Clayton (1964) which can be described by the one-step reaction:



Unlike the case for the experiments of Bertenrath et al. (1973) and Downs et al. (1981), the newly formed magnetite in this experiment would not have undergone a stage of hematite formation like in reaction (2). It may be either of the inverse spinel-type structure or isotopically reset since its crystallization. As a result, the oxygen isotope fractionation in the magnetite determined by O'Neil and Clayton (1964) is responsible for that in the magnetite of the inverse spinel-type structure.

In the oxygen isotope exchange experiments of Chiba et al. (1989), magnetite from the Brockman Iron Formation of the Hamersley Range in Western Australia was used as starting material. The starting magnetite was placed at high temperature and pressure to exchange oxygen isotopes with calcite, and recrystallization occurred. The oxygen isotope exchange reaction took place for 82% at 800°C and more at higher temperatures. If both theoretical and experimental calibrations have correctly predicted the behavior of oxygen isotope partitioning in the magnetites, the oxygen isotope data of Chiba et al. (1989) may imply that hematite would have been involved in the course of the formation of the starting magnetite. It is known that siderite occurs in the Hamersley Range iron-formation (Becker and Clayton, 1976). Thus, the following two-step reactions could have taken place:



Similar to the case in the laboratory experiments of Downs et al. (1981), the starting magnetite in the experiments of Chiba et al. (1989) would have been formed via reactions (9) and (10) in nature. It has thus inherited the oxygen isotope signature of the precursors Fe_2O_3 and FeO . The product magnetite in their isotope-exchange experiments may be still of the spinel-type structure in the infancy of its recrystallization.

5. Conclusions

Calculation of oxygen isotope fractionation in the two different structures of magnetite demonstrates that the magnetite of the spinel-type structure has the nearly identical behavior of oxygen isotope partitioning to hematite, but it is significantly depleted in ^{18}O relative

to the magnetite of the inverse spinel-type structure. In this regard, the systematic discrepancy in the quartz–magnetite fractionation between the theoretical calculation of Zheng (1991) and the experimental determination of Chiba et al. (1989) can be resolved by assuming the oxygen isotope inheritance, i.e. the magnetite used in the experiments have inherited the oxygen isotope feature of a precursor mineral hematite. The assumption of the oxygen isotope inheritance can also resolve the discrepancy in the magnetite–water fractionation between the theoretical calculation and the experimental measurement of Bertenrath et al. (1973). Most magnetite would be of the spinel-type structure in the infancy of its crystallization. The oxygen isotope composition of magnetite may be influenced by the starting materials and the reaction paths. This provides an insight into the possible origin of structural units of precursor minerals in mineralogical reactions by means of oxygen isotope approach, because structural re-equilibration in mineral crystals can be a much faster process than isotopic re-equilibration in natural systems or under experimental conditions. The preservation of intact oxygen units and thus the oxygen isotope inheritance from precursor minerals may be common in the formation of secondary minerals. The oxygen isotope study on magnetite can be used to trace the mechanism of mineralogical reactions during its formation.

Acknowledgements

This study was supported by funds from the Chinese Academy of Science within the framework of the project ‘‘Stable Isotope Geochemistry of the Earth’s Crust and Mantle’’. Discussion with Dr. Z.D. Sharp helped to clarify the thought about oxygen isotope inheritance. Comments by Drs. H. Chiba and F.J. Longstaffe lead to improvement of the manuscript.

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