Stable Oxygen and Hydrogen Isotope Fractionation Factors for the Goethite (hematite)-water System

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ABSTRACT

This paper reports experimental results on the low-temperature (<100 ºC) $\delta^{18}O$ and $\delta^{2}H$ fractionation of goethite (hematite)-water in a closed system. Both goethite (α-FeOOH) and hematite (α-Fe$_2$O$_3$) exhibited closer fractionation factor values but the $\alpha_{Hematite-Water}$ value is slightly higher (~0.9932) than the $\alpha_{Goethite-Water}$ (~0.9924) for the ^{18}O isotope. The average fractionation factor (1000ln$^2\alpha$; at 70 ºC) value for ^2H in the goethite-water is determined to be -115.78 which is more negative than the 1000ln$^{18}\alpha$ values for ^{18}O. The isotopic change from initial waters to the final waters in which these minerals were synthesized, was observed to be larger for the δ^2H (average~2.02‰) than the $\delta^{18}O$ (average~0.55‰). Variations in the fractionation factors of goethite and hematite reported in various studies is probably related to the procedures such as drying, washing, type of reactants, pH, and extraction and measurement of ^{18}O and ^2H isotopes and, therefore, invite further research for the understanding of α-T relation. Formation temperatures of goethite (~70 ºC) and hematite (~90 ºC) seem to have less impact in altering mineral-water fractionation as compared to the formation water.

Key words: Goethite; Hematite; Hydrogen and Oxygen isotope; Fractionation factor; Temperature.

INTRODUCTION

The high reactivity of iron with oxygen results in various Fe-(hydr)oxides in surface and near surface environments. Among these commonly occurring Fe-minerals, the low solubility of the goethite (α-FeOOH) and hematite (α-Fe$_2$O$_3$), under oxidizing conditions preserve the isotopic information on ancient environments[1,2]. The isotopic ratios (e.g., $^{18}O/^{16}O$, D/H) of these crystallized Fe^{III}-minerals reflect the original temperature of formation and the isotopic signature of the formation water[3,4]. Isotopic ratios of goethite and hematite may closely mimic the isotopic fractionation exhibited in many natural environments and, therefore, are required to understand

paleotempratures and isotopic composition of the waters present at the time Fe-(hydr)oxide formation. Being authigenic minerals in both continental and oceanic settings, goethite and hematite are important repository of knowledge of geologic environments. A well defined fractionation-temperature relation is, therefore vital if isotopic composition of goethite and hematite are to provide quantitative information.

This work investigates into the isotopic signature of both oxygen and hydrogen in synthetic goethite and hematite. It includes an attempt to determine fractionation factor at a specific temperature, and isotopic composition of waters present at the time of mineral formation.

MATERIAL AND METHODS

Hematite (α-Fe$_2$O$_3$) and goethite (α-FeOOH) were prepared by aging 2-line ferrihydrite from the alkaline Fe^{III} systems following the methods of Schwertmann and Cornell [5]. Goethite was synthesized from 100 mL of 1 M Fe(NO$_3$)$_3$.9H$_2$O in 2 L polyethylene bottle. About 180 mL 5 M KOH was added and the suspension was diluted to 2L. The suspension was held at 70 ºC (pH~ 13) for 60 hours. Reactants were preheated to the designated temperature before mixing. Hematite was synthesized by dissolving 40 g of Fe(NO$_3$)$_3$.9H$_2$O in 500 mL distilled water and adding 300 mL of 1M KOH. To this was added 50 mL 1M NaHCO$_3$ and the suspension was kept in a closed polyethylene flask at 90 ºC for 48 hours (pH~ 8-8.5). Both hematite and goethite were synthesized in two types of waters such as Milli Q (type-I) and ultra pure (type –II) with different isotopic values. The end products were centrifuged and washed to remove electrolyte (OH, NO$_3$, CO$_3$, Na and K) repeatedly. Separation of phases (precipitate) of the synthesized minerals was performed using an ultra speed centrifuge. Samples were then dried under vacuum in a freeze drier and grounded. The presence of NO$_3$ was tested qualitatively with diphenylamine.

Oxygen and hydrogen isotopes of initial and final waters (type-I and type-II; n= 12) in which goethite and hematite were synthesized were also measured along with the solid end products (n =4; GI, GII, HI and HII). The isotope analysis of samples

was conducted at the BayCEER laboratory, University of Bayreuth, Germany. The samples were ground (<100µm), dried and the TC-IRMS coupling was used for the simultaneous determination of oxygen (ä^{18}O) and hydrogen (ä^{2}H) isotope abundances. Each sample was weighed into the silver capsule, tightly closed and introduced into the pyrolysis oven. There sample was thermally converted to CO and H$_2$ for the H and O isotope analysis, respectively, under the oxygen free conditions. The gases thus produced were purified in a chemical trap and separated by gas chromatography subsequently. The relative abundances of the H and O isotopes were analyzed by the isotope ratio mass spectrometry (IRMS). The isotope ratios are presented in the delta notation as given below:

$$\delta X = [R_{sample}/R_{standard} - 1] \ X \ 1000‰$$

Where δX is the δ value of the heavy isotope X (δ^{18}O or ä^{2}H) and R is ^{18}O/^{16}O or ^{2}H/H .The standard is V-SMOW (Vienna Standard Mean Ocean Water)[6]. Overall analytical precision is ±0.2‰ for δ^{18}O and ±0.3‰ for ä^{2}H measurements. Specific surface areas of goethite and hematite samples were determined by gas adsorption using Brunauver-Emmett-Teller (BET) specific surface analysis instrument (Micromeritics, USA). Each dried sample was treated in a mixed-gas flow (N$_2$ 31% and He 70%; flow rate 70ml/min) at 150 ºC for 15 min and cooled to liquid nitrogen temperature (-196 ºC). The mineralogy and purity of the samples were investigated by X-ray powder differaction (XRD), Fourier Transform Infra Red (FT-IR) spectroscopy and SEM.

RESULTS

Product description

This method produced 8.21 g goethite and 7.43 g hematite with the average surface areas of 23.5 and 30.9 m^2/g, respectively. X-ray diffractograms and IR spectra of goethite and hematite samples are shown in Figure 1 and 2. Both goethite and hematite samples showed sharp identifiable X-ray diffraction (XRD) peaks. All peaks in the IR spectra correspond to hematite and goethite and are indistinguishable from each other revealing uniformity of the experimental conditions. The

Table 1: Oxygen and hydrogen isotope data for the synthesized goethite and hematite.

Mineral	Sample ID	Temperature (°C)	Duration (hr)	Surface area (m²/g)	Isotope type	Initial water	Final water [‰]	Mineral	α Mineral-Water [(1000 + δ_Mineral)/(1000 + δ_Water)]	10³ ln α Mineral-Water	ε Mineral-Water [‰]
Goethite	G-I	70	60	25.21	^{18}O	-6.7271	-9.1157	-16.7524	0.99229		-7.74
Goethite	G-II	70	60	25.8	^{18}O	-6.841	-7.4769	-14.9928	0.99243		-7.60
Goethite	G-I	70	60	25.21	^{2}H	-65.6805	-65.9549	-167.2954	0.83075		-115.59
Goethite	G-II	70	60	25.8	^{2}H	-55.2056	-56.6973	-160.1428	0.83059		-115.57
Hematite	H-I	90	48	51.80	^{18}O	-6.4521	-6.9564	-15.6534	0.99522		-6.51
Hematite	H-II	90	48	50.14	^{18}O	-6.4518	-7.1527	-15.9512	0.99514		-6.55
Hematite	H-I	90	48	51.80	^{2}H	-60.4615	-60.5095				-
Hematite	H-II	90	48	50.14	^{2}H	-56.0954	-56.1359				-

goethite consists of relatively large acicular crystals (300 ~ 600 nm long; 60 ~ 100 nm wide: 15 ~ 20 nm thick.). Hematite crystals were fairly uniform in size (30 ~ 60 nm) and diamond shaped. SEM images of four samples are shown in Figure 3.

Goethite

Oxygen and hydrogen isotope data for pure synthetic minerals and water samples are listed in Table 1. The $\delta^{18}O_{Goethite}$ values varied from -16.75 to -14.99‰ and the corresponding waters in which goethites were synthesized varied between -9.114 (final water) and -6.84‰ (initial water). The $\delta^{2}H_{Goethite}$ varied from −167.10 to -160.14‰, while the corresponding waters ranged from -65.96 to -55.20‰.
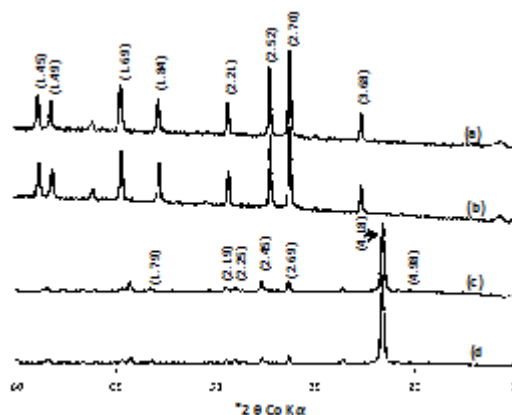

Fig. 1: X-ray diffractograms of pure hematite ((a) in type-1 and (b) in type-II water) and goethite ((c) in type-1 and (d) in type-II water) synthesised from F^{III} salt solutions. The Å spacings are in parentheses (in Å)
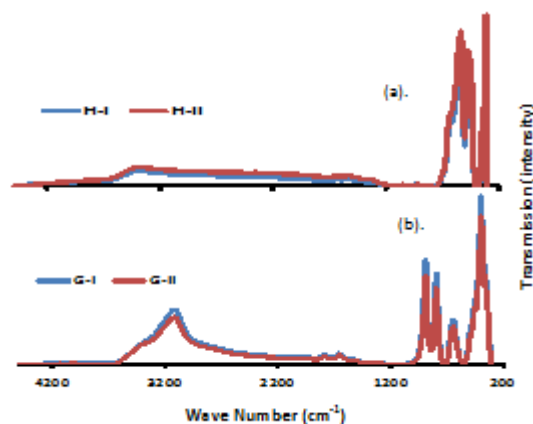

Fig. 2: Infrared spectra of pure hematite (a) and goethite (b) samples

The average isotopic separation, defined here as $\Delta_{Goethite-Water} = \delta_{Goethite} - \delta_{Water}$, between goethite and water was -7.58 ‰ for ^{18}O and -102.61‰ for ^2H. The average fractionation factor ($\alpha_{Goethite-Water}$) is measured to be 0.9924 for the ^{18}O isotope and 0.8907 for the ^2H isotope. Yapp [7] reported $^{18}\alpha$Goethite-$_{Water}$ value of 1.0022‰ at 62 ºC which is higher than the value measured in this study. The

average fractionation factor ($^2\alpha_{Goethite-Water}$) for the ^2H isotope is measured to be 0.8907. Yapp [8] reported the fractionation factor ($^2\alpha_{Goethite-Water}$) value of 0.905 at 62 ºC which is much higher than the value measured in this study. At present there are no other published experimental values of $^2\delta_{Goethite-Water}$ available for comparison.

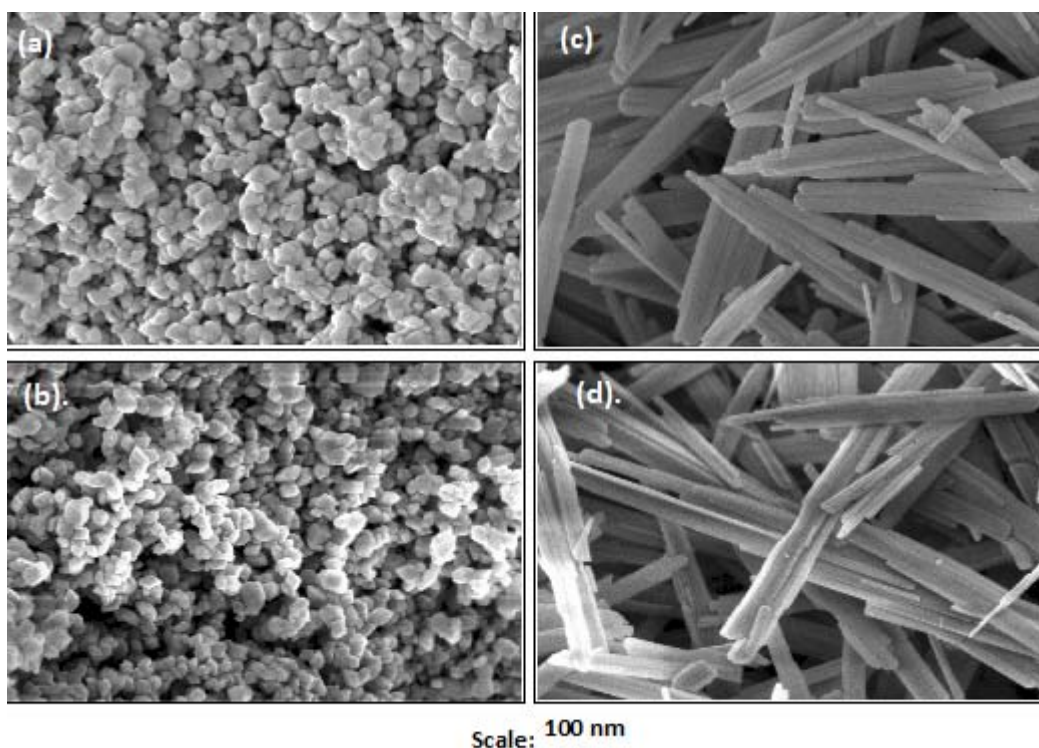Scale: 100 nm

Fig. 3: SEM images of pure hematite ((a) in type-1 and (b) in type-II water) and goethite ((c) in type-1 and (d) in type-II water). Hematite crystals are small platelets with some diamond shaped. Acicular goethite crystals (c & d) cut perpendicular to the needle axis
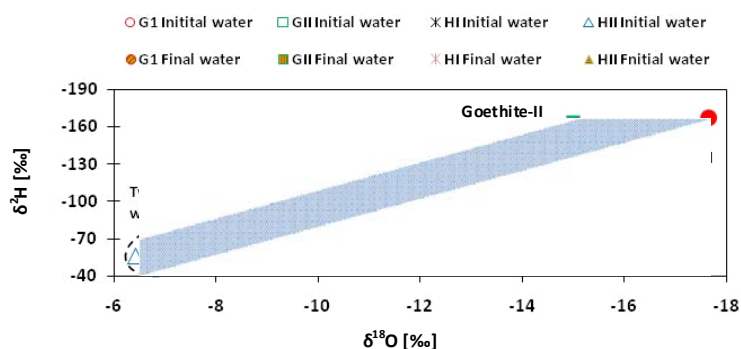

Fig. 4: Plot of $\delta^{18}O$ vs. δ^2H of water and iron oxide samples

Hematite

The $\delta^{18}O_{Hematite}$ values varied between -15.66 and -13.96‰ (range~ 1.7‰) and the corresponding waters in which hematite was synthesized varied from -8.94 to -6.43‰ (Table 1). No ä²H values were measured for hematite. The ä²H values for initial and final water in which hematites were synthesized did not show any significant change ($\leq$ 0.048‰) revealing no active role of hydrogen during the mineral formation.
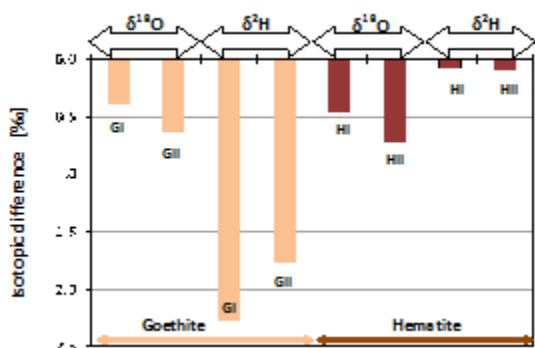

Fig. 5: Isotopic difference [$\delta_{Final\ water}$ - $\delta_{Initial\ water}$] in ^{18}O and ^{2}H values between the initial and final water in which goethite and hematite were synthesized
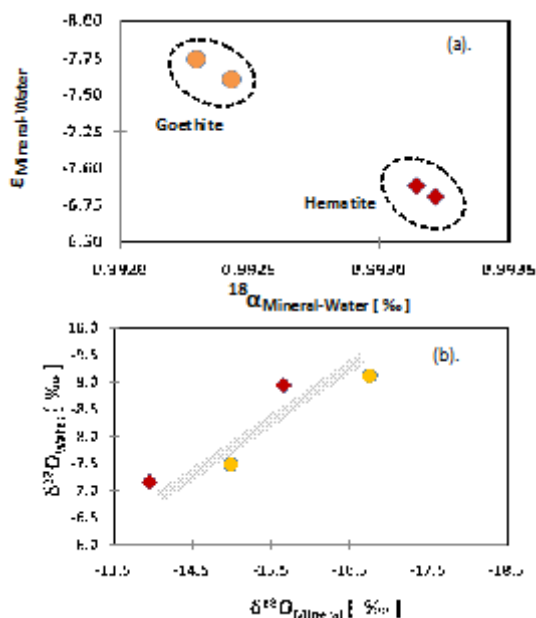

Fig. 6: Plots of the fractionation factor against the enrichment factor of mineral-water system (a) and 18O of mineral against water (b)

The average isotopic separation ($\Delta_{Hematite-Water}$) between hematite and water is -6.77‰ for ^{18}O isotope. The average fractionation factor ($\alpha_{Hematite-Water}$) for the ^{18}O isotope is measured to be 0.9932‰. Zheng [9] reported a much lower $^{18}\alpha_{Hematite-Water}$ value of 0.9889 ‰ at 90 ºC and Yapp [7] reported a much higher value of 0.9998 ‰ at 92 ºC.

DISCUSSION

The Λ^{18}O values showed a positive correlation with δ^2H in both water and iron oxide samples. The δ^{18}O and δ^2H values of all goethite and hematite samples shifted in apparent response to the isotopic composition of the initial water in which the mineral was in contact (Fig. 4). The magnitude of the change in δ^{18}O is slightly lower for the goethite (0.39 and 0.64‰) than the hematite (0.45 and 0.72‰) samples. The magnitude of change in δ^2H is much larger than d^{18}O (Fig. 5). A slight change in temperature results in a larger variation in hydrogen than the oxygen due to the large difference in masses. Both δ^{18}O and δ^2H values of final waters were lower than the initial waters which indicated the incorporation of heavy O- and H- isotopes into the solid products, goethite and hematite. The δ^2H values of initial and final waters

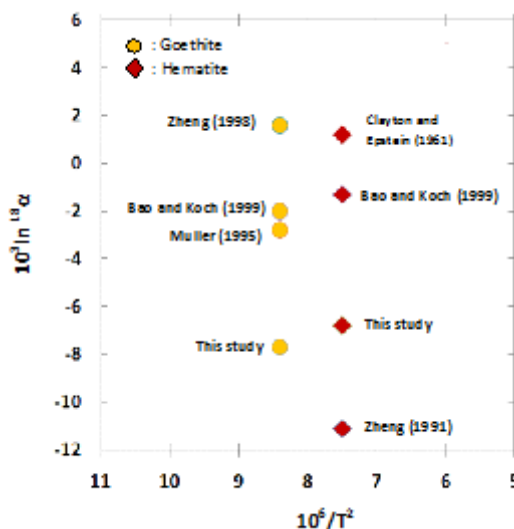**Fig. 7: Plots of 10³ln $^{18}\alpha$ *vs.* 10⁶/T² for goethite-water (~70 ºC) and hematite-water (~90 ºC) fractionation factors determined by synthesis experiments and calculations**

did not change due to no active role playing in the hematite (Fe_2O_3) crystal growth.

The goethite and hematite exhibited closer fractionation factor values with water. The higher isotopic values of the type-II water showed relatively higher fractionation factors ($\alpha > 0.9915$‰) as compared to the type-I water. The $\alpha_{Hematite\text{-}Water}$ value is slightly higher (~0.001; Fig. 6(a)) than the $\alpha_{Goethite\text{-}Water}$ for the ^{18}O isotope. The hematite was synthesized at higher temperature (~90 ºC) than the goethite (~70 ºC). Two minerals also differ in the synthesis pathway after the initial formation of ferrihydrite ($Fe_5HO_8.H_2O$ approx.). The hematite is formed by the direct solid state transformation from the ferrihydrite by internal reorganization. Therefore, the ^{18}O isotope of hematite is solely related to the ^{18}O isotope of the initial water from which precursor ferrihydrite formed. The goethite is formed by the dissolution of ferrihydrite and subsequent precipitation as goethite [10]. In the goethite crystal growth process the isotopic composition of the initial ferrihydrite may be lost. Also, goethite crystals took longer (~60 h) to form than the hematite (~48 h) and, therefore, mineral-water isotopic equilibrium may have been approached. The enrichment factor ($\varepsilon_{Fe\text{-}oxide\text{-}Water}$) decreased systematically with the increase of fractionation factor reflecting isotopic signature of the initial water in which the minerals were synthesized. Hematite samples showed both higher fractionation and enrichment factors as compared to the goethite samples (Fig. 6(a)). The $\delta^{18}O_{Mineral}$ showed a positive correlation with $\delta^{18}O_{Water}$. In terms of mineral-water relationship both goethite and hematite showed a similar trend by plotting along the line (Fig. 6(b)).

The fractionation factor ($1000ln^{18}\alpha$) and temperature relation revealed slightly lower value of the goethite-water as compared to the hematite-water (Fig. 7). The two ferric (hydr)oxides were synthesized at different temperatures which may explain differences in $1000ln^{18}\delta$ values. Various studies presented $1000ln^{18}\delta$ values for goethite-water and hematite-water which differ from the values determined in this study. A comparison is shown in Figure 7. The mineral-water oxygen isotope fractionation factors calculated from the α-T relations given by various researchers ranged from -8 to 2 for goethite (at 70 ºC) and -11.0 to 1.5

for hematite (at 90 ºC). Yapp[7, 8] presented the α-T relation for both goethite and hematite-water system and he concluded that O-isotope fractionation factors for these two minerals are identical. Zheng[9,11] calculated the $1000ln^{18}\alpha$ values for goethite-water which are significantly different from the hematite-water (Fig. 7). The average fractionation factor ($1000ln^2\alpha$) value for hydrogen in the goethite-water is determined to be -115.78‰ which is more negative than the $1000ln^{18}\alpha$ values for oxygen.

The most likely reasons for a wide range in fractionation factors at the same temperature are due to the difference in procedures followed to obtain $\delta^{18}O$ and δ^2H data. Which include drying, washing, type of reactants, pH, and extraction and measurement of ^{18}O and ^2H isotopes in a sample. Moderate to low temperatures synthesis experiments may never reach isotopic equilibrium due to the extremely low rates of mineral-water exchange [4] so α-T relation at lower temperature may not represent the true equilibrium. Formation temperatures of goethite (~70 ºC) and hematite (~90 ºC) seem to have less impact in altering mineral-water fractionation as compared to the formation water.

CONCLUSIONS

Goethite-water fractionation factor values for ^{18}O and ^2H isotopes are measured to be 0.9924 and 0.8907, respectively. Hematite-water fractionation factor value for the ^{18}O is measured to be 0.9932. These values differ from the values reported in the literature probably due to the differences in the synthesis conditions. The isotopic change is much larger for the δ^2H than the $\delta^{18}O$ in waters in which minerals were synthesized. Formation temperatures of goethite and hematite seem to have less impact in altering mineral-water fractionation as compared to the formation water.

ACKNOWLEDGMENTS

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