



Article Potential Reference Materials for Hematite Oxygen Isotope Analysis

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Received: 5 October 2020; Accepted: 4 November 2020; Published: 6 November 2020



Abstract: Hematite is a potential mineral for reconstructing the oxygen isotope composition and paleotemperature of paleowater. A highly accurate analysis of oxygen isotopes is essential. However, relative to other oxygenated minerals, we lack hematite reference materials that allow for internationally comparable analyses between different laboratories. To address this issue, we attempted to perform bulk rock oxygen isotope analysis on five hematite reference materials (GBW07223a, GBW07825, YSBC28740-95, YSBC28756-2008, Harvard 92649). Meanwhile, the oxygen isotope ratios of iron oxides (GBW07223a, GBW07825, YSBC28740-95, YSBC28756-2008) were obtained by mass balance involving other oxygen-bearing minerals such as quartz and silicates. In addition, the oxygen isotope ratios of iron oxides in an oolitic hematite (ca. 1.65 billion years ago) are consistent with the results of previous analyses of this class of minerals.

Keywords: hematite; iron oxides; oxygen isotopes; isotope ratio mass spectrometry (IRMS); laser fluorination

1. Introduction

Hematite, siderite, goethite and magnetite are iron-bearing minerals that are relatively widely distributed in nature. The oxygen isotope of iron oxides is an important tool for reconstructing the paleo-temperature, oxygen isotopes of fluids, etc. during mineral formation or climate on land [1–15]. Hematite is a relatively common iron-bearing mineral, especially from the Precambrian period, and is the most important constituent mineral of Banded Iron Formation (BIF) [16–22]. Among these iron-bearing minerals, an oxygen isotope of hematite has been used to reconstruct paleotemperature variations during the Paleocene–Eocene Thermal Maximum (PETM) [1]. More recently, a systematic analysis of iron oxides of oxygen isotopes in hematite over 2 billion years was performed [7].

To date, the oxygen isotope of a large number of hematite samples has been analyzed by the laser fluorination method [23], with a few laboratories testing for hematite oxygen isotopes using secondary-ion mass spectrometry (SIMS) [24,25]. However, many laboratories lack an intercomparable reference material (RM) for hematite oxygen isotopes. To address the lack of stable isotope analysis RMs for hematite, we attempted to standardize the oxygen isotope values of a number of hematite RMs procured for principal analysis to assess whether they could be used as potential reference material for comparison between laboratories.

2. Experimental Section

2.1. Samples

In this study, we selected five samples of hematite. Two (GBW07223a, GBW07825) were purchased from the China National Standards, and two (YSBC28740-95, YSBC28756-2008) were purchased from NCS Testing Technology Co. They were previously used as reference materials for primary or trace element analysis (see https://www.ncrm.org.cn/Web/Home/Index; http://icloud.ncscrm.com/catalog. aspx). One is a granular reference material of hematite (Harvard 92649), which has previously been used as an RM for electron probe analysis [21]. We also collected a piece of oolitic hematite (Chuan), as shown in Figure 1, from the Chuanlinggou Formation (ca. 1.65 Ga.) in North China, which was crushed into < 63 μ m powder. Oxygen isotope composition of hematite has been analyzed on similar such samples by previous researchers [7].



Figure 1. Oolitic hematite from the Chuanlinggou formation (ca. 1.65 Ga), North China.

2.2. Laser Fluorination Extraction System and Oxygen Isotope Analysis

We designed and built a laser-based fluorination oxygen extraction line (Figure 2) at the Institute of Geology and Geophysics, Chinese Academy of Sciences. This line was made with a stainless steel tube. BrF_5 was purchased from Tianjin Special Gas Company and placed in Kel-F Teflon distillation traps (Figure 2). The laser fluorination system utilizes a New Wave Research MIR10-30 laser coupled to a vacuum extraction system. The sample chamber in the laser fluorination system is made of nickel metal and has 36 circular cavities with diameters of 3 mm. The whole system consists of 2 cold fingers, 2 cold traps and one hot trap. Both the cold fingers and the cold traps were immersed in liquid nitrogen during the reaction. KBr was added to the hot trap and heated to 100 °C to react with the F_2 possibly present in BrF_5 and to collect the Br_2 in the later cold trap.

One zircon, Penglai (PL) (IGGCAS; $\delta^{18}O = +5.17\%)$ [26] and one garnet, 04BXL07 garnet (University of Science and Technology of China; $\delta^{18}O = +3.70\%$) [27] were used in the standard set and were $\pm 0.08\%$ and $\pm 0.05\%$, respectively. The measured ${}^{18}O/{}^{16}O$ ratios were normalised using the value for Standard Mean Ocean Water (SMOW). A ca. 2 mg sample was weighed and placed into the sample chamber. The sample chamber is designed to hold up to 36 samples at a time, with a batch of 10 RMs, including garnet (04BXL07) and zircon (PL) for the analytical test procedure. An excess of BrF₅ was added, and the reaction took approximately 10 minutes to remove adsorbed moisture from the air. The reaction gas was purified and withdrawn from the sample. Usually, two PL zircon samples are analyzed consecutively until the specific value of the PL sample reaches its given value (+5.17‰) before the other samples are analyzed.



Figure 2. BrF₅ laser oxygen isotope fluoridation preparation system.

The fluorination of minerals is usually performed by adjusting the diameter of the CO₂ laser beam to 3 mm and the power of the reaction to between 10 and 20 W. In the presence of BrF₅, the reaction usually emits a bright white light, and the reaction time is usually 5 minutes, until no white light is emitted and the oxygen of the sample is completely released. Furthermore, the amount of oxygen obtained from the reaction is used to calculate the yield, which is usually > 99%, indicating a complete reaction. The remaining BrF₅ from the reaction is first collected in cold finger 1 and cold trap 1, and trace F₂ gas passes through a hot well containing KBr at 100 °C to produce Br₂, which is collected in cold trap 2 (Figure 2). The reference O₂ gas used was purchased high-purity oxygen (99.999%). The oxygen isotope values (δ^{18} O) were –9.91‰, which ere obtained by calibrating to the international RM quartz (NBS-28). The O₂ gas was analyzed on a MAT 252 mass spectrometer. The mass spectrometer is equipped with three Faraday cups for simultaneous measurement of 32, 33 and 34.

2.3. Chemical Treatment

The fluorination of natural ironstones releases oxygen not only from iron-bearing minerals like hematite but also from other oxygen-bearing minerals like quartz and silicate minerals. Therefore, in order to analyze oxygen isotopes of iron oxides in natural ironstones, it is necessary to analyze the oxygen content and isotope of quartz and silicate minerals present in natural ironstones.

Sedimentary hematite usually contains significant amounts of silicates, including quartz, and different oxygen-bearing silicate minerals have a significant effect on the determination of oxygen isotopes of iron oxides. Methods for the assessment of oxygen isotopes of iron oxides for hematite are numerous [1,7,11]. In this study, we used the 12N HCl dissolution treatment method. About 1.5 g of the powder sample was weighed and placed in a 15 mL centrifuge tube, and 10 mL HCl was added. To avoid the possible exchange of oxygen from the reagent with the silicate as much as possible, the reaction condition was room temperature at 25 °C for 24 hours. However, we found that at room temperature, even for pure ferric oxide (metal basis), complete dissolution was still not achieved (only 83.4% dissolution), whereas at 90 °C, complete dissolution can be achieved. Therefore, the reaction temperature is very critical for the dissolution of hematite. Previous studies have also shown that a temperature range of 60–80 °C ensures the complete dissolution of hematite in the presence of sufficient HCl [28]. After the 24-hour reaction is completed, the tube was centrifuged for 10 minutes at 4000 rpm. After pouring off the upper clear liquid, secondary ionized water was added for repeated washing and centrifugation more than four times. The residue was then dried in a freeze dryer or oven (60 °C). The weight of the residue as a percentage of the whole rock sample was calculated (Table 1).

Sample Number	Reaction Temperature	Residue Content (%)	Oxygen Content of Residue (%)	δ ¹⁸ O _{Residue} (‰, SMOW)	δ ¹⁸ O _{Oxides} * (‰, SMOW)
GBW07223a	25 °C	32.8	30.04 ± 0.55	4.53 ± 0.2	1.33 ± 0.12
GBW07223a	90 °C	8.5	45.3 ± 1.3	11.74 ± 0.04	1.2 ± 0.08
GBW07825	25 °C	19.6	35.7 ± 1.8	10.87 ± 0.18	-0.29 ± 0.13
GBW07825	90 °C	17.0	45.6 ± 1.2	11.84 ± 0.16	-0.89 ± 0.11
YSBC28740-95	25 °C	58.2	31.7 ± 1.33	0.57 ± 0.42	1.09 ± 0.7
YSBC28740-95	90 °C	13.0	33.8 ± 0.7	5.59 ± 0.16	-0.01 ± 0.34
YSBC28756-2008	25 °C	15.9	42 ± 1.02	9.8 ± 0.2	9.08 ± 0.28
YSBC28756-2008	90 °C	14.3	46.6 ± 0.5	10.21 ± 0.12	8.81 ± 0.28
Chuan	90 °C	16.1	48.7 ± 0.1	12.68 ± 0.3	-4.71 ± 0.07

Table 1. Oxygen isotope ($\delta^{18}O_{\text{Residue}}$) and oxygen content of residue after HCl dissolution treatment and oxygen isotope values of iron oxides ($\delta^{18}O_{\text{Oxides}}$).

* $\delta^{18}O_{Oxides}$ obtained through Equation (3).

2.4. Measument of CO_3^{2-}

In natural hematite samples, $CO_3^{2^-}$ -bearing minerals, such as siderite, calcite or dolomite are common. Therefore, it is necessary to measure the oxygen content of these kinds of minerals. In this study, we used GasBench II system (ThermoFisher company) which is commercial equipment to measure carbon and oxygen isotope of carbonate.

In order to measure the total inorganic carbon, approximately 300 μ g of pure carbonate RM and 4 mg of hematite samples were reacted with 100% phosphoric acid at 70 °C within a 12 mL vial tube filled with He, and generated CO₂ gas was introduced into an isotope ratio mass spectrometer.

3. Results and Discussions

3.1. Oxygen Isotope of Bulk Rocks ($\delta^{18}O_{Bulk}$)

The oxygen isotopes of bulk rocks tested in this study were mainly in the range of -1.12 to 2.25‰ (Table 2). The two RM of GBW07223a and GBW07825 had consistent bulk rock δ^{18} O values within the error ranges of 2.20 ± 0.02‰ and 2.25 ± 0.08‰, respectively. Whereas YSBC28740-95 has a slightly lower value of 0.76 ± 0.26‰, it is less reproducible relative to the oxygen isotope values of the other samples. This indicates its possible inhomogeneity. There are two extremes of δ^{18} O values: one sample (YSBC28756-2008) has a high δ^{18} O value (9.51 ± 0.03‰), and the hematite RM (Harvard 92649) has the lowest δ^{18} O value (-1.12 ± 0.07 ‰). With the exception of RM YSBC28740-95, the analytical repeatability of the oxygen isotopes of the other whole rock samples analyzed in this analysis is high, which also indicates that the samples have good homogeneity, at least within the 2 mg sample size range.

Table 2. Oxygen isotopes and oxygen content data in bulk rock samples.

Sample Number	Analytical Number	δ ¹⁸ O _{Bulk} (‰, SMOW)	Oxygen Content ^a (%)	Iron Content ^b (%)	Oxygen Content from CO_3^{2-} (%)
GBW07223a	3	2.20 ± 0.02	32.43 ± 1.06	61.73	0.04
GBW07825	3	2.25 ± 0.08	31.02 ± 0.51	49.50	3.90
YSBC28740-95	3	0.76 ± 0.26	31.93 ± 0.77	66.15	ND
YSBC28756-2008	3	9.51 ± 0.03	31.01 ± 0.68	55.81	0.45
Chuan	3	-0.57 ± 0.05	34.09 ± 0.76	NM	0.03
Harvard 92649	4	-1.12 ± 0.07	30.87 ± 0.50	69.06	NM

^a The oxygen contents do not include the oxygen content of carbonate minerals such assiderite, carbonate or dolomite. ^b Data are from the website (https://www.ncrm.org.cn/Web/Home/Index; http://icloud.ncscrm.com/catalog.aspx) and McGuire et al. (1992) [29]. NM—not measured. ND—not detected. The bulk rock δ^{18} O values for the newly collected samples (Chuan) are $-0.57 \pm 0.05\%$. In addition, it is very noteworthy that this sample (Chuan) has the highest oxygen content (34.09 \pm 0.76%) compared to the other standard samples, which indicates that the sample contains more silicates or quartz.

We should note that one of the selected samples (GBW07825) contained high CO_3^{2-} content, with 3.9% (GBW07825) of its oxygen from CO_3^{2-} . Since this sample contains low Ca and Mg, the mineral could not have been calcite or dolomite, but rather siderite for GBW07825, given that these samples were rich in iron. The oxygen content from CO_3^{2-} in the other four samples (YSBC28756-2008, GBW07223a, YSBC28740-95, Chuan) was less than 0.45%, and the oxygen content from CO_3^{2-} in YSBC28740-95 was not detectable at all. Because the oxygen content of the CO_3^{2-} -bearing minerals could not be detected through faraday cup (32, 33, 34) of MS, the presence of CO_3^{2-} -bearing minerals also does not affect the bulk oxygen isotope of the sample to be tested [30–32]. The oxygen content of iron-bearing mineral obtained by the fluoridation method will underestimate the total oxygen content of the sample. The sum of the oxygen content obtained by fluoridation and the oxygen content of the carbonate minerals is representative of the total oxygen content of the sample.

3.2. Oxygen Isotopes of Residues After HCl Dissolution

Dissolution of hematite at room temperature was used to avoid possible oxygen isotope exchange as much as possible. However, our HCl dissolution experiments for pure hematite (metal basis) showed that pure hematite could not be completely dissolved at 25 °C, and about 16.6% could not be dissolved. For samples (GBW07223a, YSBC28740-95, Chuan), the red mineral (hematite) was clearly present in the residue, which indicates that room temperature is not sufficient to completely dissolve hematite. In contrast, the red hematite residue was clearly not present in the residue, and the pure hematite was completely dissolved at 90 °C, indicating that the temperature of the reaction directly determined the degree of dissolution of hematite. Oxygen isotope analysis of the residues at both temperatures also showsed that 90 °C is the more valid temperature for the complete dissolution of iron oxides.

Except for hematite RM (Harvard 92649), we performed HCl dissolution treatment on all other samples (GBW07223a, GBW07825, YSBC28740-95, YSBC28756-2008, Chuan). The four samples (GBW07223a, GBW07825, YSBC28740-95, YSBC28756-2008, Chuan) were treated with HCl under 25 °C and 90 °C conditions. The percentage content of the residue of hematite at 25 °C was significantly higher than that at 90 °C. The oxygen content of the residue nferred from its molar amount of oxygen (Table 1) is significantly higher at 90 °C than that at 25 °C due to the high oxygen content of silicate minerals compared to Fe₂O₃ (30.06%).

It is also important to note that because we used two temperature conditions (25 °C and 90 °C) for hematite dissolution, δ^{18} O values for both residues were obtained for each sample (Table 1, Figure 3). It is noteworthy that the content of residue at 90 °C is lower than that at 25 °C (Table 1), and the content of residue in these two samples (GBW07223a, YSBC28740-95) is significantly lower than that in the other two samples (GBW07825, YSBC28756-2008). Correspondingly, the sample with the largest change in residue amount (GBW07223a, YSBC28740-95) had the largest change in oxygen isotope value (Figure 3, Table 1). The residue δ^{18} O values at 25 °C are much closer to those of the bulk rock samples (Figure 3, Table 1), which also indicates that hematite is not completely dissolved at 25 °C. The oxygen isotope ratios of the residues of the two samples (GBW07825, YSBC28756-2008) with small residue variation are very similar, which indicates that the dissolution of Fe_2O_3 was nearly achieved in these two samples at 25 °C. However, we can also see that the δ^{18} O values of the residues at 25 °C are obviously lower, which also reflects that a small portion of the Fe_2O_3 exists in the residue. In addition, we noted that the δ^{18} O values of the residues of three (GBW07223a, GBW07825, YSBC28756-2008) of the four RMs and one other collected sample (Chuan) were all in the positive range of 10–13‰ at 90 °C (Table 1). The δ^{18} O values of the residues of one RM (YSBC28740-95) were relatively low (5.59‰) (Table 1).

The Hematite RM (Harvard 92649) is known from previous testing that this RM is a relatively pure hematite and that total iron and oxygen are essentially the main elemental composition of this sample, so the low and negligible amount of residue can be expected.



Figure 3. Oxygen isotope ratios of iron oxide reference materials (RMs) and residues after the HCl dissolution treatment at room temperature (25 °C) and 90 °C. The orange rhombi represent the bulk rock δ^{18} O. The blue rhombi represent the reaction at room temperature. The green rhombi represent the 90 °C condition. The error bars represent 1 σ .

3.3. Oxygen Isotope of Iron Oxides ($\delta^{18}O_{Oxides}$)

By measuring the moles of O_2 gas released from oxides during fluorination, we can calculate the oxygen content of the bulk rock from the oxygen production. In addition, the oxygen content of the residue from the oxygen yield was obtained. In this way, without distinguishing the specific mineral composition of the residue, mass balance calculation was expressed as

$$N_{Bulk} \times \delta^{18} O_{Bulk} = N_{Oxides} \times \delta^{18} O_{Oxides} + N_{Residue} \times \delta^{18} O_{Residue}$$
(1)

$$N_{Oxides} = N_{Bulk} - N_{Residue} \tag{2}$$

where N_{Bulk} refers to the moles of oxygen in the bulk rock, $N_{Residue}$ refers to the moles of oxygen in the residue and N_{Oxides} refers to the moles of oxygen in iron oxides, which can be calculated from Equation (2). $\delta^{18}O_{Residue}$ refers to the oxygen isotope of the residue remaining after HCl dissolution of hematite.

With Equation (2) we can obtain the oxygen isotope values for iron oxides by following equation

$$\delta^{18}O_{Oxides} = \left(N_{Bulk} \times \delta^{18}O_{Bulk} - N_{Residue} \times \delta^{18}O_{Residue}\right) / \left(N_{Bulk} - N_{Oxides}\right) \tag{3}$$

In addition, we also tried to perform a calculation of $\delta^{18}O_{Oxides}$ by Equation (3) after HCl dissolution treatment at 25 °C (Table 1), although the residue under 25 °C includes part of the iron oxides.

Ironstones in nature are not composed of iron-containing minerals such as hematite and magnetite, but also contain other oxygen-containing minerals such as quartz, calcite and other minerals. Thus, it is impossible to directly get the oxygen isotope values of iron oxides. In contrast, a pure hematite RM (Harvard 92649) is composed mainly of Fe and O. The oxygen isotope analysis of iron oxides shows a good homogeneity ($1\sigma = 0.07\%$). It is an ideal RM for inter-laboratory comparisons.

The other samples also had more than 16% of the residue undissolved in HCl, so the oxygen isotopes of the residue and the percentage content of the residue need to be evaluated for calculating the oxygen isotope of iron oxides. In sum, the $\delta^{18}O_{Oxides}$ values of hematite obtained at 25 °C were all higher than those at 90 °C (Table 1, Figure 4). The difference between the $\delta^{18}O_{Oxides}$ value (-0.89 ± 0.11‰) and the bulk rock $\delta^{18}O$ is the largest in GBW07825, an RM, relative to the small deviation between $\delta^{18}O_{Bulk}$ and $\delta^{18}O_{Oxides}$ of the other samples.



Figure 4. Ratio of bulk rock δ^{18} O and corrected $\delta^{18}O_{Oxides}$ for hematite RMs. The orange rhombi represent the bulk rock δ^{18} O. The red rhombi represent the corrected $\delta^{18}O_{Oxides}$ after HCl dissolution treatment at room temperature (25 °C). The black rhombi represent the $\delta^{18}O_{Oxides}$ after HCl dissolution treatment at 90 °C. The error bars represent 1 σ .

In this study, the $\delta^{18}O_{\text{Oxides}}$ value of hematite sample (Chuan) is -4.71 ‰ (Table 1). It is worth noting that the $\delta^{18}O_{\text{Oxides}}$ values of some samples collected from the same location range from -3.41‰ to -5.67‰, which is close to those of the present study [7].

4. Conclusions

The hematite sample (Harvard 92649) is an ideal hematite RM for inter-laboratory comparisons, and our study shows that it not only has good primary element homogeneity but also has good oxygen isotope homogeneity.

In addition, we analyzed other samples from China (GBW07223a, GBW07825, YSBC28740-95, YSBC28756-2008, Chuan), three of which (GBW07223a, GBW07825, YSBC28756-2008, Chuan) had better homogeneity, while YSBC28740-95 had poorer homogeneity.

In the present study, ironstones were subjected to HCl dissolution chemistry. By further analysis of the oxygen content and oxygen isotopes of the insoluble residue, the oxygen isotope ratios of iron oxides can be obtained by mass balance calculations.

Author Contributions: Conceptualization, L.F.; Funding acquisition, L.F.; Methodology, L.F., H.L. and T.L.; Writing—original draft, L.F., H.L. and T.L. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by National Key R&D Program of China (No.2018YFF0215400), Instrument Function Developing Project of the Chinese Academy of Sciences (No.IGG201603), CAS Key Technology Talent Program and the Key Research Program of the Institute of Geology & Geophysics, CAS, Grant No. IGGCAS-201905.

Acknowledgments: Thanks to Chaofeng Li for providing the sample GBW07825 and to Lanzhen Guo for his help in the sample analysis.

Conflicts of Interest: The authors declare no conflict of interest.

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