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Oxygen isotopic composition of ferric oxides from recent soil, hydrologic, and marine environments

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Abstract—Low-temperature synthesis experiments on ferric oxide–water systems have resulted in disparate oxygen isotope fractionation–temperature (α -T) curves. In this study, recent ferric oxides, mostly goethites of Holocene age, were collected and analyzed from a variety of modern soil, stream, and marine environments, where formation temperature and the oxygen isotopic composition ($\delta^{18}\text{O}$) of the water from which ferric oxides precipitated can be independently measured or estimated. This allows comparison of experimental α -T relationships with data from natural systems.

Selective dissolution methods were refined for the pretreatment of fine-grained minerals in order to obtain reliable $\delta^{18}\text{O}$ values for pure and crystalline ferric oxides. The difference ($\Delta\delta^{18}\text{O}$) between the $\delta^{18}\text{O}$ value of goethite and that of local mean meteoric water ranges from -1.5 to $+6.3\%$ for soil goethites from New Jersey, Indiana, Michigan, Iowa, South Dakota, and Taiwan. We argue that these variations are largely the result of differences between the $\delta^{18}\text{O}$ of formation water and that of local mean meteoric water, induced probably by ^{18}O -enrichment of soil waters by evaporation or other processes in soil horizons where ferric oxides are forming. A marine goethite sample from Scotland and a subaqueous bog iron sample from New Jersey, which can not be biased by evaporative processes, provide crucial natural evidence that the difference in $\delta^{18}\text{O}$ between goethite and formation water is $\sim -1.5\%$ at $\sim 10^\circ\text{C}$. This result is consistent with our prior laboratory synthesis results (Bao and Koch, 1999), but in conflict with other experimental calibrations. Given the highly variable $\delta^{18}\text{O}$ value of soil or other surface water, as well as the potential of initially formed ferric oxides for reequilibration with subsurface burial fluids during maturation to crystalline phases, an understanding of formational and diagenetic conditions is absolutely essential when attempting to use the oxygen isotope composition of ferric oxides as a paleoclimatic proxy. Copyright © 2000 Elsevier Science Ltd

1. INTRODUCTION

Ferric oxides are the most common stable phases for iron at Earth surface conditions. Ferric oxides occur in an enormous variety of forms (e.g., α -FeOOH, γ -FeOOH, α -Fe₂O₃, Fe₂O₃·nH₂O, etc.). Banded iron formations, ooidal ironstones, laterites, bog irons, and iron concretions are examples of Fe(III)-rich deposits. In modern soils, ferric oxides occur throughout a wide spectrum of climates and are often associated with Fe-rich parent materials.

Recent studies on the $\delta^{18}\text{O}$ of authigenic minerals have demonstrated the potential of ferric oxide as a proxy for paleoclimatic reconstruction (Yapp, 1987, 1990b, 1993a,b; Bird et al., 1992, 1993; Bao et al., 1999). There are, however, uncertainties in the literature over the appropriate ferric oxide–water fractionation values. Experimental and theoretical determinations of the oxygen isotopic fractionation at low temperatures have yielded different results (Clayton and Epstein, 1961; Yapp, 1987; Müller, 1998; Zheng, 1991, 1998; Bao and Koch, 1999). Natural ferric oxides usually form over several to hundreds of thousands of years, and natural processes are difficult to simulate in the laboratory. Analysis of natural samples from modern environments, where temperature and the $\delta^{18}\text{O}$ of

formation water can be monitored, provides an alternate strategy for the determination of fractionation relationship.

Several studies have reported that natural ferric oxides form in oxygen isotopic equilibrium with local mean meteoric water (Yapp, 1987, 1997; Bird et al., 1992; Girard et al., 1997). Most of these studies have been conducted on oxides that have formed over a long period of time (i.e., several millions of years), typically at a single locality. The $\delta^{18}\text{O}$ of ambient water has rarely been measured. Yet it is known that evaporation enriches the ^{18}O of soil water, which may complicate assessment of the fractionation of oxygen isotopes between ferric oxides and local mean meteoric water. For example, pedogenic carbonates precipitate from waters that have $\delta^{18}\text{O}$ values systematically higher than those formed in isotopic equilibrium with mean meteoric water. Evaporative loss of soil water and/or seasonal precipitation of carbonates have been posited as sources of this bias (Quade et al., 1989; Cerling and Quade, 1993; Liu et al., 1996).

This study represents a survey of the $\delta^{18}\text{O}$ of modern and Holocene ferric oxides from different surface settings, including both land and marine environments. Because the samples used in this study are recent or, at most, of Holocene age, the temperature and the $\delta^{18}\text{O}$ of meteoric water experienced by iron oxides during their formation should be relatively stable and similar to recent average values. Our goal is to examine the modern relationship between the $\delta^{18}\text{O}$ of ferric oxides and local

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mean meteoric water. Samples with well-understood formation conditions can provide key tests of the different experimentally determined fractionation relationships. If we detect large variations in the difference between the $\delta^{18}\text{O}$ of ferric oxide and meteoric water that can not be explained by temperature differences, other factors, such as ^{18}O -enrichment of soil water due to evaporation and other processes, or kinetic effects during precipitation, must be considered.

2. MATERIALS

The samples consisted of ferric oxides, including bog irons in water-logged soil and stream beds, soil ferric-oxide nodules, ferric-oxide cemented sands in soils, ortstein oxide coatings on gravel, disseminated ferric oxides in bulk soils, deep-ocean hydrothermal deposits, and shallow marine cements. Ortstein is a hardened spodic horizon in which the cementation is due to sesquioxides (mostly iron) and illuviated organic matter. All the ferric oxides reported here are recent and are actively forming today. Geographically, these samples are from Michigan, Iowa, Indiana, New Jersey, South Dakota, Scotland, Taiwan, and the Pacific Ocean. Samples from tropical regions were not studied because it is difficult to obtain concentrated, crystalline ferric oxide from young tropical soils. In addition, highly concentrated ferric oxide samples from systems with relatively simple mineral compositions were selected to simplify sample purification and analytic procedures.

Whenever possible, local shallow groundwater was collected for oxygen isotope analysis. The $\delta^{18}\text{O}$ of shallow groundwater is regarded as a good representation of the average isotope composition of local meteoric water (Yonge et al., 1985; Fritz et al., 1987). A total of 16 water samples were analyzed. Most shallow groundwater samples were collected while sampling ferric oxides. Some sites were sampled repeatedly over the course of a year. Of course, the soil water or pore fluids immediately adjacent to oxide samples are most likely to be representative of the $\delta^{18}\text{O}$ of the water from which oxides precipitate. Because ferric oxides usually record water signature of an integrated time period and the $\delta^{18}\text{O}$ of these soil waters or pore fluids have large temporal variation, several measurements are not sufficient to draw a conclusion. Therefore, we did not collect these fluids for further laboratory extraction. Our ultimate goal was not to test for equilibrium precipitation in all surface settings. Rather, we were trying to determine if it is plausible that oxides formed in equilibrium with a fluid that has a composition similar to local mean meteoric water, as the $\delta^{18}\text{O}$ of mean meteoric water, is a valuable proxy for paleoclimatic and paleohydrologic research.

3. METHODS

Nearly all natural ferric oxide samples from surface deposits contain silicates and other minerals. Because fluorination, the method used to extract oxygen for $\delta^{18}\text{O}$ measurement, fuses the mixed sample and releases oxygen from all mineral phases, the $\delta^{18}\text{O}$ of pure ferric oxide must be calculated by mass balance using 1) the oxygen mole fraction (OMF) for each mineral phase in the mixture, 2) the $\delta^{18}\text{O}$ of the mixture, and 3) the $\delta^{18}\text{O}$ of the residue phase remaining after ferric oxide has been dissolved from the mixture with HCl or dithionite-citrate-bicarbonate solution (DCB) (Bird et al., 1992; Bao et al., 1999; see Appendix I for details). One difference from analyses involving more ancient geological samples is that ferric oxide in recent sediments is often a mixture of amorphous, poorly crystalline, and

crystalline phases. Noncrystalline phases pose additional difficulties during oxygen extraction by laser fluorination. They should be removed by the initial pretreatment steps. In cases where some of the Fe in the mixture was derived from Fe-bearing silicates, rather than from ferric oxide, the DCB method was employed to extract Fe from just the ferric oxides (Mehra and Jackson, 1960), so that the OMF of ferric oxide in the mixture was not overestimated. X-ray diffraction (XRD) analysis was conducted to identify the ferric oxide phase present (e.g., goethite or hematite) which permits appropriate OMF calculation. The error in the estimated $\delta^{18}\text{O}$ value for pure ferric oxide is largely determined by the concentration of ferric oxide in the mixture, with large standard deviations at lower concentrations.

Because the OMF of ferric oxide is calculated from the Fe content of ferric oxide in the mixture, the effect of Al-substitution on the $\delta^{18}\text{O}$ value of pure ferric oxide can be removed by assuming that Al-substitution shifts the $\delta^{18}\text{O}$ value of Al-substituted ferric oxides toward that of aluminum silicates (Bird et al., 1992; Yapp, 1993b). The error associated with this assumption should be minimal because, as it turns out, all our reported goethite samples have low Al-content (Appendix 2).

Oxygen isotope analyses of ferric oxides and silicates were conducted at the Geophysical Laboratory, Carnegie Institution of Washington. A few samples were analyzed at the University of California, San Diego, and the $\delta^{18}\text{O}$ of our reference sample showed no difference between the two CO_2 -laser systems. Sputtering during laser heating was a problem for samples containing a significant amount of silicate minerals. To avoid partial reaction and sample contamination, samples were widely spaced in the sample holder and small amounts of sample were used (<2 mg). The results are highly reproducible, with the difference between duplicates < 0.3‰.

Oxygen isotope analysis of water was performed by equilibration with CO_2 using a VG-Isoprep18 linked to an Optima mass spectrometer (Department of Geosciences, Princeton University). The standard notation for $\delta^{18}\text{O}$, referenced to V-SMOW (Vienna Standard Mean Ocean Water), was used for all ferric oxides and water samples.

4. SAMPLE DESCRIPTIONS AND OXYGEN ISOTOPE RESULTS

More than 30 samples were examined for this project. Most of the ortstein samples from soils in New England and the Great Lake region, including samples from the Pullup Series, Finch Series, Naumburg Series, and Success Series did not contain significant amounts of crystalline ferric oxide in their fine fractions. One ortstein sample from Nova Scotia contained a significant amount of highly crystalline hematite, which is apparently associated with a nearby red Triassic sandstone. We also excluded some soil ferric oxide samples due to their poor crystallinity, including several surface soil samples from New Jersey and one ferric oxide-cemented sandstone sample from Ohio. Several ferric oxide samples from deep ocean hydrothermal vents (Alt, 1988) and one ooidal iron sample from a shallow-marine volcanic setting (Heikoop et al., 1996) were treated and analyzed. Unfortunately, these recent deep ocean samples contained mostly amorphous and poorly crystalline phases, which dissolve readily in oxalate treatment (Appendix 1).

Ultimately, we are reporting the elemental compositions and $\delta^{18}\text{O}$ values for 12 natural ferric oxide samples, all of which are moderately crystalline (Tables A1, A2, and Table 1) and most of which have low levels of Al-substitution (Appendix 2 and Table A3). The occurrences of ferric oxide in these 12 cases differ in many ways, making a case-by-case description necessary.

Table 1. The $\delta^{18}\text{O}$ values of modern ferric oxides in a variety of locations.

Sample	$\delta^{18}\text{O}$ mixture	$\delta^{18}\text{O}$ silicates	OMF as FeOOH ^a	$\delta^{18}\text{O}$ pure oxide	Error ±‰	$\delta^{18}\text{O}$ of mean meteoric water measured or estimated	MAT ^e °C	AST ^e °C
G97-1	-8.10	14.80 ^b	0.9809	-8.5	0.1	-7.0 ± 0.3 (<i>n</i> = 7)	11.4	23
G97-3	6.70	14.80	0.4684	-2.5	0.8	-7.0 ± 0.3 (<i>n</i> = 7)	11.4	23
Vincentown	2.70	9.20	0.5547	-2.5	0.5	-7.0 ± 0.3 (<i>n</i> = 7)	11.4	23
Batsto-Bog1 ^c	-0.20	14.09	0.9664	-0.7	0.2	-7.0 ± 0.3 (<i>n</i> = 7)	11.4	23
Batsto-Bog2	-2.50	12.04	0.9402	-3.5	0.2	-7.0 ± 0.3 (<i>n</i> = 7)	11.4	23
UP-Bogiron	-5.90	10.30 ^b	0.9869	-6.1	0.1	< -8.4	4.7	17.5
Jordan-G	-2.90	4.30 ^b	0.8739	-3.9	0.3	-8.0 to -8.5 (Simpkins, 1995)	8.1	22
Jordan-H ^d	-2.50	4.30	0.8314	-3.9	0.3	-8.0 to -8.5 (Simpkins, 1995)	8.1	22
Zadog-IN	-0.30	9.40	0.8907	-1.5	0.2	-7.8 ± 0.1 (<i>n</i> = 4)	10.3	22
BLKH-Bog	-5.06	8.83	0.6805	-11.6	0.4	-14 to -15	8	22
Taiwan	-0.30	10.50	0.7006	-4.9	0.4	-6.0 ± 2.6 (<i>n</i> = 60) (C.-H. Wang)	20.6	
Aslay	-0.50	7.95	0.9271	-1.2	0.2	0.0 ± 0.1 (Ganssen)	10	14

^a Oxygen mole fraction as FeOOH (except samples Batsto-Bog1 and Jordan-H) in mixture.

^b Data for similar samples are used here due to extremely small content of non-oxide residues.

^c 100% hematite.

^d Calculated assuming hematite/goethite ratio of 4:1.

^e MAT = mean annual temperature; AST = average summer temperature.

4.1. New Jersey: A Variety of Soil Ferric Oxides

We examined a suite of soil ferric oxides (including bog irons) from central New Jersey. Central New Jersey had a periglacial environment during the late Wisconsinan, as inferred from features such as boulder fields, fossil ice wedges, and patterned ground (Wolfe, 1953; Judson, 1965; Minard and Rhodehamel, 1969; Walters, 1978). Ridge et al. (1992) argued that the periglacial climate inhibited soil development and accelerated erosion and redeposition by freeze-thaw processes and mass transport, including slope erosion, fan deposition, and eolian sedimentation. Their model of late Quaternary landscape development suggests that, after the recession of late Wisconsinan ice, significant soil development and landscape stability were delayed until the Holocene (~10 kyr ago). Two radiocarbon dates also suggest that soils in central New Jersey are less than 20 kyr old (Chris Smith, USDA Natural Resource Conservation Service [NRCS], New Jersey, personal communication). It is probable, therefore, that most of the soil ferric oxides from central New Jersey formed under climatic conditions and from water with similar compositions to those measured at the sites today.

G97-1 is a bog iron collected in situ from Marsh Land (USDA soil classification), Georgetown. This area is covered with water 8 to 10 months of the year, and can not be much improved by drainage (Markley and Hutchins, 1971). The sample contains highly concentrated goethite of moderate crystallinity.

G97-3 is a goethite-cemented, glauconite-rich sandstone on a stream bank (not in situ), southeast of Georgetown, NJ.

Vincentown is a loose sand from the B horizon of the Evesboro Sand (USDA soil classification), near Vincentown, NJ. The sample was taken from an upland pit where sand was removed for construction. The Evesboro Soil Series consists of a high fraction of deep, loose, and excessively drained sands with low available water capacity that is usually too dry to be suitable for crops (Markley and Hutchins, 1971). The loose sand is coated with yellowish goethite of moderate crystallinity.

Batsto-Bog1 and Batsto-Bog2 are cemented sand and gravel

samples collected from Batsto, NJ. Ferric oxides act as cement between poorly sorted quartz sand and gravel. Clay minerals are virtually absent. Blood-red rocks are cemented by hematite, whereas rusty-brown ones are cemented by goethite. Often in a single rock, the surface portion that is exposed to the atmosphere is red, whereas the partially buried portion is brown. Here, sample Batsto-Bog1 is hematite and sample Batsto-Bog2 is goethite.

4.2. Upper Peninsula, Michigan: Bog Iron

Sample UP-Bogiron was collected from a burned field, west of Newberry, Michigan. The upper peninsula of Michigan was glaciated during the Last Glacial Maximum, thus these soils must be younger than 10 kyr old. Shallow groundwater with a $\delta^{18}\text{O}$ of -8.4‰ was collected at 90 cm below the surface at this site during the summer of 1996. Another groundwater sample collected 40 miles east from a poorly drained soil (Finch Series) had a $\delta^{18}\text{O}$ value of -13.7‰, significantly more negative than that from the bog iron site. The large difference between these two sites is puzzling, but may be explained by the observation that the bog iron site has much less vegetation cover and is much better drained than the Finch Series site. The bog iron occurs sporadically as yellowish, sheet-like deposits (0.5 to 2 cm in thickness) on the soil surface. Plant root and stem traces are abundant in the bog iron deposits. The soil at the sample location is developed on well-drained sands (Spodosol). There have been no prior reports of this type of ferric oxide deposit in this region. Highly concentrated goethite (>99%) was obtained from the fine fraction of the bog iron. The goethite is moderately crystalline.

4.3. Northeastern Iowa: Weathering Crust

Two indurated sandstones from immediately beneath the modern soil horizon (Boone Series) were sampled at a road-cut, 1/4 mile east of Church, Iowa, where the Cambrian Jordan Sandstone is exposed. The Jordan Sandstone is widespread in western Wisconsin, Minnesota, and eastern Iowa. Johnson and

Swett (1974) studied the origin and diagenesis of calcite and hematite nodules in the Jordan sandstone in northeastern Iowa and concluded that the calcite/hematite nodules are a weathering feature closely related to recent soil processes. Although Wisconsinan ice sheets did not cover this area, the locality was only 100 miles southwest of the glacial. The periglacial environment resulted in severe erosion of this Paleozoic terrace. Soils from previous interglacials and interstadials are unlikely to have survived late Wisconsinan erosion. The soil development and formation of iron-rich weathering crusts on the sandstone are most likely a relatively recent phenomenon, probably less than 15,000 years old (Art Bettis, personal communication).

Both pieces of sandstone are strongly cemented by yellow and red ferric oxides. XRD reveals that the yellowish sample is cemented by goethite, whereas the reddish one is cemented mostly by hematite with a minor component of goethite. Sample Jordan-G, the pure goethite cement, has a $\delta^{18}\text{O}$ value of $-3.9 \pm 0.3\%$. Sample Jordan-H, the hematite cement, contains a minor portion of goethite. Knowledge of the hematite/goethite ratio in the mixture is required to calculate the $\delta^{18}\text{O}$ of this ferric oxide due to slightly different oxygen content between goethite and hematite. On the basis of the relative XRD peak intensities of hematite and goethite, we estimate that goethite represents <25 wt% of the mixture. Using a 4:1 hematite/goethite ratio, the $\delta^{18}\text{O}$ of ferric oxide (hematite + goethite) in sample Jordan-H is calculated as $-3.9 \pm 0.3\%$. The estimate of the hematite/goethite ratio may have an error of $\pm 10\%$. However, even if the ratio is 3:2, the calculated $\delta^{18}\text{O}$ of ferric oxide would be $-3.8 \pm 0.3\%$. In samples with high concentrations of ferric oxide, such as these cements, the calculated $\delta^{18}\text{O}$ of ferric oxide is relatively insensitive to hematite/goethite ratio.

4.4. Kankakee Valley, Indiana: Calcite/Goethite Nodules

Iron nodule samples were collected from a corn field, Jasper County, Indiana. In northern Indiana, the Zadog Series consists of deep, poorly drained soils formed on sandy outwash in broad depressions. Iron nodules occur mostly in the upper B horizon, but are concentrated in localized patches. Frequently, they are found on the surface of cultivated soils. These soils were mined for iron during World War II. Most Zadog soils are now drained and planted in corn and soybeans. The Zadog soil is usually 3 m above the Snider glacial till from the Michigan lobe of the Wisconsinan ice sheet, which is only 22,000 years old. Thus the Zadog soil is probably not more than 10,000 to 15,000 years old in this region (Shane McBunett, Purdue University, personal communication).

Field and laboratory examinations reveal that these nodules are actually calcite nodules. Most nodules have a goethite rim 2–4 mm thick on their surface, and sometimes as patches in the interior, as seen in thin-sections and polished slabs. Detrital quartz sand is common and often coated with goethite. Snail shells are frequently found inside these nodules. Isotopic evidence suggests that the calcite nodules are pedogenic (Bao, 1998). These observations suggest that calcite nodules may have formed in a different environment, when the climate was probably much drier, whereas recent wetter conditions may favor the formation of ferric oxides on preexisting calcite

nodules. XRD patterns confirmed that the ferric oxides are nearly pure goethite (sample Zadog-IN), with only a trace of quartz.

4.5. Black Hills, South Dakota: Bog Iron

A bog iron sample (BLKH-Bog), loosely goethite-cemented sands and gravel, was collected from a construction site, west of Rochford, Pennington County, South Dakota. The soil could be very old, because the Black Hills region was not glaciated during the Last Glacial Maximum. On the other hand, it is likely that these bog iron deposits are quite recent because of its relatively poor crystallinity (Appendix 2). The $\delta^{18}\text{O}$ of stream water collected after a storm in summer 1997 was -15.9% . A mean stream water $\delta^{18}\text{O}$ value is not available at this site. On the basis of nearby groundwater $\delta^{18}\text{O}$ data from Wall, SD (-13.9%) and Douglas, WY (-16.3%) (Lander, 1991), a mean meteoric water value of -14 to -15% is a reasonable estimate for the Black Hills region.

4.6. Central Taiwan: Iron Concretions in a Forest Soil

Iron concretion samples were collected from a forest soil in the Lien-Hua-Chi drainage basin, central Taiwan. King et al. (1990) reported a detailed study of these ferric oxides, which are morphologically different from ortstein, placic horizon, plinthite, or any Fe-rich soil nodules reported in the soil literature. The concretions are forming pedogenically by in situ weathering of a Tertiary shale bed on an east-facing, 60% slope at an elevation of 680–780 m. The present climate of central Taiwan is humid and warm-temperate. Torrential summer rainfall associated with typhoons is the main source of precipitation. The vegetation is typical warm-temperate montane rain forest. Iron concretions are mostly forming at 50 to 100 cm depth, and occur mainly as fragments above 30 cm (King et al., 1990). The high erosion rate associated with the high rainfall and steep slope suggests that the iron concretions at this site are likely to be very young.

Oxygen isotope data for meteoric water in central Taiwan are available through the work of C.-H. Wang (Institute of Earth Sciences, Academia Sinica, Taipei), and T.-R. Peng (Department of Geology, National Taiwan University). XRD examination reveals that goethite is the only ferric oxide phase in the fine fraction of the sample (Taiwan). Muscovite and quartz were present in the sample after pretreatment.

4.7. Islay, Scotland: A Marine Goethite Cement

A cemented sample (Islay) containing sand, gravel, and bivalve shells was obtained from seawater near Islay, Scotland. The material is associated with the wreckage of a boat that sank in 1857. Submarine aragonite, magnesian calcite, and ferric oxide are the cementing agents and their petrology and geochemistry were studied by Adams and Schofield (1983). This sample was recovered from a depth ~ 8 m below midwater, near the base of a cliff. Sea surface temperature variation is small in this area. Temperature ranges from $\sim 14^\circ\text{C}$ in July and August, to 8°C in January and February (U.S. Navy, 1981). There are no measurements of the $\delta^{18}\text{O}$ of sea water at this site. However, data from nearby North Atlantic sites, obtained in April 1988 at depth of ~ 5 m follow the relationship:

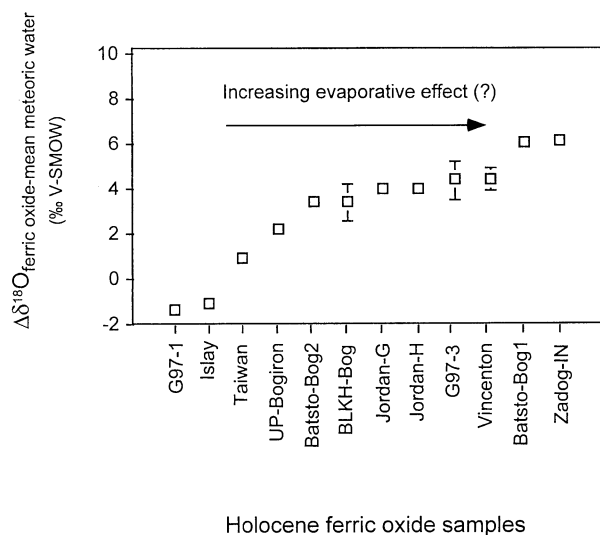


Fig. 1. Holocene ferric oxide samples.

$$\delta^{18}\text{O} = -13.74 + 0.39 \times \text{salinity} \quad (r^2 = 0.68)$$

(Ganssen, unpublished data). (1)

Salinity can decrease to 34.5 practical salinity units (psu) near the coast in this region. An estimate of 35 psu is reasonable at this site because it experiences extremely rough water and there are no major rivers nearby. The regression relationship yields a seawater $\delta^{18}\text{O}$ estimate of $0.0 \pm 0.1\text{‰}$. A highly concentrated goethite sample was obtained by pretreatment of the cemented rock.

5. DISCUSSION

5.1. Do Ferric Oxides Form in Oxygen Isotopic Equilibrium with Local Mean Meteoric Water?

Among the 12 samples, only Batsto-Bog1 and Jordan-H are hematite. Batsto-Bog1 has a $\delta^{18}\text{O}$ value 2.8‰ higher than that of goethite (sample Batsto-Bog2) at the same locality, whereas Jordan-H, a hematite sample with a minor component of goethite, has nearly the same $\delta^{18}\text{O}$ value as Jordan-G, a goethite sample from the same locality. From the discussion below on the goethite–water fractionation relationship, we believe the most likely explanation is that hematite and goethite exhibit very similar fractionations with water, and that hematite has higher $\delta^{18}\text{O}$ values than co-occurring goethite because of hematite formation favored by drier conditions (Schwertmann and Taylor, 1989). We will now focus on goethite, the dominant recent ferric oxide phase.

The difference in $\delta^{18}\text{O}$ value between goethite and shallow groundwater (equivalent to mean meteoric water), defined here as $\Delta\delta^{18}\text{O}_{\text{goethite-meteoric water}}$ for New Jersey samples ranges from -1.5‰ to $+6.3\text{‰}$ (Table 1). There are essentially no differences in annual temperature and precipitation among these bog iron sites. Other reported samples are from regions with similar mean annual temperature (5–10°C), but the $\Delta\delta^{18}\text{O}_{\text{goethite-meteoric water}}$ varies too (Fig. 1).

Several factors may contribute to the large variation, such as

different degrees of soil–water evaporation at different sites (related to position in the solum), water–mineral interaction and exchange, differences in Al-substitution, and true disequilibrium (i.e., kinetic isotope effects). Al-substitution is low for all samples reported here, and its effect should have been removed by our correction procedure.

The precipitation kinetics for crystalline ferric oxides are complex, determined by pH, Fe(III) concentration, and solution temperature. Fe(III) hydrolysis results in the formation of mono-, di-, and labile polynuclear species, which eventually age to an intermediate amorphous precipitate or to a variety of crystalline phases (Cornell et al., 1989). For many natural crystalline ferric oxides, the rate-limiting step is the transformation from the poorly crystalline to the crystalline phase. We do not have quantitative information on how fast the crystalline ferric oxide formed in our 12 samples. However, a crude division can be made among them based on local pH of soil solution. Samples Islay, Zadog-IN, and Jordan-G, and Jordan-H probably precipitated in weakly alkaline conditions, where pH is buffered by sea water, nodular calcite, or calcite cement, respectively. Other samples formed under acidic conditions. The $\Delta\delta^{18}\text{O}$ values from both groups exhibit large variations (from -1.5‰ to $+6.3\text{‰}$). There are no consistent patterns in $\Delta\delta^{18}\text{O}$ values between these two groups of ferric oxides, as expected if isotopic disequilibrium due to precipitation kinetics had played a significant role. Although it is difficult to rule out kinetic effects entirely, we argue that the most likely cause of the observed $\Delta\delta$ variability is due to differences between the $\delta^{18}\text{O}$ of local shallow groundwater and that of the actual soil water immediately adjacent to the ferric oxide in question. Analysis of subaqueous samples, which formed in water body close to local mean meteoric water in terms of its $\delta^{18}\text{O}$ value, should provide the most robust measure of the goethite–water fractionation relationship.

Samples G97-1 and Islay are the only two samples that are forming below the water table among those reported in this paper. Thus they are the only samples for which we have reliable information for both formation water and formation temperature. The average $\Delta\delta^{18}\text{O}_{\text{goethite-water}}$ value is $-1 \pm 1\text{‰}$ in these settings with an average temperature of 10°C. This value is close to that expected from the fractionation relationships of Bao and Koch (1999) and the base-added experiment of Müller (1998), but is far from the values predicted by other experimental or theoretical estimates for the goethite–water fractionation. For example, the fractionation relationship from Yapp (1990a), the hydrolysis experiment of Müller (1998), and Zheng (1998) would predict positive $\Delta\delta^{18}\text{O}$ values (6–7‰) for the goethite–water system at 10°C. The fractionation relationship of Clayton and Epstein (1961) would predict a slightly positive $\Delta\delta^{18}\text{O}$ value ($\sim 2.6\text{‰}$) at 10°C. In general, the different oxygen isotope fractionation relationships for ferric oxide–water systems in the literature exhibit low sensitivity to temperature at surface conditions.

Many of the $\Delta\delta^{18}\text{O}_{\text{goethite-water}}$ values in our data set appear to match those expected from α -T relationships that have large, positive values at earth surface temperatures (e.g., Yapp, 1990a; the hydrolysis experiment of Müller, 1998; and Zheng, 1998). However, even if we assume these relationships represent equilibrium fractionation, the high variance in $\Delta\delta^{18}\text{O}_{\text{goethite-water}}$ values, and the low $\Delta\delta^{18}\text{O}_{\text{goethite}}$ values

observed in subaqueous samples, remain unexplained. We suggest, as an alternative hypothesis, that the goethite–water fractionation is close to -1‰ at Earth surface temperatures, as indicated by the subaqueous goethites analyzed here, and that for goethites that have formed even partially subaerially, evaporative ^{18}O -enrichment of ferric oxide formation waters may be responsible for unexpectedly high $\delta^{18}\text{O}_{\text{goethite}}$ values and highly variable $\Delta\delta^{18}\text{O}_{\text{goethite-water}}$ values. The ^{18}O -enrichment of soil water resulting from exchange with soil minerals is less likely in low-temperature surface environments where the precipitation of ferric oxides demands open and oxidizing conditions.

It has long been recognized that evaporation causes the oxygen isotope value of water to shift toward more positive values in the upper portions of soil profiles (Barnes and Allison, 1988). The position of maximally ^{18}O -enriched values and the degree of the positive shift depend on, among other things, climate, soil properties, and vegetation coverage. Soil water $\delta^{18}\text{O}$ values can be $+5\text{‰}$ to $+12\text{‰}$ more positive than those from shallow groundwater (Allison and Hughes, 1983; Walker and Brunel, 1990). Therefore, minerals forming near the surface of a soil will often equilibrate with a water that has a higher $\delta^{18}\text{O}$ value than shallow groundwater. Since evaporation and dehydration are important factors promoting the crystallization of ferric oxides in nature, we should not be surprised to find many examples of natural ferric oxides forming from ^{18}O -enriched waters. Indeed, all the samples in our study that are forming above the water table have more positive $\Delta\delta^{18}\text{O}_{\text{goethite-water}}$ than those of the two subaqueous samples (Fig. 1).

The range of $\Delta\delta^{18}\text{O}_{\text{goethite-water}}$ values may reflect relative differences in evaporative effects among the different sample sites. Sample Taiwan has a $\Delta\delta^{18}\text{O}$ value of only $\sim 1\text{‰}$, indicating a small evaporative effect that could be explained by the wet and heavily vegetated locality. Likewise, relatively large evaporative effects should be expected for samples from the soil surface and upper soil horizons (e.g., Georgetown-3, Vincentown, G97-3, and Zadog-IN) (Fig. 1). Quantitative testing of this hypothesis, however, requires systematic measurement of both the $\delta^{18}\text{O}$ and δD of soil water and goethite. Combined oxygen and hydrogen isotope data for soil water will reveal the extent of evaporation by comparison to data for local meteoric water (Gat, 1996). To establish a reliable relationship between the oxygen isotope compositions of soil minerals and soil water, and the extent of evaporative water loss from soils, it is essential to obtain the $\delta^{18}\text{O}$ of the water from which the minerals precipitate and transform. Unfortunately, such a project requires not only improved accuracy in measuring water isotopic composition for relatively dry soils, but also year-round and long-term monitoring, which is beyond the scope of this study.

5.2. Prior Studies of Natural Ferric Oxides

A significant amount of data on the $\delta^{18}\text{O}$ of natural ferric oxides has been collected over the past several decades. Before Yapp's systematic efforts, analysis of the $\delta^{18}\text{O}$ of ferric oxides was often the by-product of isotopic studies on silicates. Analytical methods, especially those related to purification of ferric oxides, differ among the studies. It is also possible that some of

the reported $\delta^{18}\text{O}$ values are not for pure ferric oxide phases, but rather are for mixtures containing minor amounts of silicate. Many recent attempts to examine the oxygen isotope relationship between soil iron oxides and local meteoric water (e.g., Bird et al., 1992; Girard et al., 1997; Yapp, 1997) appear to be in agreement with the fractionation relation of Yapp (1987, 1990a), which is $6\text{--}7\text{‰}$ more positive than the relationship reported here for subaqueous samples, and the experimental relationship reported in Bao and Koch (1999).

As indicated by natural ferric oxides from this study, samples formed above the water table, or in zones that are periodically exposed to evaporative processes, are not ideal candidates for examination of the relationship between ferric oxides and mean meteoric water. Here we discuss two cases in which ferric oxides formed and aged under water or deep in soil profiles. We argue that these natural data fit our expectations well.

First, Hein et al. (1994) analyzed the $\delta^{18}\text{O}$ of three "pure goethite ironstones" (D27-B1-2, D27-B5-2, and CD1-16B) recovered from seamounts in the central Pacific, and found the $\delta^{18}\text{O}$ value to vary between 3.8 and 6.5‰ . On the basis of the major element composition of the samples listed in Table 3 of Hein et al. (1994), however, it is clear that the samples are not 100% goethite. If other elements, such as Ca, P, Si, Al, Mg, Mn, K, Ti, and Na are taken into account in the calculation of the OMF for pure FeOOH, as in the mass-balance approach used here, the OMF for FeOOH is only 0.861 for sample D27-B1-2. Assuming the nongoethite minerals (carbonates and silicates) in these samples have a $\delta^{18}\text{O}$ value of 20‰ , the average $\delta^{18}\text{O}$ of non-ferric-oxide minerals in hydrothermal deposits, the calculated $\delta^{18}\text{O}$ of pure FeOOH is 1.4‰ . This value is much closer to that expected for goethite formed from seawater (with a $\delta^{18}\text{O}$ value $\approx 0\text{‰}$) using our relationship than that expected using the relationship of Yapp (1990a). The second example is the study by Bird et al. (1993) of eastern Amazon hematite/goethite ores. The $\delta^{18}\text{O}$ values of pure hematite/goethite ores deep in the soil profiles (below 20 m) range from -2.9‰ to -6.5‰ , very close to the $\delta^{18}\text{O}$ values (-3.6 to -5.6‰) of the modern meteoric water in this region.

5.3. Implication for Paleoclimatic Research

The conclusions drawn from this study of modern/Holocene goethites are consistent with the oxygen isotope fractionation relationship obtained from our synthesis experiments for the goethite–water system at near-surface conditions (Bao and Koch, 1999). Both studies suggest that the $\delta^{18}\text{O}$ of goethite is $\sim 1\text{‰}$ lower than that of its formation water under surface condition ($10\text{--}20^\circ\text{C}$). However, application of this fractionation relationship to continental paleoclimatic reconstruction will be complicated by the fact that ferric oxides that have formed above the water table are likely to have unpredictably ^{18}O -enriched values, owing to evaporative effects on the $\delta^{18}\text{O}$ value of surface waters from which ferric oxides precipitate and age. On the other hand, due to the extremely slow transformation from noncrystalline ferric oxide phases to crystalline phases in many natural settings, some geological samples may record values that reflect a long-term equilibration with surface fluids. If ferric oxides formed below water table, or if early poorly crystalline ferric compounds undergo the majority of their maturation to highly crystalline phases below the water

table, where formation water is representative of the local mean meteoric water, then the $\delta^{18}\text{O}$ of mean meteoric water can be estimated from the $\delta^{18}\text{O}$ of goethite. A detailed understanding of formation conditions and subsequent diagenesis of ferric oxides in geological settings is essential to the application of ferric oxides as paleoclimatic proxies.

6. CONCLUSIONS

Unlike other recent minerals in soil or marine environments, ferric oxides often remain as poorly crystalline phases that are kinetically stable and transform only slowly into crystalline phases. This behavior poses problems for the examination of the oxygen isotope fractionation relationship in the ferric oxide–water system using recent natural samples. Separation, concentration, and pretreatment techniques have been developed and refined in this study to allow determination of the oxygen isotope composition of a series of modern fine-grained ferric oxide samples (mostly goethite) from around the USA and several other locations. The results suggest that the oxygen isotope fractionation under surface conditions is small for the goethite–water system ($\delta^{18}\text{O}_{\text{goethite}} - \delta^{18}\text{O}_{\text{water}} \approx -1 \pm 1\%$). A similar result is likely for the hematite–water system, although we have much less data on naturally occurring hematites. These results are in accord with expectations for the fractionation relationships derived in our synthesis experiments (Bao and Koch, 1999). Our results from goethites that have precipitated wholly in a subaqueous environment do not support the fractionation relationship developed by Yapp (1990a). We suggest that evaporative effects may shift the $\delta^{18}\text{O}$ of surface waters toward values higher than those for local mean meteoric water, contributing to the large variations observed in the $\delta^{18}\text{O}$ of ferric oxides in continental environments.

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APPENDIX 1: DESCRIPTION OF ANALYTICAL PROCEDURES

Pretreatment

1. Obtain concentrated goethite or hematite from fine fraction using ultrasonic stirring of raw samples.
2. Remove organic matter from the fine fraction by treating sample for >12 h in NaOCl (2–3%) solution. Ferrihydrite may form during this step if samples contain large amounts of organic–Fe complexes (Schulze, 1988).
3. Dissolve ferrihydrite, iron oxyhydroxysulfate, poorly crystalline ferric oxides, and Mn oxides/hydrates using ammonium oxalate in the dark (pH = 3) (McKeague and Day, 1966; McKeague et al., 1971). This treatment should have little effect on crystalline ferric oxides. Ferrihydrite (including that formed in Step 2) or other poorly crystalline phases may transform into crystalline goethite or hematite in late hot NaOH treatment (Goodman, 1988). We also found that hot NaOH treatment without prior oxalate-leaching of the noncrystalline ferric oxide phases resulted in exchange of oxygen isotopes between ferric oxides and hot NaOH solution. Therefore, it is essential to remove them prior to any hot treatment.
4. Soak the sample in 5 M NaOH solution at $\sim 90^\circ\text{C}$ for 3–5 h. This step removes a fraction of the silicates in the mixture (Kämpf and Schwertmann, 1982; Yapp, 1991). The amount of silicate dissolved by this treatment is determined by its mineralogy. Quartz is least susceptible to attack by NaOH, whereas amorphous phases, smectite, and berthierine/chamosite are readily dissolved. Norrish and Taylor (1961) reported complete removal of kaolinite and gibbsite, while ferric oxides, quartz, anatase, rutile, mica, and vermiculite were found in the residue. Phase changes, reduction in Al-substitution, and change of the crystallinity of ferric oxides are minimized when Si is present in the solution (Kämpf and Schwertmann, 1982), as is the case for most natural samples in this study.
5. After washing once with deionized water, treat the sample with ~ 0.5 M HCl solution for 15–20 min to dissolve newly formed, poorly crystalline phases as well as sodalite (Singh and Gilkes, 1991). Wash twice before freeze-dry.

Table A1. Results of ICP elemental analyses prepared by DC extraction and fusion methods.

Sample	mg	Fe(1) ^a	Si(1)	Al(1)	Ca(1)	Ti(1)	Mg(1)	Mn(1)	K(1)	Fe(2)	Si(2)	Al(2)	Ca(2)	Ti(2)	Mn(2)	Mg(2)	K(2)	OH ^b	Total-O	OMF-Fe ^c	Mean OMF-Fe	Error (±)
Vincentown-1	38.54	501.34	115.70	117.87	0.75	ND	ND	ND	ND	4.76	65.86	22.96	0.25	16.20	0.07	0.00	0.79	62.590	909.15	0.551	0.555	0.002
Vincentown-2	39.15	508.50	129.94	125.37	0.50	ND	ND	ND	ND	2.69	51.33	16.73	0.15	12.40	0.04	0.00	0.41	63.158	911.22	0.558		
G97-3-1	41.54	434.20	33.82	22.96	0.55	2.46	3.29	1.53	8.25	47.45	232.04	66.55	0.40	17.79	0.11	8.19	1.37	39.783	920.73	0.472	0.468	0.002
G97-3-2	40.12	427.04	57.17	30.02	0.77	2.88	4.11	1.53	7.06	43.33	216.45	61.16	0.60	14.61	0.11	7.94	2.51	40.524	917.81	0.465		
Batsto-Bog1	ND ^e	175.64	4.69	0.98	ND	ND	ND	0.00	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.437	181.75	0.966	0.966	0.001
Batsto-Bog2	ND ^e	197.02	10.39	1.48	ND	ND	ND	0.00	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.660	209.56	0.940	0.940	0.001
Taiwan-1	39.04	636.53	84.23	38.53	2.52	1.63	2.88	0.25	8.21	3.76	69.06	30.08	0.22	2.42	0.00	0.53	0.18	30.492	911.53	0.698	0.701	0.001
Taiwan-2	37.52	657.12	95.98	41.70	2.45	2.05	3.29	0.29	7.62	2.65	62.58	26.02	0.42	1.88	0.00	0.25	0.43	30.096	934.83	0.703		
BLKH-Bog-1	35.05	506.27	40.94	15.90	1.87	2.46	2.47	0.22	1.80	21.67	87.08	26.52	0.22	2.59	0.07	2.38	2.38	18.853	733.69	0.690	0.681	0.005
BLKH-Bog-2	33.45	464.64	39.87	14.07	1.80	2.25	2.47	0.22	1.36	30.62	84.51	25.35	0.27	2.59	0.03	2.22	2.68	17.520	692.47	0.671		

^a Micromole of oxygen in FeOOH. (1) refers to the content extracted by DCB method, and (2) to the content measured by fusion method on residues of DCB extraction. For other elements, oxygen mole contents are calculated as $\text{SiO}_2/\text{Al}_2\text{O}_3$, CaO , TiO_2 , MgO , MnO_2 and K_2O .

^b Calculated by assuming $\text{Al}:\text{H} = 3:2$ for silicate minerals.

^c Oxygen mole fraction as FeOOH, using only Fe from DCB extraction.

^d Not determined.

^e The two Batsto samples were analyzed by acid digestion (6 M HCl) and fusion method.

Table A2. Results of ICP elemental analysis prepared by "MgO + Fusion" method.

Sample	mg	Fe ^a	Si	Al	OH ^b	Ca	Ti	Mn	K ^c	Total-O	OMF-Fe ^d	Mean OMF-Fe	Error (±)
G97-1-1	15.69	264.55	3.8	0.22	0.10	1.75	0.13	0.25	0.05	270.90	0.977	0.981	0.002
G97-1-2	11.51	211.49	1.78	0.33	0.15	0.25	0.13	0.22	0.32	214.67	0.985		
UP-Bogiron-1	13.63	280.21	1.85	0.00	0.00	0.75	0.00	0.62	0.14	283.58	0.988	0.987	0.001
Up-Bogiron-2	12.03	250.67	1.99	0.00	0.00	1.00	0.17	0.47	0.03	254.33	0.986		
Jordan-H-1 ^e	14.49	284.24	35.96	6.56	2.92	0.00	2.67	0.18	0.42	332.95	0.854	0.856	0.001
Jordan-H-2 ^e	12.77	261.86	31.83	5.84	2.59	0.00	2.71	0.18	0.28	305.30	0.858		
Jordan-H-1 ^f	14.49	213.18	35.96	6.56	2.92	0.00	2.67	0.18	0.42	261.89	0.814	0.816	0.001
Jordan-H-2 ^f	12.77	196.40	31.83	5.84	2.59	0.00	2.71	0.18	0.28	239.83	0.819		
Jordan-G-1	13.97	247.09	26.13	3.89	1.73	1.50	1.80	0.04	0.18	282.35	0.875	0.874	0.001
Jordan-G-2	11.95	226.05	24.35	3.56	1.58	1.50	1.71	0.07	0.20	259.03	0.873		
Zadog-IN-1	15.7	276.63	19.37	5.73	2.55	3.00	0.71	2.26	0.40	310.63	0.891	0.891	0.000
Zadog-IN-2	14.84	260.07	18.01	5.50	2.45	2.50	1.00	2.11	0.26	291.90	0.891		
Islay-1	12.34	244.85	16.73	1.06	0.47	0.50	0.33	0.25	0.13	264.33	0.926	0.927	0.000
Islay-2	14.56	297.67	19.94	1.50	0.67	0.25	0.38	0.29	0.12	320.81	0.928		

^a Micromole of oxygen in ferric oxides (FeOOH and/or Fe₂O₃). For other elements, oxygen mole contents are calculated as SiO₂, Al₂O₃, CaO, TiO₂, MnO₂ and K₂O. Note that Mg was not determined due to the addition of MgO in the method.

^b Calculated oxygen mole content in OH Group, assuming Al:H = 3:2.

^c Measured using atomic absorption spectrometer (Perkin Elmer Model 3100).

^d Oxygen mole fraction as ferric oxides.

^e Calculated assuming 100% FeOOH.

^f Calculated assuming 100% Fe₂O₃.

Inductively Coupled Plasma (ICP) Elemental Analysis

1. In ~40 mg of freeze-dried sample, dissolve ferric oxides using the DCB method. Repeat the procedure if necessary until the residue becomes milky white. This treatment should extract most Fe from ferric oxides with minimal from Fe-bearing clay minerals.
2. After centrifugation, collect the supernatant in a flask. Wash sample 4 times with deionized water and combine all the supernatants. Drops of saturated NaBr can be used for flocculation. Measure Fe, Al, Si, Mn, K, Ca, Mg, and Ti concentration in solution. Fe content is usually high, but other elements are low, in the DCB-extracted solution.
3. Oven-dry the residue at 50°C, then mix with LiBO₂ for fusion. Measure Fe, Al, Si, Mn, K, Ca, Mg, and Ti concentrations. Usually, Si and Al are the dominant elements.
4. Combine elemental data from the two sets of ICP results. The Fe measured in the DCB extract represents ferric oxide (Table A1).

For samples with a low content of Fe-bearing clay minerals, such as certain bog irons and sandstone cements, the DCB step is unnecessary. However, samples should be mixed with LiBO₂ and MgO with a volume ratio of ~1:10:10 for fusion at 1100°C. MgO is used in this step because it prevents adhesion of fused material to the wall of the graphite crucible, particularly iron, which may otherwise stick to the bottom of the crucible (Figueroa et al., 1997) (Table A2).

Elemental concentration was measured using ICP-OES (Optical Emission Spectrometry, Perkin Elmer 6000) and was converted to oxide concentration and reported as oxygen mole content of oxides for all elements (Tables A1 and A2). After pretreatment, Fe, Si, Al, and sometimes Ti are the most abundant elements in the mixture associated with the oxygen. In most cases, contribution of oxygen from other elements is minimal. As indicated in the mass balance calculation, the calculated δ¹⁸O value of pure oxide would only be shifted by -0.1 to -0.2‰ if oxygen contributions from minor elements were not considered. The difference in weight percent (wt%) between duplicates in the wet chemistry procedures is <1% for Fe, <5% for Si, and <3% for Al and other minor elements.

APPENDIX 2: AL-SUBSTITUTION AND CRYSTALLINITY OF NATURAL GOETHITE

The Al³⁺ ion (0.53 Å) is slightly smaller than the Fe³⁺ ion (0.65 Å). The ionic substitution of Al for Fe in ferric oxides is well-studied both in the laboratory and in soils (Fitzpatrick and Schwertmann, 1982;

Cornell and Schwertmann, 1997). Al substitution ranging from 0 to ~33 mole% is reported for soil goethite (Siehl and Thein, 1989), and from 0 to ~15 mole% for soil hematite (Schwertmann et al., 1977; Fontes and Weed, 1991; Prasetyo and Gilkes, 1994).

The effect of Al substitution on oxygen isotope fractionation in ferric oxides has not been experimentally determined. Bird et al. (1992) and Yapp (1993b) assumed that increasing Al substitution increases the fractionation factor for goethite linearly toward that of diaspore (α-ALO₃), which should be significantly enriched in ¹⁸O relative to pure α-FeOOH. However, Zheng (1998) predicts a negative shift in δ¹⁸O value for Al-substituted goethite.

The mole% Al substitution of natural goethite samples was estimated using the method developed by Schulze (1984), which requires 1) an estimate of the *c* dimension, calculated from the formula: $c = [1/d(111)^2 - 1/d(110)^2]^{-1/2}$, and 2) an estimate of Al substitution from the relationship: mole% Al = 1730 - 572 × *c*. Schulze (1984) argues that the estimate using this method has a 95% confidence interval of ± 2.6 mole% Al. Because many of our goethite samples have only moderate crystallinity, peak broadening introduces another source of error. We conclude that a precision of ± 3–5 mole% Al is a reasonable estimate. The XRD patterns were obtained using Scintag PAD-V θ-2θ diffractometer with α Cu Kα radiation source at a scan rate of 1° or 2° 2θ/min at the Department of Geosciences, Princeton University.

Table A3. FWHM and estimated content of Al-substitution in comparison to the maximum Al-substitution estimated from ICP analysis.

Sample	FWHM(°2θ)	d(110)	d(111)	<i>c</i>	Mole% Al (XRD)	Mole% Al (ICP)
G97-1	0.569	4.181	2.448	3.020	2.7	0.2
G97-3	0.243	4.18	2.446	3.016	4.6	7.6
Vincetown	0.295	4.176	2.437	3.001	13.4	24.3
Batsto-Bog2	0.307	4.191	2.452	3.023	0.6	1
UP-Bogiron	0.578	4.19	2.449	3.018	3.6	0
Jordan-H	0.253	4.183	2.451	3.025	-0.1	2.9
Jordan-G	0.662	4.171	2.444	3.016	4.9	2.1
Zadog-IN	0.287	4.176	2.444	3.014	5.9	2.7
BLKH-Bog	0.57	4.187	2.452	3.025	-0.3	4.0
Islay	0.461	4.194	2.453	3.024	0.1	0.6
Taiwan	0.437	4.185	2.444	3.011	7.9	7.6

In general, lower levels of Al substitution are found in goethite from highly concentrated bog irons and coarse sandstone cements, and higher levels are found in goethite from clay-rich soil horizons. As shown in Table A3, most samples have <10 mole% Al substitution.

The Al content from the DCB extract can set an upper limit on the degree of Al substitution in ferric oxides, as some Al in the extract is generated by dissolution of Al silicates, not goethite. As shown in Table A3, estimates from the two methods are consistent, except that

the upper limits given by ICP estimates are higher for some of the clay-rich samples, e.g., Vincentown, as expected when Al silicates make an important contribution.

We noted that different goethite samples had different peak XRD intensities. A crude method to estimate mineral crystallinity (crystal size) is to measure the full width at half maximum (FWHM) of a major peak. The (110) peak was measured for all goethite samples (Table A3). Note that goethite associated with quartz sand has a higher crystallinity than goethite associated with clay-rich deposits.