

THE STABLE ISOTOPE COMPOSITION OF SEDIMENTARY  
IRON OXIDES WITH SPECIAL REFERENCE  
TO BANDED IRON FORMATIONS

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Iron-rich sedimentary rocks, which are deposited intermittently throughout earth history can be divided into four groups according to their different mineralogical facies: oxides, carbonates, silicates, and sulfides. The present chapter deals exclusively with the stable isotope composition of Fe oxide minerals with special emphasis on Banded Iron Formations (BIFs). This type of deposit is virtually the only one which is mined today for Fe.

As is well known BIFs occur on all continents in Precambrian shield areas. Some of the largest and best known deposits are found in the Labrador Trough in North America, the Hamersley Range in Western Australia, the Quadrilatero Ferrifero in Brazil, the Transvaal Basin of South Africa and the Krivoy Rog areas in the USSR. With respect to their geologic ages three main periods of formation can be differentiated: mid Archean (3.4-2.9 Ga), early Proterozoic (2.5-1.9 Ga), late Proterozoic (0.75-0.5 Ga). Early Proterozoic deposits far outweigh those of all other ages.

The origin of BIFs is still a major controversial subject as exemplified, for instance, by a recent discussion of Garrels (1988) and Morris and Trendall (1988). Because H and especially O isotope

data can provide insight into environments and temperatures of formation, this article summarizes the relevant literature to elucidate the depositional environment and the diagenetic-metamorphic history of BIFs. At first, however, some generalizations about the formation and the stability of the different iron oxide minerals are presented.

#### STABILITY AND OCCURRENCE OF IRON OXIDES

Under to day's weathering conditions  $\text{Fe}^{+2}$  is released from rocks and oxidized to  $\text{Fe}^{3+}$ . Because  $\text{Fe}^{3+}$  is extremely insoluble in water under naturally occurring conditions (only in very acid solutions does it reach higher concentrations) it will hydrolyze to form ferric oxides/hydroxides. The first Fe precipitate from solution is a highly hydrous oxide of indefinite water content. As is well known, such first precipitates are seldom stable and transform to stable phases by splitting out most of its water.

Stable phases are goethite ( $\alpha\text{-FeOOH}$ ), lepidocrocite ( $\gamma\text{-FeOOH}$ ), hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ) and maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ). By far the most common in sediments are goethite and hematite. There has been considerable debate about the relative stabilities of goethite and hematite in rocks. According to Schwertmann (1969), environmental conditions play a decisive role in determining which of the two forms are produced. Fischer and Schwertmann (1975) presented experimental evidence that goethite and hematite are not inter-related genetically by a simple hydration-dehydration type of reaction, but are formed by separate pathways from  $\text{Fe}(\text{OH})_3$ . In the case of some soils, there is evidence that much of the hematite forms directly from dehydration of the initial ferrihydrite precipitate (Fischer and Schwertmann, 1975). Nevertheless, it is a well established fact that in progressively older rocks hematite becomes more abundant than goethite. Therefore, it appears likely that much of the sedimentary hematite in older rocks was formed by dehydration of pre-existing goethite (James, 1966).

## BRIEF CHARACTERIZATION OF BANDED IRON FORMATIONS

According to the nomenclature of James (1966), Fe-rich sedimentary rocks can be divided into two broad classes: ironstone, which occurs mainly as thin beds of Phanerozoic age, and BIFs, mainly of Precambrian age and representing by far the greatest concentration of Fe of sedimentary origin. Both have originated as chemically precipitated sediments. With respect to their isotopic composition, BIFs have only been studied so far, with the exception of the study by Hangari et al. (1980), who determined the isotope composition of siderite and magnetite from the Wadi Shatti District in Lybia, which are regarded to be equivalent to other minette-type Phanerozoic ironstones.

As defined by James (1954, p.239) a banded iron formation is a "chemical sediment, typically thin-bedded or laminated, containing 15% or more Fe of sedimentary origin, commonly but not necessarily containing layers of chert". James proposed a classification into 4 facies: oxide, carbonate, silicate and sulfide. In the following, we will restrict ourselves to the oxide facies: the cherty banded iron formation. Recent literature has been summarized for instance by Trendall and Morris (1983).

Fe oxides and  $\text{SiO}_2$  together constitute over 90% of the rock. The main mineral components -magnetite, hematite and finely crystalline quartz (usually called chert)- are banded as to easily recognize Fe-rich and Fe-poor layers of varying thickness. Bands of varying scale and prominence represent the fundamental structures in all BIFs. Banding sometimes occurs on a scale of 1 mm or less (microbanding), but alternation on a larger scale also occurs (mesobanding and macrobanding; Trendall, 1983). The regularity in banding, with individual bands sometimes continuing over distances of tens or hundreds of kilometers, suggests deposition in large, quiescent water bodies. The favored model of BIFs involves a water column with an upper oxic layer overlying a much larger volume of anoxic water. Most investigators favor a marine origin, but there is a strong minority opting for a freshwater origin. Garrels

(1987), for instance, assumed that banded iron formations were deposited by evaporation of stream water in restricted basins. The microbanding is the result of initial deposition of iron minerals during evaporation followed by deposition of silica after saturation with that substance. If the concept of annual varves is accepted, the average varve thickness is about 0.15mm/y, which requires removal of 26 mg of Fe and 21 mg of  $\text{SiO}_2$  for each  $\text{cm}^2$  of the depositional basin by evaporation of about 500 cm of water (Garrels, 1987).

With the exception of small occurrences of bog ores found in small lakes of higher latitudes, there is no example in present-day environments of Fe deposition approaching in composition the Fe rich units of the geological past. Therefore, it is extremely difficult to obtain first-hand information on the primary phases that were originally precipitated. The principal problem seems to be to permit the deposition of Fe phases, but inhibit the precipitation of carbonates and prevent the introduction of clastic material. With respect to the Precambrian BIFs, there is a real dilemma: how to transport Fe to its sites of deposition if the hydrosphere and atmosphere were then oxidizing and how to precipitate it if they were reducing (Cloud, 1983)?

Based on thermodynamic stability calculations, one can, of course, attempt to deduce what the original depositional phases may have been. Therefore, on Eh-pH diagrams at 25°C and 1 atm total pressure, the stability fields of mineral assemblages can be calculated (Garrels and Christ, 1965). However, such equilibrium diagrams must be applied with caution to an evaluation of environmental conditions of the geological past, because it is common to find that the first formed phases are metastable species and it is only with the passage of time that these assemblages adjust through dehydration and crystallization to yield thermodynamically more stable phases.

A different and promising approach to obtain information on ancient sedimentary environments is to study the stable isotope composition of Fe oxide/hydroxide phases. As is well known, stable isotope ratios are especially useful for deducing possible sources

of water and for calculating temperatures of mineral formation. Thus, O and H isotopes could be used to provide data on the isotopic composition of the waters present at the time of mineral formation and temperatures of formation could be calculated if fractionation factors between minerals and water at the respective temperatures are accurately known.

#### PRIMARY ISOTOPE COMPOSITION OF GOETHITE AND HEMATITE

The isotopic composition of most low temperature minerals (carbonates, silicates, sulfates, phosphorites) is generally well known. This cannot be said for the Fe oxide/hydroxide family. Only in recent years due to the efforts of Yapp and his coworkers, this deficiency is beginning to change. Yapp (1983; 1987a and b), Yapp and Pedley (1985) and Yapp and Poths (1986) analyzed the H, C, and C isotope composition of "museum quality" and synthesized goethites. The  $\delta D$  values of 24 natural goethites varied between -202 and -94 per mil (Yapp, 1987a). Yapp and Pedley (1985) demonstrated that H isotope fractionation between goethite and water is approximately constant over the temperature range from 25 to 145°C, the fractionation factor being about 0.90. This suggests that goethite  $\delta D$ -values may be a direct temperature independent measure of the  $\delta D$ -values of the waters with which goethite last equilibrated. However, it might be impossible to decide whether goethites, which formed some million years ago, had preserved their original  $\delta D$ -values or had, instead, exchanges with modern waters. Yapp and Pedley (1985) suggested that substitution of  $Al^{3+}$  and/or  $Mn^{3+}$  for  $Fe^{3+}$  in the goethite structure might produce changes in the D/H fractionation factor.

The natural goethites analyzed so far have a  $\delta^{18}O$  range of about 14 per mil. Scatter in the data could be due to different water compositions and/or to different temperatures of formation. Because Yapp (1987a) observed a temperature dependent  $\delta^{18}O$  fractionation between 25°C, 44°C and 62°C and the corresponding water, he concluded that temperature is a dominant factor in determining the

O isotope composition of goethite. A plot of  $\delta D$  vs.  $\delta^{18}O$ -values of different hydroxyl bearing minerals reveals that the 25° goethite line is closest to the Meteoric Water Line while the 25° chert line is farthest for the Meteoric Water Line (Fig. 1). Figure 1 indicates that goethite can be used in combination with other low temperature minerals as a geothermometer.

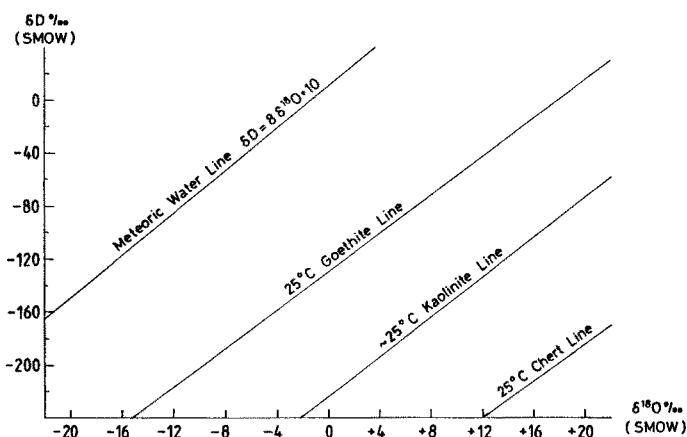


Figure 1: Variation of  $\delta D$  vs.  $\delta^{18}O$  for different minerals relative to the meteoric water line (from Yapp, 1987)

One complication may arise from the fact that, as is well known, bacteria might be causal factors in the precipitation of Fe oxides/hydroxides. However, whether bacteria are necessary or directly involved in the precipitation of Fe is still unanswered (Nealson, 1982). Therefore, it is assumed that during Fe precipitation vital effects do not have any significant influence on the isotope composition of sedimentary oxides.

During their investigation of O and H isotope composition of natural goethites, Yapp and Poths (1986) noted that goethites contain variable amounts of C (2wt%  $CO_2$ ). They concluded that C exists in two different forms: "trapped  $CO_2$ " and organic matter. Total  $^{13}C$ -values range from -27.2 to -8.10 per mil. This large range could be explained by different ratios of trapped  $CO_2$  to organic matter. According to Yapp (1987b), the amount of trapped  $CO_2$  depends on the  $CO_2$  partial pressures at the time of mineral formation, and thus represents a potential  $CO_2$ -geobarometer. It, therefore, seems possible that the analyses of "trapped  $CO_2$ " may

give quantitative information on CO<sub>2</sub>-partial pressures in the earth's geologic history.

Let us now discuss possible fractionation effects that might happen during the conversion of iron hydroxides to Fe oxides. Yapp (1983) demonstrated experimentally that partial dehydration of goethite to hematite is accompanied by a systematic H isotope fractionation, which results in a progressive decrease in the  $\delta D$ -values of the residual mineral water with increasing degree of hydration. Dehydration under open system conditions produces a smaller degree of isotope fractionation than under closed system conditions. There are no systematic experiments which studied the behaviour of O isotopes, but from comparison of data on natural goethites (Yapp, 1983) and on hematite from low temperature banded iron formations, there should be only a relatively small fractionation effect. This can also be deduced by mass balance considerations: even if dehydration goes to completion three quarters of O remain in the solid phase. This relationship does not speak for large fractionation effects.

#### ISOTOPE FRACTIONATION PROCESSES DURING BURIAL HISTORY OF BANDED IRON FORMATIONS

##### Interpretation of Temperatures

Cherty banded iron formations consist of two phases only: quartz and Fe oxides, which are stable over a wide range of temperatures and pressures. Therefore, petrologic criteria used generally to distinguish between diagenetic and metamorphic assemblages are inadequate in such rocks.

As is well known, stable isotope ratios can be used to calculate "temperatures of formation". However, there are a few problems when applying such geothermometers. The first condition which has to be fulfilled is isotope equilibrium. Secondly, it is generally assumed that the various Fe oxide minerals - magnetite, hematite,

martite - do not show any difference in their O isotope fractionation behaviour. And indeed, by separating different concentrates of hematite, magnetite and martite from Fe ores in Minas Gerais, Hoefs et al. (1982) did not find any differences between these minerals. Thirdly, temperature calibrations must exist.

Based on spectroscopic and heat capacity measurements, Becker and Clayton (1972) gave a calculated magnetite-water curve. Such theoretical calculations are very difficult, because all vibrational frequencies of the crystalline lattice must be taken into account. Therefore, the most promising approach seems to be the experimental determination which, however, has not been performed below temperatures of 300°C, because exchange rates are so slow. Blattner et al. (1983) determined the O isotope fractionations between magnetite crystallized from hydrothermal steam at Wairakei (New Zealand), and the corresponding hydrothermal fluid at 175°C and 112°C. Their data support the earliest proposed magnetite-H<sub>2</sub>O fractionation curve of O'Neil and Clayton (1964). Nevertheless, fractionation curves are still not very well defined at low temperatures. Therefore, the temperatures calculated from the quartz-Fe oxide fractionations will, to some extent, depend on the calibration curves that are used for the calculations. Recently, Muller et al. (1986) have compiled all available literature data on O isotope fractionations between quartz and Fe oxide in banded iron formations and have recalculated temperatures on the basis of the computer programme of Hoernes (1980). The thus obtained temperatures vary from 140 to 810°C., which encompass the whole range of temperatures which is found in the earth's crust. Temperatures for the least metamorphosed deposits vary from 200 to 300°C (Muller et al., 1986). Considering the uncertainties in temperature calibrations and in attainment of isotope equilibrium, these low temperatures should not be overinterpreted, but they indicate a low grade burial metamorphism.

#### Reconstruction of Depositional Environment

For an attempt to reconstruct the original sedimentary environment, the least metamorphosed banded iron formations represent

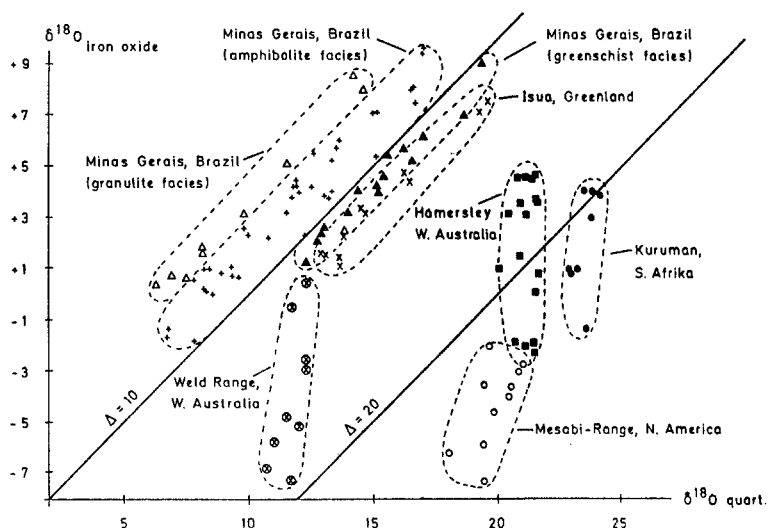


the most suitable deposits. Based on O isotope fractionations, these are the Mesabi-Range, North America (Perry et al., 1973), the Hamersley Basin, western Australia (Becker and Clayton, 1976), the Kuruman deposit, South Africa (Perry and Ahmad, 1983), and the Urucum district in western Brazil (Hoefs et al., 1987). However, Becker and Clayton (1976) and Hoefs et al. (1987) concluded that isotope effects during diagenetic and metamorphic fluid/rock interactions are so pronounced that the initial isotopic composition of the sedimentary environment is no longer reflected in the  $\text{SiO}_2$  and in the Fe-oxide phases. Gregory (1986) modelled these changes in terms of two major constraints on isotopic systems: conservation of mass and the kinetics of exchange equilibria.

It is convenient to treat fluid/rock interactions by simple endmember models: (a) closed systems, where interactions may occur between mineral phases and a coexisting fluid, all of which being present in constant relative proportions, and (b) open systems, where complex isotopic interactions occur between mineral phases and externally-derived fluids.

In cases, where open-system processes are suspected, it is useful to construct plots of  $\delta^{18}\text{O}$  of one mineral vs. the  $\delta^{18}\text{O}$  of a coexisting mineral (Gregory, 1986). Such graphs reflect bulk  $\delta^{18}\text{O}$  variations, as well as  $^{18}\text{O}/^{16}\text{O}$  fractionation data on coexisting minerals. Gregory (1986) has shown that for mineral assemblages with different bulk compositions equilibrated under closed system conditions, coexisting minerals should exhibit  $\Delta x-y$  values that define linear arrays of  $45^\circ$  slope on a  $\delta-\delta$  diagram which parallel the  $\Delta = 0$  fractionation line. In contrast, under open system conditions mineral pairs lie along steep (nearly vertical), positively sloped arrays indicating disequilibrium.

A summary of Fe oxide quartz data from Precambrian iron formations is shown in figure 2. There appear to be two major classes of data: mineral pairs from Minas Gerais (Brazil) and from Isua (Greenland) lie along slope 1 arrays, which is suggestive of equilibration under greenschist to granulite facies conditions, and mineral pairs from Hamersley and Weld Range (Australia), Kuruman (S. Africa) and Mesabi Range (North America) lie along



**Figure 2:** Closed and open system-behavior of quartz-Fe oxide pairs from various BIFs of different metamorphic grade. Closed system equilibrium arrays are indicated for the Iron Quadrangle deposits (Hoefs et al., 1982) and Isua, Greenland (Perry et al., 1978). The low grade deposits of Weld Range, West Australia (Perry and Ahmad, 1983), Hamersley, W. Australia (Becker and Clayton, 1976) and Mesabi Range, N. America (Perry et al., 1973) show open system disequilibrium arrays, that are characteristic of hydrothermally exchanged rocks (modified after Gregory, 1986)

sloped arrays indicative of disequilibrium exchange under open system conditions. These data indicate that under some high temperature conditions quartz readily exchanges  $^{18}\text{O}$  with its surroundings. In low-grade, relatively undeformed areas, the data lie along steep disequilibrium arrays that are characteristic of hydrothermally exchanged rocks. These positions of the disequilibrium arrays indicate that different initial  $^{18}\text{O}$  compositions are required for the precursors. The major conclusion that can be derived from the disequilibrium arrays shown in figure 2, is that the rocks have behaved as open systems and that fluid/rock interactions have erased the isotopic record of the surface history of the rocks. An open question is whether the samples which have been metamorphosed under higher temperatures and whose minerals appear to exhibit oxygen isotope equilibrium, initially passed through an open-system burial history analogous to the low temperature terranes. Nevertheless, in the following a scenario is presented which

is by no means unique, but may represent plausible conditions.

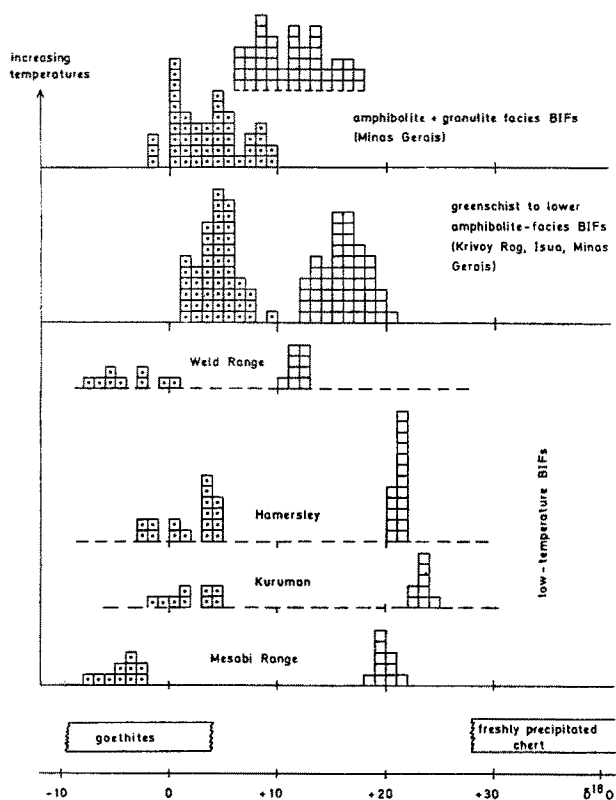


Figure 3: Variation of  $\delta^{18}\text{O}$  values of cherts and Fe oxides from different BIFs

The initial  $^{18}\text{O}$  composition of quartz and Fe oxide should be uniform when precipitated from ocean water or should have restricted compositional variations within single terranes when precipitated from evaporated fresh-water bodies. Assuming the original water composition was around 0 per mil and water temperatures were similar to those of today, then the amorphous precursor of the chert should have an isotopic composition around 35 per mil (Knauth and Epstein, 1976). A compilation of the O isotope variations of cherts and Fe oxides observed in BIFs of different metamorphic grade demonstrates that  $^{18}\text{O}$  contents of cherts from the least metamorphosed deposits are at least 10 per mil lower (Fig. 3). This  $^{18}\text{O}$  shift by 10 per mil or more, occurs obviously during phase transformations to an ordered  $\text{SiO}_2$  polymorph via isotope exchange

with a low  $^{18}\text{O}$  fluid.

The  $^{18}\text{O}$  contents of the original Fe phases are also unknown. Goethites from different geologic environments vary between +4.4 to -4.9 per mil with one low  $\delta^{18}\text{O}$  value of -9.5 per mil (Yapp, 1987). This range is also found in the least metamorphosed banded iron formations (Fig. 3). Therefore, the Fe oxide system behaves much more inert than the  $\text{SiO}_2$ -system, which could be due to the fractionation behaviour of the Fe-oxide-water system. Although the exact fractionation curve between Fe oxide and water is still a matter of debate, in any case there should be a cross-over at rather low temperatures (Blattner et al. 1983) making the system rather insensitive towards temperature changes. Another reason why Fe oxides tend to maintain rather constant  $\delta^{18}\text{O}$  values independent of metamorphic grade might be that the amount of O in the Fe oxides "buffers" the isotopic composition of  $\text{SiO}_2$  which reaches in granulite facies banded iron formations from Minas Gerais unusual values as low as 6‰ per mil (Fig. 3).

#### Possible Paleoclimatoloical Significance

There has been much debate about the paleoclimatological significance of  $^{18}\text{O}$  contents of banded iron formations. The observed  $^{18}\text{O}$  decrease with geological time in cherts, together with the corresponding trends in carbonates and phosphorites, has lead to the conclusion that Precambrian oceans were depleted in  $^{18}\text{O}$  (Perry et al 1973) relative to today's ocean or were warmer (Knauth and Epstein, 1976; Karhu and Epstein, 1986), the two alternatives not being exclusive. On the other hand, Muehlenbachs and Clayton (1976) and Gregory and Taylor (1981) have proposed that the  $\delta^{18}\text{O}$  value of the ocean remains constant because of the buffering effect of ocean water-basalt interactions.

Fe oxide data discussed here do not add any decisive evidence to the pros and cons of this controversial subject. Nevertheless, the light  $\delta^{18}\text{O}$  values from the Mesabi and Weld Range (Fig. 3) do not exclude the possibility of the precipitation in a fresh water environment, a conclusion which has been already made by Garrels

(1987) on totally different grounds. If this is so, an important implication is that the Precambrian was characterized by a hydrologic regime much like the present one.

## CONCLUSIONS

The isotopic composition of goethites may provide insight into their environments of formation. After transformation into hematite, however, the primary record obviously erases; such a conclusion arises from analysis of the least metamorphosed banded iron formations.

Potentially Fe oxides besides quartz represent the most suitable minerals for geothermometry. Calculated temperatures from quartz-Fe oxide pairs of banded iron formations of all metamorphic grades vary from 140 to 810°C, which encompass the whole range of crustal temperatures. Because of ill-defined calibration curves at low temperatures calculated temperatures below 400°C should not be taken too seriously and may need refinement and revision.

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