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Geochimica et Cosmochimica Acta 227 (2018) 186–210

Geochimica et Cosmochimica Acta

www.elsevier.com/locate/gca

Miocene weathering environments in Western Australia—Inferences from the abundance and $^{13}C/^{12}C$ of $Fe(CO_3)OH$ in CID goethite

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Received 7 August 2017; accepted in revised form 14 February 2018; available online 21 February 2018

Abstract

The channel iron deposits (CID) of the Hamersley Province in Western Australia are dominated by pedogenic goethite/hematite-rich ooids and pisoids that were transported to, and deposited in, the meandering channels of Miocene rivers. Information about the Miocene weathering environments that produced the Fe(III) oxides is archived in the mole fraction (X) and $\delta^{13}C$ of the $Fe(CO_3)OH$ component in solid solution in oolitic CID goethite (α-FeOOH).

Values of X and $\delta^{13}C$ were measured for 12 oolitic goethite samples from different depths in two cores drilled in CID of the Robe Formation of Mesa J. The weighted-average plateau values of X ranged from 0.0098 to 0.0334, which suggest ambient CO_2 concentrations that ranged from ~50,000 ppm V to perhaps as much as ~200,000 ppm V at the time of goethite crystallization. In a vadose zone characterized by in situ production of CO_2 with steady-state Fickian diffusive transport of the gas, such concentrations would correspond to modeled soil respiration rates (Q) ranging from about 10 to 30 mmol/m^2/h. Values for Q of about 10 mmol/m^2/h are reported for soils in modern tropical forests with MAP $\geq$ ~2000 mm. However, model-derived values of Q that exceed 15 mmol/m^2/h are larger than observed in modern systems. This could indicate that some of the CID goethites crystallized in conditions that were phreatic or near phreatic rather than vadose.

The $\delta^{13}C$ values of the $Fe(CO_3)OH$ component in these 12 CID samples ranged from −24.0‰ to −22.3‰, which are among the most negative measured to date. If they reflect steady-state diffusive transport of CO_2 in vadose environments, the soil CO_2 would have been derived from a source with $\delta^{13}C$ values that ranged from ~−31‰ to −29‰. If, on the other hand, the goethites crystallized in a nearly phreatic environment that was moderately acidic, the inferred $\delta^{13}C$ of the ancient CO_2 source would have been about −27.6‰ to −25.8‰. In either case, the $\delta^{13}C$ values point to in situ oxidation of C_3 organic matter as the predominant source of the ambient CO_2.

The Fe(III) oxides in the CID ooids suggest crystallization in aerobic environments. However, even in aerobic environments, many microbial species can reduce the Fe^{3+} in oxides to relatively soluble Fe^{2+} and may have facilitated progressive Fe enrichment during multiple cycles of Fe(III) oxide dissolution and recrystallization. At the same time, microbially mediated oxidation of organic matter could have produced the high concentrations of soil CO_2 with the very negative $\delta^{13}C$ values recorded in the $Fe(CO_3)OH$ component in oolitic goethite.

More frequent summer storms in the Miocene, may have been a significant factor in forming and eroding these soil systems and in concentrating large volumes of oolitic Fe(III) oxides in the local river systems to form channel iron deposits. However,

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https://doi.org/10.1016/j.gca.2018.02.023

published (U-Th)/He ages indicate that the oolitic CID goethites of Mesa J became closed systems after ~7 Ma, which suggests a change in local climate and/or conditions of burial at about that time in the Miocene.

Keywords: Goethite; Miocene; Carbon isotopes; CID; $Fe(CO_3)OH$; Weathering; Paleosols; CO_2; Solid solution; Paleoclimate

1. INTRODUCTION

Iron (Fe) undergoes oxidation-reduction (redox) reactions in the surface and near-surface conditions found on Earth (Garrels and Christ, 1965). In oxidizing environments, iron occurs as Fe^{3+}—most commonly in the minerals goethite (α-FeOOH) and hematite (α-Fe_2O_3). Goethite and hematite are widely distributed and occur in soils; ironstones; bog-iron deposits; mineral spring and acid stream deposits; ferromanganese nodules; secondary precipitates on fossils; marine chemical sediments associated with hydrothermal vents; and as radiating, botryoidal, and stalactitic masses, and pseudomorphs after pyrite, siderite, and/or magnetite (James, 1966; Spears, 1989; Young and Taylor, 1989; Bao et al., 1998; Yapp, 2001b, and references therein).

Some microorganisms exploit the redox properties of iron to catalyze metabolic reactions (Fredrickson and Gorby, 1996; Lovley, 1997; Masse et al., 2007), and it has been suggested that biological mediators played important roles in the formation of iron-rich deposits such as banded-iron formations and certain oolitic ironstones (Dahanayake and Krumbein, 1986; Holm, 1989; Widdel et al., 1993; Yapp and Poths, 1993; Søgaard et al., 2000; Kappler et al., 2005; Li et al., 2015). The widespread occurrence of goethite and hematite and the fact that their ages of crystallization can be determined by (U-Th)/He dating (e.g., Shuster et al., 2005) points to the significance of these Fe(III) oxides as geochemical archives of paleoenvironmental information.

Among the more spectacular accumulations of Fe(III) oxides on Earth are the channel iron deposits (CID) in the Hamersley Province of Western Australia. The CID are composed predominantly of oolitic goethite and hematite, which are presumably pedogenic (Morris and Ramanaidou, 2007). They are also an economically important source of iron (Kneeshaw and Morris, 2014)—recently estimated to contain >15 Gt of ore. Gt = 10^9 metric tons.

These CID include the Miocene oolitic Robe Formation (Robe Pisolite) located near the modern Robe River. The oolitic goethite and hematite of the Robe Formation appear to have been deposited in meandering river channels during the Miocene. However, because the Fe(III) oxides were more resistant to subsequent erosion than were the surroundings, the CID of the Robe Formation now commonly occur as mesas—i.e., inverted topographic features (Morris and Ramanaidou, 2007). Analogues of the Western Australian CID have only been reported in less extensive Oligocene-age deposits in Kazakhstan. This apparently limited occurrence suggests that the development of CID is restricted to a very specific set of paleoenvironmental conditions, and there has been discussion of a possible role for microbial mediation in the formation of the CID (e.g., Morris and Ramanaidou, 2007). Stable carbon isotopes can indicate the presence of biologically derived carbon (Cerling, 1984; Amundson et al., 1988; O'Leary, 1988; Hayes et al., 1999), and in this context, the goethite of the CID is of particular interest.

Yapp and Poths (1986, 1991) observed a correlated loss of H_2O and CO_2 during incremental vacuum dehydration of natural goethites to hematite at temperatures of ~200 °C. It was postulated that the source of this CO_2 is a ferric (Fe^{3+}) carbonate component in solid solution in the goethite (Yapp, 1987a; Yapp and Poths, 1991). The carbon in ambient CO_2 molecules presumably binds to structural O^{2-} exposed on the goethite surface to form a distorted carbonate molecule (Russell et al., 1975). As crystal growth proceeds, this weakly chemisorbed CO_2 may be occluded in the mineral as a ferric carbonate component in solid solution. The process is summarized in the following reaction (Yapp, 1987a):

$$FeOOH + CO_2 = Fe(CO_3)OH$$

Infrared spectra indicate the existence of a distorted carbonate molecule in goethite (Yapp and Poths, 1990; Boily et al., 2006), which supports the idea of an $Fe(CO_3)OH$ component in solid solution in the mineral structure. Therefore, the solid-state dehydration-decarbonation of goethite can be written as (e.g., Yapp, 2015):

$$2FeO_{(1-X)}(CO_3)_XOH = Fe_2O_3 + H_2O + 2XCO_2$$

If equilibrium conditions are approached during crystallization, the partial pressure and $\delta^{13}C$ of CO_2 in the local environment should be systematically related to the mole fraction (X) and $\delta^{13}C$ of the $Fe(CO_3)OH$ component in solid solution in the goethite (Yapp, 1987a). Published studies of ancient goethites have provided insights into the carbon cycle in oxidizing weathering environments and groundwater systems in Earth's past (Yapp, 1987a, 2001a, 2002, 2004; Yapp and Poths, 1992, 1993, 1996; Tabor et al., 2004; Tabor and Yapp, 2005a; Feng and Yapp, 2009; Yapp and Schuster, 2011; Gulbranson et al., 2011).

No previous studies have investigated the $Fe(CO_3)OH$ component in goethite of the CID. The current work presents abundance and carbon isotope data for the $Fe(CO_3)OH$ component in oolitic goethite from two drill cores extracted from CID of the Robe Formation in the Hamersley Province. The results provide (*i*) insight into the climatic/hydrologic conditions at the time of goethite crystallization and (*ii*) evidence suggestive of a possible role for biological activity in the formation of these ore-grade