Miocene Weathering and the Stable Carbon Isotope Geochemistry of Goethite in CID of Western Australia

Tyler O. Fritz[1] , Crayton J. Yapp[1]

1. Huffington Department of Earth Sciences, Southern Methodist University, Dallas TX, 75275

INTRODUCTION

The Hamersley Province of Western Australia contains some of the most expansive and economically important iron-ore bearing geological formations in the world. Current estimates of iron ore mining in Australia indicate that about 40-50% of total production derives from channel-iron deposits (CID), which are the result of weathering and erosion of terrane that includes the probable source of the CID iron -- Proterozoic-age banded-iron formations of the Hamersley Group (Morris et al. 1993, Ramanaidou et al., 2003). The dominant minerals in the ore-grade CID are hematite and goethite. The stable isotope composition of these iron(III) oxides can be a source of information on the environment in which the CID formed (Yapp, 2001). In particular, the mineral goethite (α-FeOOH) contains small amounts of occluded CO_2 which is present as an $Fe(CO_3)OH$ component in solid solution. Incremental vacuum dehydration methods yield measurements of the mole fraction (X) and $\delta^{13}C$ of $Fe(CO_3)OH$, which are related, respectively, to the concentration and $\delta^{13}C$ of CO_2 in the local environment at the time of crystallization. Previous workers have used this proxy to estimate biological productivity, CO_2 pressures in soil or groundwater, and under certain circumstance, partial pressures of atmospheric CO_2 in ancient environments. We applied this approach to the goethite of the CID of the Miocene-age Robe River Formation to investigate the conditions under which those deposits formed.
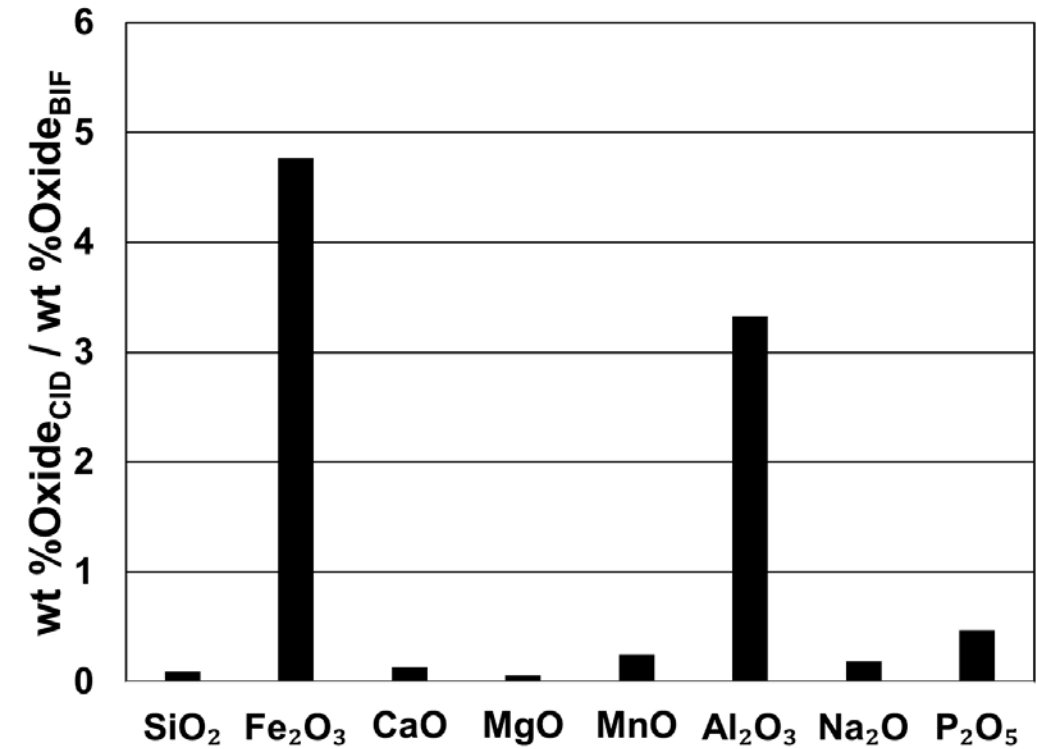
Weathering processes have extensively concentrated Fe and Al while removing SiO_2 in CID deposits relative to local Hamersley banded iron formations (BIF data from Klein, 2005).

SAMPLES and BACKGROUND

Eight oolitic/pisolitic samples from a diamond drill core were provided by the CSIRO of Western Australia (CSIRO core J6087). The core was drilled as part of the mining activity on Mesa J (21°44′27.23″S 116°15′13.46″E) in the Hamersley province of Western Australia (Figure 1). Mesa J is an example of inverted topography resulting from the differential weathering and erosion of the geologic formations hosting these channel-iron deposits. The CID of the Robe River Fm includes a spectrum of iron-rich fluvial and fluvial-lacustrine rocks which can range in lithology from gravelly mudstones and ooid-rich granular rocks to intra-formational boulder conglomerates. These were deposited in Paleogene-aged channels incised in Precambrian granitoids, volcanics, metasediments, banded iron formations, and Paleogene-aged ferruginous valley fill (Morris and Ramanaidou, 2007). The ore-grade CID of Mesa J generally consist of Miocene-age pedogenically derived pelletoids with hematite nuclei and goethite cortices, abundant goethite-replaced wood and charcoal fragments, and minor goethitic matrix composed of secondary re-precipitated goethite (Morris and Ramanaidou, 2007). Published (U-Th)/He ages of Robe River deposits from Mesa J indicate a 4 – 8 Ma time frame for deposition in three phases: (1) formation of hematitic centers (cores) of ooids at ~ $14.3_{(± 3.7)}$ Ma and ~ $18.3_{(± 3.5)}$ Ma; (2) formation of the goethitic cortices of the ooids at ~ $11.6_{(± 3.0)}$ Ma; and (3) ferruginization of wood fragments from ~ $9.4_{(± 0.5)}$ Ma to $8.2_{(± 0.4)}$ Ma (Danisik et al., 2013).

METHODS

Previous workers have observed that the isothermal, solid state transformation of goethite to hematite in vacuum yields correlated losses of incrementally evolved structural, stoichiometric hydrogen (as water) and non-stoichiometric, occluded carbon dioxide. The small amounts of occluded CO_2 are present as a ferric carbonate component at $[Fe(CO_3)OH]$ in solid solution in the goethite. Thus,

$$2FeO_{(1-X)}(CO_3)_XOH = Fe_2O_3 + H_2O + 2XCO_2$$
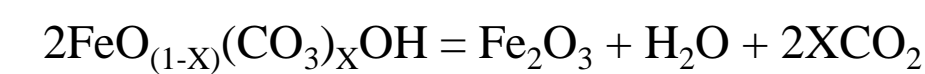
X is the mole fraction of the $Fe(CO_3)OH$ component in goethite. The following Henry's Law formulation has been used to deduce ancient ambient CO_2 partial pressures at the time of crystallization:

$$\log P_{CO_2} = \log X + 6.04 - 1570/T$$

During incremental isothermal vacuum dehydration-decarbonation goethite, the $\delta^{13}C$ of the evolved CO_2 and the molar ratio (F) of CO_2 to co-evolved H_2O are measured for each increment. If they exhibit plateau values, the measured values of F and $\delta^{13}C$ are presumed to represent the concentration and $\delta^{13}C$ of the $Fe(CO_3)OH$ component (Yapp and Poths, 1991, 1992, 1993).

Note: for plateau values, X = 0.5F.

The eight oolitic CID samples from Mesa J analyzed for this work represent depths from 5 m to ~ 36.2 m in the drill core.
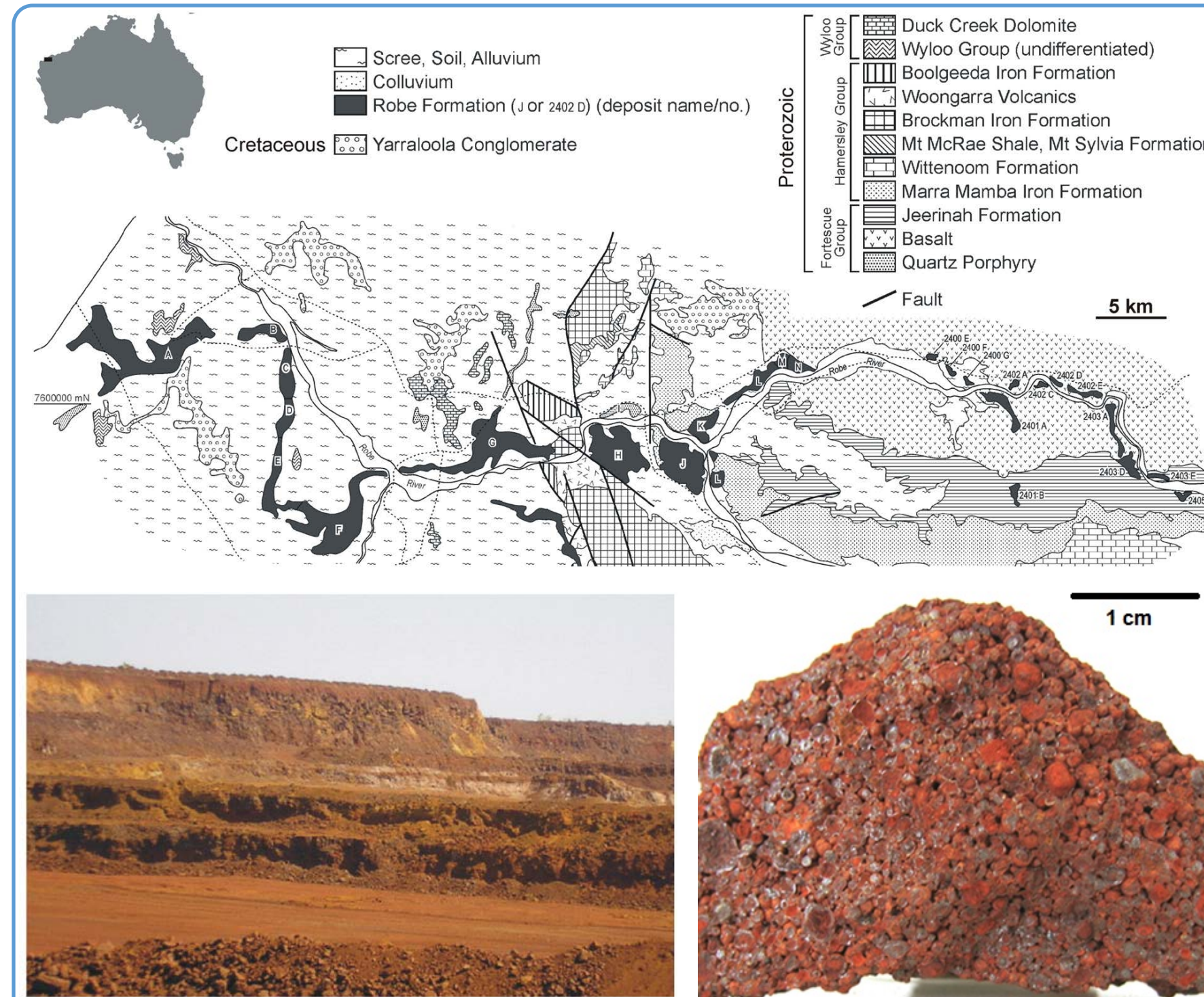
Figure 1: Simplified geological map (above) of the Robe River CID and a photograph (left) of Mesa J. Reproduced from Danisik et al., 2013 and Morris and Ramanaidou (2007). Photograph (right) depicting oolitic CID ore material comprised of goethite, hematite, and minor quartz

RESULTS

Plateau values for X and $\delta^{13}C$ of the $Fe(CO_3)OH$ component for these samples ranged from 0.0082 to 0.0334 and -22.5‰ to -24.2‰, respectively. The values of X and $\delta^{13}C_{PDB}$ include the highest concentrations and among the more negative $\delta^{13}C$ values observed to date (Fig. 3). The values for X imply ancient ambient CO_2 concentrations that ranged from about 40,000 ppmV to more than 160,000 ppmV. If the weathering environment was a vadose zone system, the $\delta^{13}C$ values of the $Fe(CO_3)OH$ imply soil CO_2 $\delta^{13}C$ values that ranged from ~ -31‰ to -29‰. If phreatic, the ancient CO_2 $\delta^{13}C$ was ~ -27‰ to – 25‰.
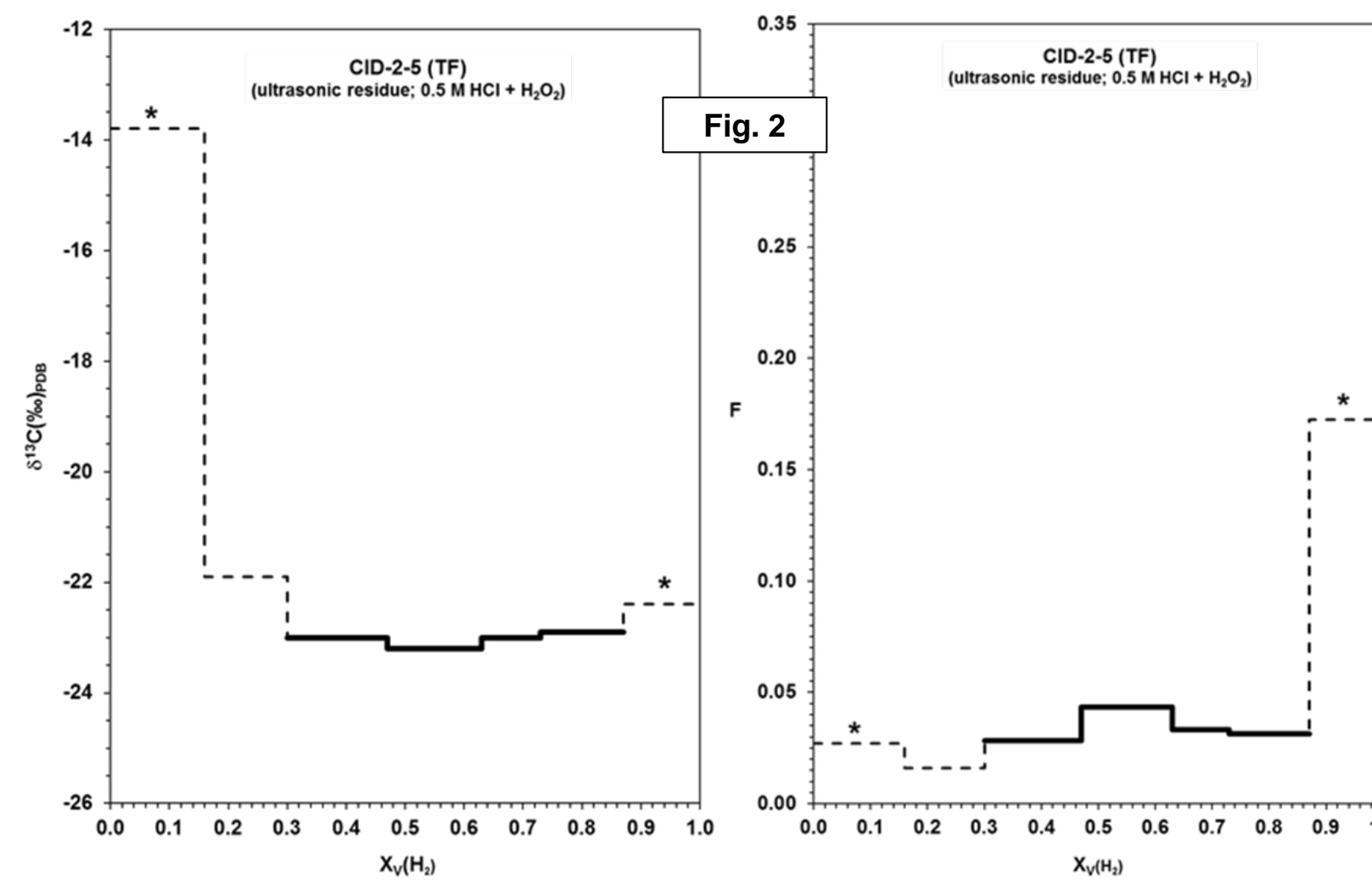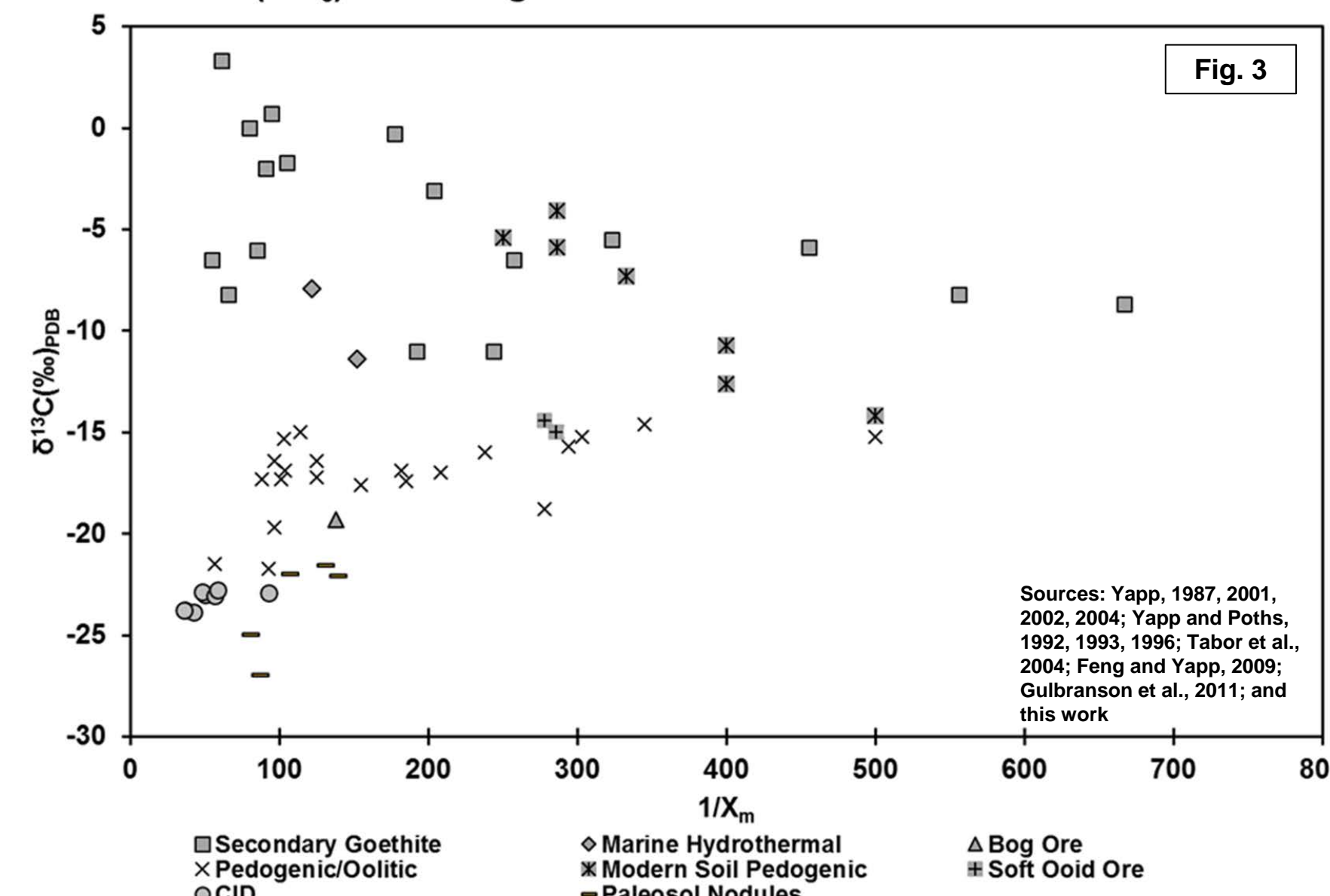

Figure 2: Example of spectra produced from an incremental, isothermal, open system dehydration experiment. Bold segments indicate "plateau" values. Asterisks denote closed-system conditions. $X_o(H_2)$ is the cumulative sum of evolved hydrogen as a mole fraction of the total hydrogen in the goethite sample.

Fe(CO3)OH Average Plateau Values from Various Studies

Sources: Yapp, 1987, 2001, 2002, 2004; Yapp and Poths, 1992, 1993, 1996; Tabor et al., 2004; Feng and Yapp, 2009; Gulbranson et al., 2011; and this work
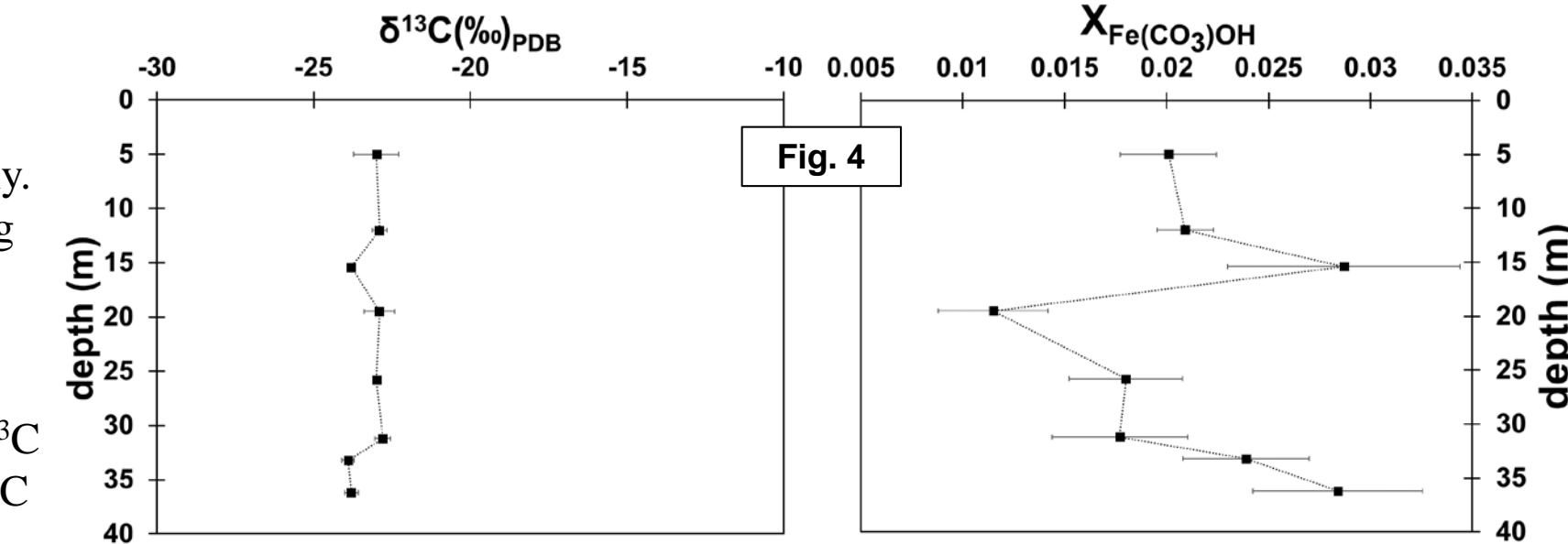
Legend: ☐ Secondary Goethite, ✕ Pedogenic/Oolitic, ☐ CID, ◆ Marine Hydrothermal, ✳ Modern Soil Pedogenic, ─ Paleosol Nodules, △ Bog Ore, ✳ Soft Ooid Ore

Fig. 4. Although the range of the very negative $\delta^{13}C$ values of $Fe(CO_3)OH$ in the CID goethites is relatively narrow, the range for the values of X is comparatively large. This seemingly paradoxical result may indicate that, prior to transport and deposition in the ancient river channel, the various oolitic goethites formed in Miocene soils from different locales in the drainage basin. The $\delta^{13}C$ of the organic matter may have been similar among the soils, but the soils may have differed in porosity, permeability, biological productivity, etc. Such differences could have been manifested in differences in diffusion coefficients and/or soil respiration rates (i.e., CO_2 fluxes). A simple steady-state Fickian diffusion model with constant D_S illustrates the circumstances under which the foregoing scenario could account for the small range of $\delta^{13}C$ values and the large range of X among the CID-2 goethites of this study:

$$C_s = \frac{z^{*2}\phi_0}{D_s}\left(1 - e^{\frac{-z}{z^*}}\right) + C_a$$

Figure 5 depicts model curves of the concentrations of soil CO_2 for different values of the diffusion coefficient (D_S) and the net diffusive CO_2 flux, Q, out of the soil for z* = 30 cm (note: Q = z*ϕ_0). Although not uniquely constrained, small values of D_S from ~ 0.005 to 0.01cm^2/s and high values of Q from ~ 10 mmol/m²/hr to ~ 40 mmol/m²/hr generate model soil CO_2 concentrations (C_S) that approximate (for z > ~ 50 cm) the soil CO_2 concentrations inferred for the Miocene weathering systems of the CID. Corresponding curves (not shown) calculated for $\delta^{13}C$ of the soil CO_2 indicate that the range of Q and D_S values which yield the inferred soil CO_2 concentrations do not predict much difference among the $\delta^{13}C$ values of the model soils (for z > 50 cm) if the oxidizing organic matter has about the same $\delta^{13}C$ among those soils.
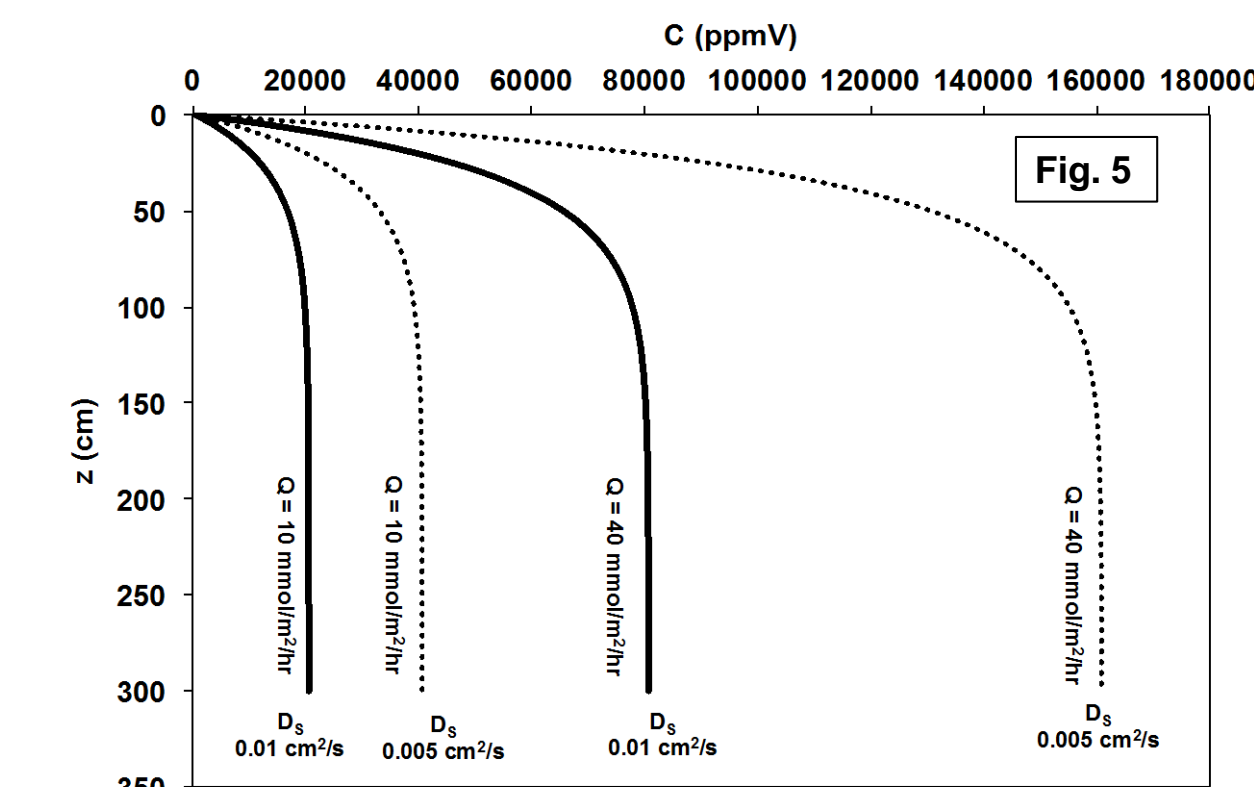
The subtropical Miocene paleolatitude (~ 31°S) of Mesa J would have been the first order influence on the local climate (Veevers et al., 1991). At present, the subtropics of Western Australia (e.g., Perth) are dry in the summer months. Yet, the existence of lateritic weathering with abundant goethite and indications of high rates of oxidation of soil organic matter suggest wetter climates at those latitudes in the Miocene. This may indicate increased frequency and/or intensity of rainfall from summer storms that were features of a consistent shift in regional atmospheric circulation at that time in Earth's history.

CONCLUSIONS

The high concentrations and very negative $\delta^{13}C$ values inferred for ambient CO_2 in those Miocene weathering systems imply high rates of oxidation of *in situ* organic matter. Such high rates were probably microbially mediated and if so, could be indicative of widespread biological activity in the soil systems of the Hamersley province during the Miocene.

Previous workers have suggested that biological activity may have played a role in the weathering processes that generated the scale of iron enrichment and accumulation seen in channel-iron deposits (Danisik et al., 2013; Morris and Ramanaidou, 2007). Ancient microbial fauna may have included species with adaptations similar to *Shewanella putrafaciens* or *Shewanella oneidensis*, which are capable of dissimilatory iron reduction in aerobic environments. Thus, even in oxidizing weathering environments, microbial activity can induce local, reductive dissolution of iron (III) oxides at the microbe/mineral interface (Grantham et al., 1997; Hersman et al., 1996). Upon cessation of that biological activity, the reduced iron could be released into the larger ambient environment, where it would re-oxidize and crystallize as iron (III) oxides.

If the two foregoing categories of microbially mediated processes operated in the Miocene and acted in tandem, one set could have facilitated progressive Fe enrichment over multiple cycles of Fe(III) oxide dissolution and re-crystallization, while the other left evidence of high concentrations of soil CO_2 with very negative $\delta^{13}C$ values. However, as indicated by the (U-Th)/He ages, the Fe recycling processes have not been in widespread operation in these CID over the past ~ 8-12 Ma.

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Legend (map): Scree, Soil, Alluvium; Wyloo Group (undifferentiated); Colluvium; Boolgeeda Iron Formation; Robe Formation (J or 2402 CI) (deposit name/no.); Woongarra Volcanics; Cretaceous – Yarraloola Conglomerate; Brockman Iron Formation; Mt McRae Shale, Mt Sylvia Formation; Wittenoom Formation; Marra Mamba Iron Formation; Jeerinah Formation; Basalt; Quartz Porphyry; Fault; Duck Creek Dolomite