Dating paleochannel iron ore by (U-Th)/He analysis of supergene goethite, Hamersley province, Australia: COMMENT

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Despite their laudable efforts to date the channel iron deposits (CID) of the Pilbara of Western Australia (WA), Heim et al., (2006) need to reassess their sampling and the statistical strategy behind their conclusions. Many details they report conflict with data from a major CSIRO-industry research program on CID (Morris et al., 1993; Ramanaidou et al., 2003) and other research (e.g., Stone et al., 2003).

Miocene fluvial goethite/hematite CID of the WA Pilbara range from gravelly mudstones and ooid-rich granular rocks with abundant ferruginized wood fragments, to intraformational pebble, cobble, and occasional boulder conglomerates. Clays and non-ore polymictic basal and marginal conglomerates are also present. The largely pedogenically derived iron-rich sediments occupy numerous meandering paleochannels in a mature surface on Precambrian granitoids, volcanics, metasediments, banded iron formation, and Paleogene valley fill. The porous, consolidated, ooid-rich fine gravels and their intraformational conglomerates from the Yandi and Robe deposits are a >7 billion ton resource of export iron ore.

Heim et al. (2006) make a number of erroneous assertions. To begin, our CID reports do not describe the goethitized cortex of the ooids and pisoids as "vitreous" (as reported by Heim et al. on p. 174). We never used "botryoidal," nor did we describe matrix as "late-stage cement," though some post-depositional solution voids in the matrix contain late-stage infill. Yet Heim et al. attribute these and other incorrect statements to Ramanaidou et al. (2003). "Botryoidal" is Greek for "bunches of grapes," a texture rare in CID ore. Colloform texture, however, is common in late-stage goethite which fills or lines some solution voids in the matrix, and at times appears vitreous. Goethite infill can appear very similar to original matrix in reflected light—see Heim et al.'s Figure A1 (DR1) in the GSA Data Repository 2006032. They wrongly regard this normally minor component as "the ore matrix" (p. 174).

Though shown as "typical Yandi ore," Figure A1b (DR2006032) is from *non-ore*, polymictic marginal conglomerate, and Figure A1a, although ore, is from intraformational conglomerate. Original channel-fill contains a "large percentage…of Fe-rich clasts" including, the authors claim, "partially weathered, banded iron-formation" (p. 175). This, in fact, is very rare in CID ore, though common in non-ore marginal conglomerates. CID are ferruginous sediments, not "ferruginized" or "Fe-metasomatized" as claimed (p. 173); however, it is likely some wood/charcoal was goethitized in the channels.

Sampling CID goethite for dating. The use of "botryoidal" by Heim et al. (p. 174) to describe their sampling sources implies masses of pure secondary goethite, which is misleading. So is the 1.5 mm sample spot in Heim et al.'s Figure A1c (DR2006032), since they used "4 mm diameter" drill cores (p. 174), and both are incompatible with the >10 mm fragment of Figures A1e and A1f. Even 1.5 mm cores could include cortex from adjacent ooids as well as original matrix. From crushed cores, Heim et al. selected 0.1–3 mm fragments "devoid of detrital phases," but said, "None of the samples analyzed in duplicate yields statistically reproducible results" (p. 174). The authors offered three possible explanations, ignoring the most likely. Despite apparently rigorous inspection of duplicates, and without similar data from the analyzed samples, Heim et al. cannot be sure they avoided look-alike primary matrix or ooid cortex. Both are older than the infill goethite they were trying to date, probably by millions of years, and could include even older U/Th in former soil components. Note the wide range in group ages in Heim et al's Figure 1.

The validity of the goethite dating is critically dependent upon what was actually sampled. We suggest Heim et al. included unrecognized original matrix and cortex with the infill goethite.

Statistical forcing of data. Heim et al. used progressively larger age corrections (their Fig. 2), to improve the statistical fit for their conclusions. For example, the 20% correction that they used as a He loss "worst-case scenario" (p. 175), increased the calculated ages of the samples by 30%–32.8%. These ages were used to argue that "ca. 36 Ma" valley fill was ferruginized and cemented from the top down as water levels fell, reaching completion in the Pliocene or later (p. 176). Their extrapolated ~28–36 Ma dates for the start of "ferruginization" assumed an "original channel surface" at 505 m (p. 175), but the overlying Iowa Eastern Member CID is largely absent from their deposit (their Fig. 1). Thus, the original surface was at least 15 m higher, and likely much more, assuming continuous erosion since Heim et al.'s "ca. 36 Ma" date. Extrapolating to this more likely surface could thus support an unrealistic Paleocene or even Cretaceous start for CID sedimentation.

Contemporary deposition of CID matrix. Many features, including partial alluvial matrix and matrix-supported samples with up to 75% matrix, contradict the top-down infill model. Episodic post-consolidation partial leaching of matrix with refilling of some voids is demonstrated by various generations of infill goethite, silica, and oxidized siderite. Scours filled by later CID and well-preserved bedding surfaces confirm lithification occurred soon after sedimentation (Stone et al., 2003). The scours at Yandi are 2–10 m deep, to 20 m wide and over 200 m long, with typically steep, sometimes near-vertical margins. In unconsolidated granule material, such margins would soon slump into the scours to disappear from the CID record. Intraformational conglomerate horizons comprising well-rounded pebble- and cobble-sized clasts of granular CID confirm a contemporary matrix.

Downward younging of CID "infill" goethite. The altered Lower CID basal zone (Heim et al.'s Fig. 1), with its large ochre patches and cavities, is evidence of major leaching due to prolonged basal channel water flow in the past, and the current high water table confirms changing water levels. The presence of unrecognized contemporary CID matrix, altered variably by later episodic solution and by lesser infill events as flow levels fell erratically, as well as by imprecise sampling, is a more valid explanation for the wide-ranging group dates and different younging trends than the top-down infill model of Heim et al.

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Morris et al. correctly point out that we misquoted their work and attributed to them observations that they did not report in Ramanaidou et al. (2003). Eager to acknowledge nearly two decades of descriptive work on Yandi-type orebodies by the Commonwealth Scientific and Industrial Research Organization, we inadvertently attributed both their and our textural observations to them. We apologize for that mistake. As for the petrographic descriptions, minerals and textures identified, and implications for the evolution of the Yandi deposit, we stand by our data and interpretations.

Morris et al. state that the terms "vitreous," "botryoidal," and "late-stage" cement do not accurately describe typical ore textures at Yandi or other channel iron deposits (CIDs). They also suggest that the material that we describe does not constitute typical Yandi ore.

The samples used for geochronology were collected from active mine faces at the Yandi deposit. Most samples were collected at the middle of the Yandi paleochannel, with some samples collected from the channel margins, as shown in Heim et al. (2006), Figure 1. Because it is a polymictic marginal conglomerate, the sample shown in Data Repository Figure A1b (Heim et al., 2006) is not typical Yandi ore. However, it is a CID-facies and thus genetically linked to CID formation.

The Yandi CID samples contain fragments of detrital hematite, goethite, and ferruginized wood; some samples also contain ferruginized clay pods. All detrital grains are cemented together by late-stage goethite. Goethite cement varies from microns to centimeters in thickness, invariably shows a finely laminated texture, is highly crystalline and indurated, varies from dark brown to black on freshly broken surfaces, and has a vitreous lustre (DR Appendix 1, Heim et al., 2006). Concentric goethite cement surrounding clasts could be described as having a "colloform" texture. Clasts surrounded by colloform goethite and cemented by colloform late-stage goethite form a mass that resembles a "bunch of grapes;" therefore, "botryoidal texture" accurately describes this material. We interpret the goethite cement to be "late-stage" based on paragenetic relationships. Vitreous goethite binds together clastic grains and partially or completely fills pores (DR Appendix 1, Heim et al., 2006). When more than one generation of vitreous goethite exists, cross-cutting relationships are clear.

Therefore, we maintain that (1) Yandi-type ore contains vitreous goethite, (2) vitreous goethite is a late-stage cement, and (3) samples composed of detrital grains surrounded by vitreous goethite display a botryoidal texture.

Morris et al. suggest that we mixed original matrix and cortex with our late-stage goethite and doubt our ability to recover pure goethite from 1.5-mm growth zones with a 4-mm-diameter drill core. As described by Heim et al. (2006), the 4-mm drill core is the first stage of a systematic sample recovery and characterization process. After drilling, the 4-mm core is crushed to 0.1–3 mm grain size and sieved, washed in ethanol, and only pure goethite grains (easily recognized with the aid of a binocular microscope) are picked. We select 5–10 grains for geochronology, while an aliquot of visually pure grains are mounted in epoxy disks, described petrographically, and investigated under a SEM and an EM. Bench-top and synchrotron-based XRD of goethite cement extracted by this procedure confirms pure goethite concentrates.

We cannot completely reject the suggestion made by Morris et al. that some of goethite grains could be partially mixed with goethite from the cortices of pisoliths. However, even if small amounts of cortices were included, none of the samples that we have analyzed so far contain significant amounts of this detrital goethite. We stringently excluded texturally distinctive cortex phases from the picked sample aliquots, so any conceivable contamination must be very small. The poorest (U-Th)/He age reproducibility is observed for a sample with a 1-cm-thick late-stage goethite vein, which is petrographically devoid of any detrital phase. Therefore, the small but statistically significant age irreproducibility cannot be explained by admixture of pisolith cortices and warrants further investigation.

Morris et al. also accuse us of statistically forcing our data. There is very little statistical treatment of the data. We used linear regressions simply to illustrate how the (U-Th)/He age reproducibility for duplicate samples affects an extrapolation of the (U-Th)/He dates to the projected original surface of the channel. As stated in Heim et al. (2006), duplicate aliquots yield a narrow range of ages, but the uncorrected ^{4}He ages are not within analytical uncertainty. This irreproducibility could have various possible sources: (1) we underestimated errors in ^{4}He extraction and measurement, (2) we underestimated errors in U and Th analysis, (3) the samples lost various amounts of U and/or Th, (4) the samples lost different amounts of ^{4}He during their geologic history or during sample preparation, and (5) the finely laminated vitreous goethite samples contain various generations of supergene goethite, spanning a range in ages. Procedures and the statistics for the treatment of analytical error in U and Th analysis by ICP-MS, and ^{4}He analysis by mass spectrometry, are well-established and treated in Farley (2002). As stated in our paper, we cannot and do not address possible U and Th gains or losses. Some grains may indeed contain various proportions of supergene goethite from different generations; we can only address this issue by increasing spatial resolution. On the other hand, we can quantify ^{4}He loss through ^{4}He/^{3}He geochronometry.

^{4}He/^{3}He experiments routinely show that natural goethites have diffusively lost 0% to a maximum of 20% of radiogenic ^{4}He since precipitation. We applied the worst-case scenario to all samples. Extrapolating the geochronological data to the original channel surface illustrates an approach to estimate the end of aggradation and the onset of post-depositional goethite cementation of the channel sediments; we can only estimate this age within ± 20% margin of error.

Since the goethite cements that we investigated are demonstrably late-stage phases, they also provide clear *minimum* ages for the host sediments. The downward decrease in goethite cement ages evident in our data is not explained by any conceivable sediment depositional mechanism, as proposed by Morris et al. The geochronological results strongly suggest a pre-Miocene age for the channel sediments, which were subsequently altered by post-deposition weathering and goethite cementation to form CID ore at Yandi.

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