

## Development and Application of Synthetic Hematite Reference Material for U-Pb Geochronology

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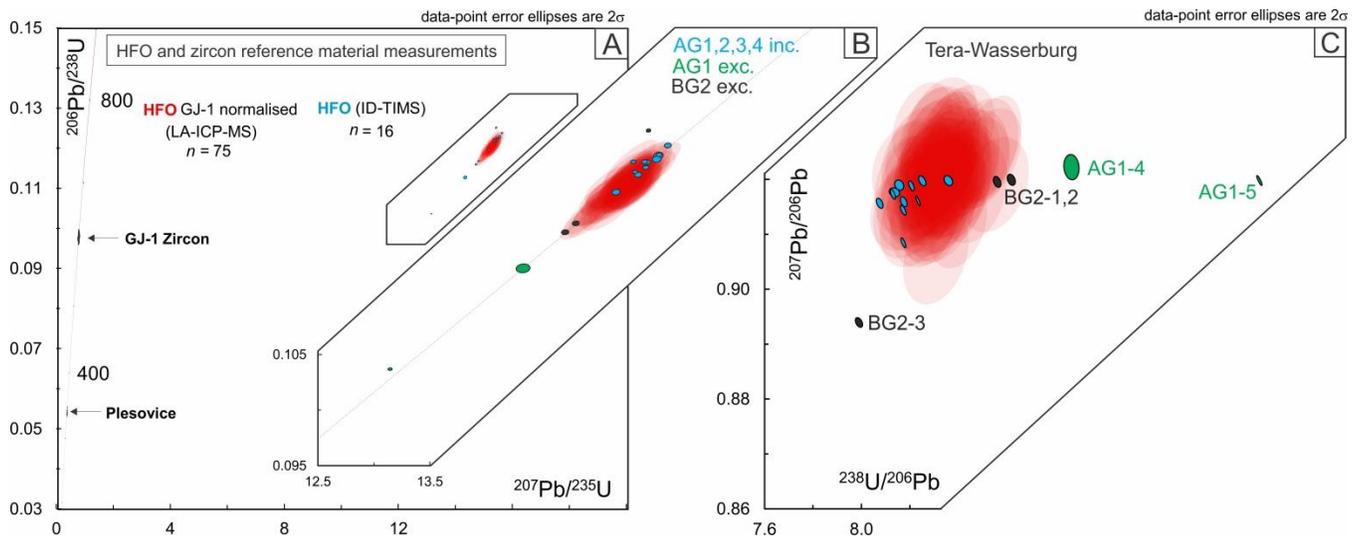
The common iron oxide hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ) can incorporate significant concentrations of U into its crystal structure and retain radiogenic Pb over geological time (Duff et al., 2002; Ciobanu et al., 2013). Hematite is a ubiquitous component of planetary crusts (e.g. ore deposits, banded iron formations, regolith), and represent a valuable geochronometer allowing direct constraints to be placed on the timing of mineral precipitation (e.g. Courtney-Davies et al., 2019a; Keyser et al., 2019). Development of the hematite mineral geochronometer is important because, unlike accessory minerals routinely used to track hydrothermal mineralization, hematite has been shown in certain cases to incorporate negligible common Pb and appears resistant to radiation damage accumulation (Courtney-Davies et al., 2020). Most hematite U-Pb dating studies have utilized laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), due to its relatively high spatial resolution, speed and low cost. However, no suitable natural haematite reference material has been identified, necessitating use of a variety of primary and secondary zircon reference materials. Here, a hematite U-Pb reference material, named MR-HFO, was synthesised and then characterised using LA-ICP-MS and isotope dilution-thermal ionization mass spectrometry (ID-TIMS), to test the materials homogeneity.

Synthetic  $\alpha\text{-Fe}_2\text{O}_3$  co-doped with U and Pb was prepared from a solution of ferric nitrate precipitated with ammonia solution (Courtney-Davies et al. 2019b). This reaction produced a suspension of colloidal hydrated ferric oxide that was washed with water several times by decantation until it peptised. A doping solution of uranyl and lead nitrates was then added to adsorb the U and Pb onto the colloidal hydrated ferric oxide particles. After settling, the doped material was dried at 50 °C to produce solid chips, each several millimetres in thickness, followed by heating to 700 °C. The material was held at 700 °C for 10 h, after which it was furnace-cooled to ambient temperatures, resulting in conversion of doped hydrated ferric oxide to  $\alpha\text{-Fe}_2\text{O}_3$ .

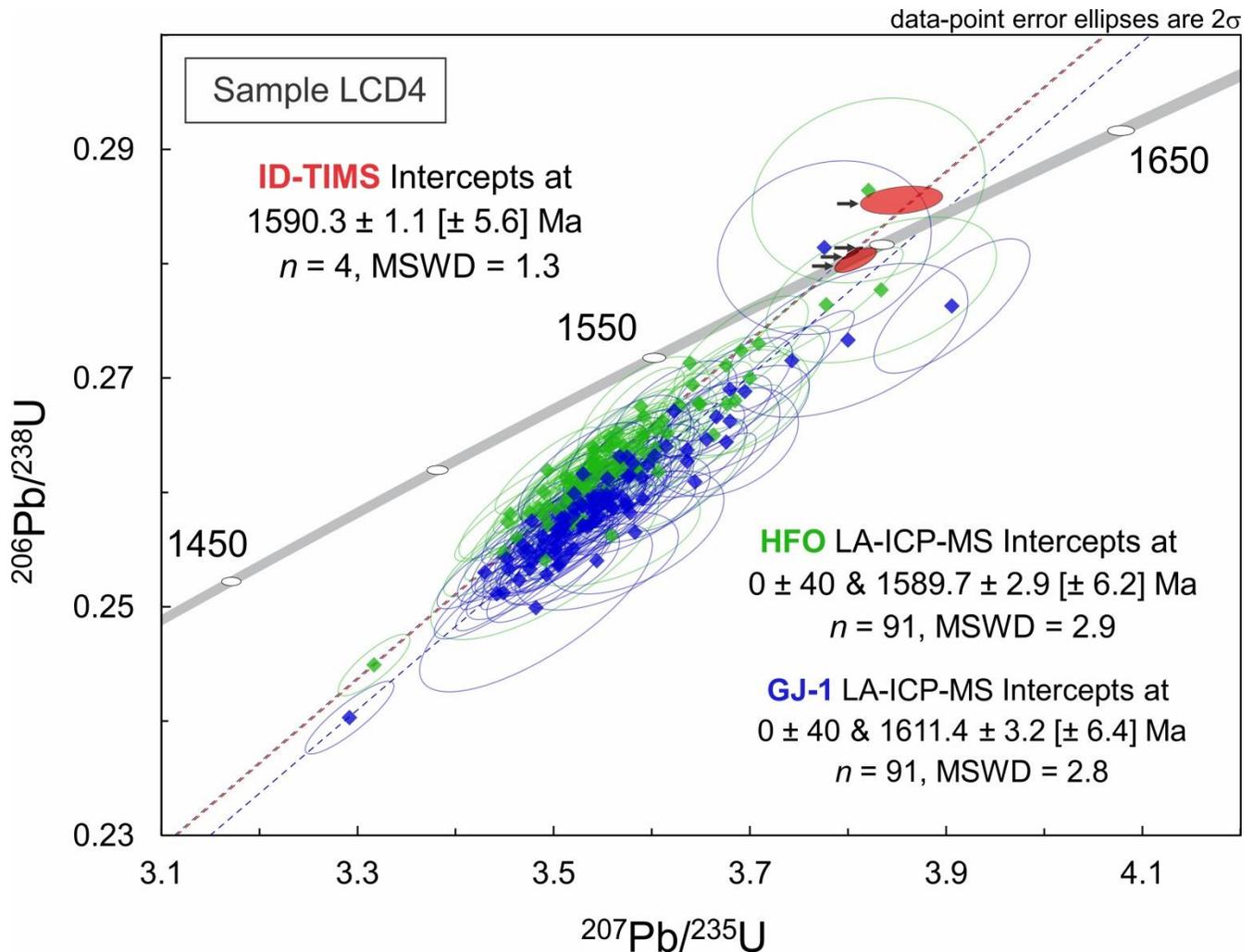
Centimetre-scale chips of synthesised  $\alpha\text{-Fe}_2\text{O}_3$  were randomly microsampled via ‘laser ablation-extraction’ and analysed using ID-TIMS at the British Geological Survey. Reproducible U/Pb and Pb/Pb ID-TIMS measurements were obtained across four separate chips ( $n = 13$ ). Data obtained from MR-HFO is displayed in Figure 1.

Subsequently, an evaluation of the suitability of MR-HFO in constraining U-Pb data via LA-ICP-MS (performed at Adelaide Microscopy) was carried out using a selection of natural samples derived from iron oxide-Cu-Au systems, including Olympic Dam (Australia), Carajás (Brazil) and Mantoverde (Chile), which range from Cenozoic to Proterozoic in age. The MR-HFO normalised U-Pb ratios were more concordant and ages more accurate versus the same LA-ICP-MS spot analyses normalised to zircon reference material, when compared with independently acquired ID-TIMS data from the same natural hematite grains (Figure 2). These results establish MR-HFO as a

suitable reference material for LA-ICP-MS hematite U-Pb geochronology, and represent the first ever synthetic U-Pb reference material (Courtney-Davies et al., 2021).



**Figure 1.** (A) Wetherill Diagram showing LA-ICP-MS measurements of secondary zircon reference materials (GJ-1 and Plešovice) and MR-HFO (red ellipses) normalised to GJ-1 zircon. (B) inset of (A), displaying the ID-TIMS measurements of MR-HFO. Blue ID-TIMS ellipses represent analyses used for calibration of MR-HFO, green and blue ellipses were excluded analyses from more heterogeneous chips. (C) The same data displayed in (B) transformed into a Tera-Wasserburg diagram. Note the slight offset between ID-TIMS (blue) and GJ-1 (red) normalised LA-ICP-MS measurements of MR-HFO.



**Figure 2.** Wetherill diagram displaying a comparison of ID-TIMS data versus LA-ICP-MS data, which has been normalised using both MR-HFO (green ellipses) and GJ-1 zircon (blue ellipses). All ID-TIMS measurements and LA-ICP-MS spot analyses were obtained from the same grain of hematite at Olympic Dam. Note the improved accuracy of MR-HFO normalised data in terms of the upper intercept date versus GJ-1 normalised, when compared with the independent ID-TIMS intercept.

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