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# The early formation of the IVA iron meteorite parent body

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ABSTRACT

The IVA iron meteorites are magmatic cumulates from the core of a small asteroid, which broke apart ~400 Ma ago. As the depletion of this planetary body in volatile elements is expected to be reflected in high U/Pb ratios of its minerals, we embarked on analyzing the isotope composition of Pb in the cm-sized troilite inclusions of Muonionalusta and Gibeon, both iron meteorites belonging to the IVA family. The bulk of the data for nine troilite subsamples of Muonionalusta scatter with an apparent age of 4.57 Ga, which is shown to reflect the presence of both primordial and common terrestrial Pb components, in addition to radiogenic Pb. The most radiogenic subsample, however, has fractions with $^{206}Pb/^{204}Pb$ ratios as high as over 1000 and gives a statistically significant $^{207}Pb^*/^{206}Pb^*$ age of 4565.3 ± 0.1 Ma (MSWD = 0.08), consistent with the $^{182}Hf$–$^{182}W$ metal–silicate segregation age of 2.4 ± 2.0 Ma. These data make the age of Muonionalusta the oldest documented yet for all differentiated bodies in the Solar System and constitute the first high-precision Pb–Pb age determined for crystallization of a phase contained within an iron meteorite group, hence advancing our understanding of early Solar System chronology. Using literature values for the cooling rate, and assuming a closure temperature for Pb of 300 °C, it is further estimated that the IVA parent body accreted within 1 Ma of CAI formation and had cooled to the Pb closure temperature within an additional 1–2 Ma. The overlap between the high-precision Pb–Pb and Hf–W ages points to a small, or rapidly fragmented, planetary body. The isotopic composition of Pb in Gibeon troilite yields a significantly younger age of 4544 ± 7 Ma (MSWD = 1.5), consistent with evidence from the $^{107}Pd$–$^{107}Ag$ chronometer, but we believe this age has been reset by melting upon shock. One puzzling observation is that the apparent $^{232}Th/^{238}U$ of Muonionalusta troilite is particularly low (~0.32), requiring a mechanism capable of efficiently fractionating Th from U, presumably the reduction of U to its trivalent form or the crystallization of phosphate. Average Pb concentrations of the order of 5–10 ppb and high $^{238}U/^{204}Pb$ ratios of >1000 require U concentrations in troilite in the sub-ppb to one ppb range. This may indicate that troilite inclusions in IVA meteorites do not represent metal-sulfide unmixing, but rather correspond to late-stage S-rich liquid residues from extreme crystallization of the interstitial melts.



## 1. Introduction

Observations and measurements made on meteorites offer rare clues about the numerous processes taking place during the first few million years of the history of the Solar System. Isotopic measurements in particular shed light on the chronology of these processes. Over the last several decades, the assumption that iron meteorites likely formed in bodies with lengthy accretionary histories and protracted periods of differentiation and crystallization has gradually given way to accumulating isotopic evidence that the crystallization of at least some of these bodies occurred within a very few million years of the start of the Solar System (Chen and Wasserburg, 1990; Horan et al., 1998; Lee, 2005; Markowski et al., 2006; Scherstén et al., 2006; Qin et al., 2008; Schönbächler et al., 2008). The emerging testimony for the rapid progression of early planetary processes requires that some iron meteorites were extracted from small, very early-formed asteroids. The nature of these bodies and their evolution in the rapidly evolving solar nebula are not well understood. Although the debris disk left by accretion of planetary bodies from the solar nebula appears to have dissipated in less than a few Ma (Wyatt, 2008), firsthand records of old ages in planetary objects are scarce, mostly because radiometric ages reflect cooling ages, while heating by the radioactive decay of $^{26}Al$, tidal dissipation, and repeated impacts were keeping planetary interiors hot. Exceptions exist, such as the angrite d'Orbigny with a documented Pb–Pb age of 4564.4 Ma (Amelin, 2008). Core segregation within the parent asteroids of at least some iron meteorites seems to have started very early, but has been variably dated depending on which chronometer is considered. Presumably, $^{187}Re$–$^{187}Os$ (Horan et al., 1998) and $^{107}Pd$–$^{107}Ag$ (Chen and Wasserburg, 1990; Schönbächler et al., 2008) ages are those of

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metal crystallization or subsolidus closure, whereas $^{182}Hf$–$^{182}W$ (Horan et al., 1998; Lee, 2005; Markowski et al., 2006; Scherstén et al., 2006; Qin et al., 2008) dates silicate–metal segregation. The latter chronometer in particular strongly suggests that iron meteorites are very old differentiated objects that formed within only a few Ma of Allende CAIs. However, the limiting precision on W and Ag ages of, respectively, ~2 and ~4 Ma, and the current range of 1.6 Ma on the age of CAIs used to anchor both the $^{182}Hf$–$^{182}W$ and $^{107}Pd$–$^{107}Ag$ chronometers, stand in the way of finding out precisely how old.

Although some iron meteorites, such as, most famously, Canyon Diablo, have been found to contain the least radiogenic (i.e., primitive or primordial) Pb in the Solar System (Patterson, 1956; Tatsumoto et al., 1973; Chen and Wasserburg, 1983; Göpel et al., 1985), others contain Pb radiogenic enough to allow for an investigation into their chronological potential in terms of absolute ages (Chen and Wasserburg, 1983), which is why we set out to date some of these objects using the Pb–Pb chronometers. The $^{207}Pb/^{206}Pb$ chronometer has the unique property that ages are independent of measured parent/daughter ratios and, therefore, largely insensitive to recent resetting. In addition, and contrary to extinct radioactivities, the $^{207}Pb/^{206}Pb$ chronometer defines an absolute time scale that renders it independent of CAI age constraints. In fact, it is the $^{207}Pb/^{206}Pb$ chronometer itself which is used to date the CAIs in the first place (Bouvier et al., 2007; Amelin and Krot, 2007; Connelly et al., 2008; Jacobsen et al., 2008; Wadhwa and Bouvier, 2009). The final advantage of the $^{207}Pb/^{206}Pb$ chronometer is its remarkable precision (due to the combination of a short-lived, almost extinct ($^{235}U$) and a long-lived ($^{238}U$) parent nuclide and the parent element being common to both chronometers), potentially better than 1 Ma, even for ages as old as that of the Solar System.

Among the magmatic iron meteorites, the IVA group is known to be depleted in volatiles, such as Ga and Ge (Wasson and Richardson, 2001). This group is not, however, adequately accounted for by a simple fractional crystallization model with a unique initial S content (Chabot, 2004). The IVA group is also known for its broad and somewhat controversial range of cooling rates, between 30 and 6600 K per Ma (Rasmussen et al., 1995; Haack et al., 1996; Wasson and Richardson, 2001; Yang et al., 2007, 2008), which has been interpreted as the disruption and reassembly of the core of an early planet 5–200 km in diameter. Low-Ni members of this group may have cooled down as fast as 1500 K $Ma^{-1}$. Oxygen isotopes suggest that the IVA irons and the L and LL ordinary chondrites may have been extracted from the same parent body (Wang et al., 2004). Because of its large range in Pd/Ag ratios, Gibeon, which belongs to the IVA group, has become the reference for $^{107}Pd$–$^{107}Ag$ ages (Chen and Wasserburg, 1990; Schönbächler et al., 2008). Muonionalusta is another, but less well known member of the IVA group, with large fragments excavated in Sweden from north of the Arctic Circle. It is an octahedrite that contains large, cm-sized inclusions of troilite (Lagerbäck and Wickman, 1997). The presence of stishovite signifies that this meteorite was heavily shocked, possibly during the 0.4 Ga old breakup event indicated by cosmic ray exposure (Voshage, 1967; Lavielle et al., 1999) and the associated shower (Holtstam et al., 2003). The Pb–Pb dating of troilite inclusions from two separate samples of Muonionalusta and the implications of their ages for the early history of the Solar System is the main focus of the present work, although we also show Pb–Pb isotope data for a troilite inclusion from Gibeon, and Hf–W isotope data for Muonionalusta iron.

## 2. Samples and analytical techniques

Two large samples of Muonionalusta (thin slabs, one rectangular and one triangular, of ~350 g each measuring, respectively, 8×10×0.7 cm and 12×14×15×0.3 cm) were acquired from an anonymous German meteorite dealer (the rectangular slab hereafter referred to as ML1) and from Luc Labenne, a French meteorite dealer (the triangular slab hereafter referred to as ML2). Each slab contained a single large troilite inclusion, one only slightly elongated, the other ellipsoidal, with dimensions of about 3.5×2×0.7 cm (ML1) and 6×3×0.3 cm (ML2). The following sample characteristics are largely reproduced from the descriptions by Buchwald (1975) and Holtstam et al. (2003) of different pieces of Muonionalusta. The iron shows a fine Widmanstätten pattern with long kamacite lamellae. Wasson and Richardson (2001) reported an average Ni content of the iron of 8.48 wt.%. Troilite varies from schreibersite, with the composition of $Fe_{0.97}Cr_{0.02}S$, to kamacite near the edge, with the composition of $Fe_{1.56}Ni_{1.44}P$. The troilite is accompanied by subhedral grains of chromite, elongated grains of daubreelite ($Fe^{2+}Cr_2S_4$), and rare stishovite, all up to 100 μm long.

A 120 g piece of Gibeon in the form of a thick slab measuring 5×4×1.2 cm with half of a single large, nearly circular (3.5×3×1.2 cm) troilite inclusion comprising about a third of the iron meteorite sample also was obtained from Luc Labenne. The troilite inclusion itself contained small (~0.5 cm) spherical metal blebs scattered within the sulfide matrix with a conspicuous metal-sulfide eutectic rim. From the detailed petrological descriptions given by Buchwald (1975) and Teshima et al. (1986), the two meteorites, Muonionalusta and Gibeon, and their troilite inclusions, are similar, with the sole difference that stishovite has not been found in Gibeon troilite. Teshima et al. (1986) argued that Gibeon underwent some event of flash heating followed by rapid cooling. Wasson and Richardson (2001) report a range of Ni content in the metal of 7.9–8.2 wt.%.

Several troilite subsamples (nine for Muonionalusta and one from Gibeon) in the form of massive chunks (1.6–3.5 g) were extracted from the troilite inclusions of the two slabs of Muonionalusta and the single slab of Gibeon using a stainless steel chisel. One of the Muonionalusta subsamples and the Gibeon sample were first analyzed on an Element 2 LA-ICP-MS at Rice University to verify their true troilite nature and determine their depletion levels for Pb, U, and Th. As expected, high concentrations of Fe, S, Cr, and Ni (of the order of wt.%), as well as Mn, Co, Cu, P, and Zn (of the order of ppm), and very low concentrations of Pb, U, and Th (of the order of ppt to ppb) were found (Table 1). The laser ablation measurements were done on a ThermoFinnigan Element 2 single-collector magnetic sector ICP-MS using a 213 nm New Wave laser. Samples were ablated with an energy flux of 16–18 J/cm$^2$ at a 10 Hz repetition rate. Spot diameters varied from 55 to 110 μm. $^{57}Fe$, $^{60}Ni$, $^{33}S$, $^{52}Cr$, $^{59}Co$, $^{31}P$, $^{55}Mn$, $^{63}Cu$, and $^{66}Zn$ were determined in medium mass resolution mode (m/Δm ~ 3000), which was sufficient to resolve all relevant

**Table 1**
Major and trace element abundances in Muonionalusta and Gibeon troilites.

| Sample | Muonionalusta all ($n$ = 21) | | Muonionalusta[a] ($n$ = 14) | | Gibeon ($n$ = 4) | |
|---|---|---|---|---|---|---|
| | Mean | 2s | Mean | 2s | Mean | 2s |
| Fe (wt.%) | 59.2 | 7.78 | 60.2 | 7.6 | 58.3 | 2.88 |
| S (wt.%) | 40.1 | 6.43 | 39.6 | 7.6 | 41.4 | 2.83 |
| Cr (wt.%) | 0.264 | 0.0357 | 0.26 | 0.039 | 0.246 | 0.0381 |
| Ni (wt.%) | 0.326 | 0.755 | 0.0294 | 0.00558 | 0.0238 | 0.0041 |
| Mn (ppm) | 300 | 81 | 300 | 55 | 350 | 260 |
| Cu(ppm) | 200 | 190 | 170 | 130 | 110 | 51 |
| Co (ppm) | 630 | 660 | 22 | 11 | 16 | 8.7 |
| P (ppm) | 170 | 800 | 5.2 | 3.6 | 380 | 740 |
| Zn (ppm) | 1.4 | 3.5 | 0.78 | 0.56 | 66 | 150 |
| Pb (ppm) | 0.04 | 0.29 | 0.0077 | 0.0074 | 0.097 | 0.24 |
| Th (ppm) | 0.0014 | 0.0035 | 0.0019 | 0.0042 | 0.00054 | 0.00024 |
| U (ppm) | 0.0015 | 0.0078 | 0.00081 | 0.0038 | 0.0028 | 0.0044 |

[a] Homogeneous domain within the same inclusion ($n$ = number of analyses; 2s = 2 sigma).