

## More old news from Martian meteorites.

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The consensus that the magmatic ages of shergottites are young (<500 Ma) [1] is inconsistent with crater density evidence that most of the Martian surface is old (> 3 Ga) [2]. Bouvier and co-workers [3-5], however, obtained old Pb-Pb ages on basaltic shergottites (4.1-4.3 Ga), which they used to challenge the interpretation of Rb-Sr and Sm-Nd internal isochrons, as well as K-Ar ages. Here we report new Pb isotopic data on whole-rocks and mineral separates from the enriched shergottite RBT 04262, the nakhlite MIL 03346, and the orthopyroxenite ALH 84001, which previously provided Sm-Nd ages of 4.5 Ga [6,7] on silicates and Pb-Pb ages of ~ 3.9-4.0 Ga on carbonates [8].

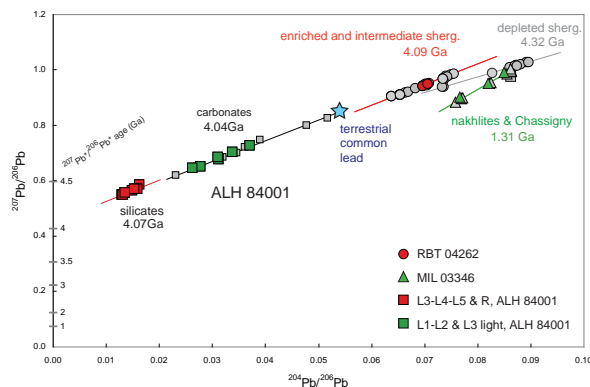


Figure 1: New Pb-Pb results on Martian meteorites (in color). Literature data [3-5, 8, 10] in grey. Terrestrial Pb from [11].

### Samples and analytical techniques

As a follow-up to an earlier report [5], we present additional Pb isotopic data for mineral separates (pyroxene and/or maskelynite) of the enriched shergottite RBT 04262 and the nakhlite MIL 03346. The shergottite and nakhlite mineral separates (63-150 m) were successively leached in 1.5M HBr (60°C, 1h), 1M HF (60°C, overnight), and 6M HCl (60°C, 4h). We also processed a ~0.8 g sample of the orthopyroxenite ALH 84001 to obtain the Pb isotopic composition of the whole-rock powder and silicate separates, which hence differs from an earlier Pb-Pb study of ALH 84001 carbonates [8]. We separated carbonates, maskelynite and glass from the orthopyroxene on the 63-150 m fraction (~0.6g) using heavy liquids (methylene iodide) and hand-picking. We

processed the heavy and light fractions separately for leaching and chemistry. We leached the bulk and mineral separates using a longer protocol than for shergottite and nakhlite separates to first remove terrestrial contamination, and then dissolved progressively the most to least soluble phases. The ALH 84001 samples were successively leached in 0.25M HCl (20°C, 1h), 2.5M HCl (90°C, 6h), 6M HCl (110°C, 12h), 1M HF (110°C, 1h), and finally for the orthopyroxene separates only in 4M HF (110°C, 16h). Leachates and residues of the whole-rock and orthopyroxene separates were analyzed, whereas only leachates were analyzed for the small light fraction. The procedures for Pb separation chemistry and isotope measurement using the Nu Plasma HR MC-ICPMS at ENS-Lyon are described in [4]. Total procedural blanks were ~1-2 pg and isotopic compositions were corrected according to the method described in [9].

### Results

The new Pb isotope data for the shergottite RBT 04262 fall on the ~4.1 Ga enriched and intermediate shergottite isochron defined by 23 other residues of maskelynite separates and whole-rocks of shergottites (Zagami, Los Angeles, Shergotty, EETA79001, NWA 480, NWA 1068 from [4,5] and references therein) (Fig. 1). When regressing all the Pb-Pb data of maskelynite and whole-rock residues of enriched and intermediate shergottites, we find an age of  $4092 \pm 74$  Ma (MSDW=34). The residues of the depleted shergottites (QUE 94201 [10] and NWA 1195 [5]) define a different isochron at  $4319 \pm 47$  Ma (MSWD=11). The whole-rock and mineral separates of MIL 03346 fall on the ~1.3 Ga nakhlite and chassignite isochron defined by literature and unpublished data on Nakhla ([4] and references therein), and Yamato-000593 and Chassigny [5]. The first two leachates of the ALH 84001 whole-rock and orthopyroxene, and also the third leachate of the light fraction, fall on the 4.04 Ga Pb-Pb isochron defined by the carbonates from ALH 84001 [8]. The last leachates and residues of the bulk and orthopyroxene separates of ALH 84001 have more radiogenic compositions and define a Pb-Pb array with an age of  $4074 \pm 99$  Ma (MSWD=47).

### The issue of terrestrial contamination

We previously argued that, although terrestrial common Pb plots near the shergottite alignments, these are unlikely to be due to terrestrial contamination [4]. First,

contaminated samples should define a 3-component mixing domain (initial, radiogenic, and terrestrial contaminant) rather than a binary mixing array. Second, the nakhlite array indicates an age of 1.3 Ga consistent with Rb-Sr, Ar-Ar, and Sm-Nd results, and yet does not pass through the terrestrial Pb composition. Again, the terrestrial common Pb plots near the ALH 84001 isochrons. This situation is very similar to that observed for terrestrial  $^{207}\text{Pb}/^{204}\text{Pb}$  vs  $^{206}\text{Pb}/^{204}\text{Pb}$  isochrons [11], which all converge to the terrestrial common Pb: bundling isochrons simply reflect that secondary isochrons intersect on the Pb isotope composition of the mantle source, i.e., on the geochron, and do not record massive yet elusive 'contamination'.

### A younger age for ALH 84001

The new results do not confirm the well-entrenched 4.5 Ga Sm-Nd ages [6,7] of ALH 84001. The age of the carbonate isochron is consistent with previous ages on leachates [8] and indistinguishable from the silicate internal isochron. ALH 84001 seems to be just another petrographic variant from the  $\sim 4.1$  Ga old crust, and carbonate deposition may be contemporaneous with or only slightly younger than the magmatic emplacement age.

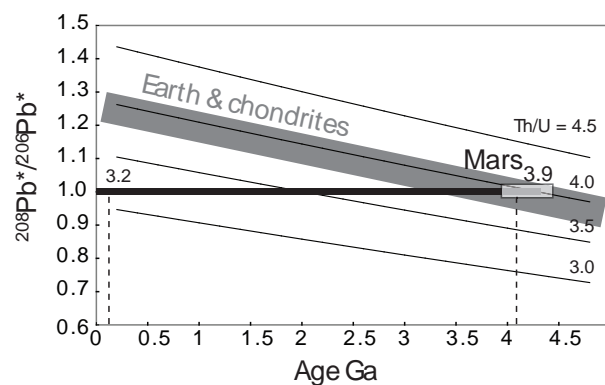


Figure 2: The contrasting Th/U ratios inferred at 4.1 and 0.2 Ga from the  $^{208}\text{Pb}^*/^{206}\text{Pb}^*$  intercept in the  $^{208}\text{Pb}/^{206}\text{Pb}$  vs  $^{204}\text{Pb}/^{206}\text{Pb}$  plot.

### $^{208}\text{Pb}/^{206}\text{Pb}$ evidence of old shergottite ages

Th and U are highly refractory and therefore very unlikely to be fractionated during accretion. Further evidence for Noachian shergottites is provided by the ratio of radiogenic  $^{208}\text{Pb}^*$  to  $^{206}\text{Pb}^*$  of  $1.02 \pm 0.05$  (Fig. 2): this ratio corresponds to a Th/U ratio of 3.9 for 4.1-4.3 Ga old shergottites, and to 3.2 if they are  $<0.5$  Ga old. The ratio for an age of 4.1-4.3 Ga is indistinguishable from the Th/U ratio of  $3.9 \pm 0.2$  found for the Earth, the Sun, and carbonaceous chondrites [12], and also from the time-integrated Th/U ratio derived from the Pb isotope compositions of most lunar rocks [13].

### Conclusions

The accumulated Pb isotopic evidence shows that all Martian meteorites formed in three episodes dated at  $\sim 4.3$ , 4.1, and 1.3 Ga. The  $\sim 4.5$  Ga Sm-Nd age of ALH 84001 is not confirmed by our new Pb-Pb data.

### References

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