

LEAD IN MARTIAN METEORITES — OBSERVATIONS AND INCONSISTENCIES: I. CHASSIGNY

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Introduction: The history of Pb isotope analyses of the martian meteorites (SNC) and their interpretations is laden with difficulties. Two different analytical groups have interpreted their ancient (≥ 4 Ga) shergottite Pb ages as primary [1-5]. A Nakhla age of ~ 4.3 Ga has been interpreted to be primary as well [2]. This is in stark contrast to the young (≤ 1.4 Ga) crystallization ages defined by the Rb-Sr, Sm-Nd, Lu-Hf, and K-Ar systems [6]. Possibly, a better interpretation for the ancient Pb ages is that they reflect the formation times of the various SNC source regions [7].

A difficulty in dealing with Pb is that terrestrial contamination is ubiquitous, unlike the other chronometer systems noted above. This issue is complicated by the fact that radioactive decay causes localized mineral damage. So washing and leaching to remove Pb contamination tends to remove *in situ* radiogenic Pb. This issue is further compounded because U and Th are often concentrated in phosphates and other minor phases, so the leaching process tends to remove these, especially phosphates.

Another difficulty is that it is not clear whether the observed Pb isotopic variation in leachates, residues, and ion-microprobe analyses is due to terrestrial or to indigenous martian Pb contamination [e.g., 8].

A third difficulty is that the shergottites on the one hand, and the nakhlites and chassignites on the other, appear to have come from separate source regions with different chemical compositions [e.g., 7]. Thus, it is expected that their Pb isotopic characteristics would be different. And even if all these meteorite types came from the same source region, their igneous ages differ considerably. The nakhlites and chassignites are ~ 1.4 Ga and the shergottites are ≤ 600 Ma [e.g., 6]. This age difference alone should assure that the two distinct SNC groups have differing Pb isotopic signatures.

Pb in Chassigny: Figure 1 summarizes Pb analyses for Chassigny. For comparison, there are two estimates of modern terrestrial Pb [1, 9] and a solar system primordial Pb (PAT; [10]).

Many issues become apparent in Figure 1. First, the **plagioclases**, **pyroxenes**, and **olivines** of Chassigny appear to fall on a separate trend from that of the Chassigny **K-spar** and **sulfides**. These are all ion probe analyses [8], which are less precise than isotope dilution TIMS analyses; but the differences appear systematic and are unlikely analytical. The TIMS analyses of Chassigny [5] fall along and extend the olivine-pyroxene-plagioclase trend.

Further, there are two distinct plagioclase groups. Figure 2 illustrates that these two groups appear to be

unrelated to *in situ* decay of U. Therefore, there are three isotopically distinct feldspar groups: (1) a high $^{206}\text{Pb}/^{204}\text{Pb}$ plagioclase group; (2) a low $^{206}\text{Pb}/^{204}\text{Pb}$ plagioclase group; and (3) a K-spar group. The plagioclases appear to define a mixing between high and low $^{206}\text{Pb}/^{204}\text{Pb}$ endmembers. The K-spars (and sulfides) form a sub-parallel trend to the plagioclases, having higher $^{207}\text{Pb}/^{206}\text{Pb}$ ratios. The K-spar and sulfide data regress to near PAT; the plagioclases regress to a composition having a lower $^{207}\text{Pb}/^{206}\text{Pb}$ than PAT.

Chassigny **olivines** are very radiogenic and are consistent with the plagioclase trend. And all Chassigny analyses either have higher $^{207}\text{Pb}/^{206}\text{Pb}$ ratios than are typical for modern terrestrial Pb [1,9] or regress to such compositions. This demonstrates that the radiogenic signatures of the Chassigny olivines are not due to terrestrial contamination.

Pb in Chassigny Olivine, Pyroxene, and High $^{206}\text{Pb}/^{204}\text{Pb}$ Plagioclase: Bellucci et al. [8] gave special attention and discussion to the radiogenic Pb signature of their olivine analyses. The extreme incompatibility of U in olivine make it highly unlikely that this signature is due to *in situ* decay of U. Therefore, Bellucci et al. concluded that this “unsupported” radiogenic Pb was due to hydrothermal alteration, incorporation into the olivine by shock, and/or residence in olivine fractures that were subsequently annealed.

We find all of these possibilities to be highly improbable. There is no mineralogical evidence for hydrothermal alteration [11]. Shock incorporation would presumably affect olivine rims more than cores, since shock temperatures and pressures are both extremely transient. And it would be odd that none of the analyses of [8] managed to totally avoid an annealed fracture or grain boundary, i.e. why are there no olivines that plot within the low $^{206}\text{Pb}/^{204}\text{Pb}$ plagioclase group? Therefore, it seems reasonable that the radiogenic Pb in the Chassigny olivines is magmatic. And because olivine was apparently the liquidus phase, this would imply that the Chassigny parent liquid contained highly radiogenic Pb that was incorporated into olivine, pyroxene, and plagioclase. That said, the spread in $^{206}\text{Pb}/^{204}\text{Pb}$ among all these phases suggests that there was never Pb isotopic equilibration and that the system was not closed. The high $^{206}\text{Pb}/^{204}\text{Pb}$ reservoir must have had a $^{238}\text{U}/^{204}\text{Pb}$ (μ) of ≥ 13 .

This interpretation is complicated by the observation that the mafic phases in Chassigny appear to have equilibrated subsolidus [12]. So therefore, it is not clear that primary isotopic compositions should have been preserved. But the isotopic heterogeneity of Pb

in Chassigny is manifest. It is possible that the mass and size of Pb^{2+} prevented diffusive Pb equilibration. Armoring of olivine by poikilitic pyroxene may also have helped to preserve isotopic heterogeneity [13].

Pb in Low $^{206}\text{Pb}/^{204}\text{Pb}$ Plagioclase: The leaches and residue of Chassigny from [5] fall mainly at the low $^{206}\text{Pb}/^{204}\text{Pb}$ end of the plagioclase trend. This implies that the Pb mass balance in Chassigny is dominated by a low $^{206}\text{Pb}/^{204}\text{Pb}$ component. These analyses emphasize the unequilibrated nature of Chassigny Pb.

It is not easy to understand the origin of these low $^{206}\text{Pb}/^{204}\text{Pb}$ plagioclases. A 2-stage model of $\mu \sim 0.5$ for 2 Ga from PAT and a μ of ~ 7 for 1.1 Ga suffices to provide an acceptable isotopic composition that falls on the plagioclase regression line (Fig. 1). Although this model is not unique, it is near impossible to produce the observed trend(s) in a single stage from PAT.

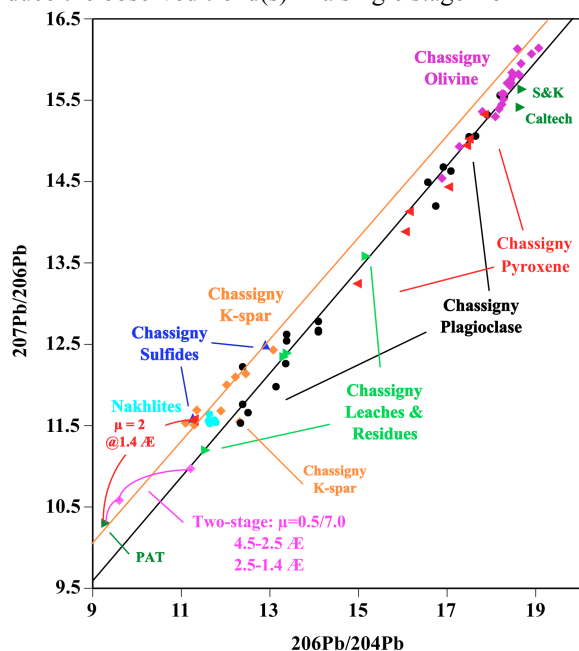


Figure 1. Chassigny Pb Summary. A K-spar analysis, nearly hidden by a plag analysis, is pointed out. Light green and light blue analyses by TIMS [3,5] — others by ion probe [8].

Pb in K-spar and Sulfide: These phases fall on a sub-parallel trend to that of the plagioclases and that passes through or near PAT, suggestive of special significance. The fact that nakhlite residues plot near the K-spar/sulfide same trend is perplexing. The nakhlites and chassignites appear to be extremely similar in terms of their Sr and Nd initial isotopic signatures [12], but the nakhlites here show similarities to Pb in the depleted shergottites. Further, because the residues and leaches of [5] do not resemble the Pb in K-spar and sulfides, this Chassigny Pb component must be minor. A single stage of growth for 1.4 Ga from PAT with a μ of 1.5-2.0 would serve to produce Pb at the low $^{206}\text{Pb}/^{204}\text{Pb}$ end of the K-spar/sulfide trend.

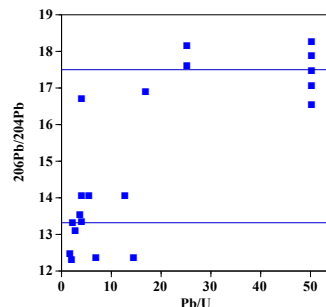


Figure 2. Two $^{206}\text{Pb}/^{204}\text{Pb}$ plagioclase populations in Chassigny. See also Figure 1.

Possible Pb-based Petrogeneses for Chassigny:

Scenario I: Olivine was the liquidus phase of an Ur-parent liquid that had a high $^{206}\text{Pb}/^{204}\text{Pb}$, most likely from a very small degree of crustal assimilation. The amount of olivine crystallization was probably small; the best composition for the Chassigny parent is slightly silica-normative [13]. Plagioclase and augite appear soon thereafter as magma recharge(?), which decreases the $^{206}\text{Pb}/^{204}\text{Pb}$ of the system, and plag continues to crystallize after augite is exhausted. In the latest stages of crystallization, Pb from a different reservoir dominates as K-spar and sulfides crystallize. This last reservoir had affinity to the nakhlites and depleted shergottites. In short, the petrology of Chassigny was dominated by continual open system evolution.

Scenario II: The Ur-parent was olivine saturated but had low $^{206}\text{Pb}/^{204}\text{Pb}$. Low $^{206}\text{Pb}/^{204}\text{Pb}$ plagioclase followed olivine on the liquidus as the melt assimilated high $^{206}\text{Pb}/^{204}\text{Pb}$ crust. Augite followed plagioclase and its Pb became increasingly radiogenic. A late recharge(?) of non-radiogenic Pb produced K-spar and sulfide. Subsolidus equilibration then partially reset the isotopic signature of olivine, making it highly radiogenic. Sub-solidus equilibration did not greatly affect the other phases. The gap in plagioclase $^{206}\text{Pb}/^{204}\text{Pb}$ is attributed to poor sampling. Again, open system behavior pertains.

References: [1] Chen J.H. & Wasserburg G.J. (1986a) *G.C.A.* **50**, 955-968. [2] Chen J.H. & Wasserburg G.J. (1986b) In *Lunar Planet Sci. XVII* (Abstract). 113-114. [3] Bouvier A. et al. (2005) *E.P.S.L.* **240**, 221-233. [4] Bouvier A. et al. (2008) *E.P.S.L.* **266**, 105-124. [5] Bouvier A. et al. (2009) *E.P.S.L.* **280**, 285-295. [6] Nyquist L.E. et al. (2001) *Space Sci. Rev.* **96**, 105-164. [7] Jones J.H. (2015) *MAPS* **50**, 674-690. [8] Bellucci J.J. et al. (2016) *E.P.S.L.* **433**, 241-248. [9] Stacey J.S. & Kramers J.D. (1975) *E.P.S.L.* **26**, 207-221. [10] Tatsumoto M. et al. (1973) *Science* **180**, 1279-1283. [11] Floran R.J. et al. (1978) *G.C.A.* **42**, 1213-1229. [12] Misawa K. et al. (2006) *E.P.S.L.* **246**, 90-101. [13] Longhi J. & Pan V. (1989) *Proc. Lunar Planet. Sci. Conf. 19th*, 451-464.