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A Pb isotopic resolution to the Martian meteorite age paradox

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ABSTRACT

Determining the chronology and quantifying various geochemical reservoirs on planetary bodies is fundamental to understanding planetary accretion, differentiation, and global mass transfer. The Pb isotope compositions of individual minerals in the Martian meteorite Chassigny have been measured by Secondary Ion Mass Spectrometry (SIMS). These measurements indicate that Chassigny has mixed with a Martian reservoir that evolved with a long-term $^{238}\text{U}/^{204}\text{Pb}$ (μ) value $\sim$ two times higher than those inferred from studies of all other Martian meteorites except 4.428 Ga clasts in NWA7533. Any significant mixing between this and an unradiogenic reservoir produces ambiguous trends in Pb isotope variation diagrams. The trend defined by our new Chassigny data can be used to calculate a crystallization age for Chassigny of 4.526 ± 0.027 Ga (2σ) that is clearly in error as it conflicts with all other isotope systems, which yield a widely accepted age of 1.39 Ga. Similar trends have also been observed in the Shergottites and have been used to calculate a >4 Ga age or, alternatively, attributed to terrestrial contamination. Our new Chassigny data, however, argue that the radiogenic component is Martian, mixing occurred on the surface of Mars, and is therefore likely present in virtually every Martian meteorite. The presence of this radiogenic reservoir on Mars resolves the paradox between Pb isotope data and all other radiogenic isotope systems in Martian meteorites. Importantly, Chassigny and the Shergottites are likely derived from the northern hemisphere of Mars, while NWA 7533 originated from the Southern hemisphere, implying that the U-rich reservoir, which most likely represents some form of crust, must be widespread. The significant age difference between SNC meteorites and NWA 7533 is also consistent with an absence of tectonic recycling throughout Martian history.

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1. Introduction

Quantifying the formation and interactions of geochemical reservoirs is critical to understanding relationships and chronology of planetary bodies. Mars is the only planet other than Earth for which we have physical samples, in the form of the Martian meteorites. Pb isotopes can be used to define the crystallization age of a rock and to quantify time-integrated geochemical variables of the source from which that rock was derived ($\mu = ^{238}\text{U}/^{204}\text{Pb}$ and $\kappa = ^{232}\text{Th}/^{238}\text{U}$). These ratios have been used on Earth to define mantle and crustal reservoirs and their interactions (e.g., Hart et al., 1992; Zartman and Haines, 1988). The U–Th–Pb history of the Martian mantle has been investigated using the Pb isotope system of the Martian meteorite suite including the Sher-

gottites, Nakhilites, and Chassignites (SNCs), as well as orthopyroxenite ALH 84001 (Borg et al., 2003, 2005; Bouvier et al., 2005, 2008, 2009; Chen and Wasserburg, 1986; Gaffney et al., 2007; Nakamura et al., 1982). Results from these studies indicated that the Martian mantle has a relatively limited range in μ -values (1–5) and the best estimate of μ -value for bulk silicate Mars is determined as ~ 3 (Gaffney et al., 2007). The limited range in composition, rock type, and ages of the SNCs (0.16–1.3 Ga, e.g., Nyquist et al., 2001) precludes a detailed investigation of the complexity of the Martian U–Th–Pb system. Nonetheless, a recent investigation into the micrometer-scale Pb isotope systematics of 4.428 Ga clasts in Martian regolith breccia NWA7533 indicated a complicated resetting history and derivation from a crustal source with a μ -value of 13.4 at 4.4 Ga (Bellucci et al., 2015). Additionally, Moser et al. (2013) measured the Pb isotope systematics of minerals and melt pockets from shergottite NWA 5298, demonstrating micrometer scale heterogeneities in a non-brecciated Martian meteorite. As these heterogeneities were only revealed by *in situ* analyses,

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Fig. 1. Backscatter electron image of Chassigny with locations of analytical spots.

a similar approach is clearly warranted for the Pb isotope systematics of the rest of the SNCs. Secondary Ion Mass Spectrometry (SIMS), used here to investigate the *in situ* Pb isotope systematics of individual minerals in Chassigny, has the distinct advantage of resolving micrometer scale heterogeneities that are inaccessible to bulk solution analyses and combined with demonstrably negligible laboratory contamination, provides a large number of data points that yield statistically significant populations.

Chassigny was seen to fall in France and was collected on October 3, 1815, thus its terrestrial history is relatively well constrained. It is classified as a dunite with minor phases of Ca-rich pyroxene, plagioclase that has been converted to maskelynite, and interstitial K-feldspar (Fig. 1 and Fig. 2). The crystallization age

for Chassigny has been previously determined by K–Ar, Rb–Sr, and Sm–Nd analyses, with reasonable agreement on an age of ~ 1.39 Ga (Misawa et al., 2006; Lancet and Lancet, 1971). The cosmic ray exposure age of ~ 11 Ma, a proxy for ejection age, has been determined by noble gas isotope systematics (Terribilini et al., 1998).

2. Analytical methods

Elemental and x-ray maps were made using a FEI Quanta FEG 650 scanning electron microscope at Stockholm University, Sweden (Fig. 1 and Fig. 2). The Pb isotope compositions of plagioclase, alkali-feldspar, pyroxene, sulfide, and olivine grains were determined using SIMS on a polished epoxy mount of Chassigny prepared, in house, from a rock chip. Before analysis, Chassigny was cleaned in alternating 1-minute baths of water and ethanol. After thorough washing, a 30 nm coating of Au was applied to the surface. All measurements were conducted using a CAMECA IMS1280 instrument at the Swedish Museum of Natural History, Stockholm (NordSIM facility) using the experimental protocol from Whitehouse et al., 2005 and Bellucci et al., 2015. An area of $35 \times 35 \mu\text{m}$ was rastered for 70 s prior to Pb isotope analysis to eliminate surface contamination (Fig. 3a). A 300 μm aperture was used resulting in a 12–15 nA O_2^- primary beam and a 30 μm , slightly elliptical spot on the surface of the sample. All analyses were conducted in multi-collector mode at a mass resolution of 4860 ($M/\Delta M$), using an NMR field sensor in regulation mode to control the stability of the magnetic field. Lead isotope ratios were measured in low noise (<0.01 cps) ion-counting electron multipliers for 160 cycles with a count time of 10 s, resulting in a total collection time of 1600 s. The extremely low noise detectors obviate the need for a background correction. Isotope ratios were calculated using integrated means for all analyses. A single, linear correction factor that accounts for mass fractionation and gain differences between detectors was performed by bracketing the unknowns with analyses of USGS basaltic glass reference material BCR-2G ($\sim 11 \mu\text{g/g}$ Pb), assuming the accepted Pb

Fig. 2. Corresponding elemental maps of Chassigny in Mg, Fe, Al, and Ca for Fig. 1.

Fig. 3. a) Time resolved spectra of Chassigny and San Carlos olivine including time during rastering the surface. San Carlos olivine is a terrestrial olivine that contains an undetectable concentration of Pb. Each sample was prepared in the exact same manner at the Swedish Museum of Natural History. The increased count rate at the beginning of the raster is due to enhanced ionization of Pb by the Au coating. Once the Au coat is removed, the San Carlos olivine signal drops to background (~ 0.01 cps), while the Chassigny olivine maintains its high count rate. These results confirm that the radiogenic Pb in Chassigny resides inside the olivine crystal and it cannot be on the surface. b) CPS vs. time (in s) for the Pb isotope signal measured in an olivine from Chassigny. The signal for all isotopes is constant through $3 \mu\text{m}$ confirming the composition in the crystal center.

isotope ratios (Woodhead and Hergt, 2000). Pb isotope fractionation between different materials in SIMS analysis is extremely low, typically being within the level of individual analytical uncertainties (Shimizu and Hart, 1982; Belshaw et al., 1994). External reproducibility in $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ was 0.3% (2σ). External reproducibility in $^{208}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{206}\text{Pb}/^{204}\text{Pb}$ was 0.90%, 0.7%, and 1% (2σ), respectively. Relative concentration estimates for Chassigny were determined by normalizing the ratio of counts of ^{208}Pb (cps) to the primary beam current (I_p in nanoamps). This value is a qualitative measure of the relative concentrations in an individual mineral phase. Direct concentration measurements cannot be determined due to the lack of matrix-matched standards. Isochron calculations were made with Isoplot 4.15 (Ludwig, 2012).

3. Results

Measured Pb isotope compositions and relative signal intensities are presented in Fig. 4 and Table 1. Signal intensities vary by orders of magnitude between crystals of each silicate phase. $^{206}\text{Pb}/^{204}\text{Pb}$ in Chassigny ranges from 11.07 to 19.04 and the Pb isotope arrays observed in $^{207}\text{Pb}/^{206}\text{Pb}$ vs. $^{204}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ vs. $^{204}\text{Pb}/^{206}\text{Pb}$ are triangular (Fig. 4), indicating three-component mixing. The mixing end-members are: 1) initial Pb, 2) radiogenic Pb produced in the analyzed minerals by the *in situ* decay of U and Th from 1.39 Ga to present, and 3) an extremely radiogenic reservoir that cannot be supported by primary, igneous U/Pb ratios (Table 1). The initial Pb (mixing end-member 1) pre-

Fig. 4. Pb-isotope data for Chassigny. Dashed lines represent the permissible limits of mixing trends with the proposed radiogenic end-member. The red curve represents Pb growth from 4.567 to 1.39 Ga (μ of 2) beginning with CDT (Chen and Wasserburg, 1983) and constrains the composition of Chassigny at the time of crystallization. Included in this diagram is the minimum estimate for the Martian radiogenic reservoir with a modern composition, derived from a long-term single stage reservoir with a μ -value of at least 9.25. Additionally, the projected modern composition of the reservoir recorded in the 4.428 Ga clasts observed in NWA7533 is plotted (Bellucci et al., 2015). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

served in K-feldspar and one sulfide grain ($^{206}\text{Pb}/^{204}\text{Pb} = 11.07$) plots close to the 1.39 Ga Geochron, and reflects the Pb isotope composition at the time of the crystallization of Chassigny. This value is significantly less radiogenic than corresponding residue analyses from progressive leachates of Chassigny ($^{206}\text{Pb}/^{204}\text{Pb} = 11.5550$, Bouvier et al., 2009). Since the least radiogenic data plot near the 1.39 Ga Geochron, which represents all predicted Pb isotope compositions for a given time, μ and κ values for the mantle from which Chassigny was derived can be determined assuming the simplest, single-stage Pb evolution model from Canyon Diablo Troilite between 4.567 and 1.39 Ga (Chen and Wasserburg, 1983; Holmes, 1946; Houtermans, 1946). This estimation yields μ and κ values of the mantle from which Chassigny was derived of 2 and 4.5, respectively (Fig. 4), which are in good agreement with previous studies (Bouvier et al., 2009). Pb resulting from the radiogenic decay of U (mixing end-member 2) is preserved in some K-feldspar and plagioclase and lies on a line with a slope corresponding to the accepted age of 1.39 Ga (1.39 Ga-present line shown in Fig. 4). The contribution of this Pb component is clearly visible when comparing analyses of K-feldspar and plagioclase with the highest $^{204}\text{Pb}/^{206}\text{Pb}$ (Fig. 4), which are unmistakably resolvable beyond analytical uncertainties. Heterogeneous mixing between the initial Pb, 1.39 Ga *in situ* accumulated Pb, and the unsupported radiogenic component (mixing end-member 3) is evident in some K-feldspar, pyroxene, plagioclase, a sulfide grain, and in particular olivine grains, where it cannot be explained by an *in situ* accu-

Table 1
Pb isotopic compositions of mineral phases in Chassigny.

	$^{204}\text{Pb}/^{206}\text{Pb}$	1σ (%)	$^{207}\text{Pb}/^{206}\text{Pb}$	1σ (%)	$^{208}\text{Pb}/^{206}\text{Pb}$	1σ (%)	$^{206}\text{Pb}/^{204}\text{Pb}$	1σ (%)	$^{207}\text{Pb}/^{204}\text{Pb}$	1σ (%)	$^{208}\text{Pb}/^{204}\text{Pb}$	1σ (%)	^{208}Pb ((cps)/lp(na))	U/Pb	1σ (%)
K-Feldspar-1	0.089	0.8	1.019	0.32	2.76	0.27	11.26	0.8	11.51	0.8	31.20	0.8	45	1.76	1
K-Feldspar-2	0.081	0.8	0.937	0.31	2.60	0.26	12.29	0.8	11.55	0.8	32.10	0.8	85	1.50	1
K-Feldspar-3	0.077	0.5	0.950	0.18	2.49	0.15	13.05	0.5	12.43	0.5	32.61	0.5	147	0.01	6
K-Feldspar-4	0.088	0.7	1.030	0.27	2.78	0.23	11.32	0.7	11.69	0.7	31.57	0.7	56	0.02	4
K-Feldspar-5	0.090	1.2	1.038	0.46	2.81	0.38	11.07	1.2	11.53	1.2	31.18	1.2	26	0.00	100
K-Feldspar-6	0.084	0.3	0.981	0.12	2.70	0.10	11.87	0.3	11.68	0.3	32.12	0.3	271	0.05	1
K-Feldspar-7	0.080	0.3	0.974	0.10	2.63	0.08	12.43	0.3	12.14	0.3	32.79	0.3	413	0.64	1
K-Feldspar-8	0.082	0.6	0.990	0.22	2.62	0.18	12.19	0.6	12.10	0.6	32.07	0.6	101	0.02	12
K-Feldspar-9	0.083	0.6	0.998	0.23	2.65	0.19	12.00	0.6	12.00	0.6	31.94	0.6	75	0.02	13
Olivine-01	0.055	0.2	0.854	0.05	2.10	0.04	18.33	0.2	15.71	0.2	38.67	0.2	1597	0.00	16
Olivine-02	0.055	0.2	0.855	0.07	2.11	0.05	18.34	0.2	15.71	0.2	38.75	0.2	884	0.00	13
Olivine-03	0.054	0.2	0.853	0.06	2.10	0.05	18.40	0.2	15.75	0.2	38.85	0.2	1209	0.00	14
Olivine-04	0.054	0.2	0.854	0.05	2.11	0.04	18.46	0.2	15.80	0.2	39.06	0.2	1776	0.00	15
Olivine-05	0.054	0.1	0.853	0.05	2.11	0.04	18.64	0.1	15.95	0.1	39.47	0.1	2340	0.00	21
Olivine-06	0.054	0.2	0.857	0.05	2.11	0.04	18.44	0.2	15.84	0.2	39.10	0.2	1789	0.00	18
Olivine-07	0.059	2.2	0.862	0.74	2.16	0.61	16.86	2.2	14.54	2.2	36.49	2.2	7	N/A	N/A
Olivine-08	0.054	2.9	0.859	0.81	2.12	0.67	18.56	2.9	16.13	3.0	39.70	3.0	5	N/A	N/A
Olivine-09	0.054	2.6	0.855	0.79	2.11	0.65	18.41	2.6	15.71	2.6	38.33	2.4	5	N/A	N/A
Olivine-10	0.053	2.0	0.849	0.70	2.11	0.59	19.04	2.0	16.14	2.0	40.08	2.0	8	N/A	N/A
Olivine-11	0.054	2.1	0.852	0.68	2.10	0.56	18.58	2.1	15.82	2.0	38.94	2.0	8	N/A	N/A
Olivine-12	0.053	1.2	0.852	0.40	2.09	0.33	18.88	1.2	16.07	1.2	39.31	1.2	22	N/A	N/A
Olivine-13	0.054	2.0	0.849	0.60	2.11	0.51	18.61	2.0	15.81	1.9	39.20	1.9	12	N/A	N/A
Olivine-14	0.054	1.3	0.855	0.46	2.11	0.33	18.40	1.3	15.72	1.2	38.79	1.2	31	N/A	N/A
Olivine-15	0.055	0.8	0.851	0.27	2.10	0.22	18.21	0.8	15.45	0.8	38.14	0.8	37	N/A	N/A
Olivine-16	0.056	1.3	0.864	0.40	2.12	0.33	17.77	1.3	15.36	1.3	37.72	1.3	19	N/A	N/A
Olivine-17	0.054	1.1	0.851	0.34	2.10	0.32	18.39	1.1	15.68	1.1	38.70	1.0	29	N/A	N/A
Olivine-18	0.054	1.3	0.855	0.46	2.11	0.38	18.37	1.3	15.70	1.3	38.68	1.3	23	N/A	N/A
Olivine-19	0.055	0.8	0.853	0.27	2.11	0.22	18.25	0.8	15.58	0.8	38.49	0.8	46	N/A	N/A
Olivine-20	0.058	1.5	0.865	0.51	2.15	0.42	17.25	1.5	14.93	1.5	37.07	1.4	16	N/A	N/A
Olivine-21	0.055	0.7	0.853	0.25	2.11	0.20	18.21	0.7	15.58	0.7	38.43	0.7	51	N/A	N/A
Olivine-22	0.055	0.9	0.848	0.29	2.09	0.24	18.24	0.9	15.51	0.9	38.15	0.9	35	N/A	N/A
Olivine-23	0.055	1.4	0.848	0.44	2.09	0.36	18.06	1.4	15.30	1.3	37.81	1.3	23	N/A	N/A
Olivine-24	0.055	1.2	0.848	0.42	2.09	0.34	18.14	1.2	15.39	1.2	38.00	1.2	23	N/A	N/A
Plagioclase-01	0.059	0.8	0.856	0.27	2.12	0.22	17.05	0.8	14.63	0.8	36.33	0.8	38	0.02	11
Plagioclase-02	0.076	1.9	0.912	0.70	2.39	0.58	13.10	1.9	11.98	1.9	31.43	1.9	12	0.39	19
Plagioclase-03	0.080	3.3	0.933	1.24	2.47	1.02	12.47	3.3	11.66	3.3	30.89	3.2	3	0.67	15
Plagioclase-04	0.074	2.6	0.930	0.95	2.50	0.78	13.54	2.6	12.62	2.6	34.00	2.6	4	0.29	11
Plagioclase-05	0.071	2.3	0.899	0.84	2.41	0.68	14.06	2.3	12.67	2.3	33.99	2.3	5	0.26	16
Plagioclase-06	0.075	2.3	0.938	0.83	2.47	0.68	13.34	2.3	12.54	2.3	33.04	2.2	5	0.36	23
Plagioclase-07	0.081	2.1	0.935	0.79	2.51	0.65	12.30	2.1	11.53	2.1	31.00	2.0	9	0.55	12
Plagioclase-08	0.057	0.8	0.853	0.27	2.12	0.22	17.61	0.8	15.06	0.8	37.52	0.8	36	0.04	20
Plagioclase-09	0.056	0.7	0.855	0.22	2.11	0.18	17.87	0.7	15.32	0.7	37.75	0.7	123	0.02	8
Plagioclase-10	0.057	1.0	0.860	0.32	2.15	0.26	17.46	1.0	15.05	1.0	37.63	1.0	34	0.03	11
Plagioclase-11	0.081	0.5	0.987	0.19	2.61	0.15	12.35	0.5	12.22	0.5	32.38	0.5	108	0.07	8
Plagioclase-12	0.071	1.9	0.897	0.68	2.32	0.55	14.06	1.9	12.65	1.9	32.77	1.9	14	0.08	10
Plagioclase-13	0.055	0.5	0.849	0.15	2.10	0.12	18.26	0.5	15.55	0.5	38.38	0.5	121	0.02	7
Plagioclase-14	0.060	1.9	0.847	0.63	2.17	0.52	16.71	1.9	14.20	1.9	36.46	1.9	10	0.26	16
Plagioclase-15	0.081	1.4	0.949	0.52	2.60	0.43	12.35	1.4	11.76	1.4	32.17	1.4	32	0.15	11
Plagioclase-16	0.075	2.3	0.918	0.83	2.50	0.67	13.32	2.3	12.26	2.3	33.40	2.2	12	0.50	22
Plagioclase-17	0.071	1.6	0.906	0.57	2.39	0.47	14.06	1.6	12.78	1.6	33.73	1.6	16	0.19	8
Plagioclase-18	0.055	0.8	0.855	0.24	2.11	0.20	18.16	0.8	15.56	0.8	38.43	0.7	41	0.04	20
Plagioclase-19	0.059	1.1	0.867	0.36	2.16	0.30	16.88	1.1	14.68	1.1	36.60	1.1	31	0.06	7
Plagioclase-20	0.060	1.2	0.874	0.39	2.19	0.32	16.53	1.2	14.49	1.2	36.32	1.2	25	0.02	12
Pyroxene-1	0.062	0.7	0.874	0.23	2.21	0.19	16.12	0.7	14.13	0.7	35.73	0.7	65	0.02	9
Pyroxene-2	0.057	2.5	0.855	0.81	2.14	0.66	17.41	2.5	14.94	2.5	37.38	2.4	6	0.01	35
Pyroxene-3	0.056	1.1	0.858	0.37	2.11	0.31	17.81	1.1	15.32	1.1	37.63	1.1	27	0.04	101
Pyroxene-4	0.062	2.7	0.863	0.93	2.18	0.76	16.03	2.7	13.88	2.7	35.01	2.7	6	0.04	41
Pyroxene-5	0.057	1.3	0.857	0.44	2.12	0.36	17.47	1.3	15.02	1.3	37.19	1.3	27	0.03	24
Pyroxene-6	0.059	0.7	0.847	0.23	2.13	0.19	17.00	0.7	14.43	0.7	36.29	0.7	55	0.06	10
Pyroxene-7	0.067	2.2	0.884	0.76	2.24	0.62	14.94	2.2	13.24	2.2	33.62	2.1	6	0.14	20
Sulfide-1	0.089	0.6	1.032	0.25	2.76	0.21	11.23	0.6	11.60	0.6	30.99	0.6	76	n.m.	N/A
Sulfide-2	0.078	0.8	0.970	0.29	2.54	0.24	12.87	0.8	12.50	0.8	32.67	0.8	62	n.m.	N/A

Fig. 5. High-resolution BSE (before) and SEM images (after) of pits in the highly enriched Pb grain and the Pb isotopic composition of field blanked analyses. No cracks appear in any of the pits, pit bottoms, or sample surfaces, aside from the slight overlap in the left corner in the upper panels. However, this analysis has the same exact composition as the smaller extraction area and therefore, likely did not contribute any Pb with a different composition.

mulation of radiogenic Pb because the compositions fall off the 1.39 Ga–Present evolution line illustrated in Fig. 4. Mixing with this unsupported radiogenic component stretches the data into a triangular array.

4. Discussion

The Pb isotope compositions of the olivine, plagioclase, and pyroxene crystals measured in Chassigny are the most radiogenic and similar, within error, despite location in the sample and the relative signal intensities of Pb being highly variable (5–2340 cps/lp(na), Table 1). This is in contrast to the major element compositions, which appear to be homogeneous (Fig. 2). The range of signal intensities, a proxy for concentration, measured in the olivine crystals in Chassigny is strikingly different from the concentrations of igneous olivine in terrestrial samples, which contains virtually no Pb because Pb is extremely incompatible in olivine (e.g., Eggins et al., 1998). This implies that the unsupported radiogenic Pb must be a non-igneous, secondary feature in Chassigny, which is consistent with the observation that its isotope composition lies off the 1.39 Ga–Present line in Fig. 4.

The composition and nature of the reservoir from which the unsupported radiogenic Pb component was derived can be estimated assuming the olivine hosted no igneous Pb and therefore, its measured Pb isotope composition represents the introduced radiogenic end-member. The composition of the unsupported radiogenic Pb in olivine is only possible if this reservoir is of modern age, due to its proximity to the present-day Geochron and evolved with a long-term a μ -value of at least 9.25 (Fig. 4). Likewise, the necessary κ -value in the mixing contaminant is 4.4. This estimated μ -value is ~ 5 times higher than that of the mantle from which Chassigny was derived, while the κ -value appears to be similar between the Chassigny mantle reservoir and the unsupported radiogenic Pb.

The unsupported radiogenic Pb potentially has three sources: 1) laboratory contamination, 2) terrestrial contamination during entry into Earth's atmosphere/curation, and 3) alteration on the Martian surface. Laboratory contamination from SIMS preparation techniques can introduce unsupported Pb during cutting, polishing and gold coating. In this case, the Pb would be concentrated only

on the surface or in open cracks and topographic features that can be readily detected during reflected-light optical microscope and SEM-based secondary and/or back-scattered electron (BSE) imaging. Pre-sputtering in the SIMS to remove the gold coating prior to data acquisition effectively removes all surface contamination (Fig. 3), and provided that surface cracks are avoided during analysis, there should be no introduced laboratory contamination (e.g., Harrison and Schmitt, 2007). Fig. 5 demonstrates the crack- and topographic feature-free nature of two targeted areas of the olivine grain that displays the highest concentration of Pb in the investigated section of Chassigny, before and after and SIMS analyses. To further confirm that the high-Pb analyses are representative of the olivine itself and not due to a minor beam overlap onto a crack hosting a highly contrasted Pb concentration, a field aperture blanking method was applied to two analyses (white squares in Fig. 5) in order to limit to an area on the sample surface from which ions can be admitted to the mass spectrometer (i.e., the sample surface field of view). Two sequential field aperture-blanking analyses were conducted, using 2000 μm and 1000 μm field apertures to respectively define $\sim 13 \mu\text{m}$ and $\sim 6.5 \mu\text{m}$ fields of view. Both of these areas are crack-free in both pre- and post-analytical images and yield compositions (Fig. 5 and Table 1) that are within error identical to all other olivine analyses (Fig. 5), suggesting that the same Pb is being sampled. The high intensity of the Pb signal is apparent from the beginning of each analysis and the sampled depth is less than a few micrometers, approximately an order of magnitude less than the lateral resolution. It is, therefore, highly unlikely that a hidden crack (not observable in the pre- and post-analysis imaging) is consistently responsible for the Pb signal given both the number of analyses ($n = 26$) and lateral/depth-resolution contrast. Additionally, the signal intensities do not vary in direct proportion to the sampled area in Fig. 5, as would be expected for homogeneously distributed crystal lattice hosted Pb, in one analysis even yielding a higher count rate from the smaller area (Table 1). This suggests that the unsupported Pb is heterogeneously distributed within the crack-free olivine, which could occur for example if it is hosted in annealed cracks. The heterogeneously distributed Pb is also evident in the large variation in signal intensity throughout the sample, which must be a reflection of a heterogeneous mixing process. Additionally, a terrestrial

Fig. 6. $^{207}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ isochron (blue dashed line) through all Chassigny data. Additionally, shown on this diagram, but not included in calculation, are data for Chassigny from Bouvier et al., 2009. A linear regression through Bouvier et al., 2009's data (black solid line) intersects the composition of the SIMS most radiogenic olivine but not terrestrial Pb (Stacey and Kramers, 1975). Included in the plot but not in the calculation are all literature Pb isotope compositions plotted against Chassigny isotopic compositions measured via SIMS. All plotted data (grey squares) are residue values from progressive leachates of individual Martian meteorites (Borg et al., 2003, 2005, Bouvier et al., 2005, 2008, 2009, and Gaffney et al., 2007). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

olivine (San Carlos) was prepared in exactly the same way and yields background level Pb signal intensities after pre-sputtering (Fig. 3), which validates the efficiency of our cleaning procedures prior to analyses. Therefore, laboratory contamination cannot be the origin of the unsupported radiogenic Pb and it must have come from Earth entry/curation or from alteration on Mars.

Terrestrial contamination introduced via entry to Earth or during curation is a possible source of the unsupported radiogenic Pb but seems unlikely. The unsupported radiogenic Pb clearly resides in the center of most of the minerals analyzed here, as shown both by our study (Figs. 3 and 5) and in progressive leachates of Chassigny (Bouvier et al., 2009, Fig. 6). Leaching effectively removes surface contamination, which should yield pristine Pb isotopic compositions, similar to SIMS surface cleaning and pre-sputtering techniques employed here. The only plausible mechanism by which unsupported radiogenic Pb can enter a solid crystal is via diffusion during thermal alteration. The total weight of Chassigny was ~4 kg and it fell in 1815, long before the introduction of leaded gasoline substantially increased the potentially fluid mobile surface and atmospheric Pb budget of the Earth (Tatsumoto and Patterson, 1963), where continental crust has on average 17 $\mu\text{g/g}$ Pb (Rudnick and Gao, 2003). The transient thermal perturbation during entry into Earth's atmosphere and subsequent rapid cooling of its small mass on the Earth's surface, are highly unlikely to introduce Pb via exposure to fluid mobile Pb diffusion. Additionally, Chassigny was immediately museum curated after its fall, which has protected it from any additional thermal and aqueous alteration. Lastly, the most radiogenic Pb in Chassigny plots outside of error of the best estimation of terrestrial surface Pb on Earth (Stacey and Kramers, 1975). While this cannot be taken strictly at face value because the Pb isotope composition of the continental crust is highly variable, it plots slightly above modern (Stacey and Kramers, 1975) Pb composition in $^{207}\text{Pb}/^{206}\text{Pb}$ vs. $^{204}\text{Pb}/^{206}\text{Pb}$, which implies that this reservoir is older and distinct from modern terrestrial Pb. Lastly, a linear regression through Bouvier et al. (2009)'s high precision data intersects the composition of the most radiogenic olivine measured here and not terrestrial Pb, as determined by Stacey and Kramers, 1975.

In contrast to the relatively mild conditions that Chassigny has endured during and after its fall to Earth, ejection from Mars would have been considerably more violent. Although the bulk rock did not experience high post shock temperatures (Malavergne et al., 2001; Fritz et al., 2005), these calculations were made assuming a non-porous target. The presence of wadsleyite (Malavergne et al., 2001; Fritz et al., 2005), amorphous material with olivine-composition as veins or at contacts between olivine grains (Malavergne et al., 2001), and localized shock melt pockets (Fritz et al., 2005), argue that at fine scale the PT record in Chassigny is much more complex. Wadsleyite requires temperatures in excess of 1500 °C, and temperatures in excess of 1750 °C are required to form an olivine melt (Fritz et al., 2005). The evidence for extreme heterogeneity in post shock temperature in Chassigny indicates that it had some porosity at the time of the impact. Porous objects respond very differently to impact than non-porous objects (Kieffer et al., 1976; Sharp and DeCarli 2006; Bland et al., 2014). Crushing out the pore space requires extra work; after release that 'waste heat' generates much higher temperatures than in a non-porous target. In a natural material there is also see significant heterogeneity in post shock temperature (Kieffer et al., 1976; Bland et al., 2014). Chassigny is an olivine cumulate. It is unlikely that the porosity was primary. The morphology of the amorphous phases, and the heterogeneity in post shock heating, suggest that Chassigny was a highly fractured rock at the time of impact. Those fractures were likely annealed, with local formation of high T phases, during the impact that launched it. Under such conditions, fluid mobile Pb on the Martian surface may have entered via diffusion and/or along subsequently annealed (during ejection) fractures, open fractures, pore space, and crystal imperfections. The presence of substantial amounts of Pb on the Martian surface have been revealed by the Curiosity rover, recent estimates for some parts of Gale Crater yielding Pb concentrations that range from 50–100 $\mu\text{g/g}$ (Gellert et al., 2015) with accompanying, daily transient aqueous activity (Martin-Torres et al., 2015). Therefore, it is possible that the radiogenic Pb could have been introduced into Chassigny while on the surface of Mars as a result of recent interaction with hydrothermal fluids, brines, ground water, and/or during ejection at ~11 Ma. Thus, the simplest and preferable explanation for the presence of unsupported, radiogenic Pb that resides in the center of most of the Chassigny minerals is that the Pb was introduced on the Martian surface recently and mixed with igneous initial and supported radiogenic Pb resulting in the triangular mixing array measured by new SIMS data.

4.1. Effect of mixing a non-radiogenic sample with a radiogenic reservoir in Pb–Pb data

As Chassigny was derived from a low- μ source region, similar to the rest of the SNCs (Borg et al., 2005, Bouvier et al., 2005, 2008, 2009, Gaffney et al., 2007), any mixing with a more radiogenic component, either terrestrial or Martian, will result in ambiguous trends in Pb isotope diagrams. The important observation here is that the radiogenic end-member Pb in Chassigny resides in the crystals of plagioclase, pyroxene and, in particular, olivine where it cannot be accumulated *in situ* from U decay. Therefore, irrespective of the origin of Pb the arrays here cannot be interpreted to represent the age of Chassigny. Similar sets of arrays are evident in the previously published Pb–Pb solution data for some of the SNC meteorites (Borg et al., 2005, Bouvier et al., 2005, 2008, 2009, Gaffney et al., 2007, Fig. 6), including progressive leachates of Chassigny (Bouvier et al., 2009, Fig. 6). The data of Bouvier et al. (2009) is in complete agreement with the data presented here (Fig. 6). However, the mixing array observed in Chassigny by Bouvier et al. (2009, Fig. 6) is not as pronounced as in the SIMS data set. This is the inevitable result of homogenization of sub-grain

scale heterogeneities during solution analysis of multi-grain fractions or even single grains. For example, SIMS analyses of multiple plagioclase grains from Chassigny show a spread of $^{206}\text{Pb}/^{204}\text{Pb}$ between 12 and 18 (Fig. 4), which would be averaged and therefore undetectable in a multigrain fraction of plagioclase analyzed using traditional solution methods.

Arrays in Pb isotope data obtained for a number of Shergottite samples have been interpreted as an isochron, which has age significance (Bouvier et al., 2005, 2008, 2009), terrestrial Pb acquired during impact, and/or residence of the samples on the Earth's surface and/or laboratory handling, which would have no age significance (Borg et al., 2005; Gaffney et al., 2007). If the Bouvier et al., 2005, 2008, and 2009 interpretation is correct than the Shergottites are implied to have an undisturbed, closed U–Pb system and a crystallization age of >4 Ga (Bouvier et al., 2005, 2008, 2009). If a similar approach is taken for the Chassigny data presented here and a slope is fitted through the analytical points, an age of 4.521 ± 26 Ga (2σ) can be calculated (Fig. 6). These old ages for Chassigny and the Shergottites are, however, in conflict with every other radiogenic isotope system by 3 Ga, and 4 Ga, respectively (Borg et al., 2003; Niihara et al., 2011; Misawa et al., 2006; Moser et al., 2013; Symes et al., 2008; Zhou et al., 2013). The new SIMS Pb isotope data from Chassigny offer a unified explanation for these apparently conflicting datasets, implying that recent alteration or shock from ejection incorporated unsupported radiogenic Pb into mineral centers in almost every Martian meteorite. This unsupported radiogenic Pb accessed by solution analyses in the Shergottites, yielding conflicting >4 Ga ages, is likely just representative of a similar process that affected Chassigny and is documented here. Lastly, all Martian data for the residues from subsequent leaching of the SNCs seem to converge at an apex that is measured in Chassigny's olivine, plagioclase, and pyroxene (Borg et al., 2003, 2005, Bouvier et al., 2005, 2008, 2009, and Gaffney et al., 2007). These meteorites were curated differently, fell in different places, analyzed by several different labs and yet, and the majority of data converge to the same radiogenic apex, including Chassigny (Fig. 6). Additionally, there were vastly different sources of anthropogenic lead when these meteorites fell and the continental crust, dust, and laboratory blanks are also very heterogeneous. Therefore, the best explanation is that these meteorites were altered very recently on Mars by interaction with a radiogenic, likely crustal, Pb reservoir shortly prior to and/or during their ejection to Earth.

4.2. Distribution and formation of a high- μ reservoir

Martian regolith breccia NWA7533 contains clasts that were derived from a crustal reservoir with μ -value of 13.5 at 4.428 Ga (Bellucci et al., 2015). This is the first evidence of a high- μ reservoir on Mars and is explicitly crustal. The predicted Pb isotope composition for a Martian reservoir evolving with a μ -value of 13.5 from 4.567 Ga-present is plotted in Fig. 4. While, the predicted composition of the NWA7533 high μ -reservoir does not overlap with the radiogenic Pb measured in Chassigny it does approach its composition. The 4.428 Ga ages obtained for clasts in NWA7533 indicate that it likely came from the southern hemisphere of Mars (Agee et al., 2013; Humayun et al., 2013). In contrast, the unambiguous 1.39 Ga age for Chassigny suggests an origin from the younger, northern hemisphere of Mars (Nyquist et al., 2001; Tanaka, 1986; Tanaka et al., 1992). Since a similar mixing trend is seen in some of the Shergottites, the signature of this high- μ reservoir appears to be present in almost every single Martian sample and therefore, must be spatially widespread.

Possible mechanisms for creating a high- μ reservoir on planetary bodies, either by enriching U or depleting Pb, includes subduction, inter-crustal differentiation, loss of volatiles, and late stage crystallization of a highly differentiated magma ocean. The first

two scenarios require 1) protracted time, which is limited in the case of the Martian reservoir inferred here due to the minimum formation age of NWA7533 at 4.428 Ga, 2) a significant concentration of water, and 3) the requirement of taking place on both hemispheres, as this reservoir is widespread. Pb is a volatile element and a large volatilization event or series of volatilization events (i.e., impacts) could increase the μ -value of early crust. This mechanism has been invoked to explain the high- μ character of the lunar crust (Tera and Wasserburg, 1972). Additionally, U is an incompatible element during mantle crystallization/melting and it is possible to concentrate U in a late-stage crystallization product of a large magma volume, which is the mechanism by which the K, Rare Earth Elements, and P rich (KREEP) reservoir on the Moon likely formed (e.g., Warren and Wasson, 1979). Regardless of the petrogenesis of this high- μ reservoir, it had to have formed by at least 4.428 Ga and is still currently present on the Martian surface. Therefore, operation of modern Earth-style crustal recycling can be ruled out for the bulk of Martian history. These observations are in agreement with previous studies from Lu–Hf and SIMS Pb–Pb and U–Pb (e.g., Lapen et al., 2010 and Moser et al., 2013).

The inference of a globally widespread, early high- μ reservoir on Mars has potential implications for understanding the evolution of other terrestrial planets. On Earth, the Hadean rock record has been completely obliterated by more than 4 billion years of intense exogenic and endogenic activity. Eoarchean rocks on Earth preserve evidence for a similar high- μ reservoir that required U/Pb differentiation at ca. 4.1–4.3 Ga (Kamber et al., 2003), raising the possibility that formation of an early-enriched reservoir and subsequent stagnant lid tectonic regime may be fundamental processes during planetary formation. On Earth this reservoir was effectively destroyed by the onset of plate recycling after 4 Ga, but it has clearly remained present on the surface of Mars. Further investigation into the chemistry of the Martian high- μ reservoir may thus yield insights into the early tectonics (stagnant lid vs. crustal recycling) and geochemical evolution on early Earth.

5. Conclusions

This study presents evidence for a highly radiogenic, potentially global-scale crustal reservoir on Mars. This reservoir is recorded in the Pb isotope composition(s) of individual minerals measured by SIMS in Chassigny. These results require three-component mixing between initial Pb, supported radiogenic Pb, and unsupported radiogenic Pb. The latter component creates a trend that can be used to define an incorrect >4 Ga Pb–Pb isochron age. Similar trends have been observed in the Shergottites and converge on our measured unsupported radiogenic end-member. The composition of the unsupported radiogenic Pb has been estimated as being modern (as it lies close to the modern Geochron) but resulting from a prolonged evolution in a reservoir with a long-term μ of at least 9.25, which is ~ 5 times greater than that of the mantle from which Chassigny was derived. This Pb reservoir is most likely crustal and mixed with Chassigny recently during alteration, ejection from the surface, or a combination of both. The composition of this Pb is approaching that inferred from 4.428 Ga monzonite clasts in NWA7533, which originates from the southern hemisphere of Mars. Chassigny and the Shergottites are derived from the northern hemisphere of Mars indicating that this high- μ reservoir is potentially global, formed early, and has not been recycled at any time during Martian history. Given the similarity between the high- μ reservoir on both the Earth and Mars, further investigations into this ancient Martian reservoir could yield significant insights into the Hadean Earth that have been lost due to plate tectonic activity.

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