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Early oxidation of the martian crust triggered by impacts

Zhengbin Deng1†, Frédéric Moynier1, Johan Villeneuve2, Ninna K. Jensen3, Deze Liu1, Pierre Cartigny1, Takashi Mikouchi1, Julien Siebert1, Arnaud Agranier5, Marc Chaussidon1, Martin Bizzarro1,3

Despite the abundant geomorphological evidence for surface liquid water on Mars during the Noachian epoch (>3.7 billion years ago), attaining a warm climate to sustain liquid water on Mars at the period of the faint young Sun is a long-standing question. Here, we show that melts of ancient mafic clasts from a martian regolith meteorite, NWA 7533, experienced substantial Fe-Ti oxide fractionation. This implies early, impact-induced, oxidation events that increased by five to six orders of magnitude the oxygen fugacity of impact melts from remelting of the crust. Oxygen isotopic compositions of sequentially crystallized phases from the clasts show that progressive oxidation was due to interaction with an $^{17}$O-rich water reservoir. Such an early oxidation of the crust by impacts in the presence of water may have supplied greenhouse gas $\text{H}_2$ that caused an increase in surface temperature in a $\text{CO}_2$-thick atmosphere.

INTRODUCTION

The NWA 7533/7034 regolith breccia and other 15 paired meteorites contain igneous clasts with noritic, basaltic to monzonitic compositions (1). These clasts have been proposed to be the products of an early remelting, likely by impacts (2–4), of the primary crust derived from the martian mantle. Hence, these igneous clasts can provide insights into the ancient surface of Mars, allowing us to investigate the physicochemical conditions that existed at the surface of the planet, including the oxygen fugacity at the time of crustal reworking. This information is critical to constrain the timing of establishment of Mars’ hydrosphere and atmosphere and, hence, the potential for early habitability. On Earth, oxidized lavas with ΔFMQ (i.e., oxygen fugacity in logarithmic deviation relative to the fayalite-magnetite-quartz buffer) values as high as +5 occur in arc systems due to the recycling into the sub-arc mantle of crustal material that experienced interactions with seawater (5, 6). Differentiated meteorites typically have ΔFMQ values below zero (6), among which martian meteorites including shergottites, nakhlites, and chassignites (i.e., SNC meteorites) are the most oxidized ones, with ΔFMQ ≈ −4 to −1 for shergottites and ≈ 0 for nakhlites and chassignites (6, 7). In contrast, some igneous clasts from the NWA 7533/7034 meteorites are reported to be highly oxidized with ΔFMQ values of up to +4 (8, 9), but it is unclear whether the oxidized nature of these clasts represents early magmatic or late postmagmatic processes (8).

Titanium isotopic variations in magmatic rocks are mainly controlled by Fe-Ti oxide crystallization (10, 11). Because of the different coordination numbers of Ti in Fe-Ti oxides (sixfold) and silicate melts (four-, five-, and sixfold depending on the melt composition) (12), Fe-Ti oxides preferentially incorporate light Ti isotopes such that fractional crystallization of Fe-Ti oxides produces isotopically heavy residual melts (10, 11, 13–15). At Fe-Ti oxide saturation, Fe-Ti oxide crystallization is promoted by the decreasing solubility of total FeO (FeOt) due to a change in either melt composition or oxygen fugacity (16–18). In terms of melt composition, cooling leads to crystallization of olivine or pyroxene, thereby lowering the Mg# and the FeOt contents at Fe-Ti oxide saturation in silicate melts. Instead, an increase in oxygen fugacity leads to a decrease in the FeOt contents but an increase in the Mg# values of the silicate melts due to fractional crystallization of Fe-Ti oxides (see equation 5 in 16). Thus, the combination of chemical and Ti isotopic compositions can be used to determine the magmatic thermal and/or redox histories of igneous rocks, in other words, the T–$\text{FeO}$ paths during magma evolution (16).

RESULTS AND DISCUSSION

Fifteen igneous clasts of the NWA 7533 meteorite selected from a larger set studied for petrology (12 basaltic clasts, 1 phono-tephritic clast, and 1 foiditic clast, as well as an orthopyroxene crystal; figs. S7 to S14 and data files S1 and S2) were chosen for detailed chemical and isotopic investigations. Alkali and SiO2 contents of the studied NWA 7533 igneous clasts match with the global gamma ray spectrometry (GRS) data (19, 20) and the rover data of surface rocks and soils in Gusev (21, 22) and in Gale (23, 24) craters, which have higher alkali contents compared with SNC meteorites (Fig. 1) (25, 26). The present basaltic clasts are characterized by enrichments in light rare earth and siderophile elements, which is consistent with earlier work (fig. S1 and data file S2) (3, 27–31). Zircons extracted from the basaltic clast C27 yield ancient and overlapping $^{207}\text{Pb}/^{206}\text{Pb}$ dates, with one zircon defining nearly concordant U-Pb systematics corresponding to a $^{207}\text{Pb}/^{206}\text{Pb}$ age of 4443.6 ± 1.2 million years (Ma) (32). These data, combined with existing U-Pb systematics of zircons from the NWA 7533/7034 meteorite (3, 30, 31, 33), confirm the antiquity of the igneous clasts. This is in line with the interpretation that these ages reflect the remelting of the primary crust during the first 100 Ma of the planet’s history (2, 3). Hence, the magmatic
histories of these clasts provide insights into the processes and conditions of reworking of Mars’ first crust.

The NWA 7533 igneous clasts are characterized by elevated $\delta^{49}$Ti values ranging from $+0.055 \pm 0.025$ per mil to $+0.432 \pm 0.032\%$ (i.e., a delta notation of $^{49}$Ti/$^{47}$Ti ratio relative to OL-Ti standard) at high Mg# values of 39.5 to 55.5 (Fig. 2). This is in contrast with (i) terrestrial rocks like the lavas from Agung volcano in the Sunda Arc [$\Delta$FMQ $\approx +2.4$] and those from Hekla volcano in Iceland [$\Delta$FMQ $= +0.9$] that became saturated in Fe-Ti oxides at low Mg# values, and (ii) magmatic meteorites like shergottites (including the most differentiated shergottite, Los Angeles) and angrites that have lower oxygen fugacity with $\Delta$FMQ $= -4$ to $-1$ and did not ever approach Fe-Ti oxide saturation even at Mg# values as low as 23.8 (Fig. 2 and data file S1). It is unlikely that the high $\delta^{49}$Ti values of the NWA 7533 clasts reflect contamination by chondrite-like impactors given that the various chondrite groups have $\delta^{49}$Ti values that are within $\pm 0.050\%$ of known oxide-undersaturated mafic and ultramafic rocks ($10, 11, 34–36$). Thus, the observed $\delta^{49}$Ti-Mg# systematics indicates that Fe-Ti oxide crystallization occurred during the evolution of the melts parental to NWA 7533 clasts, implying that the oxidized features of the clasts are fingerprints from early magmatic processes rather than postmagmatic resetting. Substantial Fe-Ti oxide crystallization without any systematic decrease in Mg# value suggests that the decrease in magnetite solubility in silicate melts of the clasts is mainly caused by an increase in oxygen fugacity rather than by a change in melt composition due to cooling. This interpretation is in line with the higher magmatic $\Delta$FMQ values of +1.6 to +3.9 of these clasts relative to that of the martian mantle as sampled by SNC meteorites (6) [$\Delta$FMQ $= -4$ to $-1$; see (12)]. In support of our inference, we reproduced experimentally such an oxidation-induced Fe-Ti oxide removal. In our experiments, an increase in the $\Delta$FMQ values from $-2.9$ to $+2.6$ or to +6.5 resulted in notable magnetite crystallization from Fe-rich basaltic parental melts and, therefore, decreasing FeOtot contents in the oxidized melts [see (16)]. The increased $\delta^{49}$Ti values of $+0.056 \pm 0.025\%$ to $+0.160 \pm 0.020\%$ in nakhlites with a cumulate origin suggest that their parental magmas have also experienced fractionation of Fe-Ti oxides, which is consistent with the more oxidized nature of these meteorites relative to shergottites (6, 7). Considering that some of the studied clasts date back to 4443.6 $\pm$ 1.2 Ma (32), oxidation of the parental magmas of these igneous clasts by up to six orders of magnitude requires an oxidizing agent, likely water, at the surface of the planet at the time of reworking of the crust.

Taking a conservative approach and assuming that the clasts’ crustal precursors likely had $\Delta$FMQ values and FeOtot contents close to those of shergottites (i.e., at equilibrium with the martian mantle), progressive oxidation of the magmas generated by melting of the primary crust will result in fractional crystallization of Fe-Ti oxides. This magnetite fractionation scenario is in agreement with the correlated decrease in the concentration of FeOtot and that of elements compatible in magnetite, namely, Ni, V, Co, and some highly siderophile elements like Ir, Rh, Ru, and Os (with Pt as an exception due to its low partition coefficient between magnetite and silicate melt under oxidized conditions) (Fig. 3 and fig. S2) (37). Combined V-Fe systematics in these igneous clasts implies on average a low partition coefficient of $\sim 2.5$ for V between Fe-Ti oxides.

Fig. 1. Alkali ($Na_2O + K_2O$) versus SiO$_2$ classification diagram for volcanic rocks modified after Agee et al. (4) and McSween et al. (19). The NWA 7533 clasts in this study (the red solid circles), whole-rock NWA 7034 meteorite in Agee et al. (4) (the green solid circle), and SNC meteorites (25, 26) (the orange field) are compared with the gamma-ray spectrometer (GRS) data of the Mars Odyssey orbiter (20) and those of rocks and soils in Gusev Crater (the gray dots) from the alpha particle x-ray spectrometer (APXS) on the Spirit Rover (21, 22) and in Gale Crater (the grey crosses) from APXS (23) and laser-induced breakdown spectrometer (ChemCam) (24) on the Curiosity Rover. Note that clast C4 is plotting outside the figure due to its high alkali content (data file S1).
and melts, which independently confirms the oxidized nature of the equivalent magmas ($\Delta$FMQ $\geq +3$) based on the calibrations in 38. The basaltic clasts with the least magnetite fractionation (e.g., clast C3) have high Ni and Ir concentrations of $\approx 1500$ parts per million (ppm) and $\approx 80$ parts per billion (ppb) [this study and (3)], respectively. Assuming Ni $\approx 150$ ppm and Ir $\approx 0$ ppb for the reduced primary crust derived from martian mantle (25), and Ni $\approx 10,500$ ppm and Ir $\approx 455$ ppb for the chondritic impactor (39), the high Ni and Ir concentrations in the NWA 7533/7034 igneous clasts (Fig. 3) require the addition of $\approx 15$ weight % (wt %) of chondritic material to their parent magmas, which is higher than the values estimated directly from the apparent Ni and Ir contents of the bulk clasts (3, 4, 6, 27, 28). The various enrichments in Ni observed for rocks and soils in Gusev and Gale craters suggest that addition of Ni to the primary crust of Mars by impacts was likely a general process (Fig. 3). Tracking ferrous-ferric iron budgets in the melts over oxidation shows that 2.4 to 2.9% of total oxygen in the oxidized melts of the clasts would originate from the oxidant (16), corresponding to a consumption of 1.2 to 1.4 wt % water.

Such an oxidation scenario for the origin of the NWA 7533/7034 igneous clasts is corroborated by their triple O isotope compositions, from both this study and literature (4, 40). In detail, a pyroxene crystal (i.e., P3 from this study) and a pyroxene separate (in (40)) have $\Delta^{17}$O values ($+0.27 \pm 0.05\%_o$ and $+0.33\%_o$, $n = 1$, respectively) within experimental error identical to that of SNC meteorites ($\Delta^{17}$O = $+0.318 \pm 0.016\%_o$, 2 SD, $n = 56$) (41). This confirms that the crustal precursors of the NWA 7533/7034 igneous clasts likely derive from a martian mantle reservoir with $\Delta^{17}$O value similar to that of SNC meteorites, in line with the petrological and chemical constraints. Note that our samples were analyzed only once and, hence, the resulting errors are comparatively large. Yet, $\Delta^{17}$O values different from other SNC meteorites are identified for two clast samples (C16 and C17) having values of $\approx -0.4\%_o$. These values in the NWA 7533 igneous clasts are inconsistent with the concept of $\Delta^{17}$O homogeneity of differentiated bodies. These O-isotope data require a late partial exchange of oxygen between the parent melts of the basaltic clasts and oxidizer having a distinctively high $\Delta^{17}$O value to explain the higher bulk clast $\Delta^{17}$O values and the dependence of maximal $\Delta^{17}$O values of minerals with the order of magnetite $\leq$ pyroxene $\leq$ apatite $\leq$ plagioclase $\leq$ zircon $\leq$ K-feldspar for six studied holocrystalline clasts (i.e., C11, C16, C4, C7, C18, and C27) (Fig. 4, fig. S3, and data file S3). It is also noteworthy that the magnetite, pyroxene, and plagioclase phenocrysts have systematically lower maximal $\Delta^{17}$O values than those making the groundmass (Fig. 4). As proposed by Nemchin et al. (42), the $\Delta^{17}$O variability in the $\approx 4.43$–billion year (Ga)–old zircons from the NWA 7533 meteorite can result either from an early ($\approx 4.43$ Ga) assimilation of a high-$\Delta^{17}$O component into the parental magmas of the clasts or, alternatively, from a late ($\approx 1.7$ Ga) oxygen exchange between the minerals in the clasts and a hydrothermal fluid with high $\Delta^{17}$O values. Our $\Delta^{17}$O data for minerals of various types and textures allow us to differentiate between the two models. Under hydrothermal conditions, oxygen diffuses much faster in feldspar and apatite than in magnetite, pyroxene, and zircon (43), and therefore, feldspar and apatite are predicted to
reach oxygen isotopic equilibrium with the fluid much earlier than zircon and pyroxene. The mineralogical control on $\delta^{17}$O depicted in Fig. 4 is not consistent with this prediction, thereby supporting a progressive input of high-$\delta^{17}$O material during early ($\sim$4.43 Ga) magmatic processes as an explanation for the $\delta^{17}$O variability in the NWA 7533/7034 basaltic clasts. This is in agreement with the observation that heat-released water from the NWA 7034 meteorite, which likely reflects late-stage hydrothermal fluids, has an SNC meteorite--like $\delta^{17}$O value of $+0.330 \pm 0.011\%$ (4) rather than an elevated $\delta^{17}$O composition. The addition of heavy oxygen into the magmatic systems, as inferred from the mineral O-isotope data, is indicative of interaction with a high-$\delta^{17}$O oxidant (i.e., oxidation), which, as described above, also results in magnetite crystallization. Using a $\Delta^{17}$O value of $+2.6\%$ for the composition of the oxidant (Fig. 4), and a basaltic magma having initially a Martian mantle--like $\Delta^{17}$O value ($+0.318\%$) (41) and $\Delta$FMQ $\leq-2.5$, an increase in $\Delta$FMQ to +2 to 4 (i.e., 2.4 to 2.9% oxygen from oxidant) would lead to a 0.054 to 0.066% increase in melt $\Delta^{17}$O [see (16)]. This is consistent with the shift in bulk $\Delta^{17}$O observed for three oxidized clasts (i.e., C16, C7, and C27; $\Delta^{17}$O = $+0.383 \pm 0.042\%$; Fig. 4 and data file S4). Thus, our data establish that a water reservoir (either liquid or ice) characterized by a $\Delta^{17}$O value $\sim$2% higher than the Martian mantle was present at the surface of the planet by $\sim$4.44 Ga. We infer that interaction of magmas produced during reworking of the crust with this reservoir is responsible for the $\Delta^{17}$O variability observed in ancient igneous components on Mars.

The high-$\Delta^{17}$O water component on early Mars may represent either water delivered by impacting material such as water-rich asteroidal bodies (44) or, alternatively, water equilibrating with photochemical products from the early martian atmosphere (4, 42, 45). Our data cannot discriminate between these two possibilities. Nonetheless, an impact origin for the NWA 7533/7034 basaltic clasts is established from their enrichment in highly siderophile elements. This interpretation is consistent with recent seismic observations indicating that the first 8 to 11 km of the Martian crust is intensely fractured (45). It has been proposed that such early bombardment episodes may have induced elevated surface temperatures on Mars, resulting in a warm and wet early climate that is implied by the ancient records of fluvial activity (47, 48). However, the heat flux solely resulting from impacting bodies as large as 100 km in diameter can only induce transient warm periods lasting years on the martian surface (47), which is too short-lived to account for the geological evidence for long-lived fluvial activity [hundreds of million years (49)]. In contrast, the reducing greenhouse gases CH$_4$ and H$_2$ emitted during impact-induced remelting and oxidation of the primary crust may strongly modify the composition of the martian atmosphere, leading to a warm climate on early Mars that can potentially be sustained for millions of years (50, 51). As a conservative
estimate, we consider the effect of a single crustal remelting event associated with a 100-km-diameter impactor of chondritic composition, which would result in the remelting of a crustal reservoir of \(\sim 1.6 \times 10^{19}\) kg for an impact melt-to-impactor volume ratio of \(\sim 10\). Using the NWA 7533/7034 igneous clasts as a proxy for the level of oxidation of the primary crust \(\text{i.e.}, \sim 1.2 \text{ to } 1.4 \text{ wt } \% \text{ water consumption (16)}\), this would result in the consumption of \(\sim 2 \times 10^{17}\) kg of \(H_2\) and release \(\sim 6\) mole \% \(H_2\) in a 2-bar martian atmosphere, which is enough to raise the surface temperature by \(\sim 60^\circ\text{C}\) \((51)\). In addition to this supply of \(H_2\), there can be also other sources of \(H_2\) on early Mars, e.g., Fe oxidation by \(H_2O\) in the impact vapor plumes \((48)\) or degassing from volcanism \((50)\). Integrating these potential supplies of \(H_2\) predicts that a high amount of \(H_2\) can accumulate in the martian atmosphere. This could raise the surface temperature of early Mars above the freezing point of water for several or tens of millions of years (or even longer) despite the faint young Sun \((48, 50–53)\), therefore making the early habitability of the planet possible.

**MATERIALS AND METHODS**

**Scanning electron microprobe and quadrupole inductively coupled plasma mass spectrometer**

The NWA 7533 hand specimens were cut into \(\approx 1.3\)-mm-thick sections with a diamond wire saw at the Centre for Star and Planet Formation, University of Copenhagen. For the large igneous clasts showing up in at least two sections, the igneous clasts of interest were extracted from one of the sections and mounted into epoxy for in situ chemical and isotopic characterization, and the counterpart section was then used for destructive sampling. All the studied clasts were first characterized for petrology by scanning electron microprobe (SEM) at the Institut de Physique du Globe de Paris (IPGP) \((\text{figs. S7 to S14)}\). For a well-polished and flat sample surface, SEM can provide major element compositions for the sample that are reliable in a sub–weight percent uncertainty, as corroborated by the results from basaltic glass BHVO-2G \((\text{data files S2 and S5)}\). The mapped igneous clasts were sampled by a microdrilling instrument at IPGP applying a tungsten carbide bit of 200 \(\mu\text{m}\) in diameter, and Mille-Q \(H_2O\) and pipette were used to transport the sample powders into precleaned Savillex beakers. The powders of the NWA 7533 igneous clasts and angrites, as well those of shergottites, nakhlites, and chassignites (SNC meteorites), were digested via a protocol using 26 M HF and 16 M \(HNO_3\) acids \((2:1 \text{ in volume)}\) or/and an \(NaOH\) fusion method described in Deng et al. \((36)\). With respect to \(NaOH\) fusion, \(\sim 10\) mg of sample powder for each sample was weighed into an Ag crucible with the addition of \(\sim 200\) mg of \(NaOH\) pellets \((99.99\% \text{ trace metal basis, Sigma-Aldrich Company)}\) and was fused at 720°C in a furnace for 15 min, after which the sample was dissolved in \(\sim 1\) M \(HNO_3\). For the digestions with HP and \(HNO_3\) acids, the samples were heated in 6 M HCl at 135°C for 3 days to decompose the fluorides forming from HF dissolution. For the NWA 7533 igneous clasts, an aliquot containing 5% dissolved material of each sample was dried down and dissolved in 0.5 N \(HNO_3\) for major and trace element measurements on the Agilent quadrupole inductively coupled plasma mass spectrometer (Q-ICP-MS) at...
samples was lost as SiF₄ during HF digestion. Over the whole analytical session, the composition of BHVO-2 was measured three times as unknown, and the comparison of the measured values and certified values suggests an external reproducibility of ≤5% for most elements (data file S2).

Laser ablation–high-resolution–ICP-MS

The igneous clasts showing up in at least two sections were measured for major and trace element compositions by laser ablation (LA)–ICP-MS at the Institut Universitaire Européen de la Mer (Brest), which couples a Coherent COMPex 102 Laser Ablation System (193-nm wavelength), with an Element XR high-resolution (HR)–ICP-MS. Multiple ablation spots of 160 μm in diameter were conducted on the clasts with a laser energy output of 10 J/cm² and a repetition rate of 10 Hz. The generated aerosols were transported by He gas into HR-ICP-MS, before which the sample aerosols were mixed with Ar gas. The analysis on each ablation spot contained 40 cycles with 3.2 s per cycle (i.e., ~1280 laser pulses), making a spot of ~150 μm in depth. The typical washout time was less than 10 s, and a pause time of 1.5 to 2 min between two analyses was applied to minimize memory effects. Data reduction on each spot was conducted by integrating the cycles except for the transient cycles at the beginning of ablation. For each igneous clast, intensity signals of all the spots were integrated, and MgO content of each clast by SEM was used as an internal normalization standard to overcome yield effects from ablation. The composition of the basaltic glasses BCR-2G, BHVO-2G, and BIR-1G was analyzed at the beginning and at the end of each session confirmed that these instrumental Ca isotopic ratios were estimated from the natural Ca isotopic ratios (44Ca/46Ca = 657.03 and 44Ca/48Ca = 11.14) by assuming a similar instrumental mass bias for Ca as that for Ti. This correction of Ca isotopic interferences, together with double-spike inversion to calculate Ti isotopic compositions of the samples, was implemented with an Isospike software developed in (54). A spiked Ti standard solution (referred to as IPGP-Ti) was used as the bracketing standard for secondary normalization. The IPGP-Ti standard has a δ⁴⁹Ti = +0.140 ± 0.011% (95% confidence interval, n = 8) (36), where δ⁴⁹Ti represents per mil deviation of the 49Ti/47Ti ratio of the sample relative to the OL-Ti standard (10). Reference materials including BHVO-2, AGV-1, BIR-1, and BCR-2 were processed in parallel following the same protocols, which provide the δ⁴⁹Ti values well consistent with those reported previously (data file S1) (10, 11, 34–36).

Secondary ion mass spectrometry for in situ triple O isotopic measurements

Seven igneous clasts (C11, C16, C4, C7, C18, C27, and C3) were measured for triple O isotopic composition by secondary ion mass spectrometry (SIMS) using the CAMECA IMS 1270 E7 housed at Centre de Recherches Pétrographiques et Géochimiques (CRPG)–Centre National de la Recherche Scientifique (CNRS). The epoxy mounts hosting the samples were coated with gold and degassed in a vacuum chamber overnight. A ~5.5- to 6-nA Cs⁺ primary ion beam of ~15 μm in diameter was used for sputtering to produce ¹⁶O⁻, ¹⁸O⁻, and ¹⁸O⁺ ions, and the charge was compensated using an electron gun. An N₂ trap was used to maintain a high vacuum over the analytical sessions (<4×10⁻⁹ torr), which maintains a low production of ¹⁸O²⁻. To further minimize ¹⁸O²⁻ interference on ¹⁷O⁻, a mass resolving power (MRP) of ~10,000 was achieved on the central Faraday cup for ¹⁷O⁻ analysis, and ¹⁶O⁻ and ¹⁸O⁻ were measured on L2 and H1 off-axis Faraday cups with MRP ≈ 5000 (slit 2). By doing that, the ¹⁸O²⁻ tailing contribution on ¹⁷O⁻ was kept negligible. Six standards (San Carlos olivine, KL2-G basaltic glass, Miyake anorthite, GoldEns enstatite, JV1 diopside, and BHVO-2G basaltic glass) were used to generate the instrumental mass fractionation (IMF) line at the beginning and the end of each analytical session, and three of the standards (San Carlos olivine, JV1 diopside, and BHVO-2G) were inserted into the epoxy mounts hosting the NWA.
The NWA 7533 igneous clasts were extracted from the meteorite in distilled H2O and ethanol in steps. Milligram-size (0.939 to \(10^{-6}\) g) clasts were cleaned using ultrasonic washing in distilled H2O and ethanol and then reacted in a BrF5 atmosphere. Samples were then reacted using laser fluorination, with the released O2 being purified and analyzed by a dual-inlet ion-ratio mass spectrometer. The typical external errors on mil deviation of 17O/16O and 18O/16O ratios relative to those of the international SMOW standard using the conventional delta notation, where 

\[ \Delta^{17}O = \left( \frac{^{18}O / ^{16}O}_{\text{sample}} / ^{18}O / ^{16}O_{\text{standard}} - 1 \right) \times 1000 \]

are ~1.7 \times 10^{-6} to 2.3 \times 10^{-6} counts per second (cps) on 16O−, ~6.7 \times 10^{-6} to 8.8 \times 10^{-6} cps on 17O−, and ~3.6 \times 10^{-6} to 4.8 \times 10^{-6} cps on 18O− for silicates, which are 50% higher for magnetite (data file S3). Therefore, we consider that typical uncertainty for SIMS measurements in this study be ±0.5‰ for the \(\Delta^{17}O\) value.

Ion-ratio mass spectrometer for triple O isotopic measurements

The NWA 7533 igneous clasts were extracted from the meteorite slices with a 250-μm diamond-coated wire saw, and the matrix attached to the igneous clasts was removed with diamond-coated bits. The extracted clasts were cleaned by ultrasonication and rinsing in distilled H2O and ethanol in steps. Milligram-size (0.939 to 1.325 mg) fragments of four extracted clasts, including three high-MgO igneous clasts (C16, C7, and C27) and one pyroxene crystal (P3), were used for the bulk oxygen isotope analyses at IPGP. Given the amount of material available, the data shown here represent single analyses. Analytical methods are similar to those documented in Rumble et al. (55). Before analyses, samples were prefluorinated overnight in a BrF5 atmosphere. Samples were then reacted using laser fluorination, with the released O2 being purified and analyzed for O isotopic compositions using a dual-inlet ion-ratio mass spectrometer (IRMS; Thermo Fisher Delta V). Samples were analyzed along with garnet standard UWG-2 from the Gore Mountain mine, Adirondack Mountains, New York (56), and reported versus the international SMOW standard using the conventional delta notation, where 

\[ \Delta^{18}O = \left( \frac{^{18}O / ^{16}O}_{\text{sample}} / ^{18}O / ^{16}O_{\text{standard}} - 1 \right) \times 1000 \]

are ~1.7 \times 10^{-6} to 2.3 \times 10^{-6} counts per second (cps) on 16O−, ~6.7 \times 10^{-6} to 8.8 \times 10^{-6} cps on 17O−, and ~3.6 \times 10^{-6} to 4.8 \times 10^{-6} cps on 18O− for silicates, which are 50% higher for magnetite (data file S3). Therefore, we consider that typical uncertainty for SIMS measurements in this study be ±0.5‰ for the \(\Delta^{17}O\) value.

### SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at [http://advances.sciencemag.org/cgi/content/full/6/4/eabc4941/DC1](http://advances.sciencemag.org/cgi/content/full/6/4/eabc4941/DC1)

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