

# Unique Meteorite from Early Amazonian Mars: Water-Rich Basaltic Breccia Northwest Africa 7034

Carl B. Agee,<sup>1,2\*</sup> Nicole V. Wilson,<sup>1,2</sup> Francis M. McCubbin,<sup>1,2</sup> Karen Ziegler,<sup>1</sup> Victor J. Polyak,<sup>2</sup> Zachary D. Sharp,<sup>2</sup> Yemane Asmerom,<sup>2</sup> Morgan H. Nunn,<sup>3</sup> Robina Shaheen,<sup>3</sup> Mark H. Thiemens,<sup>3</sup> Andrew Steele,<sup>4</sup> Marilyn L. Fogel,<sup>4</sup> Roxane Bowden,<sup>4</sup> Mihaela Glamoclija,<sup>4</sup> Zhisheng Zhang,<sup>3,5</sup> Stephen M. Elardo<sup>1,2</sup>

We report data on the martian meteorite Northwest Africa (NWA) 7034, which shares some petrologic and geochemical characteristics with known martian meteorites of the SNC (i.e., shergottite, nakhlite, and chassignite) group, but also has some unique characteristics that would exclude it from that group. NWA 7034 is a geochemically enriched crustal rock compositionally similar to basalts and average martian crust measured by recent Rover and Orbiter missions. It formed  $2.089 \pm 0.081$  billion years ago, during the early Amazonian epoch in Mars' geologic history. NWA 7034 has an order of magnitude more indigenous water than most SNC meteorites, with up to 6000 parts per million extraterrestrial H<sub>2</sub>O released during stepped heating. It also has bulk oxygen isotope values of  $\Delta^{17}\text{O} = 0.58 \pm 0.05$  per mil and a heat-released water oxygen isotope average value of  $\Delta^{17}\text{O} = 0.330 \pm 0.011$  per mil, suggesting the existence of multiple oxygen reservoirs on Mars.

The only tangible samples of the planet Mars available today for study in Earth-based laboratories are the so-called SNC (shergottite, nakhlite, and chassignite) meteorites (1) and a single cumulate orthopyroxenite (Allan Hills 84001). The SNCs currently number 110 named stones and have provided a treasure trove for elucidating the geologic history of Mars (2). But, because of their unknown field context and geographic origin on Mars and their fairly narrow range of igneous rock types and formation ages (3), it is uncertain to what extent SNC meteorites sample the crustal diversity of Mars. In fact, geochemical data from NASA's orbiter and lander missions suggest that the SNC meteorites are a mismatch for much of the martian crust exposed at the surface (4). For example, the basalts analyzed by the Mars Exploration Rover Spirit at Gusev Crater (5, 6) are distinctly different from SNC meteorites, and Odyssey Orbiter gamma-ray spectrometer (GRS) data (7) show that the average martian crust composition does not closely resemble SNC.

NWA 7034, on deposit at the Institute of Meteoritics in Albuquerque, was purchased by Jay Piatek from Aziz Habibi, a Moroccan meteorite dealer, in 2011. It is a 319.8-g single stone,

porphyritic basaltic monomict breccia, with a few euhedral phenocrysts up to several millimeters and many phenocryst fragments of dominant andesine, low-Ca pyroxene, pigeonite, and augite set in a very fine-grained, clastic to plumose, groundmass with abundant magnetite and magnetite; accessory sanidine, anorthoclase, Cl-rich apatite, ilmenite, rutile, chromite, pyrite, a ferric oxide hydroxide phase, and a calcium carbonate were identified by electron microprobe analyses on eight different sections at the University of New Mexico (UNM). X-ray diffraction (XRD) analyses conducted at UNM on a powdered sample and on a polished surface show that plagioclase feldspar is the most abundant phase ( $38.0 \pm 1.2\%$ ), followed by low-Ca pyroxene ( $25.4 \pm 8.1\%$ ), clinopyroxenes ( $18.2 \pm 4.0\%$ ), iron oxides ( $9.7 \pm 1.3\%$ ), alkali feldspars ( $4.9 \pm 1.3\%$ ), and apatite ( $3.7 \pm 2.6\%$ ). The x-ray data also indicate a minor amount of iron sulfide and chromite. The data are also consistent with magnetite and magnetite making up  $\sim 70\%$  and  $\sim 30\%$ , respectively, of the iron oxide detected (8).

**Petrology and geochemistry.** Numerous clasts and textural varieties are present in NWA 7034, including gabbros, quenched melts, and iron oxide- and ilmenite-rich reaction spherules (figs. S1 to S4) (8). However, the dominant textural type is a fine-grained basaltic porphyry with feldspar and pyroxene phenocrysts. NWA 7034 is a monomict brecciated porphyritic basalt that is texturally unlike any SNC meteorite. Basaltic breccias are common in Apollo samples, lunar meteorites, and HED meteorites but are wholly absent in the world's collection of SNC meteorites (9). The absence of shock-produced SNC breccias seems curious at face value, because nearly all of them

show evidence of being subjected to high shock pressures, with feldspar commonly converted to maskelynite. Martian volcanic breccias are probably not rare, given the observed widespread occurrence of volcanism on Mars. However, launch and delivery of such materials to Earth as meteorites has not been observed (9). Although NWA 7034 is texturally heterogeneous, both in the hand specimen and microscopically (Fig. 1), it can be considered a monomict breccia because it shows a continuous range of feldspar and pyroxene compositions that are consistent with a common petrologic origin (figs. S5 and S6). We find no outlier minerals or compositions that would indicate the existence of multiple lithologies or exotic components. We also see no evidence for polymict lithologies in either the radiogenic or stable isotope ratios of NWA 7034 solids. However, many clasts and some of the fine-grained groundmass have phases that appear to have been affected by secondary processes to form reaction zones. We observed numerous reaction textures, some with a ferric oxide hydroxide phase; this phase and apatite are the main hosts of the water in NWA 7034 (fig. S2). Impact processes are likely to have affected NWA 7034 by virtue of the fact that this meteorite was launched off of Mars, exceeding the escape velocity—presumably by an impact—although the shock pressures did not produce maskelynite. One large (1-cm) quench melt clast that was found could originate from shock processes (fig. S3). On the other hand, the very fine groundmass with the large phenocrystic feldspars and pyroxenes strongly suggests an eruptive volcanic origin for NWA 7034; thus, it is likely that volcanic processes are a source of the brecciation.

It has been shown (10) that Fe-Mn systematics of pyroxenes and olivines are an excellent diagnostic for classifying planetary basalts. The Fe-Mn systematics of NWA 7034 pyroxenes, as determined by electron microprobe analyses, most resemble the trend of the SNC meteorites from Mars (Fig. 2); other planetary pyroxenes such as in lunar samples and basalts from Earth are poor matches for NWA 7034. Furthermore, feldspar compositions (fig. S5) (8) and compositions of other accessory phases in NWA 7034 are consistent with mineralogies commonly found in SNC meteorites (11) but not with any other known achondrite group. However, the average bulk chemical composition of NWA 7034 does not overlap in major element space with SNC; instead, it is remarkably similar to the geochemistry of the rocks and soils at Gusev Crater and the average martian crust composition from the Odyssey Orbiter GRS (Fig. 3 and figs. S7 and S8). NWA 7034, Gusev rocks, and the GRS average martian crust all have higher concentrations of the alkali elements sodium and potassium than do SNC meteorites. Other major and minor element ratios such as Mg/Si, Al/Si, and Ni/Mg have similarly good matches between NWA 7034 and Gusev Crater rocks (figs. S7 and S8). Although some

<sup>1</sup>Institute of Meteoritics, University of New Mexico, Albuquerque, NM 87131, USA. <sup>2</sup>Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque, NM 87131, USA. <sup>3</sup>Department of Chemistry and Biochemistry, University of California, San Diego, La Jolla, CA 92093, USA. <sup>4</sup>Geophysical Lab, Carnegie Institution of Washington, Washington, DC 20005, USA. <sup>5</sup>School of Environmental Science and Engineering, Sun Yat-Sen University, Guangzhou 510275, China.

\*To whom correspondence should be addressed. E-mail: agee@unm.edu

experimental work has been conducted to link martian meteorites to surface rocks analyzed by the Mars Exploration Rovers (12–14), and aside from the exotic “Bounce Rock” (15) at Meridiani Planum and a hypothesized martian soil component in Tissint melt pockets (16), there has been no direct link between the bulk chemical compositions of martian meteorites and surface rocks to date.

The rare-earth element (REE) abundances of NWA 7034 were determined by multicollector inductively coupled plasma mass spectrometry (Neptune MC-ICP-MS) at UNM. They are enriched relative to chondritic abundances, with a marked negative europium anomaly ( $\text{Eu}/\text{Eu}^* = 0.67$ ) (fig. S9 and table S2). The REE pattern has

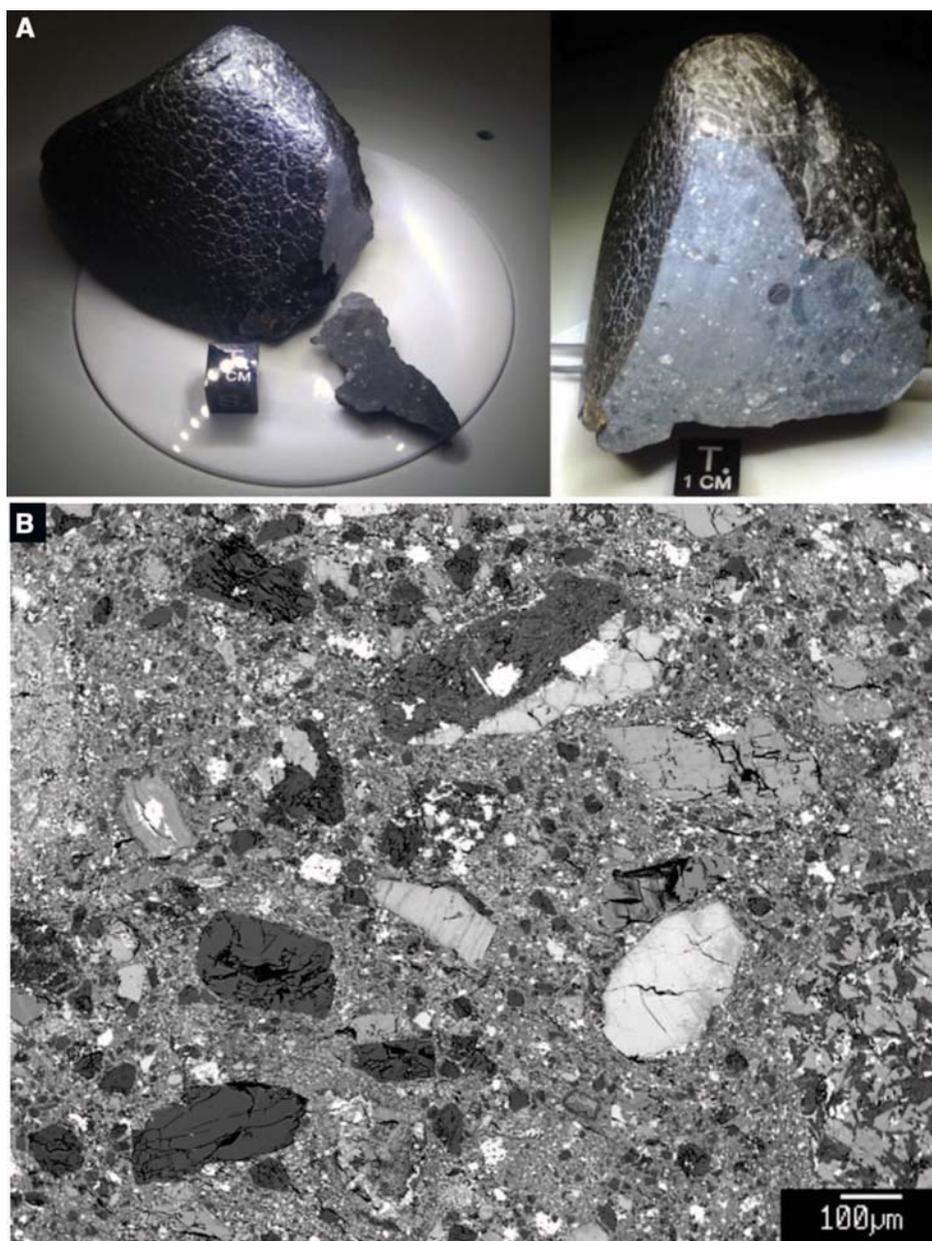
a negative slope, and light rare-earth elements (LREE) are elevated relative to the heavy rare-earth elements (HREE) [CI-chondrite normalized lanthanum-ytterbium ratio  $(\text{La}/\text{Yb})_{\text{N}} = 2.3$ ]. Bulk SNC meteorites are much less enriched in REE (17) than is NWA 7034 (fig. S10); although LREE enrichment relative to HREE and REE patterns with negative slopes are seen in nakhlites, only magmatic inclusions and mesostasis in nakhlites and estimated nakhlite parent magmas have LREE enrichments comparable to those of NWA 7034 (17, 18). We observed ubiquitous, relatively large (up to  $\sim 100 \mu\text{m}$ ) Cl-rich apatite grains in NWA 7034 that presumably harbor a substantial fraction of the REEs in this meteorite, as neither merrillite nor whitlockite were identi-

fied in any of the investigated thin sections or probe mounts.

**Radiometric age.** A five-point isochron gives an Rb-Sr age for NWA 7034 of  $2.089 \pm 0.081$  billion years ago (Ga) [ $2\sigma$ ; mean square weighted deviation (MSWD) = 6.6], an initial  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of  $0.71359 \pm 54$  (Fig. 4), and a calculated source  $^{87}\text{Rb}/^{86}\text{Sr}$  ratio of  $0.405 \pm 0.028$  (Fig. 5). The Sm-Nd data for the same samples result in an isochron of  $2.19 \pm 1.4$  Ga ( $2\sigma$ ). The high uncertainty in the latter is due to minimal separation between the data points generated from analysis of mineral separates. The small error on the Rb-Sr age may come from the abundance and variety of feldspar compositions in NWA 7034 (fig. S5). Furthermore, we are confident that the Rb-Sr isochron and variations in the  $^{87}\text{Sr}/^{86}\text{Sr}$  values are the result of the time-integrated radiogenic growth from  $^{87}\text{Rb}$  and not the results of mixing between end members with different  $^{87}\text{Sr}/^{86}\text{Sr}$  values (figs. S11 to S14). The combined REE and isotopic data show that NWA 7034 is an enriched martian crustal rock (Fig. 5). The whole rock has  $^{143}\text{Nd}/^{144}\text{Nd} = 0.511756$  and  $^{147}\text{Sm}/^{144}\text{Nd} = 0.1664$ , giving a calculated initial (source value)  $^{143}\text{Nd}/^{144}\text{Nd} = 0.509467 \pm 0.000192$  (initial  $\epsilon_{\text{Nd}} = -9.1 \pm 1.7$ , calculated using the Rb-Sr age). This requires that NWA 7034 was derived from an enriched martian reservoir (19), with an inferred time-integrated  $^{147}\text{Sm}/^{144}\text{Nd} = 0.1680 \pm 0.0061$ , assuming separation from a chondrite-like martian mantle at 4.513 Ga (18). Data for each of our analyses are available in table S3. An age of  $\sim 2.1$  Ga for NWA 7034 would make it the only dated meteorite sample from the early Amazonian (19) epoch in Mars’ geologic history.

NWA 7034 is derived from the most enriched martian source identified to date; it is even more enriched than the most enriched shergottites (20–23) (Fig. 5). On the basis of REE enrichment, isotopic values, and match to rover elemental data, NWA 7034 may better represent the composition of Mars’ crust than other martian meteorites. Although NWA 7034 may not be representative of a magmatic liquid, the negative europium anomaly and the absence of merrillite or whitlockite (24) suggest either that the magma(s) parental to basaltic breccia NWA 7034 underwent plagioclase fractionation before eruption or that feldspar was left in the residuum during partial melting. Because of the instability of plagioclase at high pressure (25), these processes would have necessarily occurred in the crust or upper mantle of Mars. Consequently, the geochemically enriched source that produced NWA 7034 could have originated from the martian crust or mantle, much like the geochemically enriched reservoir(s) that are recorded in the shergottites (26–30).

**Carbon.** Confocal Raman imaging spectroscopy conducted at the Carnegie Institution Geophysical Laboratory in Washington, DC, identified the presence of macromolecular carbon (MMC) within mineral inclusions in the groundmass minerals of NWA 7034 (8). This MMC is spectrally



**Fig. 1.** (A) Two views of the NWA 7034 hand specimen. (B) Backscatter electron image of porphyritic texture in NWA 7034. Large dark crystals are feldspar; large light-colored crystals are pyroxene. A portion of a gabbroic clast is shown above the scale bar.

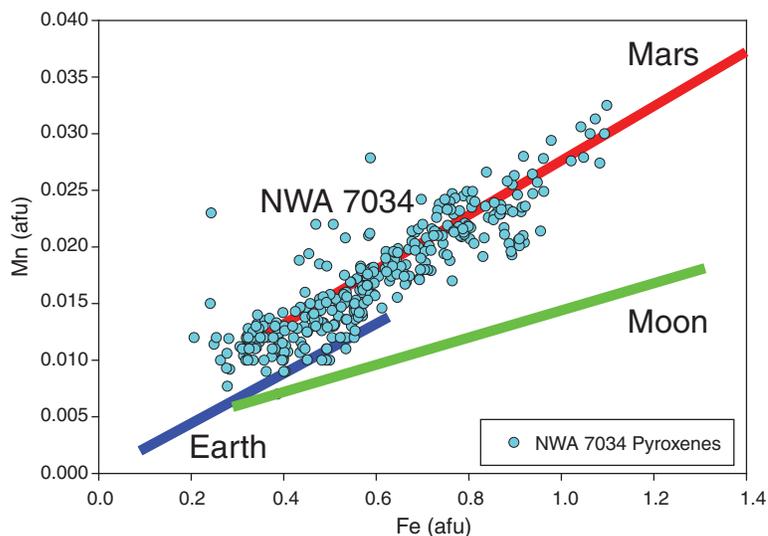
similar to reduced organic macromolecular carbon that has been identified in several shergottites and a single nakhlite meteorite (fig. S15) (30), indicating that the production of organic carbon from abiogenic processes in the martian interior may not be unique to SNC-like source regions in Mars. Steele *et al.* (31) also demonstrated that the formation mechanism of MMC requires reducing magmatic conditions consistent with oxygen fugacities below the fayalite-magnetite-quartz (FMQ) buffer. Consequently, much of the ferric iron in the oxides of NWA 7034, as evidenced by electron probe microanalysis and XRD, was likely a product of oxidation subsequent to igneous activity as a result of secondary processes.

Bulk carbon and carbon isotopic measurements on NWA 7034 were also carried out at Carnegie, using combustion in an elemental analyzer (Carlo Erba NC 2500) interfaced through a ConFlo III to a Delta V Plus isotope ratio mass spectrometer (ThermoFisher) in the same manner as the data reported by (31, 32) [see (8)]. These data indicate that carbon is present within mineral inclusions in NWA 7034 at concentrations of at least  $22 \pm 10$  ppm, and that the  $\delta^{13}\text{C}$  isotopic value of this carbon is  $-23.4 \pm 0.73\text{‰}$ , which is very similar to previous bulk C and  $\delta^{13}\text{C}$  analyses of carbon included in shergottite meteorites analyzed in the same manner (31, 32). These data indicate that multiple geochemical reservoirs in the martian interior may have similarly light  $\delta^{13}\text{C}$  values. The bulk C concentration in the untreated sample performed in these measurements was  $2080 \pm 80$  ppm C, with a corresponding  $\delta^{13}\text{C}$  value of  $-3.0 \pm 0.16\text{‰}$ . Scattered carbonate veinlets from desert weathering were observed by backscatter electron imaging and element mapping with the electron microprobe, especially in the near-surface material but less frequently in the deeper interior slices of NWA 7034. Although this carbonate is below the detection limits of our XRD analyses of the bulk sample and is thus a minor phase within the meteorite, we believe that this weathering product is sampled in our bulk carbon and carbonate analyses (8) (fig. S16).

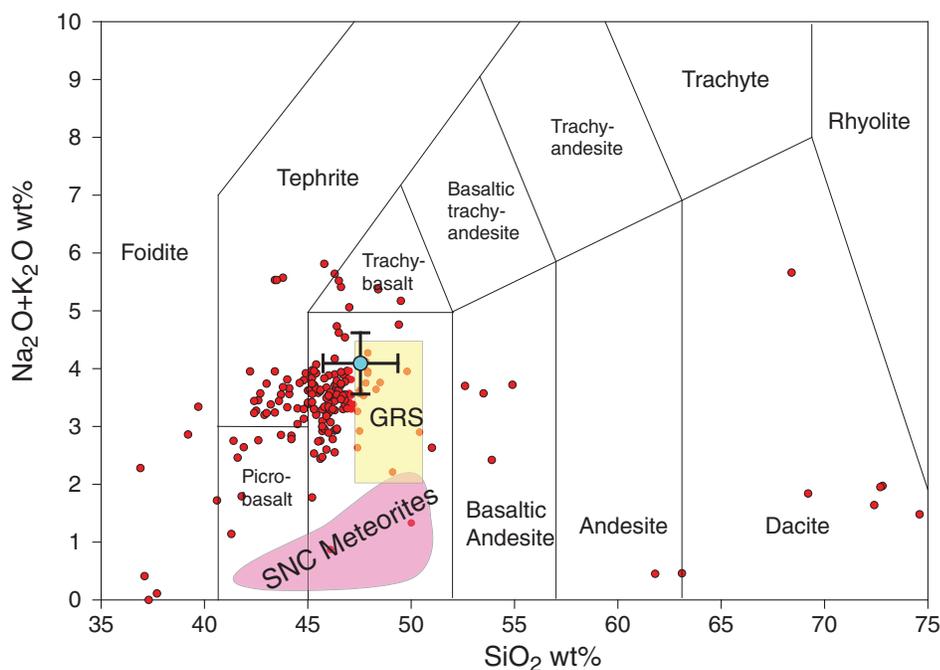
**Oxygen isotopes.** Measurements of oxygen isotopic composition were performed by laser fluorination at UNM on acid-washed and non-acid-washed bulk sample and at the University of California, San Diego (UCSD), on vacuum preheated ( $1000^\circ\text{C}$ ) bulk sample (table S4). The triple oxygen isotope precision on San Carlos olivine standard [ $\delta^{18}\text{O} = 5.2\text{‰}$  versus standard mean ocean water (SMOW);  $\Delta^{17}\text{O} = 0\text{‰}$ ] analyzed during sessions at UNM was  $\Delta^{17}\text{O} = \pm 0.03\text{‰}$ ; the precision at UCSD using NBS-28 quartz standard ( $\delta^{18}\text{O} = 9.62\text{‰}$ ) was also  $\Delta^{17}\text{O} = \pm 0.03\text{‰}$ . In total, we carried out 21 analyses of bulk NWA 7034 (Fig. 6). The mean value obtained at UNM was  $\Delta^{17}\text{O} = 0.58 \pm 0.05\text{‰}$  ( $n = 13$ ) for acid-washed samples and  $\Delta^{17}\text{O} = 0.60 \pm 0.02\text{‰}$  ( $n = 6$ ) for non-acid-washed samples; at UCSD the mean value was  $\Delta^{17}\text{O} = 0.50 \pm 0.03\text{‰}$  ( $n = 2$ ) for vacuum preheated samples that were de-watered and decarbonated. The combined data give

$\Delta^{17}\text{O} = 0.58 \pm 0.05\text{‰}$  ( $n = 21$ ). These interlab values of bulk samples are in good agreement but are significantly higher than literature values for SNC meteorites ( $\Delta^{17}\text{O}$  range 0.15 to 0.45‰) (33–36). Figure 6 shows that the  $\delta^{18}\text{O}$  values (5.5 to 7.0‰ versus SMOW) of NWA 7034 are higher than any determination from the SNC group. The  $\Delta^{17}\text{O}$  values of the non-acid-washed samples measured at UNM are similar to and within

error of the acid-washed samples; this indicates that NWA 7034 has, at most, only minor terrestrial weathering products, which would drive the non-acid-washed values closer to  $\Delta^{17}\text{O} = 0.00$ . The slope of the best-fit line to the combined UNM acid-washed and non-acid-washed data is  $0.517 \pm 0.025$ , which suggests that the oxygen isotopic composition of NWA 7034 is the result of mass-dependent fractionation processes.



**Fig. 2.** Fe versus Mn (atomic formula units) showing the trend for all NWA 7034 pyroxenes (cyan dots, 349 microprobe analyses) and, for comparison, pyroxene trends from Mars (red), the Moon (green), and Earth (blue) (10).



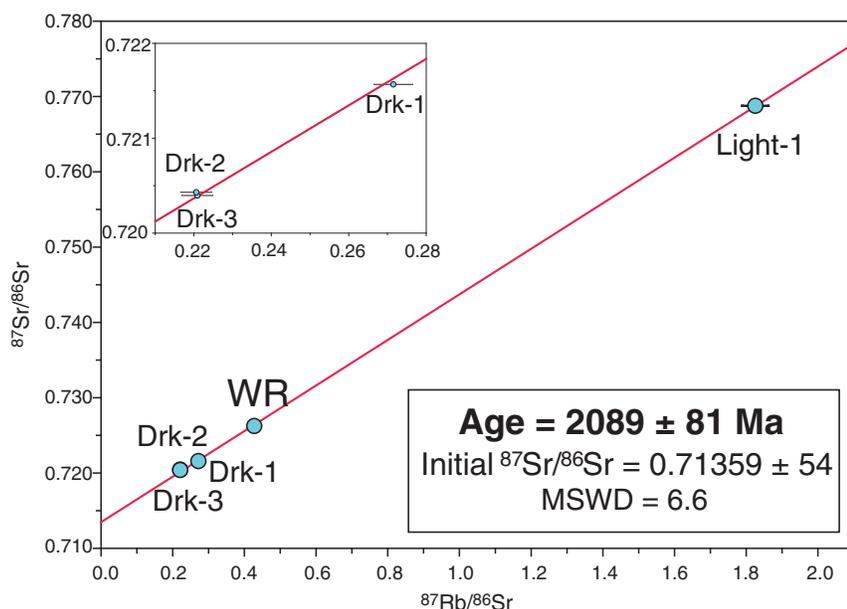
**Fig. 3.** Volcanic rock classification scheme based on the abundance of alkali elements and  $\text{SiO}_2$ , modified after McSween *et al.* (4). Red dots denote analyses of rocks and soils at Gusev Crater by the Alpha Particle X-ray Spectrometer (APXS) onboard the Spirit rover (5, 6). The yellow rectangle is the average martian crust as measured by the GRS onboard the Mars Odyssey orbiter (7). The pink field is the known range of martian meteorite (SNC) compositions. The cyan dot is the mean value of bulk NWA 7034 as determined by 225 electron microprobe analyses of fine-grained groundmass; error bars denote SD.

There are no other known achondrites or planetary samples with bulk oxygen isotope values similar to those of NWA 7034. Most achondrite groups have negative or near-zero  $\Delta^{17}\text{O}$  values, as do rocks from Earth and the Moon. The oxygen isotope compositions of Venus and Mercury are currently unknown, but NWA 7034 is too oxidized and iron-rich to be derived from Mercury (37–39), and it seems to be a poor match for

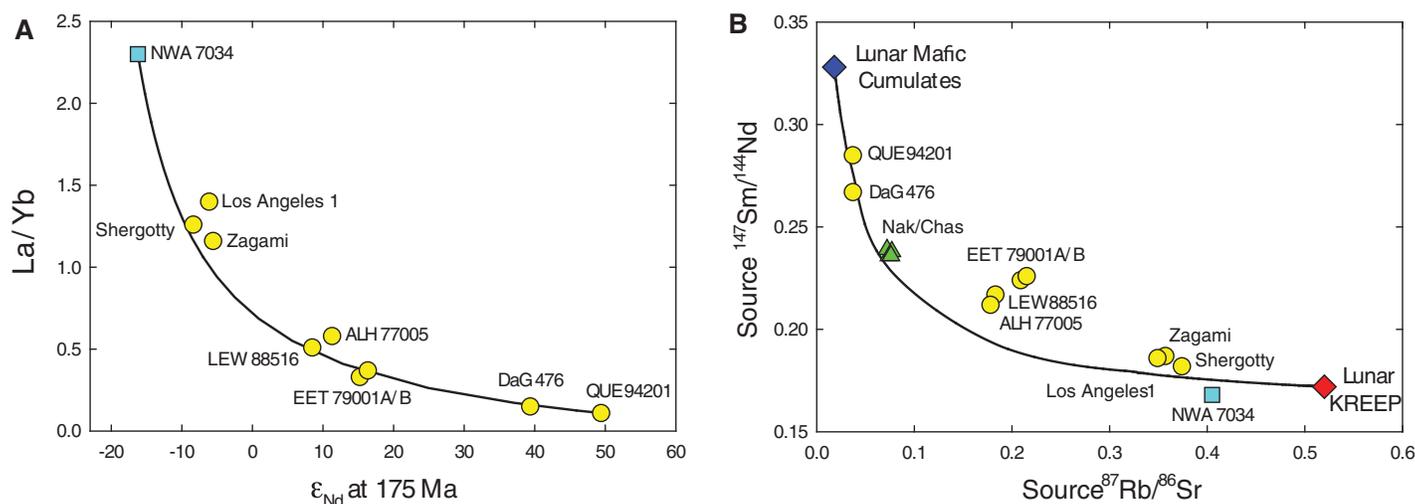
Venus because it experienced low-temperature alteration on its parent body and has significant indigenous water, which would not persist with the high surface temperatures on Venus (40).

The distinct  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values relative to other martian meteorites can be explained by multiple reservoirs—either within the martian lithosphere or between the lithosphere and a surficial component (41, 42)—or by incorporation of ex-

otic material. The idea of separate long-lived silicate reservoirs is supported by radiogenic isotope studies (21, 23). The distinct  $\Delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  values of the silicate fraction of NWA 7034 relative to all SNC meteorites measured to date further support the idea of distinct lithospheric reservoirs that have remained unmixed throughout martian history. A near-surface component with high  $\Delta^{17}\text{O}$  values has been proposed on the basis of analysis of low-temperature alteration products (41–43), and this may in part explain the  $\Delta^{17}\text{O}$  differences between the bulk and “water-derived” components of NWA 7034. However, the  $\Delta^{17}\text{O}$  value of 0.58‰ for the bulk silicate is different from the  $\Delta^{17}\text{O}$  value of 0.3‰ found in all SNC samples measured to date. If materials with a  $\Delta^{17}\text{O}$  value other than 0.3‰ are attributed to a surficial (atmospheric) component, then the bulk of NWA 7034 would have necessarily undergone extensive exchange with this reservoir. This is a possibility, given the abundance of low-temperature iron oxides. The ramifications of distinct lithospheric reservoirs are very different from those attributed to a different surficial reservoir. The latter could be explained by photochemical-induced isotope fractionation and/or hydrodynamic escape (44–46), whereas the former is consistent with a lack of initial planet-wide homogenization and an absence of plate tectonics (41). Isolated lithospheric oxygen isotope reservoirs are inconsistent with a global magma ocean scenario for early Mars, which would have very efficiently homogenized oxygen isotopes in the planet, as occurred for Earth and the Moon. Instead, Mars’ differentiation could have been dominated by basin-forming impacts that left regional or even hemisphere-scale magmatic complexes (47, 48) with distinct and varied isotopic and geochemical characteristics.



**Fig. 4.** Rb-Sr whole-rock mineral isochron of NWA 7034. The mineral fractions are labeled as Light-1, Drk-1, Drk-2, and Drk-3 according to abundance of dark magnetic minerals. Light-1, with high  $^{87}\text{Rb}/^{86}\text{Sr}$ , was the least magnetic fraction. An MSWD value of 6.6 suggests that the small scatter in the values cannot be explained by analytical errors and may include slight isotopic heterogeneities in the rock.  $2\sigma$  measurement errors were used for the  $^{87}\text{Sr}/^{86}\text{Sr}$  data; 2% errors for the  $^{87}\text{Rb}/^{86}\text{Sr}$  data were used for age calculation. Larger errors were assigned to the  $^{87}\text{Rb}/^{86}\text{Sr}$  ratios because of the inability to perform internal mass fractionation on Rb isotopic measurements (Rb only has two isotopes). There was not enough Sm and Nd in the mineral fractions to provide a meaningful age.



**Fig. 5.** (A) Plot of bulk rock La/Yb ratio versus  $\epsilon_{\text{Nd}}$  calculated at 175 Ma for NWA 7034 and basaltic shergottites. Solid line represents two-component mixing line between NWA 7034 and QUE 94201. (B) Plot of calculated parent/daughter source ratios for NWA 7034, basaltic shergottites, nakhilites including Chassigny (which has values similar to nakhilites) (Nak/Chas), and lunar

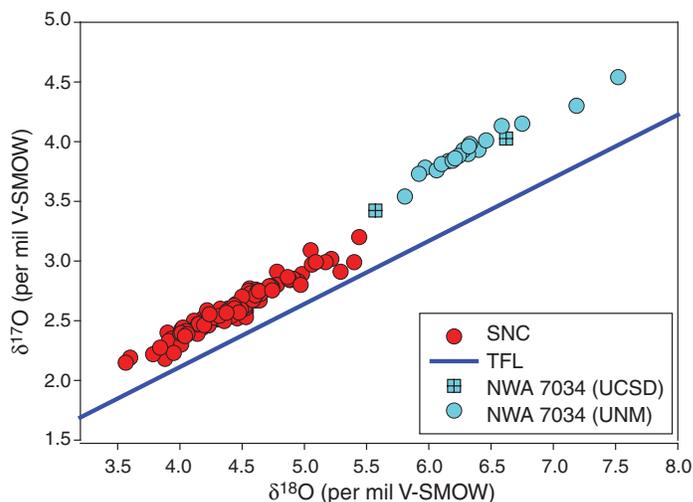
mantle sources. Solid line represents two-component mixing line between depleted lunar mafic cumulates and lunar potassium, rare-earth elements, and phosphorus (KREEP). Depleted lunar mafic cumulates are estimated by (54–56). Lunar KREEP is estimated by (56). Data for basaltic shergottites, nakhilites, and Chassigny are from (22, 23) and references therein.

Another possibility is that NWA 7034 originally had oxygen isotope values similar to or the same as SNC, but a cometary component with higher  $\delta^{18}\text{O}$ ,  $\delta^{17}\text{O}$ , and  $\Delta^{17}\text{O}$  was mixed with it through impact processes on Mars, thus producing a  $\Delta^{17}\text{O}$  excess relative to SNC. Until we find clear evidence of such an exotic component in NWA 7034, this scenario seems less likely than the other two.

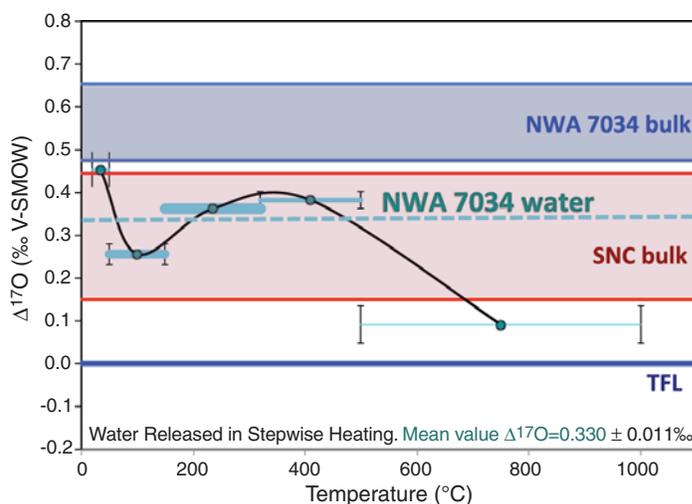
**Water.** The oxygen isotope ratio of water released by stepped heating in a vacuum at UCSD (table S5) shows that most, possibly all, of the water in NWA 7034 is extraterrestrial, with  $\Delta^{17}\text{O}$  values well above the terrestrial fractionation line (Fig. 7). NWA 7034 water falls primarily within the range of values for bulk SNC meteorites, with a weighted mean value of  $\Delta^{17}\text{O} = +0.33 \pm 0.01\%$ ;  $\delta^{18}\text{O}$  and  $\delta^{17}\text{O}$  values give a slope of 0.52, indicating mass-dependent fractionation. Note that the  $\Delta^{17}\text{O}$  value for NWA 7034 water is lower than, and outside the range of, the  $\Delta^{17}\text{O}$  for bulk NWA 7034, offering clear evidence that there are multiple distinct oxygen isotope sources for this sample. The  $\Delta^{17}\text{O}$  value of the water released at the 500° to 1000°C range (+0.09‰) approaches terrestrial values, possibly because of decomposition of the terrestrial carbonate veins in the meteorite and equilibration of the produced  $\text{CO}_2$  with the released water. Karlsson *et al.* (41) reported oxygen isotope values of water from several SNC meteorites and also saw that they differed from the  $\Delta^{17}\text{O}$  of the bulk SNC samples. However, their observed  $\Delta^{17}\text{O}$  relationship between bulk rock and water is reverse to the one seen in NWA 7034, with waters in general having more positive  $\Delta^{17}\text{O}$  values than their respective host rocks (Nakhla, Chassigny, and Lafayette). Only two shergottites (Shergotty and EETA-79001A) have waters with  $\Delta^{17}\text{O}$  values more negative than the host rock, and Nakhla has water similar to its host rock. Romanek (43) analyzed iddingsite, an alteration product of olivine and pyroxene, in Lafayette and found the  $\Delta^{17}\text{O}$  value is 1.37‰ for a 90% iddingsite separate, supporting the positive  $\Delta^{17}\text{O}$  shift of Lafayette water relative to host rock. Karlsson (41) argued that this  $\Delta^{17}\text{O}$  difference suggested a lack of equilibrium between water and host rock, with the lithosphere and hydrosphere having distinct oxygen isotopic reservoirs. Our data support this conclusion but suggest that the  $\Delta^{17}\text{O}$  value of the “water” reservoir is not always heavier than the rock reservoir.

We determined the deuterium/hydrogen isotope ratio ( $\delta\text{D}$  value versus SMOW) and the water content of whole-rock NWA 7034 at UNM by both bulk combustion and stepped heating in a continuous-flow helium stream with high-temperature carbon reduction (49) (Fig. 8 and table S6). Six whole-rock combustion measurements yielded a bulk water content of  $6190 \pm 620$  ppm. The mean  $\delta\text{D}$  value for the bulk combustion analyses was  $+46.3 \pm 8.6\%$ . The maximum  $\delta\text{D}$  values in two separate stepwise heating experiments were  $+319\%$  and  $+327\%$ , reached

**Fig. 6.** Oxygen isotope plot showing the values of NWA 7034 from this study. Cyan dots, 13 analyses of acid-washed and six analyses of non-acid-washed bulk samples (UNM); cyan squares, two analyses of dry, decarbonated bulk preheated to 1000°C (UCSD). Red dots are SNC meteorites from the literature (33–36, 41). TFL, terrestrial fractionation line (slope 0.528).



**Fig. 7.** Plot of  $\Delta^{17}\text{O}$  versus temperature, showing values for NWA 7034 water released by stepped heating. Vertical error bars are given for each data point; horizontal line segments show the temperature range for each step, and the thickness of the line segment indicates the relative proportion of water released at each step. Dashed line is the mean value of  $\Delta^{17}\text{O}$  for NWA 7034 water. Also shown are ranges of  $\Delta^{17}\text{O}$  for bulk NWA 7034 analyses and for bulk SNC values from the literature.

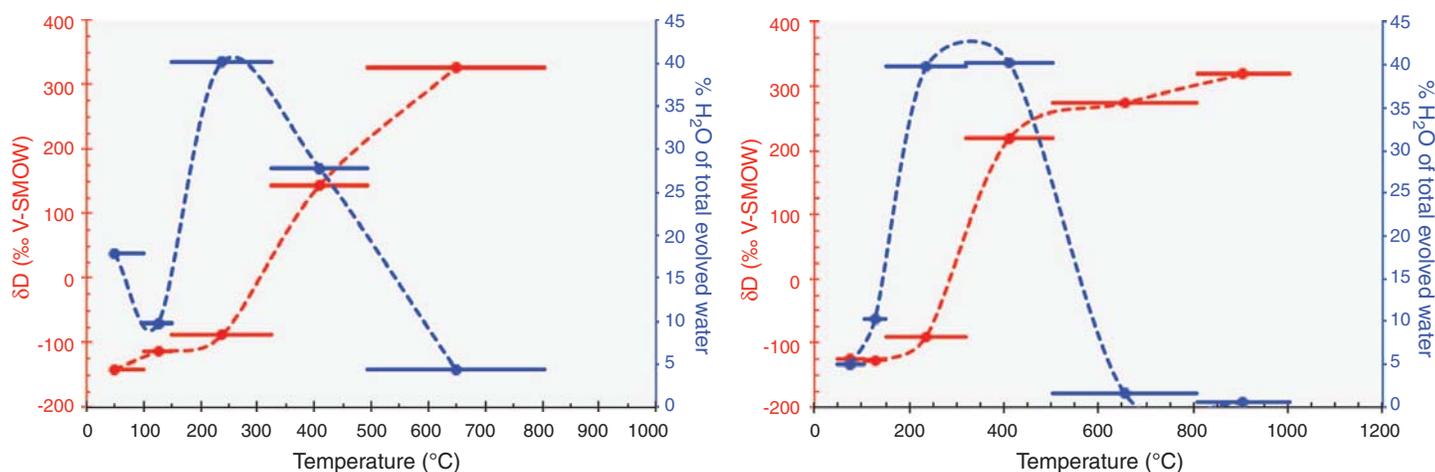


at 804°C and 1014°C, respectively (table S6), similar to values seen in the nakhlites (50). Figure 8 shows that most of the water in NWA 7034 is released between approximately 150° and 500°C, and that there are two plateaus of  $\delta\text{D}$  values, one around  $-100\%$  at 50° to 200°C and a second around  $+300\%$  at 300° to 1000°C. This suggests that there are two distinct  $\delta\text{D}$  components in NWA 7034: a low-temperature negative-value component and a high-temperature positive-value component. One possibility is that the low-temperature negative values are from terrestrial water contamination, although the  $\Delta^{17}\text{O}$  values in water released at even the lowest temperature step of 50°C have a 0.3‰ anomaly (Fig. 7). It is also possible that protium-rich water is released at the lowest steps of dehydration, although such fractionation is not observed on terrestrial samples. Alternatively, the hydrogen but not the oxygen isotope ratios could have been affected by terrestrial alteration. Finally, it is possible that nearly all the released water from NWA 7034 is in fact martian and not terrestrial. In this case, the hydrogen isotope ratios have

fractionated as a function of temperature, or there are two distinct hydrogen isotope reservoirs.

Our data show that NWA 7034 has more than an order of magnitude more indigenous water than most SNC meteorites. The amount of water released at high temperature ( $>320^\circ\text{C}$ ) is  $3280 \pm 720$  ppm. Leshin *et al.* (50) measured an average of  $249 \pm 129$  ppm  $\text{H}_2\text{O}$  released above 300° to 350°C in seven bulk SNC meteorites, with the exception of the anomalous Lafayette nakhlite (which released 1300 ppm  $\text{H}_2\text{O}$  above 300°C). They (50) argued that some of the water released at temperatures as low as 250°C could in fact be from martian alteration products. Given our oxygen water analyses, this could also be the case for NWA 7034 at temperatures as low as 50°C. Hence, the total amount of martian water in NWA 7034 could be in the vicinity of 6000 ppm, possibly supporting hypotheses that aqueous alteration of near-surface materials on Mars occurred during the early Amazonian epoch (2.1 Ga) either by magmatically derived or meteoric aqueous fluids (51–53).

**Conclusions.** The young crystallization age of NWA 7034, 2.1 Ga, requires that it is planetary



**Fig. 8.** Plots of  $\delta D$  versus temperature, showing data for the NWA 7034 bulk sample during stepped heating. The horizontal solid lines represent the temperature intervals; circles are mid-interval temperatures. The two plots represent two aliquots of the NWA 7034 sample.

in origin. Its major, minor, trace, and isotopic chemistry is inconsistent with originating from Earth, the Moon, Venus, or Mercury, and it is most similar to rocks from Mars. Nonetheless, NWA 7034 is uniquely different from any other known martian meteorite, as it is the most geochemically enriched rock from Mars found to date. Moreover, the bulk chemistry of NWA 7034 is strikingly similar to recently collected orbital and lander data collected at the martian surface, allowing for a direct link between a martian meteorite and orbital and lander spacecraft data from Mars. NWA 7034 is also distinct from the SNC meteorites because it has higher bulk  $\delta^{18}O$  and  $\Delta^{17}O$ , suggesting the existence of multiple oxygen isotopic reservoirs within the lithologic portion of Mars.

#### References and Notes

- A. H. Treiman, J. D. Gleason, D. D. Bogard, *Planet. Space Sci.* **48**, 1213 (2000).
- H. Y. McSween, T. L. Grove, J. Wyatt, *J. Geophys. Res. Planets* **108**, 5135 (2003).
- L. E. Nyquist *et al.*, in *Chronology and Evolution of Mars*, R. Kallenbach, J. Geiss, W. K. Hartmann, Eds. (Springer, New York, 2001), p. 105.
- H. Y. McSween Jr., G. J. Taylor, M. B. Wyatt, *Science* **324**, 736 (2009).
- R. Gellert *et al.*, *J. Geophys. Res. Planets* **111**, E02505 (2006).
- D. W. Ming *et al.*, *J. Geophys. Res. Planets* **113**, E12S39 (2008).
- W. V. Boynton *et al.*, *J. Geophys. Res. Planets* **112**, E12S99 (2007).
- See supplementary materials on Science Online.
- S. P. Wright, P. R. Christensen, T. G. Sharp, *J. Geophys. Res. Planets* **116**, E09006 (2011).
- J. J. Papike, J. M. Karner, C. K. Shearer, P. V. Burger, *Geochim. Cosmochim. Acta* **73**, 7443 (2009).
- F. M. McCubbin, H. Nekvasil, *Am. Mineral.* **93**, 676 (2008).
- J. Filiberto, *Geochim. Cosmochim. Acta* **72**, 690 (2008).
- H. Nekvasil, F. M. McCubbin, A. Harrington, S. Elardo, D. H. Lindsley, *Meteorit. Planet. Sci.* **44**, 853 (2009).
- F. M. McCubbin, H. Nekvasil, A. D. Harrington, S. M. Elardo, D. H. Lindsley, *J. Geophys. Res. Planets* **113**, E11013 (2008).
- J. Zipfel *et al.*, *Meteorit. Planet. Sci.* **46**, 1 (2011).
- H. Chennaoui Aoudjehane *et al.*, *Science* **338**, 785 (2012).
- M. Wadwa, G. Crozaz, J.-A. Barrat, *Antarct. Meteorite Res.* **17**, 97 (2004).
- J. M. Day, L. A. Taylor, C. Floss, H. Y. McSween Jr., *Meteorit. Planet. Sci.* **41**, 581 (2006).
- W. K. Hartmann, G. Neukum, in *Chronology and Evolution of Mars*, R. Kallenbach, J. Geiss, W. K. Hartmann, Eds. (Springer, New York, 2001), p. 165–194.
- L. E. Borg, D. S. Draper, *Meteorit. Planet. Sci.* **38**, 1713 (2003).
- L. E. Borg, L. E. Nyquist, L. A. Taylor, H. Wiesmann, C.-Y. Shih, *Geochim. Cosmochim. Acta* **61**, 4915 (1997).
- L. E. Borg, L. E. Nyquist, H. Wiesmann, Y. Reese, *Geochim. Cosmochim. Acta* **66**, 2037 (2002).
- L. E. Borg, L. E. Nyquist, H. Wiesmann, C.-Y. Shih, Y. Reese, *Geochim. Cosmochim. Acta* **67**, 3519 (2003).
- C. K. Shearer *et al.*, *Am. Mineral.* **96**, 1418 (2011).
- C. B. Till, T. L. Grove, M. J. Krawczynski, *J. Geophys. Res.* **117**, B06206 (2012).
- M. D. Norman, *Meteorit. Planet. Sci.* **34**, 439 (1999).
- C. D. K. Herd, L. E. Borg, J. H. Jones, J. J. Papike, *Geochim. Cosmochim. Acta* **66**, 2025 (2002).
- A. B. Sarbadhikari, J. M. D. Day, Y. Liu, D. Rumble III, L. A. Taylor, *Geochim. Cosmochim. Acta* **73**, 2190 (2009).
- A. B. Sarbadhikari, C. A. Goodrich, Y. Liu, J. M. D. Day, L. A. Taylor, *Geochim. Cosmochim. Acta* **75**, 6803 (2011).
- C. D. K. Herd, *Meteorit. Planet. Sci.* **38**, 1793 (2003).
- A. Steele *et al.*, *Science* **337**, 212 (2012).
- M. M. Grady, A. B. Verchovsky, I. P. Wright, *Int. J. Astrobiol.* **3**, 117 (2004).
- R. N. Clayton, T. K. Mayeda, *Earth Planet. Sci. Lett.* **62**, 1 (1983).
- I. A. Franchi, I. P. Wright, A. S. Sexton, C. T. Pillinger, *Meteorit. Planet. Sci.* **34**, 657 (1999).
- D. W. Mittlefehldt, R. N. Clayton, M. J. Drake, K. Righter, *Rev. Mineral. Geochem.* **68**, 399 (2008).
- D. Rumble *et al.*, *Proc. 40th Lunar Planet. Sci. Conf.* **40**, 2293 (2009).
- F. M. McCubbin, M. A. Riner, K. E. Vander Kaaden, L. K. Burkemper, *Geophys. Res. Lett.* **39**, L09202 (2012).
- M. A. Riner, F. M. McCubbin, P. G. Lucey, G. J. Taylor, J. J. Gillis-Davis, *Icarus* **209**, 301 (2010).
- L. R. Nittler *et al.*, *Science* **333**, 1847 (2011).
- K. Lodders, B. Fegley, *The Planetary Scientist's Companion* (Oxford Univ. Press, Oxford, 1998).
- H. R. Karlsson, R. N. Clayton, E. K. Gibson Jr., T. K. Mayeda, *Science* **255**, 1409 (1992).
- J. Farquhar, M. H. Thiemens, T. Jackson, *Science* **280**, 1580 (1998).
- C. S. Romanek *et al.*, *Meteorit. Planet. Sci.* **33**, 775 (1998).
- E. D. Young, R. D. Ash, P. England, D. Rumble 3rd, *Science* **286**, 1331 (1999).
- Y. L. Yung, W. B. Demore, *Photochemistry of Planetary Atmospheres* (Oxford Univ. Press, Oxford, 1999).
- J. Farquhar, M. H. Thiemens, *J. Geophys. Res. Planets* **105**, 11991 (2000).
- C. C. Reese, V. S. Solomatos, *Icarus* **184**, 102 (2006).
- F. Nimmo, S. D. Hart, D. G. Korycansky, C. B. Agnor, *Nature* **453**, 1220 (2008).
- Z. D. Sharp, V. Atudorei, T. Durakiewicz, *Chem. Geol.* **178**, 197 (2001).
- L. A. Leshin, S. Epstein, E. M. Stolper, *Geochim. Cosmochim. Acta* **60**, 2635 (1996).
- L. Borg, M. J. Drake, *J. Geophys. Res. Planets* **110**, E12503 (2005).
- B. L. Ehlmann *et al.*, *Nature* **479**, 53 (2011).
- F. M. McCubbin *et al.*, *Earth Planet. Sci. Lett.* **292**, 132 (2010).
- G. A. Snyder, L. A. Taylor, C. R. Neal, *Geochim. Cosmochim. Acta* **56**, 3809 (1992).
- G. A. Snyder, D.-C. Lee, L. A. Taylor, A. N. Halliday, E. A. Jerde, *Geochim. Cosmochim. Acta* **58**, 4795 (1994).
- P. H. Warren, J. T. Wasson, *Rev. Geophys. Space Phys.* **17**, 73 (1979).

**Acknowledgments:** We thank J. Piatek for acquiring the NWA 7034 specimen and for his generous donation to the UNM Meteorite Museum, which has enabled this research and sample allocations for future research on NWA 7034. We also thank M. Spilde, V. Atudorei, and J. Connolly at the University of New Mexico for assistance with data collection. Supported by NASA Cosmochemistry Program grants NNX11AH16G (C.B.A.) and NNX11AG76G (F.M.M.). S.M.E. acknowledges support from the New Mexico Space Grant Consortium, NASA Earth and Space Science Fellowship NNX12A015H, and NASA Cosmochemistry grant NNX10AI77G to Charles K. Shearer. M.H.T. and R.S. acknowledge NSF award ATM0960594, which allowed the development of an analytical technique to measure oxygen triple isotopic composition of small (<1  $\mu$ M) sulfate samples.

#### Supplementary Materials

www.sciencemag.org/cgi/content/full/science.1228858/DC1  
Materials and Methods  
Figs. S1 to S16  
Tables S1 to S6  
References (57–71)

15 August 2012; accepted 14 December 2012  
Published online 3 January 2013;  
10.1126/science.1228858