

Hydrogen isotope geochemistry of Iherzolitic shergottite in Martian meteorite GRV99027 from the Grove Mountains in Antarctica

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Abstract Hydrogen isotopic composition was measured using an ion microprobe for Iherzolitic shergottite in Martian meteorite GRV 99027 from the Grove Mountains in Antarctica. The D/H ratios of phosphate whitlockites were analyzed and water concentrations of tested points were calculated. The result show that their δD values vary from +1300‰ to +4700‰, and water contents from 0.04 wt% to 0.43 wt%. Comparing the results with the hydrogen isotopic compositions of whole rock, hydrous minerals and phosphates in SNC meteorites indicates that water highly enriched in deuterium is a unique feature of Martian meteorites, especially the phosphates prominent. It is interpreted as the result of isotopic exchange between magmatic water and Martian crustal fluids. The high D/H ratios observed in GRV 99027 phosphates indicate that they have hydrogen isotopic compositions similar to those of apatite in other Martian meteorites. The results further confirmed the association of GRV 99027 with the Martian meteorite group.

Keywords: Antarctica, Martian meteorite, Iherzolitic shergottite, hydrogen isotope, ion microprobe.

Whether life vestige existed in Martian meteorites or not has provoked a hot tide toward Mars exploration. Among the other things, whether water existed in Mars

or not again becomes a hot point of contemporary scientific exploration. Analyzing the hydrogen isotopic compositions and water concentrations of Martian meteorites is an effective method for investigating this important scientific issue. Some foreign scholars have done much work in this field.

The current Martian atmosphere contains water with a D/H ratio five times greater than the terrestrial water, corresponding to a δD of +4200‰ relative to mean terrestrial ocean water^[1]. It is generally assumed that Mars originally had a D/H similar to the terrestrial values (+100‰ to -300‰) and to those in most primitive meteorites^[2-4]. The mechanism fractionating the Martian D/H ratio from its initial value to that observed today is not well understood, but people generally assume that preferential loss of H relative to D from the Martian atmosphere experienced early hydrodynamic escape and later jeans escape^[5].

Leshin *et al.*^[6] studied hydrogen isotope geochemistry of SNC meteorites. They reported the yields and hydrogen isotopic compositions of water extracted by stepwise heating of eight whole-rock SNC meteorites. The data are consistent with the water in the samples originating from two sources: a terrestrial component/contaminant, released largely at low temperature, and an extraterrestrial component, released at high temperature. The variation in δD values of the high-temperature hydrogen (~ +250—+900 for nakhlites, ~ +1200—+2100 for the shergottites, and ~ +800 for ALH 84001) could represent true variation of the δD of the extraterrestrial water in the samples, or may reflect varying contributions of the terrestrial endmember, even at high temperature. The high δD values are consistent with a Martian origin for the meteorites since the current Martian atmosphere contains water with a δD of ~ +4000. The D-enriched water was probably incorporated into the rocks through interaction at low temperature with aqueous crustal fluids that had exchanged with the Martian atmosphere.

Using an ion microprobe, Watson *et al.*^[7] studied magmatic, hydrous amphibole, biotite, and apatite in SNC meteorites, and observed elevated and variable D/H values of water in these minerals (δD +500‰—+4300‰). They suggested that after minerals crystallization, magmatic water in these minerals intermixed or isotopically exchanged with Martian crustal fluids with near atmospheric D/H to cause D enrichment.

Leshin^[5] analysed D/H and water content of mag-

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matic, hydrated apatite from the QUE94201 shergottite, which were carried out with the cameca IMS 1270 ion microprobe at UCLA. The data suggest that either mixing (with atmosphere-derived and D-enriched waters) or shock would tend to increase the δD values of the minerals. Eleven apatite measurements (δD) range from $\sim +1680\%$ to $+3570\%$, which also fall within the range observed in other Martian meteorites. The isotopic data show a striking negative correlation between δD and OH content of these apatites.

Boctor *et al.*^[8] measured H isotope of carbonate, phosphate, feldspathic and mafic glasses, and post-stishovite silica phase in the shergottites, as well as in Chassigny and ALH 84001. They show that all these phases contain D-enriched water of extraterrestrial origin. The minerals and glasses analyzed may contain an initial primary hydrogen component, but their isotopic composition was modified to varying degrees by three different processes: interaction with a fractionated water reservoir on Mars, hydrogen devolatilization by impact melting, and terrestrial contamination.

The maximum advantage of ion microprobe is to *in situ* directly analyze isotope and trace element at micro-area ($<10\ \mu\text{m}$) in an individual mineral grain. Phosphates are the best minerals for analyzing hydrogen isotope by ion microprobe. This paper uses ion microprobe to study the hydrogen isotopic geochemistry of the first Martian lherzolitic shergottite Grove Mountains 99027 found in Antarctica by China.

1 Experimental methods

Sample GRV 99027 was collected from the ice field of the Grove Mountains in Antarctica, by the 16th Chinese Antarctic Research Expedition in 1999/2000. It weighs 9.97 g and is partially covered by fusion crust. Its petrology, mineralogy and rare earth element geochemistry have been reported^[9-16]. This meteorite is cumulation consisting mostly of olivine and pigeonite with minor amounts of augite, maskelynite, and trace amounts of phosphates, and opaque minerals. GRV 99027 shows almost identical characteristics to other lherzolitic shergottites^[17-20].

The sample used in this study is provided by Chinese National Antarctic Research Institute. The polished thin section was firstly examined with an optical transmission and reflectance microscope and a JEOL-845 scanning electron microscope (SEM) equipped with an IXRF energy-dispersive (EDS) detector system. Min-

eral chemistry was determined with an electron microprobe (JEOL JXA-8800M) at State Key Laboratory for Mineral Deposits Research, Department of Earth Sciences, Nanjing University. Accelerating voltage was 15 KeV with a 20 nA beam current. Both synthetic (NBS) and natural mineral standards were used, and matrix corrections were based on ZAF procedures.

Hydrogen isotopes and water concentrations in phosphates were measured using the IMS-6f ion microprobe at Arizona State University. Due to the extensive occurrence of small cracks in the phosphate grains, a small ($\sim 2-5\ \mu\text{m}$) Cs primary beam had to be used to avoid contamination from surrounding epoxy material. In order to increase transmission, secondary ion signals were collected at 9 KeV with an ion image field of $75\ \mu\text{m}$. Sample charging was compensated by an incident electron-flooding gun. Instrumental mass fractionation and hydrogen background corrections were made using terrestrial apatite standards and olivine in the GRV 99027 thin section. Water contents in spots analyzed for D/H were also determined using terrestrial apatite standards, with P as the reference element. The relative uncertainties of water concentration are between $\sim 5\ \text{wt}\%$ and $18\ \text{wt}\%$. The principle, method and application of ion microprobe testing on hydrogen isotopes have been described by Hsu^[21].

2 Results

2.1 Petrography

GRV99027 contains three distinct petrographic units in the thin section: poikilitic, non-poikilitic, and glassy to partially crystalline melt pocket (Fig. 1). In the central poikilitic areas, olivine occurs as euhedral or subeuhedral crystals ($0.1-0.5\ \text{mm}$) enclosed by large (up to several mm) oikocrysts of pigeonite. On the right edge, non-poikilitic areas consist of larger olivine, pigeonite, and augite. Maskelynite and phosphates usually occur interstitially between olivine and pyroxenes. On the left edge, shock-melt pockets consist predominantly of melt glass, quenched olivine. Needle-shaped, crypto-crystalline materials are also commonly set in melt glasses.

2.2 Hydrogen isotope

The phosphate grains found in the GRV99027 thin section occur interstitially between olivine and pyroxene grains. Their sizes range from less than $10\ \mu\text{m}$ to about $150\ \mu\text{m}$ (Fig. 2(a)). Some of the phosphate grains

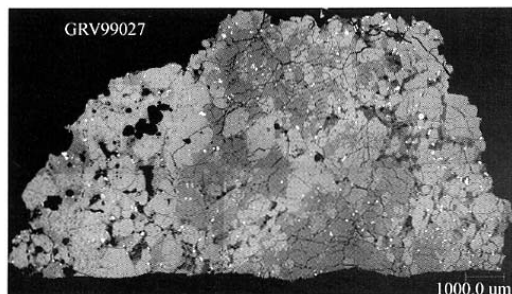


Fig. 1. Backscattered electron image of the GRV 99027. In the central poikilitic texture, the gray pyroxenes grains enclose light gray olivines crystals. In the right non-poikilitic texture, maskelynite (dark gray) occurs interstitially between olivine and pyroxene. On the left edge is melt glass pocket.

are crosscut by plagioclase (maskelynite) veins (Fig. 2(b)). Most of the phosphate grains in GRV99027 are whitlockite. The electrical microprobe analyses of chemical compositions of phosphates are shown in Table 1. Small and tiny amounts of apatite can be found in a few whitlockite grains.

Table 1 Chemical composition of whitlockite in GRV99027 (wt%)

	Analysis point						
	50	51	52	53	54	55	56
SiO ₂	0.10	0.18	0.11	0.19	0.19	0.14	0.11
Al ₂ O ₃	0.05	0.01	0.00	0.05	0.05	0.04	0.07
TiO ₂	0.04	0.03	–	–	0.04	0.03	–
Cr ₂ O ₃	0.00	0.01	–	0.07	–	0.04	–
FeO	2.59	2.62	2.36	2.24	1.73	2.36	1.60
MnO	–	0.16	0.04	0.03	0.12	0.05	0.03
MgO	3.61	3.74	3.75	3.70	3.60	3.49	3.65
CaO	47.14	46.75	46.62	47.33	46.67	46.18	47.42
Na ₂ O	0.49	0.34	0.37	0.40	0.61	0.44	0.63
K ₂ O	0.01	0.02	0.03	–	0.02	0.02	0.02
P ₂ O ₅	44.12	44.42	44.39	44.48	43.99	44.01	44.66
F	2.36	1.68	2.29	1.24	1.68	1.57	1.98
Cl	–	0.02	0.03	0.01	0.03	0.03	0.02
Total	100.50	99.98	100.00	99.22	98.72	98.39	100.18

Hydrogen isotopes of GRV99027 were measured at Arizona State University. Six of the phosphate grains were analyzed for their D/H ratios and water concentrations by using the IMS-6f ion microprobe. The analyzing results are listed in Table 2, δD values are from +1300‰ to +4700‰, and water contents from 0.04 wt% to 0.43 wt%. A light negative correlation exists between D/H ratios and water contents in these GRV 99027 phosphate whitlockite grains. Because GRV 99027 has tiny amounts of apatite, analyzing data of tested point 6 are approximately similar to those of

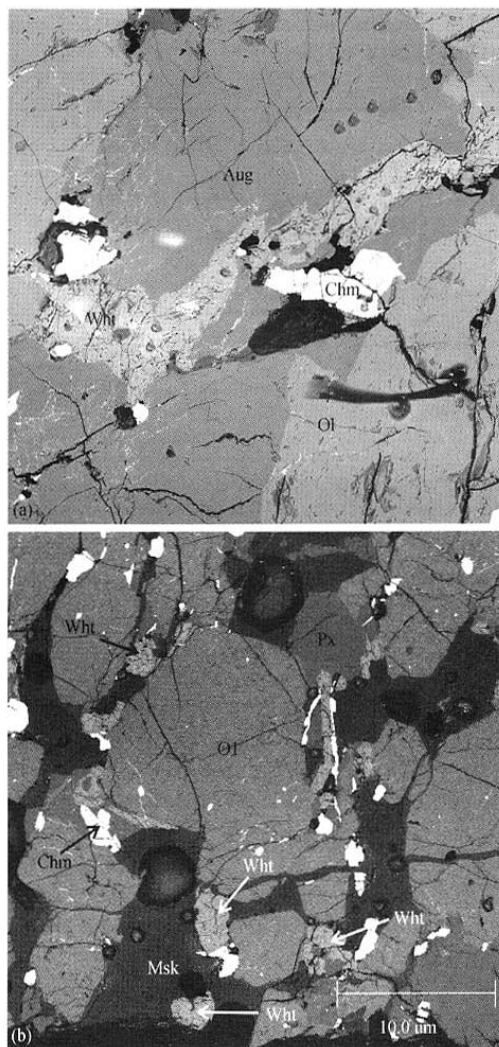


Fig. 2. Backscattered electron image of whitlockites (Wht). (a) Whitlockite (Wht) occurs interstitially between olivine (Ol) and pyroxene (Aug). The field of view is about 500 μm . (b) the phosphate grains (Wht) are crosscut by maskelynite (Msk) tiny veins.

Table 2 D/H and water contents of GRV99027 phosphates

Sample	δD (‰) $\pm 2\sigma$	H ₂ O (wt%)
Grain 1	4745 \pm 309	0.04
Grain 2,a	2179 \pm 246	0.10
Grain 2,b	2153 \pm 251	0.07
Grain 3	2387 \pm 271	0.06
Grain 4	1902 \pm 167	0.24
Grain 5	1326 \pm 193	0.10
Grain 6	4064 \pm 283	0.43

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apatites of other Martian meteorites such as Zagami and QUE94201 (Fig. 3).

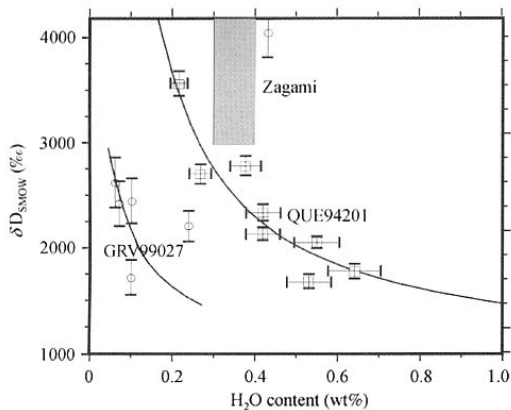


Fig. 3. Comparison between δD values and water contents of phosphates grains from GRV99027 and other Martian meteorite QUE94201, Zagami (QUE94201 and Zagami data from ref. [6]).

3 Discussion

(1) GRV99027 phosphate grains yield high and variable δD ratios, δD values are from 1326 ‰ to 4745‰, and water concentrations from 0.06% to 0.43%. These δD values are similar to those of apatite in other Martian meteorites^[5,7], δD of apatites in QUE94201 varied from 1683‰ to 3565‰, and water contents from 0.22% to 0.64%. δD of apatites in Zagami is 2962‰–4358‰, while relative references only provided a range of ~0.3%–0.4% for water contents. The results of our study have further confirmed the association of GRV99027 with the Martian meteorite group.

(2) Comparing δD values of GRV99027 whitlockites with hydrous silicates and apatites in SNC meteorites (Fig. 4), two striking characteristics can be found out: 1) δD values of kaersutites, biotite, and apatite in the SNC meteorites are more enriched, from 1000‰–4000‰, than that of terrestrial water (left in Fig. 4). In these hydrous minerals, the δD values of phosphates are maximum, up to ~+4400 (right in Fig. 4); 2) Large variability in the D/H ratio occurs among different mineral groups, for example, the above silicates and phosphates have greater variable δD values; in same mineral group, δD variability of different mineral crystals is also large.

The high but variable D/H values of these minerals

originated from isotopic exchange of magmatic water in minerals and D-enriched Martian crustal fluids mixing. It is generally thought that Martian magmatic crystallized minerals initially were poor in D, their magmatic water had lower δD , about $900‰ \pm 250‰$. While because of interaction, mixing or isotopic exchange with Martian atmosphere (right in Fig. 4), Martian crustal fluids became high δD water reservoir with near Martian atmosphere.

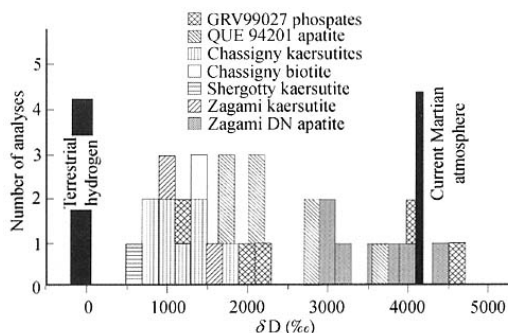


Fig. 4. Histogram comparison of the δD values of hydrous minerals from GRV 99027 and other Martian meteorite QUE94201, Chassigny, Shergotty and Zagami^[7].

(3) Comparing δD and water content of whitlockite in GRV99027 with those of apatite in QUE94201 (Fig. 3), it is noticeable that: 1) δD apparently negatively correlates to water content in latter, while slight negative correlation in GRV99027 is approximately parallel to the curve of QUE94201; 2) δD values of two meteorites equal basically, but water content of GRV99027 decreases dramatically.

Except their mineralogical textures of apatite in QUE94201 and whitlockite in GRV99027 causing these differences, they experienced different stages of shock metamorphism. Whitlockite in GRV99027 suffered stronger shock metamorphism than apatite in QUE94201. In GRV99027, mafic melt pockets indicate stronger shock metamorphism about 60–80 GPa pressure, and presence of maskelynite represents ~30 GPa pressure, as a result, GRV99027 experienced shock pressure of 30–80 GPa. In addition, whitlockite is crosscut by maskelynite and whitlockite has plastic flow phenomena in polished slice of GRV99027.

There are different perspectives about shock metamorphism's influence on δD values, Watson suggested that shock devolatilization could make δD value

change more greatly. Otherwise, an experiment^[22] could not confirm that this physical mechanism could produce detectable $\sim 2000\%$ δD variability. Our data comparison between GRV99027 and QUE94201 indicates that shock metamorphism had minor effect on δD values of two meteorites, which basically remained primary level, and evident effect on dehydration, causing obvious decrease of water concentrations of minerals. It is possible that dehydration is stronger than hydrogen isotopic exchange equilibration under instant intensive shock.

4 Results

(1) Hydrogen isotopes hydrous phosphates in GRV99027 were measured by using ion microprobe. Their δD varies from $+1300\%$ to $+4700\%$, water contents from 0.04 wt% to 0.43 wt%. The high but variable δD values are distinctive characteristics of Martian meteorites, which have further confirmed that GRV99027 is a Martian meteorite.

(2) Comparing δD values and water concentrations of hydrous minerals of GRV99027 with those of other Martian meteorites indicates that δD values of phosphates are generally higher. The higher δD values of hydrous minerals originated from isotopic exchange of magmatic water in minerals and D-enriched Martian crustal fluids.

(3) Study on variability of δD values and water content of GRV99027 indicates that shock metamorphism had minor effect on δD values of meteoritic minerals, while dehydration- and degassing-shock metamorphism had evident effect on water concentrations of minerals of Martian meteorites.

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