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## Hydrogen Isotopes of Glassy and Phyllosilicate Spherules in Al Rais (CR) and Orgueil (CI) Chondrites

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**Abstract** The hydroxyl in phyllosilicate minerals is the most common occurrence of water in primitive meteorites. Direct hydrogen isotopic analysis of this water component using an ion microprobe has been made in some glassy or phyllosilicate spherules from the Al Rais (CR) and Orgueil (CI) chondrites. The spherules from Al Rais show large deuterium excesses ( $\delta D = +200 - +800\text{‰}$ ) relative to terrestrial standards, whereas deuterium-enrichments in the spherules from Orgueil are much smaller ( $\delta D = +40 - +130\text{‰}$ ). The phyllosilicate spherules are products of aqueous alteration of glassy precursors. In Al Rais the phyllosilicate spherules have relatively higher  $\delta D$  values than the glassy ones, indicating that water introduced during aqueous alteration was deuterium-enriched. The deuterium-enrichments in the phyllosilicate spherules from Orgueil could result from isotopic exchange under thermodynamic conditions within the solar nebula. The much larger  $\delta D$  excesses of the Al Rais spherules, however, cannot be attributed to the similar process; instead, an interstellar origin needs to be invoked.

**Key words:** isotope, hydrogen, meteorite, chondrite, ion microprobe

### 1 Introduction

It has been well established that highly deuterium-enriched materials occur in some primitive meteorites and interplanetary dust particles (IDPs) (Zinner, 1988; Messenger and Walker, 1997; Messenger, 2000; Aleon et al., 2001). Unlike the isotopic anomalies observed in presolar grains of circumstellar origin (commonly referred to as “stardust”), the large deuterium enrichments are believed to have resulted from chemical isotope fractionation in cold interstellar molecular clouds prior to the formation of the solar system (Geiss and Reeves, 1981). The preservation of these deuterium-rich materials could be used to extract important information on their evolutionary history and to gain insights into the formation of the solar system.

Most of the hydrogen in primitive meteorites is carried by organic components and phyllosilicate minerals. Organic matter can be broadly divided into an acid-insoluble component, often referred to as “kerogen”, and a soluble component. The bulk kerogen is the dominant carrier of excess deuterium in most meteorites, with  $\delta D$  values from  $\sim +1000\text{‰}$  to  $\sim +6000\text{‰}$  (Robert and Epstein, 1982; Kerridge, 1983; Yang and Epstein, 1983; Kerridge et al., 1987). From the soluble component, specific organic compounds, including individual amino acids,

hydrocarbons, and carboxylic acids, were successfully identified and analyzed for their hydrogen isotopic compositions, yielding  $\delta D$  values from  $\sim +200$  to  $\sim +3500\text{‰}$  (Pizzarello et al., 1991; Cronin et al., 1993; Pizzarello and Huang, 2004). The evidence for the existence of deuterium-rich phyllosilicate minerals, however, is more circumstantial. They come from stepwise pyrolysis of bulk meteorite samples (McNaughton et al., 1981; McNaughton et al., 1982b), and from the positive correlations between the D/H ratios and the chemical compositions ( $H_2O$ , K, Si) of unseparated mineral phases analyzed using ion microprobe (Deloule and Robert, 1995; Guan et al., 1998; Aleon et al., 2001). No direct measurement of hydrogen isotopic composition of any phyllosilicate mineral in primitive meteorites has yet been made.

Zolensky et al. (1996) observed many glassy or phyllosilicate spherules in some CI and CR chondritic meteorites. The authors concluded that these spherules might be among the most primitive objects present in the early solar system. The round phyllosilicate aggregates probably formed from aqueous alteration of pre-existing glassy spheres. Therefore, if in some primitive meteorites water is indeed another deuterium-rich carrier that has survived the formation of the solar system, these glassy and phyllosilicate spherules may represent the best candidates

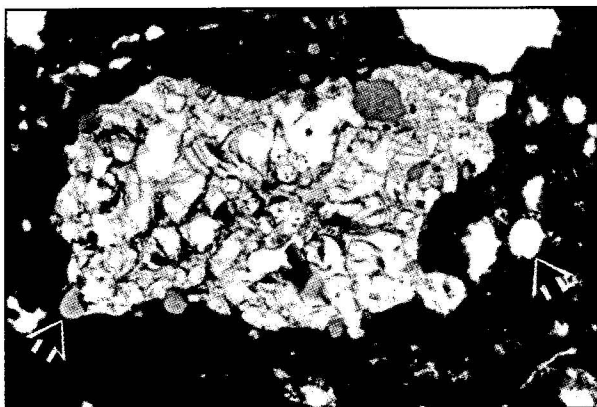


Fig. 1. Transmitted light view of glassy or phyllosilicate spherules in Al Rais.

Many of the rounded objects are shown. Two spherules sampled for this study are arrowed. The field of view is about 2.5 mm across.

for direct survey of the D/H ratios of water in meteorites. In this paper, we report the results and implications of hydrogen isotopes of these spherules.

## 2 Samples and Analytical Techniques

We studied 27 spherules from two carbonaceous chondrites: Orgueil (CI) and Al Rais (CR). Under an optical microscope, the yellow or brown spherules, generally smaller than 100  $\mu\text{m}$ , were found within or rimming chondrules, as well as scattering loosely within the matrix (Figs. 1 and 2). These spherules are particularly abundant in Al Rais. Individual spherules were selected and pressed into Au foils for subsequent examinations using scanning electron microscope (SEM), ion microprobe, transmission electron microscope (TEM), and electron microprobe.

Hydrogen isotopic analysis was carried out with the extensively modified CAMECA ims-3f ion microprobe at Washington University in St. Louis. A  $\text{Cs}^+$  primary ion beam was used to sputter negative secondary ions from the surface of the sample. Comparing with the measurement of positive secondary ions, the analysis of negative secondary ions has the advantages of higher ion yields and negligible  $\text{H}^{2-}$  interference. The negligible interference from  $\text{H}^{2-}$  enables measurements to be performed at low mass resolution, which results in an additional gain in sensitivity by about a factor of three relative to positive ion analyses. In order to further optimize sensitivity, the high magnification transfer lenses were set to produce a 75- $\mu\text{m}$  image field. D/H ratio measurements were performed in an automatic peak-jumping mode. Using terrestrial amphibole as a standard, the exact peak positions of hydrogen and deuterium were determined by averaging the magnetic field values corresponding to the half-maximum of the mass peaks. All the hydrogen isotopic measurements were made

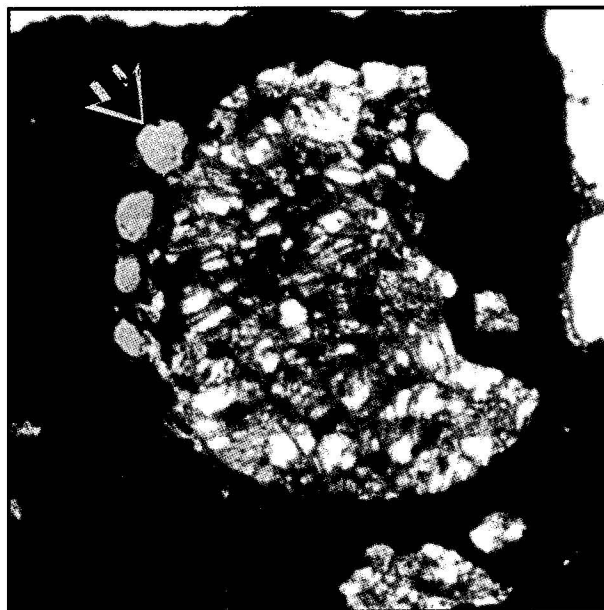


Fig. 2. Transmitted light view of glassy or phyllosilicate spherules in Al Rais.

The four spherules rimming a chondrule are shown. The one sampled for this study is arrowed. The field of view is about 1.8 mm across.

by utilizing a program that offers the option of centering both hydrogen and deuterium peaks in the middle of the exit slit of the ion microprobe. The secondary ions were detected by an electron multiplier operating in pulse counting mode, and corrected for system dead time that was determined by independent measurements on a Ti standard. The energy distribution of the secondary ions was automatically monitored during each run, and any sample charging was compensated for by offsetting the secondary accelerating voltage. To reduce background counts, which mostly come from the edge of the focused beam because the hydrogen contaminant migrates easily along the sample surface, a field aperture was used and the primary beam was defocused so that its image was slightly larger than the field aperture.

The instrumental mass fractionation ( $F$ ) is corrected by measuring an amphibole standard with known isotopic composition. Numerically, the instrumental mass fractionation is defined as:

$$F = \left[ \frac{R_m}{R_t} - 1 \right] \cdot 1000 \quad (1)$$

where  $R_m$  and  $R_t$  are the measured and true isotopic ratios of the amphibole standard, respectively.

All the isotopic ratios are reported as  $\delta$ -values, deviation (‰) from the D/H ratio of the Standard Mean Ocean Water (SMOW). The true  $\delta\text{D}$  values ( $\delta_t$ ) of samples can be calculated from their measured values ( $\delta_m$ ) and  $F$ :

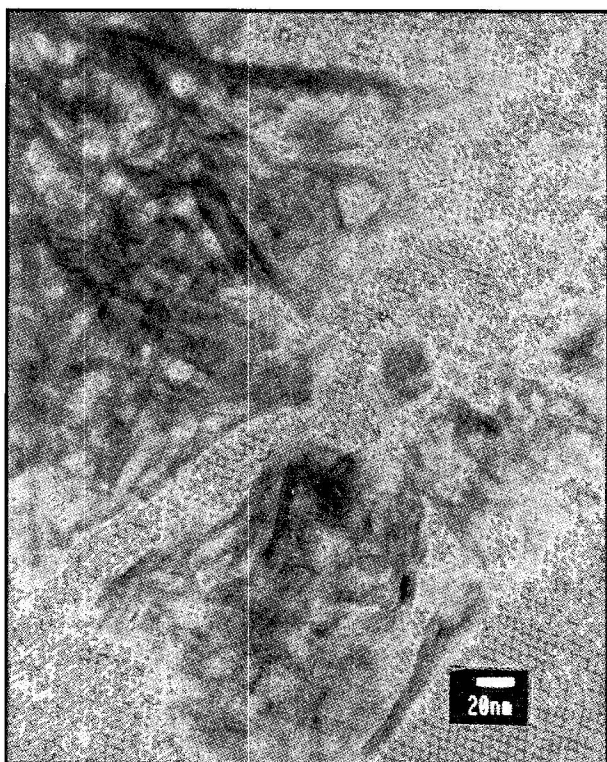


Fig. 3. TEM view of serpentine and saponite in a spherule from Al Rais.

$$\delta_t = \frac{\delta_m + 1000}{1 + \frac{F}{1000}} - 1000 \quad (2)$$

The associated total error of  $\sigma_t$  is:

$$\sigma_t = \frac{1}{1 + \frac{F}{1000}} \cdot \sqrt{\sigma_m^2 + \left(1 + \frac{\delta_t}{1000}\right) \cdot \sigma_F^2} \quad (3)$$

where  $\sigma_m$  is the counting statistics error and  $\sigma_F$  is the standard deviation of instrumental mass fractionation determined by repeated measurements of the standards.

After the isotopic measurements, the remaining samples were removed from the Au foil for subsequent TEM and electron microprobe examination. Prior to electron beam analysis, all fragments were embedded in EMBED-812 low-viscosity epoxy. We microtomed the grains only partially through the samples, leaving a potted butt for each sample appropriate for electron microprobe analysis. We observed the thin microtomed sections using a JEOL 2000FX STEM equipped with a LINK EDX analysis system, operating at 200 kV. Natural mineral standards and in-house determined k-factors were used for the reduction of compositional data, which are considered to be accurate

only to within  $\pm 6\%$  (relative). A Cliff-Lorimer thin-film correction procedure was employed (Goldstein, 1979). In the case of phyllosilicates, mineral identifications were made on the basis of both composition and electron diffraction data whenever possible.

The spherules from Al Rais and Orgueil were analyzed for major elements using a CAMECA CAMEBAX electron microprobe operating at 15 kV and 30 nA. A focused beam was used for mineral analyses. Natural mineral standards were utilized, and corrections were applied using the CAMECA on-line PAP program. These probe analyses are accurate to within  $\pm 0.5\%$  (relative).

### 3 Results and Discussion

#### 3.1 Mineralogy

In the CR chondrite Al Rais, TEM examination showed that some spherules are completely non-crystalline (glass), some consist almost entirely of serpentine with accessory saponite (Fig. 3), and some contain mixtures of non-crystalline material and phyllosilicates. The serpentine-rich spherules are remarkable in their homogeneous texture, consisting almost entirely of flaky phyllosilicates, with only a few inclusions of submicron olivine (Zolensky et al., 1996).

In the CI chondrite Orgueil, these rounded objects consist mainly of two components: (1) Rather fine-grained, flaky phyllosilicate with basal lattice spacing  $\sim 0.7$  and  $1.1$ – $1.4$  nm and compositions indicating intergrown serpentine and saponite. (2) Very poorly-crystalline ferromagnesian material with the same approximate composition as the phyllosilicate. This could be ultra-fine grained phyllosilicates damaged by the electron beam (Zolensky et al., 1996). In fact, these two materials dominate the bulk of the host CI chondrites as well (Bass, 1971; Tomeoka and Buseck, 1988). In any case, saponite clearly is predominant over serpentine in the crystalline, flaky material. Also present in the thin sections we examined were a few sub-micrometer sized grains of chromite and magnetite. These spinels are common byproducts of the aqueous alteration of ultramafic material when the resultant phyllosilicates cannot accommodate all the available Fe and Cr. In fact, with the exception of these sparse spinels, the rounded phyllosilicate objects are remarkably free of other minerals. This suggests that the precursor from which the phyllosilicates were derived was a simple, homogeneous material as well.

#### 3.2 Major chemistry

The major chemical compositions were obtained for 15 spherules of those analyzed for hydrogen isotopes (Table 1). The others were either sputtered away during ion

**Table 1** Major chemical compositions of the glassy or phyllosilicate spherules from Al Rais and Orgueil

Spherule	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	FeO	MgO	MnO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	NiO	Cr <sub>2</sub> O <sub>3</sub>	SO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	Total
ALRS-3	47.51	0.09	0.76	5.98	44.11	0.15	0.33	0.04	0.02	0.07	0.67	0.08	0.01	99.81
ALRS-4	37.31	0.10	3.66	20.15	18.77	0.18	0.21	0.06	0.20	0.33	1.42	0.44	0.04	82.87
ALRS-5	30.57	0.07	3.33	21.08	20.61	0.12	0.17	0.19	0.14	0.16	3.11	0.44	0.10	80.09
ALRS-6	36.04	0.11	3.57	21.21	21.57	0.20	0.37	0.24	0.12	0.17	1.18	0.55	0.10	85.42
ALRS-7	32.27	0.09	2.90	19.63	18.39	0.21	1.42	0.99	0.18	1.89	0.36	2.86	0.48	81.66
ALRS-8	39.46	0.08	3.00	14.17	33.41	0.16	0.24	0.15	0.09	0.14	1.08	0.16	0.08	92.24
ALRS-10	33.13	0.07	4.40	22.18	21.75	0.15	0.16	0.19	0.14	0.10	2.10	0.29	0.09	84.76
ORGL-1	34.92	0.10	1.82	17.67	16.26	n.d.	1.22	0.11	0.02	0.77	0.86	0.60	n.d.	74.36
ORGL-2	33.78	0.09	1.91	14.32	13.03	n.d.	1.21	0.08	0.02	0.66	0.28	0.50	n.d.	65.89
ORGL-3	32.90	0.05	1.72	15.39	16.10	n.d.	1.16	0.04	0.00	0.67	0.24	0.34	n.d.	68.63
ORGL-4	25.82	0.33	1.43	43.08	12.91	n.d.	0.68	0.03	0.00	0.64	0.18	0.29	n.d.	85.40
ORGL-5	31.49	0.05	1.88	25.30	14.43	n.d.	1.10	0.02	0.02	0.68	0.30	0.49	n.d.	75.77
ORGL-6	37.24	0.02	1.98	15.72	20.10	n.d.	1.21	0.02	0.01	0.67	0.30	0.41	n.d.	77.69
ORGL-7	38.02	0.03	1.99	10.95	16.55	n.d.	1.05	0.42	0.06	0.47	0.29	0.38	n.d.	70.21
ORGL-9	26.74	0.03	1.57	11.05	12.07	n.d.	0.90	0.08	0.03	0.85	0.33	0.71	n.d.	54.34

n.d. – not detected. Most of the data listed in the table are average values of 2 to 8 measurements of each spherule.

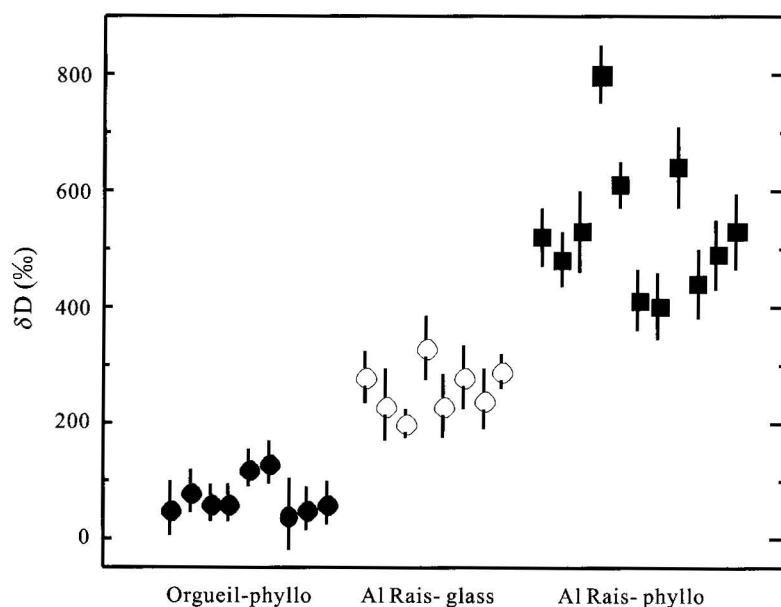


Fig. 4. Hydrogen isotopic compositions of glassy or phyllosilicate spherules in Al Rais and Orgueil.

Filled square: phyllosilicates in Al Rais; open circle: glassy objects in Al Rais; solid circle: phyllosilicates in Orgueil.

microprobe measurement, or lost during transfer and microtome processes. Most of the data listed in the table are average values of 2 to 8 measurements of each spherule.

The major chemical compositions of the phyllosilicate spherules in Al Rais are consistent with the TEM observation that they are composed mainly of serpentine with minor saponite, whereas the high total of the glass

spherule (ALRS-3) reflects its anhydrous nature.

The 8 spherules from Orgueil have relatively low cation totals, which are typical for CI meteorites, reflecting high porosity and the hydrated nature of this material. Their major chemical compositions indicate that they are a mixture of serpentine and saponite, containing minor Fe-Ni sulfides and magnetite. These electron probe data are in general agreement with the results of our TEM examination (Zolensky et al., 1996).

### 3.3 Hydrogen isotopes

A total of 27 spherules (18 from Al Rais and 9 from Orgueil) were analyzed for their hydrogen isotopic composition. The results are listed in Table 2 and plotted in Fig. 4. For each spherule, its  $\delta D$  value is an average of 2 to 7 spot analyses.

#### 3.3.1 Spherules from Al Rais

All the spherules from Al Rais exhibit clear deuterium excesses ( $\delta D = +200\text{‰}$  to  $+800\text{‰}$ ) relative to the terrestrial standard SMOW. The spherules show a larger  $\delta D$  range than that of the bulk Al Rais ( $+520\text{‰}$  to  $+690\text{‰}$ ) (McNaughton et al., 1982a; Kerridge, 1985). No hydrogen isotope data is available for organic components from Al

**Table 2 Hydrogen isotopic compositions of the spherules from Al Rais and Orgueil**

Spherule	Mineral	$\delta D_{SMOW} (‰)$	Error (2 $\sigma$ )
ALRS-2 (4)	Phyllosilicate	520	50
ALRS-4, A (4)	Phyllosilicate	480	48
ALRS-4, B (2)	Phyllosilicate	530	62
ALRS-5 (4)	Phyllosilicate	800	48
ALRS-6(7)	Phyllosilicate	610	38
ALRS-7 (6)	Phyllosilicate	410	52
ALRS-8 (2)	Phyllosilicate	400	58
ALRS-10 (4)	Phyllosilicate	640	65
ALRS-12 (2)	Phyllosilicate	440	60
ALRS-15 (2)	Phyllosilicate	490	60
ALRS-16 (2)	Phyllosilicate	530	66
ALRS-3 (5)	Glass	280	46
ALRS-9 (3)	Glass	230	64
ALRS-11 (6)	Glass	200	26
ALRS-13 (4)	Glass	330	56
ALRS-14 (2)	Glass	230	54
ALRS-17 (2)	Glass	280	56
ALRS-18 (2)	Glass	240	52
ALRS-1 (5)	?	290	30
ORGL-1 (3)	Phyllosilicate	50	46
ORGL-2 (3)	Phyllosilicate	80	36
ORGL-3 (2)	Phyllosilicate	60	34
ORGL-4 (2)	Phyllosilicate	60	34
ORGL-5 (3)	Phyllosilicate	120	32
ORGL-6 (2)	Phyllosilicate	130	38
ORGL-7 (3)	Phyllosilicate	40	47
ORGL-8 (2)	Phyllosilicate	50	38
ORGL-9 (2)	Phyllosilicate	60	38

? – unidentified. In parenthesis are numbers of spot analysis.

Rais to compare with the results from this study. The duplicate fragments from spherule ALRS-4 (A, B) give similar  $\delta D$  values of about +500‰.

Except for ALRS-1, which has little unspattered material left, all the other fragments were successfully removed from the Au foil and examined by TEM after ion microprobe analysis. Seven of them are identified as glass, while the others are phyllosilicate spherules composed mainly of serpentine with accessory saponite. Interestingly, the  $\delta D$  values (+400‰ to +800‰) of phyllosilicate spherules are higher than those (+200‰ to +330‰) of

glassy ones.

### 3.3.2 Spherules from Orgueil

The 9 phyllosilicate spherules in Orgueil have  $\delta D$  values ranging from +40‰ to +130‰ (Table 2; Fig. 4), which are much lower than those from Al Rais. The bulk values  $\delta D$  values (+170‰ to +235‰) of Orgueil (Kerridge, 1983; Yang and Epstein, 1983) are also lower than those of Al Rais (+520‰ to +690‰) (McNaughton et al., 1982a; Kerridge, 1985). Acid residues of Orgueil are characterized by high D/H ratios, with  $\delta D$  values from +400‰ to +1100‰ (Kerridge, 1983; Yang and Epstein, 1983).

### 3.4 Origin of the hydrogen isotopes in spherules

While it may be conceivable, there is no compelling evidence that hydrous minerals are present in the interstellar medium or that they could be condensed from the proto-solar nebula (Zolensky and McSween, 1988; Zolensky et al., 1993). Thus, the formation of hydrated minerals in meteorites is normally regarded as a result of aqueous alteration of pre-existing anhydrous silicates. Whether the aqueous alteration is a nebular or meteorite parent body process is a complicated and controversial topic, which is beyond the scope of this paper. Zolensky et al. (1996) interpreted the spherules in Al Rais and Orgueil as glassy, pre-accretionary objects caught in various stages of aqueous alteration. The extremely homogeneous texture of phyllosilicates supports the contention that they were derived from such a homogeneous siliceous glass, as opposed to merely a fine-grained assemblage of anhydrous, crystalline silicates.

Previous stepwise pyrolysis measurements of bulk unequilibrated ordinary chondrites revealed that the water released at 600–1000°C, which is most likely from phyllosilicate minerals, is highly enriched in deuterium (with  $\delta D$  values up to +4500‰) (McNaughton et al., 1981; McNaughton et al., 1982b; Robert and Epstein, 1982). Ion microprobe analyses of IDPs and matrix material in chondrites (McKeegan and Zinner, 1984; Deloule and Robert, 1995; Guan et al., 1998) also suggested that the hydroxyl in phyllosilicate minerals carries large deuterium excesses. The direct isotopic analysis of phyllosilicate spherules presented in this study has confirmed that they are indeed one of the deuterium-rich carriers in primitive meteorites. The large deuterium excesses (+400 to +800‰) observed in the phyllosilicate spherules from Al Rais imply that the water introduced during the aqueous alteration could be highly deuterium-enriched. The highest  $\delta D$  values (+800‰) measured in ALRS-5 may represent the lower limit for the D/H ratios of the water source.

In general, the deuterium excesses of glassy and phyllosilicate spherules observed in this study are lower



than those ( $\sim +1000\text{‰}$ ) suggested for phyllosilicates in matrix of another CR chondrite Renazzo (Deloule and Robert, 1995; Guan et al., 1998), and substantially less than the large deuterium excesses (with  $\delta D$  values up to  $\sim +4500\text{‰}$ ) suggested for phyllosilicates in the ordinary chondrites Semarkona and Bishunpur (McNaughton et al., 1981; Deloule and Robert, 1995; Sears et al., 1995). Especially, the deuterium enrichments in the phyllosilicate spherules from Orgueil ( $+40$  to  $+130\text{‰}$ ) and in the glassy ones from Al Rais ( $+200$  to  $+330\text{‰}$ ) are much smaller. There is a slight chance that organic components, which are highly deuterium enriched, might contribute to the higher  $\delta D$  values from pyrolysis and ion microprobe measurements of unseparated samples. A more plausible explanation, however, is that it merely reflects the variation of hydrogen isotopes in meteorite water, which can range from  $\sim -400\text{‰}$  to  $+4500\text{‰}$  (McNaughton et al., 1981; Deloule and Robert, 1995).

The hydrogen isotopes of the protosolar nebula are strongly depleted in deuterium ( $\delta D = \sim -870\text{‰}$ ) (Geiss and Reeves, 1981). The large hydrogen isotopic variations, especially the extreme deuterium enrichments, in meteoritic water cannot be produced by isotope fractionation at variable temperatures associated with chondrite formation in the solar nebula. McNaughton et al. (1981) first pointed out that it is conceivable that a practically "pure" sample of interstellar water has survived into the solar system. Deloule and Robert (1995) also suggested that the high  $\delta D$  values of phyllosilicate minerals in Semarkona and Renazzo could not have resulted from thermal isotopic exchange in the solar nebula, and ion-molecule reactions in an interstellar environment are presumably the only alternative mechanism. Kinetic modeling (Lecluse and Robert, 1994) indicated that in the proto-solar nebula with an overall normal hydrogen isotopic composition the  $\delta D$  values of water condensed as ice cannot exceed  $+160\text{‰}$ . The deuterium-enrichments in the glassy and phyllosilicate spherules from Al Rais analyzed in this study are clearly beyond this limit. Thus, an interstellar origin for the water in these spherules needs to be invoked. The deuterium-enrichments in the phyllosilicate spherules from Orgueil, on the other hand, are well within the range that could be produced by isotopic exchange under thermodynamic conditions within the solar nebula. However, Robert et al. (2000) pointed out that water in the solar system cannot be produced by thermal reactions in the solar nebula. Instead, it probably originated from an interstellar environment. The large  $\delta D$  variations of phyllosilicates in meteorites result from variable sampling of this interstellar water as it isotopically evolves from a high- $\delta D$  component with time and space in the nebula through progressive isotopic exchange with

protosolar hydrogen. Based on this proposition, the hydrogen isotopes of the glassy or phyllosilicate spherules from Al Rais and Orgueil reported in this study imply evolved water with variable histories in the nebula or on meteorite parent bodies. For water with large deuterium enrichments ( $> +160\text{‰}$ ), both models (Lecluse and Robert, 1994; Robert et al., 2000) require an interstellar origin, as the one suggested for the highly deuterium enriched organic components (Geiss and Reeves, 1981). From interstellar medium to their final destination in meteorites, both the water and organic components must have undergone an extremely complex journey, which is still little understood.

## 4 Conclusions

Hydrogen isotopic analysis with an ion microprobe demonstrates that the glassy or phyllosilicate spherules from Al Rais contain large deuterium excesses ( $\delta D = +200\text{‰}$ – $+800\text{‰}$ ) relative to terrestrial standards. The deuterium-enrichments in the phyllosilicate spherules from Orgueil are relatively smaller ( $\delta D = +40\text{‰}$ – $+130\text{‰}$ ).

Petrologic and TEM examination suggests that the phyllosilicate spherules from Al Rais and Orgueil were formed by aqueous alteration of pre-existing glassy precursors. Hydrogen isotopes of the glassy and phyllosilicate spherules indicate that the water introduced during aqueous alteration could be highly deuterium-enriched. While the relatively smaller deuterium excesses in phyllosilicate spherules from Orgueil could result from isotopic exchange under thermodynamic conditions within the solar nebula, the much larger deuterium enrichments of the Al Rais spherules, however, cannot be attributed to the similar process; instead, an interstellar origin needs to be invoked.

## Acknowledgements

We thank the reviewers for valuable comments. Y. Guan is grateful to G. Crozaz and the late R. Walker of the Laboratory for Space Sciences of Washington University in St. Louis for their encouragement and support for this work. M. Zolensky was supported by the NASA Cosmochemistry Program. We thank Marian Hyman for the Orgueil samples and valuable discussions.

Manuscript received June 15, 2004

accepted Aug. 31, 2004

edited by Xie Guanglian

## References

Aleon, J., Engrand, C., Robert, F., and Chaussidon, M., 2001.

- Clues to the origin of interplanetary dust particles from the isotopic study of their hydrogen-bearing phases. *Geochim. Cosmochim. Acta*, 65: 4399–4412.
- Bass, M.N., 1971. Montmorillonite and serpentine in Orgueil meteorite. *Geochim. Cosmochim. Acta*, 35: 139–147.
- Cronin, J.R., Pizzarello, S., Epstein, S., and Krishnamurthy, R.V., 1993. Molecular and isotopic analyses of the hydroxy acids, dicarboxylic acids, and hydroxydicarboxylic acids of the Murchison meteorite. *Geochim. Cosmochim. Acta*, 57: 4745–4752.
- Deloule, E., and Robert, F., 1995. Interstellar water in meteorites? *Geochim. Cosmochim. Acta*, 59: 4695–4706.
- Geiss, J., and Reeves, H., 1981. Deuterium in the solar system. *Astronomy and Astrophysics*, 93: 189–199.
- Goldstein, J. I., 1979. Principles of thin-film X-ray microanalysis. In: Hren, J.J., Goldstein, J.I., and Joy, D.C. (eds.), *Introduction to Analytical Electron Microscopy*. New York: Plenum Press, 813–820.
- Guan, Y., Hofmeister, A., Messenger, S., and Walker, R.M., 1998. Two types of deuterium-rich carriers in Renazzo matrix. *Lunar and Planetary Institute Conference Abstracts*, 1760.
- Kerridge, J.F., 1983. Isotopic composition of carbonaceous-chondrite kerogen: Evidence for an interstellar origin of organic matter in meteorites. *Earth Planet. Sci. Lett.*, 64: 186–200.
- Kerridge, J.F., 1985. Carbon, hydrogen and nitrogen in carbonaceous chondrites: Abundances and isotopic compositions in bulk samples. *Geochim. Cosmochim. Acta*, 49: 1707–1714.
- Kerridge, J.F., Chang, S., and Shipp, R., 1987. Isotopic characterization of kerogen-like material in the Murchison carbonaceous chondrite. *Geochim. Cosmochim. Acta*, 51: 2527–2540.
- Lecluse, C., and Robert, F., 1994. Hydrogen isotope exchange reaction rates: Origin of water in the inner solar system. *Geochim. Cosmochim. Acta*, 58: 2927–2939.
- McKeegan, K.D., and Zinner, E., 1984. On the distribution of excess deuterium in Renazzo and Semarkona: An ion microprobe study. *Lunar and Planetary Institute Conference Abstracts*, 534–535.
- McNaughton, N. J., Borthwick, J., Fallick, A.E., and Pillinger, C. T., 1981. Deuterium/hydrogen ratios in unequilibrated ordinary chondrites. *Nature*, 294: 639–641.
- McNaughton, N.J., Hinton, R.W., Pillinger, C.T., and Fallick, A. E., 1982a. D/H ratios of some ordinary and carbonaceous chondrites. *Meteoritics*, 17: 252.
- McNaughton, N.J., Pillinger, C.T., and Fallick, A.E., 1982b. Deuterium enrichments in type 3 ordinary chondrites. *J. Geophys. Res.*, 87(Suppl.): A297–A302.
- Messenger, S., 2000. Identification of molecular-cloud material in interplanetary dust particles. *Nature*, 404: 968–971.
- Messenger, S., and Walker, R.M., 1997. Evidence for molecular cloud material in meteorites and interplanetary dust. In: Bernatowicz, T.J., and Zinner, E.K. (eds.), *Astrophysical Implications of the Laboratory Study of Presolar Materials*. New York: AIP Press, 545–564.
- Pizzarello, S., and Huang, Y., 2004. The deuterium content of individual Murchison amino acids. *Lunar and Planetary Institute Conference Abstracts*, 1212.
- Pizzarello, S., Krishnamurthy, R.V., Epstein, S., and Cronin, J.R., 1991. Isotopic analyses of amino acids from the Murchison meteorite. *Geochim. Cosmochim. Acta*, 55: 905–910.
- Robert, F., and Epstein, S., 1982. The concentration and isotopic composition of hydrogen, carbon and nitrogen in carbonaceous meteorites. *Geochim. Cosmochim. Acta*, 46: 81–95.
- Robert, F., Gautier, D., and Dubrulle, B., 2000. The solar system D/H ratio: Observations and theories. *Space Science Reviews*, 92: 201–224.
- Sears, D.W.G., Morse, A.D., Hutchison, R., Guimon, R.K., Jie, L., Alexander, C.M.O.D., Benoit, P.H., Wright, I., Pillinger, C., Xie, T., and Lipschutz, M.E., 1995. Metamorphism and aqueous alteration in low petrographic type ordinary chondrites. *Meteoritics*, 30: 169–181.
- Tomeoka, K., and Buseck, P.R., 1988. Matrix mineralogy of the Orgueil CI carbonaceous chondrite. *Geochim. Cosmochim. Acta*, 52: 1627–1640.
- Yang, J., and Epstein, S., 1983. Interstellar organic matter in meteorites. *Geochim. Cosmochim. Acta*, 47: 2199–2216.
- Zinner, E., 1988. Interstellar cloud material in meteorites. In: Kerridge, J.F., and Matthews, M.S. (eds.), *Meteorites and the Early Solar System*. Tucson: University of Arizona Press, 956–983.
- Zolensky, M.E., Barrett, R.A., and Browning, L., 1993. Mineralogy and composition of matrix and chondrule rims in carbonaceous chondrites. *Geochim. Cosmochim. Acta*, 57: 3123–3148.
- Zolensky, M.E., Hyman, M., Rowe, M.W., and Weisberg, M.K., 1996. The origin of round phyllosilicate aggregates in CR2 and CI1 chondrites. *Lunar and Planetary Institute Conference Abstracts*, 1505.
- Zolensky, M.E., and McSween, H.Y., 1988. Aqueous alteration. In: Kerridge, J.F., and Matthews, M.S. (eds.), *Meteorites and the Early Solar System*. Tucson: University of Arizona Press, 114–143.