

## THE ISOTOPIC SIGNATURE OF HYDROGEN IN LUNAR BASALTS: SPALLOGENIC OR PRIMORDIAL?

Michel STIEVENARD\*, Jean JOUZEL\*, François ROBERT\*\*.

\* Lab. Géochimie Isotopique. CEN Saclay, DLPC, Bat. 522. 91191 Gif-sur-Yvette Cedex. France.

\*\* Lab. Géochimie Isotope Stables, Paris 7, Tour 54-64 1<sup>er</sup> étage, 2 Place Jussieu 75251 Paris Cedex 05, France.

Because of the extremely low concentration of hydrogen in lunar basalts (0.5  $\mu\text{mole/g}$ ) only one attempt has been made to determine their D/H ratio [1]. In this previous step-wise heating experiment, water and molecular hydrogen were separated and high  $\delta\text{D}$  values were found in the molecular hydrogen pyrolysed between 725 and 1000°C. In this fraction, the measured absolute deuterium concentration was in agreement with the calculated production rate of spallogenic deuterium. Therefore the following interpretation was proposed: during step-wise heating pyrolysis, the spallogenic deuterium is extracted from the rock as HD and mixed with  $\text{H}_2$  derived from the reduction of water. Because the isotopic composition of this water was essentially similar to that of the terrestrial moisture, its origin was ascribed to terrestrial contamination. The aim of the present study is to re-examine these interpretations by means of a new experimental protocol.

### I. Experimental.

Marked and recent improvements [2] of the technique developed by Robert et al. [3] has made this experiment possible. The rock sample was heated in a helium flow. Water in helium was reduced into molecular hydrogen by passing through uranium at 800°C and  $\text{H}_2$  was separated from helium by a palladium thimble at 500°C. The hydrogen leaked directly into the mass-spectrometer with no capillary between the palladium and the ion-source. Such an experimental protocol permitted detailed step-wise heating experiments (i.e. 300 temperature steps) on an absolute amount of hydrogen as low as 0.2  $\mu\text{mole}$ . This represents an improvement in sensitivity of approximately a factor of 1000 relative to other hydrogen extraction procedures. The reproducibility on the D/H ratio in rock or in gas samples was as good as obtained by routine vacuum pyrolysis techniques. The instantaneous concentration and isotopic composition of hydrogen were continuously recorded as it was progressively released from a sample while temperature increased. The data were obtained in real time and automatically processed by the computer.

Two aliquots from the basalt 70 215 were analysed. In sample (1) water and molecular hydrogen were analysed together and in sample (2) molecular hydrogen was analysed separately by keeping the uranium furnace cold. By subtracting (2) from (1), the water temperature release pattern can be calculated.

### II. Results.

Sample temperature, instantaneous hydrogen concentration and isotopic composition (expressed in  $\delta\text{D}(\text{‰})$  relative to SMOW) are reported versus the duration of the experiment in Fig. 1 and 2.

Fig. 1: At the 200°C temperature plateau, the first peak corresponds to the release of terrestrial adsorbed water. Above 200°C, the second peak is probably the remaining contribution of the non-outgassed terrestrial water fraction. The peak in  $\delta\text{D}$  (up to +300‰) at 140 min. corresponds to a slight increase in concentration superimposed to the exponential decrease of the low temperature hydrogen, indicating that a new component begins to pyrolyse.

Fig. 2: The analysis of molecular hydrogen shows that the increase in concentration of the deuterium-rich component appearing in Fig. 1 can be entirely attributed to the release of  $\text{H}_2$ . This implies that this hydrogen fraction is of lunar origin. This lunar component exhibits  $\delta\text{D}$  values up to c.a. +1000‰. The isotopic release pattern is governed by a mixing of two compounds: a low  $\delta\text{D}$  hydrogen ( $\delta\text{D} < -400\text{‰}$ ) probably resulting from the reduction of water during pyrolysis, and a high  $\delta\text{D}$  extraterrestrial hydrogen ( $\delta\text{D}$  up to +1000‰).

### III. Discussion.

Since a peak in molecular hydrogen does exist in this sample, it is no longer possible to argue that pure spallogenic deuterium is mixed with H of terrestrial origin (reduction of water into  $\text{H}_2$  during the pyrolysis). Several interpretations are possible each one of these having their own problems and consequences:

1) The [D] and [H] in the deuterium-rich  $H_2$  ( $0.5 \mu\text{mole} \cdot \text{g}^{-1}$  with a mean  $\delta D$  value of  $+450\text{‰}$ ) are  $1.5 \cdot 10^{14} \cdot \text{g}^{-1}$  and  $6.7 \cdot 10^{17} \cdot \text{g}^{-1}$ , respectively. Although not reported in the figures, it should be noted that no peak in the D/H ratio or in the hydrogen concentration appears at temperature higher than  $800^\circ\text{C}$  (up to  $1500^\circ\text{C}$ ). The [D] is quite in agreement with theoretical calculations:  $6 \cdot 10^{13} \cdot \text{g}^{-1}$  for an exposure age of  $10^8$  years [4,5]. At a first glance, the H can be supposed to be the non-reactive energetic protons implanted along with the in-situ produced D. However if one assumes that all the incoming protons ( $70 \text{H} \cdot \text{cm}^{-2} \cdot \text{sec}^{-1}$  i.e.  $2.2 \cdot 10^{17} \text{H} \cdot \text{cm}^{-2}$  for  $10^8$  years) are distributed in the first 10 cm. of depth, the spallogenic D/H ratio can be calculated:  $6 \cdot 10^{13} / (2.2 \cdot 10^{17} / 30) \approx 10^{-2}$ . This calculated isotopic ratio is in disagreement with the presently reported value: the D/H ratio in the deuterium-rich hydrogen is  $2.3 \cdot 10^{-4}$ . Consequently the lunar basalts exhibit at least 40 times too much hydrogen and it seems difficult to ascribe these H to solar or galactic energetic protons. Hence our first interpretation: primordial hydrogen, which is known to be deuterium-free ( $\delta D = -900\text{‰}$ ; [6]), is still trapped in these lavas. When this primordial component pyrolyses, the spallogenic deuterium is extracted...

2) A second interpretation is possible: the deuterium-rich molecular hydrogen represents an indigenous lunar component both for H and D. The spallogenic deuterium would not be concentrated in the molecular hydrogen but mixed with the main hydrogen fraction extracted as water from the sample. In such a case an important question remains unsolved: why is the lunar hydrogen  $+450\text{‰}$  instead of  $-900\text{‰}$  as predicted by astrophysical models?

#### References

[1]. Merlivat L., Lelu M., G. Nief & E. Roth (1976) *Proc. Lunar Sci. Conf. VII*, 649. [2] Stievenard M., Jouzel L., Merlivat L. & Javoy M. *Chem. Geol.*, **70**, 57 (1988). [3]. Robert F., Javoy M, Halbout J., Dimon B. & Merlivat L. (1987) *Geochim. Cosmochim. Acta*, **51**, 1787. [4]. Yokoyama Y. personal communication reported in [1]. [5]. Badhwar G.D. & Daniel R.R. (1963) *Prog. Theor. Phys.* **30**, 615. [6]. Gautier J. & Owen T. (1983) *Nature* **302**, 215.

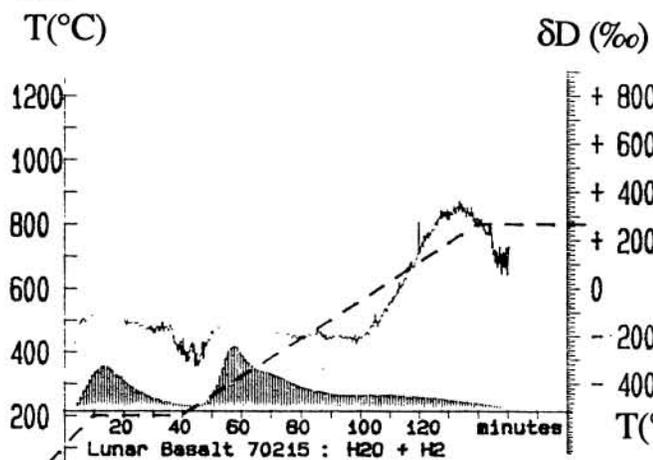


Fig. 2: Right side. Basalt 70215; 600 mg. Total molecular hydrogen:  $0.48 \pm 0.01 \mu\text{mole} \cdot \text{g}^{-1}$ ,  $\delta D = +455\text{‰}$ . See fig. 1 for units. The isotopic pattern is governed by the mixing of two components: the deuterium-rich hydrogen represents a lunar component while the deuterium depleted H is attributed to terrestrial contamination water reduced during its outgassing from the sample. The origin of these high  $\delta D$  values remains unclear: spallogenic or primordial?

