

D/H RATIO ION PROBE MEASUREMENTS ON MAGMATIC MINERALS FROM MARTIAN METEORITES : IMPLICATIONS FOR DEGASSING OF THE MARTIAN MANTLE. Etienne Deloule, CRPG-CNRS BP 20, 15 rue Notre Dame des Pauvres, 54501 Vandoeuvre-lès-Nancy Cedex France (deloule@crpg.cnrs-nancy).

### Introduction

The presence in the past of large quantities of water on the surface of Mars has been inferred from the study of valley networks and other morphological features. The identification and characterization of water reservoirs (internal and external) on Mars can also be done indirectly through petrographic and chemical studies of pre-terrestrial alteration products in the SNC meteorites. Hydrogen isotope studies indicate that Martian crustal rocks have been altered by a fluid that has exchanged with the Martian atmosphere and/or hydrosphere with

D values up to +1500 [1-3]. Investigation of the North West Africa 817 (NWA817) nakhlite [4] demonstrated that magmatic minerals have preserved their initial mantellic water contents with a D value of -170, providing information on the evolution of the Martian mantle in terms of water content and exchange. The present study provides hydrogen isotope measurements of magmatic minerals on sections from 5 other Martian meteorites: NAKLA, CHASSIGNY, ZAGAMY, the new shergotites NWA480 "Theodore Monod" [5] and NWA856 "Djel Ibone" [6]

### Experimental

**Hydrogen isotopic compositions** were measured in situ on polished sections with the Cameca IMS 1270 ion microprobe at CRPG-CNRS, Nancy. A 13 kV, 10 nA O<sup>-</sup> primary beam was focused onto the sample to a 30 μm diameter area. The secondary beam mass resolution was set at 2000, with an energy window of 55 eV, without energy filtering. Secondary ions of H<sup>+</sup>, D<sup>+</sup> and H<sub>2</sub><sup>+</sup> were measured for 20 mn each by ion-counting and peak switching. Statistical precisions ranging from ±30‰ for samples with low water contents to less than 10‰ for those with high water contents were attained. Amphibole and pyroxene standards were used to correct for instrumental isotopic fractionation, calculated as a function of the Mg number of the analyzed phases. Samples were carefully degassed before introduction in the analytical chamber. The H<sub>2</sub><sup>+</sup>/H<sup>+</sup> ratio was always below 10<sup>-3</sup>, attesting to a minimal instrumental contribution [7]. Results are given in D<sub>SMOW</sub> with a precision of 20 to 40 ‰, including the instrumental calibration uncertainty. The background level measured on terrestrial NAM standards is lower than 10 ppm of water.

**Chemical compositions** in major elements were measured with a Cameca SX50 electron microprobe at

University of Nancy 1, using 15 kV accelerating voltage and a beam current of 10 nA.

### Results

Hydrogen isotope measurements have been carried out on feldspar (Fd), pyroxene (Px), olivine (Ol) and maskelinite (Mk) on the different sections.

**Water contents** of the minerals can be roughly calculated from the H<sup>+</sup> secondary beam intensity for samples and standards. An internal standard of Px NSH12 (1200 ppm H<sub>2</sub>O, D = -72) was measured at the same time as the samples to test the hydrogen ionization yield and the stability of the instrumental calibration. The water contents of the Martian meteorite minerals were estimated to range from 400 ppm to up to 10 000 ppm, the lower values being observed for NAKLA and ZAGAMI, the higher for NWA 480. ZAGAMI and NWA 856 display a small range of water contents, from 400 to 2000 ppm and from 800 to 2400 respectively. For these two meteorites, Mk displays lower water contents than Px. CHASSIGNY display larger water contents, from 2000 to 4000 ppm. NAKLA and NWA 480 both display a large range of variation, from 200 ppm up to 8000 ppm and from 1000 ppm to 10000 ppm respectively.

Of these five meteorites, CHASSIGNY is the only one displaying systematically high water contents. This could be interpreted as resulting from terrestrial contamination, as demonstrated for sulfate by Gounelle and Zolensky [8]. In contrast, ZAGAMI and NWA 856 seem to be well preserved, with only low water contents. The

D values of NAKLA and NWA 480 need to be carefully examined due to their large range of variations.

**The δD values** measured on standard NSH12 range between -66 and -95, with a mean of -78±12, in agreement with the known value. The D values measured on the Martian meteorites range from -170 to +100, with variable distributions. NAKLA displays values from -105 to +80, with one low value of -170. Taken separately, the values measured in Ol and in Px display positive trends (figure 1) between D values and water contents, suggesting that a D rich water has been added to minerals with an initially D poor low water content. This is consistent with the high D measured in alteration phases [1-2]. NWA 856 displays a more limited range of D values, ranging from -141 to -91 in Px, with one value at -171, and from -68 to -4 in Mk. Zagami, which is comparable in water content to NWA 856, displays a

large range of  $\delta D$  values, from -88 to +67 with a single point at -136 in Px, and from -35 to +61 in Mk. In both samples, Mk displays low water contents and high  $\delta D$  values, but in ZAGAMI Px seems also to have been affected by interaction with the martian surface water. NWA 480 displays a large range of  $\delta D$  values, from -152 to +99. As shown in figure 1 the data for this sample could be interpreted as 3 end-member mixing between 1) a low  $\delta D$ , low water content volcanic pole, 2) a high  $\delta D$  martian surface water pole and 3) a low  $\delta D$  high water content pole. CHASSIGNY displays a lower range of  $\delta D$  values, from -142 to -27, which could be interpreted in the same way as NWA 480. Nevertheless, the higher  $\delta D$  values measured on CHASSIGNY are in the terrestrial range, and then terrestrial contamination can not be excluded, as already suggested [2, 8]. This could also apply for the end member 3 of NWA 480.

### Discussion and conclusion

**Surface contamination :** Possible surface contamination during sample preparation and measurement has little effect on our results (Robert and Deloule, this volume). Terrestrial alteration cannot be excluded in two cases, NWA480 and CHASSIGNY. However as already discussed for NWA 817 [4], the low  $\delta D$  value end member present in most of the samples has a too low value to result from terrestrial contamination. This end member is observed in meteorites collected as both "falls" and "finds". Thus the data on NAKLA, ZAGAMI, and NWA 856 can be interpreted as a mixture between Martian magmatic water and Martian surface water, and both end-members are still observable in NWA 480.

The preservation of a magmatic water reservoir with a low  $\delta D$  value on Mars has several implications. This low value is similar to the mean value of carbonaceous chondrites and the primitive value of Earth [9]. This shows that the Martian mantle is not completely degassed, and that the surface water had a limited interaction with the interior. This may imply that the Martian surface  $\delta D$  enrichment did not occur during the early history of the planet.

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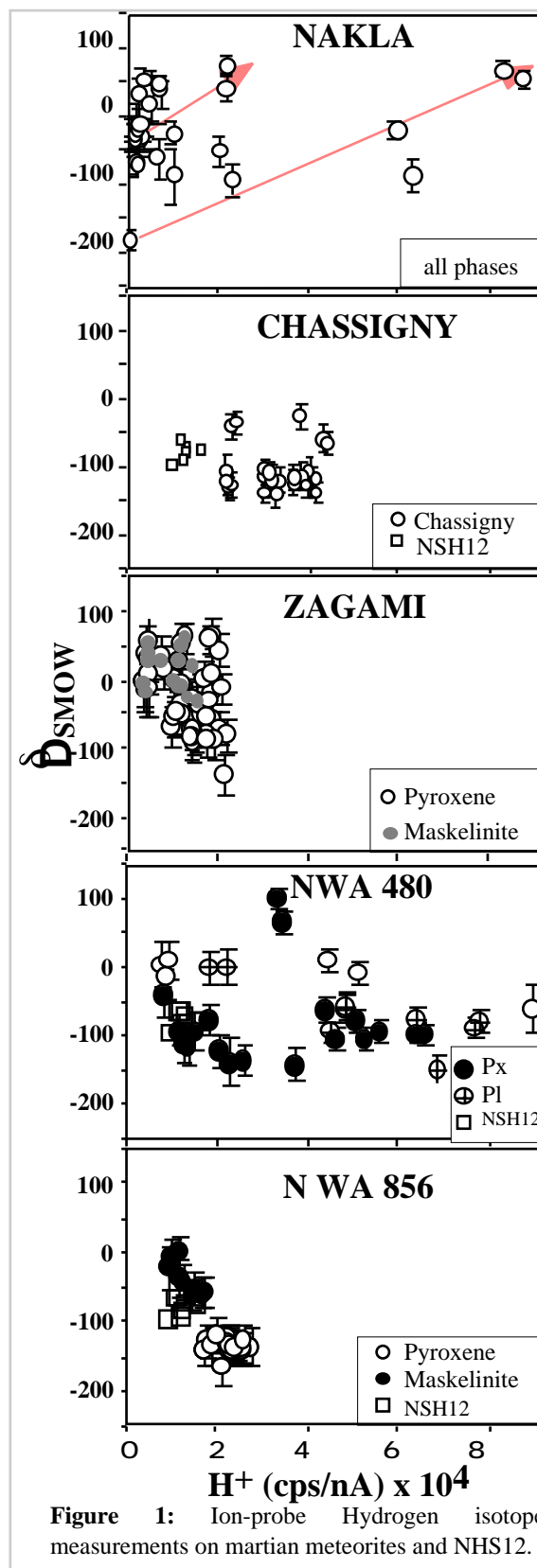


Figure 1: Ion-probe Hydrogen isotope measurements on martian meteorites and NHS12.