

RECOGNIZING THE EFFECTS OF TERRESTRIAL CONTAMINATION ON D/H RATIOS IN SHERGOTTITE PHOSPHATES. D. K. Ross¹, M. Ito^{2,3}, R. Hervig⁴, M. N. Rao¹ and L. E. Nyquist³, ¹ESCG-Jacobs Technology, 2224 Bay Area Blvd. Houston TX 77058, *Daniel.Ross@nasa.gov*. ²Lunar and Planetary Institute-USRA, Bay Area Blvd, Houston TX, 77058. ³NASA Johnson Space Center, NASA Parkway 77058. ⁴SESE-Arizona State University, Tempe AZ. 85287.

Introduction: Hydrogen isotope ratios in shergottite phosphate minerals have been investigated by SIMS in the meteorites Queen Alexandra Range (QUE) 94201 and Los Angeles. We have also collected electron probe data on these phosphates in order to characterize the phosphate minerals and attempt to document any potential hydrogen isotopic differences between chlor-apatite and whitlockite. In the section of Los Angeles we studied (748), we found both chlor-apatite and whitlockite, but in the section of QUE 94201, 38 studied, we found only whitlockite. In both meteorites, D/H ratios (expressed in units of δD_{SMOW}) vary, from terrestrial values up to $\sim 5400\%$ in QUE 94201, and to $\sim 3800\%$ in Los Angeles. We have carefully examined the ion probed pits with high-resolution FE-SEM. In most cases where the D/H ratios are low, we have identified cracks that intersect the ion probe pit. These cracks are not visible in the optical microscope attached to the SIMS instrument, making them impossible to avoid during SIMS data collection. We contend that the low ratios are a function of substantial terrestrial contamination, and that similar contamination is a likely factor in previously published studies on D/H ratios in martian phosphates. Here we highlight the difficulty of attempts to constrain the martian mantle D/H ratio using phosphate data, given that both terrestrial contamination and martian mantle hydrogen will move phosphate D/H ratios in the same direction, toward lower values. We note that our data include some of the most deuterium-rich values ever reported for martian phosphates. It is clear that some of our measurements are only minimally or totally uncontaminated, but the question arises, are intermediate values diminished because of true martian variability, or do they reflect contamination?

Hydrogen Isotopes, the Martian Atmosphere and Mantle: It is well established from previous studies (refs. 1-6) that martian phosphates in SNC meteorites show D/H ratios that extend to very high values (~ 3000 - 4800%). The widely accepted model that explains these high D/H ratios is that preferential loss of the light isotope during erosion of the atmosphere by solar-wind sputtering has left a residual hydrogen inventory substantially enriched in deuterium. Assimilation of high-D/H materials by the magmas that crystallized phosphates, or interaction between groundwaters and martian basalts has produced high D/H ratios in phosphate minerals and other phases in the basalts.

Measurements of the modern day martian atmosphere show it to be enriched in deuterium with δD_{SMOW} ratio of $\sim +4200\%$ [7, 8]. One attempt at constraining the D/H ratio of the Martian mantle [2], based on correlations between hydrogen isotopes and H₂O contents in Martian phosphates produced a suggested D/H ratio in the Martian mantle of $\sim 800\%$. This remains a matter of considerable debate, and it is clear that further work will be needed to arrive at a robust determination of the Martian mantle hydrogen isotope ratio. We suggest that the problems of terrestrial contamination, and of assimilation make it unlikely that phosphate measurements will yield accurate mantle D/H ratios, and that melt inclusion studies will be required to successfully attack this problem.

Ion probe measurements: Hydrogen isotopic analyses of phosphates in QUE 94201 and Los Angeles were performed, *in situ*, using the IMS-6f ion microprobe at Arizona State University. A Cs⁺ primary ion beam with a diameter of ~ 3 - $5 \mu\text{m}$ was used. The primary beam current was ~ 0.4 nA. Negative secondary ions of ¹H and D were measured by a single electron multiplier (EM) detector in peak-switching mode at a mass resolution of $M/\Delta M = \sim 600$. Count rates were limited in order to minimize deadtime effects on the EM. The deadtime was 42 ns, and deadtime corrections were applied to the data. An incident electron-flooding gun and carbon coat on the sample surface prevented sample charging. Instrumental mass fractionation correction was made using terrestrial standards of macusanite glasses [9] and San Carlos kaersutitic amphibole [10] with different H₂O wt % and known D/H ratios.

Ion and Electron Probe Results: Our δD_{SMOW} values in QUE 94201 range from ~ 100 to ~ 5400 and in Los Angeles they range from ~ -100 to ~ 3800 (Table 1). δD in QUE 94201 is most readily interpretable as terrestrial contamination (low values), Martian signature (high values), or a mixture of these two signals (intermediate values). Los Angeles phosphates show a bimodal distribution of δD , interpretable as terrestrial contamination (values near zero), as Martian hydrogen (values from 3400 to 3800), with two points that appear to be mixtures (~ 2500 in Cl-apatite and ~ 1800 in mesostasis). What is uncertain is whether the intermediate values in QUE 94201, ~ 700 - 1300% , reflect true Martian variation, or if they are also contaminated, and Martian variations are obscured. It is also uncertain whether the lower values in the high deuterium group

in Los Angeles, relative to the high group in QUE 94201, reflect greater terrestrial contamination in Los Angeles, or assimilation on Mars of a less-deuterium rich assimilant. We emphasize here the great difficulty in discussing Martian variations in δD in these rocks, given considerable evidence for the influence of terrestrial contamination.

Finally, we note that there are no systematic differences seen between Cl-apatite and whitlockite in our data set from the Los Angeles meteorite, although it would require a more extensive data set to fully test the issue of systematic differences between the two phosphates.

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meteorite	phase	δD	Error (2 sm)
Los Angeles	Cl-apat	3424	± 151
Los Angeles	Cl-apat	3249	± 64
Los Angeles	Cl-apat	2493	± 56
Los Angeles	Cl-apat	390	± 50
Los Angeles	whit	3820	± 168
Los Angeles	whit	3361	± 67
Los Angeles	whit	116	± 45
Los Angeles	whit	110	± 61
Los Angeles	whit	-2	± 39
Los Angeles	whit	-48	± 40
Los Angeles	whit	-92	± 41
Los Angeles	mesostasis	1844	± 114
QUE 94201	whit	5390	± 91
QUE 94201	whit	5301	± 96
QUE 94201	whit	5299	± 130
QUE 94201	whit	4583	± 103
QUE 94201	whit	3766	± 196
QUE 94201	whit	3700	± 352
QUE 94201	whit	3441	± 452
QUE 94201	whit	3377	± 219
QUE 94201	whit	1287	± 118
QUE 94201	whit	1089	± 178
QUE 94201	whit	1033	± 87
QUE 94201	whit	723	± 205
QUE 94201	whit	295	± 80
QUE 94201	whit	87	± 63

Table 2: Representative Probe Analyses of Phosphates

QUE 94201,38						
wt. %	whitlockite					
F	0	0	0.01	0.04	0	0
Na ₂ O	0.48	0.63	0.68	0.66	0.56	0.53
MgO	0.65	0.42	0.7	0.13	0.75	0.58
Al ₂ O ₃	0.08	0.04	0.08	0.55	0.02	0.04
SiO ₂	0.13	0.15	0.14	0.13	0.13	0.13
P ₂ O ₅	44.91	44.62	44.62	43.68	44.70	44.20
Cl	0	0	0	0.01	0	0.05
CaO	47.45	48.32	47.77	48.07	48.27	48.51
TiO ₂	0.02	0.01	0.05	0.02	0	0
MnO	0.27	0.29	0.21	0.32	0.24	0.25
FeO	5.74	5.77	5.62	6.14	5.1	5.52
Total	99.73	100.25	99.88	99.75	99.87	99.81
Los Angeles						
wt. %	chlor-apatite			whitlockite		
F	0.44	1.12	0.27	0.06	0	0.01
Na ₂ O	0.26	0.09	0.16	1.2	1.29	1.13
MgO	0	0	0	0.87	0.62	0.79
Al ₂ O ₃	0.01	0.06	0.02	0.05	0.04	0.02
SiO ₂	0.79	0.56	0.88	0.13	0.09	0.09
P ₂ O ₅	41.04	41.77	40.57	45.26	45.89	45.62
Cl	3.0	1.37	3.45	0.02	0.01	0.01
CaO	53.84	54.35	53.55	47.32	47.32	47.08
TiO ₂	0.04	0.04	0.05	0.01	0.03	0
MnO	0.11	0.09	0.11	0.23	0.22	0.24
FeO	1.02	1.01	0.98	4.64	5.16	4.99
Total	100.55	100.47	100.04	99.79	100.67	99.98

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