Chlorine Abundances In Martian Meteorites. D. D. Bogard<sup>1</sup>, D. H. Garrison<sup>2</sup>, and J. Park<sup>3</sup>. 1-Code KR, NASA-JSC, Houston, TX 55058 (<u>donald.d.bogard@nasa.gov</u>). 2- Barrios Technology JE23, 2224 Bay Area Blvd., Houston, TX 77058. 3-NASA-MSFC, Huntsville, AL.

Chlorine measurements made in martian surface rocks by robotic spacecraft typically give Cl abundances of  $\sim 0.1$ -0.8% (1, 2). The average Mars global surface abundance of Cl measured from orbit is estimated at 0.48% (3). In martian rocks, Cl correlates with S, and both likely were concentrated on the martian surface by volcanic emissions and in martian rocks by near-surface water interactions (1,2,4). In contrast, Cl abundances in martian meteorites appear lower, although literature data are limited, and martian nakhlites were also subjected to Cl contamination by Mars surface brines. Chlorine abundances reported by one lab for whole rock (WR) samples of Shergotty, ALH77005, and EET79001 range 108-14 ppm, whereas Cl in nakhlites range 73-1900 ppm (Table 1). Measurements of Cl in various martian weathering phases of nakhlites varied 0.04-4.7 percent and reveal significant concentration of Cl by martian brines (7).

At JSC we have performed Ar-Ar age dating of whole rock and separated mineral phases of several martian meteorites (e.g., 8,9). Neutron irradiation of these samples produce <sup>38</sup>Ar from <sup>37</sup>Cl. Although terrestrial atmospheric <sup>38</sup>Ar, trapped martian <sup>38</sup>Ar, and <sup>38</sup>Ar produced by cosmic ray interactions are also present in these samples, we previously showed how consideration of the Ar isotopic data as a function of stepwise temperature release of Ar can be used to identify these individual <sup>38</sup>Ar components (10). Briefly summarized, we adopt the <sup>36</sup>Ar/<sup>37</sup>Ar ratio (<sup>37</sup>Ar is produced in the reactor by neutron capture on Ca) measured in high-temperature Ca-rich phases as being a pure nuclear component, and subtract this ratio from measured <sup>36</sup>Ar/<sup>37</sup>Ar at all extractions to give trapped (terrestrial and martian) <sup>36</sup>Ar. For each extraction, we then multiple <sup>36</sup>Ar<sub>cos</sub> by 1.5 to obtain <sup>38</sup>Ar<sub>cos</sub> and trapped <sup>36</sup>Ar by 0.188 to obtained trapped <sup>38</sup>Ar. Subtracting these <sup>38</sup>Ar components from measured <sup>38</sup>Ar gives excess <sup>38</sup>Ar produced from Cl (<sup>38</sup>Ar<sub>Cl</sub>) for each extraction. Because this technique permits determination of  $^{38}Ar_{C1}$  with increasing temperature, and because all terrestrial and at least some martian Cl incorporated onto grain surfaces by weathering is expected to degas from the sample at lower extraction temperatures, this method permits, to some degree. separation of primary Cl indigeneous to the minerals from Cl on weathered grain surfaces. The uncertainty in these Cl abundance calculations are estimated at  $\sim 10\%$  for measuring relative abundances of <sup>38</sup>Ar in the meteorite and the co-irradiated Cl standard, and about

8% for absolute Cl in the irradiation standard (10), or  $\sim$ 18% overall.

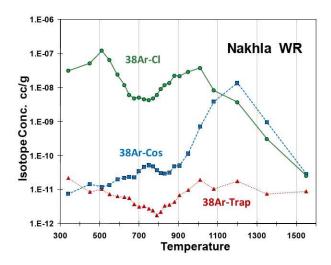
Figure 1 shows the result of using this technique to divide the temperature release of 38 Ar from Nakhla WR into three <sup>38</sup>Ar components – cosmogenic, trapped, and <sup>38</sup>Ar<sub>Cl</sub>. Because 96% of the total <sup>38</sup>Ar was produced from Cl, subtraction of minor cosmogenic and trapped <sup>38</sup>Ar do not significantly affect the calculation. For Nakhla, <sup>38</sup>Ar<sub>Cl</sub> is primarily released in two peaks centered at  ${\sim}500^{\circ}\mathrm{C}$  and  ${\sim}1000^{\circ}\mathrm{C}$ . The  ${^{36}\mathrm{Ar}}/{^{37}\mathrm{Ar}}$  ratios indicate that terrestrial Ar is released only in the first extraction (Nakhla is a fall), and thus most of this <sup>38</sup>Ar<sub>Cl</sub> is martian. Calculated total martian Cl is 268 ppm, of which 131 ppm released at higher temperature was certainly incorportated into the rock at formation, whereas 137 ppm released at lower temperature may represent Cl introduced by martian weathering. Some nakhlites, including Nakhla, are known to contain significant martian weathering phases (7), and even higher Cl reported for Nakhla (Table 1) probably represent martian weathering.

Table 1 presents Cl abundance calculations for WR and mineral separates of several nakhlites and shergottites, as well as Chassigny. The second column (total-Cl) is the total calculated Cl derived from <sup>38</sup>Ar<sub>Cl</sub>, the third column (Mars-Cl) subtracts out low-temperature Cl that is likely grain surface contamination, and the last column (% <sup>38</sup>Ar) is the percent of the total <sup>38</sup>Ar that arises from neutron capture on Cl. For most samples, these last values are >80%, and cosmogenic and trapped <sup>38</sup>Ar are relatively minor. Argon isotopic ratios for most samples show complex variability with extraction temperature, and our martian Cl values may contain some secondary martian Cl introduced by weathering.

The primary observation to be made from Table 1 is that martian meteorites contain much lower Cl that that measured in martian surface rocks and give further confirmation that Cl in these surface rocks was introduced by brines and weathering. A secondary observation is that nakhlites tend to show higher Cl than shergottites. However, this difference may, in part, be produced by greater abundance of martian weathering product in nakhlites compared to shergottites. Except for probable Cl contamination in the first few extractions, WR and Plag samples of nakhlites MIL03346 and Y-000593 each released their <sup>38</sup>Ar<sub>Cl</sub> in a single broad peak at mid-to high-

temperatures, and primary (igneous) Cl cannot be separated from secondary (retentive weathering) phases, if any is present. Much of the primary Cl in martian meteorites probably resides in phosphate minerals. This is consistent in Fig. 1 with 38Ar<sub>Cl</sub> degassing at lower temperatures than 38Arcos, which primarily resides in feldspar. During mineral separation according to magnetic properties, phosphate accompanies the feldspar, which probably explains higher Cl in most Plag separates compared to WR and pyroxene. As feldspar rarely exceeds ~30% abundance in shergottites, Cl in Plag separates probably is considerably higher than in WR. An exception is Los Angeles, where Cl in Plag is lower Data in Table 1 suggest that Cl than in WR. abundances in shergottites are typically <100 ppm, consistent with earlier literature data on three shergottites (Table 1).

It has been argued that Cl is twice as effective as water in lowering the melting point and promoting melting at shallower martian depths, and that significant Cl in the shergottite source region would negate any need for significant water (11). However, this conclusion was based on experiments that utilized Cl concentrations more analogous to martian surface rocks than to shergottite meteorites, and may not be applicable to shergottites. Lower Cl concentrations for shergottites are generally consistent with their K contents and an estimated K/Cl ratio for Mars of ~7 (5).



1) Rieder et al. 2004 Science 306, 1746; 2) Haskin et al. 2005 Nature 436, 66; 3) Taylor and Boynton, LPSC 40<sup>th</sup>. 2009. #1411; 4) Rao et al. 2009. EPSL doi:10.1016; 5) Dreibus & Wänke 1985 Meteoritics 20, 367; 6) Dreibus & Wänke 1999. MaPS 34, A33; 7) Bridges et al. 2000 EPSL 176, 267; 8) Park et al. 2009. GCA 73, 2177; 9)

Bogard et al. 2009. MaPS 44, 905; 10) Garrison et al. 2000. MaPS 35, 419; 11) Filiberto and Treiman 2009. Chemical Geology 263, 60; 12) Dreibus et al. 2006. LPSC 37, #1180; 13) Anand et al. 2006. MaPS 41, A16.

Sample Te	otal-Cl	Mars-Cl	% <sup>38</sup> Ar
Nakhla WR	286	268	96
MIL03346 WR	225	210	98.5
MIL03346 Px	29	26	65
MIL03346 Plag	847	753	34
Y-000593 WR	95	87	92
Y-000593 Px	12	11	42
Y-000593 Plag	1336	1320	99.6
NWA 998 Plag	210	180	96.4
Chassigny WR	39	38	93
Zagami FG-Plag	85	84	96
Zagami FG-cPx	24	24	84
Zagami FG-Px	27	27	88
Zagami CG-Plag	48	48	76
Zagami CG-Px	30	29	87
NWA2975 Plag	34	26	92
NWA 1460 Plag	131	126	98
NWA 3171 Plag	91	71	96
NWA 3171 Glass	54	43	92
Dho 378 Plag	30	23	84
NWA 1068 WR	16	13	89
Los Angeles WR	137	131	98
Los Angeles Px	5.2	3	52
Los Angeles Plag	6.2	5.7	66
Dag 476 Plag	26	12	90
Dag 476 Px-dk	17	12	82
Dag 476 Px-lt	18	13	92
Literature Data:			<u>References</u>
Shergotty		108	5,6,12,13
EET79001- $A$		26	
EET79001-B		48	
<i>ALH77005</i>		14	
Lafayette		100	
	876, 114.	5, 1900	
NWA 998		88	
Y-000593		101	
Y-000749	<u></u>	73	
MIL03346	24	<i>48, 156</i>	