STABLE CHLORINE ISOTOPES AND ELEMENTAL CHLORINE BY THERMAL IONIZATION MASS SPECTROMETRY AND ION CHROMATOGRAPHY: MARTIAN METEORITES, CARBONACEOUS CHONDrites AND STANDARD ROCKS. N. Nakamura1,2, L. E. Nyquist1, Y. Reese2, C-Y Shih3, T. Fujitani4 and O. Okano1. 1NASA Johnson Space Center, ARES Mail Code KR, 2101 NASA Pkwy, Houston, TX 77058, USA (noboru.nakamura@nasa.gov); 2Mail Code JE-23, ESCG/Muniz Engineering, Houston, TX 77058. 3ESCG Jacobs-Sverdrup, Houston, TX 77058. 4Marine Tech. College, Ashiya 659, Japan; 5Okayama University, Okayama 700, Japan, 6Kobe University, Nada, Kobe 657, Japan (nakamuransjp@yahoo.co.jp).

Introduction: Recently significantly large mass fractionation of stable chlorine isotopes has been reported for terrestrial and lunar samples [1,2]. In addition, in view of possible early solar system processes [3] and also potential perchlorate-related fluid/microbial activities on the Martian surface [4,5], a large chlorine isotopic fractionation might be expected for some types of planetary materials. Due to analytical difficulties of isotopic and elemental analyses, however, current chlorine analyses for planetary materials are controversial among different laboratories, particularly between IRMS (gas source mass spectrometry) and TIMS (Thermal Ionization Mass Spectrometry) groups [i.e. 1,6,7] for isotopic analyses, as well as between those doing pyrohydrolysis and other techniques [i.e. 8,9]. Additional careful investigations of Cl isotope and elemental abundances are required to confirm real chlorine isotope and elemental variations for planetary materials.

We have developed a TIMS technique combined with HF-leaching/ion chromatography at NASA JSC that is applicable to analysis of small amounts of meteoritic and planetary materials. We present here results for several standard rocks and meteorites, including Martian meteorites.

Analytical Technique: Chemical Procedures. For silicate samples, a HF-leaching method modified from that of [9] was employed in this work. Chemical steps: (1) HF-leaching and neutralization by Ca(OH)₂ slurry, (2) chlorine was converted to MgCl₂ via AgCl precipitation (3) Cl recovered as CsCl by treatment of cation-exchange resin (AG 50Wx16 200-400 mesh) and activated-charcoal. Most of the chemical steps and reagent blanks were monitored by Ion Chromatography (IC). Total blank contribution is less than 1% for most cases. The chemical yield of the first stage 1) is about 100% for most cases except for samples with low Cl contents (≤120ppm) (and higher organic materials). In those cases, the total chemical yield of Cl was about 90%. We noted that 10% or more losses of Cl was caused mainly by the difficulty of physically handling small amounts of AgCl precipitates (200-400 µg) in a dark room, but these procedures are now significantly improving.

Mass Spectrometry. Isotopic measurements were carried out by static mode using an MAT 262 mass spectrometer in a similar way (but modified in many details) to our previous work [10]. The isotopic ratio of masses 303 to 301 (133Cs²/131Cl⁴, 133Cs²/35Cl₅) was measured at intensity of 40-50mV (10⁰Ω) on the mass 301 for 15 scans/10 blocks (total 150 ratios) in 35 minutes/run. Isotopic measurements are repeated up to normally 6 to 8 runs until systematic mass fractionations (more than 0.6‰) are noted. Seawater (together with a laboratory isotope standard) were repeatedly analysed before, between and after samples.

Results and Discussion: Chlorine abundances. The IC results for step (1) for standard rocks are particularly interesting to know if the recovered Cl is representative of samples or not, and also to obtain Cl concentrations in samples if the recovery yield is 100%. In Table 1, our results are compared with those from previous works. Note that our results for all standard rocks analysed are in complete agreement with the recommended values given by [11].

Table 1. Chlorine abundances (in ppm) obtained by Ion Chromatography (combined with HF-leaching) in this work, compared with those of previous works.

<table>
<thead>
<tr>
<th>Sample</th>
<th>This work</th>
<th>Previous works*</th>
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<tbody>
<tr>
<td></td>
<td>MSID</td>
<td>NA, PA Pyro Recom</td>
</tr>
<tr>
<td>JB-1</td>
<td>185 ±13</td>
<td>166 159 175±17 152 176±18</td>
</tr>
<tr>
<td>JB-2</td>
<td>316</td>
<td>266 297 302±18 295 281±58</td>
</tr>
<tr>
<td>JB-3</td>
<td>328</td>
<td>260 336±7</td>
</tr>
<tr>
<td>JR-1</td>
<td>986 ±33</td>
<td>1008 972 992±90 920±81</td>
</tr>
<tr>
<td>AGV-1</td>
<td>138</td>
<td>156 118 119±24</td>
</tr>
<tr>
<td>GSP-1</td>
<td>364</td>
<td>273 330±24</td>
</tr>
<tr>
<td>Allende</td>
<td>336 ±22</td>
<td>372±34 237 216 223</td>
</tr>
<tr>
<td>Murchison</td>
<td>739 ±5</td>
<td>180 242</td>
</tr>
<tr>
<td>Kobe</td>
<td>257</td>
<td>261±12</td>
</tr>
<tr>
<td>Zagami</td>
<td>114±10</td>
<td>145</td>
</tr>
<tr>
<td>Nakhla</td>
<td>550±50</td>
<td>1891# 1145±9 563#</td>
</tr>
<tr>
<td></td>
<td>40</td>
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</tbody>
</table>

and Allende meteorite were calculated using [10] within cited errors. In addition, it is also noted that our results for Allende and Kobe meteorites, as well as 4 standard rocks (JB-1,-2, -3, JR-1) also perfectly agree with those of NAA and PAA results given by [8]. On the other hand, we note that CI contents in all the standard rocks and Allende obtained by HPLC/NAA/Ic determination combined with Pyrohydrolysis [6,12,13] are systematically (20±10%) lower than ours, although these data are still within the variations of recommended values of standard rocks. In any case, we strongly suggest that the recovery yield of stage (1) is 100% (with possible errors of 3-5%) and in turn that our concentration results are reasonable for those samples. The repeated analyses of Mur elected show too high CI content compared to those of previous work such as NAA results [12]. The reason is not currently clear but two possibilities (heterogeneous distributions of chlorine in Mur chison sample and/or terrestrial contamination) may be considered. Nakhla results indicate quite heterogeneous CI distribution as expected from the previous works [12].

CI isotopic compositions of meteorites and standard rocks: Definition:

\[ \delta^{37}\text{Cl}_{\text{sample}} = \left( \frac{^{37}\text{Cl}_{\text{sample}}}{^{37}\text{Cl}_{\text{SMOC}}} - 1 \right) \times 10^3 \] (SMOC: Standard Mean Ocean Chloride).

The \( \delta^{37}\text{Cl} \) values are calculated using well-established seawater value: 0.318870± 0.000062 (1σ) (for past few months). Our previous analyses for JB-1,-2, -3 and Allende meteorite were calculated using our labor atory standard (Nacalai tesque CsCl reagent) which was well established in our previous work: \( \delta^{37}\text{Cl}_{\text{SMOC}} =-2.49 \pm 0.21\% \) [10]. External (1σ) errors for mean of 6-runs were normally about 0.2‰ except for some samples mentioned later.

As shown in Fig. 1, variations of \( \delta^{37}\text{Cl} \) values for terrestrial (igneous) standard rocks are relatively limited, ranging from -1.1‰ for JB-1 to +0.5‰ for JB-3. Meteorites show much more variations in \( \delta^{37}\text{Cl} \), ranging from -1.5‰ for Allende (CV3) to +3.3‰ for Kobe (CK4). Kobe is a metamorphosed carbonaceous chondrite. It is, therefore possible that chlorine was lost during thermal metamorphism on the CK parent body, yielding to lower CI content (260ppm) and higher \( \delta^{37}\text{Cl} \). Our results for Murchison (0.5‰) and Allende (-1.5‰) are relatively similar to those reported by Sharp et al. (2008) [11] and Bonifacie et al (2007) [6] but significantly different from previous TIMS values [13]. So, the earlier suggestion [1,16] that the earlier TIMS \( \delta^{37}\text{Cl} \) values for these meteorites reported by [13] were too high is confirmed. As found in Fig. 1, most of our TIMS results for standard rocks and some meteorites are relatively similar to and/or agree well with previous IRMS results.

One of Martian igneous meteorites, Zagami (shergottite) shows low CI abundance (see Table 1) but the \( \delta^{37}\text{Cl} \) value of +0.09± 0.25‰, is in perfect agreement with seawater. This is the first case showing that one Martian sample has similar CI isotopic composition to a representative terrestrial material, seawater. In addition, our tentative results for Nakhla appears to be also similar to or not too much different from seawater. Fig. 1. Chlorine isotopic compositions obtained by TIMS in this work (full green circles), compared with those from previous works [1,13, 16]. Nakhla results are only tentative.

In conclusion, our results strongly suggest that the TIMS technique established here is potentially applicability to small quantities of planetary materials including Martian meteorites.