

STABLE CHLORINE ISOTOPES AND ELEMENTAL CHLORINE BY THERMAL IONIZATION MASS SPECTROMETRY AND ION CHROMATOGRAPHY; MARTIAN METEORITES, CARBONACEOUS CHONDRITES AND STANDARD ROCKS. N. Nakamura^{1,6}, L. E. Nyquist¹, Y. Reese², C-Y Shih³, T. Fujitani⁴ and O. Okano⁵. 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 groups [i.e. 6,8]. 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 MgCl 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 step (1) is about 100% for most cases except for samples with low Cl contents (≤ 120 ppm) (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 μ g) 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 ($^{133}\text{Cs}_2^{37}\text{Cl}^+ / ^{133}\text{Cs}_2^{35}\text{Cl}^+$) was measured at intensity of 40-50mV ($10^{11}\Omega$) 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 analyzed are in complete agreement with the recommended

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

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

*Analytical techniques and/or data sources; MSID: Mass Spectrometric Isotope Dilution [8,15]; NA: Neutron Activation Analysis and PA: Photon Activation Analysis [8]; Pyro: High Performance Liquid Chromatography combined with Pyrohydrolysis [1], NA combined with Pyrohydrolysis [12] and IC combined with Pyro [13]; Recomn: Recommended values given by [11]. #High Cl is explained as terrestrial contamination [11].

values [11] 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 Cl 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 Murchison showed too high Cl 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 Murchison sample and/or terrestrial contamination) may be considered. Nakhla results indicate quite heterogeneous Cl distribution as expected from the previous works [12].

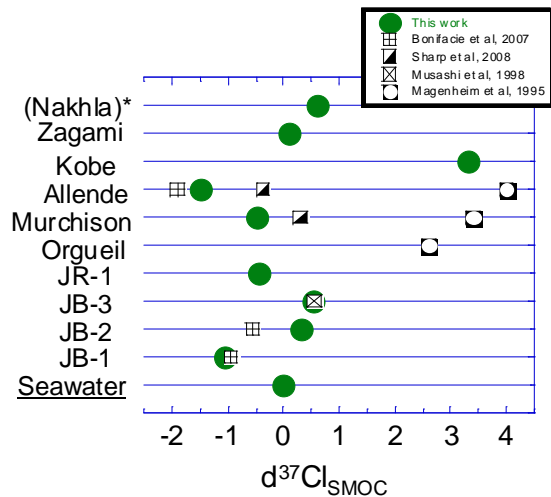
Cl isotopic compositions of meteorites and standard rocks: Definition: $\delta^{37}\text{Cl} (\text{‰})_{\text{SMOC}} \equiv \left\{ \frac{[^{37}\text{Cl}/^{35}\text{Cl}]_{\text{Sample}}}{[^{37}\text{Cl}/^{35}\text{Cl}]_{\text{Seawater}}} - 1 \right\} \times 10^3$ (SMOC: Standard Mean Ocean Chloride).

The $\delta^{37}\text{Cl} (\text{‰})_{\text{SMOC}}$ values are calculated using well-established seawater value; 0.318870 ± 0.000062 (1 σ) (for past few months). Our previous analyses for JB-1, -2, -3 and Allende meteorite were calculated using our laboratory standard (Nacalai tesque CsCl reagent) which was well established in our previous work; $\delta^{37}\text{Cl}_{\text{SMOC}} = -2.49 \pm 0.21\text{‰}$ [10]. External (1 σ) errors for mean of 6-8 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 Cl 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 (shergotite) shows low Cl abundance (see Table 1) but the $\delta^{37}\text{Cl}$ value of $+0.09 \pm 0.25\text{‰}$, is in perfect agreement with seawater value. This is the first case showing that one Martian sample has similar Cl 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.

too much different from seawater. So, no possible fluid-related [17] Cl isotope fractionations are noted. Because of unexpectedly lower Cl contents in our samples compared to previous works [12,], our isotopic analyses for Nakhla were not sufficiently successful, so further careful work is required to establish a precise $\delta^{37}\text{Cl}$ value.

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

References: [1] Bonifacie M. et al. (2008), Science 319, 1518-1520. [2] Sharp Z D et al (2010) LPSXXX #1211. [3] Nakamura N. et al. (2007) LPS XXXIII #1929 [4] Hecht M H et al. (2009). [5] Ader M et al (2008). [6] Bonifacie M. et al. (2007) Chem Geol, 242, 187-201. [7] Sharp et al. (2009), [8] Shinonaga T et al (1994) Chem. Geol. 115, 213-225; Oura Y. et al (2002) Geochem. J. 36, 295-308. [9] Musashi M. et al. (1998), Anal. Chim. Acta 362 261-269. [10] Numata M. et al. (2001), Geochem. J. 35, 89-100. [11] Imai N et al (1995) Geostandard Newsletter 19, 135-213; Gladney ES et al (1992) Geostandar Newsletter 16, 111-300. [12] Dreibus G et al (1979) Origin & Distri. Elements 33-38; Dreibus G & Wanke H. Icarus 71, 225-240. [13] Magenheim A J (1994) Geochim. Cosmochim. Acta 58, 3117-3121; EPSL 131, 427-432. [14] Sharp Z. D. et al. (2007), Nature 446, 1062-1614. [15] Fujitani T & Nakamura N (2006) Geostandard Geoanal Res 30, 113-120. [16] Sharp Z. D. et al. (2007), Nature 446, 1062-1614. [17] Sautter V et al (2006) EPSL 252, 45-55.