

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, 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 [e.g. 1,6,7] for isotopic analyses, as well as between pyrohydrolysis and other groups for elemental analyses [e.g. 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, an HF-leaching method modified from that of [9] was employed in this work. Chemical steps: (1) Chlorine was extracted by HF leaching, (2) Cl was converted to MgCl via AgCl precipitation, (3) Cl was recovered as CsCl by treatment of cation-exchange resin (AG 50Wx16 200-400 mesh). Most of the chemical steps and reagent blanks were monitored by Ion Chromatography (IC). The 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 treated for larger amounts (≥ 500 mg) and/or with higher organic materials. In those cases, the total chemical yield of Cl was about 90%. We noted that 10% or more losses of Cl were caused mainly by the difficulty of physically handling small amounts of AgCl precipitates (200-400 μ g), 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 important to knowing if the recovered Cl is representative of samples or not, and also to obtain Cl concentrations in samples if the recovery yield is shown to be 100%. In Table 1, our results are compared with those from previous work. Note that our results for all standard rocks analyzed are in agreement with the recommended values [11] within cited errors. In addition, it is noted that our results for the Allende and Kobe

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±13*	166 159	175±17	152	176±18
JB-2	316	266 297	302±18	295	281±58
JB-3	328	260	336±7		
JR-1	986±33*	1008 972	992±90		920±81
AGV-1	138	156		118	119±24
GSP-1	364	273			330±24
Allende	336±22*		372±34	237 216 223	
Murchison	739±5*			180 242	
Kobe	257		261±12		
Zagami	114			145	
Nakhla	40, 550			1890 876	
MIL03346	214			248	

*1 σ error of replicate analyses. [#]Analytical techniques and/or data sources; Mass Spectrometric Isotope Dilution [8,14]; NA: Neutron Activation Analysis and PA: Photon Activation Analysis [8]; Pyro: High Performance Liquid Chromatography combined with Pyrohydrolysis [6], NA combined with Pyrohydrolysis [12] and IC combined with Pyro [13]; Recom: Recommended values given by [11].

meteorites, as well as 4 standard rocks (JB-1,-2, -3, JR-1) also agree perfectly with 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 [6,7,12,13] are systematically (~20%) lower than ours, although these data are still within the variations of recommended values of standard rocks. In any case, we conclude that the recovery yield of stage (1) is 100% (with possible errors of 3-5%) and that our concentration results are reliable for those samples. The repeated analyses of Murchison showed Cl contents that are too high compared to NAA results [12]. The reason is not currently clear, but two possibilities are heterogeneous Cl distributions for samples from different sources, and/or terrestrial contamination may be considered. The Nakhla results indicate heterogeneous Cl distribution as expected from prior work [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 a seawater value of 0.318870 ± 0.000062 (1σ) stably measured over the past few months. Our previous analyses for JB-1, -2, -3 and the Allende meteorite were calculated using our laboratory standard (Nacalai tesque CsCl reagent). Its value was well established in our previous work: $\delta^{37}\text{Cl}_{\text{SMOC}} = -2.49 \pm 0.21\text{‰}$ [10]. External (1σ) errors for means of 6-8 runs were normally about 0.2-0.3‰ 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 -1.3‰ for JB-1 to +0.6‰ for JB-3. Meteorites show more variations in $\delta^{37}\text{Cl}$, ranging from -1.6‰ 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, producing lower Cl content (260 ppm) and higher $\delta^{37}\text{Cl}$. Our results for Murchison (-0.5‰) and Allende (-1.6‰) are similar to those reported by Bonifacie et al [6] and Sharp et al. [7], but significantly different from previous TIMS values [13]. So, we confirm the earlier suggestions [6,7] that the TIMS $\delta^{37}\text{Cl}$ values reported by [13] for these meteorites were too high. As shown in Fig. 1, most of our TIMS results for standard rocks and some meteorites are quite similar to and/or agree well with previous IRMS results.

The Zagami igneous Martian shergottite shows lower Cl abundance than the terrestrial basalts (Table 1) but the $\delta^{37}\text{Cl}$ value of $+0.09 \pm 0.25\text{‰}$ agrees with the seawater value. This is the first example of a Martian sample with similar Cl isotopic composition to representative terrestrial materials. In addition, our prelimi-

nary results for Nakhla also appear to be similar to the terrestrial seawater value. So, no possibly fluid-related [5] isotope fractionations are recognized as yet. Because of the unexpectedly lower Cl content in our samples compared to previous work [e.g., 12], the isotopic analyses for Nakhla were not sufficiently definitive, so further work is required to establish a precise $\delta^{37}\text{Cl}$ value for Nakhla.

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

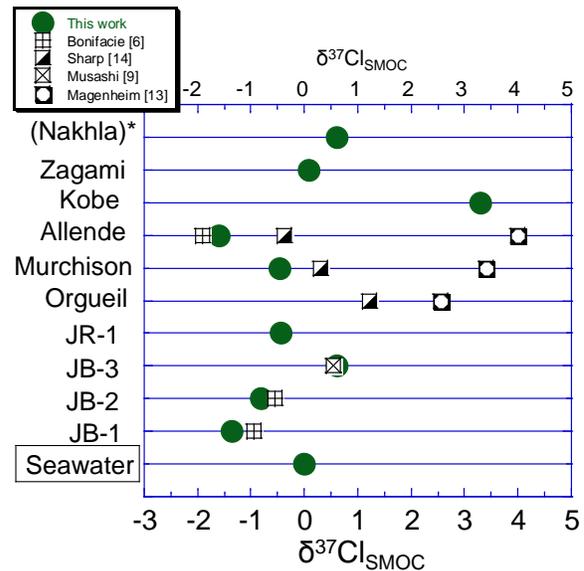


Fig. 1. Chlorine isotopic compositions obtained by TIMS technique in this work (green full circles), compared with those from previous works [1,7,13]. *Preliminary result.

References: [1] Bonifacie M. et al. (2008), Science 319, 1518-1520. [2] Sharp Z. D. et al. (2010) Science 329, 1050-1053. [3] Nakamura N. et al. (2007) LPS XXXIII Abstract #1929 [4] Hecht M. H. et al. (2009) Science 325, 64-67. [5] Ader M. et al. (2008) EPSL 269, 605-613. [6] Bonifacie M. et al. (2007) Chem. Geol., 242, 187-201. [7] Sharp Z. D. et al. (2007) Nature 446, 1062-1614. [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 Newslet 19, 135-213; Gladney E. S. et al. (1992) Geostandard Newslet 16, 111-300. [12] Dreibus G. et al. (1979) Origin & Distrib. Elements 33-38; Dreibus G. et al. (2006) LPS XXXVII #1180. [13] Magenheim (1994) GCA 58, 3117-3121; EPSL 131, 427-432. [14] Fujitani T. & Nakamura N. (2006) Geostandard. Geoanal. Res. 30, 113-120. [16] Sautter et al. (2006) EPSL 252, 45-55.