DETERMINATION OF STABLE CHLORINE ISOTOPIC COMPOSITION FOR PLANETARY MATERIALS BY TIMS

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Introduction: Light, volatile elements can be expected to have undergone significantly large isotopic mass fractionations in the early solar system recorded in present day isotopic heterogeneities. Thus, heterogeneity in the isotopic composition of Cl in planetary materials might be expected [1]. Due to analytical difficulties, however, chlorine isotope studies on planetary materials are controversial [2-4]. Also, studies on primitive and differentiated meteorites are quite limited. We have initiated development of the TIMS (Thermal Ionization Mass Spectrometry) technique at NASA JSC applicable to analysis of small amounts of meteoritic and planetary materials. We report here results for reference materials (JB-1, -2, -3, and Allende) as well as seawater and a laboratory Cl standard and discuss the consistency between TIMS and IRMS (Gass-source Mass Spectrometry) techniques.

Analytical Technique: The HF-leaching method [5] was employed and high whole chemical recovery (~90%) and low blank contribution (≤1%) of Cl were attained in this work. For the isotopic analysis by TIMS similar to [6], the sample-loading technique and data-acquisition system for the MAT-262 were also improved: Cl was loaded as CsCl (2μg Cl) on a wide Ta-filament together with fine-grained graphite powder as an emitter and $^{133}Cs_2^{35,37}Cl^+$ ions (m/z =301, 303, resp.) were measured. A well-qualified laboratory standard (CsCl reagent with $\delta^{37}Cl_{SMOC}$ =-2.49‰ [7]; $\equiv \{[^{37}Cl/^{35}Cl]_{Sample}/[^{37}Cl/^{35}Cl]_{seawater} -1\} \times 10^3$) was monitored before, between, and after the analyses of samples.

Results and Discussion: It is remarkable that stable signals (controlled to ~3E-13A) of $^{133}Cs_2^{35}Cl^+$ lasted for normally 5~8 runs (each run; 60min, 300ratios) per one-filament loading without significant fractionation. Our typical internal errors ($2\sigma_m$) for the mean $^{37}Cl/^{35}Cl$ ratios is ≤0.20‰ and external errors (1σ) is 0.2~ 0.3‰ for the past several months. The mean values of $\delta^{37}Cl$ (‰)$_{SMOC}$ were 0.32 ±0.07 (1 σ) for JB2 and 0.53 ±0.20 (1 σ) for JB3, resp. The JB3 value is in agreement with IRMS by [4] (0.55 ±0.10) within 1σ error. The JB2 value is ~0.8 ‰ higher than that of [1]. Preliminary analyses of Allende give $\delta^{37}Cl_{SMOC}$ = -1.41 ± 0.15‰ similar to -1.90 reported by [1]. A few persistent problems in chemical procedures have been recognized and should be improved for future work on smaller samples. In view of the controversial status of chlorine isotope studies among different laboratories, our TIMS data that are consistent with those of IRMS provide a possible basis for future development of advanced study of planetary materials with even lower Cl contents.

References: [1] Nakamura N. et al. 2007. Abstract #1929. 33rd Lunar & Planetary Science Conference. [2] Bonifacie M. et al. 2007. Chemical Geology 242: 187-201. [3] Bonifacie M. et al. 2008. Science 319: 1518-1520. [4] Sharp Z. D. et al. 2007. Nature 446: 1062-1614. [5] Musashi M. et al. 1998. Analytica Chimica Acta 362: 261-269. [6] Xiao Y.-K. and Zhang C.-G. 1992. International Journal of Mass Spectrometry and Ion Processes 116: 183-192. [7] Numata M. et al. 2001. Geochemical Journal 35: 89-100.