

CHLORINE ISOTOPES AS A POSSIBLE TRACER OF FLUID/BIO-ACTIVITIES ON MARS AND A PROGRESS REPORT ON CHLORINE ISOTOPE ANALYSIS BY TIMS.

N. Nakamura¹, L. E. Nyquist¹, Y. Reese¹, C-Y Shih¹, M. Numata², T. Fujitani³ and O. Okano⁴. ¹NASA JSC, Mail Code KR, 2101 NASA Parkway, Houston, TX 77058-3696, USA (nakamuransjp@yahoo.co.jp; laurence.e.nyquist@nasa.gov); ²National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki 305-8563, Japan, ³Marine Tech. College, Ashia 659-0026, Japan. ⁴Okayama University, Okayama 700-8530, Japan

Introduction: Significantly large mass fractionations between chlorine isotopes (³⁵Cl, ³⁷Cl) have been reported for terrestrial materials including both geological samples and laboratory materials [1, 2]. Also, the chlorine isotopic composition can be used as a tracer for early solar system processes [3]. Moreover, chlorine is ubiquitous on the Martian surface [4,5]. Striking variations among outcrop rocks at Meridiani were reported with some chlorine abundances as high as ~2% [6]. Characterizing conditions under which chlorine isotopic fractionation may occur is clearly of interest to planetary science. Thus, we have initiated development of a chlorine isotopic analysis technique using TIMS at NASA-JSC. We present here a progress report on the current status of development at JSC and discuss the possible application of chlorine isotopic analysis to Martian meteorites in a search for fluid- and possibly biological activity on Mars.

Chlorine Isotopic Analysis by TIMS: Mainly two techniques, gas-source isotope ratio mass spectrometry (IRMS) and thermal ionization mass spectrometry (TIMS), have currently been employed for stable chlorine isotope analysis of geological samples [1]. The IRMS technique is most precise in determining the ³⁷Cl/³⁵Cl ratio ($\pm 0.1\%$) but requires large amounts of Cl (~1 mg per analysis) and so is applied mostly to geological samples that are relatively enriched in Cl. On the other hand, the TIMS technique (precision: $\pm 0.2 \sim 0.3\%$) needs only ~2 μg Cl per analysis and has been found to be sufficiently applicable to planetary materials with a wide variety of chlorine isotopic compositions.

Current status at JSC. We have initiated development of the TIMS technique to investigate tiny amounts of planetary materials with low chlorine contents (10s to 100s of ppm). To establish the lab value for the Finnigan-MAT 262 mass spectrometer at JSC, we have carried out repeated analyses of CsCl reagent (Nacclai tesque) [2]. Chlorine "loads" of 2, 3 and 4 μg were loaded on wide (in a few cases normal, narrow) Ta-filaments as CsCl together with graphite powder [7] and subjected to repeated mass spectrometric runs. Currently, more than 100 runs (typically, 20 cycles and 20 blocks) have been carried out for more than 30

samples separately loaded. In order to test various conditions, measurements were carried out for varying intensities of $(2-5) \times 10^{-13}$ A of $\text{Cs}_2^{35}\text{Cl}^+$ ($m/z=301$) and $^{133}\text{Cs}^+$ was monitored before and after the runs. The signals increased steadily at filament currents of ~1400 mA and were thus controlled to a specific range in intensity from ~20-45mV in most cases. It was found that during filament heating, the $\text{Cs}^+/\text{Cs}_2\text{Cl}^+$ ratio changed steadily, normally from 0.9 to 1.1 and up to > 1.2 in some cases. The measured ³⁷Cl/³⁵Cl ratio correlated positively with the $\text{Cs}^+/\text{Cs}_2\text{Cl}^+$ ratio, indicating significant isotopic fractionation of chlorine occurs during the measurements. The least mass fractionation was obtained for $\text{Cs}^+/\text{Cs}_2\text{Cl}^+ \sim 0.9-1.1$. Ratios obtained for standard runs under these favorable conditions are shown in Fig. 1.

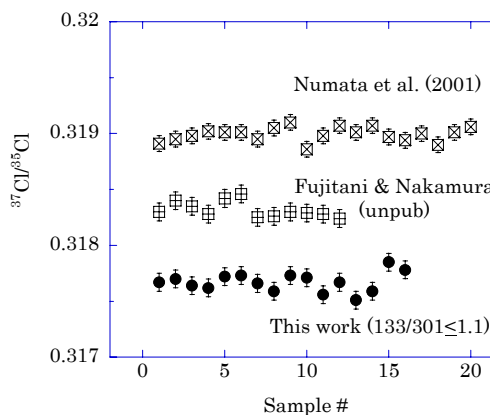


Fig. 1 Results for the CsCl reagent (Nacclai tesque) at JSC for the period 9-11/2008. Each data point represents the mean of 3 to 4 runs. The mean ³⁷Cl/³⁵Cl ratio of 0.317659 ± 0.000071 (1σ) obtained in this work is significantly (4.2% in ³⁷Cl/³⁵Cl ratio) lower than that by Numata et al. [2] and also 2.2% lower than that of Fujitani & Nakamura (unpublished).

Chlorine isotope fractionations produced by anaerobic bacteria: Using a similar TIMS technique, Numata et al. (2001; 2002b) [8,9] developed an analytical technique for chlorinated organic compounds and carried out laboratory experiments of reductive

dechlorination of chlorinated ethenes by anaerobic bacteria in order to investigate chlorine isotopic fractionations presumably produced during environmental processes [9]. In Fig. 2, the change of chlorine isotope compositions, represented by the $\delta^{37}\text{Cl}$ permil deviation of the $^{37}\text{Cl}/^{35}\text{Cl}$ ratio relative to the initial composition, for reductive dechlorination of tetrachloroethene (PCE) and trichloroethene (TCE) to cis-1,2-dechlorinoethene (cDEC) by anaerobic bacteria (Strain T, Consortium N and Consortium F) are plotted against remaining PCE. Strain T was a sulfate reducing bacterium isolated from the drainage of a laundry, Consortium F was an enrichment culture obtained from PCE contaminated soil, and consortium N was an enrichment culture from TCE contaminated soil. It is remarkable that significant chlorine isotope fractionation was observed [9]. Fig. 2 shows that Numata et al. very reproducibly measured the Cl isotopic fractionation produced in chlorinated organic compounds by anaerobic bacteria. This result is relevant to evaluating the role of bio-activities in terrestrial environments, and suggests in turn that chlorine isotopic composition potentially can be used as an indicator of fluid- and, if

present, bio-activity in planetary environments like the Martian surface.

Possible applications: There are potential applications of these results to high-Cl Martian environments. As demonstrated in [2], only a few milligrams of a halogen-rich salt vein as found in some nakhlites would provide enough Cl for an isotopic analysis. Such measurements would be impossible by the IRMS technique. Such halogen-rich veins are abundant in nakhlites, but there are other types of halogen-rich areas in other types of martian meteorites [10,11]. The scarcity of meteoritic materials to which these techniques can be applied encourages additional developments to increase their sensitivity. In view of recent discovery of perchlorate in Mars soil (NASA Science reports) and potential microbial perchlate reduction [12], large isotopic variations of stable chlorine in martian samples might be expected. Then, the Cl-isotopic composition of Martian salts may ultimately prove to be an important biomarker for possible bacterial activity in Martian surface salts.

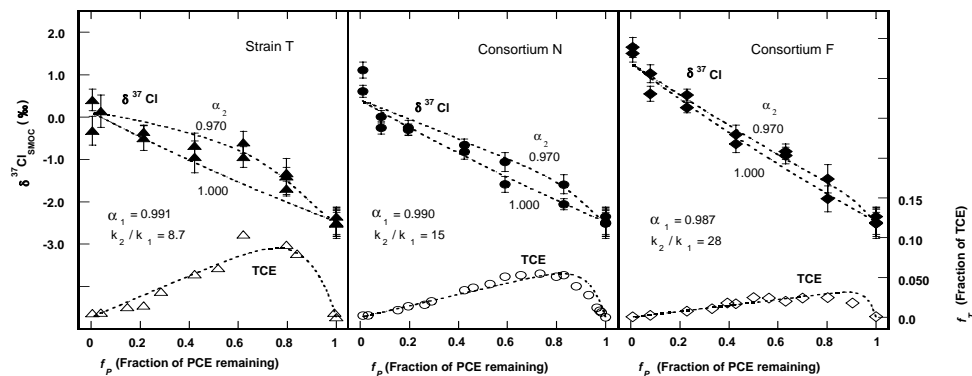


Fig. 2. Change of chlorine isotope composition ($\delta^{37}\text{Cl}$, permil deviation from the initial composition) for reductive dechlorination of tetrachloroethene (PCE) and trichloroethene (TCE) to cis-1,2-dechlorinoethene (cDEC) by anaerobic bacteria (Strain T, Consortium N and Consortium F). α_1 and α_2 represent isotopic fractionation factor for PCE and TCE dechlorination, respectively. Dotted lines represent theoretical value. The diagram was reproduced from Fig. 6 in Numata et al. (2002b) [9].

References: [1] Stewart M. A. and Spivack A. J. (2004) In “*Geochem. Non-traditional stable isotopes*” (ed Rosso J.J.), 231-254; [2] Numata M. et al. (2001) *Geochem J.* 35, 89-100. [3] Nakamura N. et al. (2007) *LPS XXX VI* #1234. [4] Haskin L. A. et al. (2005) *Nature*, 436, 66-69. [5] Keller J. M. et al. (2007) *JGR* 111, E03S08. [6] Clark B. C. et al. (2005) *EPSL* 240, 73-94. [7] Xiao Y. K. & Zhang C. G. et al (1992) *Int. J. Mass*

Spectrom. Ion Proc. 116, 183-192. [8] Numata M. et al. (2002a) *Anal. Chim. Acta* 455, 1-9. [9] Numata M. et al. (2002b) *Environ. Sci. Technol.* 36, 4389-4394. [10] Rao M. N. et al. (2005) *JGR*, 110, E12S06, doi :10.1029/2005JE002470. [11] Rao M. N. et al. (2008) *JGR* 113, E06002, doi :10.1029/2007JE002958. [12] Magali A. et al. (2008) *EPSL* 269, 605-613.