Chemical processes of zinc in aerosols inferred from the speciation and isotopic analyses

MASATOMO FUJIWARA,[1] MASAHARU TANIMIZU,[2,1]
AND YOSHIO TAKAHASHI[1*]

[1]Hiroshima University, ytakaha@hiroshima-u.ac.jp; [2]Japan Agency for Marine-Earth Science and Technology (JAMSTEC);

Supply of Zn from atmosphere to earth's surface is important considering possible deficiency of zinc (Zn) for phytoplanktons in open oceans and also toxic effects of excess Zn to various organisms in surface environment. Relative concentration of zinc (Zn) in aerosols is very high compared with the crustal abundances normalized by aluminum for other elements, showing that Zn in aerosols is originated exclusively from anthropogenic sources. In addition, Zn is largely found in finer particle fractions, since the main process of the emission is combustion in refinery factories etc. Another possible source of Zn is its emission as particles by the ablation of polyorganic materials containing zinc such as tire wears.

When Zn is provided by gaseous species into the atmosphere, finer particle of Zn in aerosol is finally formed by condensation of vapor released by the combustion, the fraction of which exhibits lighter Zn isotopic ratio enriched feature [1]. For this reason, Zn isotopic analyses may be able to quantify the contribution of Zn emitted by the volatlization. On the other hand, Zn speciation is changed in the atmosphere during long-range transport due to the reactions with water and other ligands such as sulfate and oxalate in the atmosphere. Thus, the speciation of Zn in the aerosol by X-ray absorption fine structure (XAFS) can reflect the source and behavior of Zn in the atmosphere. However, there have been no studies conducted based on both speciation and isotopic analysis for Zn in the aerosols.

In this study, aerosol samples were collected at Tsukuba, Japan. We applied XAFS to identify the speciation in the aerosols coupled with ICP-AES or ICP-MS to determine total concentration of each Zn species at each particle size. In addition, we also measured isotopic ratio of Zn using multi-collector inductively-coupled plasma mass spectrometer (MC-ICPMS; Neptune) to examine the relationship between Zn species and their isotopic ratios.

For the particles larger than 3.3 μm, ZnO and ZnS were mainly observed, which may be released from tire wear and other materials emitted originally as particles into the atmosphere. Zinc isotopic ratios in the particles are not fractionated because there is no process to induce isotopic fractionation such as volatilization for Zn when they are prduced originally as particles.

For the finer particles, main zinc species were $ZnCl_2$, Zn sulfate, and Zn oxalate. A negative correlation between zinc concentration in the atmosphere and its isotopic ratios was observed. This result suggested that most of zinc in the finer particles is anthropogenic, and that most of zinc has been emitted by the vaporization during combustion.

References

[1] N. Mattielli et al., 2009. Atmos. Environ. 43, 1265-1272.
[2] T. Furukawa and Y. Takahashi, 2011. Atom. Chem. Phys., 11, 4289-4301.

Tellurium Isotope Analysis in Sequential Acid Leachates of Carbonaceous Chondrites

YUSUKE FUKAMI[1*] AND TETSUYA YOKOYAMA[1]

[1] Department of Earth and Planetary Sciences, Tokyo Institute of Technology, fukami.y.aa@m.titech.ac.jp (* presenting author)

Nucleosynthetic isotope anomalies found in primitive chondrites give us clues for understanding the origin of materials from which our solar system has formed. Precise determination of isotopic compositions for various trace elements in meteorites now suggests heterogeneous isotopic distribution in the protosolar nebula (e.g. Cr, Ti, Mo, Ru, Sm [1-3]), yet some limited elements support isotopic homogeneity in the early solar system (e.g. Zr, Te, Os [4-6]). The inconsistent isotopic signatures would be the result of incomplete mixing and/or destruction of some "selected" presolar materials in the early solar system. To investigate this, it is important to determine the main presolar phases for individual elements that have contributed to the solar system. However, it is difficult to directly measure isotope ratios in individual presolar grains for trace elements where concentrations are at ppm level. In contrast, sequential acid leaching of bulk chondirtes enables chemical mineral separation, and it has been commonly used for detecting isotope anomalies of trace elements. Tellurium is one of the intriguing elements for the study of nucleosynthetic isotope anomalies in meteorites. It has eight stable nuclides produced by nucleosynthesis of p-process (^{120}Te), s-process ($^{122, 123, 124, 125, 126}$Te) and r-process ($^{125, 126, 128, 130}$Te). The isotopic composition of Te is also affected by the extinct nuclide of ^{126}Sn that decays to ^{126}Te with a half-life of 234.5 kyr [7]. In this study, we present preliminary data of Te isotopic compositions in acid leachates of Murchison meteorite (CM2) and Tagish Lake meteorite (C2-ung), which were subjected to the sequential acid leaching procedure described in [8] that was used for Os isotope analysis.

Te isotope analysis was performed by using thermal ionization mass spectrometry in negative mode (N-TIMS). The typical analytical reproducibility was 310 ppm for ^{126}Te/^{124}Te ratios when measured by using Faraday cups. The Te isotopic compositions in all the acid leacahtes from Murchison and Tagish Lake were not resolvable from terrestlial standard within analytical uncertainties. This is contrasting to Os isotopic results which showed larage nucleosynthetic anomalies in acid leachates of Murchison, while bulk chondrites possess no Os isotope anomalies [6, 8]. This inconsistency might indicate that dominant presolar phases carrying Te were thermally or aqueously unstable compared to those containing Os. The difference of volatility might have acted to produce not only planetary but also minral-scale isotopic homogeneity for Te, which was not the case for Os and other elements.

[1] Trinquier *et al.* (2009) *Science* **324**, 374-376. [2] Burkhardt *et al.* (2011) *EPSL* **312**, 390-400. [3] Chen *et al.* (2010) *GCA* **74**, 3851-3862. [4] Schönbächler *et al.* (2003) *EPSL* **216**, 467-481. [5] Fehr *et al.* (2006) *GCA* **70,** 3436-3448. [6] Yokoyama *et al.* (2010) *EPSL* **291**, 48-59. [7] Oberli *et al.* (1999) *Int. J. Mass. Spectrom.* **184**, 145-152. [8] Reisberg *et al.* (2009) *EPSL.* **277**, 334-344.