

Evaluation of in-house metallic standard for siderophile elements using fs-LA-ICPMS

T.D. YOKOYAMA*, T. IMAI², Y. UCHIYAMA²,
T. SUZUKI³, T. YOKOYAMA¹, M. TAKEYAMA⁴,
E. TAKAHASHI² AND T. HIRATA¹

¹Dept. Earth and Planet. Sci., Kyoto Univ., Kyoto 606-8502, Japan

(*correspondence: yokoyama@kueps.kyoto-u.ac.jp)

²Dept. Earth and Planet. Sci., Tokyo Ins. Tech., Tokyo 152-8551, Japan

³IFREE, Japan Agency for Marine Sci. and Tech., Yokosuka 237-0061, Japan

⁴Dept. Metallurgical Engin., Tokyo Ins. Tech., Tokyo 152-8551, Japan

Siderophile elements were preferentially distributed into the metallic phase or metallic core during the planetary formation sequence. Abundance data for siderophile elements can provide key information concerning the chemical evolution of metallic core or metallic phase in the meteoritic parent. However, precise determination of the siderophile elements in the metallic samples have been retarded by the analytical difficulty mainly due to poor analytical precision or sensitivities achieved by the conventional laser ablation-ICP-mass spectrometry[1]. However, most of commercially available standard materials for elemental analysis does not cover many siderophile elements. To overcome this, we have prepared the in-house calibration standard material of Fe-Ni metal for determination of siderophile elements using femtosecond laser ablation ICP-mass spectrometry. The in-house metallic standard was prepared through arc melting technique from a mixture of high purity Fe, Ni and 20 siderophile and chalcophile elements powders, and heating treatment to minimize the elemental heterogeneity. The nominal concentrations of trace elements were 150 $\mu\text{g/g}$. The resulting metal button was subsided to evaluation of major and trace element abundance using EPMA and the fs-LA-ICPMS. The abundance data for both the major elements and trace elements revealed that the abundance for trace elements did not vary measurably within the analytical precisions achieved here. In this precision, we will present the abundance data. In this presentation, we will present the abundance data for several iron meteorites to comparing the previously reported value. Availability of in-house metallic standard for meteoritic metals will be discussed in this presentation.

[1] Hirata and Kon (2008) *Anal. Sci.*, **24**, 345-353.

Effect of oxidation state on arsenic and selenium incorporation into calcite

Y. YOKOYAMA* AND Y. TAKAHASHI

Hiroshima University, Hiroshima 739-8526, Japan

(*correspondence: yoshiyuka@hiroshima-u.ac.jp)

The influences of oxidation state on arsenic (As) and selenium (Se) coprecipitation with calcite were evaluated with the information of their oxidation states both in water and calcite, and thermodynamic stability in water. To assess these reaction quantitatively, As and Se distribution coefficients (K_d) into calcite were determined using reproducible experimental system of their partition at low precipitation rates such as in natural systems.

The XAFS measurements showed that calcite selectively incorporated pentavalent As (arsenate) rather than trivalent As (arsenite)[1], and tetravalent Se (selenite) was selectively incorporated rather than hexavalent Se (selenate). Molecular geometries of dissolved selenite and selenate are similar to that of arsenite and arsenate, respectively. However, there was no relationship in their incorporation behavior into calcite. Interestingly, the XANES analysis detected arsenate and selenite in calcite precipitated only from arsenite or selenate spiked systems, respectively. Moreover, our cyclic voltammetric measurement observed arsenate stabilization in solution containing calcium ion indicating the shift of arsenite/arsenate redox boundary. These phenomena are associated with high stability of calcium arsenate and calcium selenite complexes compared with those for arsenite and selenate, respectively. Considering the abundance of calcium in natural water, the valence change effects by calcium is important as a (geo)chemical reaction which may have been overlooked so far. Hence, we conclude that the factor controlling incorporation behavior of As and Se into calcite is the stabilities of their complexes with calcium ion. These thermodynamic properties should be explained by quantum chemical approaches. In view of the valence change effects by calcium, ratios of their net K_d into calcite were determined at pH ~7: $K_{\text{As(V)}}/K_{\text{As(III)}}$ was >2500 and $K_{\text{Se(IV)}}/K_{\text{Se(VI)}}$ was 150.

Immobilization of As and Se with calcite in groundwater are of great interest for remediation of contaminated drinking water such as in Bangladesh and for inhibition of ⁷⁹Se migration from nuclear waste repositories, respectively. Therefore, the present findings should provide some insights into those concerns because As and Se oxidation states are variable in subsurface environment.

[1] Yokoyama *et al.* (2009) *Chem. Lett.* **38**, 910-911.