Improved Pd-Ag isotopic systematics by MC-ICP-MS

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The short-lived ^{107}Pd-^{107}Ag radiogenic decay system has been used to date volatile depletion, crystallization and shock in meteorites. Palladium is siderophile with a condensation temperature (T_c) similar to Fe-metal alloy, while Ag is chalcophile with T_c several hundred degrees lower. The contrasting characteristics allow Pd-Ag data to provide chronologic information on early solar system processes complementary to that provided by other long- and short-lived systems.

Early Pd-Ag measurements by thermal ionization mass spectrometry (TIMS) yielded the first internal isochron for high Pd/Ag Group IVA iron meteorites [1]. Because Ag has only two isotopes, however, the inability to correct for instrumental mass bias limited precisions in ^{107}Ag/^{109}Ag by TIMS to 10-20 ε units (parts in 10,000). Over the past decade, our group refined a technique for MC-ICP-MS measurements of Ag isotopic composition by Faraday cup using added Pd to correct for mass bias [2,3]. External precision for tens of ng of Ag initially was ±1.3 ε, which allowed resolution of the ^{107}Pd decay contribution to the Ag isotopic compositions in low Pd/Ag iron meteorites and pallasites. Subsequent use of wet plasma, instead of desolvation, produced more constant mass bias of Ag relative to Pd, yielding precisions of ±0.5 ε, and showed Pd/Ag correlated with Ag isotope compositions in carbonaceous chondrites, but also many epsilon units of natural Ag mass fractionation effects in ordinary chondrites. [3,4]

To measure low Ag abundances (100s of pg) in volatile depleted irons, we used simultaneous collection of Ag isotopes by ion multipliers on the Nu Plasma MC-ICPMS. Mass bias was corrected by comparison with Ag standards without added Pd. Although precision was only ±10 ε, a precise solar system initial ^{107}Pd/^{108}Pd of 2.8(±0.3) x 10^{-5} was obtained from the Group IVA iron Muonionalusta by assuming that the Pd-Ag system closed at its ^{207}Pb-^{206}Pb date (4565.3±0.1Ma). Pd-Ag systematics indicated the interval between volatile depletion and crystallization in the IVA parent body was short, <0.5Ma, suggesting that volatile depletion occurred during planetesimal breakup[5].

[1] Chen *et al*, GCA, 1990. [2] Carlson *et al*, 2001 GCA. [3] Schönbächler *et al*, Mass Spec Ion Proc., 2007 [4] Schönbächler *et al* GCA 2008. [5] Horan *et al*, EPSL 2012.

Reduction process of Cr(VI) by Fe(II) and humic acid using high-time resolution XAFS analysis

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The reduction of Cr(VI) to Cr(III) starts immediately when Cr(VI) is released in the soil. However, Cr(VI) species have high mobility in subsurface soil, so the behavior of Cr (VI) released in the soil is not well understood. In this study, we clarified the detailed initial reduction process at high time resolution.

Three kinds of samples were prepared, 1) Fe(II) pellet, 2) humic acid (HA) pellet, 3) Fe(II)-HA pellet which contributed to Cr(VI) reduction in soil, and then they were spiked with Cr(VI) solution. In order to estimate the initial reduction process of Cr(VI) in samples, we continuously observed the valence of Cr and the concentration of Cr(VI) in samples after spiking Cr(VI) solution by measuring consecutively by Quick X-ray absorption fine structure (QXAFS) for several hours.

The decrease of concentration of Cr(VI) was observed for all samples just after Cr(VI) was spiked to samples. However, the reduction of Cr(VI) with Fe(II)-HA experiment showed reduction process unlike both Fe(II) and HA experiment, because of HA could also reduce Fe(III) to Fe(II). 97 % of total Cr(VI) was reduced to Cr(III) in 140 min. There were three phases of reduction processes. Firstly, there was an immediate sharp decrease of concentrations of Cr(VI), which means rapid reduction reaction. And then, the concentration of Cr(VI) gradually decreased. Thereafter, the concentration of Cr(VI) decreased sharply again, the reduction reaction was rapid. In the first phase, Cr(VI) was rapidly reduced by both Fe(II) and HA. In the second phase, Cr(VI) was mainly reduced by Fe(II). In the third phase, Cr(VI) was reduced by Fe(II), which was reduced by HA. The reduction reaction became rapid again due to increase of Fe(II). We clarified that the initial reduction process consisted of three phases, and Fe(II) and HA do different contribution to reduction of Cr(VI) in each phase.

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