Development of high precision Cr-Ti stable isotope measurements for extra-terrestrial materials.

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Introduction: Extra-terrestrial materials have highly variable ⁵⁴Cr/⁵²Cr and ⁵⁰Ti/⁴⁷Ti that do not follow mass-dependent fractionation. These variations are considered to reflect nucleosynthetic heterogeneities, possibly resulting from the incomplete and/or impermanent mixing of nuclides from different nucleosynthetic sources (e.g., 1-2). In recent years, these variations have become powerful tools for tracing astrophysical environments of early solar system (e.g., 3-4). They also provide important information about the genetic relationship between the planetary materials especially when the two isotope systems are combined (5). Here, we report the first sequential chemical separation procedure for high-precision Cr and Ti isotopic ratio measurements of extra-terrestrial rocks. We also measured Cr stable isotope compositions of the silicate samples processed through the new chemical separation scheme by thermal ionization mass spectrometry (TIMS).

Results & Discussion: Both Cr and Ti were successfully purified for standard rock samples basalt (JB-1b; 15-50 mg) and Juvinas (~20 mg) monomict non-cumulate eucrite using a new four-stage column chromatographic procedure. All the dissolved silicate samples were dried down, and re-dissolved in 2 mL of 6 M HCL for the first step of column chemistry. In the first step, Fe was separated from most elements including Cr and Ti using AG1-X8 anion exchange resin. The recovery rates in this step were 97-100% for Cr, ~100% for Ti, and 0% for Fe, respectively. In the second step, Ti-fraction was separated from Cr-fraction, and matrix elements like Ca were removed using AG50W-X8 cation exchange resin modifying the Ni separation procedure developed by (6). The recovery rates were 89-100% for Cr, 89-92% for Ti and 0% for Ca, respectively. In this step, Ti was about 43-66% left in the Cr-fraction, and Cr was about 1% left in the Ti-fraction. In the third step, Cr-fraction from the second step was further separated from Ti-fraction and purified for most matrix elements (V, Na, Mn, Mg, Na, Sr etc.) using AG50W-X8 cation exchange resin. The recovery rates in this step were 89-100% for Cr, 97% for Ti and 0% for most matrix elements. In this step, Ti and V were removed from the Cr-fraction, and about 1% of Cr and V left in the Ti-fraction. In the last step, Ti-fractions from the second step and the third step were combined, and the Ti-fraction was further purified for V and Cr. This chemical separation follows the procedure using TODGA resin described by (7). The recovery rates in this step were 97% for Ti, and 0% for Cr and V. These steps decrease the problematic isobaric interferences to be sufficiently low: 56 Fe/ 52 Cr, 51 V/ 52 Cr and 49 Ti/ 52 Cr in Cr fraction were as low as 7.09×10^{-6} , 7.75×10^{-8} and 4.05×10^{-7} , respectively. The Cr stable isotope analyses yielded ε^{54} Cr = 0.16 ±0.22 (2SE) for JB-1b and ε^{54} Cr = -0.48 ±0.25 (2SE) for Juvinas. The reliability of the method was verified by the result that ε ⁵⁴Cr value for geostandard JB-1b is identical to that of Cr standard within the uncertainties. Furthermore, the ε^{54} Cr value of Juvinas eucrite is identical within analytical uncertainty to the previous reported value (ϵ^{54} Cr = -0.71 ±0.12 (2SE); (8)). The sequential chemical separation scheme developed here allows us to extract Cr and Ti from basaltic samples with fewer steps than those in the previous study (e.g., 7,9) and with high recovery rates (>80% for all steps). We will apply the method to various extra-terrestrial materials for better understanding of the origin and evolution of the solar system.

References: (1) Trinquier et al. (2009), (2) Qin et al. (2011), (5) Warren, (2011), (6) Yamakawa et al. (2009), (7) Zhang et al. (2011), (8) Trinquier et al. (2007), (9) Schiller et al. (2014)

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