

Chemical separation of Cr and Ti from a single digest for high precision isotope measurements of planetary materials

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Introduction: Extra-terrestrial materials have highly variable chromium-54 and titanium-50 anomalies 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 phases (CAIs, pre-solar spinel, etc.) including nuclides from different nucleosynthetic sources (e.g., 1-2). Moreover, these anomalies could be produced by spallation reactions on target elements like Fe during irradiation by galactic cosmic-ray exposure since the samples were near the surface of its parent body or existed as small isolated fragments in space (e.g., 3-5). Hence, for determining original isotopic composition, caution should be taken to interpret data for mineral phases with high Fe concentrations and significant cosmic ray exposure ages. Chromium-54 and titanium-50 isotope compositions provide important constraints on the genetic relationship between the planetary materials especially when the two isotope systems are combined (6). However, almost all Cr-Ti isotope data reported in the previous studies were obtained from different fragments of the same meteorite (or meteorite group). This becomes serious problem especially for samples having great internal isotopic variations such as carbonaceous chondrites and ureilites (7). Sequential chemical separation and isotope measurements of Cr and Ti in a single fraction of planetary materials is indispensable not only for understanding the astrophysical environments of early solar system but also for identifying the accretionary carrier phases that contribute to these anomalies. Here, we report the first sequential chemical separation procedure for high-precision Cr and Ti isotopic ratio measurements of extra-terrestrial rocks.

New chemical separation procedures: For the high precision determination of Cr and Ti stable isotope compositions using TIMS and/or MC-ICP-MS, the chemical separation and purification of Cr and Ti from other matrix components are required to avoid matrix effects as well as polyatomic and isobaric interference during the measurement. Problematic isobaric interferences in Cr and Ti isotope analyses are from ⁵⁰Ti, ⁵⁰V, and ⁵⁴Fe on ⁵⁰Cr and ⁵⁴Cr and from ⁴⁶Ca, ⁴⁸Ca, ⁵⁰V and ⁵⁰Cr on ⁴⁶Ti, ⁴⁸Ti and ⁵⁰Ti, respectively. Hence, these elements i.e., Fe, V, Ti, Cr, must be efficiently separated using a high recovery separation procedure. Both Cr and Ti were successfully purified for a terrestrial basalt standard (JB-1b: 50 mg), a terrestrial peridotite standard (JP-1: 10 mg), Allende (~5 mg) carbonaceous chondrite (CV) and Juvinas (~10 mg) non-cumulate eucrite using a new three-stage column chromatographic procedure. The procedure comprises three steps: (i) Fe removal using AG1-X8 anion exchange resin; (ii) Ti separation using AG50W-X8 cation exchange resin; (iii) Cr separation using AG50W-X8 cation exchange resin. 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 and Ti, and 0% for Fe, respectively. In the second step, Ti was separated from Cr-fraction, and purified for V. This chemical separation follows the procedure using TODGA resin described by (8). The recovery rates in this step were 93-100% for Ti, 96-100% for Cr and 100% for V (0% V in Ti-fraction). In the last step, Cr-fraction from the second step was further purified for matrix elements (V, Na, Ca, Mn, Mg, Al, Sr etc.) using AG50W-X8 cation exchange resin. This chemical separation is based on the procedures by (9-12). The recovery rates in this step were 88-96% for Cr, and 0% for other matrix elements. These steps decrease the problematic isobaric interferences to be sufficiently low: ⁵⁶Fe/⁵²Cr, ⁵¹V/⁵²Cr and ⁴⁹Ti/⁵²Cr in Cr fraction were as low as 7×10^{-6} , 8×10^{-8} and 4×10^{-7} , respectively. ⁴⁴Ca/⁴⁷Ti, ⁵¹V/⁴⁷Ti, and ⁵²Cr/⁴⁷Ti in Ti fraction were as low as 6×10^{-4} , 5×10^{-4} and 1×10^{-4} , respectively.

Cr and Ti isotopic ratio measurements: We have measured Cr and Ti isotope compositions of the silicate samples processed through the new chemical separation scheme. Cr isotopic data were acquired using a Thermo Finnigan *Triton-plus* thermal ionization mass spectrometer (TIMS) at the National Museum of Nature and Science. The analytical method is the same as that used by (9). The sample size of 3 µg Cr was loaded onto the filament, mixed with 3 µL of silica gel-boric acid-Al type activator (9) per filament. Cr isotopic ratios are calculated relative to a Cr standard (9) after internal normalization to reference ⁵⁰Cr/⁵²Cr ratio (13) using an exponential law. Ti isotopic data were acquired using a Thermo Fisher Scientific *Neptune-plus* (MC-ICP-MS) operated in high-resolution mode (M/ΔM > 9000) at the University of Tokyo. The samples were introduced into the mass spectrometer via an Aridus-II desolvating nebulizer using Ar as sweep gas with N₂ gas flow. Ti

solution yielded a ^{48}Ti signal of ~ 100 V/ppm. Ti isotopic ratios are calculated relative to an NIST 3162a Ti standard after internal normalization to reference $^{49}\text{Ti}/^{47}\text{Ti}$ ratio (14) using an exponential law.

The Cr and Ti stable isotope analyses for Juvinas eucrite yielded $\epsilon^{54}\text{Cr} = -0.62 \pm 0.02$ (2SE) and $\epsilon^{50}\text{Ti} = -1.34 \pm 0.13$ (2SE). These values are identical within analytical uncertainty to the previous reported values ($\epsilon^{54}\text{Cr} = -0.71 \pm 0.12$ (2SE); (2) and $\epsilon^{50}\text{Ti} = -1.25 \pm 0.05$ (2SE); (15)). The Ti isotope analyses for two different fractions of Allende carbonaceous chondrite yielded distinctive $\epsilon^{50}\text{Ti}$ values of 3.31 ± 0.18 and 6.54 ± 0.21 (2SE), respectively. The Cr stable isotope analyses for Allende are still ongoing. The $\epsilon^{50}\text{Ti}$ values of the Allende two fractions are different from the previous reported value ($\epsilon^{50}\text{Ti} = 5.01 \pm 0.29$ (2SE); (16)), exceeding the range of the error. If we assume that these variations are caused by uneven distribution of CAIs having a highly elevated $\epsilon^{50}\text{Ti}$ value of 9.14 ± 0.22 (2SE) (16), one fraction of $\epsilon^{50}\text{Ti} = 3.31 \pm 0.18$ can be explained by 2 wt% addition and the other fraction of $\epsilon^{50}\text{Ti} = 6.54 \pm 0.21$ can be explained by 12 wt% addition of CAIs to the CI chondrite composition (17), respectively. The reliability of the whole analytical method was verified by the result that $\epsilon^{54}\text{Cr}$ and $\epsilon^{50}\text{Ti}$ values for geostandard JB-1b and JP-1 are identical to those of Cr and Ti standards within the uncertainties.

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 studies (2-5 steps for each element extraction; e.g., 8-11) and with high recovery rates (~ 90 -100% for all steps). We will apply this method to various extra-terrestrial materials including samples with great isotopic heterogeneities for better understanding of the origin and evolution of the solar system.

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