

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

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Introduction: Nucleosynthetic ^{54}Cr and ^{50}Ti anomalies in meteorites and their components have become powerful tools for tracing astrophysical environments of solar system formation (e.g., Trinquier et al., 2009; Qin et al., 2010). They also provide important information about the genetic relationship between the planetary materials especially when the two isotope systems are combined (Warren, 2011). Here, we report the sequential chemical separation procedure for high-precision Cr and Ti isotopic ratio measurements of planetary materials, about which we reported preliminary results last year. We also measured Cr and Ti isotope compositions of the separated samples by thermal ionization mass spectrometry (TIMS) and multiple collector-inductively coupled plasma mass spectrometry (MC-ICPMS), respectively.

Results & Discussion: Our new separation procedure comprises three steps with additional one step of Ti-purification only for samples having high Cr/Ti as well as Ca/Ti: (i) Fe removal using AG1-X8 anion exchange resin; (ii) Ti separation using TODGA resin; (iii) Cr separation using AG50W-X8 cation exchange resin; and (additional) Ti purification using AG1-X8 anion exchange resin. We applied this new method to chemically diverse silicate samples, including terrestrial basalt (JB-1b) and peridotite (JP-1), Juvinas basaltic eucrite, Allende carbonaceous chondrite, and NWA 6704 ungrouped achondrite. Following digestion with HF-HNO₃, samples were dried down and re-dissolved in 6 M HCl for the first step of column chemistry. In the first step, Fe was separated from most elements including Cr and Ti. The recovery rates for Cr and Ti were 96-100% for all studied samples. In the second step, Ti was separated from Cr-fraction based on the procedure described by (Zhang et al., 2011). The recovery rates for Cr and Ti were 95-100% for all studied samples. Prior to the third step, we controlled the temperature and acid concentration of sample fractions recovered from the second step so that Cr(III) remains the dominant species in the acid, on the basis of the protocol of (Larsen et al., 2016). In the third step, Cr was purified from matrix elements. The recovery rates of Cr were 97-100% for JB-1b, 91% for JP-1, 83-100% for Juvinas, 95% for Allende, and 88-91% for NWA 6704, respectively. In the additional step, Ti was further purified from matrix elements, including Ca and Cr. The recovery rates for Ti were >98% for all samples including JP-1, Allende and NWA 6704. All these steps decrease the problematic isobaric interferences to be sufficiently low: $^{48}\text{Ti}/^{52}\text{Cr}$, $^{49}\text{Ti}/^{52}\text{Cr}$, $^{51}\text{V}/^{52}\text{Cr}$, and $^{56}\text{Fe}/^{52}\text{Cr}$ in Cr fraction were $<5 \times 10^{-7}$, $<6 \times 10^{-7}$, $<7 \times 10^{-8}$, and $<2 \times 10^{-6}$, whereas $^{44}\text{Ca}/^{47}\text{Ti}$, $^{51}\text{V}/^{47}\text{Ti}$, and $^{52}\text{Cr}/^{47}\text{Ti}$ in Ti fraction were $<4 \times 10^{-5}$, $<2 \times 10^{-4}$, and $<2 \times 10^{-4}$, respectively. The reliability of the method was verified by the results that $\epsilon^{54}\text{Cr}$ and $\epsilon^{50}\text{Ti}$ values for geostandard JB-1b ($\epsilon^{54}\text{Cr} = 0.00 \pm 0.16$, $\epsilon^{50}\text{Ti} = 0.05 \pm 0.36$) and JP-1 ($\epsilon^{54}\text{Cr} = 0.04 \pm 0.15$, $\epsilon^{50}\text{Ti} = -0.06 \pm 0.24$) are identical to those of Cr and Ti standards within analytical uncertainty. The combined ^{54}Cr and ^{50}Ti results revealed that Allende carbonaceous chondrites ($\epsilon^{54}\text{Cr} = 0.87 \pm 0.19$, $\epsilon^{50}\text{Ti} = 3.51 \pm 0.22$) and NWA 6704 ($\epsilon^{54}\text{Cr} = 1.27 \pm 0.16$, $\epsilon^{50}\text{Ti} = 2.03 \pm 0.43$) are characterized by excesses in neutron-rich isotopes, while Juvinas eucrites (n=5, $\epsilon^{54}\text{Cr} = -0.66 \pm 0.22$, $\epsilon^{50}\text{Ti} = -1.28 \pm 0.08$) are characterized by their depletion compared to the standards. These results are consistent with the previously published datasets, and further reveal isotopic variations in Allende carbonaceous chondrites. The external reproducibilities achieved here were ± 22 ppm and ± 8 ppm for Cr and Ti, respectively, which are markedly smaller than isotope variation among planetary materials (Cr $\sim 2 \epsilon$, Ti $\sim 7 \epsilon$). Hence, the new

sequential separation method for combined ^{54}Cr and ^{50}Ti analyses in the same sample sets will enable us to assess the nature of proto-planetary disk across multiple scale sizes from planetary-scales down to mm-scales.

Keywords: Nucleosynthetic isotope anomalies, Chemical separation, TIMS, MC-ICPMS