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A Chemical Separation and Measuring Technique for Titanium Isotopes for Titanium Ores and Iron-Rich Minerals

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Abstract: Ti-isotope fractionation on the most Ti-rich minerals on Earth has not been reported. Therefore, we present a chemical preparation and separation technique for Ti-rich minerals for mineralogic, petrologic, and economic geologic studies. A two-stage ion-exchange column procedure modified from the previous literature is used in the current study to separate Ti from Fe-rich samples, while cx-TiO_2 does not require chemical separation. Purified solutions in conjunction with solution standards were measured on two different instruments with dry plasma and medium-resolution mode providing mass-dependent results with the lowest errors. $^{49/47}$TioL-Ti for the solution and solids analyzed here demonstrate a range of >5%o far greater than the whole procedural 1 error of 0.10%0 for a synthetic compound and 0.07%0 for the mineral magnetite; thus, the procedure produces results is resolvable within the current range of measured Ti-isotope fractionation in these minerals.

Keywords: Ti-isotope fractionation; magnetite; rutile; multi-collector ICP-MS

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1. Introduction

A significant volume of literature has focused on robust means to separate and measure titanium isotope fractionation in extraterrestrial materials, with studies starting the late 1970s and progressing to today [1-6]. Titanium isotopes in these materials have been demonstrated experimentally and directly to span a large range of isotopic space in non-mass-dependent (>98%o [7,8] and mass-dependent fractionations [4,9-12]. More recently, these techniques have been used to fingerprint terrestrial processes through the analysis of whole-rock sedimentary, igneous, and metamorphic materials, where the amount of Ti fractionation is significantly less (in the order of 2-3%0) [6,11,13-16].

The focus of this contribution is to develop a method for Ti ores as a means to apply Ti-isotope geochemistry to Ti-rich minerals. Surprisingly, no comprehensive work exists documenting Ti-isotope compositions for common Ti-bearing rock-forming minerals, such as rutile (cx-TiO_2), ilmenite ((FeTi)iO_3), or (titano)magnetite. From an economic geology perspective, monitoring the Ti-isotope composition of these phases could provide a means to understand the hydrothermal and magmatic processes associated with the concentration of titanium in minerals and the formation of Fe-Ti oxide ore deposits. From a petrological perspective, titanium concentrations in magnetites and the presence/absence of rutile and ilmenite are foundational to ore-deposit and igneous-rock classifications, respectively. These phases are geochemically less diverse than whole rocks and silicate minerals in extraterrestrial materials, and thus pose fewer problems during the chemical purification process, since they lack most of the rock-forming elements that can cause isobaric interference with several of the Ti masses.

Here, we present a combination of the previously established chemical separations of Fe and Ti and apply them to the Ti-rich minerals magnetite, ilmenite, and rutile. The mass-dependent results using ^{46}Ti, ^{47}Ti, and ^{49}Ti represent the quality and reliability of the measurements. The methods for measuring Ti isotopes on a multi-collector ICP-MS are also explored. Thus, the document provides purification and measurement strategies modified from several different sources to apply Ti-isotope geochemistry to Ti-rich ores.

2. Materials and Methods

2.1. Sample Preparation and Ion-Exchange Chromatography

Several materials were prepared to be chemically processed through ion-exchange chromatography. Magnetite, an the Fe-Ti oxide compound from VWR, an Alfa Star ICP-MS standard solution, and several rutile crystals from Magnet Cove provided by the Carnegie Museum Hillman Hall of minerals (CM3218) were used. The minerals were powdered and sieved to silt-sized particles to aid in dissolution. A dried aliquot of the ICP-MS titanium concentration solution standard was also processed as a means to monitor potential titanium-isotope fractionation in the resins. Four other reference standards were used during the study: the in-house standard developed by the University of Chicago Origins Lab at 1000 ppm [13,17], NIST 3161A 1000 ppm (also reported in [2,5]), High-Purity Standard (HPS) lOppm (cat no 10-62-4-100, lot# 20009813-100), and ARISTAR 1000 ppm (Lot# J2-T102102R). All data were presented relative to the OL-Ti standard [3,6,13].

A total of 50 milligrams of mineral powder was dissolved in 4 ml of ultrapure acid (3:1 proportion of 10 molar HCl to 15.2 molar HNO_3) at 80 °C for at least 8 h. All acids were purchased from J.T. Baker and were certified ultrapure reagents. Before drying for chromatography, a 0.1 mL aliquot was removed for concentration analysis and yield checks on the columns. Concentration data were also measured on column calibrations described below, where every 2 ml fraction of the eluted column solutions was analyzed (Figure 1). Concentration measurements for these minerals and solutions from the chromatography were conducted on ICP-OES instruments at PSU and Juniata College, respectively. For both instruments, In was used as an internal check for all solutions.

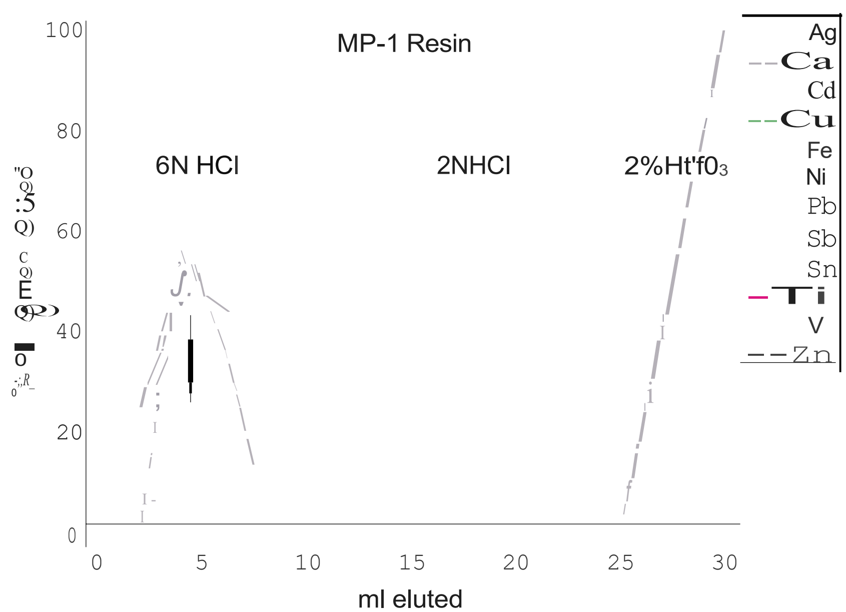

Figure 1. Plot showing the elution flux as a percentage of the cumulative solute at each elution step for the MP-1 resin.

Solutions from magnetite, rutile, and the Alfa Star ICP-MS standard were dried and processed through a 2-stage column procedure. In the first column, Fe was removed from the matrix through the use of a MP-AG-1 Bio-Rad resin, 200-400 mesh, HCl form. The column setup was identical to that in [18,19], where 1.6 to 1.8 mL of resin was loaded onto a 10 mL Bio-Rad polypropylene column. The resin was cleaned with 10 mL of ultrapure water (18 0), 10 mL of 0.5 molar HNO3 acid, and 6 mL of 6 molar HCl. The sample was loaded onto the resins as 2 mL of 6 molar HCl and 8 mL of 6 molar HCl. These 2 mL and an additional 8 ml were collected because Ti does not appreciably adhere to resin, as evidenced in the column calibration (Figure 1). However, this solution required further purification because Ca and other major cations also pass through the resin during this step. The Fe was retained on the resin and could be collected using the 2-molar HCl elution shown on the calibration.

The second column step isolated Ti from Ca and other unwanted ions in the matrix (Figure 2) using the TODGA prepacked column by Eichrom. Most Ti-separation techniques use these resins with complex silicate-dissolved mineral matrices. These column purification steps were conducted under vacuum in a 24-sample vacuum box. Flow rates were monitored to maintain a sub-1 ml-per-minute drip rate. This protocol was identical to that used in [12,16], where the resin was first cleaned with 10 mL of ultrapure water (18 0), 10 mL of 3 molar HNO_3, and 10 mL of 12 molar HNO_3. The sample was loaded in 10 mL of 12-molar HNO_3 and the matrix was eluted with the next 10 mL of 12-molar HNO_3. The Ti fraction was collected in 10 mL of nitric acid +1% ultrapure hydrogen peroxide.

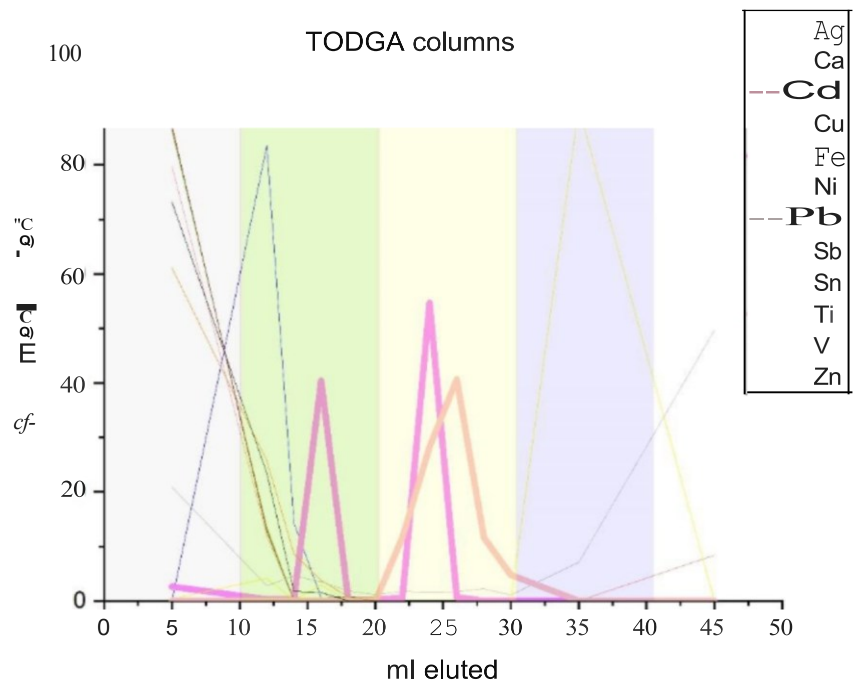

Figure 2. Plot showing the elution flux as a percentage of the cumulative solute at each elution step for the MP-1 resin. The changing colors indicate different acids eluted from the resin to purify the samples (from right to left, 12 molar nitric acid +sample, 12 molar nitric acid rinse, 12 molar nitric acid with 0.1%H2O2, and 2 molar nitric acid).

The importance of using this two-stage column procedure for Fe-rich Ti ores is that only using the TODGA resin does not eliminate all of the Fe. As seen in Figure 2, in samples with elevated Fe, Fe breaks through in multiple elutions of the profile. Significantly, 40% of the total Fe in magnetite elutes with the Ti. Given the masses that were loaded, the total Fe in the Ti aliquot would be several orders of magnitude greater than the total Ti. In this