

**MICROBEAM TITANIUM ISOTOPIC ANALYSIS BY RESONANCE IONIZATION MASS SPECTROMETRY;** D. R. Spiegel<sup>1</sup>, M. J. Pellin<sup>2</sup>, W. F. Calaway<sup>2</sup>, J. W. Burnett<sup>2</sup>, S. R. Coon<sup>2</sup>, C. E. Young<sup>2</sup>, D. M. Gruen<sup>2</sup>, A. M. Davis<sup>1</sup> and R. N. Clayton<sup>1</sup>, <sup>1</sup>Enrico Fermi Institute, University of Chicago, Chicago, IL 60637, <sup>2</sup>Materials Science Division, Argonne National Laboratory, Argonne, IL 60439.

The importance of isotopic anomalies in refractory inclusions in meteorites is well established. Measurements of the anomalies using conventional mass spectrometry are often rendered difficult, however, by isobarically interfering isotopes: for example, <sup>48</sup>Ti and <sup>48</sup>Ca. Resonance ionization mass spectrometry (RIMS) can substantially reduce isobaric interferences in a number of systems. We have employed RIMS for the *in situ* detection of Ti atoms sputtered from pure Ti metal and from several terrestrial oxides containing both Ti and Ca. Tunable lasers were employed to resonantly ionize neutral Ti atoms. We have chosen Ti specifically because of the importance of Ti isotopic anomalies in cosmochemistry.

Our experiments were carried out on the Surface Analysis by Resonance Ionization of Sputtered Atoms (SARISA) apparatus, a laser-based, time-of-flight (TOF) secondary neutral mass spectrometer, at Argonne National Laboratory [1]. To achieve highly selective photoionization of Ti, three tunable wavelengths were generated using XeCl excimer-pumped dye lasers.

Figure 1 shows the TOF spectrum obtained for 3-color resonance ionization of Ti sputtered from a Ti metal sample. The signal was averaged for 10 sec at a laser-pulse repetition rate of 23 Hz. The mass resolution ( $M/\Delta M$  for <sup>48</sup>Ti at FWHM) is about 130. Laser intensities at all three wavelengths were sufficient to saturate the Ti ionization. With the stability and sensitivity achieved using saturating intensities, we obtain better than 1% precision for Ti isotope measurements on Ti metal in under ten minutes of acquisition time.

The driving force for the use of a RIMS apparatus in *in situ* geochemical analyses is the strong enhancement of the detection of the analyte over isobarically interfering species. The enhancement is quantified by the selectivity, defined (for detection of X in the presence of isobarically interfering Y, where X and Y can be either atomic or molecular species) as  $S(X|Y) = (X_{\text{signal}}/[X])/(Y_{\text{signal}}/[Y])$ , where [X] and [Y] are molar concentrations in the sample. The selectivity is never infinite due to nonresonant ionization of isobarically interfering species, and will in general depend on the ionization scheme employed. Figure 2 shows mass spectra obtained from perovskite (CaTiO<sub>3</sub>) by secondary ion mass spectrometry (SIMS) and by RIMS using two different ionization schemes. A comparison of the relative Ti and Ca signals in the SIMS and RIMS spectra dramatically illustrates the advantages of the 3-color RIMS technique. Furthermore, the selectivity  $S(\text{Ti}|Ca)$  is clearly superior in scheme #2, which was used for all subsequent experiments.

The selectivity can be different for different matrices. We have measured the selectivities of Ti in the presence of Ca in three oxides: perovskite, sphene (CaTiSiO<sub>5</sub>) and hibonite (CaAl<sub>12-2x</sub>Ti<sub>x</sub>Mg<sub>x</sub>O<sub>19</sub>; our sample contained 1.2 at% Ti). Using scheme #2 to resonantly ionize Ti emitted from these oxides, we find selectivities of  $100 \pm 20$  (perovskite),  $200 \pm 40$  (sphene) and  $600 \pm 150$  (hibonite).

In Table 1 we show measurements of Ti isotope ratios in perovskite, sphene and hibonite, as well as pure Ti metal. The results are typically based on one minute of data acquisition time; substantial improvements in precision are observed for longer averaging times. The ratios of <sup>46</sup>Ti, <sup>47</sup>Ti, <sup>49</sup>Ti and <sup>50</sup>Ti to <sup>48</sup>Ti were normalized to terrestrial values [2] with no correction for mass fractionation. The data display a strong odd-even effect in which the even isotope ratios (<sup>46</sup>Ti/<sup>48</sup>Ti, <sup>50</sup>Ti/<sup>48</sup>Ti) are much closer to their expected value than the odd isotope ratios (<sup>47</sup>Ti/<sup>48</sup>Ti, <sup>49</sup>Ti/<sup>48</sup>Ti). This odd-even effect is not observed in nonresonant ionization of the same samples in the same apparatus, thus indicating that this effect is due to the resonant ionization process itself. Odd-even RIMS effects have been reported previously for Mo and Sn [3] and were attributed to differing ionization cross-sections for odd- and even-mass isotopes due to hyperfine structure and isotope shifts [4]. We are at present carrying out studies on the wavelength dependence of isotope ratios to address this question for Ti. It is clear that isotopic standards must be employed in RIMS measurements of isotopic abundances.

Our results show that a comprehensive understanding of laser ionization of sputtered species is crucial in the application of sputter-initiated RIMS to geochemical problems. In the present case, the selectivity of Ti over Ca can be improved with a judicious choice of ionization scheme, and is different for different matrices. Strong Ti isotopic odd-even effects also occur, probably due to hyperfine structure and isotopic shifts. Since standards can always be employed, such effects need not deter RIMS searches for isotopic anomalies. The mass resolution and sensitivity reported here show that time-of-flight RIMS can indeed be used to provide isotopic data for the important case of Ti in refractory oxides, and the selectivity obtained in hibonite quantitatively demonstrates the unique advantages provided by RIMS in isotopic analysis.

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**References:** [1] C. E. Young, M. J. Pellin, W. F. Calaway, B. Jørgenson, E. L. Schweitzer and D. M. Gruen (1987) *Nuclear Instruments and Methods* B27, 119. [2] F. R. Niederer, D. A. Papanastassiou and G. J. Wasserburg (1985) *GCA* 49, 835. [3] W. M. Fairbank, Jr., M. T. Spaar, J. E. Parks and J. M. R. Hutchinson (1989) *Phys. Rev. A* 40, 2195. [4] P. Lambropoulos and A. Lyras (1989) *Phys. Rev. A* 40, 2199.

Table 1. Ti isotopic compositions in terrestrial materials.  
 $\delta^{46}\text{Ti} = (R/R_{\text{std}} - 1) \times 1000$ , where  $R = {}^{46}\text{Ti}/{}^{48}\text{Ti}$ ;  
 $\delta^{47}\text{Ti}$ ,  $\delta^{49}\text{Ti}$  and  $\delta^{50}\text{Ti}$  are defined similarly.  
 Uncertainties are  $\pm 2\sigma$ .

Material	$\delta^{46}\text{Ti}$	$\delta^{47}\text{Ti}$	$\delta^{49}\text{Ti}$	$\delta^{50}\text{Ti}$
Perovskite	$39 \pm 11$	$354 \pm 23$	$475 \pm 17$	$-1 \pm 24$
Hibonite	$-5 \pm 29$	$240 \pm 26$	$483 \pm 25$	$41 \pm 48$
Sphene	$-2 \pm 22$	$303 \pm 13$	$425 \pm 14$	$10 \pm 20$
Ti metal	$-15 \pm 9$	$325 \pm 4$	$448 \pm 4$	$-17 \pm 8$

Fig. 1 (right). 3-color RIMS mass spectrum from Ti metal. Note that the Ti isotope peaks from 46 to 50 are well resolved.

Fig. 2 (below). Comparison of SIMS and two 3-color RIMS mass spectra of perovskite from Magnet Cove, Arkansas.

