

Measurement of isotopic ratios by resonance ionization mass spectrometry in the presence of optical isotope shifts

R. K. Wunderlich*, G. J. Wasserburg, I.D. Hutcheon and G.A. Blake

Division of Geological and Planetary Sciences, California Institute of Technology, California, CA 91125, *Physikalisches Institut Universität Augsburg, W-8900 Augsburg, FRG

ABSTRACT: The effect of optical isotope shifts on Os and Ti isotopic ratio measurements by resonance ionization mass spectrometry has been investigated. Conditions with regard to laser bandwidth and intensity and the reproducibility of laser wavelength setting have been evaluated which allowed Os and Ti isotopic ratios to be obtained with an accuracy better than 0.4%.

1. INTRODUCTION

The determination of isotopic ratios by Resonance Ionization Mass Spectrometry (RIMS) requires a thorough characterisation of laser induced isotope effects. Besides the widely discussed odd-even effects (Fairbanks et al.1989,Lambropoulos et al.1989, Payne et al. 1991, Wunderlich et al 1992 a,b) there have also been reports of laser induced shifts in even-even isotopic ratios (Joung et al.,1990 Miller et al.1990). Both effects complicate the application of RIMS to accurate measurements of isotopic ratios in geo- and cosmochemistry (Spiegel et al. 1992).

In this study we focus on the effects of the optical isotope shift (IS) on the measurement of even-even isotope ratios of Os and Ti in order to evaluate the conditions which allow the measurement of isotopic ratios by RIMS with high accuracy.

2. WAVELENGTH TUNING EFFECTS AND MASS FRACTIONATION

In the presence of optical isotope shifts the ionization efficiency of different isotopes depends on parameters such as laser bandwidth and intensity the atomic absorption width and the size of the IS. This results in a dependence of measured isotopic ratios on the precise laser wavelength tuning and intensity. By precise we mean that measured isotope ratios may change on a scale smaller than the laser bandwidth with laser tuning. In addition, mass spectrometric analyses are always characterized by pure mass fractionation which cause a shift in measured isotopic ratios as compared to the isotopic abundances present in the sample. This pure mass fractionation can be corrected by the application of a fractionation 'law':

$$R_{ijM}^{ij} \times f(\alpha) = R_{ijS}^{ij}$$

where R_{ijM}^{ij} is the measured ratio of ion currents at masses i and j , R_{ijS}^{ij} is the isotope ratio in a reference standard and $f(\alpha)$ is an empirical function of the form $(1 + n\alpha)$, $(1 + \alpha)^n$ or $\exp(n\alpha)$ with $n=i-j$. If at least two isotopes in the sample, i and j , are of known standard abundance the mass fractionation per mass unit, α , can be determined from measurements of R_{ijM}^{ij} . Pure mass fractionation is characterized by a constant, mass independent α . In order to obtain accurate isotopic ratios from RIMS measurements it is thus important to separate the shifts in isotopic ratios originating from pure mass fractionation from the effects of laser wavelength tuning.

The differences in the ionization probability of the even isotopes arise from the dependence of the effective absorption cross section of isotope i , σ_A^i , on the detuning of the laser center wavelength from the absorption maxima of isotope i . The discrete transition of isotope i is saturated if:

$$F_L \times \sigma_A^i \times t_p \gg 1$$

where F_L and t_p are the total flux of laser photons and pulse duration respectively. If this condition can be met simultaneously for isotopes i and j in a certain wavelength tuning interval, then R_{ij}^M will be constant in that interval. The value of $R_{ij}^M(\lambda) = \text{const.}$ is then considered to represent the purely mass fractionated value of that isotopic ratio. If the pair i, j has the largest IS, all other isotopes can be measured simultaneously. Alternatively, if the different isotopes are spectrally well resolved, the purely mass fractionated ratios can be obtained from measurements of the ion current at the individual isotopic ionization maxima. This procedure however considerably complicates analytical applications.

3. EXPERIMENTS AND RESULTS

The experiments were performed with a thermal atom source in a modified quadrupole mass spectrometer. Os and Ti were ionized with 1+1 photoionization schemes with resonance transitions near $40000. \text{ cm}^{-1}$. Measurements were performed with a pulsed laser system. Details of the experimental set up have been described elsewhere (Wunderlich et al. 1992 a and b).

Fig.1 shows the laser wavelength dependence of the $^{190}\text{Os}/^{188}\text{Os}$ isotope ratio, expressed as the per mil deviation from its standard reference value (δ -values) (Creaser et al. 1991). In this experiment the ratio of the laser bandwidth $\Delta\omega_L$ to the optical isotope shift of the transition ΔT was $\Delta\omega_L/\Delta T = 15$ ($\Delta\omega_L = 0.75 \text{ cm}^{-1}$, $\Delta T = 0.05 \text{ cm}^{-1}$). The measured isotope ratio is constant within a wavelength tuning interval of $\approx 0.4 \text{ cm}^{-1}$. For $\Delta\omega_L/\Delta T \approx 8$ the width of the plateau was reduced to 0.20 cm^{-1} . Similar experiments with Lu isotopes (Miller et al. 1990) performed at much lower laser intensity and with $\Delta\omega_L/\Delta T \approx 10$ did not reveal a plateau in the measured isotope ratios. The constancy of the measured isotope ratio is a result of the

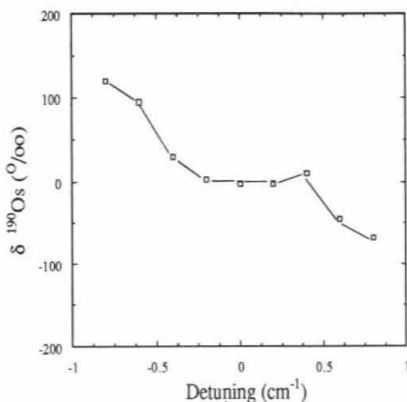


Fig. 1: Wavelength dependence of the $^{190}\text{Os}/^{188}\text{Os}$ ratio. $J=4$, 40361 cm^{-1}

strong power broadening of the resonance, following the arguments given above. The power broadening of the resonance was estimated as 0.8 cm^{-1} . The mass fractionation factor per mass unit, α , is then calculated from the value of the $^{190}\text{Os}/^{188}\text{Os}$ ratio measured in the region $R_{ij}^M(\lambda) = \text{const.}$ Table 1 shows the α -values obtained for other Os isotopes with the laser tuned in the center of the region $^{190}\text{Os}/^{188}\text{Os}(\lambda) = \text{const.}$. Within the precision of the experiment the α -values are indistinguishable, showing that these isotopic ratios differ from those present in the sample only by pure mass fractionation and can thus be simultaneously measured with high accuracy. Using the condition $^{190}\text{Os}/^{188}\text{Os}(\lambda) = \text{const.}$ for laser wavelength tuning we obtained in a series of different experiments a reproducibility of the $^{192}\text{Os}/^{188}\text{Os}$ ratio of 0.3%. After mass fractionation correction the absolute value of the $^{192}/^{188}$ ratio was indistinguishable from the standard ratio.

The width of the region $R^{ij}(\lambda)=\text{const.}$ directly shows the the required accuracy of laser wavelength setting for a given set of laser parameters required to obtain reproducible isotope ratio measurements. For the case shown in Fig.1 this accuracy is easily obtained with e.g. a pulsed wave meter or a well calibrated dye laser.

The importance of power broadening is also demonstrated in the power dependence of even-even isotope ratios shown in Fig.2. The $^{190}\text{Os}/^{188}\text{Os}$ ratio was measured with $\Delta\omega_L/\Delta T=7$ at the maximum of the ^{190}Os ion signal and for a detuning of 0.08 cm^{-1} . It is seen that in particular for lower pulse energies the effects of a small laser detuning can be very large. Both curves converge at higher laser intensities. The maximum laser intensity in this experiment was $5 \times 10^7\text{ Watt/cm}^2$.

Isotopic ratio measurements of Ti proved more difficult due to the larger IS approaching the closed neutron shell with magic neutron number 28 in ^{50}Ti . Compared to Os, the IS has a different sign. Optical isotope shifts were measured for different resonance transitions of the $3d^3 4p$ and $3d^2 4s 4p$ excited state electron configuration (Wunderlich et al. 1992 b). Fig.3 shows the wavelength dependence of the $^{50}\text{Ti}/^{46}\text{Ti}$ ratio using the 39715.5 cm^{-1} ($J=3$, $3d^3 4p$ configuration) resonance transition together with the ion signals at masses 50 and 46. In this experiment we had $\Delta\omega_L/\Delta T=3$ and $\Delta T(50-46)=0.15\text{ cm}^{-1}$. It is obvious that in this case isotopic ratios can *not* be measured with a single laser wavelength setting. For resonance states of the $3d^2 4s 4p$ electron configuration which have smaller IS, $\Delta T(50-46)=0.06\text{ cm}^{-1}$, it was possible to obtain a wavelength tuning interval with $^{50}\text{Ti}/^{46}\text{Ti}(\lambda)=\text{const.}$ Very good agreement between isotopic ratios measured in this region $R^{ij}(\lambda)=\text{const.}$ and ratios obtained from measurements of the ion current at the ionization maxima of the individual isotope for $3d^3 4p$ resonance states, have been obtained. This agreement justifies the

identification of the ratio measured in the region $^{50}\text{Ti}/^{46}\text{Ti}(\lambda)=\text{const.}$ with the purely mass fractionated value of that ratio. The α -values obtained in a series of measurements are summarized in Tab.1. Within experimental precision the values are identical and it is again seen that the measured isotope ratios are characterized by pure mass fractionation. After application of mass fractionation correction, the measured $^{50}\text{Ti}/^{46}\text{Ti}$ and $^{48}\text{Ti}/^{46}\text{Ti}$ are indistinguishable from the standard reference values (Niederer et al.).

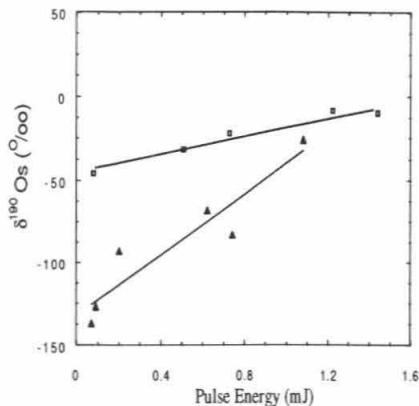


Fig.2: Power dependence of the $^{190}\text{Os}/^{188}\text{Os}$ ratio. Squares: zero detuning, triangles: detuning 0.08 cm^{-1} .

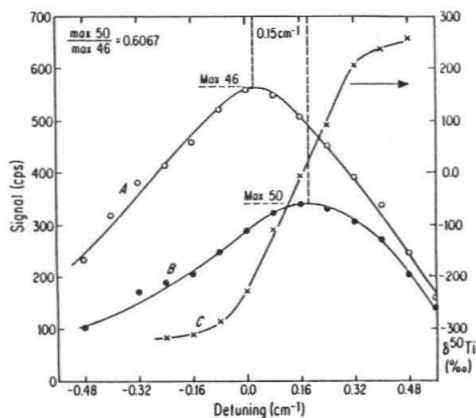


Fig.3: Wavelength dependence of the $^{50}\text{Ti}/^{46}\text{Ti}$ ratio (left) and ion signals at masses 46 and 50 (right)

Table 1: Mass fractionation per mass unit for Os and Ti ratios measured in the region $R_{ij}(\lambda)=\text{const.}$

Os Ratios	$\alpha \times 10^3$	Ti Ratios	$\alpha \times 10^3$
192/188	7.0 (2)	50/46	25 (2)
190/188	6.5 (3)	48/46	24 (7)
192/190	8.0 (3)		

3. CONCLUSIONS

We have shown that under selected conditions even-even isotopic ratios differing from the 'true' ratios only by mass dependent fractionation can be measured by RIMS. Application of the mass fractionation correction then yields very good agreement with the standard ratios. A large laser bandwidth and strong power broadening allow measurement at a single laser wavelength setting. This approach is important for analytical applications as compared to measurements of the ion intensity at the individual isotopic peaks which requires careful measurement of the ionization lineshapes of all isotopes. The accuracy of 0.3% of our best Os measurements suggests that it will be interesting to infer the absolute accuracy which can be obtained in this type of RIMS experiment. The importance of power broadening suggests that the intensity distribution in the laser beam and the focussing conditions may become limiting factors for the accuracy at a higher level of precision. The results given here, together with our measurements of the odd even effect in Os and Ti, show that it is possible to obtain isotopic ratios by RIMS with an absolute accuracy of 0.4% or better.

ACKNOWLEDGEMENTS

This work was supported by DOE grant DE FG03-88ER-1351 and NSF grant EAR-8816936 to G. J. Wasserburg. The laser system was obtained through support from the Packard and Sloan Foundations and NASA grant NAGW -1955 to G. A. Blake.

REFERENCES

- Creaser R A, Papanastassiou D A and Wasserburg G J 1991 *Cosmochim. Acta* **55** 397
 Fairbank W M Jr., Spaar M T, Parks J E and Hutchinson J M R 1989 *Phys. Rev.* **A40** 2195
 Lambropoulos P and Lyras A 1989 *Phys. Rev.* **A40** 2199
 Miller C M, Fearey B L, Palmer B A and Nogar N S 1988 *Resonance Ionization Spectroscopy 1988*, eds. J E Parks and T B Lucatorto Institute of Physics Conf. Series **94**, (Bristol UK) 297-301
 Niederer F R, Papanastassiou D A and Wasserburg G J 1981 *Geochim Acta* **45** 1017
 Payne M G, Allman S L and Parks J E 1991 *Spectrochim. Acta* **46B** 1439
 Spiegel D R, Pellin M J, Calaway W F, Burnett J W, Coon S R, Young C E, Gruen D M and Clayton R N 1992 *Anal. Chem.* **64** 469
 Wunderlich R K, Hutcheon I D, Wasserburg G J and Blake G A 1992 a *Int J. Mass Spectrom. and Ion Processes*, in press
 Wunderlich R K, Hutcheon I D, Wasserburg G J and Blake G A 1992 b submitted *Anal. Chem.*
 Young Y P, Shaw R W, Goeringer D E, and Smith D H 1988 *Resonance Ionization Spectroscopy 1988*, eds. J E Parks and T B Lucatorto Institute of Physics Conf. Series **94**, (Bristol UK) 367-371