

ISOTOPIC ANALYSIS OF OSMIUM, RHENIUM AND IRIIDIUM BY NEGATIVE THERMAL ION MASS SPECTROMETRY. R. A. Creaser, J. H. Chen, D. A. Papanastassiou, G. J. Wasserburg. The Lunatic Asylum, Div. Geol. & Planet. Sci., Caltech, Pasadena CA 91125.

The Re-Os decay scheme has been shown to have widespread application in cosmochemistry and geochemistry [1,2]. However, isotopic analysis of Os is difficult, and presently requires highly specialized analytical equipment. We have developed a technique for producing intense, stable ion beams of negatively-charged Os, Re and Ir oxides in a conventional, thermal-ionization mass spectrometer (Negative Thermal Ion Mass Spectrometry - NTIMS [3]). Solutions of hexachloro-osmate and hexachloro-iridate salts in 2.5N HCl are loaded onto a Pt filament, dried in air, and reduced to metal at  $\sim 500^\circ\text{C}$  in a vacuum of  $<10^{-5}\text{T}$ . The metal sample is then covered with Ba (as a solution of  $\text{Ba}(\text{NO}_3)_2$  in water) and dried in air prior to mass spectrometric analysis. Addition of Ba reduces the electron work function of the Pt filament and promotes the production of negative thermal ions [4]. Re is loaded onto a Pt filament as a solution in 0.1N  $\text{HNO}_3$  together with the Ba solution, and dried in air prior to analysis. Negative thermal ions of Os, Re and Ir oxides are produced at  $\sim 650 - 850^\circ\text{C}$ .

For Os, NTIMS has the capacity to determine the abundance of  $^{187}\text{Os}$  with a precision of  $\pm 1\%$  for 4ng Os ( $\sim 90$  pg  $^{187}\text{Os}$ ), and  $\pm 3\%$  for 70pg Os ( $\sim 1.5$  pg  $^{187}\text{Os}$ ) from prepared solutions (Table 1). The ionization efficiency (2-6%) is the highest yet reported for Os, and the observed mass-dependent isotope fractionation is restricted - below  $1\text{‰ amu}^{-1}$  for ng-quantities of Os. The NTIMS technique for Os isotopic analysis offers superior precision, efficiency and sensitivity to other methods presently available. Compared with SIMS, RIMS and ICP-MS, the precision obtained for Os by NTIMS is a factor of 10-20 better for equivalent analysis quantities, and the ionization efficiency is improved by  $10^2 - 10^5$ . The detection limit for Os by NTIMS is estimated to be below  $10^{-14}\text{g}$ . For Re and Ir, isotopic compositions have been determined by NTIMS with a precision of  $\pm 0.3\%$ . The  $^{185}\text{Re}/^{187}\text{Re}$  ratio determined by NTIMS ( $0.5977 \pm 4$ ) is identical to that previously measured by thermal ionization of positive metal ions ([5];  $0.5974 \pm 4$ ), and the  $^{191}\text{Ir}/^{193}\text{Ir}$  ratio ( $0.5948 \pm 4$ ) is the most precise yet measured. The Re experiments show a total range in mass-dependent isotope fractionation of  $\pm 1.2\text{‰ amu}^{-1}$  about the mean, and for Ir the range is  $<1\text{‰ amu}^{-1}$ . Ionization efficiency is  $>20\%$  for Re and 1% for Ir. Based on NTIMS, it is now reasonable to consider that ionization efficiency for Os and Re is not a limiting factor in precision and sensitivity. The total ion collection efficiency will be further improved by using simultaneous ion beam collection in a multi-collector mass spectrometer, so as to achieve a nearly 100% duty cycle for all isotopes.

$\text{OsO}_3^-$ ,  $\text{ReO}_4^-$ , and  $\text{IrO}_2^-$  are the principal ion species of Os, Re and Ir produced by the NTIMS technique. The sharp distinction in the masses of the dominant molecular species permits the measurement of isotopic compositions of each element from mixtures of platinum-group elements without significant isobaric interferences. For  $^{187}\text{Re} - ^{187}\text{Os}$  isotope studies, this technique offers the advantage of isotopic analyses without prior chemical separation of Re from Os, as no isobaric interference between the oxides of  $^{187}\text{Os}$  and  $^{187}\text{Re}$  exists under these conditions (Fig.1).

We have applied NTIMS to determine the Os isotopic composition of natural iridosmine. One sample from the Mammoth Mine, Junction City, California, was loaded directly onto a Pt filament and covered with Ba prior to analysis. The  $^{187}\text{Os}/^{192}\text{Os}$  ratio of this sample is  $0.04026 \pm 0.00002$  ( $^{187}\text{Os}/^{186}\text{Os} = 1.0315$ ), determined with a precision of  $< \pm 0.5\%$ . This demonstrates that, in some cases, geologically useful Os isotope data can be produced without any chemical treatment of the sample. Osmium has also been chemically separated from a small piece of the metal phase from the Canyon Diablo (IA) iron meteorite (acid etched prior to digestion), and  $^{187}\text{Os}/^{192}\text{Os}$  determined to be  $0.03466 \pm 0.00012$  ( $^{187}\text{Os}/^{186}\text{Os} = 0.888$ ). This value is one of the lowest yet reported from meteoritical material, and is significantly different from the values of  $\sim 1.11$  previously reported from the whole meteorite [1,6]. The result indicates that differences in Re/Os and Os isotopic heterogeneities exist within Canyon Diablo. It should, therefore, be possible to determine an internal isochron from this, and other, iron meteorites. We anticipate presenting further Os isotopic

data from iron meteorites at the meeting. Although the primary application of NTIMS is in Re-Os chronometry through the use of radiogenic  $^{187}\text{Os}$  as a tracer, the technique can also be applied to the precise determination of PGE concentrations by isotope dilution mass spectrometry.

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TABLE 1. Os, Re and Ir isotopic ratios measured by NTIMS

Osmium	<sup>186</sup> Os/ <sup>192</sup> Os	<sup>187</sup> Os/ <sup>192</sup> Os	<sup>189</sup> Os/ <sup>192</sup> Os	<sup>190</sup> Os/ <sup>192</sup> Os	<sup>187</sup> Os/ <sup>186</sup> Os
Osmium solution:					
1. 4ng	0.03901 ± 4	0.05908 ± 3	0.39536 ± 4	0.64371 ± 5	1.5137 ± 8
2. 4ng	0.03908 ± 7	0.05911 ± 5	0.39521 ± 17	0.64378 ± 8	1.5145 ± 13
3. 70pg	0.0395 ± 2	0.0591 ± 2	0.3948 ± 7	0.6443 ± 7	1.514 ± 5
4. 70pg	0.0394 ± 2	0.0589 ± 2	0.3945 ± 6	0.6436 ± 3	1.509 ± 5
Natural iridosmine. Mammoth Mine, Junction City, California:					
5. -	0.03900 ± 2	0.04026 ± 2	0.39548 ± 6	0.64362 ± 5	1.0315 ± 5
Metal phase, Canyon Diablo IA iron meteorite:					
6. -	0.03919 ± 15	0.03466 ± 12	0.3949 ± 4	0.6429 ± 7	0.888 ± 3
Rhenium and Iridium		<sup>185</sup> Re/ <sup>187</sup> Re	<sup>191</sup> Ir/ <sup>193</sup> Ir		
1. Re	1ng	0.5977 ± 2			
2. Re	1ng	0.5977 ± 2			
3. Re	350pg	0.5977 ± 2			
4. Ir	5ng		0.5948 ± 2		

Uncertainties  $2\sigma$  (mean).  $^{187}\text{Os}/^{186}\text{Os}$  calculated from  $^{187}\text{Os}/^{192}\text{Os}$  and grand mean  $^{186}\text{Os}/^{192}\text{Os}$  of 1, 2 and 5 ( $0.03903 \pm 3$ ); uncertainty in  $^{187}\text{Os}/^{186}\text{Os}$  reflects uncertainty in  $^{187}\text{Os}/^{192}\text{Os}$ . Os data normalized for mass-dependent isotope fractionation to  $^{188}\text{Os}^{16}\text{O}_3^- / ^{192}\text{Os}^{16}\text{O}_3^- = 0.323394$  (from  $^{188}\text{Os}/^{192}\text{Os}=0.3244$  [7],  $^{17}\text{O}/^{16}\text{O}=0.0003708$ ,  $^{18}\text{O}/^{16}\text{O}=0.002045$  [8]).

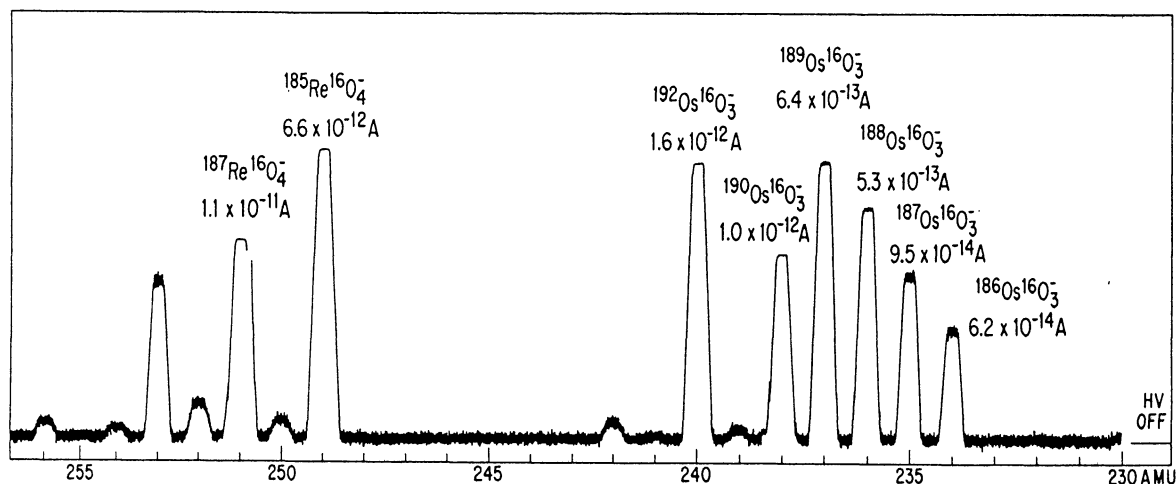


Fig 1. Mass spectrum determined by Faraday collector of 5ng Os + 3ng Re on a single Pt filament doped with Ba at  $770^\circ\text{C}$ . Rhenium is produced as  $\text{ReO}_4^-$  whereas Os is produced dominantly as  $\text{OsO}_3^-$ , effectively eliminating the isobaric interference between  $^{187}\text{Re}$  and  $^{187}\text{Os}$ . The unlabeled peaks correspond to minor oxygen species of Os and Re. Scale changes occur in spectrum.