Formation of Negative Thermal Ions from a Mixed Solution of Platinum Group Elements

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Abstract Formation behaviors of negative thermal ions from a mixed solution of platinum group elements (PGEs; Ru, Rh, Pd, Os, Ir and Pt), Mo, W, Re and Au has been explored using two thermal ionization mass spectrometers. The dominant negative thermal ions were RuO_3^-, OsO_3^-, IrO_2^-, PtO^-/Pt^-, MoO_3^-, ReO_4^- and Au^- using a Pt single filament method. The ion beam intensities were $ReO_4^- > OsO_3^- > IrO_2^- \approx RuO_3^- > MoO_3^-$. Negative ions of halogens, Cl^-, Br^- and I^-, were also observed. No negative ion species for Rh, Pd and W were, however, detected in this study. The ion currents of thermal negative ion species were reduced when one or two very strong negative ions such as Cl^-, Br^- or ReO_4^- were coexisting. Overnight baking at a low filament temperature could reduce this effect.

Key words: Negative thermal ionization, Mass spectrometry, Platinum group elements, Mo, W, Re, Au

1. Introduction

Abundances and isotopic compositions of PGEs are in great interest for geochemists because of their affinity to sulfides and metals (chalcophile and siderophile elements). Re has a long-lived radioisotope which decays to Os (^{187}Re: Half-Life $= 4.23 \times 10^{10}$ y, Lindner *et al.*, 1989) and the Re-Os systematics can be used for age determination of sulfides in ore deposits as well as metals in meteorites (Herr and Merz, 1958; Herr *et al.*, 1961). Recent development of negative thermal ionization mass spectrometry (N-TIMS) has enabled us precise determination of isotopic ratios of PGEs (e.g. Völkening *et al.*, 1991a; Creaser *et al.*, 1991; Walczyk and Heumann, 1993). We report here the exploratory results of formation behaviors of negative thermal ions from a mixed solution of PGEs and several precious or refractory metals and investigate the applicability of isotope dilution technique for elemental abundance determination (e.g. Heumann, 1992) without separation of each element.

2. Experiments

2.1 Mixed Solution

The mixed solution of PGEs and several precious or refractory metals used in this study was prepared by mixing 10 parts of a mixed standard solution of Ru, Rh, Pd, Re, Os, Ir, Pt and Au ($100 \,\mu g/ml$ each element in 20% HCl; Specpure ICP/DCP standard solution, Johnson and Matthey Alfa Co.), one part of a Mo standard solution ($990 \,\mu g/ml$; AA standard solution) and one part of a W standard solution ($1000 \,\mu g/ml$; Specpure ICP/DCP standard solution). The resulting solution contains $83.3 \,\mu g/ml$ each of Ru, Rh, Pd, W, Re, Os, Ir, Pt and Au, and $82.5 \,\mu g/ml$ Mo. A Br, I, Ru and Re mixed solution for calibration of mass spectrometers was also used.

2.2 Instrumentation

Two thermal ionization mass spectrometers, Finnigan THQ and MAT-261, at the Johannes Gutenberg-University, Mainz, were used for this study. THQ is equipped with a thermal ionization ion source, where 13 samples can be placed simultaneously, and a quadrupole mass analyser. MAT-261 is equipped with the same ion source and a 54-cm-radius sector magnet. One Faraday cup collector is placed at the end of the each mass spectrometer for ion current measurements. While the magnetic sector field type mass spectrometer is designed for precise isotope ratio measurements, the quadrupole type mass spectrometer offers a small machine size and ease of use because it doesn't require a high acceleration voltage and a high vacuum. This is suitable for isotope dilution mass spectrometry. All measurements were performed by the Pt single filament method. The filament temperatures were measured by optical pyrometers.

2.3 Filament Preparation and Sample Loading

A 99.999% Pt ribbon (H. Cross Co., 0.03937 inch wide, 0.00197 inch thick) was used for sample loading filaments. They were degassed in a vacuum for an hour with the filament current of 5 A. After they were sufficiently cooled, $2 \,\mu l$ of a $Ba(NO_3)_2$ solution (10 mg Ba/ml) was loaded as an activator on the filaments by a micro pipette and slowly dried in the air with the filament current of 1.5–2 A. Then $2 \,\mu l$ of the mixed solution was loaded in the same manner. 20 μg of Ba and ca. 170 ng of each element in the mixed solution were on the filaments.

3. Results and Discussion

3.1 Calibration Solution Measurements

Before measurements of the samples, a calibration solution, which contains Br, I, Ru and Re was measured by both mass spectrometers for calibration
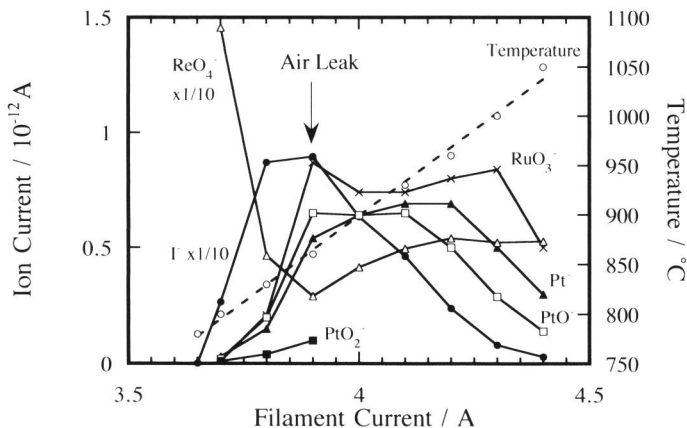
Fig. 1. The observed negative thermal ion currents from a Br, I, Ru and Re mixed calibration solution against filament currents. The measured mass numbers for I^-, RuO_3^-, Pt^-, PtO^-, PtO_2^- and ReO_4^- were 127, 150, 194, 210, 226 and 251, respectively. Filament temperatures measured by an optical pyrometer are also shown.

between mass numbers and the magnetic or electric field currents. However, it can be also considered as another sample solution. One of the results measured by MAT-261 is shown in Fig. 1. As the sample didn't contain PGEs other than Ru (and Re), we didn't detect any ion species of Rh, Pd, Os and Ir. We did, however, observed those of Pt since it was used as a sample loading filament. The dominant negative ion of Re was ReO_4^- and that of Ru was RuO_3^- as reported in literature (e.g. Heumann *et al.*, 1985; Huang and Masuda, 1997). The intensities of other oxide species of the elements were at least one order of magnitude smaller than those of ReO_4^- and RuO_3^-. For example, when the ion currents of ReO_4^- (mass 251) and RuO_3^- (mass 150) were 3.8×10^{-11} A and 8.7×10^{-13} A, respectively, those of ReO_3^- (mass 235) and RuO_2^- (mass 134) were as low as 1×10^{-13} A and 2×10^{-14} A, respectively. For Pt, we detected three negative ion species: Pt^-, PtO^- and PtO_2^-. The ion currents of PtO_2^- were about 1/4–1/5 of those of Pt^- and PtO^-. While the ion currents of PtO^- were higher than those of Pt^- at lower temperatures, Pt^- was the dominant species at higher temperatures ($>900°C$) in spite of introduction of air (i.e. oxygen) into the ion source up to 7×10^{-7} mbar. The intensity of ReO_4^- was reduced at $\sim 900°C$ probably because of production of large amounts of Br^- (more than 1×10^{-10} A; not shown in Fig. 1) and I^-, but it gradually recovered at higher temperatures as the intensity of I^- (and probably also Br^-) were getting lower.

3.2 Measurements by THQ

The negative thermal ion currents measured by THQ were shown in Fig. 2. The resolution setting of the quadrupole mass analyser affects the sensitivity. In
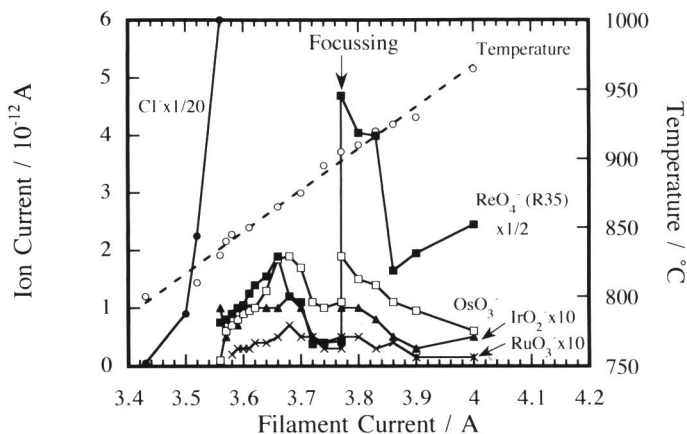
Fig. 2. The negative thermal ion currents from a PGE-mixed solution measured by THQ
against filament currents. All ion currents were measured at a low resolution setting 73
except for Re at a better resolution setting 35. The measured mass numbers for Cl^-,
IrO_2^- and OsO_3^- were 35, 225 and 240, respectively. Others were same in Fig. 1.

this figure, all ion currents were measured at a low resolution setting 73 except
for Re at a better resolution setting 35. The ion currents at resolution 73 were
about 4 times higher than those at resolution 35. At the best resolution setting
45, the intensities were too low (at least one order of magnitude lower than those
at resolution 35) to properly assess formation of negative thermal ions. Focuss-
ing the ion beams by adjusting the electric potentials of slits and plates was also
critical. By being re-focussed at the filament current 3.77 A in Fig. 2, ion beam
intensities for Os, Ir and Ru became twice and those for Re became 10 times
higher (optimized for ReO_4^-). Cl^- was the highest intensity ion beam, which
came from the HCl matrix of the solution. The dominant negative ion of Re was
ReO_4^- and that of Ru was RuO_3^- as observed at the calibration solution
measurements. OsO_3^- and IrO_2^- were the dominant ions for Os and Ir as
previously reported (Völkening *et al.*, 1991a; Walczyk and Heumann, 1993).

3.3 Measurements by MAT-261

The negative thermal ion currents measured by MAT-261 were shown in
Fig. 3. Air was introduced into the ion source to the pressure of 7×10^{-7} mbar
at the filament current 3.9 A in order to increase the Os and other PGE oxide ion
intensities (Walczyk *et al.*, 1991). In addition to the ions detected at the THQ
measurements, Au^-, PtO^- and MoO_3^- were observed. Also seen were I^- and
CrO_3^-, which were probably impurities of the HCl matrix and Pt filaments,
respectively. While the ion currents of I^- monotonically decreases when the
filament temperature goes up ($>900°C$), those of OsO_3^-, IrO_2^-, RuO_3^- and Au^-
show maxima at about 900–950°C almost simultaneously. A maximum for CrO_3^-
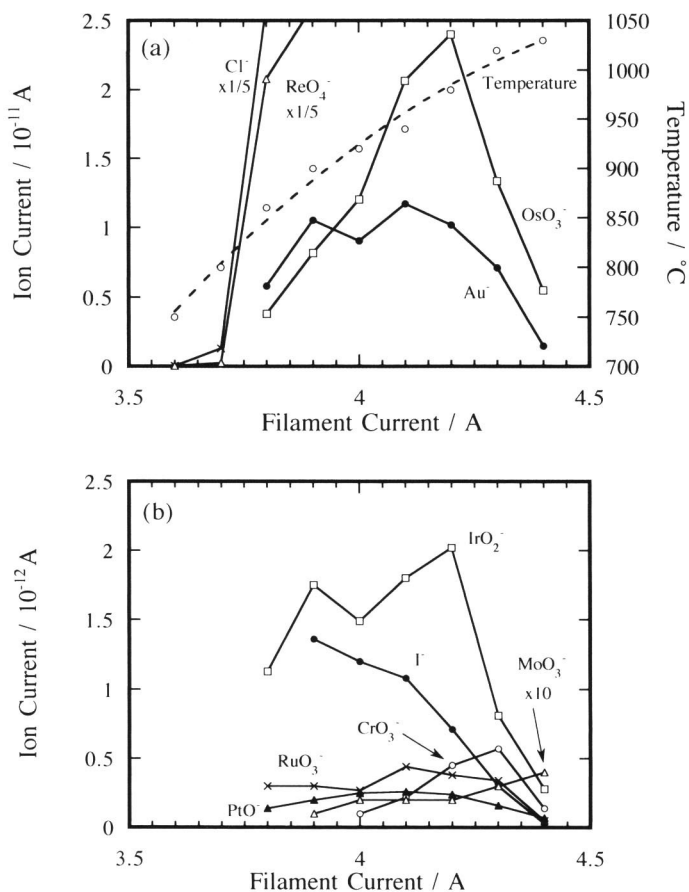
Fig. 3.   The negative thermal ion currents from a PGE-mixed solution measured by MAT-261 against filament currents.   Note that the scale of ion currents in Fig. 3(a) is ten times higher than that in Fig. 3(b).   The measured mass numbers for Cl^-, CrO_3^-, MoO_3^-, Au^- and ReO_4^- were 37, 100, 140, 197 and 249, respectively.   Others were same in Fig. 2.

is at slightly higher temperature ($\sim 1000°C$) and that for MoO_3^- could be at higher than $1000°C$.

Since intensity reduction due to coexisting very strong ion beams was observed, we tried to reduce this effect by pre-baking the sample at a low filament temperature.   The same amount of the mixed solution was loaded on a degassed Pt filament without any Ba salts.   The filament then was put in a vacuum chamber and was baked overnight at the filament current of 3.2 A.   After cooling, the sample was covered by $20\,\mu g$ of Ba as the same way.   Results are shown in Fig. 4.   While the ion currents of ReO_4^- were greatly reduced, those of OsO_3^- were reduced only slightly (e.g. the former became 1.0×10^{-10} A to 2.5×10^{-12} A
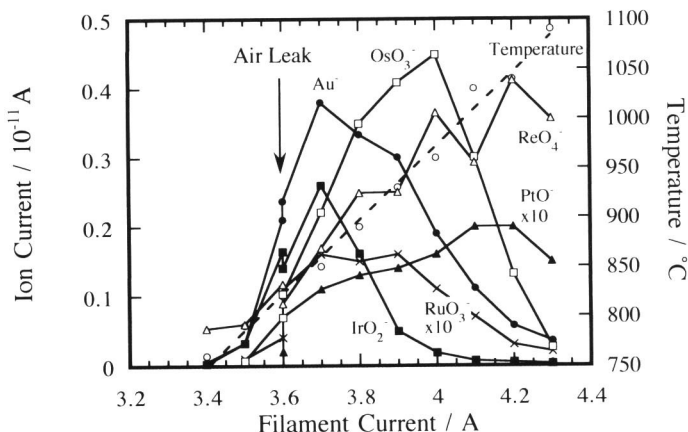
Fig. 4. The negative thermal ion currents from a PGE-mixed solution measured by MAT-261 after overnight baking at the filament current 3.2 A.

and the latter became 3.8×10^{-12} A to 3.5×10^{-12} A at the same filament current, 3.8 A). We also observed the differences between temperatures where PGE negative ions showed the ion beam current maxima ($Au^- \approx IrO_2^- < RuO_3^- < OsO_3^- < PtO^- < ReO_4^-$).

3.4 Applicability and Limitations

Using a thermal ionization mass spectrometer, RuO_3^-, OsO_3^-, IrO_2^-, PtO^-/ Pt^-, MoO_3^-, ReO_4^- and Au^- can be detected with a Pt single filament method. The ion beam intensities were $ReO_4^- > OsO_3^- > IrO_2^- \approx RuO_3^- > MoO_3^-$, produced from the same amount of each element. The negative ion species for Rh, Pd and W were, however, not observed in this study. Formation of WO_3^- was reported by Völkening *et al.* (1991b) using a Re double filament method as is the case of MoO_3^- (Köppe and Heumann, 1988). They found much less formation efficiency of negative thermal ions of W with Pt filaments compared with that with Re filaments (2 order of magnitude less). Formation of negative ions of W and Mo from a mixed PGE solution with the Re double filament method must be explored. A combination of Pt and Re filament methods may provide a good concentration determination technique by N-TIMS.

Isotope dilution technique using ICP-MS is also promising. Determination of Pt, Pd and Ir concentrations by isotope dilution method using ICP-MS was already reported by Ravizza and Pyle (1997). The abundances of mono-isotopic elements such as Rh can't be determined by the isotopic dilution technique, in principle, without the use of radioactive isotopes. But, ICP-MS can also be used for concentration determination of mono-isotopic elements using the external calibration method. For isotope ratio measurements of Os and some of PGEs, however, N-TIMS still gives results with better precision. Thus ICP-MS and

N-TIMS could be used complementarily each other.

Acknowledgments

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