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MASTER

THE MASS SPECTROMETRIC ANALYSIS OF NANOGRAM LEVELS OF RUTHENIUM

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ABSTRACT

Previous investigations have demonstrated the possibility of using ruthenium originating from the spontaneous fission of ^{238}U for geochronological purposes. Because the abundance of ruthenium is low in geologic specimens and isotopic data are required, an indepth study of the production of steady mass spectrometer ion beams from nanogram amounts of ruthenium was undertaken. The results of this continuing mass spectrometric investigation are presented with some illustrative data.

INTRODUCTION

This laboratory has been analyzing microgram level samples of various fission products, including ruthenium (Ru), by isotope dilution mass spectrometry for approximately fifteen years.[1] Based on this experience, a program was initiated in 1974 to analyze ore from the ancient natural reactors of Oklo.[2] Nine fission product elements were analyzed; three (Rb, Sr, Ba) showed natural isotopics, five (Nd, Sm, Mo, Zr, Ce) were mixed fission product-natural isotopics, and one (Ru) had an isotopic composition corresponding to that of essentially pure, stable fission product material.

This led to the speculation that if Ru is that rare and immobile in nature, perhaps ^{238}U spontaneous fission produced Ru could be measured in uranium (U) ores. This in turn could be used to study the stability of Ru in nature and possibly as an age dating tool. Subsequent measurements[3] of non-Oklo ore samples indeed showed that fission product Ru was present, and that the predominant source of Ru was from the spontaneous

fission of ^{238}U.

The analytical method had to be improved before this type of measurement could be utilized for some practical purpose. The goal, therefore, was to improve the method such that data good to at least 1% could be obtained on samples no larger than five nanograms of total Ru. This level of performance is routinely exceeded for many elements, Pu being an example. However, the physical and chemical characteristics of Ru make these objectives more difficult to achieve. While the early data was good to 5-10%, easily demonstrating the existence of ^{238}U spontaneous fission origin Ru in a wide variety of U ores, better accuracy was desired to more fully evaluate the use of Ru as a geochronology tool.[3,4,5]

With this potentential application in mind, a program was initiated to improve the Ru analytical method. The basic phases of the method are: a) sample dissolution, b) separation chemistry and c) mass spectrometry. After sample dissolution, the Ru is distilled as RuO_4[3], which gives a clean separation for Ru at the 1 PPB level for all samples except those with high organic content. The major difficulty is the generation of ion beams of sufficient intensity and stability to allow the collection of the necessary mass spectrometric data from nanogram sized samples. A 90° sector tandem magnet mass spectrometer equipped with pulse counting and a computerized data system was used. The criteria established for acceptable data were 100-200 counts/sec on the smallest peak of interest, which is about 0.5% of the total sample, and an intensity stable to within 5% per minute.

THE THERMAL IONIZATION PROCESS

Ruthenium is ionized in the mass spectrometer by the positive thermal ionization process. This involves evaporating Ru from a metallic surface that has a high affinity for electrons. This affinity for electrons is measured by the work function (W). The material which is used almost universally in the thermal generation of positive ions is rhenium (Re), because it is malleable, has good strength at high temperatures, and a desirable work function (4.7-5.1 volts). The work function is a surface property, which varies with the crystalline face or the polycrystalline character of the surface. It is also strongly affected by surface cleanness. The ability of an element to give up an electron to such a surface is measured by its ionization potential (IP), which for Ru is 7.36 volts.

When the assumption is made that the only species leaving the filament are the positively charged and neutral species of the element, the Saha-Langmuir equation may be applied:

$$n+/n^{o} \infty \exp (W-IP)/kT = \exp \delta/kT$$

Where $n+$ and n^{o} are the number of positively charged and neutral species respectively, W and IP the work function and ionization potential, respectively, δ is the difference between W and IP, k is the Boltzmann constant, and T is the absolute temperature. A more complex form of this equation exists, but efforts to verify it experimentally[6] have not been successful. This simplified form of the equation[7] has been verified experimentally,[6] including the change in temperature dependence with δ. The sign and magnitude of δ strongly effects the temperature dependence of $n+/n^{o}$. The δ for the Ru-Re system is -2.36 volts, which indicates a large increase in ion production with increased temperature. A positive δ would give the opposite temperature dependence, as is the case for cesium (IP=3.89 volts, δ=+1.11 volts).

There are two broad categories of thermal ion sources in widespread use; the single filament and the multiple filament arrangements. When using the single filament the sample is loaded directly on the ionizing filament. The major advantage of this source is that all of the sample contacts the ionizing filament. The drawbacks are: a) the possibility of the sample poisoning the work function of the ionizing surface and, b) the inability to independently vary the temperature of the ionizing surface and the vapor pressure of the element.

When using the multiple filament arrangement, the sample is loaded on one or two of the side filaments, which are heated to vaporize the sample in the direction of the ionizing filament. The ionizing filament is lined up with the optics axis of the mass spectrometer. This source has the advantage of permitting independent adjustment of the ionizing filament temperature and the vapor pressure of the element to be ionized. The major disadvantages are: 1) not all the material vaporizing from the side filament strikes the ionizing filament, and 2) a compound containing the element of interest may be too volatile to permit a sufficient residence time on the hot filament for ionization or for both dissociation and ionization of that element. Uranium is an excellent element to analyze by the multiple filament technique, because the Re filament at 2100°C can both dissociate and ionize the uranium oxide vapor species to yield U^{+} ions with good efficiency.

There are, however, two major problems when Ru is ionized using the multiple filament technique. The first problem is that the multiple filament source requires a very hot center filament to ionize a high work function element efficiently.

This requirement presents another problem which is, that at high ($\sim$2100°C) temperature, a measureable Mo spectra appears which causes a serious spectral interference with Ru. This in itself precludes the use of the multiple filament technique.

The second major difficulty with the multiple filament source is that it normally does not produce Ru ions with an efficiency that is analogous to other elements. An understanding of this phenomenon helps to explain some other anomolies as well. The compounds of the higher oxidation states of Ru are volatile, and if a volatile compound strikes a very hot surface, it will either dissociate or re-evaporate. With uranium oxides, dissociation and ionization occur because the oxides have a much lower vapor pressure which allows a longer residence time on the filament; this results in a highly efficient ion source. In contrast, the various Ru species we have worked with apparently re-evaporate, or possibly dissociate and then evaporate without ionizing. It is probable that Ru would ionize more efficiently in the multiple filament source if it were present as the metal on the side filament; this method would be worth exploring were it not for the spectral interference problem of Mo from the hot center filament.

To date the single filament ion source has been far more successful for Ru than the multiple filament ion source, provided that certain exacting conditions are met. These conditions are: a) using Re filaments that are low in Mo contamination and intensely prebaked; and b) the adjustment of sample handling and mounting conditions to prevent the formation of the higher oxidation states of Ru. The close control of these paramenters has led to the most significant improvements in sensitivity, and also offers the greatest potential for future refinements.

The presently recommended procedure entails loading Ru from a strong HCl or HBr solution directly onto a single filament. The solution must never go dry during any phase of the sample handling until the last drop evaporates on the filament. Ruthenium will be lost to the container walls if the solution goes dry during sample handling, and if repeated drops are evaporated to dryness on the filament a significant loss in Ru ion intensity results. The solution must be evaporated very slowly on the filament to obtain the best sensitivity. A 10 μL drop must be dried at a temperature that takes about forty-five minutes. Faster drying rates with higher tempatures causes a significant loss in sensitivity.

These results suggest that different chemical forms of Ru are being produced on the filament as a function of drying time or temperature. One possible explanation is that the Ru, which is predominantly in the +3 valence state in concentrated HCl or HBr, is converting to a higher oxidation state. The very gentle drying process may be preserving the +3 oxidation state. Higher oxidation state Ru compounds are more covalent, and hence more volatile. The greater volatility results in Ru vaporizing in the ion source at lower temperatures, giving reduced ion production. The increase in covalency means a decrease in the ionic character of the chemical bonds, and hence a lower probability of ionization.

The logical extension of this work is the reduction of Ru to the metal on the filament. Reduction was attempted in two different ways: a) with hydrogen reduction, and b) with the resin bead method. Both techniques producted sensitivity increases of several fold, but both also had drawbacks that prevent application unless further refinements are made. The problem with the hydrogen reduction was a migration of Mo impurities in the Re filament to the surface, negating the reduction in Mo accruing from the extensive pre-baking procedure. A major problem with the resin bead method is the requirement for the chemistry and techniques for loading 10 to 50 ng quantities of Ru nearly quantitatively onto a single resin bead.

DATA AND CONCLUSIONS

Based on the work performed to date, the preferred method is the conventional single filament method, providing the necessary precautions are taken during the sample handling and drying steps. The results given in Table 1 are representative of the analysis of a uranium ore sample which contained $\sim$40 ng of Ru prior to separation chemistry. Mass 100 is used to correct for natural Ru (^{100}Ru is not producted in fission) after subtraction of ^{100}Mo based on the analysis of ^{95}Mo. This correction must be small for the data to be acceptable. The data in Table 1 easily exceeds the criteria of 1% data for the fission product nuclides.

Developments that would provide further significant improvements in the Ru analysis are: a) Re filaments with significantly lower Mo content, and b) a technique for reducing Ru to the metal on the filament without drawbacks of the methods tested to date. In spite of these development needs, the current method, in its state of development, is adequate to allow continued evaluation of the use of Ru from ^{238}U spontaneous fission for geochronology studies.

TABLE 1. FISSION ORIGIN Ru FROM U ORE DEPOSITE

Scan	99	100	101	102	104
1	25.42	1.14	27.84	29.64	15.96
2	25.50	1.19	27.68	29.70	15.92
3	25.31	1.09	27.72	30.13	15.75
4	25.29	1.16	27.83	29.86	15.85
5	25.26	1.16	27.82	29.93	15.83
6	25.37	1.02	27.61	29.95	16.05
7	25.36	1.02	27.67	30.01	15.95
Average	25.36	1.11	27.74	29.89	15.90
St. Dev.	.03	.03	.04	.06	.04
Net Ru F.P.	26.42	0.00	28.58	29.50	15.50

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