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DETERMINATION OF IRIDIUM CONCENTRATION IN SEDIMENTARY ROCKS AND IN THE GEOCHEMICAL STANDARD PCC-1 BY RADIOCHEMICAL NEUTRON ACTIVATION ANALYSIS

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A radiochemical neutron activation analysis procedure is described for the determination of concentration levels of iridium in sedimentary rocks and in the geochemical standard PCC-1. After irradiation, the powdered rock samples and standard are dissolved with a mixture of HF, HNO_3 and $HClO_4$ in a teflon bomb. The final solution obtained, in dilute HCl, is passed through a column containing the cationic resin Bio Rad AG 50W–X8. The interfering radionuclides are sorbed by the resin. The effluent solution containing iridium is concentrated for counting by evaporation. Experiments with radioactive tracer for checking radiochemical separation yield are carried out. The accuracy of the method is evaluated by means of analysis of the USGS "standard rock" peridotite, PCC-1. The precision is about 25% in the ppb range. The method is used for the determination of iridium in 16 samples of sedimentary rocks collected at different depths in the "Campos" basin-RJ (BRAZIL).

Introduction

The discovery in 1980 by ALVAREZ et al.[1] of a clay layer marking the Cretaceous/Tertiary (65 My) boundary enriched relative to crustal abundances of noble metals such as iridium and other platinum group elements has led to a vast amount of publications concerning hypothesis on causes of extinctions that occurred at that geological time.[2-4] The iridium-enriched layer which marks this event, appears to be global in extent and was atrributed by ALVAREZ et al.[1] to the impact of a large extraterrestrial object with the Earth.

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While most of these publications deal with the interpretations of reported data, only scarce references are made to new improved measurement techniques. At the ppb level of Ir, neutron activation analysis is one of the most reliable techniques, applicable to iridium determination, due to the high thermal neutron activation cross section exhibited by this element ($\sigma = 446$ barns). However, in some cases, depending on the rock composition, it is necessary to carry out radiochemical separation procedures to cut off spectral interferences such as lanthanide elements and scandium, and to improve sensitivity before applying this technique. Interfering nuclear reactions such as described by GIJBELS[5] probably do not occur in the case of the sediment samples analyzed in the present work.

Some works have been published in which several radiochemical separation procedures were used for removal of interfering radionuclides in iridium determination by neutron activation analysis. ODDONE et al.[6] studied a method for noble metals sorption on an anionic resin. STOCKMAN[7] used noble metals coprecipitation as a group with Te, using Sn^{2+} as a reducing agent. Several works[8-10] used selective sorption of the noble metal group on Srafion NMRR ion exchange resin. The fire assay technique, which concentrates the noble metals into a nickel sulfide button was employed by BORTHICK et al.[11]

This paper presents the development of a radiochemical separation procedure for elimination of some interfering radionuclides such as lanthanide elements and scandium in iridium determination by neutron activation analysis. The accuracy of the procedure was confirmed through the use of the method for the determination of iridium in the USGS "standard rock" peridotite-PCC-1. The method was used for preliminary determination of iridium in 16 samples of marine sediment cores, collected at different depths in the "Campos" basin-RJ (BRAZIL) by the local state oil company (Petrobrás). The sediment cores correspond to the Cretaceous/Tertiary age but may not contain the gradational interface.

Experimental

Treatment of the sedimentary rocks

The rock samples were first broken in smaller fragments by using a hammer. About 100 g of rock were then ground in a manual agate mortar, until all the powder passed through a 150 mesh sieve.

Preparation of stock and standard solutions

A stock solution containing 2.13 mg Ir · ml^{-1} was prepared by dissolution of iridium tetrachloride (Pfaltz and Bauer, Inc.) in 2M HCl. The standard solution, containing 4.26 μg Ir · ml^{-1} was prepared by dilution of the stock solution. From this solution an aliquot of 100 μl was pipetted on analytical filter paper for irradiation.

Irradiation and counting

Sample (about 1 g) and standard solution (filter paper) were irradiated together in aluminium tubes, at a thermal neutron flux of approximately $5 \cdot 10^{12}$ n · cm^{-2} · s^{-1} for a period of 8 hours.

Radiochemical processing of the sample started after a delay time of about 10 to 15 days after irradiation.

Countings were carried out using a high resolution solid state ORTEC Ge(Li) detector, with a resolution of 2.8 keV for the 1332 keV peak of ^{60}Co. The detector was coupled to a 4096 – channel analyzer. The 468 keV gamma-ray emitted by ^{192}Ir (74.4 d) was used for analysis. Data reduction was carried out using minicomputers and one or both of the following software for spectral analysis: Program FALA,[12] Program Ge(Li) Gam, from ORTEC.

Radiochemical separation procedure

After the cooling period, the irradiated sample was transferred to a teflon beaker. An aliquot of stock solution was then added as carrier (2 mg Ir) followed by a mixture of concentrated acids (HF, HNO_3 and $HClO_4$). This beaker was covered with a teflon disk and placed in a stainless steel dissolution bomb. Finally, the bomb was kept in a stove at 100 °C for about 5 hours. KIMBERLIN et al.[13] have shown that complete exchange between Ir carrier and activated iridium in the sample can be obtained by prolonged heating (c.a. 150 m) of acidic mixtures used to dissolve Tocopilla iron meteorite samples.

The dissolution bomb was allowed to cool off and then the teflon beaker was removed from it. The solution was taken to almost dryness for elimination of acids. According to DE SOETE,[14] amounts of iridium in the mg order are not distilled in boiling perchloric acid (c.a. 200 °C).

The residue was taken up with 150 ml of 0.03M HCl and 3 ml of H_2O_2 (120 vol) were added in order to oxidize Ir to Ir(IV).

The resulting solution was passed through a chromatographic column (1 cm diameter and 30 cm height) containing the cationic resin Bio-Rad AG 50W-X8, previously conditioned with 60 ml of a 0.03M HCl solution containing 3 ml of H_2O_2 (120 vol), at a flow rate of approximately 0.5 ml/min.

The complex ion ($IrCl_6^{2-}$) present in solution was not sorbed by the resin, while the interfering elements (lanthanides, Sc, Na, Fe, Co) were sorbed.[15]

The effluent solution containing iridium was concentrated by evaporation to 25 cm^3 and transferred to glass penicillin type containers for counting.

The iridium standard (filter paper) was dissolved in an equal volume of 6M HNO_3 and 2M HCl solution. The activities of both sample and standard were measured and compared.

Results and discussion

Determination of radiochemical separation yield

The procedure was tested with non-irradiated marine sediments to which was added an iridium radioactive tracer. A mixture of concentrated acids (HF, HNO_3 and $HClO_4$) together with the radioactive tracer of ^{192}Ir was added to the teflon beaker containing about 1 g of the marine sediment. The radiochemical separation yield was computed by comparing the added and recovered activities.

The average yield obtained with 10 determination was (76±2)%.

Accuracy and precision of the method

In order to check the accuracy and the precision of the method, 14 determinations of iridium were made in the USGS Standard rock Peridotite – PCC-1.

Results obtained are shown in Table 1, and compared with the averages given by FLANAGAN[16] and the consensus value calculated by GLADNEY et al.[17] The precision of the method is calculated to be about 25%.

Table 1
Results of the determination of iridium
in the USGS Standard Rock-PCC-1,
using radiochemical neutron activation analysis

Ir concentration, ng/g
(6.07±1.20)
(5.14±0.71)
(4.70±1.49)
(3.42±0.67)
(6.90±0.96)
(7.18±1.42)
(3.91±0.69)
(4.38±1.39)
(6.64±1.76)
(7.32±1.03)
(5.12±0.71)
(4.05±0.70)
(3.79±0.75)
(6.54±1.74)

This work: Mean ± Standard Deviation = 5.37±1.38
GLADNEY et al.[17] = 4.8±1.9
FLANAGAN[16] = 5.2

The comparison of the obtained data with the existing values in the literature for PCC-1 showed that the accuracy and reproducibility of results for the iridium measured with the method developed is well suited for the purpose of determination of the iridium anomaly at the Cretaceous/Tertiary boundary and other geological studies employing iridium as a tracer. The practical detection limit, is of the order of 0.5 ngIr/g.

Application of the method to the analysis of Ir in marine sediment samples

The method was used for the determination of iridium in 16 samples of sedimentary borehole cores taken at several depths in the "Campos" basin in the continental platform of Rio de Janeiro, Brazil (Table 2).

The samples were chosen from a suite of borehole cores belonging to the Brazilian State Oil Company (Petrobrás) and boreholes No. 1-KJS-19 from 2834.8 to 2838.7 meters depth were selected, which contains the geological interface between the Cretaceous and the Tertiary periods, although in all but a few uncertain cases the interface in Brazil has been subjected to erosional processes, this not allowing reliable location and determination of the iridium anomaly. The present study was useful to determine the background level of iridium in the sediments. The method will be

Table 2
Results for the analysis of iridium in marine sediments of "Campos" Basin-RJ (Brazil)

Depth, m	No. of determinations	Iridium contents, ng/g (Mean ± Standard deviation)
2834.78	4	1.44±0.63
2835.0	4	1.23±0.56
2835.31	6	3.00±1.75
2835.51	4	1.14±0.32
2835.70	4	1.97±1.03
2835.93	6	4.49±0.68
2836.13	4	0.73±0.19
2836.57	4	0.93±0.17
2836.93	4	0.62±0.10
2837.20	4	1.23±0.23
2837.46	8	1.63±0.67
2837.76	4	1.87±0.06
2837.96	8	1.83±0.29
2838.27	3	3.55±1.37
2838.54	3	2.26±0.09
2838.66	4	0.66±0.28

applied later to samples containing confirmed gradational Cretaceous-Tertiary interfaces in Brazil.

The main interference found in the analysis of iridium in the marine sediment samples, came from the presence of lanthanide elements and scandium. The complexity of the γ-ray spectrum of the lanthanides and the high Sc content hindered the iridium determination by means of purely instrumental activation analysis.

Therefore, the most important steps of the radiochemical separation procedure are the sorption of interfering elements by the Bio Rad AG 50W-X8 resin and the passing of the iridium(IV) species for the adequate recuperation of iridium to the effluent solution, because the $IrCl_6^{3-}$ was found to be weakly sorbed by the resin.[15] Since the chemical yield for Ir was satisfactorily reproducible (76±2)% and the experimental conditions were carefully controlled, it was found unnecessary to determine the Ir chemical yield for each analysis.

It is believed that sample heterogeneity did not occur, since the samples were ground below 150 mesh and carefully homogenized by mixing.

Conclusions

In this work a radiochemical method for the determination of iridium at the ppb level in borehole sediment core samples was developed and applied to samples of Cretaceous-Tertiary geological interface in order to find the background level of iridium of this sedimentary basin. In order to verify the accuracy and precision, the method was tested with an USGS standard rock PCC-1.

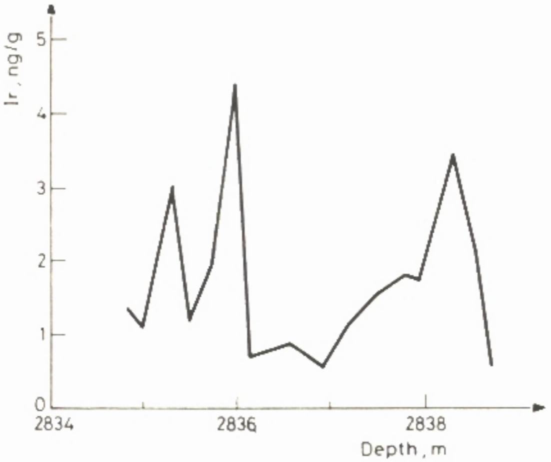

Fig. 1. Profile of iridium obtained in the region where the samples were collected

The analytical method developed has shown to be adequate for the purpose of the present work, with a relative standard deviation of about 25%, which can be considered as good for determinations at the ppb level. The agreement with the values published by FLANAGAN[16] and GLADNEY,[17] for the PCC-1 standard are also good, as can be seen in Table 1.

Results obtained for the sediments (Fig. 1) have shown wide deviations of iridium concentration for different depths. Since geological and paleontological studies of the "Campos" basin made by Petrobrās[18] indicate that the Cretaceous/Tertiary is not gradational, the peaks of iridium in Figure 1 are probably not of an "anomalous" characteristic but are related to normal sedimentation processes. The method will now be applied to a more complete set of sediment core samples and normal samples from other regions of Brazil, for which the gradational interface is known, in order to proceed wtih the studies of the unsolved Cretaceous/Tertiary interface enigma.

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