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Determination of Refractory Trace Elements in Chinese Meteorites by RNAA

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Dedicated to Prof. Hans Rudolf von Gunten on the occasion of his 60th birthday

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Abstract

Some refractory trace elements are important target elements for spallation reactions in meteorites. These elements also serve to characterize the investigated meteorites. The elements Ti, Y, Zr, Hf, W and Ta were measured after radiochemical separation in chondrites from China. After acid digestion of the irradiated samples, the group separations were obtained by precipitation reactions. The necessary radiochemical purification of the pure β emitter Y was realized on a Lewatite OC 1026 column. For all the other elements discrete gamma radiation was measured.

Introduction

Recently a large number of meteorites from China became available for investigations [1]. Due to the dense population of this huge country (about 7% of the land surface of the earth) many falls of such precious stones are observed and some material is collected every year. The chemical composition is important for the characterization of the meteorite as well as for a complete study of the history of the investigated fragments and for noble gas studies. Many rarely determined elements are important target elements for spallation reactions by the cosmic radiation. Y and Zr contribute to the formation of Kr and Ba and rare earth elements to that of Xe. The main fractions of the samples were used for a thorough study of the concentrations of the noble gases and a study of their isotopic composition [2]. The samples were provided by the Institute of Geochemistry, Academia Sinica, Beijing, to the Department of Physics of our university. The physicists themselves forwarded a small fraction of the material for direct chemical analyses of important elements to our laboratory.

The aim of this study is to present a sensitive method capable of determining low concentrations of elements not accessible by INAA, even in small samples.

Experimental

Dissolution of samples

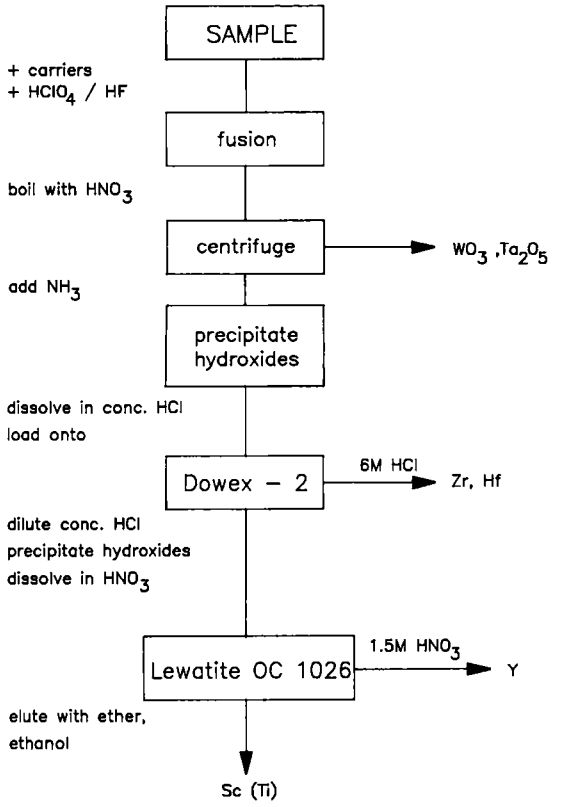
The crushed meteoritic material was sealed in Suprasil vials (synthetic quartz) and irradiated for 2 days at a thermal flux of $5 \times 10^{13} \times s^{-1}$ cm^{-2} in the swimming pool reactor SAPHIR at Würenlingen, Switzerland. After a cooling period of two days to reduce the level of activity, the gamma radiation of the samples were measured with a Ge(Li) detector connected to a multichannel system with a loss free counting unit (LFC) for the assessment of the concentrations of Na, Sc, Cr, Fe and Co. The quartz vials were then cut open and the samples were dissolved in presence of carriers of Sc, Zr, W and Ta and 1 mg La by addition of 8 ml conc. HF and 4 ml conc. $HClO_4$ in teflon crucibles (see relevant information in Table 1). The residue was then boiled for 2 hours with 5 ml of conc. HNO_3. After the evaporation to the near dryness the residue was ready for group separations.

Table 1. Analysis parameters of the measured elements

Element	Carrier	Measured radio-nuclide	Half life h	Weighing form	Chemical yield	Measured energy keV
Ti	Sc: 5 mg	Sc-48	43.7	Sc (D2EHPA)$_n$		1312 1037
Y	carrier free	Y-90	64.1	Y oxinate	Y-88 50%	β^-
Zr	5–7 mg	Zr-95	1545	Zr mandelate	85%	724 756
Ta	20 mg	Ta-182	2746	Ta_2O_5	60%	1189 1221
Hf	coprecipi-tation	Hf-181	1020	Hf mandelate	85%	482 346
W	20 mg	W-187	23.9	WO_3	60%	686 480

Group separation

A schematic representation of the chemical procedure is given in Fig. 1. The precipitate formed after the dissolution and treatment with HNO_3 contains $WO_3 \cdot n(H_2O)$ and $Ta_2O_5 \cdot n(H_2O)$, which are separated by centrifugation. In the supernate, the hydroxides are precipitated with conc. NH_3. The hydroxides are redissolved in 2 ml conc. HCl and loaded onto an anion exchange column (Dowex 2 x 8, 200 – 400 mesh, diameter 6 mm, length 100 mm). REE, Y and Sc do not stick to the resin in 10 M HCl acid. Zr and Hf are eluted with 25 ml 6 M HCl. The REE are again precipitated as hydroxides and redissolved with 0.05 M HNO_3. 1 mg each of Tb and Sm carriers are added. The resulting solution is placed on a column filled with Lewatite OC 1026 (Bayer AG, Leverkusen) [3]. This resin is produced by copolymerization of D2EHPA (di-2-ethyl hexyl phosphate) with styrene and divinyl benzene and has favourable properties for metal separations [4, 5]. Columns of a diameter of 4 mm and a length of 120 mm were filled with this resin using a grain size fraction 0.12 to 0.17 mm. From such columns La elutes in the first 40 ml of 0.5 M HNO_3. In the next 60 ml of 1 M HNO_3. Eu elutes as the main activity. Y is finally eluted with 40 ml 1.5 M HNO_3, whereas Sc remains on the Lewatite resin.



Purification of the elements

Hf: see Zr. This element follows so closely the chemical behaviour of Zr that only Zr carrier is used as group carrier [6, 7]. The chemical yield obtained for Zr is assumed to be valid also for Hf.

Ta: The residue after the dissolution of W is transferred to tubes of polyethylene. Ta is then immediately dissolved by 10 M HF [8] (after a few hours the dissolution will not work any more). The resulting solution is extracted into diethylether giving the necessary decontamination from Fe and Cr [9]. The ether is evaporated and the residue filtered off onto paper discs and dryed. After the measurement of the activity the samples are calcinated and the Ta_2O_5 weighed for the determination of the chemical yield. (When filter discs of quartz fibres are used, the calcination at 800 °C can be done before the counting.)

Ti: Since Ti only forms short lived nuclides by the irradiation with thermal neutrons, the fast neutron reaction (n, p) producing ^{48}Sc allows to dose this element a few days after the irradiation with reactor neutrons. Sc is very strongly retained by the Lewatite resin [10]. After the elution of Y from the columns, the resin is transformed to the chloride form with 5 ml of 6 M HCl. The columns are next washed with 10 ml ether. This eluate is collected in centrifuge tubes containing 1 ml of 6 M HCl. After the evaporation of the ether on a water bath, the Lewatite columns are washed with 10 ml ethanol, which is collected in the same centrifuge tubes. White flakes precipitate (probably $Sc(D2EHPA)_3$) [4], which can be filtered off after 5 to 10 minutes onto glass fibre discs and washed with 30 ml water. The precipitate is dryed at 105 °C and reaches constant weight after 3 hours.

W: The freshly formed precipitate is heated with 25% solution of ammonia to dissolve W [11]. Only about one half of the W dissolves. The remaining W is then dissolved with 5 ml conc. HCl. The resulting solution is combined with the solution of $NH_3 \cdot WO_3 \cdot x H_2O$ is reprecipitated by warming with 2 ml of conc. HNO_3. The $WO_3 \cdot n(H_2O)$ precipitate is directly filtered onto paper filter discs. The chemical yield is determined after the measurement of the activity. Since the precipitate has no stochiometric composition it needs calcination prior to the weighing.

Y: To the eluted solution from the Lewatite column containing the Y, 10 mg of Y carrier are added. The hydroxide is precipitated with NH_3, separated by centrifugation and dissolved with 4 ml of 6 M HCl. After dilution to 2 M HCl, the final precipitate is obtained by the addition of 5 ml of a 5% oxinate solution. The resulting sample is radiochemically pure. The chemical yield is determined by the measurement of ^{88}Y, added to the sample prior to dissolution. The β activity is measured on a proportional counter using an Al absorber of 677 mg/cm^2. The decay of ^{90}Y is followed. The necessary correction for the contribution of ^{88}Y and contaminates is less then 5% of the counts in the β channel.

Zr: This element is eluted from the anion resin together with Hf using 25 ml of 6 M HCl [6, 7]. The eluate is combined with 20 ml of a saturated mandelic acid solution. Hf and Zr both precipitate as the mandelate. They are filtered off, and washed with water and ether.

Table 2a. Major and trace elements measured by instrumental activation analysis (1 σ errors are ± 10%)

Chondritic meteorite	Meteorite type	Na ppm	Sc ppm	Cr ppm	Co ppm	Fe %
Guangnan	L6	6300	6.6	3180	1160	23.7
Xingyang	H5	5700	6.3	3500	840	24.6

Table 2b. Trace elements determined by radiochemical neutron activation analysis (1 σ errors: Ti ± 15%, Y ± 10%, Zr, Hf, W and Ta ± 5%)

Chondritic meteorite	Meteorite type	Ti ppm	Y ppm	Zr ppm	Hf ppm	W ppm	Ta ppm
Guangnan	L6	–	2.2	5.7	0.12	0.50	–
Xingyang	H5	–	2.2	5.2	0.08	–	–
Xingyang	H5	⩽600	2.1	5.3	0.08	0.85	0.024
Average	L6	460–810[a]	2.1[a]	5.1[b]	0.14[b]	0.12[a]	0.021[a]
chondrites	H5	510–780[a]	2.2[a]	6.2[b]	0.23[b]	0.14[a]	0.021[a]
BHVO-1		15200	28.1	190	4.3	0.26	1.0
BHVO-1 Lit.[c]		16000 ±500	28 ±2	180 ±30	4.2 ±0.2	0.28	1.1 ±0.2

[a] MASON [12]
[b] EHMANN and REBAGAY [13]
[c] Geostandards Newsletter [14]

Results and discussion

Table 2a contains the results of the measurements of the gamma radiation prior to dissolution of the samples for the meteorites investigated in this study. Only elements important for the chemical characterization are reported here. A distinct difference in composition is recognized between the two meteorites. As expected the concentration for Fe is higher for Xingyang (type H5, high iron chondrite) compared to Guangnan a L6 chondrite, whereas the concentration for H chondrites is lower compared to L chondrites for Na. As this paper mainly deals with the radiochemical determination of elemental concentrations, the results in Table 2b will be discussed more extensively. To demonstrate the reproducibility of the procedure, the values obtained for Xingyang in two different experimental series are reported individually. Excellent agreement between the two sets indicates good control of the chemical treatment of the samples. The elements Ti, W and Ta were added in the development of the chemical procedure, therefore only one value is reported for these three elements for the chondrite Xingyang. No results are reported in the literature for the radiochemically investigated elements of the analyzed meteorites. The results presented lie in the range for chondrites published by MASON [12], excepting those for W. Our values for W are very high compared to the average reported by MASON. However, our control results for the US Geological Survey reference material BHVO-1, analyzed simultaneously, are identical to those reported in the literature. Often, W is analyzed by instrumental techniques known to be more prone to contributions from other gamma lines, than our radiochemical method.

The sensitivity for Ti is rather low. Concentrations below 0.1% are difficult to assess by the technique presented here. For meteorites originating from the earth's moon, which have concentrations of Ti in the percent level, good results were obtained [15]. The value for BHVO-1 coincides within the error with the one reported in the literature.

The presented results in combination with noble gas data allow to derive specific Kr production rates for Y and Zr [16]. Y and Zr concentrations and the resulting production rates strongly vary among different meteorite classes. Therefore, the element specific production rates have to be known for the calculation of cosmic ray exposure ages of extraterrestrial samples [17].

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