High Precision Concentration Analyses of High Field Strength Elements (Nb, Ta, Zr, Hf)

M. Bizimis (NHMFL, now at U. South Carolina, Geology); V. Salters (NHMFL and FSU Geology); A. Sachi-Koscher (NHMFL, Geochemistry)

Introduction

The high field strength element (HFSE) pairs Nb-Ta and Zr-Hf are considered "geochemical twins" because they do not fractionate appreciably from each other during earth processes (e.g. mantle melting, crystallization). This leads to little overall variability in the Nb/Ta ratios of terrestrial rocks. It has been shown for some time that the Nb/Ta ratios (at a given Zr/Hf ratio) of different terrestrial reservoirs (e.g. upper mantle, continental crust) are appreciably "subchondritic". This has led to the suggestion that there exists a reservoir in the earth that is "hidden" from our sampling ability. This reservoir is thought to be eclogite, or recycled oceanic crust [1]. In order to understand the mechanisms that may lead to the formation of such a reservoir and therefore recognize its geochemical fingerprints we need very high precision determinations of Nb/Ta and Zr/Hf ratios in rock samples.

Experimental

The analytical method employed here is a modification of the Standard Addition (SA) method. In the SA, an accurately determined amount of an element is added ("spiked") to a known amount of sample solution. The unspiked and at least two spiked samples are then measured by ICP-MS (with ELEMENT -1 at the Geochemistry Division, NHMFL). The concentration of the spiked element in the sample solution is calculated by the intercept of the best-fit line on a concentration vs. intensity plot. We improve over the traditional SA by correcting for instrumental measurement with the use Y and Yb as internal standards, as these elements are already present in natural rocks, and determine $^{93}Nb/^{89}Y$, $^{90}Zr/^{89}Y$, $^{178}Hf/^{172}Yb$, $^{181}Ta/^{172}Yb$ ratios of the sample and spiked solutions. We use a York-type regression considering both measured and propagated errors. To further improve precision we simultaneously spike Nb-Ta-Zr-Hf by using spike mixtures with appropriate concentrations for different samples, prepared from pure elemental standard solutions, NIST-traceable.

Results and Discussion

		Nb	Ta	Zr	Hf	Nb/Ta	Zr/Hf
BHVO-1	n=10	17.29	1.11	170.1	4.50	15.62	37.82
	1 std	0.96%	1.02%	0.84%	0.95%	0.7%	0.5%
BCR-1	n=5	11.55	0.73	184.8	4.99	15.78	37.08
	1 std	0.5%	0.3%	0.9%	0.5%	0.6%	0.6%
BIR-1	n=11	0.498	0.038	14.43	0.601	12.97	24.00
	1 std	1.8%	1.8%	1.3%	1.3%	0.5%	0.7%
AGV-1	n=4	13.39	0.82	231.1	5.27	16.44	43.91
	1 std	0.6%	1.5%	0.9%	1.1%	0.8%	0.3%

The table shows the HFSE concentrations (in ppm) and Nb/Ta, Zr/Hf ratios of USGS standards determined by our technique. We demonstrate better than 1% external reproducibility (1 stdev) in Nb/Ta and Zr/Hf ratios. An alternative high precision method is the use of isotope dilution (ID) and chromatographic separation of HFSE [2]. While ID is generally considered as the most accurate method in determining concentrations, Nb cannot be determined by the ID method since it is monoisotopic. Therefore the Nb/Ta ratios determined by [2] must rely on 100% Nb yields through the columns and calibration against Zr concentration. Our method demonstrates similar external reproducibility in Nb/Ta as the ID method of [2], while it is faster, it does not require expensive isotope spikes and chromatographic separations and has lower blanks thereby allowing for more depleted and smaller samples to be analyzed. This method is being employed for the high precision HFSE analyses of arc lavas, ocean island basalts and kimberlites-lamproites.

Acknowledgements

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References

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[2] Munker, C., *et al*., G^3 doi:10/1029:2001GC000183 (2001).