Trace element contents in the Smithsonian reference materials collection: A program to continue Eugene Jarosewich's legacy

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New developments in microanalysis, such as secondary ion mass spectrometry (SIMS, a.k.a. ion microprobe) and LA-ICP (-MS) determination of trace elements as well as isotopes, require a new generation of calibration reference materials (RM). For many years Eugene Jarosewich of the US National Museum of Natural History carefully characterized specimens from the SI collections to be used as RM for electron microprobe analysis. However, these RM are of limited use for the new analytical techniques because they have not been characterized for trace element and isotopic compositions, and homogeneity. We have begun a program to continue the Jarosewich's legacy by characterizing natural samples, particularly mantle-derived minerals, for trace elements and isotopes. Here we present in the table below preliminary minor/trace element data (±2 sigma) for mantle derived augite, hornblende, and pyrope specimens from the famous Kakanui, New Zealand locality, comparing electron microprobe (n=40) and bulk (1.6 g) X-ray fluorescence data. Traverses by EPMA with a 40 µm interval were performed on three grains per specimen (30 kV, 200 nA, 40 µm-beam diameter). XRF analyses were performed on pressed pellets (4:1 sample to binder ratio) at 80 kV and 30 mA. The samples show a high degree of homogeneity and consistency between two analytical methods, and thus, are good candidates for further development as RM for SIMS and LA-ICP-MS. Our next step will be actual analysis of the samples by both SIMS and LA-ICP-MS

ICI -IVID.			
	143968 pyrope	122142 augite	143965 hornb.
	EPMA XRF	EPMA XRF	EPMA XRF
Sc	130±20 132±2	n.a. 37±6	n.a. 16±2
V	150±20 150±4	290±10 300±6	410±20 415±4
Cr	600±60 650±9	1040±90 1098±6	b.d.l. b.d.l.
Ni	50±20 61±2	292±12 297±2	80±20 97±2
Cu	b.d.l. 15±6	b.d.l. 9±2	b.d.l. 25±2
Zn	30±20 45±2	33±18 117±2	60±8 65±2
Ga	n.a. b.d.l.	n.a. 4±1	b.d.l. 16±2
Sr	n.a. b.d.l.	n.a. 62±1	n.a. 480±2
Zr	110±60 77±4	b.d.l. 28±2	60±40 90±2
Ba	n.a. b.d.l.	b.d.l. b.d.l.	340±20 40±30

Remobilization of REE in F-rich, low-temperature environments

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REE patterns (including Y, Th, U) of geologically young fluorites, iron hydroxides, and manganese oxides precipitated from groundwaters from the Clara mine and other deposits of the Schwarzwald ore district (SW Germany) were analyzed by LA-ICP-MS. Potential sources of these elements are primary fluorites in hydrothermal veins, their respective host rocks (granites and gneisses) and surface waters. Representative primary fluorite and water samples were analyzed along with the mineral precipitates to constrain the redistribution processes of REE under highly oxidizing, near surface conditions.

The Y/Ho ratios of all fluorites are higher than those of average crust but are highly variable in iron hydroxides, indicating relatively similar chemical conditions during formation of fluorites but more variable ones during iron hydroxide precipitation. Comparison of co-precipitated fluorites and goethites allow the calculation of differences in the Y/Ho fractionation between these minerals. The close similarity of the REE patterns of some fluorites and waters suggests surface complexation-controlled REE incorporation into fluorite.

Unexpectedly high U contents up to about 180 ppm are found in colorless, clear botryoidal fluorites and are negatively correlated with the overall REE contents and with Ce/Ce*. The Ce-anomaly suggests that U is transported as U(VI) while the negative correlation with the REE(III) indicates different transport mechanisms for U(VI) and REE(III) or reverse dependence on factors like temperature or pH. Manganese oxides show pronounced Ce anomalies, probably due to catalyzed oxidation of Ce(III) to Ce(IV) at their surface.