Electronic Supplement I

Assessment and correction of polyatomic interferences

Polyatomic interferences have detrimental effects on analytical accuracy in LA-ICP-MS, especially if the interfering element is present in much higher concentrations than the element of interest. Interference effects cannot be entirely avoided in LA-ICP-MS, but their significance and relative influence on the isotopes of interest can be evaluated. This was achieved by expanding the analytical menus to include isotopes that yield indirect information on the magnitude of interference effects affecting the isotopes of interest. For analysis of minerals, the following isotopes were added: ^{27}Al ($[^{27}Al^{16}O]^+$ interference on ^{43}Ca), ^{29}Si ($[^{29}Si^{16}O]^+$ interference on ^{44}Ca), ^{39}K ($[^{39}K^{40}Ar]^+$ interference on ^{79}Br), ^{63}Cu and ^{65}Cu ($[^{63}Cu\,^{16}O]^+$ and $[^{65}Cu\,^{16}O]^+$ interference on ^{79}Br and ^{81}Br, respectively) and ^{111}Cd ($[^{111}Cd^{16}O]^+$ interference on ^{127}I). The ^{127}I mass may further be affected by argide interferences of $[^{87}Rb^{40}Ar]^+$ and $[^{87}Sr^{40}Ar]^+$, but their influence was considered negligible because neither Rb nor Sr are major elements in the samples and because argide interference effects are orders of magnitude weaker than oxygen based ones.[43] The ^{163}Dy isotope was included to assess the possible effects of doubly charged $^{162}Dy^{++}$ on the ^{81}Br mass. Mass 162 itself is affected by an isobaric interference between ^{162}Dy and ^{162}Er, precluding direct measurement of this mass, but it was assumed that the count rates of ^{163}Dy would provide an adequate estimate for ^{162}Dy count rates due to their similar isotopic abundances. Erbium was not included, because the isotopic abundance of ^{162}Er is so low that any potential doubly charged interference effect on ^{81}Br will be outweighed by doubly charged $^{162}Dy^{++}$. Similar interference effects by doubly charged $^{158}Gd^{++}$ can affect ^{79}Br, but ^{81}Br is the preferred Br isotope due to the generally more significant interference effects on ^{79}Br caused by $[^{39}K^{40}Ar]^+$. Therefore, we have not investigated the potential effect in order to keep the number of elements included as small as possible.

For analysis of synthetic fluid inclusions, interference effects were more straightforward to predict and monitor because the starting solutions did not contain any REE or Cu. However, since the starting solutions contained 200 µg/g of Rb, ^{125}Te was included to assess the possible effect of $^{87}Rb^{40}Ar^+$ interferences affecting the ^{127}I mass. A signal on ^{125}Te coinciding with a fluid inclusion signal would indicate the presence of argide interferences caused by $^{85}Rb^{40}Ar^+$ species. Since the intensity ratios of $^{85}Rb^{40}Ar^+$ and $^{87}Rb^{40}Ar^+$ should be linked through the relative isotopic abundances of ^{85}Rb and ^{87}Rb, any potential effect on ^{127}I count rates caused by $^{87}Rb^{40}Ar^+$ interference thus be evaluated semi-quantitatively using the ^{125}Te signals.

Doubly charged REE^{++} interferences affecting Br quantification

Bromine concentrations in the scapolite samples Sca17, HAL-O and BL-Q were significantly underestimated when Durango apatite is used as external reference material (Table 6). The discrepancy between the measured and the reference values is caused by doubly charged $^{162}Dy^{++}$ interferences which significantly affect the apparent signal intensities of $^{81}Br^+$.

Figure 3 in the manuscript shows high-resolution mass spectra of Durango apatite and Sca17 for the mass over charge (m/z) range from 80 to 84.5. The peaks observed at m/z of 80.5, 81.5, 82.5 and 83.5 are caused by doubly charged ions of ^{161}Dy, ^{163}Dy, ^{165}Ho, and ^{167}Er. The mid-mass lanthanides have very low second ionization potentials around 11 eV, which is even lower than the first ionization potential of Br (11.81 eV). This causes significant production of REE^{++} ions in the plasma relative to the production rates of $^{81}Br^+$. Consequently, we can expect that doubly charged $^{162}Dy^{++}$ will significantly contribute to the count rates measured on m/z of 81, and thus increase the apparent ^{81}Br count rates in Durango apatite.

Dysprosium and Br concentrations in Durango apatite are 68 and 0.8 µg/g, respectively (Table 5),[33,48] whereas the scapolite samples contain little Dy (1 ± 0.1 µg/g) but significantly more Br (398 µg/g) (Table 5). Despite the relatively low concentrations of Dy in Durango apatite, the very high ionization efficiency of the REE still yields significant count rates in the m/z range occupied by doubly charged ions of ^{161}Dy, ^{163}Dy, ^{165}Ho and ^{167}Er (m/z of 80.5, 81,5, 82,5 and 83.5, respectively, Fig. 3). Taken together, low Br concentrations and significant REE^{++} interference effects then result in largely interference-dominated count rates on the ^{81}Br isotopes in Durango apatite, yielding too high apparent sensitivities (cps/[µg/g]) for the low reference concentration value of Br. By contrast, the REE concentrations in the three scapolite samples are so low that the signal intensities at non-integer m/z values are 3 – 4 orders of magnitude lower than the count rates on integer m/z (Fig. 3). The effect on the count rates of ^{81}Br on Sca17 are therefore practically unaffected by contributions of doubly charged lanthanide ions.

The effect of selective interferences affecting sensitivities only on the external standard reference material but not the sample is best illustrated by recalling the fundamental equation used for calculation of element concentrations in LA-ICP-MS:[50]

$$C_i^{SMP} = \frac{I_i^{SMP}}{I_{is}^{SMP}} \frac{C_{is}^{SMP}}{\left(\frac{I_i^{SRM}}{I_{is}^{SRM}} \frac{C_{is}^{SRM}}{C_i^{SRM}} \right)} \tag{1}$$

where C_{is}^{SMP} and C_i^{SMP} denote the concentrations of the internal standard (*is*) and an element (*i*) in the sample, respectively; I_{is}^{SMP} and I_i^{SMP} are the signal intensities (counts per second) of the internal standard and an element in the sample; and C_{is}^{SRM} , C_i^{SRM} , I_{is}^{SRM} and I_i^{SRM} are the concentrations and intensities of the internal standards and an element in the standard reference material (SRM). All intensities are corrected for background levels and instrumental drift. It follows that the significantly too high apparent Br sensitivities caused by the interference from doubly-charged REE species during ablation of Durango apatite results in a significant underestimation of the Br concentrations determined in scapolite. This is exactly what the data in Table 6 demonstrate.