Development of the high presicion measurement of mercury species isotopic ratios by GC-MC-ICP-MS and its validation with two other analytical aproaches

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Development of the novel technique

Mercury is transformed by microorganisms into organic forms, mainly CH_3Hg ($MeHg^+$) and $(CH_3)_2Hg$ (di-MeHg), which are highly toxic and volatile. Hence, two most abundant Hg species in the environment are Hg^{2+} and MeHg. Since gas-chromatography (GC) is one of the easiest approaches to separate this species on-line, with relatively simple sample preparation, we have estimated the suitability of the GC hyphenation with MC-ICP-MS for the precise isotopic analysis. A new protocol for the simultaneous measurement of isotopic ratios in Hg species was developed.

Validation of developed method versus other techniques

Two other analytical approaches cold-vapour generation (CVG) and continuous nebulization (CN) were chosen as reference techniques to validate the measurement of isotope ratios by GC-MC-ICP-MS. Analytical performances of these three techniques were compared, and precision for the different techniques are compared in the table below. Optimimisation of the integration approach of the transient signal and GC parameters provide a suitable precision for the Hg isotopic analysis in environmental samples.

Table 1. Comparison of precision (‰) for isotopic ratios of Hg^{2+} and MeHg using different sample introduction systems

	199/198	200/198	201/198	202/198
GC for $MeHg^+$	0.15	0.21	0.37	0.11
GC for Hg^{2+}	0.14	0.25	0.28	0.15
CN for $MeHg^+$	0.025	0.019	0.08	0.026
CN for Hg^{2+}	0.027	0.032	0.059	0.041
CVG for Hg^{2+}	0.032	0.051	0.14	0.098

Conclusions

When analysing real-world samples for Hg species isotopic analysis, preliminary sample preparation for both CVG and CN are very time- and labour-consuming in comparison with GC, while GC has a higher precision of the measurements. The precision of the GC-MC-ICP-MS measurement can be improved if a preconcentration step is applied before injection into the GC.

Stress-induced redistribution of Y and HREE in garnet during high-grade polymetamorphism

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Almandine garnet ($Alm_{62.6}Pyr_{11.4}Sps_{8.4}And_{6.5}Grs_{4.0}$) exceptionally rich in Y_2O_3 (1.8-2.3 wt%), Sc_2O_3 (0.11-0.23 wt%), $HREE_2O_3$ (1.9-2.3 wt%) and Na_2O (~ 0.3 wt%) occurs in Precambrian quartzofeldspatic granulites (*T*~ 860 °C) on Hisarøya, Western Gneiss Region, Norway. The granulites were partially reequilibrated to eclogite- (*P*: 14.9 ± 1.3 kbar, *T*: 649 ± 67 °C) and amphibolite-facies assemblages during the Caledonian Orogeny. The high Y and HREE concentrations allowed quantitative analysis and imaging of element distribution at the spatial resolution of EMPA. The granulite-facies garnet is overgrown by Caledonian garnet with Y_2O_3 and $HREE_2O_3$ both below 0.1 wt%. The granulite-facies cores are reequilibrated to lower Y_2O_3 and $HREE_2O_3$ in an outer zone, typically ~ 4 µm thick, (both Y_2O_3 and $HREE_2O_3$ ~ 1.2 wt%), and along internal deformation structures including microfaults with horsetails, en-echelon bands and splaying features around the tip of fractures (Y_2O_3 and $HREE_2O_3$ ~ 1.8 wt%). Locally, the internal reequilibrated zones, typically 10-20 µm across, have shoulders with higher Y and HREE (~ 2.9 wt%) than in the original garnet, suggesting closed-system behaviour for these elements. In addition, the garnet locally displays a m-scale complex mesh-like pattern with high and low HREE and Y bands, possibly related to straining. All features indicate ineffective Y and HREE diffusion under the present P-T conditions. Two charge-balancing mechanisms account for Y and HREE incorporation: (1) the YAG substitution involving incorporation of Al into the tetrahedral site is dominant in the granulite-facies garnet, and (2) coupled substitution with Na into the dodecahedral site is increasingly important during high-P reequilibration. The internal closed system reequilibration of the granulite-facies garnet may be due to stress concentrations build up in relict garnet during the eclogite-facies event. Possible mechanisms for reequilibration are discussed.