“ERRORS” IN HIGHLY SIDEROPHILE ELEMENT DETERMINATION

THOMAS MEISEL

General and Analytical Chemistry, University of Leoben, A-8700 Leoben, Austria.
Meisel@unileoben.ac.at

Models to explain observable distributions of HSE in the Earth’s mantle have to rely on a good database. To avoid duplicating measurements that have been done in other labs and to be able to directly and transparently compare results we need the concept of traceability. Comparable results can only be achieved by anchoring them to a common base for example a certified reference material.

To achieve traceability we need an accepted suitable reference material and an uncertainty statement for the measurement. This should enable us to judge the “fitness for purpose” of a result. To identify the composition of a late veneer component or if Pd enriched mantle regions are sought for by using element ratios (e.g. Pd/Ir), only data with sufficiently small measurement uncertainty can be used to recognize significant differences. This would require relative uncertainties on the elemental concentrations of about 2% to be fit for purpose, which is actually very difficult to achieve.

This goal is especially difficult to meet when analyzing platinum group elements, due to their low abundances in most terrestrial rocks and their high distribution coefficients causing problems with sample homogeneity that can be expressed as the so called nugget effect. But the nugget effect is **not** the only problem.

The combined uncertainty u_c is made up of four different contributions (Meisel et al. 2001):

$$u^2_c = u^2_{heterogeneity} + u^2_{segregation} + u^2_{preparation} + u^2_{measurement}$$

Variance due to sample *heterogeneity* and *segregation* can be taken care of (by taking larger subsamples and by homogenizing the sample containers before sampling, respectively), but significant variances arise from the last two terms. Although the nugget effect is recognized as a source of increased uncertainty it is often overestimated since irreproducible results can also reflect problems of *preparation* and *measurement*. In most cases the contribution of heterogeneity to uncertainty is small relative to those that come from the sample preparation and measurement process itself. Even if isotope dilution is used in combination with sensitive instruments for detection (e.g. sector field ICP-MS) many sources of error remain, one of which is incomplete digestion. It can be demonstrated that the widely used Carius tubes fail to completely liberate all Os from spinel bearing mantle rocks. Fusion and high pressure acid attack (e.g. HPA-S) are the most efficient means of achieving complete digestion to avoid problems during sample *preparation*. But even more problems arise from the actual measurement since differences of more than 30% relative have been observed on the same reference material using the same analytical procedure (e.g. isotope dilution, HPA-S and quadrupole ICP-MS) in different labs. Uncontrolled molecular interferences in an ICP-MS spectrum seem to be the major uncertainty for the determination of Ru and Pd.

In order to avoid errors and to gain confidence in the results, we thus need to put an emphasis on certifying and using reference materials to validate analytical procedures.

Meisel T., Moser J. and Wegscheider W. (2001) *Fresenius Journal of Analytical Chemistry* **370**, 566-572.