

## PGE reference material heterogeneity – Estimating minimum analytical mass

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Very small analytical masses (mg to ng) are dictated by modern analytical instruments, either because of their high sensitivity, analytical protocols or because of the small sampling volume of micro-beam techniques. But small sample masses can create problems when trace elements are major constituent in some minerals (e.g. PGE as PGM) and are irregularly distributed in samples or reference materials. Accidental inclusion or exclusion could change the spatial concentration realised simply due to spatial heterogeneity issues [1,2]. Such effects influence mass balance calculation and element budgets. Recommended minimum mass for reference materials is generally determined by analysing smaller sample mass until variance become unacceptable. Is there a way to determine minimum sample mass directly related to RM heterogeneity? And is it identical for all analytes, or unique for each analyte, in each sample? In order to systematically investigate these questions, pressed-pellets of PGE-bearing reference materials (CHR-Bkg, CHR-Pt+, MASS-1, MASS-3, WMS-1, WMS-1a) were analysed with an EDAX EAGLE III micro-XRF. Approximately 10 000 contiguous measurements were made with a beam of 50 µm covering a total area of about 25 mm<sup>2</sup>. Up to 25 analytes were measured including precious metals. Reproducibility was determined by analyzing the same location 1 000 times. In order to express the empirical heterogeneity, Angle Measure Technique (AMT) was employed [2]. The AMT transform describe the elemental map complexity as a function of geometrical scale from local to global. AMT provides a quantitative measure of the empirical heterogeneity for each element, RM, or analytical sample. From such results a minimum analytical mass for each analyte is proposed to ensure that analytical results are representative all the way down to the scale of RM fields-of-view. The proposed technique offers the advantage of defining the *effective* minimum mass for each analyte with better elemental sensitivity by allowing for a more meaningful estimation of the *global* minimum analytical mass.

[1] Savard, Barnes & Meisel (2010) *Geostandards and Geoanalytical Research* **34**, 281-291. [2] Huang & Esbensen (2000) *Chemometrics and Intelligent Laboratory Systems* **54**, 1-19.

## Groundwater flow impacts on sediment biogeochemistry: A multivariate statistical approach

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Lakes in (former) mining areas are strongly affected by Pyrite oxidation leading to high loads of iron and sulfur and the acidification of local waterbodies. Whereas the groundwater surrounding such lakes is mostly only weakly acidic, the pH of acidic mine lakes (AML) often lies below about 3 due to iron oxidation and subsequent Schwertmannite precipitation. It has been described that advective and diffusive flow through AML sediments affect the distribution of solutes and the biogeochemical driver pH in such sediments (e.g. Beer *et al.*, 2009).

To study the influence of groundwater – lake water – exchange on sediment biogeochemistry, we measured exchange rates along with sediment composition at 19 sites at an anthropogenic AML near Lauchhammer, Germany.

The pattern of the exchange rates was temporally and spatially heterogenous. Groundwater inflow dominated in the northern part of the lake and often exfiltration of acidic lake water was measured in the southern part.

To analyze the effects on the sediment, we cut sampled sediment cores according to color and texture into 3-5 layers and measured pH, sulfate reduction, contents of reduced sulfur species and carbonate, etc., and analyzed the results by multivariate statistical analysis. E.g. using cluster analysis, samples were grouped into 7 clusters which showed two different spatial patterns: 1) vertically, samples representing “fresh” sediment were observed in upper layers whereas “older” sediment samples were present at depth 2) clusters combining samples with higher biogeochemical activity and higher amounts of e.g. reduced iron sulfur species, and thus trapped acidity, prevail in the northern part of the lake. This second cluster could be related to the predominance of groundwater inflow in this part of the lake.

[1] Beer *et al.* (2009), *Geochimica et Cosmochimica Acta* **73** (13, Suppl. S), A102 (Goldschmidt 2009)