Useful ion yields and limits of SIMS analysis

RICHARD L. HERVIG

Department of Geological Sciences, Arizona State University, Tempe, AZ 85287, hervig@asu.edu

The ultimate detection levels achievable using the secondary ion mass spectrometer (SIMS, or ion microprobe) depend on how efficiently atoms of the isotope of interest can be ionized and detected. Given knowledge of the useful yield (ions detected/atom sputtered) and the volume of sample available, the analyst can determine in advance if a particular analysis is possible. Useful yields (UY) for positive secondary ions have been measured (using Cameca 3f and 6f SIMS) on NIST 610 glass (soda-lime glass containing 61 elements at \sim 500 ppm) and range from 0.0001 to 0.2 (figure). The most important influence on UYs is the ionization potential of the element. Useful yields increase linearly with sample accelerating potential (figure).

Instrumental conditions allowing maximum useful yields are rarely used in SIMS because of the need to eliminate molecular ions from interfering with the elemental ion of interest. Molecular ions are removed by using energy filtering or high mass resolution techniques. Knowing how these techniques reduce useful yields for different elements allowing the analyst to choose the analytical approach that will give highest sensitivity.



Because a sputtered cylindrical crater $\sim 30 \ \mu\text{m}$ in diameter and $\sim 1 \ \mu\text{m}$ deep will consume thousands of atoms, ppm levels of detection can be achieved even if the useful yield is much less than 0.0001. For low useful yields, increasing the sample removal rate (e.g., changing from an O⁻ to an O₂⁺ primary beam) will speed up analyses.

Trace metal concentrations in common sulfide minerals using SIMS

G. D. LAYNE¹, M.K. TIVEY² AND S.E. HUMPHRIS¹

¹MS 23, Dept. of Geology & Geophys., WHOI, Woods Hole, MA 02543, USA (glayne@whoi.edu, shumphris@whoi.edu)

²MS 8, Dept. of Marine Chemistry & Geochemistry, WHOI, Woods Hole, MA 02543, USA (mktivey@whoi.edu)

Analytical Technique

The determination of sub-ppm levels of trace metals in sulfides with SIMS is complicated by substantial isobaric interferences; e.g., ⁵⁸FeH⁺ on ⁵⁹Co⁺. However, large-format high-resolution, high-transmission ion microprobes can achieve analytically useful mass resolving powers (MRP) of 10,000 or greater - allowing elimination of these interferences by explicit mass resolution - while retaining sufficient signal levels and peak flatness to allow determination of multiple elements over an extremely large mass range (e.g., 54–209 Da) using magnetic peak switching.

Using a Cameca IMS 1270 instrument, we have demonstrated that simultaneous determination of Co, Zn, As, Se, Mo, Ag, Pb and Bi is practical, with a lateral resolution of $< 10\mu$ m in pyrite and chalcopyrite. For this set of elements, an MRP of 8500 is sufficient to resolve all significant interferences. Homogeneous reference materials are necessary to calibrate concentrations for each specific phase because matrix effects on ionization yield may be substantial.

Seafloor Hydrothermal Systems

We have applied this technique to a study of evolving physicochemical parameters and mass transfer within submarine hydrothermal systems. Our measurements have revealed meaningful variations between different seafloor systems, within the macroscopic zones of individual systems and, at a microscale level, within individual sulfide edifices.

For example, a detailed comparison of pyrite and chalcopyrite from a black smoker chimney at the Lucky Strike site shows systematic differences in the distributions of Co, Se, Zn and As. In chalcopyrite, all are relatively uniform in concentration within 1500 μ m of the inner edge of the wall (adjacent to vent fluid). In pyrite, Co and Se decrease and Zn and As increase in concentration with distance from this inner edge. This implies that chalcopyrite formed in contact with the hydrothermal fluid that filled the chimney channel, with later pyrite formed interstitially – a sequence compatible with the textural relationship of the two phases. The monotonic variations in Co, Se, As, Zn in pyrite are consistent with a decreasing T and/or change in pore fluid chemistry with distance from the chimney edge.