High Resolution–High Transmission Secondary on Mass Spectrometry (SIMS) for *in situ* microanalysis of lead isotope ratios in minerals and melt inclusions

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Large format high resolution - high transmission SIMS instruments, which include the Anutech SHRIMP and Cameca IMS 1270 ion microprobes, were designed to have the mass resolution and sensitivity required for in situ U/Pb dating of individual zircon crystals. This capability has been applied to other types of geochronology, including the U-Th-Pb dating of monazite (Harrison *et al.*, 1995). Application of the IMS 1270 at the WHOI-based Northeast Regional Ion Microprobe Facility (NERIMF) has also been successfully extended to the measurement of Pb isotope ratios in other mineral and glass phases. These include phases such as plagioclase and basalt glass which contain very low total Pb concentrations (0.1–2 ppm).

Zircon ($ZrSiO_4$) commonly contains 1–2% Hf substituting for Zr. Consequently, accurate measurement of Pb isotope ratios in zircon requires a mass resolving power (MRP) of 5000–6000 to sufficiently resolve molecular Hf species such as $HfSi^+$ from the isotopes of Pb (Schuhmacher *et al.*, 1993). However, isobaric interferences in feldspars and basalt glass generally require MRPs of only 1850 and 3500, respectively, for SIMS analysis.

For plagioclase, the most substantial isobaric interferences, tentatively identified as complexes of $Na_vCa_wAl_xSi_yO_z^+$, are easily resolved from the Pb isotopes at MRP 1850 or greater. This much lower MRP requirement is extremely advantageous since the inherent sensitivity for Pb in plagioclase is distinctly inferior to that for Pb in zircon, and because the natural Pb contents of magmatic plagioclases tend to be a maximum of only a few ppm. In plagioclase with a total Pb concentration of 1–3 ppm the ratios $^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$ can easily be determined with a precision of better than 0.5% (1 sigma) for a one hour analysis.

K-feldspars have a higher range of natural Pb concentrations - often hundreds of ppm - and appear to possess an inherently better relative sensitivity factor for Pb than plagioclase. Consequently, precisions are much higher than in plagioclase for $^{208}Pb/^{207}Pb/^{206}Pb$ analysis, and it is generally possible to extend the measurement to $^{208}Pb/^{207}Pb/^{206}Pb/^{204}Pb$ while still maintaining precisions better than 0.5-1%. Interferences on Pb peaks include $Na_vK_wAl_xSi_yO_z^+$ complexes on the low mass sides and as yet unidentified species (possibly $Li_vAl_xSi_yO_z^+$) on the high mass sides. Both sets of isobars are sufficiently resolved at 1800–2000 MRP to allow accurate Pb isotope analysis.

Analysis of basalt glasses requires a minimum MRP of 3500 to sufficiently resolve $REEO_2^+$ and HfO_2^+ species from the Pb peaks. Although basalt glass requires higher MRP, the intrinsic sensitivity for Pb in basalt under O^- bombardment is more than five times higher than that for plagioclase. Consequently, the transmission of the IMS 1270 is still sufficiently high to produce $^{208}Pb/^{207}Pb/^{206}Pb$ analyses with precisions of better than 0.4% (1 sigma) from homogeneous basalt glass for typical one hour analyses of materials with 1 ppm Pb. Reasonably precise measurements of $^{208}Pb/^{207}Pb/^{206}Pb/^{204}Pb$ can also be produced at these same resolutions with a concomitant increase in the analytical time.

Pyrite (FeS_2) and chalcopyrite ($CuFeS_2$) also require only modest MRP for Pb isotope analysis. The only substantial isobaric interferences appear to be Fe_3S^+ complexes on $^{204,206,207}Pb$ and $^{56}Fe_2{}^{32}S_3^+$ on ^{208}Pb. Both isobars require a nominal MRP of only 1000–1100. Due to inherently high natural Pb concentrations (typically 50–100 ppm), chalcopyrite can readily be analysed for $^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$ with precisions of better than 0.3%, and $^{208}Pb/^{207}Pb/^{206}Pb/^{204}Pb$ can be determined with precisions of better than 0.7% for typical 30 to 60 minute analyses.

A lateral spatial resolution of 20–30 micrometers can be maintained for most analyses. This allows studies of zoned minerals, exsolved phases, individual melt inclusions and even crystallized daughters within melt inclusions. The small inherent instrumental fractionation of measured Pb isotope ratios (0.0–0.2% per amu) allows overall accuracies which are more than adequate for many geochemical problems. The technique is thus appropriate for applications where heterogeneous Pb isotope signatures are expected from phases which cannot readily be separated for conventional mass spectrometric analysis.

In most silicate phases analysed (i.e. feldspars and basalt glass), the internal precision achieved generally approaches that inherent in the counting statistics of the Pb peak intensities. In chalcopyrite and pyrite, however, Pb routinely appears to be distributed heterogeneously on a scale comparable to that of the sputtered crater - probably due to exsolutions or microphases within the host sulphide. This causes the analytical precision to be limited instead by the short term signal intensity drift as peaks are magnetically switched into the single detector. Pb isotope analysis of sulphides is an application in which the newly available multiple collection array of the IMS 1270 (de Chambost *et al.*, 1998) will be of considerable benefit.

The microbeam analysis of Pb isotope ratios has obvious potential for widespread application to geochemical problems. Preliminary application in the WHOI facility has involved studies to typify the source and residence of an older radiogenic lead component in the 1.3 Ga Kiglapait layered intrusion in Labrador (Layne *et al.*, 1997) and to examine olivine-hosted melt inclusions from FAMOUS samples to test the 'garnet pyroxenite hypothesis' for the origin of garnet signatures in MORB (Shimizu and Layne, 1998).

References

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