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Precise Pb Isotope Analysis of Standards and Samples using an Isoprobe Multicollector ICP-MS: Comparisons with Doublespike Thermal Ionization Data

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Recent publications (Rehkämper & Halliday, 1998; Belshaw et al., 1998) on Pb isotope analysis by multicollector (MC-) ICP-MS have shown that it is possible to achieve external reproducibility on Pb standard SRM981 significantly better than conventional thermal ionization (TIMS) analyses. Improvements reported are from ca. 150 ppm/amu (1sd) at best on conventional TIMS to ca. 20-80 ppm on MC-ICP-MS, depending on the ratio. This is achieved through spiking with Tl to correct for the large mass bias in the MC-ICP-MS, using the assumption that mass bias is identical for elements of similar atomic mass. Two problems have been observed however; that a $^{205}Tl/^{203}Tl$ normalizing ratio somewhat higher than the certified value (2.38755 rather than 2.3871) is required to generate normalized Pb isotope ratios within error of "accepted" values for SRM981, and that either $^{208}Pb/^{206}Pb$ is apparently too low, or $^{207}Pb/^{206}Pb$ too high. Independently, new and near-identical reference values for SRM981 have recently been established using the double-spike (DS) technique (Galer & Abouchami, 1998; Thirlwall, 2000). A still higher $^{205}Tl/^{203}Tl$ value (ca. 2.3888 using the exponential law) is needed for the MC-ICP-MS data to conform to these, and similar inconsistencies in ratio values are observed.

The Micromass Isoprobe MC-ICP-MS at Royal Holloway, with a Cetac Aridus desolvating nebulizer, has been used to investigate this problem, and to assess whether Pb data of comparable accuracy to DS-TIMS data can be achieved. Reproducible data can only be achieved by careful attention to baseline correction. Instrument blank intensities are subtracted from sample peak intensities, and amount to <0.01% of sample Pb intensities. This corrects for most Hg: residual ion beam in the 198-202 amu spectrum is carefully checked for conformity to natural Hg abundances. At 24 ppm abundance sensitivity, accurate tail correction is essential to cope with variable Tl/Pb ratios. It cannot be achieved using half-mass zeroes, but is determined daily using Tl and Bi solutions. With a sensitivity of ca. 400V/ppm Pb, typical internal precisions of 10-35 ppm (1se) are achieved on Pb isotope ratios in ca. 4 min on ca. 4ng Pb. A $^{205}Tl/^{203}Tl$ ratio of ca. 2.3896 is required to derive ratios similar to the double spike TIMS values, and mean ratios of 16.9411±21, 0.914820±50 and 2.16753±23 (2sd, equivalent to 27-60 ppm 1sd) have been achieved on 39 analyses of a single SRM981-Tl solution over a 4-week period. These ratios are again systematically high in ^{207}Pb (or low in ^{208}Pb) relative to DS-TIMS; in view of problems in 207 analysis by TIMS (Thirlwall, 2000), the former might be suspected. However, the Tl-uncorrected Isoprobe data exhibit gradients on log-log plots significantly different from those expected from the exponential fractionation correction law (e.g. ln(208/206) vs. ln(205/203) has gradient 1.006±0.010 (2se), compared with expected power and exponential law gradients of 1.000 and 0.985 respectively). Correction using the power law requires still higher $^{205}Tl/^{203}Tl$ (=2.3903) and does not significantly change the mean ratios.

Ten samples have been analysed on the same chemical separates using both DS-TIMS and the Isoprobe. Isoprobe Pb isotope ratios are systematically 0.025±0.010%/amu higher than DS-TIMS values when corrected for the small differences in observed standard composition, and show raw $^{205}Tl/^{203}Tl$ some 0.025%/amu lower than bracketing standards. Although ReO^+ is a potential isobar with ^{203}Tl, the observed $^{205}Tl/^{203}Tl$ is not related to the Re/Tl ratio in solution, nor is it related to Tl/Pb ratios. Chemically-processed SRM981 has identical Pb isotope ratios to bracketing standards but systematically higher raw $^{205}Tl/^{203}Tl$. This strongly suggests that Tl is unable to correct for Pb mass bias on the scale of 0.03%/amu. However, the Isoprobe natural Pb isotope compositions can be corrected for mass bias using mixed runs of the sample and double spike run either on TIMS or the Isoprobe. At present, DS-corrected Isoprobe data seem able to reproduce DS-TIMS data within ca. 100 ppm on all ratios, after correction for standard differences.

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