Electronic Supplementary Information

Title: An Isotopic Approach to Mass Bias and Matrix Effects in an Argon Plasma using Multi-Collector Inductively-Coupled-Plasma Mass Spectrometry.

Jane Barling[1] & Dominique Weis[1]

Contents:

[1]University of British Columbia, Pacific Centre for Isotopic and Geochemical Research, Dept. of Earth & Ocean Sciences, 6339 Stores Road, Vancouver, BC V6T 1Z4, Canada

Matrix Effects: Batch Experiments

The results of 15 batch matrix experiments carried out over the course of a year are illustrated in Figure S1. Data have been normalized offline to the triple-spike values of Abouchami *et al.*.[1]

Experimental Details

Standard running conditions for the Nu Plasma at the PCIGR at the University of British Columbia are documented in Table S1. Instrument response to matrix has been found to vary from session to session (*e.g.* Ce in Figure S1), therefore for this study each experimental session consisted of a pair of axial plasma profiles; a matrix-free profile preceding a matrix-bearing one. This procedure allowed us to characterise the effect of the individual matrix elements on the plasma and through normalization of matrix-bearing profiles to their same session matrix-free profiles, to compare the effects of the different matrix elements run in separate sessions.

In order to ensure that torch positions were as accurate and reproducible as possible a number of precautions were taken: 1) The instrument software and in particular the Plasma Control Window, remained open throughout the period of the experiments to ensure that the stepper motor positions were not re-initialised. 2) The distance from the load coil to the tip of the sampler was measured with the torch in/out position set at 5.00mm to determine whether there was any significant offset between the digital position read from the stepper motors and the actual position of the torch with respect to the cones. 3) All profiles were carried out with the stepper motors stepping in the same direction (from 3.42 to 9.43mm for axial profiles and from 5.01 to 5.70mm for radial profiles). 4) At each step on axial profiles the radial position was checked and adjusted, if necessary, to maximize signal. 5) The torch was not changed or adjusted in its mount during the period of analysis.

To further limit the effects of variations in instrumental conditions and tuning parameters the experiments were carried out over a short period of time during which no sample material was introduced into the instrument and the instrument was not re-optimized for analysis of elements other than Pb. All m/z to be measured at each profile

point were grouped in batch runs so that the timing and sequence of measurements was identical for each step in each profile.

References

1 W. Abouchami, S.J.G. Galer and A.W. Hofmann, *Chem. Geol.*, 2000, **169**, 187-209.

Table S1: Standard Running Conditions

Instrument	**Nu Plasma MC-ICP-MS**
RF power	1300 W
Reflected power	<10 W
Accelerating potential	4000 V
Analyser pressure	< 4 x 10^{-9} mbar under full gas load
Abundance sensitivity	3 – 4 ppm
Cones	Ni (Nu Plasma Type B)
Argon gas flows:	
- coolant	13 l min^{-1}
- auxiliary	0.70 l min^{-1}
- nebuliser	35 – 40 psi
Sample introduction	**Nu Plasma DSN 100**
- hot gas flow	0.25 l min^{-1}
- membrane gas flow	2.7 – 3.1 l min^{-1}
- nebuliser	ESI PFA µflow
- sample uptake rate	70 - 80 µl min^{-1}

Figure Caption

Figure S1: Triple-spike normalized, exponentially corrected $^{208}Pb/^{204}Pb$ - $^{206}Pb/^{204}Pb$ plot for matrix batch runs (n = 5 - 18 analyses) using the SRM 981 Pb standard. Also plotted: the triple-spike values[1] for the SRM 981 Pb standard ± 2SD (square) and PCIGR annual averages ±2SD for the SRM 981 Pb standard during the period of the batch experiments (circles). Error bars: representative ±2SD for the individual batches.