

A physics-based isotope ratio estimation algorithm for geochronology by LA-ICP-MS

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Mass spectrometers do not directly measure isotopic ratios. They measure time series of electrical signals (recorded in V, A or Hz) that must be converted to isotopic ratio estimates. Nearly all currently used mass spectrometer data reduction algorithms are heuristic in nature, which makes them flexible but inaccurate:

1. The 'ratio of the means' method works well for stable signals but does not easily handle transient mass spectrometer data (e.g., caused by down-hole fractionation).

2. The 'intercept', 'mean of the ratios' and 'spline interpolation' methods are more robust to mass spectrometer drift, but are non-invertible; i.e. $\text{mean}(A/B) \neq 1/\text{mean}(B/A)$.

3. The 'logratio' method is invertible but exhibits an undesirable dwell-time dependency; i.e. $\log((n1 \text{ counts})/(d \text{ seconds}))/2 + \log((n2 \text{ counts})/(d \text{ seconds}))/2 \neq \log((n1+n2 \text{ counts})/(2d \text{ seconds}))$.

These problems degrade the accuracy of the resulting isotopic ratio estimates on a similar scale as their reported precision. Solving this issue requires abandoning the heuristic approaches in favour of bespoke methods that take into account the physical principles underlying the isotopic ratios of interest. In the case of geochronology, this physical basis is formed by the fundamental age equation.

Physics-based geochronological data reduction algorithms are based on the fact that the true isotopic composition of a matrix-matched reference material must plot on a mixing line between radiogenic and non-radiogenic components. The mass spectrometer signals are a convolution of this true isotopic composition with the effects of elemental fractionation, mass bias, drift, background and random noise. All these effects can be captured with simple functions containing a handful of parameters.

Conventional data reduction algorithms manipulate the mass spectrometer data to fit a heuristic model. The physics-based method uses the complete opposite approach, by fitting the model to the data. The new data reduction paradigm is ideally suited for analytically challenging applications of LA-ICP-MS such as in-situ Rb-Sr, Sm-Nd and Re-Os dating, as well as U-Pb dating of unconventional mineral phases that are rich in common Pb (Figure 1). It is, of course, equally capable of conventional zircon U-Pb dating.

The new algorithm has been implemented in a Julia package called 'KJ', which is available from <https://github.com/pvermees/KJ.jl>

Fig 1: U-Pb dating of WC-1 carbonate

