{MIRA: A new approach to measuring $\Delta^{47}incarbonatesandgeothermometryofMVTtypedeposits}\}

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Clumped isotope thermometry is based on the thermodynamics of the order-disorder reaction for $^{18}$O and $^{13}$C:

$$^{13}C^{16}O^{16}O^{16}O + {^{12}C^{18}O^{16}O^{16}O = ^{13}C^{18}O^{16}O^{16}O + ^{12}C^{16}O^{16}O^{16}O}$$

At high temperatures $^{18}$O is randomly distributed between $^{12}$C and $^{13}$C in the carbonate anion. However, at lower temperatures there is a tendency for the $^{18}$O to cluster together with $^{13}$C. At low temperatures ($T < 150^\circ$C) the degree of ordering, as measured by $\Delta47$ of the CO$_2$ that is produced by reaction of the carbonate with phosphoric acid ($({^{13}C^{18}O^{16}O_{sample}/^{13}C^{18}O^{16}O_{stochastic}})-1$) is a potentially useful geothermometer (Eiler, 2007). However, for reliable temperature estimates to better than +/- 1°C at near earth surface temperatures requires measurement of 1000*$\Delta47$ to better than +/-0.005. Given that the 47 isotopologue occurs at a natural abundance of just 40ppm in CO$_2$ this is a challenging measurement for stable isotope ratio mass spectrometry. We have developed a new instrument MIRA to accurately measure such small isotope ratios. MIRA is configured with a 50cm dispersion analyser, dual inlet, a high sensitivity Nier type source, 6 faraday collectors at m/z = 44, 45, 46, 47, 48 and 49 and ultra stable and linear detection and integration electronics. Using a dual inlet measurement precisions for 1000*$\Delta47$ are better than +/-0.01.

To date isotopic clusters have just been used to estimate near surface and diagenetic temperatures to 75°C. We are using MIRA and the clumped isotope thermometer to assess formation temperatures (up to 150°C) and the timing of MVT Pb/Zn mineralisation in the Pennines, UK orefield. Because temperature estimates are based on an internal order-disorder reaction, they are independent of the isotopic composition of the formation waters making it possible independently to track changes in the $\delta^{18}$O composition of mineralising fluids. With sufficient resolution (+/- 2 – 5°C) we aim to map temperature distributions in order to better constrain the hydrothermal system.

This is the first application of clumped isotopes to ‘elevated’ temperature thermometry.