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{MIRA: A new approach to measuring Δ47 in carbonates and geothermometry of MVT type deposits}

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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 ($T < 150^oC$) the degree of ordering, as measured by Δ47 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^oC at near earth surface temperatures requires measurement of 1000*Δ47 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*Δ47 are better than +/-0.01.

To date isotopic clusters have just been used to estimate near surface and diagenetic temperatures to 75^oC. We are using MIRA and the clumped isotope thermometer to assess formation temperatures (up to 150^oC) 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^oC) 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.

Eiler, J.M., 2007, ‘Clumped-isotope’ geochemistry – The study of naturally occurring multiply substituted isotopologues. *Earth and Planetary Science Letters*, **262**, 309-327