

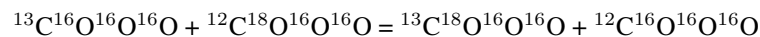


## **{MIRA: A new approach to measuring $\Delta 47$ in carbonates and geothermometry of MVT type deposits}**

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



At high temperatures  $^{18}\text{O}$  is randomly distributed between  $^{12}\text{C}$  and  $^{13}\text{C}$  in the carbonate anion. However, at lower temperatures there is a tendency for the  $^{18}\text{O}$  to cluster together with  $^{13}\text{C}$ . At low temperatures ( $T < 150^\circ\text{C}$ ) the degree of ordering, as measured by  $\Delta 47$  of the  $\text{CO}_2$  that is produced by reaction of the carbonate with phosphoric acid ( $(^{13}\text{C}^{18}\text{O}^{16}\text{O}_{\text{sample}}/^{13}\text{C}^{18}\text{O}^{16}\text{O}_{\text{stochastic}})-1$ ) is a potentially useful geothermometer (Eiler, 2007). However, for reliable temperature estimates to better than  $\pm 1^\circ\text{C}$  at near earth surface temperatures requires measurement of  $1000 \times \Delta 47$  to better than  $\pm 0.005$ . Given that the 47 isotopologue occurs at a natural abundance of just 40ppm in  $\text{CO}_2$  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  $1000 \times \Delta 47$  are better than  $\pm 0.01$ .

To date isotopic clusters have just been used to estimate near surface and diagenetic temperatures to  $75^\circ\text{C}$ . We are using MIRA and the clumped isotope thermometer to assess formation temperatures (up to  $150^\circ\text{C}$ ) 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  $\delta^{18}\text{O}$  composition of mineralising fluids. With sufficient resolution ( $\pm 2 - 5^\circ\text{C}$ ) 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.

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