

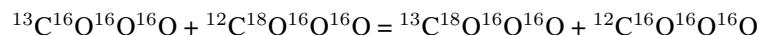


{MIRA: A new approach to measuring \$Δ\$47 in carbonates and geothermometry of MVT type deposits}

P.F. Dennis and S.J. Vinen

University of East Anglia, School of Environmental Sciences, Norwich, United Kingdom (p.dennis@uea.ac.uk)

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



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 ($T < 150^\circ\text{C}$) the degree of ordering, as measured by $\Delta 47$ of the 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 $+\text{-} 1^\circ\text{C}$ at near earth surface temperatures requires measurement of $1000 \times \Delta 47$ to better than $+\text{-} 0.005$. Given that the 47 isotopologue occurs at a natural abundance of just 40 ppm 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 50 cm dispersion analyser, dual inlet, a high sensitivity Nier type source, 6 faraday collectors at $\text{m/z} = 44, 45, 46, 47, 48$ 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 $+\text{-} 0.01$.

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 $\delta^{18}\text{O}$ composition of mineralising fluids. With sufficient resolution ($+\text{-} 2 - 5^\circ\text{C}$) 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