

New method for the on-line measurement of δD and $\delta^{18}\text{O}$ of mineral hydration waters using Cavity Ring-Down Spectroscopy

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Here we present preliminary results of a new experimental method to measure the δD and $\delta^{18}\text{O}$ of site-specific hydration water in real time. The method allows us to measure the amount and isotopic composition of hydration water as a sample is step heated alongside sample weight loss and enthalpy; in other words, to perform a differential thermal isotope analysis (DTIA).

This has been achieved by coupling a Cavity Ring-Down Laser Spectroscopy analyzer (Picarro L2130) to a Simultaneous Thermal Analyser (Netzsch STA 449 F1 Jupiter), capable of both differential scanning calorimetry and thermal gravimetric analysis. The two devices are connected via a heated transfer line and interface box, which allows the injection of water standards into the CRDS analyzer.

Previous methods to analyse hydration water have focused almost exclusively on the total hydration water extracted from the mineral. However, many minerals contain multiple forms of hydration water, so significant information is lost if only the total water is considered. In particular, more strongly bonded water is less susceptible to isotopic exchange; thus, mineral hydration water may preserve information about the isotopic composition of the fluid under which the mineral formed.

We have thus far focused on gypsum, which undergoes a two step dehydration process: gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) first dehydrates to bassanite ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$) as an intermediate form before the final dehydration product, γ -anhydrite (CaSO_4). The total water $\delta^{18}\text{O}$ and δD values are the same as results obtained by extracting the total water offline and measurement by CRDS. Analytical precision is ± 0.17 for $\delta^{18}\text{O}$ and ± 0.40 for δD (1 stdev) based on six repeated measurements of analytical grade gypsum.

We are able to separate the two peaks and measure the isotopic composition of the water released separately. Results indicate the two peaks have different oxygen and hydrogen isotope values. For $\delta^{18}\text{O}$, the first peak is more depleted in ^{18}O than the second whilst, for δD , the first peak is found to be more enriched in D than the second. Ongoing work is directed at understanding the cause of these isotopic fractionations.