## <sup>17</sup>O-excess and deuterium-excess in gypsum hydration water

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Here we present preliminary results of  $\delta^{17}O$ ,  $\delta^{18}O$ ,  $\delta D$ , and the derived <sup>17</sup>O-excess and d-excess, in the hydration water of natural gypsum samples. Our analytical method consists of the thermal dehydration of gypsum and subsequent cryogenic trapping of the released water. Subsequently, the isotopic composition of hydration water is measured by cavity ringdown spectroscopy (CRDS) using a Picarro L2140 water isotope analyzer, which permits simultaneous determination of  $\delta^{17}O,\,\delta^{18}O$  and  $\delta D.$  The analytical precision is  $\pm 0.06\%$  (1\sigma) for  $\delta^{17}O,\ \pm 0.1\%$  for  $\delta^{18}O$  and  $\pm 0.5\%$  for  $\delta D,$  whereas for  $^{17}O\text{-}$ excess and d-excess it is ±7 per meg and ±0.9 ‰ respectively, based on repeated analyses of an analytical-grade gypsum standard. We compared values of <sup>17</sup>O-excess measured by CRDS with the traditional method of fluorination followed by measurement of O2 by IRMS. We initially found the CRDS <sup>17</sup>O-excess results to be substantially different from those measured from IRMS. The problem was caused by contaminant gases (VOCs,  $H_2S$ , etc.) released from natural gypsum samples during dehydration that spectrally interfere with the wavenumber used to determine  $H_2^{17}O$  by CRDS. Use of the Picarro micro-combustion module (MCM) removes these contaminants, and 17O-excess measured by CRDS are in excellent agreement with IRMS results. We analyzed a selection of natural gypsum from different settings, including lakes, marine environments, hydrothermal systems and gypsum caves, all with different ages. <sup>17</sup>O-excess of hydration water ranged -50 to +50 per meg and is negatively correlated with  $\delta^{18}O$  across the complete dataset. Conversely, as expected, d-excess and <sup>17</sup>O-excess are positively correlated. Our results indicate that gypsum hydration water preserves <sup>17</sup>O-excess and d-excess of the mother water from which the gypsum formed. Previous studies suggest that the evolution of d-excess in water is controlled by air humidity and the temperature at the water surface, unlike <sup>17</sup>O-excess, which is only dependent on air humidity [1]. Thus, the measurement of both <sup>17</sup>O-excess and d-excess in gypsum hydration water can additional information on past humidity and provide temperature.

[1] Luz and Barkan (2010) Geochim. Cosmochim. 74, 6276–6286.