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### **ACCEPTED MANUSCRIPT**

# Triple oxygen isotope systematics of structurally bonded water in gypsum

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#### Abstract

The triple oxygen isotopic composition of gypsum mother water (gmw) is recorded in structurally bonded water in gypsum (gsbw). Respective fractionation factors have been determined experimentally for <sup>18</sup>O/<sup>16</sup>O and <sup>17</sup>O/<sup>16</sup>O. By taking previous experiments into account we suggest using <sup>18</sup> $\alpha_{gsbw-gmw}$  = 1.0037; <sup>17</sup> $\alpha_{gsbw-gmw}$  = 1.00195 and  $\theta_{gsbw-gmw}$  = 0.5285 as fractionation factors in triple oxygen isotope space.

Recent gypsum was sampled from a series of 10 ponds located in the Salar de Llamara in the Atacama Desert, Chile. Total dissolved solids (TDS) in these ponds show a gradual increase from 23 g/l to 182 g/l that is accompanied by an increase in pond water <sup>18</sup>O/<sup>16</sup>O. Gsbw falls on a parallel curve to the ambient water from the saline ponds. The offset is mainly due to the equilibrium fractionation between gsbw and gmw. However, gsbw represents a time integrated signal biased towards times of strong evaporation, hence the estimated gmw comprises elevated <sup>18</sup>O/<sup>16</sup>O compositions when compared to pond water samples taken on site. Gypsum precipitation is associated with algae mats in the ponds with lower salinity. No evidence for respective vital effects on the triple oxygen isotopic composition of gypsum hydration water is observed, nor are such effects expected. In principle, the array of  $\delta^{18}O_{gsbw}$  vs. <sup>17</sup>O<sub>excess</sub> can be used to: 1) provide information on the degree of evaporation during gypsum formation; 2) estimate pristine meteoric water compositions; and 3) estimate local relative humidity which is the controlling parameter of the slope of the array for simple hydrological situations. In our case study, local mining activities may have decreased deep groundwater recharge, causing a recent change of the local hydrology.

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