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Oxygen isotope fractionation between gypsum and its formation waters: implications for past chemistry of the Kawah Ijen volcanic lake, Indonesia.

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Abstract

Gypsum ($CaSO_4 \cdot 2H_2O$) provides an opportunity to obtain information from both the oxygen isotopic composition of the water and sulfate of its formation waters, where these components are commonly sourced from different reservoirs (e.g. meteoric vs. magmatic). Here, we present $\delta^{18}O$ values for gypsum and parent spring waters fed by the Kawah Ijen crater lake in East Java, Indonesia, and from these natural samples derive gypsum-fluid oxygen isotope fractionation factors for water and sulfate group ions of 1.0027±0.0003‰ and 0.999±0.001‰, respectively. Applying these fractionation factors to a growth-zoned gypsum stalactite that records formation waters from 1980 to 2008 during a period of passive degassing, and gypsum cement extracted from the 1817 eruption tephra fall deposit, shows that these fluids were in water-sulfate oxygen isotopic equilibrium. However, the 1817 fluid was >5‰ lighter. This indicates that the 1817 pre-eruption lake was markedly different, and had either persisted for a much shorter duration or was more directly connected to the underlying magmatic-hydrothermal system. This exploratory study highlights the potential of gypsum to provide a historical record of both the $\delta^{18}O_{water}$ and $\delta^{18}O_{sulfate}$ of its parental waters, and to provide insights into the processes acting on volcanic crater lakes or any other environment that precipitates gypsum.

Keywords: gypsum, oxygen isotopes, crystalline water, sulfate group, isotope fractionation factor, Kawah Ijen, volcanic lake

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Introduction

Sulfate minerals are common in volcanic systems, both as primary accessory minerals and secondary minerals associated with magmatic-hydrothermal fluids and sulfate in aerosols from SO_2 oxidation in the volcanic plume (Mather et al., 2006). The sulfate mineralogy is varied and includes alunite-jarosite, barite, gypsum, anhydrite, alum and leonite. Calcium sulfates (gypsum and anhydrite) are particularly common, and are found as a primary igneous mineral in the eruption products of volcanoes including El Chichon and Redoubt (Luhr et al., 1984; Rye et al., 1984; Luhr, 2008; Swanson and Kearney, 2008), as mineral encrustations or sublimate minerals around fumaroles (Africano and Bernard, 2000), as precipitates from acidic waters where volcanoes host crater lakes or acid streams (e.g. Delmelle and Bernard, 1994; Takano et al., 2004; Inguaggiato et al., 2018), and in subsurface alteration products (Fulignati et al., 1998). Hence, sulfates from volcanic environments have the potential to provide information on a multitude of volcanic processes.

In an earlier study (Utami et al., 2019), we have explored the potential of growth-zoned gypsum precipitated from crater lake effluent to provide a record of volcanic activity from a gypsum stalactite and gypsum cementing the base tephra fall deposit from the 1817 phreato-magmatic eruption, as determined from its trace elemental compositions. We showed the presence of a compositional signal that correlates with the degree of activity at the Kawah Ijen crater lake in Indonesia. Here, we investigate the potential of the complementary record provided by stable isotopes, specifically the $^{18}O/^{16}O$ oxygen isotope ratio. In particular, oxygen occurs in two different sites within the crystalline structure of gypsum; in structurally bound water, and in the sulfate group. Gypsum therefore samples two oxygen reservoirs from its formation waters; H_2O and SO_4 which commonly have different sources. Whereas H_2O is sourced from rain,

groundwater and the magmatic-hydrothermal system, SO_4 comes from volcanic gases and the subsequent disproportionation reactions to produce sulfate group ions (Kusakabe et al., 2000; Delmelle and Bernard 2015). In highly concentrated brines such as those found in the Kawah Ijen and Poás crater lakes, sulfate contains in excess of 5% by mass of oxygen (cf. Delmelle and Bernard, 1994; Martínez et al., 2000). Isotopic equilibration between these oxygen reservoirs is sluggish (Hoering and Kennedy, 1957; Chiba and Sakai, 1985, van Stempvoort and Krouse, 1994), which potentially allows for preservation of original oxygen isotopic signatures, as well as their use in geothermometry (see Seal et al., 2000). For minerals incorporating both water and sulfate and with slow intra-mineral oxygen isotopic exchange, such a signature and its differentiation between the two reservoirs would be preserved.

In this study we determined the oxygen isotopic fractionation factors between gypsum and its hyperacidic formation waters for both the crystalline water and sulfate group oxygen. We apply these data to a growth zoned gypsum stalactite precipitated over a >40 year period from seepage waters of the Kawah Ijen crater lake in Indonesia and gypsum associated with its 1817 phreato-magmatic eruption to explore whether the oxygen isotopic record can help us understand Kawah Ijen's past volcanic activity. This study forms part of a broader effort to explore the use of elemental and isotopic compositions of growth-zoned gypsum to provide information on the timing, types and characteristics of past volcanic activity of the Kawah Ijen system.

Geological setting

Ijen volcano in East Java, Indonesia, is a passively degassing basaltic to dacitic stratocone (Kemmerling, 1921; Delmelle and Bernard, 1994; Handley et al., 2007; van Hinsberg et al.,

2010, 2017) capped by the Kawah Ijen volcanic lake, the world's largest hyper-acidic crater lake (Figure 1). Historical records indicate that there has been a crater lake since at least the 19th century (Lechenault de la Tour, 1805, "Oudgast", 1820). Currently, the lake contains 2.8 x $10^7 m^3$ of pH 0-0.1 sulfate-chloride-rich brine with a total dissolved solute content of ~100mg/kg (Delmelle and Bernard, 1994; Takano et al., 2004; Caudron et al., 2015). The lake temperature is around 40°C, although surface temperature is commonly lower due to cooling by wind or rain (Lewicki et al., 2017). The extreme composition and high elemental load derives from the flux of volcanic gases into the lake and interaction between lake water and wall rocks (Delmelle and Bernard, 1994; Delmelle et al., 2000; van Hinsberg et al., 2010; 2017). The lake water seeps through the volcanic edifice and emerges in several springs on the western flank, forming the headwaters of the acidic Banyu Pahit river (Figure 1). Gypsum precipitates abundantly around these springs as a result of cooling and evaporation of the water and is present as cm-sized stalactites, efflorescences, and, at the uppermost springs, as an up to 30cm thick plateau (Utami et al, 2019). The stalactites and plateau gypsum display growth zoning, locally interrupted by sediment layers. Gypsum precipitation is a long-lived feature of the Kawah Ijen system and was already reported at the plateau site for a visit in 1796 ("Oudgast", 1820).

Ijen volcano poses significant volcanogenic hazards to communities living within the Ijen caldera, the Asambagus plain, and the nearby city of Banyuwangi, related to both volcanic activity and the metal-laden acidic effluent of the Banyu Pahit river. The most recent eruption occurred in 1817, which was a phreato-magmatic event that expelled the pre-existing lake, deepened and enlarged the crater, and led to the deposition of extensive phreatic to phreato-magmatic fall and lahars deposits (Junghuhn, 1853; Bosch, 1858; Caudron et al., 2015). Since

then, volcanic unrest at Kawah Ijen is dominated by phreatic and steam explosions, and gas emissions (Caudron et al., 2015, 2017). Only a comparatively scant historical record of its volcanic activity exists, which has led to recent efforts to improve both the active monitoring and reconstruction of its volcanic past (Gunawan et al., 2017).

Methodology

A concentrically growth-zoned gypsum stalactite was sampled in 2009 from the gypsum plateau at the seepage springs closest to the lake (Figure 1). At the time of the sampling, the gypsum stalactite was actively growing and representative of the typical stalactites found in the area. The stalactite measured 12cm in length with a 5cm base diameter. Transparent gypsum laths that form the actively growing tips were also sampled from multiple stalactites. The sampled tips represent one year of growth, as the tips were removed from these specific stalactites in 2008. The large stalactite is covered in mm-sized idiomorphic gypsum laths growing outward in all directions and also displays internal concentric growth zoning (see Fig. 3c of Utami et al., 2019). The stalactite is dense and growth appears to be restricted to its outer surface, where new gypsum laths grew on older laths that served as substrates. The tips consist of up to 5cm long, 4 mm wide idiomorphic transparent laths of gypsum, commonly twinned (Fig 3b. of Utami et al., 2019).

Gypsum cementing the base tephra fall deposit from the 1817 phreato-magmatic eruption was sampled in a separate field campaign in 2014. The tephra fall deposit consists of well-sorted, mm-sized, grain-supported, variably altered tephra fragments cemented by transparent needles of gypsum (Fig 3e of Utami et al., 2019). The gypsum needles are interpreted as precipitates from

an interstitial lake-derived fluid that was incorporated in the fall material during the initial lake expelling phreatic eruption. The tephra fall horizon is further covered by 7 to 8 m of phreatic to magmatic deposits from the later phases of the 1817 eruption, including cm-thick impermeable lahars layers.

The gypsum stalactite tips and gypsum laths from the tephra fall were crushed and transparent fragments clear of inclusions handpicked using a binocular microscope. The larger stalactite was sectioned perpendicular to its long axis and 3 growth zones representing core, mantle and rim were sampled in-situ using a small diamond rotary saw. These samples came from between the zones used by Utami et al. (2019) to date the stalactite. The sampled material was crushed, washed with distilled water, and further checked for inclusions under a binocular microscope prior to further analyses. The gypsum separates were then ground to a fine powder in an agate mortar under ethanol and dried in a desiccator. Elemental compositions for the stalactite and gypsum cement were presented in Utami et al. (2019). The seepage water from which these stalactites grow was also sampled. The water sample was filtered in the field through a 0.45 μm disposable filter and stored in cleaned HDPE bottles, free of air.

$\delta^{18}O$ analyses of the fluid sample. Sulfate in the spring water (sample KV15-006) was precipitated as $BaSO_4$ by adding an excess of dried $BaCl_2$ after a two-fold dilution with nano-pure water. This dilution was to convert HSO_4^- ions to SO_4^{2-} prior to the precipitation reaction and hence ensure a complete transfer of dissolved SO_4 to solid $BaSO_4$ as motivated by thermodynamic modeling using PHREEQC 2.17 and the Lawrence Livermore National Laboratory database (Parkhurst and Appelo, 1999). The barite and the residual fluid, as well as

the nano-pure water used to dilute the fluid were analyzed for their $\delta^{18}O$ at the Environmental Isotope Laboratory at the University of Waterloo. For further details on the barite analyses to obtain δ18OfluidSO4, see below. The δ18OfluidH2Owas determined by equilibration of the fluid samples with an injected volume of CO_2, followed by isotope ratio mass spectrometry (IRMS).

$\delta^{18}O$ analyses of oxygen in gypsum crystalline water. Thermogravimetric analysis of a Kawah Ijen gypsum sample showed loss of crystalline water in two distinct steps centred at 150 and 180˚C (for a 10˚C/min heating rate). Dehydration was completed at *ca.* 300˚C with 100% of the theoretical mass loss. Further mass changes were observed above 600˚C. There was no evidence for any absorbed water in the dried gypsum powder, nor of loss of crystalline water. The crystalline water for the isotope analyses was extracted from the dried gypsum powders by heating to 400˚C and the water subsequently captured in a cold-trap. The water was then equilibrated with an injected volume of CO_2 and measured by IRMS (Thermo GasBench-II coupled to a Thermo Delta-V) in the stable isotope laboratory of Utrecht University. The small gypsum sample amounts provided only *ca.* 50µL of water, and a correction had to be developed to account for differences in the fraction of water evaporating into the headspace (relatively more for smaller samples) and the resulting isotope fractionation. This correction was determined by measuring variable amounts (30 to 150µL) of in-house standards (RMW - distilled water, K – Kottasberggen, Greenland snow, and RSW - distilled seawater) and found to be systematic and predicatable (supplementary Figure S1), with a stronger deviation the smaller the water volume and the lower the $\delta^{18}O$ of the standard (the latter is related to the positive $\delta^{18}O$ of the CO_2, which is +0.32‰). The correction required for the gypsum crystalline water samples was minimal (supplementary Figure S1).

158
159 **$\delta^{18}O$ analyses of oxygen in the sulfate group of gypsum.** The gypsum powders were
160 dissolved overnight in nano-pure water in the presence of a small amount of dissolved $HgCl_2$ to
161 extract any sulfide, which was filtered out. The dissolved SO_4^{2-} ions in the resulting filtrate were
162 precipitated as $BaSO_4$ by adding 99.9% pure $BaCl_2 \cdot H_2O$ powder in excess (1g of $BaCl_2 \cdot H_2O$ for
163 50 mg of gypsum). The $BaSO_4$ powder was collected by filtration, washed with nano-pure water
164 and dried overnight at 60-70°C in a convection oven. The $BaSO_4$ powder was analysed for $\delta^{18}O$
165 at the Environmental Isotope Laboratory at the University of Waterloo by pyrolysis at 1450˚C
166 using an Elementar Pyrocube elemental analyzer coupled to an IsoPrime Continuous Flow
167 IRMS.

168 **Results**

169 The $\delta^{18}O^{H_2O}_{gypsum}$ and $\delta^{18}O^{SO_4}_{gypsum}$ of gypsum vary between 4.3 - 9.8‰ and 16.8 - 23.1‰,
170 respectively, whereas the corresponding values for the fluid sample are 6.9 and 23.3‰ (all
171 values relative to V-SMOW/V-SLAP - Table 1). The accuracy of analyses is between 0.2 and
172 0.5‰ (1 standard deviation) for $\delta^{18}O_{water}$ and 0.3 to 0.4‰ (1s) for $\delta^{18}O_{sulfate}$ as determined on a
173 range of certified international and cross-calibrated in-house reference materials. The precision,
174 as determined from replicate analyses is 0.1, 0.3 and 0.3, 0.1 (1s) for $\delta^{18}O_{water}$ and $\delta^{18}O_{sulfate}$ for
175 solids and fluids, respectively (Table 1). Sufficient material was available for the stalactite tip
176 sample (KV09-505) to be measured at variable sample amounts. Results are identical within
177 error after correction for extracted water amounts of 48, 55, 62 and 152µL (Table 1). The
178 $\delta^{18}O^{H_2O}_{fluid}$ and $\delta^{18}O^{SO_4}_{fluid}$ values are similar to those reported by Delmelle and Bernard (2000) for
179 the seepage area spring waters. The $\delta^{18}O^{H_2O}_{fluid}$ is within the range reported by these authors (6.9 ±
180 0.3‰ compared to 2 to 7.8‰), whereas the $\delta^{18}O^{SO_4}_{fluid}$ is about 1‰ higher. The $\delta^{18}O^{H_2O}_{gypsum}$ for

the gypsum tip and stalactite samples is similar, whereas the gypsum cement is 5.5‰ lighter. The gypsum $\delta^{18}O^{SO_4}_{gypsum}$ values are more variable, with the stalactite around 2‰ heavier and the cement 3.8‰ lighter, compared to the gypsum tips (Table 1).

Discussion

The $\delta^{18}O^{H_2O}_{fluid}$ and $\delta^{18}O^{SO_4}_{fluid}$ of Ijen seepage waters are high when compared to local meteoric water ($\delta^{18}O^{H_2O}_{meteoric}$ = -9‰, Delmelle et al., 2000; Palmer, 2009), Kawah Ijen fumaroles ($\delta^{18}O^{H_2O}_{fumaroles}$ = 3.6‰ and $\delta^{18}O^{SO_4}_{fumaroles}$ = 7.6‰, van Hinsberg et al., 2017), or seawater ($\delta^{18}O^{H_2O}_{seawater}$ = 0.2‰ and $\delta^{18}O^{SO_4}_{seawater}$ = 9.3‰, Lloyd, 1967; Schmidt, 1999). Dissolved sulfate in acidic crater lakes dominantly derives from disproportionation reactions that convert volcanic SO_2 to $SO_4^{2-}{}_{(aq)}$ via various intermediaries, with H_2S oxidation being a negligible contributor (Kusakabe et al., 2000; Delmelle and Bernard 2015). This process is likely entirely abiotic given that no sulfur-oxidizing organisms were detected in the Ijen lake or most-acidic Banyu Pahit river water samples by Löhr et al. (2006). The heavy $\delta^{18}O^{SO_4}_{fluid}$ is therefore a direct reflection of abiotic SO_2 disproportionation, and conversion of SO_2 to dissolved sulfate can indeed lead to an up to 31‰ enrichment in ^{18}O (Müller et al., 2013a,b). The heavy $\delta^{18}O^{H_2O}_{fluid}$ compared to local meteoric water has been explained by strong evaporative enrichment of the lake water combined with input of heavy water from the magmatic-hydrothermal system (Delmelle et al., 2000).

Equilibrium in water-sulfate $\delta^{18}O$. The $\delta^{18}O^{H_2O}_{fluid}$ and $\delta^{18}O^{SO_4}_{fluid}$ are close to isotopic equilibrium when compared to the sulfate-water fractionation curve of Zeebe (2010) at the ~40˚C temperature of the springs (Table 2). Oxygen isotopic disequilibrium has been reported for the

lake water and fumarole emissions at Kawah Ijen (Delmelle et al., 2000; van Hinsberg et al., 2017), although the lake disequilibrium is less pronounced when the fractionation factors of Zeebe (2010) are used. This disequilibrium could indicate preservation of a previous, higher temperature oxygen exchange equilibrium state (see Demelle et al., 2000). However, the dominant sources of water and sulfate to the lake differ, with the latter derived from the magmatic-hydrothermal system, whereas the former has a strong meteoric contribution (Delmelle et al., 2000; van Hinsberg et al., 2017). The disequilibrium could thus also reflect incomplete re-equilibration between these sources. Even at a pH of zero, the isotopic exchange half-life is approximately 11 years at a water temperature of 40˚C (Fig. 12 of Seal et al., 2000). Zeebe (2010) shows a strong difference in oxygen isotope fractionation between HSO_4^--H_2O and SO_4^{2-}-H_2O and it would seem reasonable to assume that a further difference develops when a significant fraction of sulfate is present as complexes with cations, as is the case for Ijen volcanic lake waters based on thermodynamic speciation modeling. Isotopic equilibrium would be expected for the lake given the lack of any isotopic variation with depth (Delmelle et al., 2000) and the expected long residence time of water and sulfate in the large lake volume (see also below for a discussion of residence times).

Gypsum precipitates from the seepage waters by evaporation and cooling of the fluid with an average stalactite growth rate of 340μm/year (Utami et al., 2019). Partitioning of trace elements between gypsum and its parent fluid is predictable and obeys Lattice-Strain theory (van Hinsberg and Williams-Jones 2008). This slow growth rate and systematic element partitioning suggests formation at equilibrium conditions, and we assume that this is also the case for its oxygen isotopic composition, although we acknowledge that we lack direct evidence for this. There are

no data on the kinetics of O-isotopic equilibration between H_2O and SO_4 within gypsum. However, experiments suggest it to be slow (Gonfiantini and Fontes, 1963). We therefore conclude that gypsum would preserve the isotopic composition captured from the fluid over the timescales reported here.

Oxygen fractionation between fluid and gypsum. Gypsum-fluid oxygen-isotope fractionation factors for crystalline water and the sulfate group (Figure 2) were calculated from the gypsum tip sample and its corresponding brine, as well as by combining the stalactite D growth zone with the 2009 brine, and the B-C growth zone with the seepage fluid composition reported by Delmelle and Bernard (2000). The latter two do not represent a direct equilibrium pair and are offset in time (growth zones D and B-C formed in 2008 and 1991, respectively (Utami et al*.,* 2019), and the data from Delmelle and Bernard (2000) are for 1996 seepage water). Nonetheless, the fractionation factors from these three sets are similar (Table 2). Gypsum preferentially incorporates ^{18}O in its crystalline water, but ^{16}O for the sulfate group, with mean gypsum-water fractionation factors of 1.0027 ± 0.0002 and 0.9990 ± 0.0014, respectively (uncertainties given as 1 standard deviation). The set consisting of zone B-C with the Delmelle and Bernard (2000) seepage fluid gives a fractionation factor of 1.0005 for sulfate. This is the set for which equilibrium is least constrained and with $\delta^{18}O_{sulfate}$ from two different labs, and we are therefore more confident in the fractionation factors from the other two sets. Nevertheless, it is clear from these data that the oxygen isotope fractionation between water and gypsum sulfate group is small.

Earlier studies similarly found gypsum crystalline water to be heavy compared to its parent solution in experiments, although their fractionation factors are higher at 1.0035 to 1.0041 with a preferred value of 1.0035±0.0002 (1s uncertainty, see Gazquez et al., 2017 for an overview). This difference could reflect a difference in solution pH, given that the earlier studies were at much higher, commonly circum-neutral pH, whereas the Kawah Ijen fluids have a pH of around zero. Oxygen isotope fractionation is also known to depend on speciation and species hydration (Truesdell, 1974; Horita et al., 1994), which is in turn strongly affected by pH. Unfortunately, this has yet to be quantified for acidic SO_4-rich solutions (cf. Stoffregen et al., 1994; Rouwet and Ohba, 2015). Thus, published fractionation factors between the sulfate group and water may not be directly applicable to volcanic brines like that of Ijen, in which case the observed $\alpha(SO_4\text{-}H_2O)_{fluid}$ could represent the equilibrium fractionation factor at these acidic conditions. No previous data are available on gypsum-water oxygen fractionation for sulfate group ions, but a similar, differing fractionation behaviour for sulfate group and hydroxyl groups has been reported for alunite and jarosite (Stoffregen et al., 1994; Rye and Stoffregen, 1995).

Oxygen isotopic composition of stalactite and gypsum cement formation waters. The gypsum-water fractionation factors allow for the $\delta^{18}O_{fluid}^{H_2O}$ and $\delta^{18}O_{fluid}^{SO_4}$ of the parent fluids to be calculated from gypsum (Figure 2). The $\delta^{18}O_{fluid}^{H_2O}$ compositions calculated from the growth-zoned stalactite vary from $\delta^{18}O$ = 6.2 to 7.1‰, similar to the 6.9‰ of the present-day seepage waters. The $\delta^{18}O_{fluid}^{SO_4}$ varies from 23.3 to 24.0‰, which is somewhat heavier than the crystalline water (Figure 3). In contrast, the gypsum cement formed from a fluid with significantly lighter $\delta^{18}O$ for both H_2O and SO_4 at 1.6 and 18.1 ‰, respectively. Despite these variations, the fractionation factor between $\delta^{18}O$ for H_2O and SO_4 in the fluid is near constant (Table 3). The

271 consistency in $\alpha(SO_4\text{-}H_2O)_{fluid}$, despite strong variations in $\delta^{18}O_{fluid}^{H_2O}$ and $\delta^{18}O_{fluid}^{SO_4}$, is
272 inconsistent with this representing incomplete re-equilibration; it is highly unlikely that the exact
273 same degree of temperature re-equilibration, or mixing of sources would be attained. This is
274 especially true for the 1817 gypsum cement, which samples a previous, smaller crater lake
275 (Caudron et al., 2015; Utami et al., 2019). We therefore conclude that this $\alpha(SO_4\text{-}H_2O)_{fluid}$ more
276 likely reflects oxygen exchange equilibrium for these acidic brines, with the difference from the
277 theoretical $\alpha(SO_4\text{-}H_2O)_{fluid}$ (Zeebe, 2010) reflecting the effects of pH and speciation on
278 fractionation.
279
280 **Historical $\delta^{18}O$ record from gypsum.** The historical record of seepage water $\delta^{18}O_{fluid}^{H_2O}$
281 and $\delta^{18}O_{fluid}^{SO_4}$ as based on direct fluid measurements and reconstructions from the gypsum
282 stalactite and 1817 gypsum cement is shown in Figure 4. The elemental record shows a distinct
283 change in behavior of the system around 1992, which marks the transition from quiescence to a
284 state of variable unrest (Caudron et al., 2015; Utami et al., 2019). The $\delta^{18}O$ record unfortunately
285 lacks the resolution needed to directly link the elemental and isotopic records together. The two
286 older samples that represent the period of quiescence are both lower in $\delta^{18}O_{fluid}^{H_2O}$ and higher in
287 $\delta^{18}O_{fluid}^{SO_4}$ compared to the more recent samples, but the differences are small and could represent
288 incremental variations in the lake chemistry over time. An important parameter in interpreting
289 the historical record is the residence time of water and sulfate in the lake, as this controls how
290 quickly changes will become apparent in the lake, and in the gypsum precipitating from it. To
291 estimate residence time, we use the approach of Rouwet and Tassi (2011), with elemental and
292 isotopic compositions for rain- and groundwater, volcanic gas, lake and seepage water, as well as
293 seepage flux, from van Hinsberg et al. (2017). The volcanic gas flux was estimated from the

294 change in Cl content of the lake over time and the Cl content of the volcanic gas, assuming that
295 the surface gas composition is identical to that of the gas entering the bottom of the lake. No loss
296 of Cl by evaporation was included in this calculation, and this is therefore a minimum estimate
297 (see Rodríguez et al. 2018). Annual precipitation for Kawah Ijen was taken from Blaak (1920),
298 which represents data for 1907-1917 (the annual precipitation for Banyuwangi reported by Blaak
299 (1920) is equivalent to that at present). Lake volume was taken from Caudron et al. (2015),
300 converted to mass using a density of 1.035 kg/dm^3 as calculated from lake water composition. A
301 water residence time of 1.5 years results. Although this value has a large uncertainty given the
302 assumptions and uncertainties in the input parameters, it does indicate that gypsum would be
303 able to record changes on the multi-year timescale that we have reconstructed here.
304
305 In contrast to the small variations from 1980 to 2009, the 1817 sample is distinctly
306 different (Figure 4). This gypsum records the composition of crater lake waters thrown out
307 during the 1817 phreato-magmatic eruption of Kawah Ijen (Utami et al., 2019). Both the
308 $\delta^{18}O_{water}$ and $\delta^{18}O_{sulfate}$ of the 1817 gypsum cement are lighter than the gypsum stalactite and the
309 present-day gypsum stalactite tips. Whereas the stalactite grows in an open-system, continously
310 refreshed fluid environment, the gypsum cement would likely have formed from a closed-system
311 pore fluid, resulting in $^{18}O/^{16}O$ isotope fractionation as gypsum precipitation progresses.
312 However, the above and below 1 fractionation factors for water and sulfate group, respectively,
313 would lead to diverging $\delta^{18}O_{gypsum}^{H_2O}$ and $\delta^{18}O_{gypsum}^{SO_4}$ in this case, whereas both are found to be
314 isotopically lighter. Secondary processes such as later water ingress and re-equilibration,
315 leaching of oxygen from the fall deposit rock clasts, or boiling of the fluid in the hot fall deposit
316 would almost exclusively modify $\delta^{18}O_{gypsum}^{H_2O}$ and thus introduce disequilibrium, whereas the

317 $\alpha(SO_4\text{-}H_2O)_{fluid}$ appears to be at low-temperature equilibrium (Table 3). This argument also rules
318 out a significant meteoric water contribution added in the eruption plume. Thus we conclude that
319 the observed signature reflects a fluid with a different $\delta^{18}O_{fluid}^{H_2O}$ and $\delta^{18}O_{fluid}^{SO_4}$ signature. Given
320 that the $\alpha(SO_4\text{-}H_2O)_{fluid}$ appears to be in equilibrium (Table 3), and the fact that the amount of
321 oxygen in sulfate is still subordinate to that in water in the Kawah Ijen fluids, we attribute the
322 low $\delta^{18}O_{fluid}^{SO_4}$ to disproportionation into, and equilibrating with a light $\delta^{18}O_{fluid}^{H_2O}$ reservoir. A
323 stronger fumarole contribution cannot be excluded, but this would need to be significantly larger,
324 and is not able to explain the $\delta^{18}O_{fluid}^{H_2O}$ that extends below the oxygen isotopic composition of the
325 fumaroles (Figure 4). Volatile metal ratios suggest a stronger contribution from deep, basaltic
326 magma prior to the 1817 eruption (Utami et al., 2019), but it is unclear how this would affect the
327 $\delta^{18}O$ signature. Addition of meteoric water would lower the $\delta^{18}O_{fluid}^{H_2O}$ given its $\delta^{18}O$ of around -
328 9‰ (Delmelle et al., 2000; Palmer, 2009). Water-rock interaction would also lower the $\delta^{18}O$ of
329 the fluid as ^{18}O gets enriched in the altered amorphous silica residue. However, there is no
330 evidence that the pre-eruptive lake was more dilute or more concentrated than at present (van
331 Hinsberg et al., 2017). Delmelle et al. (2000) show that the high $\delta^{18}O_{fluid}^{H_2O}$ of the current lake
332 requires significant evaporative loss of ^{16}O. This evaporation gradually increases the $\delta^{18}O$ of the
333 lake, and the lower $\delta^{18}O$ of the pre-eruptive lake may therefore indicate that it had been present
334 for a shorter duration. Less evaporation because of a lower fluid temperature can be ruled out,
335 because this would be reflected in the $\alpha(SO_4\text{-}H_2O)_{fluid}$. The lake had a smaller surface area prior
336 to the 1817 eruption (Leschenault de la Tour 1805; Caudron et al. 2015), whereas the crater itself
337 was similar in size, which would suggest a larger rain- and groundwater flux relative to
338 evaporation, compared to the present-day. Alternatively, the pre-1817 lake had a more direct
339 connection to the magmatic-hydrothermal system, and therefore a stronger contribution of

340 $\delta^{18}O^{H_2O}_{fluid}$ from the hydrothermal system. Currently, direct fluid exchange between the lake and
341 the underlying magmatic-hydrothermal system appears limited (van Hinsberg et al., 2017), but
342 fluids from the hydrothermal system do flow out at the lowermost springs with only a small
343 crater lake seepage contribution (Palmer, 2009). The $\delta^{18}O$ composition of these lowermost
344 seepage waters is significantly lighter at 0.5‰ compared to the approximately 8‰ $\delta^{18}O$ of the
345 lake water (Palmer, 2009). With the present dataset, we cannot differentiate between these
346 possibilities.
347

348 **Implications**

349 We analyzed the $\delta^{18}O$ composition of the crystalline water and sulfate group of gypsum from
350 Kawah Ijen crater lake, and determined the fractionation factors between gypsum and fluid for
351 these components. Gypsum preferentially incorporates isotopically heavy water $\delta^{18}O$, in
352 agreement with previous studies, but has a small preference for light sulfate group $\delta^{18}O$. Using
353 these fractionation factors to reconstruct the $\delta^{18}O$ of gypsum formation fluids from 1817 to 2008
354 shows a shift from positive, heavy isotopic compositions recorded by the current lake water and
355 gypsum formed during passive degassing to a lighter composition for the 1817 phreato-magmatic
356 eruption. We attribute this difference to either a shorter-lived and smaller lake prior to the 1817
357 eruption, or a lake with a more direct connection to its underlying magmatic-hydrothermal
358 system. These aspects could not be determined from the gypsum elemental record, showing the
359 value of a combined elemental and isotopic approach. The oxygen-isotopic record from gypsum
360 can thus provide insights into the state of the Kawah Ijen system in the past, and can similarly be
361 applied to other environments where gypsum precipitates from a fluid.
362

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We thank William Mark and Richard Heemskerk (University of Waterloo) for their assistance with $\delta^{18}O$ analyses of spring water and gypsum samples. We also thank Corentin Caudron, Maria Martínez-Cruz and the other participants of the Cities on Volcanoes 8 Wet Volcanoes workshop for discussion on the Kawah Ijen system. We acknowledge funding from the McGill University Graduate Mobility Award, Mineralogical Association of Canada Travel Grant, and the Cities on Volcanoes 8 Travel Grant to SBU, and the Canadian National Science and Engineering Research Council (NSERC) and le Fonds Québecois de la Récherche sur la Nature et les Technologies (FQRNT) to VvH and BG. We thank Dmitri Rouwet and an anonymous reviewer for the insightful comments that improved the manuscript,.

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List of Figure Captions

Figure 1: Panoramic view of the Kawah Ijen volcanic lake area, adapted from a Google Earth image (Google Earth, 2015). The white box indicates the location of the gypsum plateau and upper springs as well as the fall deposit. (a) Gypsum cemented tephra fall deposit above the gypsum plateau, (b) Cascading gypsum plateau, c) Gypsum stalactite tips with spring water dripping from them.

Figure 2: Conceptual model of formation and isotopic exchange for a Kawah Ijen gypsum stalactite. The gypsum stalactite tip and surface are continuously coated bin a film of the parent fluid (PF), which in this case is the crater lake seepage water. Gypsum precipitates by cooling of this fluid and its evaporation, resulting in rapid growth of a transparent tip and slower concentric growth outward. The continuous contact between the stalactite and water ensures uninterrupted growth. Determination of the isotopic compositions for parental fluids ($\delta^{18}O_{\text{fluid}}^{H_2O}$ and

579 $\delta^{18}O^{SO_4}_{gypsum}$) and gypsum ($\delta^{18}O^{H_2O}_{gypsum}$ and $\delta^{18}O^{SO_4}_{gypsum}$) allows for the fractionation factors for
580 α_{water} and $\alpha_{sulfate}$ to be determined, as well as to calculate the $\alpha(SO_4\text{-}H_2O)_{fluid}$, which is a measure
581 of the oxygen isotopic equilibrium state of the fluid. Applying the α_{water} and $\alpha_{sulfate}$ to internal
582 zones of the stalactite allows a timeseries of $\delta^{18}O^{H_2O}_{fluid}$ and $\delta^{18}O^{SO_4}_{gypsum}$ to be reconstructed.
583
584 **Figure 3**: $\delta^{18}O^{H_2O}_{gypsum}$ and $\delta^{18}O^{SO_4}_{gypsum}$ of Ijen's various gypsum samples, comprising the 1817
585 gypsum cement ('Cement'), the 2009 growth-zoned stalactite tip ('Stalactite'), 2015 spring water
586 ('Water'), and 2009 growth zoned gypsum stalactite ('Zone').
587
588 **Figure 4**: Timeseries of $\delta^{18}O^{H_2O}_{fluid}$ and $\delta^{18}O^{SO_4}_{fluid}$ for Ijen seepage waters compared to the
589 elemental record reconstructed from gypsum (data from Utami et al., 2019). Solid symbols are
590 for direct measurements, open symbols for reconstructed values. Crater lake, fumarole and
591 groundwater $\delta^{18}O$ values are shown for reference (from Delmelle et al., 2000; Palmer 2009; van
592 Hinsberg et al., 2017). The orange lines represent periods of volcanic unrest.
593
594 **Supplementary Figure S1:** Isotopic composition (a) and absolute $\delta^{18}O$ deviation (b) from the
595 certified value (dashed line) for three in-house standards measured at different water volumes
596 (symbols). The measured and corrected $\delta^{18}O$ of crystalline water extracted from variable
597 amounts of gypsum sample KV09-505 are also shown. (c) A 2nd polynomial fit surface to the
598 measured deviations in $\delta^{18}O$ as a function of sample $\delta^{18}O$, showing minimal deviation at the
599 positive $\delta^{18}O$ values of the gypsum crystalline water.

600

601 **List of tables**

602 Table 1: $\delta^{18}O$ compositions of gypsum stalactite zones, brine and gypsum cement from the 1817
603 fall deposit. The volume of crystalline water for each gypsum sample, and the age for the growth
604 zones are also listed. All values are relative to V-SMOW/V-SLAP. Uncertainties are the 1
605 standard deviation analytical uncertainty, or uncertainty on the mean.

606 Table 2: Gypsum-water $\delta^{18}O$ fractionation factors for water and sulfate group, and water-sulfate
607 group fractionation factors for water samples. The temperatures of equilibration based on the
608 water-sulfate fractionation curve of Zeebe (2010) are also listed. Water-sulfate fractionation
609 factors by Gonfiantini and Fontes (1963) and Gazquez et al. (2017) are listed for comparison.

610 Table 3: Reconstructed $\delta^{18}O$ values for gypsum formation waters ($\delta^{18}O^{H_2O}_{fluid}$ and $\delta^{18}O^{SO_4}_{fluid}$) and
611 their $H_2O\text{-}SO_4$ fractionation factors. The temperatures of equilibration based on the $H_2O\text{-}SO_4$
612 fractionation curve of Zeebe (2010) are also listed.

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Table 1.

Sample Type	Sample ID	Comment	µL	$\delta^{18}O_{H2O}$	1 s	$\delta^{18}O_{SO4}$
Gypsum stalactite	KV09-505	tip	62	9.4	0.5	
		2009	152	9.6	0.5	
			48	9.5	0.5	
			56	9.7	0.5	
						20.9
		mean		***9.6***	***0.1***	***20.9***
Gypsum stalactite	KV09-501	zone A-B	61	9.3	0.5	
		1980				22.7
						23.1
		mean		***9.3***	***0.5***	***22.9***
		zone B-C	42	8.9	0.5	
		1991				23.0
						23.1
		mean		***8.9***	***0.5***	***23.0***
		zone D	89	9.8	0.5	
		2008				22.5
						22.1
		mean		***9.8***	***0.5***	***22.3***
Gypsum cement	KS14-001	1817	59	4.3	0.5	
						17.3
						16.8
		mean		***4.3***	***0.5***	***17.1***
Seepage water	KV15-006			6.67	0.2	
				7.16	0.2	
						23.4
						23.3
		mean		***6.9***	***0.3***	***23.3***

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1 s
0.3 ***0.3***
0.3 0.3 ***0.3***
0.3 0.3 ***0.1***
0.3 0.3 ***0.3***
0.3 0.3 ***0.4***
0.4 0.4 ***0.1***

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Table 2.

Set	Sample Type	Sample ID	Comment		$\delta^{18}O_{H2O}$	1 s
1	gypsum stalactite	KV09-505	tip		9.6	0.1
1	seepage water	KV15-006			6.9	0.3
2	gypsum stalactite	KV09-501	zone D		9.8	0.5
2	seepage water	KV15-006			6.9	0.3
3	gypsum stalactite	KV09-501	zone B-C		8.9	0.5
3	seepage water	BP96 2-5	Delmelle and Bernard 2000		6	3
	fractionation factor			set 1	1.0026	0.0003
	gypsum / water			set 2	1.0029	0.0006
				set 3	1.0025	0.0029
				mean	**1.0027**	**0.0002**
			Gonfiantini and Fontes, 1963		1.0037	0.0005
			Gazquez et al. 2017		1.0035	0.0002

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$\delta^{18}O_{SO4}$	1 s	α SO_4/H_2O	Equilibration T (Zeebe 2010)
20.9	0.3		
23.3	0.1	1.016	64 ± 2 ˚C
22.3	0.3		
23.3	0.1	1.016	64 ± 2 ˚C
23.0	0.1		
22.5	0.2	1.016	65 ± 21 ˚C
0.9976	0.0003		
0.9990	0.0003		
1.0005	0.0002		
0.9990	**0.0014**		

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Table 3

Sample Type	Sample ID	Comment	Year	$\delta^{18}O_{H2O}$	1 s	$\delta^{18}O_{SO4}$	1 s
Gypsum stalactite	KV09-501	zone A-B	1980	6.6	0.4	23.9	0.3
		zone B-C	1991	6.2	0.3	24.0	0.1
		zone D	2008	7.1	0.4	23.3	0.3
Gypsum cement	KS14-001		1817	1.6	0.2	18.1	0.4

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α SO_4/H_2O	Equilibration T (Zeebe 2010)
1.017	58 ± 3 ˚C
1.018	54 ± 3 ˚C
1.016	65 ± 4 ˚C
1.016	63 ± 3 ˚C

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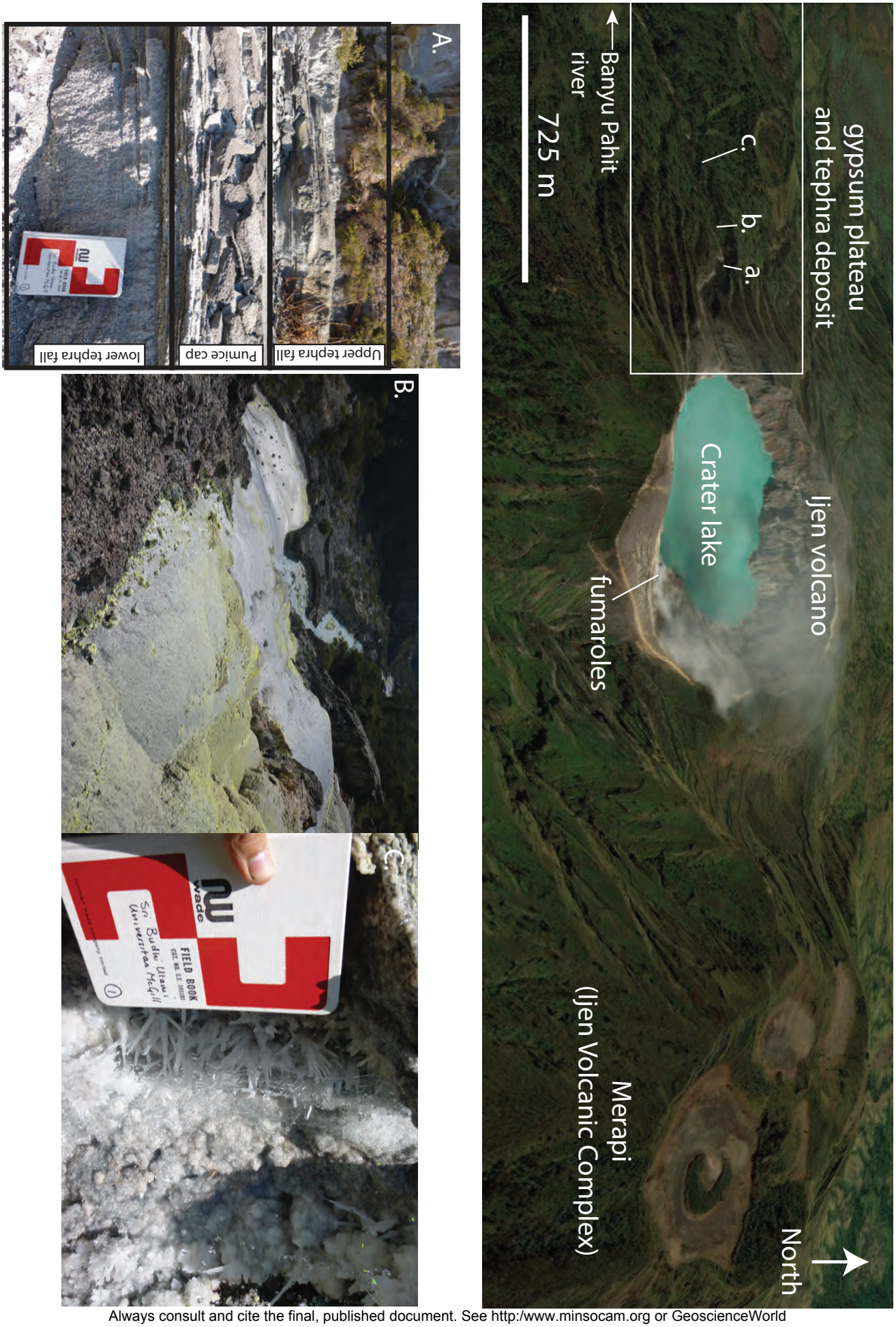
Figure 1



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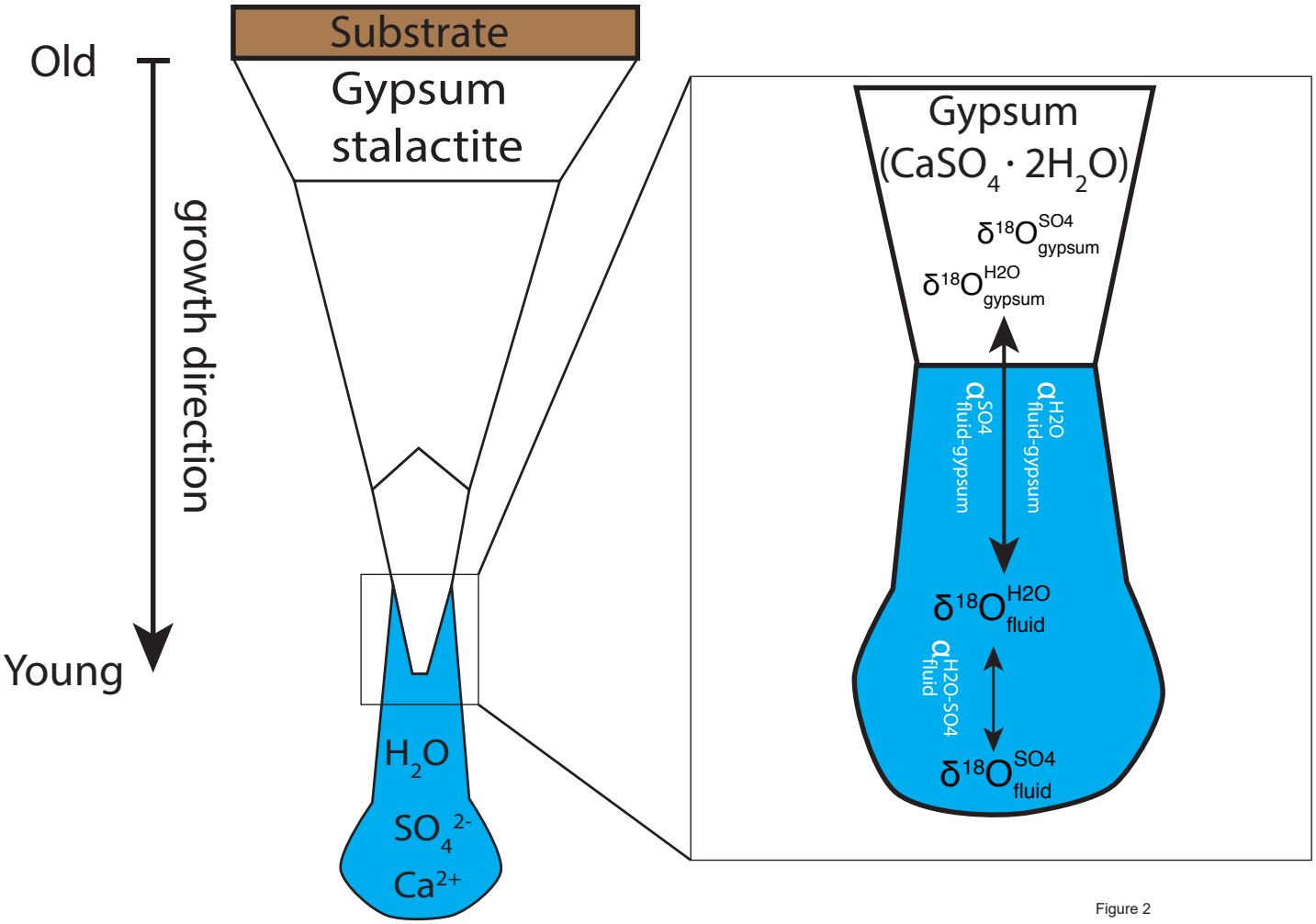

Figure 2

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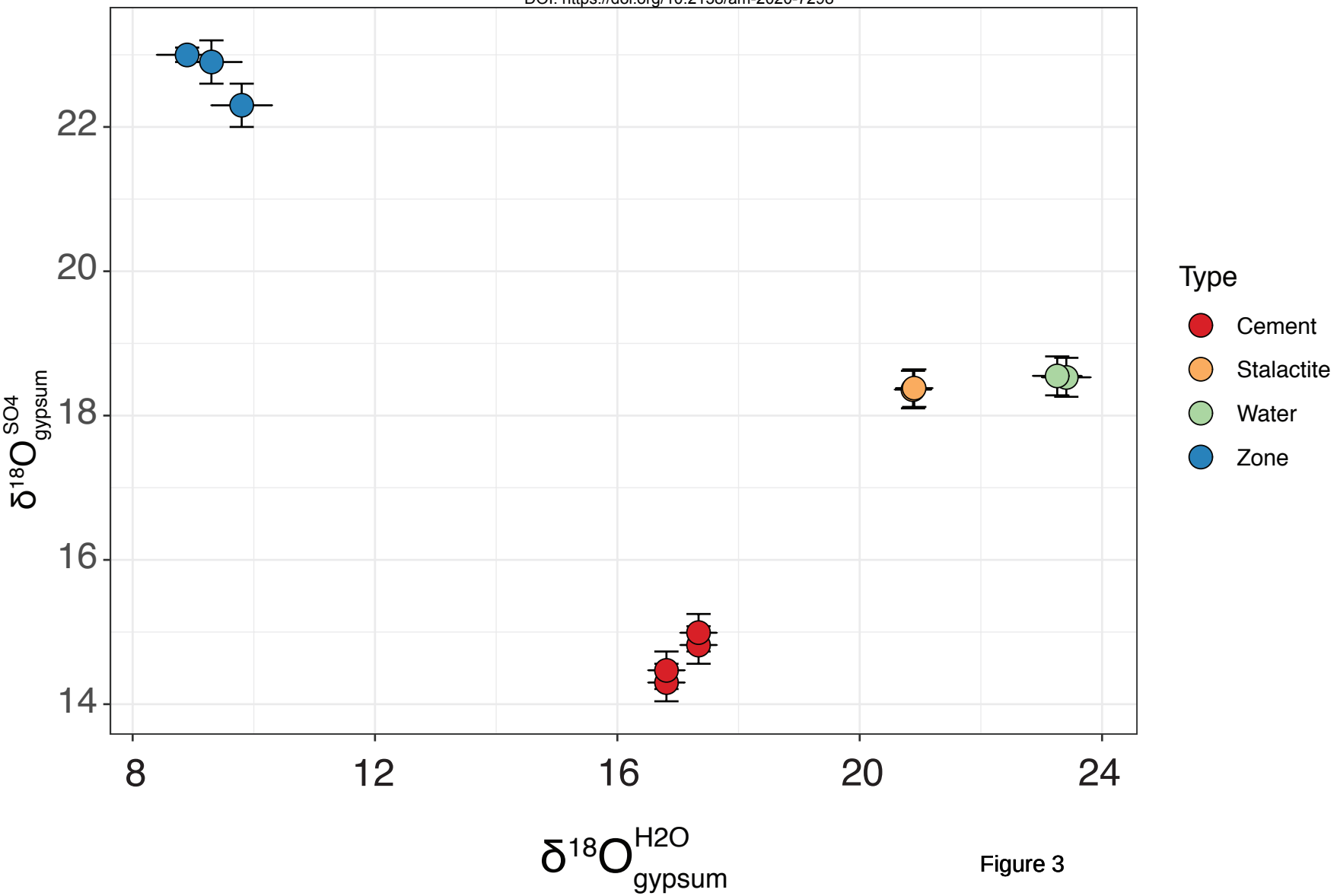

Figure 3

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Figure 4