

## 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 ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) 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  $\delta^{18}\text{O}$  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  $1.0027 \pm 0.0003\text{‰}$  and  $0.999 \pm 0.001\text{‰}$ , 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  $>5\text{‰}$  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  $\delta^{18}\text{O}_{\text{water}}$  and  $\delta^{18}\text{O}_{\text{sulfate}}$  of its parental waters, and provides 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

### 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  $\text{SO}_2$  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 primary igneous minerals 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), 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  $^{18}\text{O}/^{16}\text{O}$  oxygen isotope ratio. In particular, oxygen occurs in two different sites within the crystal-line structure of gypsum, in structurally bound water and in the sulfate group. Gypsum, therefore, samples two oxygen reservoirs from its formation waters;  $\text{H}_2\text{O}$  and  $\text{SO}_4$ , which commonly have different sources.  $\text{H}_2\text{O}$  is sourced from rain, groundwater, and the magmatic-hydrothermal system, whereas  $\text{SO}_4$  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

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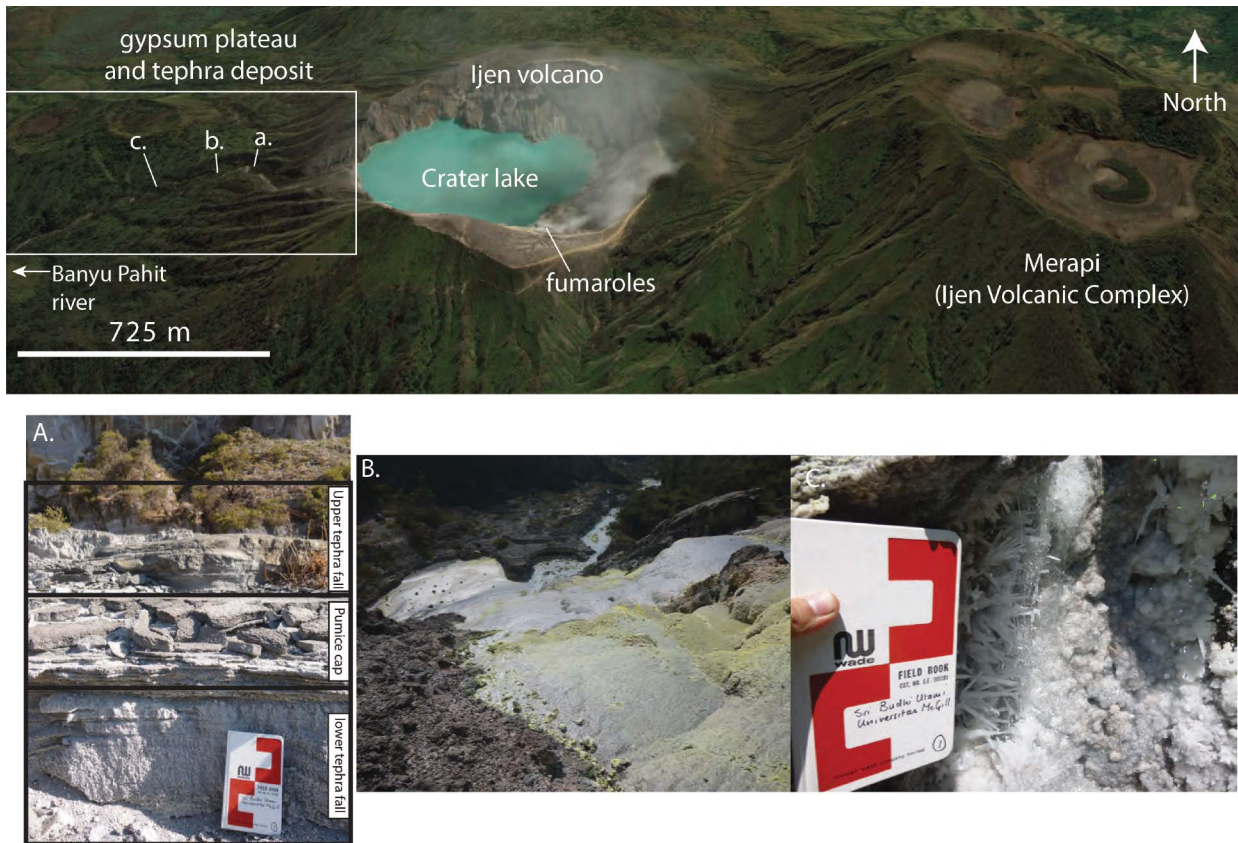
both the crystalline water and sulfate group oxygen. We apply these data to a growth zoned gypsum stalactite precipitated over a >40 yr period from seepage waters of the Kawah Ijen crater lake in Indonesia and gypsum associated with its 1817 phreatomagmatic eruption to explore whether the oxygen isotopic 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, 2016) capped by the Kawah Ijen volcanic lake, the world's largest hyper-acidic crater lake (Fig. 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  $2.8 \times 10^7 \text{ m}^3$  of pH 0–0.1 sulfate-chloride-rich brine with a total dissolved solute content of  $\sim 100 \text{ mg/kg}$  (Delmelle and Bernard 1994; Takano et al. 2004; Caudron et al. 2015). The lake temperature is around  $40^\circ \text{C}$ , although surface temperature is commonly lower due to cooling by wind or rain (Lewicki et al. 2016). 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, 2016). 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 (Fig. 1). Gypsum precipitates abundantly around these springs as a result of cooling and evaporation of the water and is present as centimeter-sized stalactites, efflorescences, and, at the uppermost springs, as an up to 30 cm 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 phreatomagmatic 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



**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. (Color online.)

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 concentric growth-zoned gypsum stalactite was sampled in 2009 from the gypsum plateau at the seepage springs closest to the lake (Fig. 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 12 cm in length with a 5 cm 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 millimeter-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 5 cm 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 phreatomagmatic eruption was sampled in a separate field campaign in 2014. The tephra fall deposit consists of well-sorted, millimeter-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 centimeter-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 three 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  $\mu\text{m}$  disposable filter and stored in cleaned HDPE bottles, free of air.

## $\delta^{18}\text{O}$ analyses of the fluid sample

Sulfate in the spring water (sample KV15-006) was precipitated as  $\text{BaSO}_4$  by adding an excess of dried  $\text{BaCl}_2$  after a twofold dilution with nano-pure water. This dilution was to convert  $\text{HSO}_4^-$  ions to  $\text{SO}_4^{2-}$  prior to the precipitation reaction and hence ensure a complete transfer of dissolved  $\text{SO}_4$  to solid  $\text{BaSO}_4$ , 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  $\delta^{18}\text{O}$  at the Environmental Isotope Laboratory at the University of Waterloo. For further details on the barite analyses to obtain  $\delta^{18}\text{O}_{\text{fluid}}^{\text{H}_2\text{O}}$ , see below. The  $\delta^{18}\text{O}_{\text{fluid}}^{\text{H}_2\text{O}}$  was determined by equilibration of the fluid samples with an injected volume of  $\text{CO}_2$ , followed by isotope ratio mass spectrometry (IRMS).

## $\delta^{18}\text{O}$ analyses of oxygen in gypsum crystalline water

Thermogravimetric analysis of a Kawah Ijen gypsum sample showed loss of crystalline water in two distinct steps centered at 150 and 180  $^\circ\text{C}$  (for a 10  $^\circ\text{C}/\text{min}$  heating rate). Dehydration was completed at ca. 300  $^\circ\text{C}$  with 100% of the theoretical mass loss. Further mass changes were observed above 600  $^\circ\text{C}$ . 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  $^\circ\text{C}$  and the water subsequently captured in a cold-trap. The water was then equilibrated with an injected volume of  $\text{CO}_2$  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. 50  $\mu\text{L}$  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 150  $\mu\text{L}$ )

of in-house standards (RMW = distilled water, K = Kottasberggen, Greenland snow, and RSW = distilled seawater) and found to be systematic and predictable (Supplementary<sup>1</sup> Fig. S1), with a stronger deviation the smaller the water volume and the lower the  $\delta^{18}\text{O}$  of the standard (the latter is related to the positive  $\delta^{18}\text{O}$  of the  $\text{CO}_2$ , which is +0.32‰). The correction required for the gypsum crystalline water samples was minimal (Supplementary<sup>1</sup> Fig. S1).

## $\delta^{18}\text{O}$ analyses of oxygen in the sulfate group of gypsum

The gypsum powders were dissolved overnight in nano-pure water in the presence of a small amount of dissolved  $\text{HgCl}_2$  to extract any sulfide, which was filtered out. The dissolved  $\text{SO}_4^{2-}$  ions in the resulting filtrate were precipitated as  $\text{BaSO}_4$  by adding 99.9% pure  $\text{BaCl}_2 \cdot \text{H}_2\text{O}$  powder in excess (1 g of  $\text{BaCl}_2 \cdot \text{H}_2\text{O}$  for 50 mg of gypsum). The  $\text{BaSO}_4$  powder was collected by filtration, washed with nano-pure water, and dried overnight at 60–70  $^\circ\text{C}$  in a convection oven. The  $\text{BaSO}_4$  powder was analyzed for  $\delta^{18}\text{O}$  at the Environmental Isotope Laboratory at the University of Waterloo by pyrolysis at 1450  $^\circ\text{C}$  using an Elementar Pyrocube elemental analyzer coupled to an IsoPrime Continuous Flow IRMS.

## RESULTS

The  $\delta^{18}\text{O}_{\text{gypsum}}^{\text{H}_2\text{O}}$  and  $\delta^{18}\text{O}_{\text{gypsum}}^{\text{SO}_4}$  of gypsum vary between 4.3–9.8‰ and 16.8–23.1‰, respectively, whereas the corresponding values for the fluid sample are 6.9 and 23.3‰ (all values relative to V-SMOW/V-SLAP; Table 1). The accuracy of analyses is between 0.2 and 0.5‰ (1s) for  $\delta^{18}\text{O}_{\text{water}}$  and 0.3 to 0.4‰ (1s) for  $\delta^{18}\text{O}_{\text{sulfate}}$  as determined on a range of certified international and cross-calibrated in-house reference materials. The precision, as determined from replicate analyses, is 0.1, 0.3, and 0.3, 0.1 (1s) for  $\delta^{18}\text{O}_{\text{water}}$  and  $\delta^{18}\text{O}_{\text{sulfate}}$  for solids and fluids, respectively (Table 1). Sufficient material was available for the stalactite tip sample (KV09-505) to be measured at variable sample amounts. Results are identical within error after correction for extracted water amounts of 48, 55, 62, and 152  $\mu\text{L}$  (Table 1). The  $\delta^{18}\text{O}_{\text{fluid}}^{\text{H}_2\text{O}}$  and  $\delta^{18}\text{O}_{\text{fluid}}^{\text{SO}_4}$  values are similar to those reported by Delmelle and

**TABLE 1.**  $\delta^{18}\text{O}$  compositions of gypsum stalactite zones, brine, and gypsum cement from the 1817 fall deposit

Sample type	Sample ID	Comment	$\mu\text{L}$	$\delta^{18}\text{O}_{\text{H}_2\text{O}}$	1s	$\delta^{18}\text{O}_{\text{SO}_4}$	1s	
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			
		<i>mean</i>		9.6	0.1	20.9	0.3	
Gypsum stalactite	KV09-501	zone A-B	61	9.3	0.5			
		1980				22.7	0.3	
						23.1	0.3	
						22.9	0.3	
		<i>mean</i>		9.3	0.5	22.9	0.3	
Gypsum stalactite	KV09-501	zone B-C	42	8.9	0.5			
		1991				23.0	0.3	
						23.1	0.3	
						23.0	0.1	
		<i>mean</i>		8.9	0.5	23.0	0.1	
Gypsum stalactite	KV09-501	zone D	89	9.8	0.5			
		2008				22.5	0.3	
						22.1	0.3	
						22.3	0.3	
		<i>mean</i>		9.8	0.5	22.3	0.3	
Gypsum cement	KS14-001	1817	59	4.3	0.5			
						17.3	0.3	
Seepage water	KV15-006			4.3	0.5			
				6.67	0.2		16.8	0.3
				7.16	0.2		17.1	0.4
							23.4	0.4
		<i>mean</i>		6.9	0.3	23.3	0.4	

Notes: The volume of crystalline water for each gypsum sample, and the age for the growth zones are also listed. All values are relative to V-SMOW/V-SLAP. Uncertainties are the 1 standard deviation analytical uncertainty, or uncertainty on the mean.

Bernard (2000) for the seepage area spring waters. The  $\delta^{18}\text{O}_{\text{fluid}}^{\text{H}_2\text{O}}$  is within the range reported by these authors ( $6.9 \pm 0.3\%$  compared to 2 to 7.8‰), whereas the  $\delta^{18}\text{O}_{\text{fluid}}^{\text{SO}_4}$  is about 1‰ higher. The  $\delta^{18}\text{O}_{\text{gypsum}}^{\text{H}_2\text{O}}$  values for the gypsum tip and stalactite samples are similar, whereas the gypsum cement is 5.5‰ lighter. The gypsum  $\delta^{18}\text{O}_{\text{gypsum}}^{\text{SO}_4}$  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  $\delta^{18}\text{O}_{\text{fluid}}^{\text{H}_2\text{O}}$  and  $\delta^{18}\text{O}_{\text{fluid}}^{\text{SO}_4}$  of Ijen seepage waters are high when compared to local meteoric water ( $\delta^{18}\text{O}_{\text{meteoric}}^{\text{H}_2\text{O}} = -9\%$ , Delmelle et al. 2000; Palmer 2009), Kawah Ijen fumaroles ( $\delta^{18}\text{O}_{\text{fumaroles}}^{\text{H}_2\text{O}} = 3.6\%$  and  $\delta^{18}\text{O}_{\text{fumaroles}}^{\text{SO}_4} = 7.6\%$ , van Hinsberg et al. 2016), or seawater ( $\delta^{18}\text{O}_{\text{seawater}}^{\text{H}_2\text{O}} = 0.2\%$  and  $\delta^{18}\text{O}_{\text{seawater}}^{\text{SO}_4} = 9.3\%$ ; Lloyd 1968; Schmidt 1999). Dissolved sulfate in acidic crater lakes dominantly derives from disproportionation reactions that convert volcanic  $\text{SO}_2$  to  $\text{SO}_4^{2-}(\text{aq})$  via various intermediaries, with  $\text{H}_2\text{S}$  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 Löhner et al. (2006). The heavy  $\delta^{18}\text{O}_{\text{fluid}}^{\text{SO}_4}$  is, therefore, a direct reflection of abiotic  $\text{SO}_2$  disproportionation, and conversion of  $\text{SO}_2$  to dissolved sulfate can indeed lead to an up to 31‰ enrichment in  $^{18}\text{O}$  (Müller et al. 2013a, 2013b). The heavy  $\delta^{18}\text{O}_{\text{fluid}}^{\text{H}_2\text{O}}$  compared to local meteoric water has been explained by strong evaporative enrichment of the lake water combined with the input of heavy water from the magmatic-hydrothermal system (Delmelle et al. 2000).

### Equilibrium in water-sulfate $\delta^{18}\text{O}$

The  $\delta^{18}\text{O}_{\text{fluid}}^{\text{H}_2\text{O}}$  and  $\delta^{18}\text{O}_{\text{fluid}}^{\text{SO}_4}$  are close to isotopic equilibrium when compared to the sulfate-water fractionation curve of Zeebe (2010) at the  $\sim 40^\circ\text{C}$  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. 2016), 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 Delmelle 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. 2016). 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 yr at a water temperature of  $40^\circ\text{C}$  (Fig. 12 of Seal et al. 2000). Zeebe (2010) shows a strong difference in oxygen isotope fractionation between  $\text{HSO}_4^-$ - $\text{H}_2\text{O}$  and  $\text{SO}_4^{2-}$ - $\text{H}_2\text{O}$  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  $340\ \mu\text{m}/\text{year}$  (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 suggest 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  $\text{H}_2\text{O}$  and  $\text{SO}_4$  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 (Fig. 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

**TABLE 2.** Gypsum-water  $\delta^{18}\text{O}$  fractionation factors for water and sulfate group, and water-sulfate group fractionation factors for water samples

Set	Sample type	Sample ID	Comment	$\delta^{18}\text{O}_{\text{H}_2\text{O}}$	1s	$\delta^{18}\text{O}_{\text{SO}_4}$	1s	$\alpha(\text{SO}_4/\text{H}_2\text{O})$	Equilibration T (Zeebe 2010)
1	gypsum stalactite	KV09-505	tip	9.6	0.1	20.9	0.3		
1	seepage water	KV15-006		6.9	0.3	23.3	0.1	1.016	$64 \pm 2^\circ\text{C}$
2	gypsum stalactite	KV09-501	zone D	9.8	0.5	22.3	0.3		
2	seepage water	KV15-006		6.9	0.3	23.3	0.1	1.016	$64 \pm 2^\circ\text{C}$
3	gypsum stalactite	KV09-501	zone B-C	8.9	0.5	23.0	0.1		
3	seepage water	BP96 2-5	Delmelle and Bernard (2000)	6	3	22.5	0.2	1.016	$65 \pm 21^\circ\text{C}$
	fractionation factor gypsum/water		set 1	1.0026	0.0003	0.9976	0.0003		
			set 2	1.0029	0.0006	0.9990	0.0003		
			set 3	1.0025	0.0029	1.0005	0.0002		
			mean	1.0027	0.0002	0.9990	0.0014		
				Gonfiantini and Fontes (1963)	1.0037	0.0005			
			Gazquez et al. (2017)	1.0035	0.0002				

Notes: The temperatures of equilibration based on the water-sulfate fractionation curve of Zeebe (2010) are also listed. Water-sulfate fractionation factors by Gonfiantini and Fontes (1963) and Gazquez et al. (2017) are listed for comparison.

incorporates  $^{18}\text{O}$  in its crystalline water, but  $^{16}\text{O}$  for the sulfate group, with mean gypsum-water fractionation factors of  $1.0027 \pm 0.0002$  and  $0.9990 \pm 0.0014$ , respectively (uncertainties given as 1s). 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  $\delta^{18}\text{O}_{\text{sulfate}}$  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  $1.0035 \pm 0.0002$  (1s uncertainty, see Gázquez 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  $\text{SO}_4$ -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  $\alpha(\text{SO}_4\text{-H}_2\text{O})_{\text{fluid}}$  could represent the equilibrium fractionation factor at these acidic conditions. No previous data are available on gypsum-water oxygen fractionation for sulfate group ions,

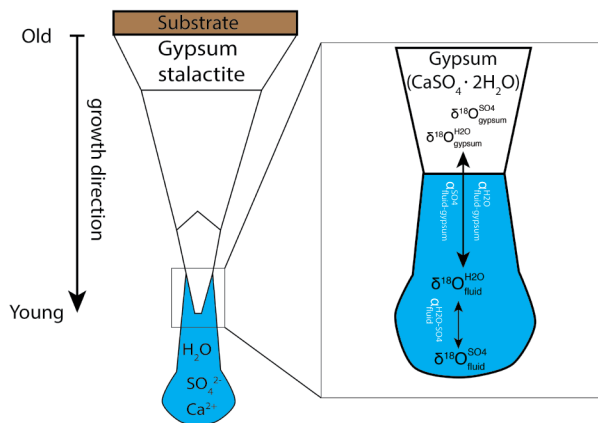
but a similar, differing fractionation behavior for sulfate group and hydroxyl groups has been reported for alunite and jarosite (Stoffregen et al. 1994; Rye and Stoffregen 1995).

### Oxygen isotopic composition of stalactite and gypsum cement formation waters

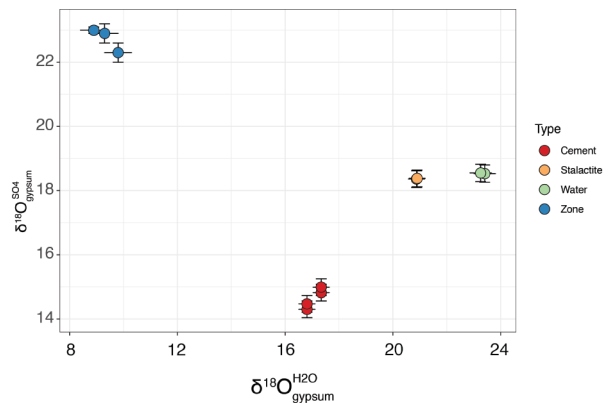
The gypsum-water fractionation factors allow for the  $\delta^{18}\text{O}_{\text{fluid}}^{\text{H}_2\text{O}}$  and  $\delta^{18}\text{O}_{\text{fluid}}^{\text{SO}_4}$  of the parent fluids to be calculated from gypsum (Fig. 2). The  $\delta^{18}\text{O}_{\text{fluid}}^{\text{H}_2\text{O}}$  compositions calculated from the growth-zoned stalactite vary from  $\delta^{18}\text{O} = 6.2$  to  $7.1\text{‰}$ , similar to the 6.9‰ of the present-day seepage waters. The  $\delta^{18}\text{O}_{\text{fluid}}^{\text{SO}_4}$  varies from 23.3 to 24.0‰, which is somewhat heavier than the crystalline water (Fig. 3). In contrast, the gypsum cement formed from a fluid with significantly lighter  $\delta^{18}\text{O}$  for both  $\text{H}_2\text{O}$  and  $\text{SO}_4$  at 1.6 and 18.1‰, respectively. Despite these variations, the fractionation factor between  $\delta^{18}\text{O}$  for  $\text{H}_2\text{O}$  and  $\text{SO}_4$  in the fluid is near constant (Table 3). The consistency in  $\alpha(\text{SO}_4\text{-H}_2\text{O})_{\text{fluid}}$ , despite strong variations in  $\delta^{18}\text{O}_{\text{fluid}}^{\text{H}_2\text{O}}$  and  $\delta^{18}\text{O}_{\text{fluid}}^{\text{SO}_4}$ , is inconsistent with this representing incomplete re-equilibration; it is highly unlikely that the exact same degree of temperature re-equilibration, or mixing of sources would be attained. This is especially true for the 1817 gypsum cement, which samples a previous, smaller crater lake (Caudron et al. 2015; Utami et al. 2019). We therefore conclude that this  $\alpha(\text{SO}_4\text{-H}_2\text{O})_{\text{fluid}}$  more likely reflects oxygen exchange equilibrium for these acidic brines, with the difference from the theoretical  $\alpha(\text{SO}_4\text{-H}_2\text{O})_{\text{fluid}}$  (Zeebe 2010) reflecting the effects of pH and speciation on fractionation.

### Historical $\delta^{18}\text{O}$ record from gypsum

The historical record of seepage water  $\delta^{18}\text{O}_{\text{fluid}}^{\text{H}_2\text{O}}$  and  $\delta^{18}\text{O}_{\text{fluid}}^{\text{SO}_4}$  based on direct fluid measurements and reconstructions from the gypsum stalactite and 1817 gypsum cement is shown in Figure 4. The elemental record shows a distinct change in behavior of the system around 1992, which marks the transition from quiescence to a state of variable unrest (Caudron et al. 2015; Utami et al. 2019). The  $\delta^{18}\text{O}$  record unfortunately lacks the resolution needed to directly link the elemental and isotopic records together. The two older samples that represent the period of quiescence are both lower in  $\delta^{18}\text{O}_{\text{fluid}}^{\text{H}_2\text{O}}$  and higher in  $\delta^{18}\text{O}_{\text{fluid}}^{\text{SO}_4}$  compared to the



**FIGURE 2.** Conceptual model of formation and isotopic exchange for a Kawah Ijen gypsum stalactite. The gypsum stalactite tip and surface are continuously coated by 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 ( $\delta^{18}\text{O}_{\text{fluid}}^{\text{H}_2\text{O}}$  and  $\delta^{18}\text{O}_{\text{fluid}}^{\text{SO}_4}$ ) and gypsum ( $\delta^{18}\text{O}_{\text{gypsum}}^{\text{H}_2\text{O}}$  and  $\delta^{18}\text{O}_{\text{gypsum}}^{\text{SO}_4}$ ) allows for the fractionation factors for  $\alpha_{\text{water}}$  and  $\alpha_{\text{sulfate}}$  to be determined, as well as to calculate the  $\alpha(\text{SO}_4\text{-H}_2\text{O})_{\text{fluid}}$ , which is a measure of the oxygen isotopic equilibrium state of the fluid. Applying the  $\alpha_{\text{water}}$  and  $\alpha_{\text{sulfate}}$  to internal zones of the stalactite allows a timeseries of  $\delta^{18}\text{O}_{\text{fluid}}^{\text{H}_2\text{O}}$  and  $\delta^{18}\text{O}_{\text{fluid}}^{\text{SO}_4}$  to be reconstructed. (Color online.)

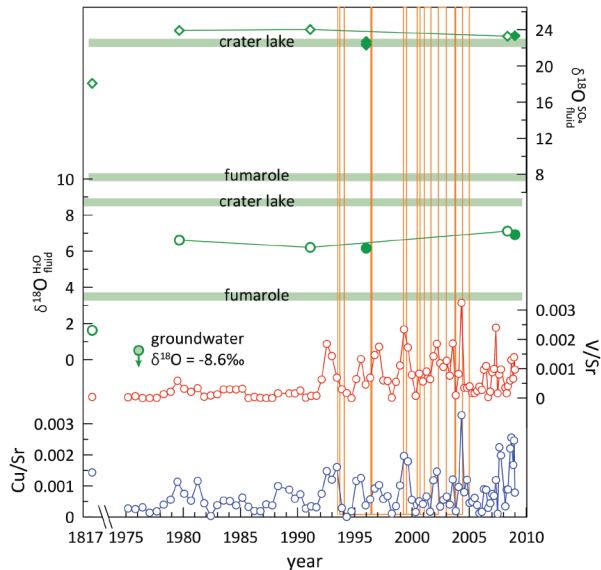


**FIGURE 3.**  $\delta^{18}\text{O}_{\text{gypsum}}^{\text{H}_2\text{O}}$  and  $\delta^{18}\text{O}_{\text{gypsum}}^{\text{SO}_4}$  of Ijen's various gypsum samples, comprising the 1817 gypsum cement ("Cement"), the 2009 growth-zoned stalactite tip ("Stalactite"), 2015 spring water ("Water"), and 2009 growth zoned gypsum stalactite ("Zone"). (Color online.)

**TABLE 3.** Reconstructed  $\delta^{18}\text{O}$  values for gypsum formation waters ( $\delta^{18}\text{O}_{\text{fluid}}^{\text{H}_2\text{O}}$  and  $\delta^{18}\text{O}_{\text{fluid}}^{\text{SO}_4}$ ) and their  $\text{H}_2\text{O}-\text{SO}_4$  fractionation factors

Sample type	Sample ID	Comment	Year	$\delta^{18}\text{O}_{\text{H}_2\text{O}}$	1s	$\delta^{18}\text{O}_{\text{SO}_4}$	1s	$\alpha(\text{SO}_4/\text{H}_2\text{O})$	Equilibration T (Zeebe 2010)
Gypsum stalactite	KV09-501	zone A-B	1980	6.6	0.4	23.9	0.3	1.017	$58 \pm 3^\circ\text{C}$
		zone B-C	1991	6.2	0.3	24.0	0.1	1.018	$54 \pm 3^\circ\text{C}$
		zone D	2008	7.1	0.4	23.3	0.3	1.016	$65 \pm 4^\circ\text{C}$
Gypsum cement	KS14-001		1817	1.6	0.2	18.1	0.4	1.016	$63 \pm 3^\circ\text{C}$

Note: The temperatures of equilibration based on the  $\text{H}_2\text{O}-\text{SO}_4$  fractionation curve of Zeebe (2010) are also listed.



**FIGURE 4.** Time series of  $\delta^{18}\text{O}_{\text{fluid}}^{\text{H}_2\text{O}}$  and  $\delta^{18}\text{O}_{\text{fluid}}^{\text{SO}_4}$  for Ijen seepage waters compared to the elemental record reconstructed from gypsum (data from Utami et al. 2019). Solid symbols are for direct measurements, open symbols for reconstructed values. Crater lake, fumaroles, and groundwater  $\delta^{18}\text{O}$  values are shown for reference (from Delmelle et al. 2000; Palmer 2009; van Hinsberg et al. 2016). The orange lines represent periods of volcanic unrest. (Color online.)

more recent samples, but the differences are small and could represent incremental variations in the lake chemistry over time. An important parameter in interpreting the historical record is the residence time of water and sulfate in the lake, as this controls how quickly changes will become apparent in the lake, and in the gypsum precipitating from it. To estimate residence time, we use the approach of Rouwet and Tassi (2011), with elemental and isotopic compositions for rain- and groundwater, volcanic gas, lake and seepage water, as well as seepage flux, from van Hinsberg et al. (2016). The volcanic gas flux was estimated from the change in Cl content of the lake over time and the Cl content of the volcanic gas, assuming that the surface gas composition is identical to that of the gas entering the bottom of the lake. No loss of Cl by evaporation was included in this calculation, and this is therefore a minimum estimate (see Rodríguez et al. 2018). Annual precipitation for Kawah Ijen was taken from Blaak (1920), which represents data for 1907–1917 (the annual precipitation for Banyuwangi reported by Blaak (1920) is equivalent to that at present). Lake volume was taken from Caudron et al. (2015), converted to mass using a density of  $1.035 \text{ kg/dm}^3$  as calculated from lake water composition. A water residence time of 1.5 yr results. Although this value has a large uncertainty given the assumptions and uncertainties in

the input parameters, it does indicate that gypsum would be able to record changes on the multi-year timescale that we have reconstructed here.

In contrast to the small variations from 1980 to 2009, the 1817 sample is distinctly different (Fig. 4). This gypsum records the composition of crater lake waters thrown out during the 1817 phreato-magmatic eruption of Kawah Ijen (Utami et al. 2019). Both the  $\delta^{18}\text{O}_{\text{water}}$  and  $\delta^{18}\text{O}_{\text{sulfate}}$  of the 1817 gypsum cement are lighter than the gypsum stalactite and the present-day gypsum stalactite tips. Whereas the stalactite grows in an open-system, continuously refreshed fluid environment, the gypsum cement would likely have formed from a closed-system pore fluid, resulting in  $^{18}\text{O}/^{16}\text{O}$  isotope fractionation as gypsum precipitation progresses. However, the above and below 1 fractionation factors for water and sulfate group, respectively, would lead to diverging  $\delta^{18}\text{O}_{\text{gypsum}}^{\text{H}_2\text{O}}$  and  $\delta^{18}\text{O}_{\text{gypsum}}^{\text{SO}_4}$  in this case, whereas both are found to be isotopically lighter. Secondary processes such as later water ingress and re-equilibration, leaching of oxygen from the fall deposit rock clasts, or boiling of the fluid in the hot fall deposit would almost exclusively modify  $\delta^{18}\text{O}_{\text{gypsum}}^{\text{H}_2\text{O}}$  and thus introduce disequilibrium, whereas the  $\alpha(\text{SO}_4-\text{H}_2\text{O})_{\text{fluid}}$  appears to be at low-temperature equilibrium (Table 3). This argument also rules out a significant meteoric water contribution added in the eruption plume. Thus we conclude that the observed signature reflects a fluid with a different  $\delta^{18}\text{O}_{\text{fluid}}^{\text{H}_2\text{O}}$  and  $\delta^{18}\text{O}_{\text{fluid}}^{\text{SO}_4}$  signature. Given that the  $\alpha(\text{SO}_4-\text{H}_2\text{O})_{\text{fluid}}$  appears to be in equilibrium (Table 3), and the fact that the amount of oxygen in sulfate is still subordinate to that in water in the Kawah Ijen fluids, we attribute the low  $\delta^{18}\text{O}_{\text{fluid}}^{\text{SO}_4}$  to disproportionation into, and equilibrating with a light  $\delta^{18}\text{O}_{\text{fluid}}^{\text{H}_2\text{O}}$  reservoir. A stronger fumarole contribution cannot be excluded, but this would need to be significantly larger, and is not able to explain the  $\delta^{18}\text{O}_{\text{fluid}}^{\text{H}_2\text{O}}$  that extends below the oxygen isotopic composition of the fumaroles (Fig. 4). Volatile metal ratios suggest a stronger contribution from deep, basaltic magma prior to the 1817 eruption (Utami et al. 2019), but it is unclear how this would affect the  $\delta^{18}\text{O}$  signature. Addition of meteoric water would lower the  $\delta^{18}\text{O}_{\text{fluid}}^{\text{H}_2\text{O}}$  given its  $\delta^{18}\text{O}$  of around  $-9\text{‰}$  (Delmelle et al. 2000; Palmer 2009). Water-rock interaction would also lower the  $\delta^{18}\text{O}$  of the fluid as  $^{18}\text{O}$  gets enriched in the altered amorphous silica residue. However, there is no evidence that the pre-eruptive lake was more dilute or more concentrated than at present (van Hinsberg et al. 2016). Delmelle et al. (2000) show that the high  $\delta^{18}\text{O}_{\text{fluid}}^{\text{H}_2\text{O}}$  of the current lake requires significant evaporative loss of  $^{16}\text{O}$ . This evaporation gradually increases the  $\delta^{18}\text{O}$  of the lake, and the lower  $\delta^{18}\text{O}$  of the pre-eruptive lake may therefore indicate that it had been present for a shorter duration. Less evaporation because of a lower fluid temperature can be ruled out, because this would be reflected in the  $\alpha(\text{SO}_4-\text{H}_2\text{O})_{\text{fluid}}$ . The lake had a smaller surface area prior to the 1817 eruption (Leschenault de la Tour 1805; Caudron et al. 2015), whereas the crater itself was similar in size, which would suggest a larger

rain- and groundwater flux relative to evaporation, compared to the present-day. Alternatively, the pre-1817 lake had a more direct connection to the magmatic-hydrothermal system, and therefore a stronger contribution of  $\delta^{18}\text{O}_{\text{fluid}}^{\text{H}_2\text{O}}$  from the hydrothermal system. Currently, direct fluid exchange between the lake and the underlying magmatic-hydrothermal system appears limited (van Hinsberg et al. 2016), but fluids from the hydrothermal system do flow out at the lowermost springs with only a small crater lake seepage contribution (Palmer 2009). The  $\delta^{18}\text{O}$  composition of these lowermost seepage waters is significantly lighter at 0.5‰ compared to the approximately 8‰  $\delta^{18}\text{O}$  of the lake water (Palmer 2009). With the present data set, we cannot differentiate between these possibilities.

### IMPLICATIONS

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

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#### Endnote:

<sup>1</sup>Deposit item AM-20-57298, Supplemental Figure. Deposit items are free to all readers and found on the MSA website, via the specific issue's Table of Contents (go to [http://www.minsocam.org/MSA/AmMin/TOC/2020/May2020\\_data/May2020\\_data.html](http://www.minsocam.org/MSA/AmMin/TOC/2020/May2020_data/May2020_data.html)).