GYPSUM AS A RECORDER OF FLUID CHEMISTRY AND TEMPERATURE AT KAWAH IJEN VOLCANO, EAST JAVA, INDONESIA

SRI BUDHI UTAMI

Department of Earth and Planetary Sciences McGill University Montreal, Québec, Canada

A thesis submitted to McGill University in partial fulfilment of the requirements of the degree of Master of Science

August 2015

 \bigodot Sri Budhi Utami, 2015

Abstract

Kawah Ijen volcano in East Java, Indonesia is an active stratovolcano capped by the worlds largest hyper-acidic lake. The lake composition is the combined product of rainwater, rock dissolution from the country rock, and magmatic gas input. The volcano has generated hazards including lava flows, lahars and acidified tephra falls in the past. Kawah Ijen also generates extreme environmental pollution as a result of leakage of extremely acidic-saline brines affecting vast areas of crops and water resources. Recent events are characterized by phreatic activity, with one phreatomagmatic eruption that threw out the entire lake in 1817. Given the potential hazards that Kawah Ijen can generate and combined with a rising population density around the volcano, the risk to human lives has increased considerably. Monitoring at Kawah Ijen is critical but requires a detailed record of past volcanic activity. Lake chemistry is an effective tool to monitor volcanic lakes, but there is currently a severely limited record of lake chemistry at Kawah Ijen. The mineral gypsum can be used to reconstruct lake chemistry history because gypsum is a direct proxy of its fluid's composition as it precipitates in equilibrium, and is abundant at Kawah Ijen, forming a plateau and stalactites that preserve past conditions in growth zoning. This research investigates the potential for gypsum as a mineralogical tool to reconstruct a historical record of lake chemistry. Trace element composition, noble gas content and uranium series dating of a cross-sectional transect across a growth-zoned gypsum stalactite yields a 50-year, high resolution record of Kawah Ijen lake chemistry. Input from rock dissolution shows seasonal variations, as well as rockslides and falls. Volatile metals track input from the shallow and deep magma reservoirs. The transition metal records a combined input from rock dissolution and magmatic gases. Analysis of the 1817 gypsum records substantially increased input from the deep-seated mafic magma, indicating mafic magmatic recharge as having driven the catastrophic 1817 eruption. Moreover, the oxygen isotopic composition of gypsum preserves isotopic disequilibrium between the sulfate and water in the lake fluids. Gypsum-reconstructed temperatures show a much stronger magmatic gas input in 1817, in agreement with trace element results. In conclusion, gypsum can be used to reconstruct lake water compositions and thermal conditions of crater lakes and build the historical record that allows monitoring to be set up. In the case of Kawah Ijen, it suggests that a catastrophic eruption, similar to that of 1817, should be accompanied by a strong signal in the volatile metals (high Cu/Rb and low Tl/Cu) and increase in lake temperature.

Résume

Le volcan Kawah Ijen dans l'est de Java (Indonésie) est un stratovolcan actif surmonté par le plus grand lac hyperacide du monde. La composition du lac est un mélange d'eaux de pluie, des roches encaissantes dissoutes, et d'un apport en gaz magmatiques. Par le passé, le volcan a déjà généré des coulées de lave, de lahars, et de chutes de tephra acides. Kawah Ijen peut également génèrer la pollution de l'environnement extrême par suite de la fuite des saumures acides et salines qui affectent les ressources en eau et agricole. Les récentes activités du volcan ont été caractérisées par une activité phréatique, avec une éruption phréato-magmatique qui a expulsé le lac entier en 1817. Le danger potentiel représenté par Kawah Ijen, combiné avec une densité de population qui ne cesse de croître entraîne une augmentation du risque pour les vies humaines. Kawah Ijen est donc nécessite dêtre sous surveillance constante, mais cette surveillance demande une connaissance accrue de l'historique du volcan. La chimie du lac est un outil efficace pour surveiller les lacs volcaniques, mais les rapports sur la chimie du lac de Kawah Ijen sont malheureusement extrêmement limités. Un outil peut cependant être utilisé pour reconstruire l'histoire de la chimie du lac: le gypse. En effet, ce minéral est un estimateur direct de la composition du fluide lors de la précipitation puisquil est alors en équilibre avec le fluide. Le gypse est aussi relativement abondant au bord du volcan, format un plateau et des stalactites qui préservent donc les conditions des zones de croissances. Ce projet ici propose de tester le potentiel du gypse comme outil minéralogique dans la reconstruction de l'histoire de la chimie du lac. L'utilisation des éléments traces, des gaz rares, et des séries d'uranium pour dater une coupe transversale prise dans une stalactite de gypse correspondant à une zone de croissance a révélé la chimie du lac de Kawah Ijen, avec une résolution sans précédent pour une période de 50 ans. L'apport de la dissolution des roches indique des variations saisonnières, ainsi que des glissements de terrain et des chutes de roches. Les métaux volatiles retracent l'apport jusqu'aux réservoirs magmatiques. Les métaux de transition enregistrent un apport provenant de la dissolution des roches et des gaz magmatiques combinés. L'analyse du gypse datant de 1817 montre une augmentation subsentielle de l'apport provenant d'un magma mafique profond, indiquant que la recharge magmatique mafique a été la cause de l'éruption de 1817. De plus, la composition isotopique du gypse en oxygène préserve le déséquilibre isotopique entre the sulfate et l'eau présents dans les fluides du lac. Les températures qui ont pu être reconstruites à l'aide du gypse montrent un apport en gaz magmatiques extrêmement important pour 1817, ce qui corrobore les données apportées par les éléments traces. En conclusion, le gypse peut être utilisé pour reconstruire les compositions des eaux lacustres et les conditions thermales des lacs de cratère. Ceci permet donc une reconstruction de l'historique du volcan, élément indispensable pour effectuer la surveillance actuelle. Dans le cas de Kawah Ijen, les données suggèrent qu'une catastrophe similaire a celle de 1817 devrait être accompagnée d'un fort signal dans les métaux volatiles (forts taux de Cu/Rb, faibles taux de Tl/Cu), ainsi qu'une augmentation de la température du lac.

Acknowledgements

My sincerest gratitude to my co-advisors Vincent van Hinsberg and Bassam Ghaleb, both of whom have generously extended their expertise, guidance and mentorship to me to ensure that I succeed during my time here. Thank you for your enthusiasm, honesty and patience; both of you were instrumental in instilling in me a deep appreciation and rigorous treatment of science.

Thanks go to Kim Berlo for discussions on the Kawah Ijen system and Daniele Pinti for discussions on noble gases. Thanks go to Corentin Caudron for extending the opportunity to take part in the Cities on Volcanoes 8 Wet Volcanoes Workshop, as well as the participants of the workshop for the fruitful discussions on volcanic lakes. Thanks also go to the people who have helped me during our fieldwork around Kawah Ijen volcano (Ibu Minarsih, Bapak and Ibu Im). Thank you especially to Bapak Jumanto for your assistance in the field. Thanks to all the technical staff at both McGill University and GEOTOP-UQAM: Anna Jung, Isabelle Richard, Lang Shi, Arisai Valadez and Jean-François Hélie who helped me with my training and analyses, as well for your guidance and expertise. Thank you also go to William Mark at the University of Waterloo for the oxygen isotope analysis. Thanks also go to current and former administrative staff Anne Kosowski, Angela Di Ninno, Kristy Thornton, Brandon Bray and Brigitte Dionne at McGill University, and Nicole Turcotte and Sandrine Solignac from UQAM for helping me with administrative duties. Thanks also go to the McGill Earth and Planetary Sciences graduate students and in particular, members of the FlexPet (Naomi, Longbo, and Charles) and MAD (Rebecca) research groups for discussions on geology and otherwise. It was a pleasure getting to know you, and I wish you all the best for the future. Thanks also to Louise Marie Meunier and Caroline Aubry-Wake for translating the abstract. Finally, thank you to my family (Bapak, Ibu, Wahyu and Riri). Your encouragement helped me through the challenging times during the past two years, and words cannot describe how much your support and encouragement mean to me.

Contents

| A | bstra | lct | i |
|----------------------------|--------------|--|----|
| Résume Acknowledgements | | | |
| | | | |
| \mathbf{Li} | st of | Figures | xi |
| 1 | Introduction | | |
| 2 Manuscript 1 | | | |
| | 2.1 | Abstract | 11 |
| | 2.2 | Introduction | 11 |
| | 2.3 | Kawah Ijen volcano | 16 |
| | 2.4 | Gypsum at Kawah Ijen | 17 |
| | 2.5 | Existing Record of Volcanic Activity at Kawah Ijen | 18 |
| | 2.6 | Methodology | 22 |
| | | 2.6.1 ²¹⁰ Pb analyses | 23 |
| | | 2.6.2 Noble gases | 23 |
| | | 2.6.3 Trace elements | 24 |
| | 2.7 | Results | 24 |

| | 2.8 | Discus | sion | | | 25 |
|---|------|---------|------------|--|------|----|
| | | 2.8.1 | Gypsum | Age | | 25 |
| | | 2.8.2 | Gypsum | as an elemental recorder of fluid chemistry | | 26 |
| | | | 2.8.2.1 | The Kawah Ijen model | | 27 |
| | | | 2.8.2.2 | Compositional time-series | | 28 |
| | | | 2.8.2.3 | Rock dissolution flux | | 31 |
| | | | 2.8.2.4 | Volatile metals | | 33 |
| | | | 2.8.2.5 | Transition metals | | 35 |
| | | | 2.8.2.6 | Comparing chemical and physical indicators of unrest at K | awah | 1 |
| | | | | Ijen | | 36 |
| | | | 2.8.2.7 | Insights into the 1817 eruption from the gypsum record . | | 37 |
| | 2.9 | Conclu | usion and | implications | | 38 |
| | 2.10 | Ackno | wledgeme | nts | | 39 |
| | 2.11 | Table | captions . | | | 40 |
| | 2.12 | Figure | Captions | | | 40 |
| 3 | Mar | nuscrip | ot 2 | | | 69 |
| | 3.1 | Abstra | ıct | | | 71 |
| | 3.2 | Introd | uction | | | 71 |
| | 3.3 | Metho | dology . | | | 73 |
| | 3.4 | Result | s | | | 74 |
| | 3.5 | Discus | sion | | | 74 |
| | 3.6 | Implic | ations | | | 77 |
| | 3.7 | Ackno | wledgeme | nts | | 78 |
| | 3.8 | List of | Figure ca | $ption \ldots \ldots$ | | 79 |
| | 3.9 | List of | Table cap | ptions | | 79 |
| | 3.10 | List of | Tables . | | | 81 |

| 4 General Summary and Conclusions | | | |
|--|--------|--|--|
| Annuality 1. Complementary T. Complementary Co. Manuality 1 (Classical | 2) 104 | | |
| Appendix 1: Supplementary Information for Manuscript 1 (Chapter | 2) 104 | | |

List of Tables

| 2.1 | Summary of the trace element transect across growth zones A-D from sta- | |
|-----|---|----|
| | lactite KV09-501 growth zones. All concentrations are in ppm, except where | |
| | indicated. ' <d.l.' below="" composition="" detection<="" element="" is="" means="" td="" the="" trace=""><td></td></d.l.'> | |
| | limit of the instrument. Hg concentrations are in counts per second (cps) | 43 |
| 2.2 | Trace element concentrations for the 1817 gypsum cement. All concentrations | |
| | are in ppm unless specified. Hg concentrations are in counts per second (cps). | |
| | ' <d.l.' below="" composition="" detection="" element="" is="" limit="" means="" of<="" td="" the="" trace=""><td></td></d.l.'> | |
| | the instrument. | 55 |
| 2.3 | ²¹⁰ Pb activities of growth zones A-D, representing the oldest to youngest, | |
| | respectively. | 57 |
| 2.4 | $^{84}\mathrm{Kr}$ and $^{132}\mathrm{Xe}$ compositions of stalactite KV09-501 with growth zones A - D. | |
| | F-values are the relative enrichment or depletion of each zone with respect to | |
| | the atmospheric noble gas composition | 58 |
| 3.1 | Table of $\delta^{18}O$ compositions of gypsum stalactites, brine and gypsum-cemented | |
| | fall deposit. | 81 |
| 3.2 | Calculated α values of gypsum and spring brine with uncertainty set at 1σ . | 82 |
| 3.3 | Reconstructed brine δ^{18} O composition for the 1817 lake water | 83 |
| 3.4 | Table of derived temperatures from the reconstructed brine compositions. | |
| | Temperatures are derived using the revised geothermometer derived by (Seal | |
| | et al. 2000), after (Mizutani and Rafter 1969) and (Lloyd 1968). \ldots | 84 |

List of Figures

| 2.1 | A) Map of East Java with Kawah Ijen highlighted. B) Modified Landsat8 | |
|-----|---|----|
| | image of the Ijen Volcanic Complex (dashed outline). Solid arrows show | |
| | the pathways of major lava flows and lahars from Kawah Ijen volcano. C) | |
| | Topographical map of Kawah Ijen and the Blau and Papak volcanoes. The | |
| | study site is highlighted. Solid and dashed arrows show the pathways of major | |
| | lava flows from Kawah Ijen volcano | 45 |
| 2.2 | A) Model of the magmatic-hydrothermal system at Kawah Ijen in its passive | |
| | degassing state, modified after (Christenson et al. 2010). B) Model of the | |
| | magmatic-hydrothermal system at Kawah Ijen volcano during periods of unrest. | 46 |
| 2.3 | A) The Kawah Ijen gypsum plateau at the uppermost seepage springs looking | |
| | back to the lake. B) Typical occurrence of gypsum stalactite growing down- | |
| | wards from brine flowing over its surface and showing the euhedral habit of | |
| | the gypsum crystals. | 47 |
| 2.4 | A) Photo of stalactite KV09-501, analysed in this study. B) Cross-section of | |
| | the base of the stalactite with growth zones chosen for $^{210}\mathrm{Pb}$ and noble gas | |
| | analyses. C) Location of the trace element transect | 48 |
| 2.5 | Gypsum cemented fall deposit from the 1817 eruption of Kawah Ijen. The | |
| | book is 19.5 cm in length. | 49 |

| 2.6 | A) Variations in 210 Pb, F(84 Kr) and F(132 Xe) in each growth zone in the | |
|------|---|----|
| | KV09-501 cross-section. B) Age model after correction using the weighted | |
| | averages of $F(^{84}Kr)$ and $F(^{132}Xe)$. | 50 |
| 2.7 | Compositions of average Kawah Ijen rock and fumarole gas relative to lake wa- | |
| | ter, normalised to their respective Mg contents, showing the dominant source | |
| | for each element. Whereas the REEs and HFSEs are mainly derived from rock | |
| | dissolution, the volatile metals are characteristically enriched in the volcanic | |
| | gas | 51 |
| 2.8 | Time-series record of trace element concentration representative of each type | |
| | of trace element group in the Kawah Ijen system: rock dissolution elements | |
| | (blue), volatile metals (red) and transition metals (purple) | 52 |
| 2.9 | Record of elemental ratios from 1964-2006, with a close-up for the 1990-2006 $$ | |
| | period for which reliable records of volcanic activity are available | 53 |
| 2.10 | Tl/Rb and Cu/Rb, representing dilution corrected input from the shallow | |
| | dacitic magma and deep basaltic magma respectively, compared with thermal | |
| | record and volcano-tectonic seismicity (VA, VB and tremor) | 54 |
| 3.1 | A) Top of the gypsum plateau, with stalactites growing on overhangs. B) | |
| | A typical gypsum stalactite recording the oxygen isotopic disequilibrium be- | |
| | tween the sulfate and water from its parent fluids. C) The pathway (dashed | |
| | line with circles) that the SO_4 and H_2O molecules take from the magmatic- | |
| | hydrothermal system to the gypsum plateau as reflected in the δ^{18} O composition. | 80 |

Chapter 1

Introduction

Evaporite minerals are abundant minerals on Earth, and their presence within the geological record provides evidence for the role played by water on the surface water on the surface or near-surface of the Earth back to the Archean (Hagemann et al. 1994). Evaporation of an aqueous solution leads to progressive concentration of the solution to its saturation point, after which the solution proceeds to precipitate evaporite minerals (Hardie and Eugster 1980). Given that evaporite minerals are closely linked to their original solution, and assuming that the minerals precipitate in chemical equilibrium with it, we can use evaporite minerals as a proxy of the composition of the original solution, or if element partition coefficients are known, to quantitatively reconstruct this composition. Knowledge of the original composition of the solution allows us to infer the fluid source, contributions to its overall composition, and track its chemical evolution through time. Applications of these tools range from reconstructing the hydrothermal fluids responsible for ore formation (Migdisov et al. 2014; Williams-Jones and Migdisov 2014) to determining the potential for water and life on Mars (Tosca and McLennan 2006; Tosca et al. 2008). Hence evaporite minerals are ideal tools to constrain fluid compositions, sources and their evolution through time.

Evaporite minerals have been used to reconstruct the composition of their original fluids, and from this deduce the tectonic, environmental and climatic controls influencing the chemical composition of the original fluids in a variety of settings (e.g. Hardie 1996; Sellwood and Price 1994; Warren 2010). For example, the composition of marine non-biogenic evaporites was used to infer oscillations in seawater chemistry (Blättler et al. 2012; Farkaš et al. 2007; Kendall and Schlager 1981). Evaporite minerals precipitated from saline meteoric groundwater in salt pans, such as the Salar de Atacama in Chile, have been found to record past groundwater influx variations and lake level changes (Bobst et al. 2001; Li et al. 1997). The assemblages of evaporite minerals found on Mars is indicative of the presence of water in its geological history, and their composition has been shown to be controlled by the weathering of basalts (Gendrin et al. 2005; Madden et al. 2004; McLennan et al. 2005). Soluble evaporite minerals such as schwertsmannite form incrustations around acidic rivers and lakes affected by acid drainage, and their chemical composition can be used to monitor the effect of contaminants on major rivers such as the Tinto river in Spain (Bigham and Nordstrom 2000; Cánovas et al. 2010; Nordstrom et al. 2000).

One important application of evaporite minerals as tools to reconstruct fluid composition is in volcanology, specifically in water-gas-rock interaction processes. Volcanogenic minerals range from hydrothermal mineral incrustations around fumaroles to evaporite deposits around acidic springs (Kawano and Tomita 2001; Stoiber and Rose 1974). The fluid composition in these systems reflects interaction between a variety of fluxes, including rainwater, groundwater, rock dissolution, and hydrothermal fluids formed by the interaction between magmatic gases and groundwater systems (Hinsberg et al. 2010a,b). Interaction between ground/rainwater and magmatic gases, which are typically rich in SO₂ and H₂S results in low pH and high ionic strength systems (e.g. Christenson (2000); Martinez et al. (2000)). The low pH leads to rock dissolution and leaching of elements from the surrounding rocks, thus contributing large amounts of cations to its elemental load (Hinsberg et al. 2010b; Varekamp et al. 2009). Where surface topography intersects these hydrothermal aquifers, surface outlets appear, comprising acidic springs, acidic rivers and in exceptional cases, volcanic lakes (Delmelle and Bernard 2000; Palmer 2009; Rowe et al. 1995). Evaporite minerals precipitate from these fluids, and given the abundance of SO_2 and H_2S from magmatic gas, the evaporite mineralogy is commonly dominated by sulfate minerals including gypsum, K-alum, jarosite and alunite (Delmelle and Bernard 2000; Zimbelman et al. 2005). These minerals can be used to reconstruct the chemistry of the acid waters, and can be used to track fluctuations in their composition through time. In turn, this allows for investigating and monitoring of the volcano-hydrothermal system and volcanic activity.

Kawah Ijen volcano in East Java, Indonesia is the system to apply this approach. This arc volcano hosts the world's largest, natural hyper-acidic lake and from which a hyperacidic river originates, the Banyu Pahit river (Delmelle and Bernard 1994). Abundant evaporite minerals are present around the lake and along the Banyu Pahit river valley. The largest evaporite deposits are found at lake seepage springs on the western flank of the volcano, which are composed of gypsum (Kemmerling 1921). This gypsum occurs as a cascading gypsum plateau, and growth-zoned gypsum stalactites. The presence of these gypsum stalactites presents a unique opportunity to reconstruct a continuous, high-resolution record of fluid chemistry for this volcano, and in doing so, track variations in element input to the lake. In particular, the input flux from the degassing magma can be used to construct a historical record of volcanic activity, which aids current monitoring attempts of the volcano. This thesis presents an investigation of gypsum's potential as a mineralogical tool to record fluid chemistry, and the first application of this tool to a volcanic system, Kawah Ijen. The thesis is structured around two manuscripts. Manuscript 1 (Chapter 2) presents the results of an analysis of a growth-zoned stalactite from Kawah Ijen volcano using noble gases composition, ²¹⁰Pb disequilibrium dating, and trace element compositions of consecutive growth zones to build a compositional time-series for Kawah Ijen crater lake water, relating fluctuations in concentration to changes in the input fluxes in the Kawah Ijen hydrothermal system. I show that the volatile metals best track volcanic activity and are therefore the best target for monitoring efforts. Moreover the Tl/Cu ratio allows for input from deep mafic magma to be differentiated from shallow dacite magma input, with the latter appearing to be responsible for small-scale phreatic activity, whereas the catastrophic 1817 eruption involved the deep mafic magma. Manuscript 2 (Chapter 3) uses disequilibrium in the δ^{18} O composition of SO₄ and H₂O in the crater lake as a thermometer and investigates whether this disequilibrium isotopic signal is preserved in gypsum.

References

- Bigham, J. and D. K. Nordstrom (2000). "Iron and aluminum hydroxysulfates from acid sulfate waters". *Reviews in mineralogy and geochemistry* 40.1, pp. 351–403.
- Blättler, C. L., G. M. Henderson, and H. C. Jenkyns (2012). "Explaining the Phanerozoic Ca isotope history of seawater". *Geology* 40.9, pp. 843–846.
- Bobst, A. L., T. K. Lowenstein, T. E. Jordan, L. V. Godfrey, T.-L. Ku, and S. Luo (2001).
 "A 106ka paleoclimate record from drill core of the Salar de Atacama, northern Chile".
 Palaeogeography, Palaeoclimatology, Palaeoecology 173.1, pp. 21–42.
- Cánovas, C., M Olías, J. Nieto, and L Galván (2010). "Wash-out processes of evaporitic sulfate salts in the Tinto river: hydrogeochemical evolution and environmental impact". *Applied Geochemistry* 25.2, pp. 288–301.
- Christenson, B. (2000). "Geochemistry of fluids associated with the 1995–1996 eruption of Mt. Ruapehu, New Zealand: signatures and processes in the magmatic-hydrothermal system". Journal of Volcanology and Geothermal Research 97.1, pp. 1–30.
- Delmelle, P. and A Bernard (2000). "Downstream composition changes of acidic volcanic waters discharged into the Banyupahit stream, Ijen caldera, Indonesia". Journal of volcanology and geothermal research 97.1, pp. 55–75.

- Delmelle, P. and A. Bernard (1994). "Geochemistry, mineralogy, and chemical modeling of the acid crater lake of Kawah Ijen Volcano, Indonesia". *Geochimica et cosmochimica acta* 58.11, pp. 2445–2460.
- Farkaš, J., F. Böhm, K. Wallmann, J. Blenkinsop, A. Eisenhauer, R. Van Geldern, A. Munnecke, S. Voigt, and J. Veizer (2007). "Calcium isotope record of Phanerozoic oceans: Implications for chemical evolution of seawater and its causative mechanisms". *Geochimica et Cosmochimica Acta* 71.21, pp. 5117–5134.
- Gendrin, A., N. Mangold, J.-P. Bibring, Y. Langevin, B. Gondet, F. Poulet, G. Bonello, C. Quantin, J. Mustard, R. Arvidson, et al. (2005). "Sulfates in Martian layered terrains: the OMEGA/Mars Express view". Science 307.5715, pp. 1587–1591.
- Hagemann, S. G., M. Gebre-Mariam, and D. I. Groves (1994). "Surface-water influx in shallow-level Archean lode-gold deposits in Western, Australia". *Geology* 22.12, pp. 1067– 1070.
- Hardie, L. A. (1996). "Secular variation in seawater chemistry: An explanation for the coupled secular variation in the mineralogies of marine limestones and potash evaporites over the past 600 my". Geology 24.3, pp. 279–283.
- Hardie, L. A. and H. P. Eugster (1980). "Evaporation of seawater: calculated mineral sequences". Science 208.4443, pp. 498–500.
- Hinsberg, V. van, K. Berlo, M. van Bergen, and A. Williams-Jones (2010a). "Extreme alteration by hyperacidic brines at Kawah Ijen volcano, East Java, Indonesia: I. Textural and mineralogical imprint". Journal of Volcanology and geothermal Research 198.1, pp. 253– 263.
- Hinsberg, V. van, K. Berlo, S. Sumarti, M. Van Bergen, and A. Williams-Jones (2010b).
 "Extreme alteration by hyperacidic brines at Kawah Ijen volcano, East Java, Indonesia: II: Metasomatic imprint and element fluxes". Journal of Volcanology and Geothermal Research 196.3, pp. 169–184.

- Kawano, M. and K. Tomita (2001). "Geochemical modeling of bacterially induced mineralization of schwertmannite and jarosite in sulfuric acid spring water". American Mineralogist 86.10, pp. 1156–1165.
- Kemmerling, G. (1921). De geologie en geomorpologie van den Idjen en analyse van merkwaardige watersoorten op het Idjen hoogland.
- Kendall, C. G. S. C. and W. Schlager (1981). "Carbonates and relative changes in sea level". Marine Geology 44.1, pp. 181–212.
- Li, J., T. K. Lowenstein, and I. R. Blackburn (1997). "Responses of evaporite mineralogy to inflow water sources and climate during the past 100 ky in Death Valley, California". *Geological Society of America Bulletin* 109.10, pp. 1361–1371.
- Madden, M. E., R. Bodnar, and J. Rimstidt (2004). "Jarosite as an indicator of water-limited chemical weathering on Mars". *Nature* 431.7010, pp. 821–823.
- Martinez, M, E Fernández, J Valdés, V Barboza, R Van der Laat, E Duarte, E Malavassi, L Sandoval, J Barquero, and T Marino (2000). "Chemical evolution and volcanic activity of the active crater lake of Poás volcano, Costa Rica, 1993–1997". Journal of Volcanology and Geothermal Research 97.1, pp. 127–141.
- McLennan, S., J. Bell, W. Calvin, P. Christensen, B. Clark, P. De Souza, J Farmer, W. Farrand, D. Fike, R. Gellert, et al. (2005). "Provenance and diagenesis of the evaporite-bearing Burns formation, Meridiani Planum, Mars". *Earth and Planetary Science Letters* 240.1, pp. 95–121.
- Migdisov, A. A., A. Y. Bychkov, A. Williams-Jones, and V. van Hinsberg (2014). "A predictive model for the transport of copper by HCl-bearing water vapour in ore-forming magmatic-hydrothermal systems: Implications for copper porphyry ore formation". *Geochimica et Cosmochimica Acta* 129, pp. 33–53.
- Nordstrom, D. K., C. N. Alpers, C. J. Ptacek, and D. W. Blowes (2000). "Negative pH and extremely acidic mine waters from Iron Mountain, California". *Environmental Science & Gamp; Technology* 34.2, pp. 254–258.

- Palmer, S. C. (2009). "Hydrogeochemistry of the upper Banyu Pahit River valley, Kawah Ijen volcano, Indonesia". MA thesis. McGill University.
- Rowe, G. L., S. L. Brantley, J. F. Fernandez, and A. Borgia (1995). "The chemical and hydrologic structure of Poa's Volcano, Costa Rica". Journal of Volcanology and Geothermal Research 64.3, pp. 233–267.
- Sellwood, B. and G. Price (1994). "Sedimentary facies as indicators of Mesozoic palaeoclimate". In: *Palaeoclimates and their modelling*. Springer, pp. 17–25.
- Stoiber, R. E. and W. I. Rose (1974). "Fumarole incrustations at active Central American volcanoes". Geochimica et Cosmochimica Acta 38.4, pp. 495–516.
- Tosca, N. J. and S. M. McLennan (2006). "Chemical divides and evaporite assemblages on Mars". Earth and Planetary Science Letters 241.1, pp. 21–31.
- Tosca, N. J., A. H. Knoll, and S. M. McLennan (2008). "Water activity and the challenge for life on early Mars". *Science* 320.5880, pp. 1204–1207.
- Varekamp, J., A. Ouimette, S. Herman, K. Flynn, A Bermudez, and D Delpino (2009). "Naturally acid waters from Copahue volcano, Argentina". Applied Geochemistry 24.2, pp. 208–220.
- Warren, J. K. (2010). "Evaporites through time: Tectonic, climatic and eustatic controls in marine and nonmarine deposits". *Earth-Science Reviews* 98.3, pp. 217–268.
- Williams-Jones, A. and A. Migdisov (2014). "Experimental Constraints on the Transport and Deposition of Metals in Ore-Forming Hydrothermal Systems".
- Zimbelman, D., R. O. Rye, and G. Breit (2005). "Origin of secondary sulfate minerals on active andesitic stratovolcanoes". *Chemical Geology* 215.1, pp. 37–60.

Contribution of Authors

This thesis consists of two co-authored manuscripts of which I am the first author. In all aspects of the research presented here, as well as in the writing, I took the lead. I sampled the gypsum stalactite and conducted fieldwork sampling at Kawah Ijen in 2014 to obtain the gypsum-cemented fall deposit, performed the trace element analyses, ²¹⁰Pb dating, and performed the chemical preparation and dehydration to obtain the crystalline water from gypsum. All data processing and interpretation was conducted principally by me. I have made substantial contributions to all papers included in the thesis and have written both manuscripts, and I wrote and compiled the thesis. My advisor Vincent van Hinsberg proposed the thesis project and collected the gypsum stalactite in a pilot study at Kawah Ijen volcano in 2009. He also contributed to all aspects of the thesis research, including providing training in analytical techniques, advising in sample analyses and experimental design, training in data analysis, and he provided critical feedback on writing. My coadvisor Bassam Ghaleb contributed by providing training in ²¹⁰Pb dating, data analysis, and provided critical feedback during the course of this project and writing in manuscript 1. My co-author on my first manuscript, Daniele Pinti and his research associate Arisai Valadez contributed by helping me analyze my growth zones for noble gases and advised during data interpretation. Jean-François Hélie from Université de Québec à Montréal and William Mark from the University of Waterloo analyzed my samples for δ^{18} O composition after I prepared the samples.

Chapter 2

Manuscript 1

Growth-zoned gypsum stalactite provides a 50-year record of volcanic activity at Kawah Ijen volcano, Indonesia

S.B. Utami^{1*}, V.J. van Hinsberg¹, B. Ghaleb², D. L. Pinti²

 Dpt. of Earth and Planetary Sciences, McGill University 3450 Rue University Montreal, Québec, Canada H3A 0E8

GEOTOP-UQAM
 Université de Québec à Montréal
 8888 Succ. Centre-Ville
 Montreal, Québec, Canada, H3C 3P8

* Corresponding author: sri.budhi.utami@gmail.com

June 2015

2.1 Abstract

Analysis of trace element and noble gas composition and ²¹⁰Pb activity from consecutive growth zones in a gypsum stalactite are used to construct a historical record of crater lake chemistry spanning 52 years at Kawah Ijen volcano in Indonesia. Rock-forming elements, including the rare earth elements and Mg originating from dissolution of crater wall rocks show trends that are consistent with seasonal variations and increased rock input from landslides. Transition elements such as Zn and Pb show trends that are most consistent with trends observed in the rock-forming elements, suggesting that these are derived mostly from rock dissolution. However, they show peaks during periods of reported unrest, indicating that input from magma degassing is also important. The volatile metals track magmatic degassing input with Tl and Sb recording variations in input from a shallow dacitic magma reservoir, whereas Cu is controlled by input from a deep-seated sulfide-saturated mafic magma. Peaks in the volatile metals occur around the same time as increases in seismicity, and are followed by sharp increases in lake temperature and tremor. Based on these findings, the volatile metals are prime candidates to monitor volcanic unrest at Kawah Ijen. Comparison of 1817 gypsum with the compositions reconstructed for 1964-2006, shows similar rock-forming and transition element contents, but markedly different volatile metal concentrations. The 1817 gypsum has the lowest Tl/Cu value and the highest Cu/Rb value compared to the gypsum stalactite. In combination with evidence of magma mingling in the 1817 pumice bombs, we therefore interpret the 1817 phreatomagmatic eruption as driven by mafic magma recharge.

Keywords: gypsum, trace elements, noble gas, U-series geochemistry, volcanic lakes

2.2 Introduction

Volcanic lakes are naturally occurring lakes that form inside depressions and craters of active and inactive volcanoes, and can be divided into two broad categories based on their

geochemistry. Marini et al. (2003) experimentally determined that compositions of volcanic lakes naturally tend to two distinct pH ranges. The first type of lakes are circumneutral lakes (pH 6-6.5) that may be dominated by meteoric water input, or are buffered by dissolved CO_2 and HCO_3^- ions. The second type of lakes are hyper-acidic lakes (pH j2) buffered by HCl and HSO_4^- ions that cap active volcanoes, and are considered to be the surface expressions of magmatic-hydrothermal systems. Circumneutral lakes are formed either by rainwater input following caldera forming eruptions infilling the caldera with water, such as in lake Toba (Indonesia) and Crater Lake (USA) (Chesner 2012; Nelson et al. 1994), or in combination with meteoric water input seeping through permeable sediments along with magmatic CO_2 gas, such as Lake Nyos and Monoun (Cameroon)(Kling et al. 1987; Tassi and Rouwet 2014). Hyper-acidic lakes on the other hand are lakes capping active volcanoes directly receiving elemental load from volcanic emissions that in turn originates from the underlying magmatic-hydrothermal system. The crater lake water comprises a concentrated aqueous solution with a low pH, composed of a wide variety of cations (e.g. Mg²⁺, Hg²⁺, Zn^{2+}) and anions (Cl⁻, F⁻, SO₄²⁻) that leads to high ionic strength conditions. The chemical composition of many hot volcanic lakes reflects the interaction of inputs including rock alteration supplying cations; magmatic gases supplying anions; and ground- and rainwater as the aqueous medium (Delmelle et al. 2000; Hinsberg et al. 2010a,b; Reed 1997; Varekamp and Kreulen 2000).

Both circumneutral and hyperacidic volcanic lakes have the potential to generate several types of volcanic hazards that pose significant risks to human life. Catastrophic hazards generated from circumneutral volcanic lakes in historical times are exemplified by the Lake Monoun and Nyos (Cameroon) disasters in 1984 and 1986, respectively (Kling et al. 1987; Sigurdsson et al. 1987). Limnic eruptions occur in stratified circumneutral volcanic lakes when these lakes harbour a deep-seated dense supersaturated gas-rich layer that has the potential to overturn in the event of a disturbance applied to this layer, such as landslides

and heavy precipitation (Kling et al. 1987; Kusakabe et al. 1989; Sigurdsson et al. 1987; Tassi and Rouwet 2014). Exsolution of gases following the overturning event allows the gases to ascend and disperse quickly to the surroundings, causing death by asphyxiation. In the case of Lake Nyos, the deep-seated layer is rich in magmatic CO_2 gas, and the limnic eruption overturned the CO_2 -rich layers, exsolving up to 1 km³ of CO_2 gas, leading to the demise of nearly all inhabitants of the nearby Nyos village (Kusakabe et al. 1989). Hyper-acidic volcanic lakes often cap craters of active volcanoes, and it is the presence of the lake that can amplify the hazards associated with volcanic eruptions. These include explosive phreatic and phreatomagmatic eruptions as the volcano erupts through the lake and associated hazards such as surtseyan jets and base surges, as observed in eruptions of Mount Ruapehu (New Zealand) and Taal volcano (the Philippines) (Kilgour et al. 2010; Manville 2015; Mastin and Witter 2000; Waters and Fisher 1971). Moreover, the involvement of hyper-acidic highly concentrated lake waters can also generate hazards such as mudflows, lahars and ash falls that deposited away from the volcano contaminating agricultural soil and water with elevated levels of toxic elements such as fluoride ions (Cronin et al. 1997, 2003). As well, eruptions can generate flows such as lahars and floods that, when channeled into valleys, can destroy settlements in the way of their flow or travel large distances (Mulyana and Effendi 2006). In addition, volcanic crater lakes can act as sources of natural pollution even when not in eruption. Seepage of crater lake brine occurs in volcanic lakes such as Póas and Rincón de la Vieja (Costa Rica) and Kawah Ijen (Indonesia), where element-laden brines feeds into springs around the volcano flanks, which may end up being used for irrigation, human and animal consumption or feed into large river systems (Palmer et al. 2011; Rouwet et al. 2008; Rowe et al. 1992). Given that the brine contains elements toxic to humans and other living organisms, harmful side-effects have been observed including fluorosis of bones and teeth and accumulation of elevated levels of these elements as observed at Ruapehu after its 1995 eruption, Ambrym volcano (Vanuatu), Iceland and Kawah Ijen volcanoes (Cronin and Sharp 2002; Cronin et al. 1998; D'Alessandro 2006; Löhr et al. 2005; Löhr et al. 2007; RotterdamLos et al. 2008). With an increase in population density in settlements near hyper-acidic volcanic lakes, more humans are now in close proximity of toxic emissions from volcanic lakes, or are situated in settlements in pathways of potentially lethal hazards from volcanic lake eruptions. Therefore, monitoring and hazard mitigation of volcanic lakes is important in order to identify signs of volcanic unrest and provide early warnings in the event that the unrest escalates into an eruption, as well as investigating the effect of volcanic lakes and volcanic outgassing on the biosphere. Hence the focus of this study is on the hyper-acidic volcanic lakes.

Volcanic crater lakes display various signs of unrest, in addition to direct observations, and these can be monitored for changes in the system's behaviour. Increasing volcanic tremors, volcano-tectonic earthquakes, changes in lake temperatures, level, colour and chemistry have all been indicated as signals of impending eruptions, and these may appear in days to months prior to the start of unrest or reported eruptions (Bryan and Sherburn 1999; Caudron et al. 2015a; Christenson 2000; Martinez et al. 2000). However, each volcanic lake system is different and no universal indicators for unrest have been identified. Effective monitoring requires a continuous and detailed monitoring record as possible using a variety of techniques. In addition to monitoring geophysical parameters such as seismicity and ground deformation, monitoring lake chemistry has become one of the most effective monitoring techniques for volcanic lakes (Martinez et al. 2000; Rouwet et al. 2014; Takano et al. 2004). Measuring specific elements and chemical species in the lake water can provide geochemical proxies for volcanic processes, for instance by measuring changes in polythionate concentrations as proxies for SO_2 and H_2 gas input from subaqueous fumaroles (Martinez et al. 2000; Takano et al. 2004). Volcanic lakes continuously receive direct input from the degassing magma, and the degassing magma brings with it elements that vary with magmatic degassing and thus are sensitive to changes in the magma body, for example mafic magmatic recharge that can trigger an eruption (Kent et al. 2010; Tepley et al. 2000). Only a minor proportion of volcanic lakes is systematically monitored; many are unfortunately not being monitored at all or have only been monitored in isolated campaigns, often after the volcano showed signs of increasing activity. These limited, and potentially biased, time-series do not allow for background quiescent activity levels to be properly defined. Nor are they likely to allow for identification of the early signals of pending unrest or eruption. Therefore, the main challenge when starting a monitoring program is the lack of a continuous historical record. Without it, the background variability is unknown and hence the probability of false positives is high, whereas the probability of recognizing early warning signs is low. This is commonly regarded as an insurmountable problem, given that the parameters and fluids needed to build such a historical record are no longer available for either measuring or sampling. In this study we therefore turn to the rock and mineral assemblages records, which are preserved, to provide this missing information. In particular, we explore the use of gypsum precipitates at Kawah Ijen volcano in Indonesia.

Gypsum has not only been continuously precipitating from springs fed directly by the seepage brine from the crater lake capping Kawah Ijen volcano for at least 200 years (Caudron et al. 2015a; Palmer 2009), it has also been shown to precipitate in equilibrium with its fluids (Hinsberg et al. 2008), thereby acting as an accurate proxy for past lake brine composition. As a result gypsum has the potential to provide a continuous record of lake chemistry for Kawah Ijen volcano. In this contribution, we show that a growth zoned gypsum stalactite precipitated from crater lake seepage at Kawah Ijen volcano provides this historical record and when complemented with seismic and thermal records, allows us to define natural background variability in composition and identify compositional signals of pending unrest.

2.3 Kawah Ijen volcano

Kawah Ijen is an active basaltic to dacitic stratovolcano located on the eastern end of the island of Java, Indonesia (Figure 2.1a), and is part of the Sunda-Banda arc (Handley et al. 2007; Hinsberg et al. 2010a,b; Kemmerling 1921; Sitorus 1990). It is the only currently active volcano within the Ijen Volcanic Complex (IVC) (Figure 2.1b), which occupies the caldera of the original Ijen stratovolcano that collapsed during the Pleistocene (Kemmerling 1921; Sitorus 1990). Kawah Ijen is capped by the world's largest natural hyper-acidic crater lake; the current lake formed after the 1817 eruption that expelled the previous lake entirely, and now comprises approximately 27.5 million m^3 pH <0.3 SO₄-Cl rich brine with an elemental load of ≥ 100 g kg⁻¹ (Caudron et al. 2015a; Delmelle and Bernard 1994; Takano et al. 2004). The surface of the lake measures approximately 1000 m \times 800 m, with a depth of up to 200 m, forming a steep-sided basin (Caudron et al. 2015a; Takano et al. 2004). The composition of the lake appears to be homogeneous with depth (Takano et al. 2004), except for seasonal dilution by rainwater (Delmelle et al. 2000; Varekamp and Kreulen 2000). It is bounded on the sides by completely altered magmatic deposits and lake sediments, and likely contains a liquid sulphur pool at depth, as evidenced by the presence of slicks of sulfur and sulfide rich spherules floating on the lake surface (Delmelle et al. 2000; Takano et al. 2004). Thermodynamic calculations of lake brine composition predict the brine is saturated in native sulfur, α -cristobalite, barite, anglesite, celestite, gypsum and amorphous silica (Delmelle and Bernard 1994). The lake and its composition is the product of a dynamic system with several input and output fluxes that can be compositionally characterized (Figure 2.2a), which vary seasonally and most importantly, with volcanic activity (Figure 2.2b). Water-rock interaction and magmatic gases comprise the main elemental inputs into the lake, whereas rain- and groundwater constitutes the main water inputs into the lake (Hinsberg et al. 2010a,b; Van Hinsberg et al. 2015). Volatiles from the underlying magma contribute anions into the lake and this flux produces the extremely low pH of the lake water (Delmelle and Bernard 1994). Berlo et al. (2014) showed that the degassing magma bodies also contribute metals, in particular Cu and Zn from a deep-seated basaltic magma and volatile metals (such as Tl and Sb) from a shallow dacitic magma body (see also Figure 2.7). Dissolution of rocks falling and sliding into the lake and landslides due to the weakening of steeply dipping crater walls contribute rock-forming elements e.g. Na, K, Fe and Mg (Hinsberg et al. 2010b) (Figure 2.7). Elemental output fluxes from the lake include evaporation, seepage and mineral precipitation. Three sets of seepage springs are present at increasing distance from the lake, with the furthest one having the largest discharge (Palmer 2009). However, only the first springs are dominantly lake seepage (95% lake water diluted with 5% meteoric water), while the other springs tap into the underlying hydrothermal system (Palmer 2009). These springs make up the headwaters of the Banyu Pahit river, which flows out from the caldera through a canyon onto the northern plains of East Java (Palmer et al. 2011). Cooling and evaporation drives the precipitation of evaporite minerals at the seepage springs and is dominated by gypsum with some Al-sulfates present as the late stage precipitated minerals at the spring outlets.

2.4 Gypsum at Kawah Ijen

The largest gypsum deposits are found around the first seepage springs closest to the lake, where they form a cascading gypsum plateau 50 m wide and 100 m long (see Figure 2.3a). Aside from gypsum, minor Al-sulfates including potassium alum and tamarugite are present just above the waterlevel.

Gypsum precipitates as *in situ* surface growths on its substrate, which was initially the valley floor, forming cascading gypsum covered terraces. At present new gypsum crystals precipitate mainly on top of these pre-existing gypsum terraces. This leads to continuous, slow, growth of the gypsum plateau, both upward and outward. More rapid growth is observed as stalactites of gypsum present on slopes and overhangs of the gypsum plateau (Figure 2.3b). Continuous flow of a thin layer of brine on the surface, evaporation and competi-

tion for open space during crystal growth promotes the formation of a variety of crystalline framework fabric texture (Spencer 2000). Common textures observed are elongated bladed gypsum crystals with varying lengths (up to 3 cm for new growths) and thickness (up to 6 cm), forming laterally continuous beds of syntaxial growths of gypsum growing upwards from the substrate as described by Spencer (2000). These regular layered gypsum deposits are interbedded with sediment and mud layers, indicating periods where sediments were washed onto the plateau. Stalactite growth commences with transparent bladed gypsum crystals growing outwards from a substrate, mostly on the gypsum plateau. Where actively growing, these are covered with a thin coating of brine. If the brine continues to coat the gypsum blade and flow, the blade provides additional substrate for smaller surface growth of gypsum crystals, whereupon progressive syntaxial growth produces a stalactite with a zoned cross-section which provides a time record of growth. Gypsum has also been found as cement in phreatomagnatic deposits downstream of the dam (Figure 2.5), where it is present as clear subhedral to euhedral crystals in a layered fall deposit that is overlain by a pumiceous layer. We interpret this sequence as deposited in the 1817 eruption of Kawah Ijen, likely as a pumice fall into acidic crater lake effluent.

2.5 Existing Record of Volcanic Activity at Kawah Ijen

Prior to discussing the existing record of volcanic activity, we shall define the terminology used to describe the different states of volcanic activity at Kawah Ijen. Volcanic activity is hereby defined as activity at an active volcano that occurs during periods of both quiescence and unrest, where the activity may be expressed in various measurable parameters such as as seismicity, volcanic emissions, and in the case of volcanic lakes, lake temperature and chemistry. If a volcano is in a state of quiescence, then that volcano may still exhibit volcanic activity, but the activity falls within the range of background variability. This variability can be quantified by calculating a background envelope for a given parameter measured from the volcano that is based on existing records, for example tremors, lake chemistry or fumarolic emissions. When a volcano is in a state of unrest, then the activity exceeds the range of background variability. States of unrest in the parameter being measured can vary from one period to another in both magnitude and its physical manifestations, such as enhanced funarolic emissions and phreatic explosions, but as long as the variations falls outside of the background envelope then the volcano is classified as being in a period of unrest. Arguably the most important state is when a volcano is during eruption, and this definition is dependent on individual volcanoes based on their eruptive histories. For Kawah Ijen, eruptions in the past involved ejection of solid juvenile magmatic material out of the immediate crater area. Moreover, we can then classify whether the occurrence is an event or an episode based on the period of time that the volcano is in a given state. An event is defined as a short, self-contained and distinct occurrence when the volcano experiences a sudden change in activity but returns quickly back to its background level of activity. On the other hand, an episode or a period is defined as an occurrence when the volcano experiences a change in activity that exceeds background variations for an extended length of time. In the context of this study due to the inherent time lag in the lake chemistry record, which is in turn built into the gypsum record, only episodes of unrest are recorded.

Field studies at Kawah Ijen yield several types of deposits corresponding to three main modes of volcanic activity (Hinsberg et al. 2010a,b; Kemmerling 1921; Sitorus 1990). The main mode of volcanic activity in the immediate vicinity of the crater lake corresponds to the cone-building phase of the volcano, characterized by a series of inter-bedded lava flows, scoria, and lapilli and ash deposits covered by a layer of sulphur-bearing mud from recent phreatic activity. These deposits can be observed on the exposed crater wall surrounding the lake and vary in thicknesses and degree of alteration, gently sloping away from the summit following the underlying topography. Moreover, large basaltic to andesitic lava flows, similar in composition to that of the lava flows near the volcanic edifice, are exposed on the flanks of the volcano where they flowed towards Gunung Blau volcano and channeled into the eastern flanks of the Ijen caldera (Figure 2.1c). The final mode of volcanic activity comprises a series of hydrothermal, phreatic and phreatomagmatic deposits suggestive of interaction between magma and lake water. The hydrothermal and phreatic eruptions are composed of altered material, native sulphur, ash fall deposits interbedded with charcoal-rich soil. Additionally magmatic ballistics, such as blocks and bombs, are found interspersed in the deposits or overlie them. Phreatomagmatic deposits, composed of fine-grained ash to lapilli sized deposits and block-and-ash deposits, are also found on the western flanks of the volcano in the Banyu Pahit river valley. These deposits are interbedded with deposits similar to that of the cone-building phase along with mud- and pyroclastic flows. Stratigraphic relationships between the three modes of volcanic activity indicate that the cone-building phase appears first, followed by alternating extrusion of lava flows and the deposition on phreatomagmatic material. Secondary deposits such as lahars and mudflows have been found around the flanks of the volcano. The presence of these deposit indicates that the volcano has had several significant explosive and potentially lethal eruptions in its geological history, with a combination of extrusion of juvenile magmatic material, phreatic/phreatomagmatic eruptions and generation of secondary hazards such as lahars and mudflows.

Historical records of Kawah Ijen volcano date back to the end of the 18^{th} century, although they have only become continuous in the late 20^{th} and early 21^{th} century. Activity during this period mostly ranged from increased seismicity, tremors and changes in lake colour to phreatic events and one phreatomagmatic eruption in 1817. Caudron et al. (2015a) compiled an up-to-date and comprehensive overview of volcanic activity at Kawah Ijen. Reports by Tour (1811) dating back to the early 18^{th} century indicate that Kawah Ijen crater lake was smaller than the present lake, bordered to the east by a plateau with fumaroles 8-10 m above the lake level. The level of activity appears to have been similar to that at the present time. The crater wall was steepest to the north, and gently sloping everywhere else. The lake flowed out through a gap in the western crater rim, and fed directly into the hyper-acidic Banyu Pahit river. Gypsum deposits were present along this outflow.

In 1817, this lake was thrown out in a phreato-magmatic eruption, which is the only known historic eruption of juvenile material at Kawah Ijen. Junghuhn (1853) and Bosch (1858), based on witness accounts and reports, wrote that the period of volcanic activity began with earthquakes and the formation of an eruption column that distributed ash as far away as the city of Banyuwangi and causing trees and huts to collapse. Additionally, the first eruption pulse generated cold lahars, flowing down the outer flanks of the volcano before being channelized in three directions: north through the Banyu Pahit-Banyu Putih valley; east to the city of Banyuwangi and depositing onto plains south of the then settlement; and northeast to the sea south of the Baluran Volcanic Complex 30 km away from Kawah Ijen (Figure 2.1b). After a short period of repose lasting 16 days, despite the sustained presence of the eruption column, a second eruption pulse triggered further ashfall followed by several mudflows, abetted by heavy rain. The mudflows deposited toxic sulphur-laden mud and debris on plains, rendering the soils unsuitable for growing crops and the water undrinkable. No human fatalities were reported owing to the low population density at the time. The morphology of the crater lake changed significantly. The crater deepened and the lake size increased together with a steepening of the eastern crater rim, and direct outflow from the lake was cut off. Seepage together with occasional spillover became the headwaters of the Banyu Pahit river.

During the 20^{th} century, activity at Kawah Ijen was characterized by predominantly phreatic events and accompanied periods of unrest between 1917 to 1940, with a phreatic eruption in 1917 that damaged a dam in the western crater wall constructed to regulate the overflow of acidic brine from the lake. The periods of unrest were characterized by significant and often sharp fluctuations in lake temperature accompanied by vigorous gas upwelling on the lake surface; fluctuations in lake levels; shift in lake colour from blue-green to milky white; water fountains up to 10 m high and vapour clouds visible on the surface. A possible trigger for the phreatic eruption in 1917 was the earthquake on the nearby island of Bali prior to the phreatic event (Kemmerling 1921), which might have destabilized the hydrothermal system, thus inducing the observed unrest and seismically triggering the phreatic event (cf.Manga and Brodsky 2006). Unrest at Kawah Ijen in the 1990s is better documented and consisted of intermittent bursts of tremors, gas bubbling, temperature fluctuations, and changes in lake colour, with minor blasts reported. In 1993-1994, phreatic eruptions occurred with increasing energy after a period of unrest involving a series of volcano-tectonic events, although their deposits were still confined to the crater area. Unrest re-commenced in 1997 with increased funarolic activity, sustained seismic tremors and changes in lake colour. In 1999, heightened seismicity typefied by 'VB'-type volcano-tectonic earthquakes and tremors were accompanied with explosions and enhanced fumarolic emissions; such unrest continued until 2004. The most recent unrest occurred in 2011 to 2014, with sharp fluctuations in temperature by as much as 17 °C and increased seismicity above background values. This latest unrest led to the establishment of a permanent monitoring network for lake level, lake temperature and seismicity (Caudron et al. 2015a), and this work is part of an effort to extend this network to continuous lake composition monitoring (cf. Gunawan et al. 2015).

2.6 Methodology

Gypsum stalactites were sampled on the gypsum plateau (Figure 2.3a) during the August 2009 dry season by cutting them at the base. These included both actively growing and "extinct" stalactites (Figure 2.3b). The former were white and commonly had a clear, often widening upwards bladed crystal with euhedral prismatic terminations, whereas the latter were grey and more rounded. These stalactites were sectioned perpendicular to their long axis to reveal their growth zoning. The gypsum stalactite (KV09-505) analyzed in this study was one of the largest actively growing stalactites in the sample suite and was selected for both

its long and continuous cross-sectional growth history, as well as having growth zones wide enough for sampling. In addition, gypsum grains were sampled from the gypsum-cemented pumice fall attributed to the 1817 eruption. The base of the gypsum stalactite was set in urethane resin, and cut into three sections of around 1 cm thickness each. A polished section of disc was explored by back-scattered electron imaging and EDS compositional analysis on a JEOL 8900 Superprobe. The selected stalactite was shown to be composed of gypsum with some (Na,K)-Al-sulfates on outer surfaces and minor interstitial syngenite. Gypsum powder was sampled *in situ* from each growth zone for ²¹⁰Pb radiometric measurements and noble gas analyses. The opposite side of the disc was polished and analysed for trace elements.

2.6.1 ²¹⁰Pb analyses

²¹⁰Pb activity was determined by alpha spectrometry of the daughter product of ²¹⁰Pb decay, ²¹⁰Po (e.g. Ghaleb 2009). 0.1g of ²⁰⁹Po tracer was dried at 85°C for 15 minutes until completely evaporated and added to 0.1g of clean, finely powdered gypsum. This mixture was dissolved in approximately 100 ml 0.5 M HCl solution at 90°C for 15 minutes while continuously stirring. HCl was chosen as it dissolves gypsum readily, but cannot digest potential silicate or oxide inclusions. No residue was however observed indicating that the gypsum samples were clean. A silver disc was lowered into the solution, and the mixture was stirred overnight for the sample and spike to plate onto the disc. The activity of ²¹⁰Po was measured by alpha spectrometry using an EGG-Ortec Type A576[™]alpha spectrometer for a period of 7-14 days until a minimum of 100 counts was reached.

2.6.2 Noble gases

Approximately 500 mg of each growth zone was put into a steel cylinder with a steel ball, pumped to a high vacuum (circa. 5×10^{-9} Pa)and purified overnight using Ti and St707 getters prior to analyses. The cylinder was subsequently gently agitated to crush the sample and release its noble gases with unspiked isotopic analyses of He, Ne, Kr, and Xe using a
Quadrupole mass spectrometer PRISMA from Pfeiffer-200. Calibrations were performed on in-house standard pipettes of purified air from Montréal (Pitre and Pinti 2010). Precision was determined using ³⁶Ar (average composition = 4.28×10^{-10} cm³ STP), and was better than 5 % for all samples. Noble gas fractions were normalized to the ³⁶Ar composition of air.

2.6.3 Trace elements

The trace element composition of a core-to-rim transect spanning the 4 main consecutive growth zones analyzed for ²¹⁰Pb and noble gases was measured using a NewWave 213 nm Nd-YAG laser coupled to a Thermo Finnigan iCAP-Qc quadrupole ICP-MS. This same setup was used to analyze gypsum cement grains from the 1817 fall deposit, which was mounted in a 1-inch block of resin and polished. The gypsum disc was triply polished and the transect was analyzed for a suite of 57 trace elements with Ca as the internal standard elements, and 60 elements for the gypsum cement. Laser operating conditions were a fluence of 3-7 J cm⁻², repetition rate of 10 Hz and ablation pit diameter of 120 μ m for the stalactite transect, and 80 μ m width and 1 mm length through for the grains in the 1817 deposit. Trace element data were processed using the Iolite software (Paton et al. 2011). Preliminary analysis with wt. % -levels of K, Na and/or Al were excluded, because these likely represent mixed analyses with Al-sulphates or syngenite inclusions. This resulted in removal of only 8 out of 89 transects spots. The relative standard deviation (RSD) for 'light' elements up to Cd is up to 0.62%, while for the remaining 'heavy' elements is up to 0.31% in the transect.

2.7 Results

A summary of the trace element concentrations are given in Table 2.1 for the gypsum stalactite, and Table 2.2 for the 1817 gypsum cement. Each element analyzed for this study has been selected to represent the reservoirs within the Kawah Ijen lake system. From these concentrations, elemental ratios are calculated from and grouped according to the source reservoirs during quiescence (Figure 2.2a) and unrest (Figure 2.2b).²¹⁰Pb activities are given in Table 2.3 and noble gases in Table 2.4.

2.8 Discussion

2.8.1 Gypsum Age

The gypsum stalactite displays concentric outward growth zoning from its core, indicating that it records a continuous time progression from core to rim. To obtain absolute ages for these growth zones, we determined their ²¹⁰Pb activity, based on the premise that ²¹⁰Pb activity would decrease with age as it decays with a half-life of 22.6 years assuming there is no in-growth of ²¹⁰Pb from the decay of its parent isotope ²²²Rn (Ghaleb 2009). Prior to calculating model ages of gypsum growth zones using ²¹⁰Pb disequilibrium, we must consider the validity of the assumption of constant initial concentration that is inherent within the decay equation. For the gypsum stalactite investigated in this study, the constant initial ²¹⁰Pb activity assumption cannot be valid because the flux of its parent isotope varies, resulting in ²¹⁰Pb activity that does not correlate with age as inferred from zone position (Table 2.3).

The main source of ²¹⁰Pb in the Kawah Ijen system is the volatile intermediary parent isotope ²²²Rn. Given that ²²²Rn is emitted from the degassing magma under active volcanoes (Condomines et al. 2010), and ²²²Rn decays to ²¹⁰Pb with a relatively short half-life of 3.8 days (Bourdon et al. 2003), variations in degassing and hence ²²²Rn flux will thus lead to variations in ²¹⁰Pb initial activity. Due to the short half-life of ²²²Rn and its fluctuating flux is dictated by the degassing rate from the underlying magma, ²¹⁰Pb activities measured do not decay from the same initial activities. The measured activities therefore need to be corrected for variations in the ²²²Rn flux. Given that the parent isotope of ²¹⁰Pb, ²²²Rn, is

a noble gas we propose a correction method for the fluctuating ²²²Rn flux using heavy and stable noble gas isotopes. In particular we use the heavy noble gases Kr and Xe. Kr and Xe concentrations show the same core-to-rim pattern as the ²¹⁰Pb activity (Figure 2.6a) which is a strong argument for a dominant control on ²¹⁰Pb activity by variations in ²²²Rn flux, in addition to age. Correction factors for variations in Rn flux were calculated from the average enrichment factor of ⁸⁴Kr and ¹³²Xe weighted to their respective analytical uncertainty. These were normalized to a ²¹⁰Pb activity with known age, which was determined by analyzing the ²¹⁰Pb activity of gypsum needles grown in 2008 at the tips of stalactites (these tips were broken off in 2007 and had regrown by 2008 -Hinsberg et al. (2008)). The corrected growth zone ages young systematically from core to rim and indicate that the stalactite records at least 37.6 $^{+16.9}_{-10.1}$ years of growth (Figure 2.6b). The age of the core could not be derived, as an accurate noble gas measurements could not be obtained. This core may either be significantly older, or may be similar due to rapid initial outward growth from the substrate. It is important to note that the non-linear progression of time in gypsum means the time resolution for the most recent year, for example 2006, is particularly high and progressively decreases with age; thus it is possible to observe long-term (6 months) and short-term (monthly) changes in the compositional record. The corrected model ages for gypsum were fitted to the gypsum trace element transect, and used to calculate the age of each transect ablation spot (Figure 2.6c).

2.8.2 Gypsum as an elemental recorder of fluid chemistry

Combining the absolute ages derived from noble gas-corrected ²¹⁰Pb activities with the composition of each growth zone allows for a continuous time-series of gypsum composition to be determined. Hinsberg et al. (2008) has shown from element partitioning systematics that gypsum grows in equilibrium with the seepage spring water, and the gypsum time-series therefore provides a record of the composition of these seepage waters. Given that the seepage waters at this location are made up of 95 % lake seepage with 5% dilution from groundwater (Palmer 2009), gypsum can be taken to record lake composition. The transect chosen for trace element analysis represents the longest uninterrupted growth cross-section from the stalactite, with no evidence of re-dissolution and re-precipitation textures that would otherwise concentrate compatible elements and re-dissolve the incompatible elements into the fluid phase. The variations in composition are interpreted in terms of the differences in compositional signature among the various sources in the crater lake system as defined in our Kawah Ijen model, outlined below.

2.8.2.1 The Kawah Ijen model

Due to the complexity of the variations in the gypsum stalactite record, interpretations of signals within the fluid chemistry must be made in the context of a model for Kawah Ijen volcano. In this study, a model of the magmatic-hydrothermal system of Kawah Ijen volcano has been constructed modified after the model proposed by Christenson (2000) for Ruapehu volcano and its lake (Figure 2.2a). Following findings by Hinsberg et al. (2010b) and Berlo et al. (2014), the elemental budget of the lake is derived from two main input fluxes: dissolution of the andesitic to dacitic rocks from surrounding flanks introduced through rock falls and flank failure, and input from a deep degassing mafic magma as well as a shallow, evolved dacitic magma. These elemental input fluxes are diluted seasonally by input of rainwater and to a limited extent, groundwater discharge from the adjacent Merapi volcano. The main output fluxes are evaporation of the brine from the lake surface, and mineral precipitation in and around the lake (Figure 2.2a). Of the output fluxes, evaporation and dilution are expected to only affect absolute concentrations, not element ratios, unless it leads to changes in the saturation state of precipitate minerals. The appearance or disappearance of a precipitate mineral will lead to a sharp change in the abundance of its constituent elements, whereas changes in volcanic gas or rock input are likely to show up as a more gradual change, because the lake is a very large element reservoir that buffers small changes, and thus is not easy to disturb.

In order to apply the model of Kawah Ijen to the record of fluid chemistry from gypsum, several assumptions must be made to enable us to interpret the geochemical signals from gypsum as representative of that of the fluid chemistry at the time of crystal growth. The first assumption for this model is that the lake composition is completely homogeneous at 40 m depth, which equates to the elevation of the springs relative to lake surface. This means fluctuations in elemental ratios from the gypsum growth zones reflect changes in the entire lake composition. Another assumption is that there is minimal lag time between the signal appearing in the lake composition and the signal being recorded in the gypsum growth zone composition. Takano et al. (2004) attempted to constrain the travel time from the lake to the springs using polythionates, and found that the travel time may be as long as 1000 days, although these authors point out that rate constants are not available for the Ijen water compositions and pH. Such a long travel time is difficult to reconcile with the short distance and the flow rate of 1 L s⁻¹, as measured by Palmer et al. (2011). Nonetheless, as the brine needs to seep through the flanks before flowing out at the springs, there is an inherent lag time built into the gypsum record. However, given that ²¹⁰Pb, used to measure the age of the gypsum, should be affected equally to the trace elements, this should cancel out any lag time. A third assumption is continuity of growth, which allows us to fit a smooth age model to the 4 age measurements that we obtained (Figure 2.6b). Whereas sediment horizons were observed in some stalactites, as well as in the gypsum plateau, which can be interpreted as breaks in growth, the stalactite investigated here does not contain these, and visually appears to show continuous growth.

2.8.2.2 Compositional time-series

The gypsum stalactite transect provides a 50-year record of lake water composition at a resolution from 1 to 6 months. It allows us to investigate both short-term behaviour and long-term trends of individual elemental concentration in the lake over time, and as shown in Figure 2.8. there are significant trends in the long-term behaviour of certain elements

in the lake. When examining the absolute concentration record, only long-term trends are examined, because short-term variations may be affected by processes other than changes in the source fluxes into the lake, the most significant of which is dilution. Dilution effects can be expected to average out over the long-term, making the large-scale trends robust.

Elements derived from rock-dissolution, such as Mg, Rb and the rare earth elements (REE) (Figure 2.7) show broadly similar fluctuations in concentrations, with significant peaks observed between 1980 to 2000, and an increase in overall concentration background levels between 1990 to 2000 (Figure 2.8a-2.8c). The gradual increase in background levels likely corresponds to increasing overall elemental load in the lake (cf. Van Hinsberg et al. 2015). In contrast, the volatile metals Cu (Figure 2.8d), Sb (Figure 2.8e), and Tl (Figure 2.8f) show their own set of peaks, which may correspond to increased input from the deep basaltic and shallow dacitic magma. Thallium is the most sensitive of the volatile metals to fluctuations and shows the most number of peaks. Interestingly, Cu and Sb show similar peaks, even though Cu is dominantly derived from sulfide breakdown in the deep basaltic magma and Sb comes from the shallow dacitic magma. This suggests that the peaks reflect an overall increase in gas input, rather than a change in gas source. The transition metal Zn (Figure 2.8g) shows a hybrid signal with peaks that correspond both to the rock dissolution input signal and volcanic degassing, reflecting its contribution from both sources (Figure 2.7). Lead (Figure 2.8h) shows a gradual increase to a maximum in 1985 followed by a consistent decrease thereafter, which is not obvious for any of the other elements and indicates a significant change in Pb input in the system. This source cannot be rock dissolution or degassing, because it is not recorded by rock-forming elements nor volatile metals.

Absolute concentrations of elements are influenced by seasonal dilution and evaporative concentration at the site of gypsum precipitation. To eliminate this effect, trace element concentrations have been divided by an element that behaves conservatively in the Kawah Ijen lake. Rubidium is suitable for this purpose because it does not form a precipitate mineral in the lake, and is not volatile during evaporation from the lake surface. Its concentration in the volcanic gas is negligible (cf. Van Hinsberg et al. 2015), it is a trace element in the rocks, and the Rb concentration in the lake is high enough that rock-dissolution will not easily disturb the Rb concentration. Eliminating the effect of variable dilution by dividing by Rb uncovers trends that more directly reflects variations in the input fluxes (Figure 2.9). It also removes the long-term trends in Pb.

The record presented by the gypsum transect consists of two components; background noise and peaks, which, in its application to volcanic monitoring can be regarded as noise and signal, respectively. Background noise is defined here as activity that corresponds to the volcano at its passively degassing state; any activity above or below this background activity is identified as corresponding to the volcano in a heightened state of activity or unrest. The background activity for each element or ratio is defined by a probability envelope. Where necessary, this probability envelope has a slope to accommodate long-term trends (e.g. Mg/Rb - Figure 2.9a). A 75 % probability interval was chosen, which means that 75% of data are assigned to background, as this appears to be a suitable interval for all elemental ratios; a higher interval would likely mask significant events, whereas a lower interval decreases the ability to discriminate between periods of passive degassing and unrest, and thereby lead to false positives in volcano monitoring. Conceptually, concentrations within the 75%probability envelope represent natural variability in background activity, or state of passive degassing at the volcano. Both peaks above and troughs below this background envelope are considered as periods of significantly increased elemental input from either rock dissolution or magmatic degassing, With the background established, we can identify peaks and correlate these with known periods of unrest, as well as with other records such as seismicity and lake temperature. This allows us to not only identify what elements track changes in volcanic activity, but also to determine the signals that indicate an impending eruptions at Kawah Ijen. In the following sections, the peaks observed for the various elements are discussed.

2.8.2.3 Rock dissolution flux

Leaching and dissolution of crater wall rocks is a major contributor of cations to the lake (Hinsberg et al. 2010b) (Figure 2.7). This material is mainly derived from rock falls from the steep walls bounding the crater lake, which are continuously weakened by acidic deposition from the fumaroles. Punctuated events also take place in the form of landslides, which can be spontaneous or triggered by rain thereby potentially having a seasonal occurrence, or tremors, which would link them to periods of unrest. The crater walls are composed of andesitic and dacitic rocks and contain the main minerals ortho- and clino- pyroxenes, plagioclase, titanomagnetite and olivine. As shown in Figure 2.7, the rock component dominates the flux of elements including Mg, Ca, and the rare earth elements (REE). These elements are therefore used to monitor variations in the rock-dissolution flux in the gypsum record. We will refer to this group of elements as the rock-forming elements in the following discussion.

The rock-forming elements show variation, but lack strong excursions in the Rb-normalized time-series. As a result, we attribute most variation to background noise resulting in a relatively large background envelope. The time-series shows a small, but significant positive slope in agreement with the 200-year increasing elemental load in the lake (Van Hinsberg et al. 2015). In more detail, the time-series shows seasonal variations with peaks in Mg/Rb and Σ REE/Rb corresponding to months in the dry season (May-September), and troughs occur during months in the rainy season (October-April). Troughs that fall outside the background envelope occur in December 1998 and January 2003, and going further back to the beginning of the gypsum record almost consistently fall in months when the rainy season peaked, although it is worth noting that the age uncertainty increases with time. The presence of seasonal effects despite the concentrations being ratioed to Rb indicates that Rb does not act as a perfectly conservative element. This is likely because gypsum incorporates high concentrations of Rb relative to the crater lake seepage (Van Hinsberg 2001). Therefore, during periods of enhanced evaporation and gypsum precipitation, such

as the dry season, there is preferential extraction of Rb from the seepage spring brine into gypsum, thereby lowering the concentrations in the brine. This effectively leads to a higher Mg/Rb peak during dry seasons. Conversely, the troughs observed in the rainy season are characterized in some years by stronger dilution at the deposition site.

The rock-forming element input flux varies by two mechanisms: rocks falling into the lake after being dislodged by volcanic tremors, and hence linked to variation in activity, or from gradual slope destabilization. Caudron et al. (2015b) have shown that during periods of unrest, for example in 2011-2012, volcano-tectonic (VT) earthquakes and tremor occur, which have the potential to dislodge rocks that fall into the lake and largely dissolve. A correlation between peaks in rock-forming elements and periods of unrest may therefore be observed. In contrast, peaks during periods of quiescence can be attributed directly to slope instability. Indeed, large land-slides have been observed at Kawah Ijen in 2014 during a period when no seismicity or increased tremor was recorded (Pers. comm. Corentin Caudron). Comparison of the Mg/Rb record with accounts of unrest in 1990-2006 yields a large peak above background that likely correspond to volcanic tremor-driven rock falls, for example in 2001-2002. However, there are many small peaks occuring in periods of quiescence, likely reflecting gradual slope destabilization. Both mechanisms thus appear to be active.

A first-order estimate of the rock flux can be obtained by comparing the bathymetry of the lake and its volume in 1922 with the lake volume at present, assuming that this change is exclusively due to sediment infill. Caudron et al. (2015a) showed that the lake volume decreased by a total of 16 million m³ since 1922. Using the density of silica sand (1522 kg m⁻³), the calculated mass of equivalent silica sand is 2.44×10^{10} kg. Hinsberg et al. (2010b) determined a 39% mass loss in complete leaching of fresh rock. Therefore, the sediment requires input of 6.24×10^{10} kg of fresh rock. Assuming that this is composed of andesite, with a density of 2660 kg m⁻³ (Johnson and Olhoeft 1984), the volume of material from rock slides and falls into the lake bottom is 2.35×10^7 m³ over this 89-year period. Finally, assuming that the crater has a circular cone shape, and the edifice recedes with the same amount along its radius, the slope has receded by as much as 25.4 m on all sides, equating roughly to a rate of 0.29 m yr⁻¹. Our assumptions mean that this is a maximum estimate, and the growing sulphur pool proposed to exist at the lake bottom (Delmelle and Bernard 1994)) is for example not accounted for. Moreover, slope recession will not be uniform around the crater, with comparison of historic topographic maps suggesting extensive recession of up to 60m of a triangular area jutting out from the southern crater wall. The recession value is high, but not unreasonable, indicating that a significant continuous rock flux is present and suggesting that the dominant control on the rock-forming elements is by landslides and slope failure.

2.8.2.4 Volatile metals

The second major contributor of elements to the lake is volcanic gases entering the lake via subaqueous fumaroles (see Figure 2.2a). These fumaroles supply the lake with SO_2 , H_2S , HF and HCl gases and volatile metals including Cu, Tl, and Sb (Berlo et al. 2014; Delmelle et al. 2000; Takano et al. 2004; Van Hinsberg et al. 2015) (Figure 2.7). Volatile elements originate from two different magma reservoirs underlying the crater lake: a deep-seated sulphide-saturated basaltic magma and a shallow dacitic magma (Berlo et al. 2014). Dacitic lava has been found to occur in a small dome on the lake shore, where the most intense fumarolic activity occurs (Hinsberg et al. 2010a). According to Berlo et al. (2014), the shallow dacitic magma is the primary source of the volatile metals Tl and Sb whereas based on the reconstruction of sulfide liquid from deep-sourced mafic melt inclusions, transition metals such Cu, Pb and Zn are sourced primarily from this deep mafic magma. The metal signature of the fumarole gases cannot be produced from one of these magma reservoirs, therefore concluding that interaction occurs when gases released from the basaltic magma pass through the shallow dacitic melt. This makes the volatile metals ideally suited to monitor Kawah Ijen because they track the magmatic degassing and hence magmatic activity, but they also allow us to differentiate between the deep mafic and shallow dacitic reservoirs. We will use Tl/Rb, Sb/Rb and Cu/Rb (Figure 2.9i-2.9h) for the former, and Tl/Cu (Figure 2.9e-2.9f) for the latter.

Figures 2.9i-2.9l show that both Rb-corrected Tl and Sb records have several peaks above the background envelope between 1960-2006 indicating increased input from the dacitic magma. In particular, peaks are observed for 1970-1985, as well as 1990, 1998 and 2000-2004. Comparison with the existing record of unrest as compiled by Caudron et al. (2015a) from 1990-2006 shows that Tl/Rb peaks occur prior to unrest. However, the uncertainty in the age does not preclude that they are contemporaneous or even postdate the unrest. The most recent and highest recorded peaks within this time frame are found prior to the 2001 and 2004 unrests. Sb (Figure 2.9k-2.9l) behaves broadly similar to Tl, meaning that the other volatile metals can be used to complement the record provided by Tl.

In order to determine whether there is input from the basaltic magma, we need to examine elements that are derived from the basaltic magma and behave similarly to the volatile metals. Berlo et al. (2014) showed that Cu is most suited for this. Copper (Figure 2.9g-2.9h)) behaves similarly to the volatile metals (Figure 2.7) rather than transition metals. Comparison of Cu/Rb and Tl/Rb shows that peaks in Tl/Rb appear to precede or are coeval with peaks in Cu/Rb above the background variations, such as the peaks observed in 2000-2002. There are also some peaks observed in Tl/Rb that do not correspond with a peak in Cu/Rb, such as the peak around 1998 that coincides with a drop in Cu/Rb that falls outside of the background variation. Similarly for the period of 2002-2003, the Tl/Rb and Sb/Rb are elevated but Cu/Rb shows background envelope. We can track the relative contribution of the deep and shallow magma in time using the Tl/Cu ratio (Figure 2.9e-2.9f). A peak in Tl/Cu indicates a relatively increased input from the shallow dacitic magma, whereas a trough suggests an increase in input from the deep-seated basaltic magma. This suggests variable input to the fumarole gas flux from the two magma reservoirs. This can be observed in 2000-2004, where there is a large drop in Tl/Cu followed by a sharp increase peaking around 2002-2003, suggesting that there is increased input from the deep-seated magma followed by increased input from the shallow magma. This sequence of signals may be explained by increased deep magmatic activity during the period of unrest, possibly magmatic intrusion or recharge, producing enhanced degassing and interaction with the overlying dacitic magma. These trends also indicate that there are instances of shallow magmatic input with no enhanced input from the deep-seated magma, as well as events where both are involved. There does not appear to be a correlation with style or severity of unrest, although no large events have taken place in the time period covered by our gypsum stalactite.

2.8.2.5 Transition metals

Transition metals are controlled by both input from rock-dissolution (Hinsberg et al. 2010b) and input from the deep, sulfide-saturated mafic magma (Berlo et al. 2014) (see also Figure 2.7). Comparison among Zn, Mg and Cu concentrations and ratios to Rb shows that Zn appears to be more consistent with Mg rather than Cu. As such, Zn is more influenced by mechanisms controlling rock dissolution, as well as seasonal variations in this record. There are also peaks in Zn/Rb that occur at the same time as Cu/Rb, such as in 2000-2002 indicating the degassing magma also exerts control on the overall Zn/Rb signal. We cannot as of yet constrain the relative contributions from rock dissolution and degassing magma, which makes Zn non-ideal as a monitoring element.

Pb concentrations increase steadily until around 1985 after which they decrease continuously, except for a large peak observed in the early 2000s (Figure 2.8h). This large-scale trend is partially removed when Pb is divided by Rb, after Pb/Rb (Figure 2.9o) largely follows $\Sigma REE/Rb$ (Figure 2.9c). Given that the REEs and Pb ratios behave similarly, rockdissolution exert the dominant control on Pb concentration. Some of the Pb/Rb peaks coincides also with peaks in the volatile metals, suggesting that the degassing magma Pb input is significant during certain periods of unrest. The long-term trend in Pb with the small peak around 1985 is not observed in any of the other elements, suggesting an additional, external source of Pb, which could be anthropogenic emissions. The trend is similar to the record of Indonesia's Pb emission from leaded gasoline, which although incomplete, shows a strong increase until around 1985 and a more gradual increase until 1995, followed by decreasing emissions until the present day (Lee et al. 2014). This trend in Pb concentration in the atmosphere may have been reached Kawah Ijen through long-range transport of aerosols, precipitation or wind (e.g. Lelieveld et al. (2001). Without additional information, for example from Pb isotopic composition, it is not yet possible to determine whether this is a possible contribution. An alternative explanation could be a change in the amount of barite precipitation from the lake, which is an important sink for Pb (Hinsberg et al. 2010b). However, this is not supported by the record of Ba concentrations.

2.8.2.6 Comparing chemical and physical indicators of unrest at Kawah Ijen

Limited monitoring data are available for Kawah Ijen in the form of seismicity, lake level and lake temperature (see Caudron et al. (2015a)). These records are by no means continuous and only rarely include a complete record prior, during and after unrest. Nonetheless, sharp fluctuations in lake level and an increase in lake temperature and seismicity have been noted prior and during episodes of unrest (Caudron et al. 2015a; Kemmerling 1921). Volcanotectonic seismicity at Kawah Ijen is subdivided into VA (earthquakes generated by brittle fracturing from a magmatic intrusion, movement of magma, or pressure from geothermal fluids) and VB (earthquakes generated from the passage of seismic waves traveling through the crust)(Caudron et al. 2015b; Scott 1989). Additionally, volcanic tremor is observed consisting of monochromatic and/or harmonic vibrations generated from the interaction of steam or gas with the shallow aquifer (Caudron et al. 2015a). Comparing the Tl/Rb and Cu/Rb record with the physical (seismicity and lake temperature) records shows moderate to good correspondence between peaks in the volatile metals (Figure 2.10a-2.10b) and sharp changes in temperature (Figure 2.10c), and elevated seismicity in both types of VT earthquakes (Figure 2.10d-2.10e) and tremors (Figure 2.10f). Best correspondence is observed for the biggest unrest events (e.g. those in 2003 and 2004). This is not surprising given that the large lake water reservoir requires a big change in input for it to be noticeable in the overall composition.

Compared to the seismic records, Tl/Rb peaks at the same time as the number of VA starts to rise, whereas peaks in Cu/Rb correspond to maximum tremor amplitudes, which peak during the reported events themselves. This is often accompanied by a significant increase in VB earthquakes (Figure 2.10e). Given that we have interpreted Cu to be dominantly derived from degassing of a deep basaltic magma whereas a shallow dacite contributes Tl, this meant that as input from the deep-seated magma increases we see a rise in temperature, and it is preceded by a rise in Tl input into the lake from the shallow magma. The agreement with seismic and lake temperature records, which are more established methods of volcano monitoring, shows that lake water composition tracks volcanic activity and can thus be used in monitoring Kawah Ijen. Moreover, the gypsum-reconstructed record of lake water composition extends much further back in time to before reliable and continuous seismic and temperature data are available.

2.8.2.7 Insights into the 1817 eruption from the gypsum record

The gypsum found in a 1817 fall deposit provides us with a unique opportunity to assess the state of the system prior to the phreatomagmatic eruption of 1817, when the volcano erupted and threw out the lake (Bosch 1858; Junghuhn 1853; Kemmerling 1921). The 1817 gypsum is similar in terms of elements derived from rock dissolution and the transition metals. The similarity in concentrations for these elements is in agreement with a total dissolved solute

content for the lake in 1805 which is the same as that at present (Van Hinsberg et al. 2015), and suggests that the lake composition had reached a similar steady state to that of the current lake. In contrast, the volatile metal contents are very different. In particular, Tl/Cu and Cu/Rb show the lowest and the highest recorded ratios respectively. The Cu/Rb exceeds background levels by over an order of magnitude, suggesting significantly increased input of volcanic gas compared to 1960-2006. Moreover, the Tl/Cu ratio is at least 1 magnitude lower than the lowest ratio from 1964-2006, indicating that the volcanic gas is dominated by input from the deep-seated basaltic magma. Strong involvement of the deep mafic magma may point to mafic magmatic recharge driving the eruption. Episodes of magmatic recharge and mixing between mafic and silicic magmas have been linked to the eruption of andesitic lava (Davidson and Tepley 1997; Kent et al. 2010), and this has been observed in eruptions in other volcanic lakes such as Ruapehu and El Chichón (Gamble et al. 1999; Tepley et al. 2000). Further support for such a scenario is the abundance of 1817 pumice fragments with mingling textures (K. Berlo, pers. comm.). The drastic difference in volatile metal concentrations, and hence degassing input, in 1817 indicates that the magmatic-hydrothermal system was in a different state prior to this large eruption. The peaks in the 1964-2006 record are much less pronounced and show that a state similar to 1817 was not encountered. We therefore interpret recent unrest as involving mainly the shallow magmatic reservoir, whereas large eruptions are triggered by involvement of the deep mafic magma.

2.9 Conclusion and implications

Growth-zoned gypsum precipitated from crater lake seepage yields a wealth of information on the past fluid chemistry of the volcanic lake at Kawah Ijen volcano, and allows a historical geochemical record spanning 50 years to be reconstructed. This record shows that elements derived primarily from rock dissolution, in particular Mg and the REE, track rock falls into the lake and seasonality in evaporation, which ultimately drives gypsum precipitation. The volatile metals act as indicators of increased gas input from the basaltic and dacitic magma reservoirs that underlie Kawah Ijen and these correlate with periods of volcanic unrest. The transition metals combine both of these sources and Pb may further be affected by anthropogenic input. Comparison with the limited seismic and thermal records that are available indicates that the geochemical record complements these records, with peaks in Tl/Rb and Cu/Rb preceding or coeval with increased seismicity and tremors. Therefore, the lake composition complement current volcano monitoring efforts at Kawah Ijen, and the historical record derived from gypsum indicates that in particular the elements Cu (representing the deep-seated basaltic magma) and Tl (representing the shallow dacitic magma) are effective indicators of volcanic activity. Finally, gypsum allowed us to characterize the geochemistry of the lake prior to the 1817 eruption, indicating a significantly elevated input of volcanic gas from the deep basaltic magma that is highly suggestive of mafic magmatic recharge and mixing driving this eruption. The gypsum tool developed here is not restricted to use at volcanic systems such as Kawah Ijen, and can be applied to reconstruct a record of fluid composition wherever gypsum grows in equilibrium with its parent fluid. As such, the approach presented here can be applied to other systems, for example gypsum stalactites in caves and even gypsum depositing from industrial effluent (e.g. García-Ruiz et al. 2007; Rutherford et al. 1994; Tayibi et al. 2009).

2.10 Acknowledgements

The authors thank Arisai Valadez for assistance in noble gas composition analysis, Kim Berlo for discussions on the Kawah Ijen system, participants of the Cities on Volcanoes 8 Wet Volcanoes workshop for discussions on the Kawah Ijen model and fieldwork. Funding for this study was received from McGill University Graduate Mobility Award, Mineralogical Association of Canada Travel Grant and Cities on Volcanoes 8 Travel Grant to SBU, and grants received to VvH and BG from the National Science and Engineering Research Council (NSERC) and le Fonds Québecois de la Récherche sur la Nature et les Technologies (FQRNT).

2.11 Table captions

Table 1: Summary of the trace element transect across growth zones A-D from stalactite KV09-501 growth zones. All concentrations are in ppm, except where indicated. '<d.l.' means the trace element composition is below the detection limit of the instrument. Hg concentrations are in counts per second (cps).

Table 2: Trace element concentrations for the 1817 gypsum cement. All concentrations are in ppm unless specified. Hg concentrations are in counts per second (cps). '<d.l.' means the trace element composition is below the detection limit of the instrument.

Table 3: ²¹⁰Pb activities of growth zones A-D, representing the oldest to youngest, respectively.

Table 4: ⁸⁴Kr and ¹³²Xe compositions of stalactite KV09-501 with growth zones A - D. Fvalues are the relative enrichment or depletion of each zone with respect to the atmospheric noble gas composition.

2.12 Figure Captions

Figure 1: A) Map of East Java with Kawah Ijen highlighted. B) Landsat8 image of the Ijen Volcanic Complex (dashed outline). Solid arrows show the pathways of major lava flows and lahars from Kawah Ijen volcano. C) Topographical map of Kawah Ijen and the Blau and Papak volcanoes. The study site is highlighted. Solid and dashed arrows show the pathways of major lava flows from Kawah Ijen volcano.

Figure 2: A) Model of the magmatic-hydrothermal system at Kawah Ijen in its passive degassing state, modified after (Christenson et al. 2010). B) Model of the magmatichydrothermal system at Kawah Ijen volcano during periods of unrest.

Figure 3: A) The Kawah Ijen gypsum plateau at the uppermost seepage springs looking back to the lake . B) Typical occurrence of gypsum stalactite growing downwards from brine flowing over its surface and showing the euhedral habit of the gypsum crystals.

Figure 4: A) Photo of stalactite KV09-501, analysed in this study. B) Cross-section of the base of the stalactite with growth zones chosen for ²¹⁰Pb and noble gas analyses. C) Location of the Trace element transect.

Figure 5: Gypsum cemented fall deposit from the 1817 eruption of Kawah Ijen. The book is 19.5 cm in length.

Figure 6: A) Variations in ²¹⁰Pb, $F(^{84}Kr)$ and $F(^{132}Xe)$ in each growth zone in the KV09-501 cross-section. B) Age model after correction using the weighted averages of $F(^{84}Kr)$ and $F(^{132}Xe)$.

Figure 7: Compositions of average Kawah Ijen rock and fumarole gas relative to lake water, normalised to their respective Mg contents, showing the dominant source for each element. Whereas the REE and HFSE are mainly derived from rock dissolution, the volatile metals are characteristically enriched in the volcanic gas.

Figure 8: Time-series record of trace element concentration representative of each type of trace element group in the Kawah Ijen system: rock dissolution elements (blue), volatile metals (red) and transition metals (purple).

Figure 9: Record of elemental ratios from 1964-2006, with a close-up for the 1990-2006 period for which reliable records of volcanic activity are available.

Figure 10: Tl/Rb and Cu/Rb, representing dilution corrected input from the shallow dacitic magma and deep basaltic magma respectively, compared with thermal record and volcano-tectonic seismicity (VA, VB and tremor).

Table 2.1: Summary of the trace element transect across growth zones A-D from stalactite KV09-501 growth zones. All concentrations are in ppm, except where indicated. '<d.l.' means the trace element composition is below the detection limit of the instrument. Hg concentrations are in counts per second (cps).

| Element | Total Spots | Minimum | Maximum | Median | 25^{th} Percentile | 75^{th} percentile |
|---------------------|-------------|---------|---------|--------|----------------------|----------------------|
| Li | 111 | 0 | 1.67 | 0.119 | 0.054 | 0.323 |
| Na | 123 | 11.5 | 1640 | 177 | 99.2 | 308 |
| Κ | 123 | 4.6 | 541 | 65.2 | 31.9 | 127 |
| Rb | 122 | 0.008 | 0.82 | 0.246 | 0.13875 | 0.41 |
| \mathbf{Cs} | 119 | 0 | 0.0422 | 0.0036 | 0.00063 | 0.0083 |
| Mg | 123 | 1.2 | 249 | 24.4 | 10.14 | 68.4 |
| Ba | 123 | 0 | 3800 | 17.1 | 2.43 | 195 |
| La | 123 | 0.769 | 21.3 | 7.38 | 5.06 | 10.73 |
| Ce | 123 | 3.9 | 56.6 | 28 | 19.68 | 37.19 |
| Pr | 123 | 0.755 | 8.29 | 4.09 | 2.93 | 5.36 |
| Nd | 123 | 3.82 | 34.6 | 17.18 | 12.31 | 21.8 |
| Sm | 123 | 0.704 | 6.03 | 2.83 | 2 | 3.45 |
| Eu | 123 | 0.153 | 1.5 | 0.66 | 0.55 | 0.809 |
| Gd | 123 | 0.293 | 5.7 | 1.51 | 1.09 | 1.98 |
| Tb | 123 | 0.0311 | 0.392 | 0.1326 | 0.104 | 0.168 |
| Dy | 123 | 0.153 | 1.85 | 0.561 | 0.42 | 0.748 |
| Но | 123 | 0.0248 | 0.302 | 0.0848 | 0.065 | 0.1086 |
| Er | 123 | 0.0397 | 0.63 | 0.191 | 0.13 | 0.244 |
| Tm | 123 | 0.0024 | 0.069 | 0.0165 | 0.0103 | 0.0217 |
| Yb | 123 | 0.01 | 0.334 | 0.085 | 0.06 | 0.116 |
| Lu | 123 | 0.0023 | 0.039 | 0.0085 | 0.0062 | 0.0116 |
| Hg^* | 123 | 19 | 186 | 71 | 52 | 90 |
| Tl | 123 | 0.0041 | 0.263 | 0.0741 | 0.044 | 0.117 |
| Pb | 123 | 3.36 | 40.76 | 16.24 | 13.89 | 23.2 |
| Bi | 123 | 0.0026 | 0.969 | 0.304 | 0.177 | 0.407 |
| In | 115 | 0 | 0.0108 | 0 | 0 | 0.0011 |
| Se | 65 | 0 | 7.3 | 0.34 | 0.16 | 0.6 |
| As | 107 | 0.01 | 4.7 | 0.34 | 0.05 | 0.29 |

| Element | Total Spots | Minimum | Maximum | Median | 25^{th} Percentile | 75^{th} percentile |
|---------------------|-------------|---------|---------|--------|----------------------|----------------------|
| Sb | 122 | 0 | 1.03 | 0.047 | 0.19 | 0.59 |
| Cr | 65 | 0 | 1.51 | 0.14 | 0.05 | 0.29 |
| Cu | 121 | 0 | 9.5 | 0.41 | 0.21 | 0.74 |
| Zn | 122 | 0.02 | 46.3 | 3.5 | 1.1825 | 8.15 |
| Ti | 115 | 0.05 | 122 | 1.5 | 0.62 | 4.8 |
| Mn | 123 | 0.02 | 15 | 1.46 | 0.55 | 3.71 |
| Sn | 123 | 0 | 0.86 | 0.072 | 0.04 | 0.142 |
| V | 115 | 0 | 1.77 | 0.196 | 0.095 | 0.49 |
| Cd | 123 | 0 | 0.014 | 0 | 0 | 0 |
| Fe | 123 | 260.4 | 595 | 321 | 297.3 | 359 |
| Co | 119 | 0.01 | 0.69 | 0.154 | 0.125 | 0.183 |
| Ni | 123 | 1.29 | 3.5 | 1.83 | 1.64 | 2.01 |
| Al | 123 | 3.3 | 9200 | 122.2 | 59.1 | 322 |
| Sc | 84 | 0.01 | 5.43 | 0.415 | 0.23 | 0.835 |
| Ga | 122 | 0 | 140 | 0.107 | 0.039 | 0.8825 |
| Ge | 121 | 0 | 1.33 | 0.18 | 0.08 | 0.31 |
| Zr | 123 | 0 | 1.34 | 0.065 | 0.0112 | 0.177 |
| Hf | 123 | 0.00 | 0.08 | 0.00 | 0.00 | 0.01 |
| Nb | 123 | 0.00 | 0.01 | 0.00 | 0.00 | 0.00 |
| Ta | 123 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Y | 123 | 0.42 | 22.02 | 1.96 | 1.37 | 2.92 |
| U | 123 | 0.00 | 0.02 | 0.00 | 0.00 | 0.01 |
| Th | 123 | 0.03 | 0.96 | 0.14 | 0.10 | 0.21 |
| Ag | 71 | 0.00 | 0.25 | 0.01 | 0.00 | 0.02 |





(a) Geographical map of East Java, Indonesia

(b) Modified landsat8 image of Ijen Volcanic Complex (IVC).



(c) Topographical map of Kawah Ijen volcano.

Figure 2.1: A) Map of East Java with Kawah Ijen highlighted. B) Modified Landsat8 image of the Ijen Volcanic Complex (dashed outline). Solid arrows show the pathways of major lava flows and lahars from Kawah Ijen volcano. C) Topographical map of Kawah Ijen and the Blau and Papak volcanoes. The study site is highlighted. Solid and dashed arrows show the pathways of major lava flows from Kawah Ijen volcano.



(c) Legend

Figure 2.2: A) Model of the magmatic-hydrothermal system at Kawah Ijen in its passive degassing state, modified after (Christenson et al. 2010). B) Model of the magmatichydrothermal system at Kawah Ijen volcano during periods of unrest.



(a) gypsum plateau



(b) gypsum stalactites

Figure 2.3: A) The Kawah Ijen gypsum plateau at the uppermost seepage springs looking back to the lake. B) Typical occurrence of gypsum stalactite growing downwards from brine flowing over its surface and showing the euhedral habit of the gypsum crystals.



(a) Stalactite KV09-501



(c) Cross-section for trace element analysis

Figure 2.4: A) Photo of stalactite KV09-501, analysed in this study. B) Cross-section of the base of the stalactite with growth zones chosen for 210 Pb and noble gas analyses. C) Location of the trace element transect.



Figure 2.5: Gypsum cemented fall deposit from the 1817 eruption of Kawah Ijen. The book is 19.5 cm in length.



(b) Corrected age of stalactite in years (c) Age in years vs. transect ablation vs. stalactite growth zone spot

Figure 2.6: A) Variations in ²¹⁰Pb, $F(^{84}Kr)$ and $F(^{132}Xe)$ in each growth zone in the KV09-501 cross-section. B) Age model after correction using the weighted averages of $F(^{84}Kr)$ and $F(^{132}Xe)$.



Figure 2.7: Compositions of average Kawah Ijen rock and fumarole gas relative to lake water, normalised to their respective Mg contents, showing the dominant source for each element. Whereas the REEs and HFSEs are mainly derived from rock dissolution, the volatile metals are characteristically enriched in the volcanic gas.

s



Figure 2.8: Time-series record of trace element concentration representative of each type of trace element group in the Kawah Ijen system: rock dissolution elements (blue), volatile metals (red) and transition metals (purple).



Figure 2.9: Record of elemental ratios from 1964-2006, with a close-up for the 1990-2006 period for which reliable records of volcanic activity are available.



Figure 2.10: Tl/Rb and Cu/Rb, representing dilution corrected input from the shallow dacitic magma and deep basaltic magma respectively, compared with thermal record and volcano-tectonic seismicity (VA, VB and tremor).

| Elements | Concentration |
|---------------------|-----------------------|
| Li | <d.1.< td=""></d.1.<> |
| Na | 0.21 |
| Mg | 0.051 |
| Al | 6.3 |
| Si | <d.1.< td=""></d.1.<> |
| Κ | 0.036 |
| Sc | <d.l.< td=""></d.l.<> |
| Ti | 0.018 |
| V | 0.0012 |
| Cr | 0.0019 |
| Mn | 0.0015 |
| Fe | 1.5 |
| Co | 0.00077 |
| Ni | 0.015 |
| Cu | 0.043 |
| Zn | 0.0080 |
| Ga | 0.0025 |
| Ge | 0.0085 |
| As | 0.0075 |
| Se | <d.l.< td=""></d.l.<> |
| Rb | 0.00031 |
| Sr | 30 |
| Υ | 0.13 |
| Zr | 0.0052 |
| Nb | <d.l.< td=""></d.l.<> |
| Mo | <d.l.< td=""></d.l.<> |
| Ag | <d.l.< td=""></d.l.<> |
| Cd | 0 |
| In | <d.l.< td=""></d.l.<> |
| Sn | 0.001 |
| Sb | 0.00018 |
| Cs | <d.l.< td=""></d.l.<> |
| Ba | 0.0018 |
| La | 0.37 |
| Ce | 1.26 |
| Pr | 0.18 |
| Nd | 0.95 |
| Sm | 0.17 |
| Eu | 0.039 |
| Gd | 0.084 |

Table 2.2: Trace element concentrations for the 1817 gypsum cement. All concentrations are in ppm unless specified. Hg concentrations are in counts per second (cps). '<d.l.' means the trace element composition is below the detection limit of the instrument.

| Elements | Concentration |
|---------------|---------------|
| Tb | 0.0092 |
| Dy | 0.0453 |
| Но | 0.0066 |
| Er | 0.015 |
| Tm | 0.0013 |
| Yb | 0.0073 |
| Lu | 0.00076 |
| $_{ m Hf}$ | 0.00020 |
| Ta | 0.000014 |
| W | 0.00014 |
| Hg (cps) | 164 |
| Tl | 0.00012 |
| Pb | 0.25 |
| Bi | 0.0080 |
| Th | 0.0032 |
| U | 0.000097 |

Table 2.2 – continued from previous page

| Sample Name | Growth Zone | Stratigraphic Position | Activity (dpm/g) | \pm total |
|-------------|--------------|------------------------|------------------|-------------|
| KV09-501-3A | А | Core (Oldest) | 1.17 | 0.09 |
| KV09-501-3B | В | | 1.23 | 0.09 |
| KV09-501-3C | \mathbf{C} | | 0.65 | 0.06 |
| KV09-501-3D | D | Rim (Youngest) | 0.73 | 0.07 |
| KV09-501 | | Present Day Value | 1.25 | 0.04 |

Table 2.3: $^{210}\mathrm{Pb}$ activities of growth zones A-D, representing the oldest to youngest, respectively.

Table 2.4: ⁸⁴Kr and ¹³²Xe compositions of stalactite KV09-501 with growth zones A - D. F-values are the relative enrichment or depletion of each zone with respect to the atmospheric noble gas composition.

| Sample Name | Growth Zone | Stratigraphic Position | $^{84}\mathrm{Kr}$ | \pm total | $^{132}\mathrm{Xe}$ | \pm total | $F(^{84}Kr)$ | \pm total | $F(^{132}Xe)$ | \pm total |
|-------------|--------------|------------------------|--------------------|-------------------|---------------------|-------------------|--------------|-------------|---------------|-------------|
| | | | $\times ~10^{14}$ | $\times ~10^{14}$ | $\times ~10^{15}$ | $\times ~10^{15}$ | | | | |
| KV09-501-3A | А | Core (Oldest) | 6.67 | 0.44 | 1534 | 299 | 1.42 | 0.2 | 9.11 | 1.9 |
| KV09-501-3B | В | | 1.08 | 0.07 | 127 | 30 | 1.43 | 0.2 | 4.70 | 1.2 |
| KV09-501-3C | \mathbf{C} | | 7251 | 268 | 274025 | 27135 | 1.05 | 0.2 | 1.11 | 0.1 |
| KV09-501-3D | D | Rim (Youngest) | 0.076 | 0.01 | 6.12 | 0.74 | 0.51 | 0.1 | 1.14 | 0.2 |
| KV09-501 | | | 100.86 | 5.86 | 4201 | 161 | 1.30 | 0.0 | 1.51 | 0.1 |

References

- Berlo, K, V. van Hinsberg, N Vigouroux, J. Gagnon, and A. Williams-Jones (2014). "Sulfide breakdown controls metal signature in volcanic gas at Kawah Ijen volcano, Indonesia". *Chemical Geology* 371, pp. 115–127.
- Bosch, C. (1858). "Uitbarstingen der vulkanen Idjin en Raun (Banjoewangi)". *Tijdschrift* voor Indische Taal-, Land- en Volkenkunde 7, pp. 265–286.
- Bourdon, B., S. Turner, G. M. Henderson, and C. C. Lundstrom (2003). "Introduction to U-series geochemistry". *Reviews in Mineralogy and Geochemistry* 52.1, pp. 1–21.
- Bryan, C. and S Sherburn (1999). "Seismicity associated with the 1995–1996 eruptions of Ruapehu volcano, New Zealand: narrative and insights into physical processes". Journal of Volcanology and Geothermal Research 90.1, pp. 1–18.
- Caudron, C., D. K. Syahbana, T. Lecocq, V. Van Hinsberg, W. McCausland, A. Triantafyllou, T. Camelbeeck, A. Bernard, et al. (2015a). "Kawah Ijen volcanic activity: a review". *Bulletin of Volcanology* 77.3, pp. 1–39.
- Caudron, C., T. Lecocq, D. K. Syahbana, W. McCausland, A. Watlet, T. Camelbeeck, and A. Bernard (2015b). "Stress and mass changes at a'wet'volcano: example during the 2011–2012 volcanic unrest at Kawah Ijen volcano (Indonesia)". Journal of Geophysical Research: Solid Earth.
- Chesner, C. A. (2012). "The Toba caldera complex". *Quaternary International* 258, pp. 5–18.
- Christenson, B. (2000). "Geochemistry of fluids associated with the 1995–1996 eruption of Mt. Ruapehu, New Zealand: signatures and processes in the magmatic-hydrothermal system". Journal of Volcanology and Geothermal Research 97.1, pp. 1–30.
- Christenson, B., A. Reyes, R Young, A Moebis, S Sherburn, J Cole-Baker, and K Britten (2010). "Cyclic processes and factors leading to phreatic eruption events: Insights from the 25 September 2007 eruption through Ruapehu Crater Lake, New Zealand". Journal of Volcanology and Geothermal Research 191.1, pp. 15–32.
- Condomines, M., O Sigmarsson, and P. Gauthier (2010). "A simple model of 222 Rn accumulation leading to 210 Pb excesses in volcanic rocks". *Earth and Planetary Science Letters* 293.3, pp. 331–338.
- Cronin, S. J. and D. S. Sharp (2002). "Environmental impacts on health from continuous volcanic activity at Yasur (Tanna) and Ambrym, Vanuatu". International Journal of Environmental Health Research 12.2, pp. 109–123.
- Cronin, S. J., M. Hedley, R. Smith, and V. Neall (1997). "Impact of Ruapehu ash fall on soil and pasture nutrient status 1. October 1995 eruptions". New Zealand Journal of Agricultural Research 40.3, pp. 383–395.
- Cronin, S. J., V. Neall, J. Lecointre, M. Hedley, and P Loganathan (2003). "Environmental hazards of fluoride in volcanic ash: a case study from Ruapehu volcano, New Zealand". *Journal of Volcanology and Geothermal Research* 121.3, pp. 271–291.
- Cronin, S., M. Hedley, V. Neall, and R. Smith (1998). "Agronomic impact of tephra fallout from the 1995 and 1996 Ruapehu Volcano eruptions, New Zealand". *Environmental Geology* 34.1, pp. 21–30.
- D'Alessandro, W (2006). "Human fluorosis related to volcanic activity: a review". Environmental Toxicology. 1, pp. 21–30.
- Davidson, J. P. and F. J. Tepley (1997). "Recharge in volcanic systems: evidence from isotope profiles of phenocrysts". *Science* 275.5301, pp. 826–829.
- Delmelle, P. and A. Bernard (1994). "Geochemistry, mineralogy, and chemical modeling of the acid crater lake of Kawah Ijen Volcano, Indonesia". *Geochimica et cosmochimica acta* 58.11, pp. 2445–2460.
- Delmelle, P., A. Bernard, M. Kusakabe, T. Fischer, and B. Takano (2000). "Geochemistry of the magmatic-hydrothermal system of Kawah Ijen volcano, East Java, Indonesia". *Journal of Volcanology and Geothermal research* 97.1, pp. 31–53.
- Gamble, J., C. Wood, R. Price, I. Smith, R. Stewart, and T Waight (1999). "A fifty year perspective of magmatic evolution on Ruapehu Volcano, New Zealand: verification of

open system behaviour in an arc volcano". *Earth and Planetary Science Letters* 170.3, pp. 301–314.

- García-Ruiz, J. M., R. Villasuso, C. Ayora, A. Canals, and F. Otálora (2007). "Formation of natural gypsum megacrystals in Naica, Mexico". *Geology* 35.4, pp. 327–330.
- Ghaleb, B. (2009). "Overview of the methods for the measurement and interpretation of short-lived radioisotopes and their limits". In: *IOP Conference Series: Earth and Envi*ronmental Science. Vol. 5. 1. IOP Publishing, p. 012007.
- Handley, H., C. Macpherson, J. Davidson, K Berlo, and D Lowry (2007). "Constraining fluid and sediment contributions to subduction-related magmatism in Indonesia: Ijen Volcanic Complex". Journal of Petrology 48.6, pp. 1155–1183.
- Hinsberg, V. van, K. Berlo, M. van Bergen, and A. Williams-Jones (2010a). "Extreme alteration by hyperacidic brines at Kawah Ijen volcano, East Java, Indonesia: I. Textural and mineralogical imprint". Journal of Volcanology and geothermal Research 198.1, pp. 253– 263.
- Hinsberg, V. van, K. Berlo, S. Sumarti, M. Van Bergen, and A. Williams-Jones (2010b).
 "Extreme alteration by hyperacidic brines at Kawah Ijen volcano, East Java, Indonesia: II: Metasomatic imprint and element fluxes". Journal of Volcanology and Geothermal Research 196.3, pp. 169–184.
- Hinsberg, V. van, A. Williams-Jones, G Mauri, N Vigouroux, G Williams-Jones, J McKenzie, S Palmer, and A Nasution (2008). "Studying the Kawah Ijen volcano-hydrothermal system-merits of an interdisciplinary approach". IAVCEI, Reykjavik, Iceland, Abstract.
- Johnson, G. and G. Olhoeft (1984). "Density of rocks and minerals". CRC Handbook of Physical Properties of Rocks 3, pp. 1–38.
- Junghuhn, F. (1853). In: Java, deszelfs gedaante, bekleeding en inwendinge structuur. Ed. byP. van Kampen. Vol. 1-4. Amsterdam.
- Kemmerling, G. (1921). De geologie en geomorpologie van den Idjen en analyse van merkwaardige watersoorten op het Idjen hoogland.

- Kent, A. J., C. Darr, A. M. Koleszar, M. J. Salisbury, and K. M. Cooper (2010). "Preferential eruption of andesitic magmas through recharge filtering". *Nature Geoscience* 3.9, pp. 631– 636.
- Kilgour, G, V Manville, F Della Pasqua, A Graettinger, K. Hodgson, and G. Jolly (2010). "The 25 September 2007 eruption of Mount Ruapehu, New Zealand: directed ballistics, surtseyan jets, and ice-slurry lahars". Journal of Volcanology and Geothermal Research 191.1, pp. 1–14.
- Kling, G. W., M. A. Clark, G. N. WAGNER, H. R. COMPTON, A. M. HUMPHREY, J. D. DEVINE, W. C. EVANS, J. P. Lockwood, M. L. Tuttle, and E. J. KOENIGSBERG (1987). "The 1986 Lake Nyos gas disaster in Cameroon, West Africa". *Science* 236.4798, pp. 169–175.
- Kusakabe, M., T. Ohsumi, and S. Aramaki (1989). "The Lake Nyos gas disaster: chemical and isotopic evidence in waters and dissolved gases from three Cameroonian crater lakes, Nyos, Monoun and Wum". Journal of volcanology and geothermal research 39.2, pp. 167– 185.
- Lee, J.-M., E. A. Boyle, I. S. Nurhati, M. Pfeiffer, A. J. Meltzner, and B. Suwargadi (2014). "Coral-based history of lead and lead isotopes of the surface Indian Ocean since the mid-20th century". *Earth and Planetary Science Letters* 398, pp. 37–47.
- Lelieveld, J. o., P. Crutzen, V Ramanathan, M. Andreae, C. Brenninkmeijer, T Campos, G. Cass, R. Dickerson, H Fischer, J. De Gouw, et al. (2001). "The Indian Ocean experiment: widespread air pollution from South and Southeast Asia". Science 291.5506, pp. 1031–1036.
- Löhr, A., T. Bogaard, A. Heikens, M. Hendriks, S. Sumarti, M. Van Bergen, K. C. Van Gestel, N. Van Straalen, P. Vroon, and B. Widianarko (2005). "Natural Pollution Caused by the Extremely Acid Crater Lake Kawah Ijen, East Java, Indonesia (7 pp)". *Environmental Science and Pollution Research* 12.2, pp. 89–95.

- Löhr, A. J., T. De Kort, N. M. Van Straalen, and C. A. Van Gestel (2007). "Unraveling the causes of the toxicity of extremely acid waters of volcanic origin". *Environment international* 33.6, pp. 743–749.
- Manga, M. and E. Brodsky (2006). "Seismic triggering of eruptions in the far field: volcanoes and geysers". Annu. Rev. Earth Planet. Sci 34, pp. 263–291.
- Manville, V (2015). "Volcano-hydrologic hazards from volcanic lakes". In: Volcanic Lakes. Springer, pp. 21–71.
- Marini, L., M. V. Zuccolini, and G. Saldi (2003). "The bimodal pH distribution of volcanic lake waters". Journal of volcanology and geothermal research 121.1, pp. 83–98.
- Martinez, M, E Fernández, J Valdés, V Barboza, R Van der Laat, E Duarte, E Malavassi, L Sandoval, J Barquero, and T Marino (2000). "Chemical evolution and volcanic activity of the active crater lake of Poás volcano, Costa Rica, 1993–1997". Journal of Volcanology and Geothermal Research 97.1, pp. 127–141.
- Mastin, L. and J. Witter (2000). "The hazards of eruptions through lakes and seawater". Journal of Volcanology and Geothermal Research 97.1, pp. 195–214.
- Mulyana, A. and W. Effendi (2006). Peta kawasan rawan bencana gunungapi Ijen, Provinsi Jawa Timur Tahun 2006 Skala 1:100.000. Geological/Hazard Map.
- Nelson, C. H., C. R. Bacon, S. W. Robinson, D. P. Adam, J. P. Bradbury, J. H. BARBER, D. Schwartz, and G. Vagenas (1994). "The volcanic, sedimentologic, and paleolimnologic history of the Crater Lake caldera floor, Oregon: Evidence for small caldera evolution". *Geological Society of America Bulletin* 106.5, pp. 684–704.
- Palmer, S. C. (2009). "Hydrogeochemistry of the upper Banyu Pahit River valley, Kawah Ijen volcano, Indonesia". MA thesis. McGill University.
- Palmer, S. C., V. J. Van Hinsberg, J. M. McKenzie, and S. Yee (2011). "Characterization of acid river dilution and associated trace element behavior through hydrogeochemical modeling: A case study of the Banyu Pahit River in East Java, Indonesia". Applied Geochemistry 26.11, pp. 1802–1810.

- Paton, C., J. Hellstrom, B. Paul, J. Woodhead, and J. Hergt (2011). "Iolite: Freeware for the visualisation and processing of mass spectrometric data". *Journal of Analytical Atomic Spectrometry* 26.12, pp. 2508–2518.
- Pitre, F. and D. L. Pinti (2010). "Noble gas enrichments in porewater of estuarine sediments and their effect on the estimation of net denitrification rates". *Geochimica et Cosmochimica Acta* 74.2, pp. 531–539.
- Reed, M. H. (1997). "Hydrothermal alteration and its relationship to ore fluid composition". Geochemistry of hydrothermal ore deposits 3, pp. 303–365.
- Rotterdam-Los, A. van, S. Vriend, M. van Bergen, and P. van Gaans (2008). "The effect of naturally acidified irrigation water on agricultural volcanic soils. The case of Asembagus, Java, Indonesia". Journal of Geochemical Exploration 96.1, pp. 53–68.
- Rouwet, D, Y Taran, S Inguaggiato, N Varley, and J. S. Santiago (2008). "Hydrochemical dynamics of the "lake-spring" system in the crater of El Chichón volcano (Chiapas, Mexico)". Journal of Volcanology and Geothermal Research 178.2, pp. 237–248.
- Rouwet, D., F. Tassi, R. Mora-Amador, L. Sandri, and V. Chiarini (2014). "Past, present and future of volcanic lake monitoring". *Journal of volcanology and geothermal research* 272, pp. 78–97.
- Rowe, G. L., S. L. Brantley, M. Fernandez, J. F. Fernandez, A. Borgia, and J. Barquero (1992). "Fluid-volcano interaction in an active stratovolcano: the crater lake system of Poás volcano, Costa Rica". Journal of Volcanology and Geothermal Research 49.1, pp. 23– 51.
- Rutherford, P., M. Dudas, and R. Samek (1994). "Environmental impacts of phosphogypsum". Science of the total environment 149.1, pp. 1–38.
- Scott, W. E. (1989). "Volcanic and related hazards". Volcanic Hazards, pp. 9–23.
- Sigurdsson, H., J. Devine, F. Tchua, F. Presser, M. Pringle, and W. C. Evans (1987). "Origin of the lethal gas burst from Lake Monoun, Cameroun". Journal of Volcanology and Geothermal Research 31.1, pp. 1–16.

- Sitorus, K. (1990). "Volcanic stratigraphy and geochemistry of the Idjen Caldera Complex, East-Java, Indonesia". PhD thesis. Victoria University of Wellington.
- Spencer, R. J. (2000). "Sulfate minerals in evaporite deposits". Reviews in Mineralogy and Geochemistry 40.1, pp. 173–192.
- Takano, B., K Suzuki, K Sugimori, T. Ohba, S. Fazlullin, A. Bernard, S. Sumarti, R Sukhyar, and M Hirabayashi (2004). "Bathymetric and geochemical investigation of Kawah Ijen crater lake, east Java, Indonesia". *Journal of volcanology and geothermal research* 135.4, pp. 299–329.
- Tassi, F. and D. Rouwet (2014). "An overview of the structure, hazards, and methods of investigation of Nyos-type lakes from the geochemical perspective". *Journal of Limnology* 73.1.
- Tayibi, H., M. Choura, F. A. López, F. J. Alguacil, and A. López-Delgado (2009). "Environmental impact and management of phosphogypsum". *Journal of Environmental Management* 90.8, pp. 2377–2386.
- Tepley, F., J. Davidson, R. Tilling, and J. Arth (2000). "Magma mixing, recharge and eruption histories recorded in plagioclase phenocrysts from El Chichon Volcano, Mexico". *Journal of Petrology* 41.9, pp. 1397–1411.
- Tour, J. Leschenault de la (1811). "Notice sur un lac d'acide sulfurique qui se trouve au fond d'un volcan du Mont-Idienne, situé dans la province de Bagnia-Vangni, côté de l'ile de Java." Am. Musm Hist. Nat 18, pp. 425–446.
- Van Hinsberg, V. J. (2001). "Water-Rock Interaction and Element Fluxes in the Kawah Ijen Hyperacid Crater Lake and the Banyu Pait River, East Java, Indonesi". MA thesis. Utrecht University.
- Van Hinsberg, V. J., N Vigouroux, S. C. Palmer, K. Berlo, S. Scher, G. Mauri, A. E. Williams-Jones, J. McKenzie, G. Williams-Jones, and T. Fischer (2015). "Element flux to the environment of the passively degassing Kawah Ijen volcano, Indonesia, and implications for estimates of the global volcanic flux". Special Issue on Volcanic Lakes.

- Varekamp, J. and R Kreulen (2000). "The stable isotope geochemistry of volcanic lakes, with examples from Indonesia". Journal of volcanology and geothermal research 97.1, pp. 309– 327.
- Waters, A. C. and R. V. Fisher (1971). "Base surges and their deposits: Capelinhos and Taal volcanoes". Journal of Geophysical Research 76.23, pp. 5596–5614.

Bridging Statement

In manuscript 1, I established that a growth zoned gypsum stalactite can be used to reconstruct a historical record of past crater lake chemistry at Kawah Ijen volcano in East Java, Indonesia. Input from rock-dissolution elements (e.g. Mg, Rb) shows seasonal variability related to variations in evaporation, whereas volatile metals (Tl, Sb, Cu) track input from shallow and deep magma. In combination with seismicity and lake temperature, chemical signals preceding periods of unrest and phreatic events in the last 20 years were identified. Moreover, gypsum from the 1817 fall deposit provided insights into the only historical phreatomagmatic eruption recorded at Kawah Ijen in 1817 (Bosch 1858). The trace element signature of this gypsum cement points to mafic magmatic recharge as a trigger of the eruption. These findings have important implications for volcano monitoring of Kawah Ijen and can further be applied to other volcanic crater lakes.

In manuscript 2, I investigate the potential of gypsum to preserve the lake water disequilibrium O-isotopic composition in the δ^{18} O of its sulfate group and crystalline water. Given that this isotopic disequilibrium in water is temperature dependent (Chiba and Sakai 1985), we can use gypsum O-isotopic composition as a geothermometer to potentially provide a thermal record, in addition to the compositional record that I presented in chapter 2.

References

- Bosch, C. (1858). "Uitbarstingen der vulkanen Idjin en Raun (Banjoewangi)". Tijdschrift voor Indische Taal-, Land- en Volkenkunde 7, pp. 265–286.
- Chiba, H. and H. Sakai (1985). "Oxygen isotope exchange rate between dissolved sulfate and water at hydrothermal temperatures". *Geochimica et Cosmochimica Acta* 49.4, pp. 993– 1000.

Chapter 3

Manuscript 2

Gypsum $\delta^{18}{\rm O}$ tracks temperature of the magmatic-hydrothermal system at Kawah Ijen volcano, East Java, Indonesia

Sri Budhi Utami^{1*}, Vincent van Hinsberg¹, and Bassam Ghaleb²

1. Dpt. Earth and Planetary Sciences, McGill University 3450 Rue University, Montréal, QC, Canada H3A 0E8

2. GEOTOP-UQAM CP 8888 Succ. Centre-Ville Montréal, QC, Canada, H3C 3P8

*Corresponding Author: sri.budhi.utami@gmail.com

Submitted August 2015

3.1 Abstract

The $\delta^{18}O$ of crystalline water and sulfate in gypsum, as well as the Kawah Ijen acid volcanic lake fluid from which it formed, preserves evidence of oxygen isotopic disequilibrium within the lake brine, which can be used as a geothermometer to track variations of the temperature of the magmatic-hydrothermal system. The fractionation factors of H₂O and SO₄ between gypsum and the brine indicate that gypsum incorporates an isotopically lighter δ^{18} O signature from the brine. Applying these fractionation factors to gypsum deposited as a result of the 1817 eruption of Kawah Ijen, it is possible to reconstruct the δ^{18} O isotopic lake water composition. The temperature derived from this reconstructed brine is 182-188 °C, which although lower than the temperature for present-day fumarole gases of 400 °C (Van Hinsberg et al. 2015), shows a marked increase from the averaged lake brine temperature of 145°C from the 1993-1996 period (Delmelle et al. 2000). The significant increase in temperature is likely due to the increased input of volcanic gas prior to the 1817 eruption. Therefore, gypsum is potentially a useful tool to estimate temperature changes within the lake, with implications for volcano monitoring of the Kawah Ijen system as well as other volcanoes and crater lakes.

Keywords: gypsum, oxygen isotope, geothermometer, volcanic lake

3.2 Introduction

Sulfate is an important constituent of magmatic-hydrothermal and geothermal fluids, and can contain almost 10% of all oxygen in these fluids in extreme cases (e.g. Póas - Martinez et al. 2000). Oxygen isotopes exchange between the dissolved sulfate group ions and water molecules (Chacko et al. 2001; Sofer 1978). The oxygen isotopic equilibrium exchange reaction is temperature and pH dependent, and in high temperature and low pH systems typical of magmatic-hydrothermal systems the reaction rate is high enough that isotopic equilibrium is attained within hours (Chiba and Sakai 1985). At low temperatures, the isotope equilibrium exchange reaction proceeds slowly, such that equilibrium is only attained in the time

scales of 10^7 years, far exceeding the residence time of the fluids. Therefore, as these ascends towards the surface, the isotopic composition of the sulfate group and water are progressively frozen in, and the SO₄-H₂O pair is at δ^{18} O disequilibrium with respect to surface fluid conditions. An important application of this SO₄-H₂O disequilibrium is in geothermometry (Lloyd 1968; Mizutani and Rafter 1969). Several δ^{18} O geothermometric formulations have been derived for the SO₄-H₂O pair (Fowler et al. 2013; Lloyd 1968; McKenzie and Truesdell 1977; Mizutani and Rafter 1969). Given the very slow equilibration at low temperature, even in extremely low pH solutions (Chiba and Sakai 1985), the δ^{18} O of the SO₄-H₂O pair in surface emissions can be used to estimate the temperature at depth in the hydrothermal system, which is an important parameter in both geothermal and volcanic settings. A limitation of this geothermometer is that it is based on fluid isotopic composition. Fluid samples are almost exclusively available for the present, and therefore do not allow this tool to be used to reconstruct temperatures in the past. In contrast, the geological record is abundant in solid samples, with rocks and minerals that preserve evidence for the presence of water dating back to the earliest geological history (e.g. Schröder et al. 2008). A mineral that could record the SO_4 -H₂O pair's δ^{18} O-isotopic disequilibrium would therefore greatly expand the applicability of this thermometer, allowing it to be used to reconstruct past temperatures and even to track the thermal evolution of a system through time. Hydrous sulfate evaporite minerals such as gypsum are common in magmatic-hydrothermal and geothermal systems. In this contribution, we investigate the potential of gypsum to record the isotopic composition of both the sulfate and crystalline water of its parent fluid. Gypsum is a hydrated sulfate with the formula $CaSO_4 \cdot 2H_2O$ and has the potential to capture the sulfate isotopic composition in its structural SO₄-group and the $H_2O \delta_{18}O$ in its crystalline water.

An ideal system to investigate the potential of gypsum as a recorder of δ^{18} O disequilibrium in a hydrothermal fluid is the crater lake of Kawah Ijen volcano in East Java, Indonesia. Kawah Ijen volcano is capped by the world's largest, natural hyper-acidic crater lake with 32 million m^3 of pH less than 0.1, SO₄-rich brine (Delmelle et al. 2000). Gypsum precipitates on the lake shore from the lake water by evaporation, but the largest gypsum deposits are found around lake water seepage springs where gypsum forms a 20m wide, 100m long cascading plateau with stalactites growing from overhangs (Chapter 3) (Figure 3.1a). Historical records indicate that gypsum has been precipitating from acid waters at this location for more than 200 years (Tour 1811), although the present plateau formed after the catastrophic 1817 eruption of Kawah Ijen, which three out the lake and deposited extensive phreatomagmatic volcanoclastics (Bosch 1858). The fall deposit of this 1817 eruption contains abundant gypsum as clear, colourless needles and interstitial grains that cement the wellsorted vesicular tephra. We interpret this as ash to lapilli-sized tephra falling into 1817 lake effluent, which became overlain by a pumice fall. The evaporation of the lake effluent within the fall deposit led to gypsum precipitation. As such, this gypsum can potentially provide temperature information on the lake prior to the 1817 eruption, and hence whether the lake temperature was elevated from increased magnatic input. In this study we shall therefore address the following questions: does present-day gypsum record the O-isotopic disequilibrium from its parent brine in its crystalline water and sulfate group? If so, can older gypsum from Kawah Ijen be used to reconstruct the brine oxygen isotopic composition and estimate the temperature of the system in the past?

3.3 Methodology

Actively-growing gypsum stalactites and associated seepage spring water were sampled on the gypsum plateau in the 2009 dry season at Kawah Ijen volcano. The water was filtered in the field through a 0.45 m disposable filter. Gypsum cement from the 1817 fall deposit was sampled in 2014. Approximately 1g of material from the clear tip of a gypsum stalactite was ground and dehydrated in a glass tube at 180-200°C for up to 120 minutes, with its crystalline water captured in an attached cold trap for analysis. Gypsum cement grains were handpicked from the crushed fall deposit and also ground and dehydrated. Water samples were equilibrated with injected CO₂ for 7 hours at 40°C, and analyzed on a Micromass Isoprime universal collector isotope ratio mass spectrometer (IRMS) in dual inlet mode to obtain the δ^{18} O of the crystalline water. Three internal water standards were included. Two ¹⁸O international standards, IAEA-601 (δ^{18} O = 23.3 ± 0.3 ‰ V-SMOW) and IAEA-602 (δ^{18} O = 71.4 ± 0.5 ‰ V-SMOW) benzoic acid standard solutions and one laboratory standard (an Ag₃PO₄ standard, see e.g. Fourel et al. 2011) were used to calibrate the instrument. Powdered gypsum from the stalactite tip and the fall deposit were dehydrated at 450 °C and the solid residue analyzed at the Environmental Isotope Laboratory at the University of Waterloo to obtain the δ^{18} O of the sulfate-group.

3.4 Results

The δ^{18} O values of gypsum are given in Table 3.1. All δ^{18} O isotopic signatures show enrichment of heavy ¹⁸O oxygen isotopes relative to V-SMOW. Duplicates indicate a 1σ uncertainty on the data of 0.05 ‰. Gypsum-water fractionation factors for SO₄ and H₂O are shown in Table 3.2. The fractionation factor between crystalline and brine water is lower than the fractionation factor between the gypsum sulfate group and the brine sulfate. Both fractionation factors suggest that gypsum incorporates an isotopically light δ^{18} O composition relative to the brine. The temperature recorded by gypsum in 2009 based on the averaged δ^{18} O composition measured by Delmelle et al. (2000) is 146 ± 0.01 °C. The reconstructed 1817 brine $\delta^{18}O_{H_{2O}}$ composition is comparable to that reported by Delmelle et al. (2000) for 1993-1996, but the sulfate δ^{18} O is lower (Table 3.3).

3.5 Discussion

Palmer 2009 found that the δ^{18} O of the spring water (8.21 ‰) show a significant isotopic shift from groundwater composition (-8.55‰), which is consistent with typical values pre-

viously measured at Kawah Ijen volcano and similar volcanoes such as Keli Mutu and Póas (Delmelle et al. 2000; Palmer 2009; Rowe 1994; Varekamp and Kreulen 2000). Furthermore, Delmelle et al. 2000 report a δ^{18} O for H₂O in the crater lake of 8.72 %, which is also significantly higher than local groundwater and magmatic water (up to +5%- Delmelle et al. 2000; Van Hinsberg et al. 2015), indicating evaporative enrichment in ¹⁸O of the lake. Measurements in 2014 showed that the Ijen upper springs recorded a δ^{18} O of 7.25-7.27 ‰, whereas the acid lake water collected from the western lake shore had a δ^{18} O of 8.56 ‰; the southeastern lake shore near the fumarolic field had a δ^{18} O of 8.51 % (M. Martinez, pers. comm.) Therefore the δ^{18} O composition of the spring brine water reflects a mixture of groundwater and magmatic water that is enriched by evaporation. Definelle et al. 2000 also measured the δ^{18} O of the dissolved SO₄ at the crater lake water surface and at different depths, with an average δ^{18} O for SO₄ of 21.9 ‰. This means the δ^{18} O of the SO₄ in the gypsum stalactite reflects the $\delta^{18}O$ for the dissolved SO₄ in crater lake, which shows strong magmatic input given that the source of SO_4 in the lake comes from degassing magma. This is reflected in the strong enrichment in $\delta^{18}O$ composition in SO₄ of crater lake, which exceeds the $\delta^{18}O$ of crystalline water, groundwater and magmatic water. The δ^{18} O for SO₄ in the gypsum stalactic is comparable to the δ^{18} O for the crater lake SO₄. Thus the δ^{18} O composition of the crater lake SO₄ and H₂O is preserved in gypsum, as the δ^{18} O of both the composition of crystalline water from the gypsum stalactite and cement also have isotopically heavy oxygen signatures. This is consistent with findings from Sofer 1978, who concluded that the gypsum δ^{18} O composition reflects the δ^{18} O of the parent fluids. Furthermore, Gonfiantini and Fontes 1963 shows that there is no evidence for δ^{18} O isotopic exchange between sulfate and crystalline water in gypsum, making re-equilibration of ¹⁸O within the gypsum structure unlikely. Therefore it is possible to derive the original $\delta^{18}O$ composition of the brine from the sulfate and crystalline water of gypsum, given the required fractionation factors between gypsum and water for SO_4 and H_2O .

The calculated fraction factors (α) for the 2009 gypsum stalactite (Table 3.2) using the δ^{18} O values for water and sulfate in the lake brine from Delmelle et al. 2000, show that gypsum incorporates an isotopically light δ^{18} O signature compared to the brine for both SO₄ and H₂O (Figure 3.1b). No fractionation factors have been previously reported for SO₄, but the value we obtain for H_2O is inconsistent with experimental data from Gonfiantini and Fontes 1963, who found gypsum to be isotopically heavy by 3‰. There are a number of possible explanations for this discrepancy: 1) The isotopic composition of the fluid in 2009 could be different from that in 1993-1996, although a δ^{18} O for lake H₂O in 2008 of +7.8% (Palmer 2009) makes this unlikely; 2) An analytical issue introduced by using δ^{18} O fluid values from the literature rather than analyzing these using the same methods and analytical instruments as for the solid samples; 3) The highly concentrated nature of the Kawah Ijen crater lake water reduces the fractionation factor compared to the simplified compositional system used in the experiments (see Chacko et al. 2001). For lack of the $\delta^{18}O$ isotopic composition of the 2009 lake water, we cannot investigate this further. However, this does not affect our ability to calculate the isotopic composition of the 1817 lake waters, because the alpha factors cancel out in this calculation.

Temperature calculations of the δ^{18} O of the reconstructed brine is based on the geothermometer equation by Seal et al. (2000), which is based on a revision of the equation derived by Lloyd (1968) and Mizutani and Rafter (1969). The temperature calculated from the averaged 1993-1996 ¹⁸O composition of the brine from Delmelle et al. (2000) is 145°C. This temperature is significantly lower than the temperature of last equilibration for the volcanic gases in Kawah Ijen's fumaroles (400 °C, Van Hinsberg et al. (2015)) and higher than the 40°C lake temperature. We interpret the 145°C δ^{18} O temperature to reflect the interaction between hot magmatic vapours from subaqueous fumaroles and the colder lake water (Figure 3.1c). As such, this temperature likely does not correspond to a reservoir at this temperature, neither in the lake nor in the hydrothermal system. It is worth noting

that this temperature exceeds the melting temperature of sulfur (116 °C), which potentially promotes the growth of sulfur pools on the lake bottom to act as a seal on the volcano's conduit (Takano et al. 1994). The seal would then prevent subsequent heat and gas release, resulting in pressurization of the shallow hydrothermal system, thus increasing the volcano's propensity for phreatic activity. Given the temperature range from the 1817 eruption also exceeds sulfur's melting temperature, this scenario is plausible during the early stages of the 1817 eruption. Although this makes the absolute temperature derived meaningless for direct volcanics monitoring purposes, relative variations in temperature will track changes in the temperature and/or amount of volcanic gas entering the lake, especially during periods of unrest and/or an eruption. The reconstructed δ^{18} O composition of the water from the lake brine prior to the 1817 eruption is comparable to the δ^{18} O measured in 1993-1996. Its SO₄ δ^{18} O is however 3 % lighter. This corresponds to a temperature of 182-188°C, which is significantly higher than in the 1993-1996 period (see Table 3.4). Given that the $\delta^{18}O$ of the water is strongly influenced by evaporation but this value was identical, and that SO_4 is derived from magmatic degassing, this indicates that there is increased input of hot magmatic gas into the lake to produce this temperature change. The increase in volcanic gas input, or its temperature, must have been significant because the brine temperature between 1993-1996 only varies between 130-150 °C, despite this period being characterized by elevated phreatic activity (Caudron et al. 2015a). Hence, by using the temperature change derived from the reconstructed $\delta^{18}O$ composition of SO₄ and H₂O in gypsum, we can construct a thermal record at Kawah Ijen volcano, identifying periods of increased input of magmatic gas that could have triggered unrest and/or eruption.

3.6 Implications

We have shown that gypsum records the oxygen isotopic disequilibrium in its parent fluid in the sulfate and crystalline water of its mineral structure. Gypsum is isotopically light for both water and sulfate, although it cannot be excluded that this is an artefact of the data sources used. Nonetheless, we can use these apparent fractionation factors for sulfate and water between gypsum and brine to reconstruct the original brine's isotopic composition. Applied to gypsum precipitating from the Kawah Ijen crater lake in Indonesia, we have been able to reconstruct its lake water isotopic composition for 1817. As in the 1993-1996 period, SO_4 and H_2O are found to be in isotopic disequilibrium. The temperature derived from this disequilibrium is 130-150°C for 1993-1996 and 182-188 °C for 1817. The significantly higher in temperature in 1817 compared to 1993-1996 suggests an increase in magmatic gases input into the lake, or in gas temperature. Such a change in the gas input would be detectable and this shows the promise of gypsum as a potential geothermometer to inform monitoring efforts at Kawah Ijen and at similar volcanic lakes. More generally, we have established gypsum as a recorder of the isotopic composition of both the sulfate and water of its parent solution, and gypsum's abundance in the geological record means that this tool can be applied to a wide variety of geological environments.

3.7 Acknowledgements

Thanks to Jean-François Hélie (UQAM) and William Mark (University of Waterloo) for $\delta^{18}O$ analyses. Thanks also go to Corentin Caudron and the participants of the Cities on Volcanoes 8 Wet Volcanoes workshop for discussion on the Kawah Ijen system and assistance in fieldwork. This project was funded by the McGill University Graduate Mobility Award 2014, Mineralogical Association of Canada Travel Grant 2014 and Cities on Volcanoes 8 Travel Grant 2014 to SBU, and grants received to VvH and BG from the National Science and Engineering Research Council (NSERC) and le Fond Québecois de la Récherche sur la Nature et les Technologies (FQRNT).

3.8 List of Figure caption

Figure 1: A) top of the gypsum plateau, with stalactites growing on overhangs. B) A typical gypsum stalactite recording the oxygen isotopic disequilibrium between the sulfate and water from its parent fluids. C) The pathway (dashed line with circles) that the SO₄ and H₂O molecules take from the magmatic-hydrothermal system to the gypsum plateau as reflected in the δ^{18} O composition.

3.9 List of Table captions

Table 1: δ^{18} O compositions of gypsum stalactites, brine and gypsum-cemented fall deposit.

Table 2: Calculated α values of gypsum and spring brine with uncertainty set at 1 sigma.

Table 3: Reconstructed brine δ^{18} O composition for the 1817 lake water.

Table 4: Derived temperatures from the reconstructed brine compositions. Temperatures are derived using the revised geothermometer derived by (Seal et al. 2000), after (Mizutani and Rafter 1969) and (Lloyd 1968).



(c) Magmatic hydrothermal system of Kawah Ijen volcano with SO_4 and H_2O pathway

Figure 3.1: A) Top of the gypsum plateau, with stalactites growing on overhangs. B) A typical gypsum stalactite recording the oxygen isotopic disequilibrium between the sulfate and water from its parent fluids. C) The pathway (dashed line with circles) that the SO₄ and H₂O molecules take from the magmatic-hydrothermal system to the gypsum plateau as reflected in the δ^{18} O composition.

3.10 List of Tables

Table 3.1: Table of $\delta^{18}{\rm O}$ compositions of gypsum stalactites, brine and gypsum-cemented fall deposit.

| Sample | Type | $\delta^{18}\mathcal{O}_{H_2O}$ | 1σ | $\delta^{18}\mathcal{O}_{SO_4}$ | 1σ |
|---|---|---------------------------------|----------------|---------------------------------|------|
| Gypsum stalactite KV09-505 KV09-505-TIP | crystalline water dehydrated gypsum | 3.44 | 0.05 | 20.88 | 0.25 |
| Gypsum-cemented KS14-H2O-OX4 KS14-H2O-OX5 KS14-001-DEOX2 | fall deposit crystalline water crystalline water gypsum cement | $3.59 \\ 2.64$ | $0.05 \\ 0.05$ | 17.34 | 0.25 |
| KS14-001-DEOX3 | gypsum cement | | | 16.81 | 0.25 |

Table 3.2: Calculated α values of gypsum and spring brine with uncertainty set at 1σ

| | lpha | 1σ |
|----------------------------------|-------|-----------|
| H_2O_{brine} - H_2O_{gypsum} | 0.996 | 0.02 |
| SO_{4brine} - $SO_{4gypsum}$ | 0.999 | 0.01 |

| Sample | Brine year | $\delta^{18}\mathcal{O}_{H_2O}$ | 1σ | $\delta^{18}\mathrm{O}_{SO_4}$ | 1σ |
|-----------------|------------|---------------------------------|-----------|--------------------------------|-----------|
| KS14-001 (min.) | 1817 | 7.9 | 0.2 | 17.8 | 0.3 |
| KS14-001 (max.) | 1817 | 8.9 | 0.2 | 18.4 | 0.3 |

Table 3.3: Reconstructed brine δ^{18} O composition for the 1817 lake water.

Table 3.4: Table of derived temperatures from the reconstructed brine compositions. Temperatures are derived using the revised geothermometer derived by (Seal et al. 2000), after (Mizutani and Rafter 1969) and (Lloyd 1968).

| Sample | Brine year | Temperature (°C) |
|----------|------------|------------------|
| KV09-505 | 2009 | 141 |
| KS14-001 | 1817 | 182 |
| KS14-001 | 1817 | 188 |

References

- Bosch, C. (1858). "Uitbarstingen der vulkanen Idjin en Raun (Banjoewangi)". *Tijdschrift* voor Indische Taal-, Land- en Volkenkunde 7, pp. 265–286.
- Caudron, C., D. K. Syahbana, T. Lecocq, V. Van Hinsberg, W. McCausland, A. Triantafyllou, T. Camelbeeck, A. Bernard, et al. (2015a). "Kawah Ijen volcanic activity: a review". *Bulletin of Volcanology* 77.3, pp. 1–39.
- Chacko, T., D. R. Cole, and J. Horita (2001). "Equilibrium oxygen, hydrogen and carbon isotope fractionation factors applicable to geologic systems". *Reviews in mineralogy and* geochemistry 43.1, pp. 1–81.
- Chiba, H. and H. Sakai (1985). "Oxygen isotope exchange rate between dissolved sulfate and water at hydrothermal temperatures". *Geochimica et Cosmochimica Acta* 49.4, pp. 993– 1000.
- Delmelle, P., A. Bernard, M. Kusakabe, T. Fischer, and B. Takano (2000). "Geochemistry of the magmatic-hydrothermal system of Kawah Ijen volcano, East Java, Indonesia". *Journal of Volcanology and Geothermal research* 97.1, pp. 31–53.
- Fourel, F., F. Martineau, C. Lécuyer, H.-J. Kupka, L. Lange, C. Ojeimi, and M. Seed (2011). "18O/16O ratio measurements of inorganic and organic materials by elemental analysis– pyrolysis–isotope ratio mass spectrometry continuous-flow techniques". *Rapid Commu*nications in Mass Spectrometry 25.19, pp. 2691–2696.
- Fowler, A., L. Hackett, and C. Klein (2013). "Reformulation and Performance Evaluation of the Sulfate-Water Oxygen Isotope Geothermometer". *GRC Transaction* 37.
- Gonfiantini, R and J. C. Fontes (1963). "Oxygen isotopic fractionation in the water of crystallization of gypsum". *Nature* 200.
- Lloyd, R. (1968). "Oxygen isotope behavior in the sulfate-water system". Journal of Geophysical Research 73.18, pp. 6099–6110.
- Martinez, M, E Fernández, J Valdés, V Barboza, R Van der Laat, E Duarte, E Malavassi, L Sandoval, J Barquero, and T Marino (2000). "Chemical evolution and volcanic activity

of the active crater lake of Poás volcano, Costa Rica, 1993–1997". Journal of Volcanology and Geothermal Research 97.1, pp. 127–141.

- McKenzie, W. F. and A. Truesdell (1977). "Geothermal reservoir temperatures estimated from the oxygen isotope compositions of dissolved sulfate and water from hot springs and shallow drillholes". *Geothermics* 5.1, pp. 51–61.
- Mizutani, Y and T. Rafter (1969). OXYGEN ISOTOPIC COMPOSITION OF SULPHATES. PART 3. OXYGEN ISOTOPIC FRACTIONATION IN THE BISULPHATE ION-WATER SYSTEM. Tech. rep. Inst. of Nuclear Sciences, Lower Hutt, NZ.
- Palmer, S. C. (2009). "Hydrogeochemistry of the upper Banyu Pahit River valley, Kawah Ijen volcano, Indonesia". MA thesis. McGill University.
- Rowe Jr, G. L. (1994). "Oxygen, hydrogen, and sulfur isotope systematics of the crater lake system of Poas Volcano, Costa Rica." *Geochemical Journal* 28.3, pp. 263–287.
- Schröder, S, A Bekker, N. Beukes, H Strauss, and H. Van Niekerk (2008). "Rise in seawater sulphate concentration associated with the Paleoproterozoic positive carbon isotope excursion: evidence from sulphate evaporites in the 2.2–2.1 Gyr shallow-marine Lucknow Formation, South Africa". Terra Nova 20.2, pp. 108–117.
- Seal, R. R., C. N. Alpers, and R. O. Rye (2000). "Stable isotope systematics of sulfate minerals". *Reviews in Mineralogy and Geochemistry* 40.1, pp. 541–602.
- Sofer, Z. (1978). "Isotopic composition of hydration water in gypsum". Geochimica et Cosmochimica Acta 42.8, pp. 1141–1149.
- Takano, B., H. Saitoh, and E. Takano (1994). "Geochemical implications of subaqueous molten sulfur at Yugama crater lake, Kusatsu-Shirane volcano, Japan." *Geochemical Journal* 28.3, pp. 199–216.
- Tour, J. Leschenault de la (1811). "Notice sur un lac d'acide sulfurique qui se trouve au fond d'un volcan du Mont-Idienne, situé dans la province de Bagnia-Vangni, côté de l'ile de Java." Am. Musm Hist. Nat 18, pp. 425–446.

- Van Hinsberg, V. J., N Vigouroux, S. C. Palmer, K. Berlo, S. Scher, G. Mauri, A. E. Williams-Jones, J. McKenzie, G. Williams-Jones, and T. Fischer (2015). "Element flux to the environment of the passively degassing Kawah Ijen volcano, Indonesia, and implications for estimates of the global volcanic flux". Special Issue on Volcanic Lakes.
- Varekamp, J. and R Kreulen (2000). "The stable isotope geochemistry of volcanic lakes, with examples from Indonesia". Journal of volcanology and geothermal research 97.1, pp. 309– 327.

Chapter 4

General Summary and Conclusions

Monitoring the crater lake chemistry at Kawah Ijen volcano can potentially be used to identify precursor geochemical signals of volcanic unrest. However, the lack of data on past lake chemistry mean that there is a severely limited record of past signals that can be used to inform current monitoring efforts. Moreover, the limited crater lake chemistry record does not allow for the integration of geochemical signals from the crater lake with other monitoring records (e.g. seismicity and lake temperature). In this research, I have shown that it is possible to use growth-zoned gypsum, precipitating from lake water seepage on the western flank of Kawah Ijen, as a mineralogical tool to reconstruct a near continuous record of past lake chemistry, which can complement the current lake chemistry record. The trace element content of gypsum has been shown to record historical variations in input fluxes into the lake from rock dissolution and magmatic input. Gypsum also records key information in its oxygen isotopic composition, where it preserves isotopic disequilibrium within its sulfate and crystalline water. This disequilibrium can be used to reconstruct the original isotopic composition of the parent fluids, and from this derive a H_2O -SO₄ disequilibrium temperature. Changes in disequilibrium temperature primarily indicate variations in magmatic gas input. With a detailed geochemical record provided by gypsum, and by integrating this with the existing seismic and thermal records, we can identify precursor signals of unrest and eruption at the volcano, and link these signals to processes occurring in the magmatic-hydrothermal system.

In manuscript 1 (Chapter 2), a growth-zoned gypsum stalactite from Kawah Ijen volcano was shown to record 50 years of lake chemistry. Using Rb-corrected trace element records, it was possible to track inputs from the degassing magma and rock dissolution fluxes, represented in volatile metals and rock dissolution elements, respectively. Rock dissolution element ratios (Mg/Rb, $\Sigma REE/Rb$) records seasonal variability and rock falls and slides into the lake. The volatile metals records input from the deep (Cu/Rb) and shallow magma (Tl/Rb, Sb/Rb), as well as the relative input from both magma reservoirs (Tl/Cu). Peaks in these records preceded periods of volcanic unrest, and also preceded or were coeval with seismicity and thermal fluctuations. The transition metals (Zn/Rb and Pb/Rb) combined both input fluxes, although the rock dissolution flux dominates the input. An exception to this is in the Pb/Rb record, which could record changes in barite saturation or leaded gasoline input, although more work is needed to constrain the Pb source reservoirs further. The same ratios were used to evaluate the lake chemistry prior to the 1817 eruption from gypsum cement found in the 1817 fall deposit. The Tl/Cu and Cu/Rb ratio both point to highly elevated input from the deep seated magma. The peaks in the Tl/Cu and Tl/Rb record from the last 50 years were minor compared to the 1817 values, indicating not only the massive input from the deep magma that occurred prior to this, but also that the escalation to such an event should be conspicuous in the lake chemistry. The gypsum record shows that variations in lake chemistry reflects volcanic activity, and that the element ratios Tl/Rb, Cu/Rb, and Tl/Cu are most sensitive to volcanic activity. Monitoring of lake water chemistry at Kawah Ijen should therefore focus on these element ratios, and can use the envelop of background variability established from the gypsum record to define the threshold values to trigger warnings. This gypsum-based approach can be applied to other active volcanoes to identify their geochemical signals of unrest, as well as any other setting, natural or industrial where gypsum precipitates.

In manuscript 2 (Chapter 3), the δ^{18} O composition of gypsum is shown to preserve the δ^{18} O of the SO₄ and H₂O in the crater lake water, both of which show strong enrichment in the heavy ¹⁸O isotope pointing to a magmatic source of the oxygen. Gypsum also preserves the isotopic disequilibrium between the SO₄ and H₂O in the crater lake water. Hence, by deriving the fractionation factors (α) it was possible to reconstruct the δ^{18} O of the parent brine from gypsum δ^{18} O composition. This disequilibrium is temperature-dependent and can be used as a geothermometer. Temperatures for the period 1993 to 1996 show minimal variation from 130 to 150°C, despite numerous phreatic events occurring during this time. In contrast gypsum-reconstructed crater lake prior to the phreatomagmatic 1817 eruption of Kawah Ijen records a much higher temperature (180-188°C). This indicates a significant magmatic gas or thermal input into the lake from subaqueous fumaroles in excellent agreement with trace element data, which was likely reflected in subaerial fumaroles and lake temperature, monitoring of which is presently being considered.

I have shown that gypsum as a mineralogical tool yields a wealth of geochemical information on the Kawah Ijen system from chemistry to temperature. This approach can be extended to other volcanoes, as well as other environments where gypsum forms, for example gypsum stalactites found in caves, gypsum depositing from industrial effluent, and even gypsum on other planets. More directly, the volatile metals have been identified as most sensitive as markers of pending unrest, and this can be expected to be true for other volcanic systems. Although the approach has proven highly successful, a range of questions remains and more work is needed to explore the tool, as well as the Kawah Ijen system further. For example it has yet to be determined how to pinpoint the source for the transition metals or establish proportions of rock dissolution and magmatic gas input for to their concentrations. Additionally the absolute temperature derived from δ^{18} O disequilibrium does not appear to represent the magmatic-hydrothermal system and more work is needed to understand what this temperature means. More work is needed to explain trends in Pb concentrations to determine whether gypsum records leaded gasoline emissions or barite saturation. Moreover, experiments are needed to constrain the partitioning of elements between gypsum and brine. Finally the record of activity at Kawah Ijen could be extended even further back in time using different dating systems, as lake-precipitated gypsum and barite have been identified in older phreatic deposits.

Bibliography

- Berlo, K, V. van Hinsberg, N Vigouroux, J. Gagnon, and A. Williams-Jones (2014). "Sulfide breakdown controls metal signature in volcanic gas at Kawah Ijen volcano, Indonesia". *Chemical Geology* 371, pp. 115–127.
- Bigham, J. and D. K. Nordstrom (2000). "Iron and aluminum hydroxysulfates from acid sulfate waters". *Reviews in mineralogy and geochemistry* 40.1, pp. 351–403.
- Blättler, C. L., G. M. Henderson, and H. C. Jenkyns (2012). "Explaining the Phanerozoic Ca isotope history of seawater". *Geology* 40.9, pp. 843–846.
- Bobst, A. L., T. K. Lowenstein, T. E. Jordan, L. V. Godfrey, T.-L. Ku, and S. Luo (2001).
 "A 106ka paleoclimate record from drill core of the Salar de Atacama, northern Chile".
 Palaeogeography, Palaeoclimatology, Palaeoecology 173.1, pp. 21–42.
- Bosch, C. (1858). "Uitbarstingen der vulkanen Idjin en Raun (Banjoewangi)". *Tijdschrift* voor Indische Taal-, Land- en Volkenkunde 7, pp. 265–286.
- Bourdon, B., S. Turner, G. M. Henderson, and C. C. Lundstrom (2003). "Introduction to U-series geochemistry". *Reviews in Mineralogy and Geochemistry* 52.1, pp. 1–21.
- Bryan, C. and S Sherburn (1999). "Seismicity associated with the 1995–1996 eruptions of Ruapehu volcano, New Zealand: narrative and insights into physical processes". Journal of Volcanology and Geothermal Research 90.1, pp. 1–18.
- Cánovas, C., M Olías, J. Nieto, and L Galván (2010). "Wash-out processes of evaporitic sulfate salts in the Tinto river: hydrogeochemical evolution and environmental impact". *Applied Geochemistry* 25.2, pp. 288–301.

- Caudron, C., D. K. Syahbana, T. Lecocq, V. Van Hinsberg, W. McCausland, A. Triantafyllou, T. Camelbeeck, A. Bernard, et al. (2015a). "Kawah Ijen volcanic activity: a review". *Bulletin of Volcanology* 77.3, pp. 1–39.
- Caudron, C., T. Lecocq, D. K. Syahbana, W. McCausland, A. Watlet, T. Camelbeeck, and A. Bernard (2015b). "Stress and mass changes at a'wet'volcano: example during the 2011–2012 volcanic unrest at Kawah Ijen volcano (Indonesia)". Journal of Geophysical Research: Solid Earth.
- Chacko, T., D. R. Cole, and J. Horita (2001). "Equilibrium oxygen, hydrogen and carbon isotope fractionation factors applicable to geologic systems". *Reviews in mineralogy and* geochemistry 43.1, pp. 1–81.
- Chesner, C. A. (2012). "The Toba caldera complex". *Quaternary International* 258, pp. 5–18.
- Chiba, H. and H. Sakai (1985). "Oxygen isotope exchange rate between dissolved sulfate and water at hydrothermal temperatures". *Geochimica et Cosmochimica Acta* 49.4, pp. 993– 1000.
- Christenson, B. (2000). "Geochemistry of fluids associated with the 1995–1996 eruption of Mt. Ruapehu, New Zealand: signatures and processes in the magmatic-hydrothermal system". Journal of Volcanology and Geothermal Research 97.1, pp. 1–30.
- Christenson, B., A. Reyes, R Young, A Moebis, S Sherburn, J Cole-Baker, and K Britten (2010). "Cyclic processes and factors leading to phreatic eruption events: Insights from the 25 September 2007 eruption through Ruapehu Crater Lake, New Zealand". Journal of Volcanology and Geothermal Research 191.1, pp. 15–32.
- Condomines, M., O Sigmarsson, and P. Gauthier (2010). "A simple model of 222 Rn accumulation leading to 210 Pb excesses in volcanic rocks". *Earth and Planetary Science Letters* 293.3, pp. 331–338.

- Cronin, S. J. and D. S. Sharp (2002). "Environmental impacts on health from continuous volcanic activity at Yasur (Tanna) and Ambrym, Vanuatu". International Journal of Environmental Health Research 12.2, pp. 109–123.
- Cronin, S. J., M. Hedley, R. Smith, and V. Neall (1997). "Impact of Ruapehu ash fall on soil and pasture nutrient status 1. October 1995 eruptions". New Zealand Journal of Agricultural Research 40.3, pp. 383–395.
- Cronin, S. J., V. Neall, J. Lecointre, M. Hedley, and P Loganathan (2003). "Environmental hazards of fluoride in volcanic ash: a case study from Ruapehu volcano, New Zealand". *Journal of Volcanology and Geothermal Research* 121.3, pp. 271–291.
- Cronin, S., M. Hedley, V. Neall, and R. Smith (1998). "Agronomic impact of tephra fallout from the 1995 and 1996 Ruapehu Volcano eruptions, New Zealand". *Environmental Geology* 34.1, pp. 21–30.
- D'Alessandro, W (2006). "Human fluorosis related to volcanic activity: a review". Environmental Toxicology. 1, pp. 21–30.
- Davidson, J. P. and F. J. Tepley (1997). "Recharge in volcanic systems: evidence from isotope profiles of phenocrysts". *Science* 275.5301, pp. 826–829.
- Delmelle, P. and A Bernard (2000). "Downstream composition changes of acidic volcanic waters discharged into the Banyupahit stream, Ijen caldera, Indonesia". Journal of volcanology and geothermal research 97.1, pp. 55–75.
- Delmelle, P. and A. Bernard (1994). "Geochemistry, mineralogy, and chemical modeling of the acid crater lake of Kawah Ijen Volcano, Indonesia". *Geochimica et cosmochimica acta* 58.11, pp. 2445–2460.
- Delmelle, P., A. Bernard, M. Kusakabe, T. Fischer, and B. Takano (2000). "Geochemistry of the magmatic-hydrothermal system of Kawah Ijen volcano, East Java, Indonesia". *Journal of Volcanology and Geothermal research* 97.1, pp. 31–53.
- Farkaš, J., F. Böhm, K. Wallmann, J. Blenkinsop, A. Eisenhauer, R. Van Geldern, A. Munnecke, S. Voigt, and J. Veizer (2007). "Calcium isotope record of Phanerozoic oceans:

Implications for chemical evolution of seawater and its causative mechanisms". *Geochim*ica et Cosmochimica Acta 71.21, pp. 5117–5134.

- Fourel, F., F. Martineau, C. Lécuyer, H.-J. Kupka, L. Lange, C. Ojeimi, and M. Seed (2011). "18O/16O ratio measurements of inorganic and organic materials by elemental analysis– pyrolysis–isotope ratio mass spectrometry continuous-flow techniques". *Rapid Communications in Mass Spectrometry* 25.19, pp. 2691–2696.
- Fowler, A., L. Hackett, and C. Klein (2013). "Reformulation and Performance Evaluation of the Sulfate-Water Oxygen Isotope Geothermometer". GRC Transaction 37.
- Gamble, J., C. Wood, R. Price, I. Smith, R. Stewart, and T Waight (1999). "A fifty year perspective of magmatic evolution on Ruapehu Volcano, New Zealand: verification of open system behaviour in an arc volcano". *Earth and Planetary Science Letters* 170.3, pp. 301–314.
- García-Ruiz, J. M., R. Villasuso, C. Ayora, A. Canals, and F. Otálora (2007). "Formation of natural gypsum megacrystals in Naica, Mexico". *Geology* 35.4, pp. 327–330.
- Gendrin, A., N. Mangold, J.-P. Bibring, Y. Langevin, B. Gondet, F. Poulet, G. Bonello, C. Quantin, J. Mustard, R. Arvidson, et al. (2005). "Sulfates in Martian layered terrains: the OMEGA/Mars Express view". *Science* 307.5715, pp. 1587–1591.
- Ghaleb, B. (2009). "Overview of the methods for the measurement and interpretation of short-lived radioisotopes and their limits". In: *IOP Conference Series: Earth and Environmental Science*. Vol. 5. 1. IOP Publishing, p. 012007.
- Gonfiantini, R and J. C. Fontes (1963). "Oxygen isotopic fractionation in the water of crystallization of gypsum". *Nature* 200.
- Hagemann, S. G., M. Gebre-Mariam, and D. I. Groves (1994). "Surface-water influx in shallow-level Archean lode-gold deposits in Western, Australia". *Geology* 22.12, pp. 1067– 1070.
- Handley, H., C. Macpherson, J. Davidson, K Berlo, and D Lowry (2007). "Constraining fluid and sediment contributions to subduction-related magmatism in Indonesia: Ijen Volcanic Complex". Journal of Petrology 48.6, pp. 1155–1183.
- Hardie, L. A. (1996). "Secular variation in seawater chemistry: An explanation for the coupled secular variation in the mineralogies of marine limestones and potash evaporites over the past 600 my". Geology 24.3, pp. 279–283.
- Hardie, L. A. and H. P. Eugster (1980). "Evaporation of seawater: calculated mineral sequences". Science 208.4443, pp. 498–500.
- Hinsberg, V. van, K. Berlo, M. van Bergen, and A. Williams-Jones (2010a). "Extreme alteration by hyperacidic brines at Kawah Ijen volcano, East Java, Indonesia: I. Textural and mineralogical imprint". Journal of Volcanology and geothermal Research 198.1, pp. 253– 263.
- Hinsberg, V. van, K. Berlo, S. Sumarti, M. Van Bergen, and A. Williams-Jones (2010b).
 "Extreme alteration by hyperacidic brines at Kawah Ijen volcano, East Java, Indonesia: II: Metasomatic imprint and element fluxes". Journal of Volcanology and Geothermal Research 196.3, pp. 169–184.
- Hinsberg, V. van, A. Williams-Jones, G Mauri, N Vigouroux, G Williams-Jones, J McKenzie, S Palmer, and A Nasution (2008). "Studying the Kawah Ijen volcano-hydrothermal system-merits of an interdisciplinary approach". IAVCEI, Reykjavik, Iceland, Abstract.
- Johnson, G. and G. Olhoeft (1984). "Density of rocks and minerals". CRC Handbook of Physical Properties of Rocks 3, pp. 1–38.
- Junghuhn, F. (1853). In: Java, deszelfs gedaante, bekleeding en inwendinge structuur. Ed. byP. van Kampen. Vol. 1-4. Amsterdam.
- Kawano, M. and K. Tomita (2001). "Geochemical modeling of bacterially induced mineralization of schwertmannite and jarosite in sulfuric acid spring water". American Mineralogist 86.10, pp. 1156–1165.

- Kemmerling, G. (1921). De geologie en geomorpologie van den Idjen en analyse van merkwaardige watersoorten op het Idjen hoogland.
- Kendall, C. G. S. C. and W. Schlager (1981). "Carbonates and relative changes in sea level". Marine Geology 44.1, pp. 181–212.
- Kent, A. J., C. Darr, A. M. Koleszar, M. J. Salisbury, and K. M. Cooper (2010). "Preferential eruption of andesitic magmas through recharge filtering". *Nature Geoscience* 3.9, pp. 631– 636.
- Kilgour, G, V Manville, F Della Pasqua, A Graettinger, K. Hodgson, and G. Jolly (2010). "The 25 September 2007 eruption of Mount Ruapehu, New Zealand: directed ballistics, surtseyan jets, and ice-slurry lahars". Journal of Volcanology and Geothermal Research 191.1, pp. 1–14.
- Kling, G. W., M. A. Clark, G. N. WAGNER, H. R. COMPTON, A. M. HUMPHREY, J. D. DEVINE, W. C. EVANS, J. P. Lockwood, M. L. Tuttle, and E. J. KOENIGSBERG (1987). "The 1986 Lake Nyos gas disaster in Cameroon, West Africa". *Science* 236.4798, pp. 169–175.
- Kusakabe, M., T. Ohsumi, and S. Aramaki (1989). "The Lake Nyos gas disaster: chemical and isotopic evidence in waters and dissolved gases from three Cameroonian crater lakes, Nyos, Monoun and Wum". Journal of volcanology and geothermal research 39.2, pp. 167– 185.
- Lee, J.-M., E. A. Boyle, I. S. Nurhati, M. Pfeiffer, A. J. Meltzner, and B. Suwargadi (2014). "Coral-based history of lead and lead isotopes of the surface Indian Ocean since the mid-20th century". *Earth and Planetary Science Letters* 398, pp. 37–47.
- Lelieveld, J. o., P. Crutzen, V Ramanathan, M. Andreae, C. Brenninkmeijer, T Campos, G. Cass, R. Dickerson, H Fischer, J. De Gouw, et al. (2001). "The Indian Ocean experiment: widespread air pollution from South and Southeast Asia". Science 291.5506, pp. 1031–1036.

- Li, J., T. K. Lowenstein, and I. R. Blackburn (1997). "Responses of evaporite mineralogy to inflow water sources and climate during the past 100 ky in Death Valley, California". *Geological Society of America Bulletin* 109.10, pp. 1361–1371.
- Lloyd, R. (1968). "Oxygen isotope behavior in the sulfate-water system". Journal of Geophysical Research 73.18, pp. 6099–6110.
- Löhr, A., T. Bogaard, A. Heikens, M. Hendriks, S. Sumarti, M. Van Bergen, K. C. Van Gestel, N. Van Straalen, P. Vroon, and B. Widianarko (2005). "Natural Pollution Caused by the Extremely Acid Crater Lake Kawah Ijen, East Java, Indonesia (7 pp)". *Environmental Science and Pollution Research* 12.2, pp. 89–95.
- Löhr, A. J., T. De Kort, N. M. Van Straalen, and C. A. Van Gestel (2007). "Unraveling the causes of the toxicity of extremely acid waters of volcanic origin". *Environment international* 33.6, pp. 743–749.
- Madden, M. E., R. Bodnar, and J. Rimstidt (2004). "Jarosite as an indicator of water-limited chemical weathering on Mars". *Nature* 431.7010, pp. 821–823.
- Manga, M. and E. Brodsky (2006). "Seismic triggering of eruptions in the far field: volcanoes and geysers". Annu. Rev. Earth Planet. Sci 34, pp. 263–291.
- Manville, V (2015). "Volcano-hydrologic hazards from volcanic lakes". In: Volcanic Lakes. Springer, pp. 21–71.
- Marini, L., M. V. Zuccolini, and G. Saldi (2003). "The bimodal pH distribution of volcanic lake waters". Journal of volcanology and geothermal research 121.1, pp. 83–98.
- Martinez, M, E Fernández, J Valdés, V Barboza, R Van der Laat, E Duarte, E Malavassi, L Sandoval, J Barquero, and T Marino (2000). "Chemical evolution and volcanic activity of the active crater lake of Poás volcano, Costa Rica, 1993–1997". Journal of Volcanology and Geothermal Research 97.1, pp. 127–141.
- Mastin, L. and J. Witter (2000). "The hazards of eruptions through lakes and seawater". Journal of Volcanology and Geothermal Research 97.1, pp. 195–214.

- McKenzie, W. F. and A. Truesdell (1977). "Geothermal reservoir temperatures estimated from the oxygen isotope compositions of dissolved sulfate and water from hot springs and shallow drillholes". *Geothermics* 5.1, pp. 51–61.
- McLennan, S., J. Bell, W. Calvin, P. Christensen, B. Clark, P. De Souza, J Farmer, W. Farrand, D. Fike, R. Gellert, et al. (2005). "Provenance and diagenesis of the evaporite-bearing Burns formation, Meridiani Planum, Mars". *Earth and Planetary Science Letters* 240.1, pp. 95–121.
- Migdisov, A. A., A. Y. Bychkov, A. Williams-Jones, and V. van Hinsberg (2014). "A predictive model for the transport of copper by HCl-bearing water vapour in ore-forming magmatic-hydrothermal systems: Implications for copper porphyry ore formation". *Geochimica et Cosmochimica Acta* 129, pp. 33–53.
- Mizutani, Y and T. Rafter (1969). OXYGEN ISOTOPIC COMPOSITION OF SULPHATES. PART 3. OXYGEN ISOTOPIC FRACTIONATION IN THE BISULPHATE ION-WATER SYSTEM. Tech. rep. Inst. of Nuclear Sciences, Lower Hutt, NZ.
- Mulyana, A. and W. Effendi (2006). Peta kawasan rawan bencana gunungapi Ijen, Provinsi Jawa Timur Tahun 2006 Skala 1:100.000. Geological/Hazard Map.
- Nelson, C. H., C. R. Bacon, S. W. Robinson, D. P. Adam, J. P. Bradbury, J. H. BARBER, D. Schwartz, and G. Vagenas (1994). "The volcanic, sedimentologic, and paleolimnologic history of the Crater Lake caldera floor, Oregon: Evidence for small caldera evolution". *Geological Society of America Bulletin* 106.5, pp. 684–704.
- Nordstrom, D. K., C. N. Alpers, C. J. Ptacek, and D. W. Blowes (2000). "Negative pH and extremely acidic mine waters from Iron Mountain, California". *Environmental Science & Gamp; Technology* 34.2, pp. 254–258.
- Palmer, S. C. (2009). "Hydrogeochemistry of the upper Banyu Pahit River valley, Kawah Ijen volcano, Indonesia". MA thesis. McGill University.
- Palmer, S. C., V. J. Van Hinsberg, J. M. McKenzie, and S. Yee (2011). "Characterization of acid river dilution and associated trace element behavior through hydrogeochemical

modeling: A case study of the Banyu Pahit River in East Java, Indonesia". *Applied Geochemistry* 26.11, pp. 1802–1810.

- Paton, C., J. Hellstrom, B. Paul, J. Woodhead, and J. Hergt (2011). "Iolite: Freeware for the visualisation and processing of mass spectrometric data". *Journal of Analytical Atomic Spectrometry* 26.12, pp. 2508–2518.
- Pitre, F. and D. L. Pinti (2010). "Noble gas enrichments in porewater of estuarine sediments and their effect on the estimation of net denitrification rates". *Geochimica et Cosmochimica Acta* 74.2, pp. 531–539.
- Reed, M. H. (1997). "Hydrothermal alteration and its relationship to ore fluid composition". Geochemistry of hydrothermal ore deposits 3, pp. 303–365.
- Rotterdam-Los, A. van, S. Vriend, M. van Bergen, and P. van Gaans (2008). "The effect of naturally acidified irrigation water on agricultural volcanic soils. The case of Asembagus, Java, Indonesia". Journal of Geochemical Exploration 96.1, pp. 53–68.
- Rouwet, D, Y Taran, S Inguaggiato, N Varley, and J. S. Santiago (2008). "Hydrochemical dynamics of the "lake-spring" system in the crater of El Chichón volcano (Chiapas, Mexico)". Journal of Volcanology and Geothermal Research 178.2, pp. 237–248.
- Rouwet, D., F. Tassi, R. Mora-Amador, L. Sandri, and V. Chiarini (2014). "Past, present and future of volcanic lake monitoring". *Journal of volcanology and geothermal research* 272, pp. 78–97.
- Rowe, G. L., S. L. Brantley, M. Fernandez, J. F. Fernandez, A. Borgia, and J. Barquero (1992). "Fluid-volcano interaction in an active stratovolcano: the crater lake system of Poás volcano, Costa Rica". Journal of Volcanology and Geothermal Research 49.1, pp. 23– 51.
- Rowe, G. L., S. L. Brantley, J. F. Fernandez, and A. Borgia (1995). "The chemical and hydrologic structure of Poa's Volcano, Costa Rica". Journal of Volcanology and Geothermal Research 64.3, pp. 233–267.

- Rowe Jr, G. L. (1994). "Oxygen, hydrogen, and sulfur isotope systematics of the crater lake system of Poas Volcano, Costa Rica." *Geochemical Journal* 28.3, pp. 263–287.
- Rutherford, P., M. Dudas, and R. Samek (1994). "Environmental impacts of phosphogypsum". Science of the total environment 149.1, pp. 1–38.
- Schröder, S, A Bekker, N. Beukes, H Strauss, and H. Van Niekerk (2008). "Rise in seawater sulphate concentration associated with the Paleoproterozoic positive carbon isotope excursion: evidence from sulphate evaporites in the 2.2–2.1 Gyr shallow-marine Lucknow Formation, South Africa". Terra Nova 20.2, pp. 108–117.
- Scott, W. E. (1989). "Volcanic and related hazards". Volcanic Hazards, pp. 9–23.
- Seal, R. R., C. N. Alpers, and R. O. Rye (2000). "Stable isotope systematics of sulfate minerals". *Reviews in Mineralogy and Geochemistry* 40.1, pp. 541–602.
- Sellwood, B. and G. Price (1994). "Sedimentary facies as indicators of Mesozoic palaeoclimate". In: *Palaeoclimates and their modelling*. Springer, pp. 17–25.
- Sigurdsson, H., J. Devine, F. Tchua, F. Presser, M. Pringle, and W. C. Evans (1987). "Origin of the lethal gas burst from Lake Monoun, Cameroun". Journal of Volcanology and Geothermal Research 31.1, pp. 1–16.
- Sitorus, K. (1990). "Volcanic stratigraphy and geochemistry of the Idjen Caldera Complex, East-Java, Indonesia". PhD thesis. Victoria University of Wellington.
- Sofer, Z. (1978). "Isotopic composition of hydration water in gypsum". Geochimica et Cosmochimica Acta 42.8, pp. 1141–1149.
- Spencer, R. J. (2000). "Sulfate minerals in evaporite deposits". Reviews in Mineralogy and Geochemistry 40.1, pp. 173–192.
- Stoiber, R. E. and W. I. Rose (1974). "Fumarole incrustations at active Central American volcanoes". Geochimica et Cosmochimica Acta 38.4, pp. 495–516.
- Takano, B., K Suzuki, K Sugimori, T. Ohba, S. Fazlullin, A. Bernard, S. Sumarti, R Sukhyar, and M Hirabayashi (2004). "Bathymetric and geochemical investigation of Kawah Ijen

crater lake, east Java, Indonesia". *Journal of volcanology and geothermal research* 135.4, pp. 299–329.

- Takano, B., H. Saitoh, and E. Takano (1994). "Geochemical implications of subaqueous molten sulfur at Yugama crater lake, Kusatsu-Shirane volcano, Japan." *Geochemical Journal* 28.3, pp. 199–216.
- Tassi, F. and D. Rouwet (2014). "An overview of the structure, hazards, and methods of investigation of Nyos-type lakes from the geochemical perspective". *Journal of Limnology* 73.1.
- Tayibi, H., M. Choura, F. A. López, F. J. Alguacil, and A. López-Delgado (2009). "Environmental impact and management of phosphogypsum". *Journal of Environmental Management* 90.8, pp. 2377–2386.
- Tepley, F., J. Davidson, R. Tilling, and J. Arth (2000). "Magma mixing, recharge and eruption histories recorded in plagioclase phenocrysts from El Chichon Volcano, Mexico". *Journal of Petrology* 41.9, pp. 1397–1411.
- Tosca, N. J. and S. M. McLennan (2006). "Chemical divides and evaporite assemblages on Mars". Earth and Planetary Science Letters 241.1, pp. 21–31.
- Tosca, N. J., A. H. Knoll, and S. M. McLennan (2008). "Water activity and the challenge for life on early Mars". *Science* 320.5880, pp. 1204–1207.
- Tour, J. Leschenault de la (1811). "Notice sur un lac d'acide sulfurique qui se trouve au fond d'un volcan du Mont-Idienne, situé dans la province de Bagnia-Vangni, côté de l'ile de Java." Am. Musm Hist. Nat 18, pp. 425–446.
- Van Hinsberg, V. J. (2001). "Water-Rock Interaction and Element Fluxes in the Kawah Ijen Hyperacid Crater Lake and the Banyu Pait River, East Java, Indonesi". MA thesis. Utrecht University.
- Van Hinsberg, V. J., N Vigouroux, S. C. Palmer, K. Berlo, S. Scher, G. Mauri, A. E. Williams-Jones, J. McKenzie, G. Williams-Jones, and T. Fischer (2015). "Element flux to the

environment of the passively degassing Kawah Ijen volcano, Indonesia, and implications for estimates of the global volcanic flux". *Special Issue on Volcanic Lakes*.

- Varekamp, J. and R Kreulen (2000). "The stable isotope geochemistry of volcanic lakes, with examples from Indonesia". Journal of volcanology and geothermal research 97.1, pp. 309– 327.
- Varekamp, J., A. Ouimette, S. Herman, K. Flynn, A Bermudez, and D Delpino (2009). "Naturally acid waters from Copahue volcano, Argentina". Applied Geochemistry 24.2, pp. 208–220.
- Warren, J. K. (2010). "Evaporites through time: Tectonic, climatic and eustatic controls in marine and nonmarine deposits". *Earth-Science Reviews* 98.3, pp. 217–268.
- Waters, A. C. and R. V. Fisher (1971). "Base surges and their deposits: Capelinhos and Taal volcanoes". Journal of Geophysical Research 76.23, pp. 5596–5614.
- Williams-Jones, A. and A. Migdisov (2014). "Experimental Constraints on the Transport and Deposition of Metals in Ore-Forming Hydrothermal Systems".
- Zimbelman, D., R. O. Rye, and G. Breit (2005). "Origin of secondary sulfate minerals on active andesitic stratovolcanoes". *Chemical Geology* 215.1, pp. 37–60.

Appendix 1: Supplementary Information for Manuscript 1 (Chapter 2)

Summary of the trace element transect across growth zones A-D from stalactite KV09-501 growth zones. All concentrations are in ppm, except where indicated. '<d.l.' means the trace element composition is below the detection limit of the instrument. Hg concentrations are in counts per second (cps).

| | 0000 0000 0000 0000 0000 0000 0000 0000 0000 |
|---|---|
| Th Th 0.0011 0.0012 <td>0.1147 0.1167 0.1167 0.1167 0.0173 0.</td> | 0.1147 0.1167 0.1167 0.1167 0.0173 0. |
| A 4 14111111111111111111111111111111111 | 2011 2012 2012 2012 2012 2012 2012 2012 |
| Y 2010 200 | 1000 1000 1000 1000 1000 1000 1000 100 |
| | 888888888888888888888888888888888888888 |
| | 888888888888888888888888888888888888888 |
| | |
| | |
| | |
| | |
| | 2775 2775 2775 2775 2775 2775 2775 2775 |
| | |
| | |
| | |
| | 8422442442828282828282846428 |
| | 2.260 2.2000 2.200 2.200 2.200 2.200 2.200 2.200 2.200 2.200 2.200 2.200 2.200 2.200 2.200 2.200 2.2000 2.2000 2.2000 2.2000 2.2000 2.2000 2.2000 2.2000 2.2000 2.2000 2 |
| 24 25 25 25 25 25 25 25 25 25 25 | 0.050 0.050 0.050 0.040 0.040 0.010 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.00000 0.00000 0.00000 0.00000000 0.0000000000 |
| C C <thc< th=""> <thc< th=""> <thc< th=""> <thc< th=""></thc<></thc<></thc<></thc<> | 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.0 |
| Ph Ph Ph Ph Ph Ph Ph Ph Ph Ph | 14.00 14.82 17.05 |
| Control of the contro | 0.13 0.13 0.13 0.13 0.13 0.13 0.13 0.13 |
| 8 8 100 100 100 100 100 100 100 100 100 | 0001 0001 0007 0007 0007 0007 0007 0007 |
| A A A (1997) (19 | Control Con |
| \$ | 0.03 441 541 541 541 541 541 541 541 |
| | |
| B1 11 11 11 11 11 11 11 11 11 11 11 11 1 | 0.22 0.23 0.25 0.25 0.25 0.25 0.25 0.25 0.25 0.25 |
| | 000 0017 0017 0017 0017 0017 0017 0017 |
| ([C193]) (C193) (C19 | 2228822888222822222222282882288 |
| | |
| | 22882228288288282222222228888222 |
| | |
| | |
| 110 100 100 100 100 100 100 100 | |
| Iby Iby 11777 11777 11777 11777 11777 11777 11777 11777 11777 11777 11777 11777 11777 11777 11777 1177 11777 1177 11777 1177 11777 1177 11777 1171 11717 1171 11717 1171 11717 1171 11717 1171 11717 1171 11717 1171 11717 1171 11717 1171 11717 1171 11717 1171 11717 1171 11717 1171 11717 1171 11717 1171 11717 1171 11717 1171 11717 1171 11717 1171 11717 1171 | 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.00000 0.00000 0.000000 |
| Th T T | 010 017 017 017 017 017 017 017 017 017 |
| 64 258 1258 1258 1258 | 1577 1570 1570 1570 1570 2576 2576 2576 2576 1581 1581 1581 1583 1586 1586 1586 1586 1586 1586 1586 1586 |
| Ru 1 1233 1233 1234 1233 1235 1233 1235 1233 1235 1233 1235 1233 1235 1233 1235 1233 1235 12333 1235 | 0.057 0.047 0.047 0.047 0.0480000000000 |
| Simulation Simulation 1 | |
| Not 2012 (2012) | 24.8 26.0 25.0 25.0 27.4 27.4 27.4 27.4 27.4 27.4 27.4 27.4 |
| | |
| | 222 22 22 22 22 22 22 22 22 22 22 22 22 |
| 14. 14. 15. 15. 15. 15. 15. 15. 15. 15. 15. 15 | 2000 000 000 000 000 000 000 000 000 00 |
| | 000000000000000000000000000000000000000 |
| | |
| 0.01 0.01 0.01 <td>0000 0000 0000 0000 0000 0000 0000 0000 0000</td> | 0000 0000 0000 0000 0000 0000 0000 0000 0000 |
| Met Met 1111 1111 1111 | 600 000 000 000 000 000 000 000 000 000 |
| A 1 4 4 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 | 77.90 225.10 225.10 227.70 200 200 200 200 200 200 200 200 200 2 |
| | |
| | |
| | 2010 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 |
| | 0.00 0.001 0.002 0.0 |
| | 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.0 |
| | 11 22 21 23 12 22 21 23 23 13 23 23 23 23 14 23 23 23 23 15 23 23 23 23 15 23 23 23 23 15 23 23 23 23 15 23 23 23 23 15 23 23 23 23 16 23 23 23 23 16 23 23 23 23 16 23 23 23 23 16 23 23 23 23 16 23 23 23 23 16 23 23 23 23 17 23 23 23 23 17 23 23 23 23 16 |
| | |
| | |
| (1) (1) (1) (1) (1) (1) (1) (1) (1) (1) | 13155 8 18 18 18 18 18 18 18 18 18 18 18 18 1 |
| Alla | |