## Hydrogeochemistry of the upper Banyu Pahit River valley, Kawah Ijen volcano, Indonesia

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#### Abstract

The largest naturally-occurring lake of hyperacid brine in the world is located in the crater of Kawah Ijen volcano in East Java, Indonesia. The hyperacid Banyu Pahit River flows down the side of Kawah lien and is a major source of regional natural pollution. Hydrothermal fluid, meteoric derived groundwater, seepage from the hyperacid crater lake, and water-rock interaction are the major sources and sinks of water and solutes from the volcano to the surrounding environment. The current research is focused on the upper Banyu Pahit River valley (within 3 km of the summit) which has been understudied to date. Detailed chemical analyses of the Banyu Pahit River, the crater lake, and all observed springs (neutral and acid) that contribute water to the river were made, including 46 major, minor and trace elements. The distinct chemical signature of each water source, as well as that of water-rock interaction, is determined. Several elements have been identified as conservative tracers of hydrologic sources and sinks as they enter the surface water system. Mass balance mixing analysis using the conservative tracers, combined with discharge measurements, is used to quantify the fluid and solute mass contribution of each source. The results of this analysis indicate that fluid from the deep hydrothermal system contributes the majority of the solute flux from Kawah Ijen, and that it also forms the headwaters of the Banyu Pahit River. The flux of crater lake seepage, which was previously assumed to be both the main source

of acid water for the Kawah Ijen hydrologic system and the headwaters of the Banyu Pahit River, has now been determined to be a full order of magnitude lower than that of hydrothermal fluid (total calculated flux = 1.2 l/s crater lake seepage versus 15.4 l/s hydrothermal fluid).

## Hydrogéochimie de la vallée du cours supérieur de la rivière Banyu Pahit, volcan Kawah Ijen (Indonésie)

#### Résumé

Le plus grand lac naturel de saumure hyperacide du monde est situé dans le cratère du volcan Kawah Ijen, dans la province de Java Est, en Indonésie. La rivière hyperacide Banyu Pahit s'écoule sur le flan du Kawah ljen et constitue une importante source de pollution naturelle régionale. Les fluides hydrothermaux, l'eau souterraine d'origine météorique, les eaux d'exfiltration provenant du lac du cratère et les interactions eauroche représentent les principaux puits et sources d'eau et de solutés de ce basin. La présente étude est centrée sur la vallée du cours supérieur de la rivière Banyu Pahit (dans un rayon de 3 km du sommet), une région sur laquelle peu d'études se sont penché. Des analyses chimiques détaillées (incluant 46 éléments majeurs, mineurs et en traces) ont été effectuées sur les eaux de la rivière Banyu Pahit, du lac du cratère et de toutes les sources observées (neutres et acides) qui contribuent à l'écoulement de la rivière. La signature chimique distincte de toutes les sources d'eau, ainsi que celle des interactions eau-roche, a été établie. Plusieurs éléments s'avèrent être des traceurs conservatifs de sources et puits hydrologiques du système d'écoulement de surface. L'analyse de mélange basée sur le bilan massigue des traceurs conservatifs, combinée aux mesures de débit d'écoulement, est utilisée pour quantifier la contribution massique de fluides et solutés de chaque source. Les résultats de cette analyse indiquent que les fluides provenant du système hydrothermal profond sont responsables de la majeure partie de l'apport de solutés provenant du Kawah lien et qu'ils constituent également la

source de la rivière Banyu Pahit. Il est maintenant établi que l'apport du lac aux eaux de surface du basin, apport qui jusqu'à present était considéré comme dominant, est largement inférieur à l'apport associé aux fluides hydrothermaux (débit calculé total = 1,2 l/s pour l'apport du lac contre 15,4 l/s pour les fluides hydrothermaux).

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#### **Contributions of Authors**

The manuscripts included for submission in this thesis are co-authored by Stephanie Palmer, Jeffrey McKenzie, Vincent van Hinsberg, and Willy Williams-Jones. The project was formed to supplement on-going multidisciplinary earth science research involving VvH and WJ at Kawah Ijen volcano through hydrologic and hydrogeochemical contributions. Sample collection in 2008 was done by SP with the guidance and supervision of VvH. 2009 sample collection was done by SP with the guidance and supervision of JM and VvH. Sample preparation and analysis using ICP-MS and Atomic Absorption was done by SP, as was submission of prepared samples for analysis using ion chromatography at the Hydrogeology Laboratory (McGill University), and for analysis of oxygen isotopic composition at the GEOTOP Stable Isotope Geochemistry Laboratory. Dataset analysis and interpretation was done by SP with the guidance and collaboration of JM and VvH. Initial manuscript preparation was done by SP with guidance and subsequent revisions of JM, VvH, and WJ, except section 5.2 of the second manuscript submission (Hydrogeological Constraints), which was written primarily by VvH.

#### Introduction

#### Volcanic hydrology and hydrogeochemistry

The chemistry of hydrologic features occurring on and around active volcanoes is well studied. More than 100 active crater lakes exist at present (Delmelle and Bernard, 2000). Pasternack and Varekamp (1997) describe processes occurring in and below active crater lakes of high-, medium-, and low-activity hazard assessment classifications. Generally heat, and magmatic and/ or hydrothermal fluid is transported more or less continuously toward and into the bottom of these lakes, and heat may also be transported separately through a heat pipes (Pasternack and Varekamp, 1997). Meteoric water often supplies a significant amount of the lake water by volume, and is trapped in a relatively impermeable crater condensing magmatic volatiles (mainly SO<sub>2</sub>, H<sub>2</sub>S, HCl, and HF) and absorbing heat (Delmelle and Bernard, 1994).

Crater lakes that have formed relatively recently, such as at Mount Pinatubo (Philippines; 1991) and El Chichón volcano (México; 1982), allow the opportunity to follow the evolution of such systems from the time of their formation, and therefore allow the examination of the immediate post-eruption readjustment of the underlying magmatic-hydrothermal system through its influence on the chemical and physical parameters of the lake (Stimac *et al.*, 2003; Rouwet *et al.*, 2008). Major and trace chemistry, isotopic systematics, and temperature of longer-established crater lakes have also been used to monitor changes in volcanic activity toward predicting eruptive periods. Observations of distinct chemical precursors to eruptive activity were noted in the cases the crater lakes associated with Mount Ruapehu, New Zealand (eruption

1995 – 1996; Christenson, 2000), Kelut volcano (eruption 1990; Badrudin, 1994), Popocatepetl, Mexico (eruption 1994; Armienta *et al.*, 2000), Soufriere, West Indies (eruption 1972; Sigurdsson, 1977), Kusatsu-Shirane, Japan (eruption 1976; Ossaka *et al.*, 1980), Copahue, Chile/ Argentina (eruption 2000; Varekamp *et al.*, 2001), Rincón de la Vieja, Costa Rica (phreatic eruption 2002; Tassi *et al.*, 2005), and Yugama, Japan (eruption 1982; Takano and Watanuki, 1990). These include increases in Al, Fe, Na, Mg, Cl, F, and especially SO<sub>4</sub> concentrations.

Other parameters directly related to volcanic activity, such as seismicity, plume height, and fumarole temperature, have also been correlated with crater lake chemistry, particularly pH and major anion concentrations (S, Cl), at Poás volcano in Costa Rica (Martinez *et al.*, 2000). General stage of volcanic activity (e.g. dormant, pre-, and posteruption) has been reported to be observed in crater lake water chemistry of dormant and active volcanoes of both pre- and post-eruption stage in Mexico (Nevado de Toluca, Popocatepetl, and El Chichón volcanoes respectively (Armienta *et al.*, 2000). Low level activity or precursors to activity, however, are often obscured in crater lake chemistry due to interaction with the atmosphere and water-rock interaction, and large lake volume diluting the signature of increased activity (Armienta *et al.*, 2008).

Additional surface hydrologic features commonly present at sites of volcanic activity are acid and thermal springs. Giggenbach and Corrales-Soto (1992) describe the potential distribution of the different water types expected to be associated with a typical volcanic-magmatic-hydrothermal system, as observed in their case study of the three volcanoes of the Guanacaste geothermal province in Costa Rica (Rincón de la Vieja, Miravalles, and Tenorío). Summit fumaroles and sometimes crater lakes are

found to occupy the crater area, and lateral fumaroles are found in some cases to occur on the upper, outer flanks of the volcanic edifice. Spring water types occurring with increasing distance from the summit are acid sulfate springs, bicarbonate springs, and chloride springs (Giggenbach and Corrales Soto, 1992). This pattern has also been observed at Los Azufres (Mexico), Zunil, Moyuta, and Amatitlán (Guatemala) (Giggenbach and Corrales Soto, 1992), Nevado del Ruiz (Colombia) (Giggenbach *et al.*, 1990), and Mount Pinatubo (Philippines) (Stimac *et al.*, 2003). Springs formed of hydrothermal fluid present a possible opportunity to understand the associated magmatic-hydrothermal system at depth and to more precisely monitor volcanic activity. Freshly emerging spring fluid is not exposed to and affected by atmospheric conditions to the extent that most crater lakes are if at all.

Water runoff from springs or lakes associated with active volcanoes has been observed to form acid streams and rivers in several cases, such as the Whangaehu River draining the crater lake of Mt. Ruapehu, New Zealand (Giggenbach, 1974; Deely and Sheppard, 1996), the Ciwidey River draining the Patuha crater lake in West Java, Indonesia (Sriwana *et al.*, 1998), numerous acid springs of Poás volcano, Costa Rica discharging into the Rio Agrio (Rowe *et al.*, 1992; Sanford *et al.*, 1995), and the Banyu Pahit (*"Acid River"*) River draining the side of Kawah Ijen volcano in East Java, Indonesia (Kemmerling, 1921; Delmelle and Bernard, 1994, 2000). Contamination of subsurface (i.e. groundwater) as well as surface water resources has the potential to transport the highly acidic and potentially highly toxic volcanic waters at the landscape scale (Sanford *et al.*, 1995). Impacts on local ecosystems and human populations in contact with such waters have been noted (Parnell and Burke, 1990; Pringle *et al.*,

1993; Heikens *et al.*, 2005; Löhr *et al.*, 2005; van Rotterdam-Los *et al.*, 2008), such as fluorosis and contamination of food crops and soils by heavy metals, particularly Al. Similar conditions and processes as observed in association with fluid from acid mine drainage are present in volcanic waters such as those mentioned above (Salomons, 1995).

#### Kawah ljen magmatic – hydrothermal system

Kawah Ijen volcano is located on the north-western flank of Merapi volcano, just inside the eastern rim of the Ijen caldera in East Java, Indonesia. The Ijen caldera formed more than 50,000 years ago upon the collapse of the stratovolcano of the same name, and is part of the Sunda Arc, resulting from the subduction of the Indian oceanic plate beneath the Sundaland craton (Kemmerling, 1921; Sitorus, 1991). To the north a semi-circular caldera wall bounds the caldera. To the south there are three post-caldera formation event rim volcanoes: Merapi, Ranteh, and Jampit. An east-west directional trend of smaller volcanoes transects the caldera, and Kawah Ijen is located at the intersection of the intra-caldera volcano trend and the rim volcano trend. A large lake seems to have occupied almost the entire north half of the caldera based on lacustrine sediment deposits in this area (van Hinsberg *et al. in review* a), and a break in the northern caldera wall near the town of Blawan acts to drain the caldera.



Overview map of Ijen caldera. Thesis study area is outlined in red.

The volcanic edifice of Kawah Ijen is comprised of a number of alternating scoria, lava, ash, and lapilli layers, as well as phreatic and phreato-magmatic deposits representing diverse stages of activity (van Hinsberg *et al., in review* a,b). Current activity within the Ijen caldera is restricted to Kawah Ijen volcano. The most recent major eruption took place in 1817, displacing the full volume of the lake and causing acidic mudslides reaching the city of Banyuwangi more than 25 kilometers from the volcano. Smaller-scale, phreatic activity is limited to the confines of the crater and has taken place more recently in 1916-17 (Kemmerling, 1921), 1936, 1952, and 1993-94 (Delmelle *et al.*, 2000).

Volcanic activity at the surface is evidenced in part by actively degassing fumaroles emitting white-yellow fumes. These form a mound approximately 20 meters

high at the western, inside edge of the crater, and are located beside an old, currently inactive dome. Fumarole temperature in recent years has been measured between ~200 and ~600°C (BGVN 32:09). Pipes have been inserted into the active fumaroles for the purpose of mining the native sulphur emissions. Fumes condense in the pipes and the native sulphur pools as a liquid at the bottom of the pipes. This cools, takes the solid form, and is collected by the miners. Fumaroles are thought to be associated with activity related to at least one magmatic intrusion.

#### Kawah Ijen – Banyu Pahit River system

The crater of Kawah Ijen also hosts a lake of hyperacid brine, possibly the largest naturally-occurring such lake in the world. pH of the lake is currently ~ -0.06, and TDS has been estimated at > 100 g/kg (> 100,000 ppm) (Delmelle and Bernard, 1994, 2000). The water component of the crater lake is predominantly meteoric, and magmatic fluid dominated by the vapour phase condenses into it. High concentrations of cations and some trace metals (Ca, Al, K, Mg, Li, Be, Co) are derived from rapid rock alteration in the hyperacid brine. It has recently been determined that rock material, in addition to that of the crater walls along the lake, must fall into the lake in order to achieve such concentrations of total dissolve solids (van Hinsberg *et al., in review* b). The lake is approximately 1500 by 950 meters in diameter, and its depth is estimated at approximately 180 to 200 meters (Takano *et al.*, 2004), with the walls of the crater rising 200 to 250 meters above the level of the lake. A low point in the crater wall (rising only approximately 50 above the level of the lake) had been dammed to control flow of crater

lake water to the Banyu Pahit River valley on the western flank of the volcano. Lake level has since fallen to such a level that the dam no longer functions.

Water from the crater lake leaks through the rock basement of the crater emerging on the western flank. Crater lake seepage of this form was to date considered to form the headwaters of the Banyu Pahit River. Due to the relative inaccessibility of the river valley between the perceived headwaters and approximately 3 kilometers downstream (elevation > 1895 m.a.s.l.), this section of the river valley has not been intensely studied. A notable discrepancy in the volume of water discharging at the headwaters and in the stream ~ 3 kilometers downstream, and in the chemical composition suggested that additional sources of water to the Banyu Pahit must be present over this unstudied stretch. Downstream of this stretch (> 3 km from the crater lake seepage springs; < 1895 m.a.s.l.) the Banyu Pahit continues to flow over the same (andesitic) lava flow for ~ 9 km until the village of Watu Capil, with only slight variations in the chemical composition due to dilution by circum-neutral groundwater with relatively very low concentrations of all elements. pH over this 9 km river section increases from 0.4 to 0.9 (Delmelle and Bernard, 2000).

Approximately 8 km beyond Watu Capil, the river passes the town of Blawan, near the southern rim of the Ijen caldera. Between Watu Capil and Blawan dilution by neutral groundwater is again noted as the predominant control on river chemistry, and pH increases again from 0.9 to 2.4 (Delmelle and Bernard, 2000). The Banyu Pahit flows out of the Ijen caldera after its confluence with two, major neutral tributaries: the Kali Sat and, several hundred meters downstream, the Kali Senggon. pH at this point increases to 4.6 (Delmelle and Bernard, 2000). The river changes name at this point to

Banyu Putih (White River) because of the white precipitate that materializes in the water upon the addition of the circum-neutral river water from the tributaries, as well as from several cation-rich, thermal springs. Further, on the Asembagus coastal plains, water from the Banyu Putih is dammed and used for irrigation (Delmelle and Bernard, 2000; Löhr *et al.*, 2005; Heikens *et al.*, 2005a,b,c; van Rotterdam-Los *et al.*, 2008).

#### Thesis research

The research presented in this thesis, carried out as partial requirement for my M.Sc. degree in Earth and Planetary Sciences at McGill University, is part of a broader, multidisciplinary earth science research effort toward understanding various components and surface expressions of the active Kawah Ijen volcanic system. Researchers from groups at Simon Fraser University (Vancouver, Canada), Institut Teknologi Bandung (Bandung, Indonesia), and McGill University (Montreal, Canada) study the geochemistry of volcanic fluids in aqueous and vapour phases and of volcanic rocks from Ijen and throughout the caldera, and use geophysical approaches to monitor and constrain the foci of the subsurface hydrothermal system. Communication and collaboration between researchers from these diverse fields within the earth sciences has enabled a more complete understanding of the past, present, and potential future activity, environmental contamination, and ore forming potential of the volcano.

My contribution to research at Kawah Ijen has been through the use of hydrologic and hydrogeochemical approaches to understanding subsurface fluid flow through hydrogeologic surface manifestations such as springs. The system is hypothesized to consist of four hydrogeochemical end members: circum-neutral groundwater ultimately

of meteoric origin, hydrothermal fluid, water-rock interaction, and seepage from the hyperacid crater lake to the outer flanks of the volcano. Water samples were taken of neutral and acid waters primarily from the upper western side of Kawah Ijen volcano. Signature chemical compositions are determined for the four acid spring end members mentioned above, which are considered to fully account for spring hydrogeochemistry in this study and notably for the hydrothermal fluid at depth in the system (see the first submitted paper contribution in the thesis). Mass balance mixing models were then developed for each set of springs to determine (1) what the source fluids of the springs are, and (2) what the relative proportions, in terms of elements and water, contributed by each source are (second submitted paper).

The following thesis components address the following questions regarding the Kawah Ijen – Banyu Pahit River system: What hydrological features do we observe in the upper Banyu Pahit River valley (> 1895 m.a.s.l. elevation) on the western side of Kawah Ijen and how can the hydrologic features be understood and described in terms of their hydrogeochemistry? In answering these questions we determine the sources and sinks of water and elements to surface hydrology over this section, and to what extent each source contributes to fluid flux to the surface environment relative to the others and absolutely. We also determine the composition of Kawah Ijen hydrothermal fluid at depth and spatially describe the flow of different fluid types in the subsurface using the hydrogeochemistry of the surface fluids.

Manuscript 1

# Hydrogeochemical insights into the nature of magmatic-hydrothermal fluid at Kawah Ijen volcano, Indonesia

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#### Abstract

Surface expressions of the magmatic-hydrothermal system of Kawah ljen volcano include three sets of hyperacid springs located at progressively lower elevations on the western flank of the volcano. While the first two consist partially of crater lake water, the third set of springs, which is the subject of this paper, emerges directly from the hydrothermal system, and is dominated by hydrothermal fluid. Three main sources and sinks of elements to this hydrothermal fluid have been identified: rock which interacts with the fluid, meteoric-derived groundwater, and magmatic fluid. Detailed chemical analyses of the third set of springs have been undertaken and the sources of water and solutes for them evaluated. The oxygen isotopic composition and concentrations of 46 major and trace elements have been determined for the hydrothermal springs and the meteoric-derived groundwater. The flux of elements between the rock and the hydrothermal fluid has also been determined. Using the conservative tracers,  $\delta^{18}$ O, CI, SO<sub>4</sub>, and F, we reconstruct the proportions of meteoric groundwater and magmatic fluid in the hydrothermal fluid mixture. These proportions are then used, in conjunction with the flux of elements between rock and fluid, and a mass-balanced mixing model, to determine the composition of the exsolved magmatic fluid. The composition obtained is consistent with a vapour-dominated magmatic fluid, and the concentrations of metals suggest that both the vapour and the associated brine have ore-forming potential.

Keywords: hydrology; volcano; magmatic-hydrothermal fluid; groundwater; Kawah Ijen

#### 1. Introduction

Magmatic intrusions are associated with the circulation of a surrounding hydrothermal system consisting of meteoric water that is deeply circulated and mixed with the exsolved magmatic fluid. Very low pH fluids are commonly produced and extensive host rock dissolution and alteration occur, producing fluid with high concentrations of many ions and heavy metals (Hedenquist and Lowenstern, 1994; Hurwitz *et al.*, 2003). Whereas magmatic fluid predominately contributes metals, water, and ligands (S, Cl) to the hydrothermal fluid, by volume there is considerably more meteoric derived groundwater than magmatic fluid (Hedenquist and Lowenstern, 1994). The chemical signature of the magmatic fluid is further diluted by meteoric water with increasing distance from the intrusion. As a result, the relative contributions of magmatic and meteoric water, and host-rock, to the chemistry of the hydrothermal fluid are difficult to assess (Hedenquist and Lowenstern, 1994).

Improved understanding of the processes and sources of water involved in hydrothermal fluid chemistry is important to several areas of geologic and hydrologic research. Surface manifestations of active magmatic-hydrothermal systems include acidic springs, crater lakes, and fumaroles. The impact on air and water quality of volcanic fluids released from these sites to the surrounding environment can be substantial (Parnell & Burke, 1990; Pringle et al. 1993; Löhr et al. 2005; Schaefer et al. 2008; van Rotterdam-Los et al. 2008). These fluids, which are directly linked to the subsurface degassing magmatic system, may also be used to monitor volcanic activity (ex. Rowe et al. 1992; Badrudin, 1994; Carapezza and Federico, 2000; Christenson, 2000). Magmatic hydrothermal systems are linked with the formation of several ore

deposit types including high- and low-sulphidation epithermal ore deposits, of which several modern analogues have been identified (Clark and Williams-Jones, 1990; Christenson, 1993; Arribas, 1995; Raymond et al. 2005; Boyce et al. 2007). Studying the modern, active magmatic hydrothermal system analogues will therefore lead to better understanding and predicting the extent of pre-existing hydrothermal ore deposits (Hedenquist and Lowenstern, 1994; Boyce et al. 2007). Understanding the sources and characteristics of hydrothermal fluids associated with ore formation is also crucial to advancing theories of ore formation itself (Taylor, 1974).

Kawah Ijen volcano in East Java, Indonesia, provides an ideal setting to study an active hydrothermal system from a hydrogeologic perspective as there are numerous surface manifestations of the magmatic-hydrothermal system. These include actively degassing fumaroles, a very low pH river (the Banyu Pahit River), a hyperacidic crater lake, and three sets of springs discharging hyperacidic water on the western flanks of the volcano. One of these sets of springs, which is characterized for the first time in this study, emerges directly from the hydrothermal system, rather than from seepage from the crater lake surface reservoir. The goal of this study was to characterize the magmatic contribution to surface outflow from the Kawah Ijen hydrothermal system from the chemistry of this set of hydrothermal springs. Using chemical analyses of the hydrothermal springs, and of the rock and meteoric groundwater end-members contributing to the spring water composition, we have determined the element contribution of the magmatic fluid end member. As a result, this study has provided new perspectives on how spring discharge may be used to monitor volcanic activity, allows for a better understanding of the pollution from Kawah Ijen volcano, and illustrates the

role that springs may play as windows to active analogues of low sulphidation epithermal ore-forming systems.

#### 2. The Kawah Ijen – Banyu Pahit system

#### 2.1 Volcano and crater lake

Kawah Ijen volcano is an actively degassing stratovolcano (≈ 2,346 m.a.s.l.) located near the eastern rim of the Ijen caldera in East Java, Indonesia (08°03'S, 114°14'E) (Fig. 1a). Fumaroles form a mound approximately 20 m high on the western inside edge of the crater. Current volcanic activity is phreatic, the last magmatic eruption taking place in 1817, and causing considerable damage up to 25 km from the volcano through mud flows (Kemmerling, 1921). The cone of Kawah Ijen volcano consists of alternating basaltic to andesitic lava flow units, lahar and pyroclastic flows, and scoria deposits from various eruptive phases of the volcano. Contacts between layers, as well as relatively permeable units, serve as conduits for subsurface flow of fluid. The mineralogy and geochemistry of the different rocks and fluids of Kawah Ijen, as well as general geology and tectonic setting of the volcano, have been described by Kemmerling (1921), Delmelle and Bernard (1994; 2000), Delmelle et al. (2000), Takano et al. (2004), and van Hinsberg et al. (in review a, b).

The summit crater of Kawah Ijen volcano is occupied by a lake, which is the world's largest naturally-occurring body of hyperacidic brine (Delmelle and Bernard, 2000). Sulphur-rich magmatic volatiles continuously condense into the lake and cause it to have a hyperacidic pH of -0.1 to 0.3, which fluctuates as a result of varying seasonal rainwater recharge, the predominant source of water to the lake (Delmelle and Bernard,

2000; van Hinsberg et al., in review). Dissolution of rocks falling into the lake from erosion of the crater walls is the main control on lake cation chemistry (van Hinsberg et al., in review). Two, hot acidic springs (temperature of 35 and 50°C, pH 1.7 and 2.6) are also located inside the crater, adjacent to the eastern side of the lake.

#### 2.2 Banyu Pahit River valley

Hyperacidic spring water is discharged at three locations in the upper Banyu Pahit River valley. Water from the crater lake emerges as springs on the outer western side of Kawah Ijen (elevation  $\approx$  2090 m.a.s.l.), with a pH < 0.1. The location of this first set of springs is characterized by extensive gypsum terraces, which extend across an area approximately 50m wide and 100m long, and are up to 40 cm thick. Gypsum precipitation occurs at the location of spring outflow due to evaporation of spring fluid (Delmelle and Bernard, 2000; van Hinsberg et al., in review). Flow from the first springs disappears into the sediment and a second set of acid springs is observed to emerge at an elevation  $\approx$  2075 m.a.s.l. Flow from these springs also disappears into the sediment after flowing on the surface for approximately 200 m.

A third set of acid springs is located at an elevation  $\approx$  1975 m.a.s.l. and is characterized by bright, yellow-green coloured water. The three springs comprising the third set of acid springs appear to represent outflow from the same fluid source. This is supported by the occurrence of the springs at the same elevation and geological contact, between impermeable lahar and lava flows over a length of approximately 10 m, and from fractures in the overlying lava flow unit, as well as by their similar chemical composition. Water from the springs mixes to form the headwaters of the Banyu Pahit

stream, which drops several tens of meters into an incised valley where it then flows west and northwest over a single lava flow to the waterfall at Watucapil (Fig. 1).

At the town of Blawan, approximately 17 km northwest of Kawah Ijen volcano, two major, neutral tributaries the Kali Sat and the Kali Senggon, join the Banyu Pahit, (Fig. 1a). The Banyu Pahit River then becomes known as the Banyu Putih (discharge ~4000 l/s). The river flows out of the Ijen caldera onto the Asembagus plain, where the water is used for agricultural irrigation (Löhr et al. 2005; van Rotterdam-Los et al. 2008). The stream eventually reaches the Strait of Madura, and the Java Sea.

#### 3. Methods and approach

Fieldwork during July and August of 2008 and 2009 took place during the dry season. Water samples were taken from all observed water emissions associated with the magmatic-hydrothermal system, including the crater lake, acid springs in the crater, and each acid spring located in the upper Banyu Pahit River valley. We also sampled a neutral spring on the southern flanks of Kawah Ijen near Paltuding (Fig. 1). Samples were collected in 60 ml sample-rinsed polyethylene bottles and filtered on site to 0.45 µm. The groundwater sample was acidified using two drops of dilute nitric acid (HNO<sub>3</sub>). Electrical conductivity, pH, and temperature were measured *in situ* as close as possible to the source of each spring. The cumulative discharge of the springs in each set was measured using the area-velocity method, with channel dimensions measured to the nearest centimetre. Velocity measurements were made along a transect perpendicular to the direction of flow with a Global Water FP101-FP201 Flow Probe.

The detailed chemical composition of each sample was determined through the analysis of a suite of 46 major and trace elements (Table 1). Concentrations of anions (CI, F, Br, and SO<sub>4</sub>) were analyzed by ion chromatography at the Hydrogeology Laboratory at the Department of Earth and Planetary Sciences, McGill University, with sample dilutions and standards prepared in distilled water. Cations (AI, Si, Ca, Fe, K, Li, Mg, and Na) were analyzed by flame Atomic Absorption Spectrometry at the Trace Element Analysis Laboratories (TEAL) at McGill University, using a Perkin Elmer AAnalyst 100 Flame atomic absorption spectrometer. Samples and standards were prepared in a 3% trace metal grade nitric acid (HNO<sub>3</sub>) matrix. Concentrations of trace and rare earth elements were analyzed using ICP-MS at the Trace Element and Analysis Laboratory (TEAL) at McGill University using a Perkin Elmer Elan 6100 DRCplus. Samples and standards were prepared in a 3% analytical grade (nanopure) HNO<sub>3</sub> matrix. All samples were also analyzed for oxygen isotopic composition ( $\delta^{18}$ O) by equilibration with injected CO<sub>2</sub> gas using the Micromass Isoprime DI Aquaprep at the GEOTOP stable isotopes geochemistry laboratory at the Université du Québec à Montréal, Montreal.

#### 3.1 Approach

The Kawah Ijen hydrothermal system is hypothesized to consist of three distinct chemical end members: acidic magmatic fluids from the degassing magmatic intrusion(s), meteoric-derived groundwater, and rock that releases components to the system through interaction with the other two end-members. Our hypothetical schematic of the surface water, hydrogeologic, and hydrothermal features and interactions at Ijen

is presented in Fig. 2. Owing to the acidic nature of the fluids and the elevated temperatures, water-rock interaction results in intense in situ leaching of components, mainly cations, from the host-rock. Some elements are removed from the fluid solution by mineral precipitation (van Hinsberg et al. in review).

Mass balance mixing models were used to distinguish and quantify the sources and sinks in the hydrothermal spring water mixture. The concentrations of individual elements, and of some elements relative to others, serve to distinguish the different end-member sources and sinks influencing hydrothermal fluid composition (rock, magmatic fluid, and meteoric groundwater). Although a minimum of n - 1 conservative tracers are required to determine the input of each n end members, we overparameterized our mixing model to avoid problems due to non-uniqueness of the end members.

Hydrothermal spring water and meteoric groundwater were sampled and their chemical compositions were analyzed directly, whereas the contributions of rock and the magmatic fluid were determined based on the element fluxes from Ijen andesite to acid water established by van Hinsberg et al. (submitted), and mass balance calculations. Equation 1 describes the mass balance of element sources and sinks, in which the concentration of any element (*C*) in the hydrothermal spring fluid (*hs*) is a function of the mixing of meteoric groundwater (*gw*), magmatic fluid (*mag*), rock (*r*), mineral precipitation (*min. precip.*), and the relative contribution of each end member to the hydrothermal fluid (*Q*), as follows:

$$Q_{hs}C_{hs} = Q_{gw}C_{gw} + Q_{mag}C_{mag} + Q_rC_r - Q_{min. precip}C_{min. precip.}$$
Eqn. 1

#### 4. Results and data treatment

The results of pH, temperature, and electric conductivity measurements taken in situ during the 2008 fieldwork season are presented in Table 1, as are major and trace element concentrations and oxygen isotopic values. The statistical error associated with major ions analyzed using ion chromatography and atomic absorption spectrometry is less than 5% for both standards and duplicates. The statistical error of ICP-MS analyses of trace elements is less than 10% except for Be (19%), and Sb (34%).

The spring water sampled near Paltuding (Fig. 1b) appears to be in equilibrium with soil and host rock, and is taken to be representative of local meteoric-derived groundwater, based on a measured pH of 8.17, and high concentrations of Ca and Mg (Table 1), typical of groundwater in equilibrium with volcanic soil (Mizota and van Reeuwijk, 1989). Three sets of acid springs are located along the western side of the volcano. Two of these sets were previously unreported, in addition to the highest elevation crater lake seepage springs. The first set of springs (1AS) (crater lake seepage) was at a temperature of 35°C and a pH of 0.06. The second set of springs (2AS) had a temperature of 22.2°C, and a pH of 0.28, and is associated with sulphate deposits, including gypsum precipitation. The temperature of the third set of springs (3AS) was between 22 and 27°C and the pH between 0.39 and 0.49.

The third set of springs is the focus of this study. Anion concentrations measured in the three individual acid springs of this third set range between 30,133 and 44,404 ppm SO<sub>4</sub>, 9,124 and 13,952 ppm Cl, and 473.7 and 833.1 ppm F. The corresponding concentrations in the meteoric groundwater springs were 31.50 ppm SO<sub>4</sub>, 3.616 ppm Cl, and 0.771 ppm F. Values of  $\delta^{18}$ O ranged from -1.99 to +1.18 ‰ in the third acid

water, and was -8.55 ‰ in the meteoric groundwater spring. The small variation in the chemistry of the outflows of the third set of springs is attributed to late-stage dilution by neutral groundwater, as spring outflow is from the same unit, suggesting that these springs are derived from the same source.

Chloride, sulphate, and fluoride behave conservatively in this system, as is evident from their constant SO<sub>4</sub>/Cl and SO<sub>4</sub>/F for samples taken from the springs and over the length of the river; the only change observed with distance from the springs is dilution by neutral, meteoric water (this study and Delmelle and Bernard, 2000). Meteoric groundwater concentrations of SO<sub>4</sub>, F, and Cl are negligible and SO<sub>4</sub>, F, and Cl are not contributed by dissolution of rock (van Hinsberg et al. in review). Thus the source of SO<sub>4</sub>, F, and Cl in the springs is magmatic fluid alone. It therefore follows that concentrations of Cl, SO<sub>4</sub>, and F can be used to quantify the dilution of the magmatichydrothermal signature by neutral water relative to the most concentrated hydrothermal spring fluid sampled. After correcting for differences due to dilution, the mean concentration of each element in the three springs was taken as being representative of the hydrothermal spring water composition. This average normalized composition is presented in Table 1 and is used in all further interpretation of the data.

#### 5. Discussion

#### 5.1 Crater lake seepage vs. hydrothermal origin

An important first step in this study was to identify a magmatic fluid type directly linked to the magmatic-hydrothermal system, as distinct from the crater lake, which is a surface reservoir in constant contact with the atmosphere. Sulphate, chloride, and

fluoride are conservative components, unaffected by neutral groundwater, mineral precipitation, or water-rock interaction, and thus are derived from the magmatic fluid alone. Differences in volatile ratios,  $SO_4/CI$  and  $SO_4/F$ , must therefore reflect differences in the magmatic source fluid resulting from different partitioning of the species between liquid and vapour (Giggenbach et al. 1974; Rowe et al. 1992). Whereas CI and F partition more readily into the vapour,  $SO_4$  tends to remain preferentially in the liquid. High  $SO_4/CI$  and  $SO_4/F$  ratios would indicate that the magmatic fluid is liquid-dominated and low  $SO_4/CI$  and  $SO_4/F$  ratios that it is vapour-dominated (Giggenbach et al. 1974).

The SO<sub>4</sub>/Cl and SO<sub>4</sub>/F ratios therefore allow us to identify the nature of the magmatic fluid component in the acid springs. The first set of springs has previously been interpreted to be the result of seepage from the crater lake (Delmelle and Bernard, 2000; Delmelle et al. 2000). This conclusion is supported by our measurements of the anion ratios for the first set of springs, which, within analytical error, are indistinguishable from those of the crater lake (Fig. 3). The third set of springs have significantly different anion ratios from those of the crater lake and first set of springs. These ratios indicate a distinct magmatic fluid source with relatively elevated SO<sub>4</sub>/Cl and SO<sub>4</sub>/F of the second set of springs are intermediate between those of the first and the third sets, suggesting that there was mixing of these fluid types in the second set of springs (Fig. 3).

Discharge estimates also suggest that outflow from the third springs is not simply a renewal of flow from the crater lake seepage of the springs at higher elevation. The estimated discharge of the third set of springs is 31 l/s, which is much greater than the estimated discharge of the first set of springs,  $\sim$  1 to 2 l/s. Furthermore the third set of

springs is located in a valley unconnected with the crater of Kawah Ijen, and thus instead of crater lake seepage, these springs are likely to have had another source of magmatic fluid.

#### 5.2 Rock-sourced hydrothermal spring water component

A recent study by van Hinsberg et al. (in review) has characterized acid sulphate rock alteration and the resulting flux from the rock to the associated fluid of a large suite of elements. This study showed that the flux from the rock found at the surface is a good proxy for alteration occurring in the subsurface environment, and we were therefore able to use their data to determine the contribution of the rock to the hydrothermal fluid. The measured composition of the hydrothermal spring water was combined with the calculated flux of elements from the rock to determine the water-rock ratio, defined as the mass of dissolved rock material per mass of acid water.

The concentrations of elements in the hydrothermal spring water were plotted against the flux of elements from the rock during immature, mature, and complete alteration of basalt, andesite, dacite and rhyolite. A least squares regression was applied to reduce the overall cumulative uncertainty associated with the analysis of each individual element. The best fit to the data ( $R^2 = 0.97$ ) was obtained using a composition corresponding to complete alteration of andesite, and produced a consistent dataset comprising concentrations that varied over six orders of magnitude (Fig. 4). This indicates that the dominant rock-type interacting with the hydrothermal fluid is andesite and that the complete alteration of this rock controls the contribution of rock-sourced elements to this fluid.

The water-rock ratio of the spring water calculated using the above data predicts that 33.4(±1.1) g of rock are dissolved in each kilogram of hydrothermal fluid; corresponding concentrations of the rock-derived elements in the spring water are reported in Table 2. The calculated concentrations of Si, Ca, Ba, and Cu are negative and fall outside the bounds of accepted error, indicating that these elements are mostly removed from the fluid by mineral precipitation. This result is consistent with the observation of precipitates of silica (cristobalite), barite and gypsum at the spring outflow.

#### 5.3 Aqueous sources of hydrothermal spring water

Once the rock-sourced component of the springs is accounted for and removed, the remaining fluid composition consists of a mixture of magmatic fluid and meteoric groundwater. The local meteoric-derived groundwater composition, including the oxygen isotopic composition, is well characterized by the current analysis (Table 2). The  $\delta^{18}$ O values for waters associated with andesitic volcanic systems are also well constrained at between 7 – 13‰ VSMOW (Taran et al. 1989; Giggenbach, 1992), which provides a means to determine through a mass balance approach the potential composition of the magmatic end member.

In addition to  $\delta^{18}$ O, Cl, F, and SO<sub>4</sub> also can be used to distinguish between the meteoric groundwater and magmatic end members (concentrations of these components are several orders of magnitude lower in the meteoric groundwater). Moreover, as discussed previously, their relative concentrations are conserved during mixing enabling them to be used as natural tracers. The conservative nature of Cl, F,

and SO<sub>4</sub>, and  $\delta^{18}$ O coupled with the measured concentrations of Cl, F, and SO<sub>4</sub> in meteoric groundwater made it possible to use the concentrations of Cl, F, and SO<sub>4</sub> relative to  $\delta^{18}$ O in meteoric and hydrothermal samples to constrain the Cl, F, and SO<sub>4</sub> concentrations in the magmatic fluid end member (Fig. 5). This was done for each of the tracers independently using the mixing model described by the following equation.

Results for each of the tracers are in good agreement (within 3%) and show that the proportion of magmatic water comprising the hydrothermal spring water ranges from  $41(\pm 2)$  to  $56(\pm 3)$ % for the maximum and minimum possible  $\delta^{18}$ O values respectively; the average proportion of magmatic fluid is 48.5%. Magmatic element concentrations for hydrothermal fluid with 41% and 56% magmatic water (59% and 44% meteoric groundwater) are reported in Table 2. Differences between these two projected scenarios are illustrated in Figure 6, and are well within one order of magnitude of each other. Fig. 7 shows the relative (%) contributions of all elements analyzed in this study by the two aqueous end-members and the rock end-member to the hydrothermal fluid. Whereas anions and some trace metals are derived completely, or in large part, from the magmatic fluid, cations and rare earth elements (REE) are derived in large part from the host rock. Whereas REE chemistry in volcanic fluids has previously been considered useful volcanic monitoring, this approach will not work where REE concentrations are controlled by water-rock interaction.

#### 6. Ore forming potential of the magmatic-hydrothermal fluid

Having determined the composition of the magmatic component of the Kawah Ijen hydrothermal fluid made it possible to explore the ore forming potential of the system. Comparison of this composition to the compositions of fluids in known ore forming systems was particularly helpful in this regard. The Ladolam gold deposit located on the flanks of the extinct Luise volcano on Lihir Island, Papua New Guinea is an outstanding example of a low-sulphidation ore-forming system associated with a currently active magmatic-hydrothermal system (Simmons and Brown, 2006). Although we could not compare the composition of the Kawah ljen magmatic fluid interpreted in this study to that of the Ladolam system in terms of the most important ore-forming elements (i.e., Au, Cu, and As, due to mineral precipitation (Cu) or an unknown contribution from altered rock (As, and Au)), we were able to show that the Kawah Ijen magmatic fluid is considerably richer in a number of associated trace metals than the Ladolam fluid. For example, the concentration of TI at Kawah Ijen is ~900 – 1300 ppb versus ~70 ppb at Ladolam, that of Sb is ~70 – 100 ppb versus 3 ppb, that of Sn is  $\sim$ 1800 – 2500 ppb versus 715 ppb, that of Pb is  $\sim$ 16 000 – 20 000 ppb versus 32 ppb, and that of V is ~15 000 – 20 000 ppb versus 820 ppb (Simmons and Brown, 2006). Condensates of Kawah ljen fumarole gases (van Hinsberg, unpublished data) that were sampled concurrently with this study have similarly high concentrations of these elements.

An issue of considerable importance to interpretations of how epithermal deposits form (primarily of gold and silver) is whether the magmatic fluid widely considered responsible for metal transport is a liquid or vapour (Williams-Jones and

Heinrich, 2005). Assuming a temperature of 600°C for the exsolved magmatic fluid (Hedenquist and Lowenstern, 1994), it is evident from the proportion of NaCl in our calculated magmatic fluid and phase relationships in the system NaCl-H<sub>2</sub>O (Driesner and Heinrich, 2003), that the magmatic component of the spring fluid is initially a vapour (Fig. 8). As this vapour rises toward the surface it cools, and either condenses or contracts (by crossing above the critical curve) to liquid, and then mixes with meteoric groundwater and interacts with the host rocks before leaving the subsurface at the third set of springs. If these springs are a window on an epithermal deposit in formation, then it is likely that this deposit is of the low-sulphidation variety and that the initial medium of metal transport is a magmatic vapour.

#### 7. Conclusions and implications

Based on our analysis, the third and lowest (elevation) set of acid springs on the western flanks of the Kawah Ijen volcano is fed by hydrothermal fluid emerging directly from the subsurface magmatic-hydrothermal system. Understanding of this system has been improved through the characterization and subsequent quantification of the sources of water and solutes to the hydrothermal fluid. Three sources of solute have been identified, namely andesite, meteroric water and magmatic vapour. The relative proportions of meteoric groundwater and magmatic vapour and their contribution of solutes has been determined within a bracketed range of potential magmatic fluid compositions, projected with the use of conservative tracers of magmatic fluid, CI, SO<sub>4</sub>, F, and  $\delta^{18}$ O. The input of solutes from interaction of this combined fluid with andesite

was determined by combining measurements made during this study with those of an earlier study of rock alteration and water-rock interaction (van Hinsberg et al. in review).

Although meteoric groundwater is a relatively small contributor of most elements by concentration, it is volumetrically an important component of the hydrogeologic system, contributing between 44 and 59% of the water. The total volume of fluid and the total solute load of the hydrothermal fluid are thus decoupled, and an increase in hydrothermal spring discharge does not necessarily mean more pollution. The major and trace element chemistry of the spring water are controlled by fluid-rock interaction, mainly through the input of cations and the rare earth elements, and by magmatic vapour, mainly through the input of anions and some metals, such as Pb, Sn, Sb, Tl, and V. Changes in the concentrations of the anions and these metals potentially may be used to monitor volcanic activity, whereas the absolute metal concentrations of the metals provide evidence of possible ore formation involving magmatic vapour in a low sulphidation epithermal system.

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# **Figure captions**

Figure 1a. Map of the Ijen volcanic complex, with Kawah Ijen located near the eastern rim of the caldera.

Figure 1b. Map of the Kawah Ijen crater lake (elevation  $\approx$  2,200 m.a.s.l.) and hydrologic features on the western side of Kawah Ijen volcano, including three sets of hyperacid springs (1AS, 2AS, 3AS), a neutral spring (NS), and the hyperacid Banyu Pahit stream. Flow from both 1AS and 2AS disappears into the subsurface, whereas 3AS forms the headwaters of the Banyu Pahit stream. Modified from van Hinsberg et al. (in review). Transect labelled A – D indicates the cross-section direction of Figure 2.

Figure 2. Hypothetical cross-section of the subsurface Kawah Ijen magmatichydrothermal-groundwater system and associated surface features: crater lake, fumaroles, three sets of acid springs (1AS, 2AS, and 3AS), and the Banyu Pahit steam. Cross-section transect from Fig. 1b labelled A – D.

Figure 3. Volatile ratios, SO<sub>4</sub>/ CI and SO<sub>4</sub>/ F, of the Kawah Ijen crater lake and each of the three sets of acid springs on the western flanks of the volcano, showing different magmatic fluid sources (crater lake and hydrothermal water) for the 3AS and the 1AS acid springs (indistinguishable from crater lake fluid), and a mixture of the two sources forming the 2AS springs.

Figure 4. Concentrations of 40 elements in the sampled hydrothermal spring water (3AS) plotted against the predicted flux of elements from Ijen andesite determined by van Hinsberg et al. (in review). Predicted concentrations of Ca, Si, Cu, and Ba are significantly higher than the concentrations measured in the spring water, suggesting

the precipitation of these elements from the fluid. The flux of elements from rock to the hydrothermal fluid determined using the intercept of the fit line indicates that  $33.4(\pm 1.1)$  g of rock dissolved in each kg of spring water.

Figure 5. Groundwater-magmatic fluid mixing models for  $\delta^{18}$ O, and F, Cl, and SO<sub>4</sub>. The range of projected magmatic end member values is based on the  $\delta^{18}$ O composition range of andesitic waters reported by Taran et al. (1989) and Giggenbach (1992) (between 7 and 13‰ VSMOW).

Figure 6. Range of determined chemical compositions of the magmatic fluid end member assuming projected maximum (59% of total volume) and minimum (43% of total volume) magmatic contributions to the hydrothermal fluid. The difference between the two projected compositions is within one order of magnitude for all analysed elements.

Figure 7. Percentage contributions of analysed elements to hydrothermal fluid by rock, groundwater, and magmatic fluid.

Figure 8. The calculated NaCl content of the magmatic fluid in the context of phase relationships in the system NaCl-H<sub>2</sub>O system at 600  $^{\circ}$ C (Driesner and Heinrich, 2003). Based on this diagram, the magmatic fluid in the third set of springs is vapour-dominated.



Figure 1a.



Figure 1b.





Figure 3.



Figure 4.



Figure 5.



Figure 6.



Figure 7.



Figure 8.

	Acid spring					Average normalized	Meteoric	
	1a	1b	3a	3b	3c <sub>i</sub>	3c <sub>ii</sub>	hydrothermal spring	Groundwater
Field measurements								
pH	0.15	0.11	0.49	0.39	0.41	0.45	n.a.	8.17
Water temperature (°C)	34	35	22	26	26	27	n.a.	14
Electric conductivity (S·m <sup>-1</sup> )	325.1	365.1	152.6	210.1	202.6	180.1	n.a.	0.1
δ <sup>18</sup> Ο	5.87	5.72	-1.99	1.18	0.16	0.18	n.a.	-8.55
Flame Atomic Absorption Spectrometry (ppm)								
Si	35.1	34.6	54.3	40.4	41.8	42.8	53.0	29.2
AI	4959	4772	2785	3823	3401	3506	3865	0.014
Fe	2409	2432	1739	2248	2012	2119	2329	0.092
Mg	557.1	566.5	368.5	469.5	471.5	450.9	504.4	44.59
Са	436.7	465.0	433.8	541.3	518.8	481.7	567.3	<d.l.< td=""></d.l.<>
Na	941.1	915.9	562.7	756.9	685.1	689.7	771.2	8.83
К	1062	1027	622.8	826.9	744.4	770.3	849.2	3.696
Li	0.576	0.593	0.416	0.497	0.472	0.475	0.535	<d.l.< td=""></d.l.<>
Pb	4.059	3.906	2.498	1.807	2.964	2.550	2.869	0.001
Ion Chromatography (ppm)								
F	1212.57	1110	473.7	833.1	728.6	744.33	753.1	0.771
CI	19348	17943	9124	13952	12409	11980.2	13175	3.616
Br	53.91	46.91	54.15	60.9216	86.33	55.4869	63.60	<d.l.< td=""></d.l.<>
SO <sub>4</sub>	58918	54023.6	30133	44403.8	39850	38972.6	42345	31.50
ICP-MS (ppm)								
Mn	40.32	42.25	24.61	20.31	30.35	29.66	30.49	0.198
Со	0.638	0.609	0.382	0.505	0.475	0.447	0.518	0.002
Ni	0.327	0.293	0.182	0.255	0.395	0.229	0.300	0.002
Cu	0.150	0.140	0.250	0.320	0.280	0.310	0.333	<d.l.< td=""></d.l.<>
V	10.467	10.78	6.518	5.371	7.848	8.087	8.089	n.a.
Cr	0.297	0.279	0.157	0.223	0.186	0.200	0.219	0.002

Table 1. Field and laboratory measurements of neutral and acid springs, including average, normalized element concentrations for the third set of acid springs.

	Acid spring					Average	Meteoric	
	1a	1b	3a	3b	3c <sub>i</sub>	3c <sub>ii</sub>	hydrothermal spring	Groundwater
Ga	1.200	1.144	0.685	0.943	0.843	0.870	0.955	0.005
Cs	0.109	0.105	0.059	0.086	0.074	0.080	0.085	<d.l.< td=""></d.l.<>
Rb	3.389	3.247	1.819	1.610	2.269	2.241	2.302	0.016
Ве	0.069	0.065	0.063	0.096	0.082	0.096	0.096	<d.l.< td=""></d.l.<>
Sr	13.91	14.50	10.00	7.95	12.34	12.68	12.50	0.078
Zr	1.800	1.821	0.934	1.381	1.140	0.966	1.261	<d.l.< td=""></d.l.<>
Hf	0.035	0.036	0.009	0.015	0.015	0.010	0.014	<d.l.< td=""></d.l.<>
Cd	0.045	0.044	0.023	0.031	0.028	0.028	0.031	0.002
Sn	0.205	0.208	0.118	0.264	0.199	0.137	0.201	<d.l.< td=""></d.l.<>
Sb	0.05875	0.053	0.002	0.004	0.005	0.002	0.003	<d.l.< td=""></d.l.<>
ТІ	0.70708	0.702	0.377	0.530	0.470	0.465	0.527	n.a.
Ва	0.0511	0.043	0.116	0.053	0.051	0.043	0.081	0.004
Y	0.94808	0.908	0.526	0.733	0.653	0.658	0.734	<d.l.< td=""></d.l.<>
La	0.61932	0.597	0.351	0.481	0.429	0.433	0.484	<d.l.< td=""></d.l.<>
Ce	1.37813	1.327	0.809	1.117	0.996	1.024	1.128	<d.l.< td=""></d.l.<>
Nd	0.76245	0.73468	0.457	0.630	0.563	0.581	0.638	<d.l.< td=""></d.l.<>
Sm	0.17208	0.163	0.089	0.125	0.111	0.115	0.125	<d.l.< td=""></d.l.<>
Eu	0.050	0.047	0.026	0.036	0.032	0.034	0.037	<d.l.< td=""></d.l.<>
Gd	0.18154	0.174	0.094	0.134	0.118	0.124	0.134	<d.l.< td=""></d.l.<>
Tb	0.02789	0.026	0.015	0.020	0.018	0.019	0.020	<d.l.< td=""></d.l.<>
Dy	0.16105	0.154	0.081	0.111	0.100	0.103	0.113	<d.l.< td=""></d.l.<>
Но	0.03569	0.03138	0.016	0.022	0.020	0.021	0.023	<d.l.< td=""></d.l.<>
Er	0.09943	0.095	0.049	0.068	0.061	0.063	0.069	<d.l.< td=""></d.l.<>
Yb	0.09229	0.089	0.047	0.064	0.058	0.059	0.065	n.a.
Lu	0.01453	0.014	0.007	0.010	0.009	0.009	0.010	<d.l.< td=""></d.l.<>
Th	0.25313	0.247	0.193	0.208	0.179	0.185	0.222	n.a.
U	0.05172	0.051	0.036	0.056	0.048	0.053	0.055	n.a.

Table 2. Concentrations (ppm) of all analysed elements contributed from each end member (rock, meteoric groundwater, and magmatic fluid). Estimated precipitation of Ca, Si, Cu, and Ba is quantified as a percentage of the concentration of each measured in the water of the third set of acid springs.

	Average hydrothermal spring (ppm)	Rock Flux (ppm)	Mineral precipitation (% hydrothermal spring)	Magmatic + meteoric groundwater (ppm)	Meteoric groundwater (ppm)	Minimum magmatic contribution (41%) (ppm)	Maximum magmatic contribution (56%) (ppm)
Si	53.0	419.5	691%	0	29.2	-	-
AI	3865	2801	-	1064	0.014	2596	1900
Fe	2329	1338	-	991.2	0.092	2417	1770
Mg	504.4	519.2	-	0	44.59	-	-
Са	567.3	1478	161%	0	<0.2	-	-
Na	771.2	814.0	-	0	8.83	-	-
К	849.2	540.3	-	308.9	3.696	748.1	548.7
Li	0.535	0.542	-	0	<0.07	-	-
Pb	2.87	-6.14	-	9.009	0.001	21.97	16.09
F	753.1	0	-	753.1	0.771	1836	1344
CI	13175	0	-	13175	3.616	32129	23524
Br	63.60	0	-	63.60	<0.1	155.0	113.5
$SO_4$	42345	0	-	42345	31.50	103234	75590
Mn	30.49	34.68	-	0.000	0.198	-	-
Со	0.518	0.473	-	0.045	0.002	0.11	0.08
Ni	0.300	0.189	-	0.111	0.002	0.27	0.20
Cu	0.333	1.578	374%	0	<0.0001	-	-
V	8.089	0.000	-	8.089	<0.0001	19.729	14.444
Cr	0.219	0.119	-	0.100	0.002	0.24	0.18
Ga	0.955	0.543	-	0.412	0.005	1.00	0.73
Cs	0.085	0.083	-	0.002	<0.0001	0.00	0.00
Rb	2.302	1.976	-	0.326	0.016	0.77	0.57
Be	0.096	0.045	-	0.051	<0.0001	0.12	0.09
Sr	12.50	12.00	-	0.499	0.078	1.10	0.83
Zr	1.261	1.487	-	0.000	<0.0001	-	-
Hf	0.014	0.034	-	0	0.0001	-	-
Cd	0.031	0	-	0.031	0.002	0.07	0.05
Sn	0.201	-0.837	-	1.038	<0.0001	2.53	1.85
Sb	0.003	-0.036	-	0.039	<0.0001	0.10	0.07

	Average hydrothermal spring (ppm)	Rock Flux (ppm)	Mineral precipitation (% hydrothermal spring)	Magmatic + meteoric groundwater (ppm)	Meteoric groundwater (ppm)	Minimum magmatic contribution (41%) (ppm)	Maximum magmatic contribution (56%) (ppm)
ті	0.521	0	-	0.521	<0.0001	1.27	0.93
Ва	0.081	6.002	7290%	0.000	0.004	-	-
Y	0.734	0.954	-	0.000	<0.0001	-	-
La	0.484	0.402	-	0.082	<0.0001	0.20	0.15
Ce	1.128	0.981	-	0.147	<0.0001	0.36	0.26
Nd	0.638	0.525	-	0.113	<0.0001	0.28	0.20
Sm	0.125	0.111	-	0.014	<0.0001	0.04	0.03
Eu	0.037	0.041	-	0	<0.0001	-	-
Gd	0.134	0.101	-	0.033	<0.0001	0.08	0.06
Tb	0.020	0.016	-	0.004	<0.0001	0.01	0.01
Dy	0.113	0.094	-	0.019	<0.0001	0.05	0.03
Но	0.023	0.020	-	0.003	<0.0001	0.01	0.00
Er	0.069	0.055	-	0.014	<0.0001	0.03	0.02
Yb	0.065	0.055	-	0.010	<0.0001	0.02	0.02
Lu	0.010	0.009	-	0.001	<0.0001	0.00	0.00
Th	0.222	0.287	-	0	<0.0001	-	-
U	0.055	0.077	-	0	<0.0001	-	-

Water emerging from the third set of hyperacidic springs in the upper Banyu Pahit River valley on the western side of Kawah Ijen volcano has been determined to be distinct from the seepage of crater lake water. Based on chemical and hydrogeologic evidence it is hypothesized to emerge directly from the subsurface magmatic-hydrothermal system, with no hydrologic contributions from the crater lake. The results of these findings have important implications with respect to constraining the composition of the magmatic-hydrothermal fluid at depth, using water composition to monitor volcanic activity, and assessing the ore forming potential of the fluid at depth in the system.

The volcanic controls on the lake water composition are obscured by meteoric inputs as the lake represents a large surface reservoir in constant contact with the atmosphere, thereby limiting the potential to understand the magmatic-hydrothermal fluids and system at depth using the lake water composition. In contrast, the third set of springs provide a more direct observation window on changing volcanic activity, and on the fluid chemical composition at depth. Having determined the magmatic-hydrothermal fluid composition at depth by removing the addition spring hydrogeochemical end members (meteoric derived groundwater and water-rock interaction), we are also able to explore the ore forming potential of the system.

An additional application of the calculated magmatic-hydrothermal fluid composition is in hydrogeochemical mass-balance mixing models applied to the other two sets of hyperacidic springs in the upper Banyu Pahit River valley. In the first paper these springs were determined to have a crater lake water component. In the second paper

proportions of each volcanic water type, in addition to meteoric derived groundwater in each set of springs are determined. The proportions of each water type are combined with measurements of discharge from each of the sets of springs to determine the absolute and relative fluxes of crater lake water and hydrothermal fluid from the springs, and to compare their potential environmental impacts. Manuscript 2

# Characterizing and quantifying hyperacidic water of volcanic origin

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#### Abstract

Hydrothermal fluid emerging from a set of springs on the western side of Kawah Ijen volcano, East Java, Indonesia, (1995 m.a.s.l.) has been determined to form the headwaters of the Banyu Pahit River. Previously it was assumed that the headwaters of the Banyu Pahit were seepage from the hyperacidic crater lake, which emerges from another set of springs (2090 m.a.s.l.). Both crater lake seepage and hydrothermal fluid have been determined to also emerge as part of yet another set of springs (2075 m.a.s.l.). Anion ratios of SO<sub>4</sub>/Cl and SO<sub>4</sub>/F are used in mixing models to determine the proportion of magmatic fluids discharged from each set of springs. Mixing models using the following conservative anions, CI, SO<sub>4</sub>, and F, were used to determine the proportions of meteoric derived groundwater and magmatic fluid in each spring. The discharge of the uppermost springs, which is derived primarily from crater lake seepage, is 1.2 l/s and infiltrates the sediment bed approximately 100 m from the outflow location. The springs at 2075 m.a.s.l. have a discharge of 0.9 l/s and also completely infiltrate the sediment bed. The discharge from the lowermost springs, composed primarily of hydrothermal fluid, is 15.4 l/s and represents a major source of contamination at a regional scale; the Banyu Pahit River flows ~45 km before discharging into the Madura Strait (connected to the Java Sea), and is used for agricultural irrigation. The flux of Al, Be, Cd, Cl, Cr, F, Fe, Pb, Mn, Na, and SO<sub>4</sub> through the Banyu Pahit River exceeds health guidelines of the World Health Organization and may pose a substantial health risk to populations living in the downstream environment and to the quality of agricultural production using the toxic water for irrigation.

Keywords: hydrogeochemistry; volcano; crater lake; hydrothermal fluid; Kawah Ijen; Banyu Pahit

## 1. Introduction

Water associated with volcanic activity is commonly characterized by low pH due to interaction with magmatic volatiles (e.g. SO<sub>2</sub>, H<sub>2</sub>S, HCl, CO<sub>2</sub>). Such volcanic waters transport elevated concentrations of heavy metals and other toxic elements derived from either the magmatic fluid itself or from accelerated rock alteration and/or dissolution due to the low pH fluid (Rowe et al., 1995; Deely and Sheppard, 1996; Sriwana et al., 1998; Delmelle and Bernard, 2000; Gammons et al., 2005). Volcanogenic fluids are similar to acid mine drainage waters in terms of acidity, toxicity, and resulting environmental impact on proximal ecosystems (Delmelle and Bernard, 2000; Parnell and Burke, 1990; Pringle et al., 1993; Schaefer et al. 2008). In particular, degraded soils and crops containing elevated levels of metals have been observed to result from agricultural irrigation using volcanic-derived acidic stream waters, with subsequent secondary human health impacts due to elevated heavy metal consumption (Parnell & Burke, 1990; Deely and Sheppard, 1996; Sriwana et al., 1998; Heikens et al., 2005a,b,c; Löhr et al. 2005, 2006; van Rotterdam-Los et al. 2007, 2008).

Element concentrations in the surface volcanic fluid can be used to observe changes in volcanic activity because volcanic fluid composition is linked to the deeper magmatic system. For crater lake fluids, the situation is more complex, as these types of lakes are exposed continuously to the atmosphere and meteoric inputs and thus have their magmatic signatures modified by diurnal and seasonal processes such as evaporation and rainfall (Armienta et al., 2008). Understanding the sources and controls of volcanic fluid exposed in the surface environment can also be used to develop a

conceptual model of the hydrogeologic-hydrothermal system at depth. Outflow of different water types (i.e., crater lake water, hydrothermal fluid, meteoric derived groundwater, etc.) at different locations, when linked to the geology and topography, provides constraints on the hydrogeologic-hydrothermal system. Understanding such systems is difficult as they tend to have a complex hydrogeology due to variable density flow driven by solute and temperature gradients between the meteoric- and magmatic-derived fluid, in addition to flow driven by hydraulic pressure and elevation (Ingebritsen et al., 2006).

Volcanic fluid on and around Kawah ljen volcano consists of a hyperacidic crater lake, three sets of hyperacidic springs, and the hyperacidic Banyu Pahit River, which has its headwaters on the western side of the volcano. All of these hydrologic components were previously assumed to be connected. Specifically, the springs were all thought to be derived from the crater lake seepage, this seepage was thought to form the headwaters of the Banyu Pahit River, and any differences among the springs were thought to result from differences in the extent of water-rock interaction and dilution by meteoric-derived groundwater (Kemmerling 1921; Delmelle and Bernard 1994, 2000; Delmelle et al., 2000; Löhr et al., 2007). Recent analyses by Palmer et al. (in preparation) of previously unstudied acid springs in the Banyu Pahit River valley has led to the identification of a second type of volcanic water at Kawah lien. This water has a chemical composition different from that of crater lake water and likely constitutes fluid derived directly from the magmatic-hydrothermal system. Contrary to previous interpretations, these hydrothermal springs are the true headwaters of the Banyu Pahit River (Palmer et al., in preparation).

Additional complexity is introduced by the presence of multiple volcanic fluid types with differing origins and compositions, something that is important when considering the transport and fate of elements in the surrounding region and monitoring or characterizing toxicity. It is also important for understanding processes within the subsurface hydrologic system. The current study was designed to undertake a hydrogeochemical survey of all surface hydrologic features on the western side of Kawah Ijen volcano in order to understand the origins of, and connections between, the different fluid types present in the surface environment of the volcano, and in particular the source of elements and fluid to the Banyu Pahit River.

The Banyu Pahit River flows past several towns and villages within the Ijen caldera and is used on the Asembagus plains for agricultural irrigation. Understanding the origin and chemistry of the river is important for people living and growing food, particularly with respect to toxicity (Heikens et al., 2005a, b, c; Löhr et al., 2005, 2006; van Rotterdam-Los et al., 2008a, b). The potential to use the chemistry of the Banyu Pahit River in developing a volcanic activity monitoring system also has important implications for the local population; acidic mudslides associated with the 1817 eruption of Kawah Ijen resulted in devastating damage as far as the city of Banyuwangi, more than 25 km southeast of Kawah Ijen (Kemmerling, 1921), and current volcanic activity and the potential for eruptive activity poses an ongoing threat to local people. In order to both monitor volcanic activity and understand the potential toxicity of the volcanic fluids in the environment during different stages of volcanic activity, it is important to understand the sources and controls of volcanic fluid in the surface environment.

Questions of particular importance are "where is the fluid coming from?" and "how would its composition change during periods of increased volcanic activity?"

The detailed hydrogeochemical compositions of the crater lake, acid springs, neutral springs sourced by local meteoric derived groundwater, and the upstream section of the Banyu Pahit River have been analyzed to address these questions. The results of these analyses, in addition to those for the Kawah Ijen hydrothermal fluid (Palmer et al., in preparation) and the flux of elements from the rock to the acid water (van Hinsberg et al., in review), were used with mass-balance mixing models of the hydrogeochemical end members (meteoric groundwater, crater lake water, hydrothermal fluid, and rock). The geographic distribution and flux of each water type to the environment was thereby constrained and a conceptual model of the Kawah Ijen – Banyu Pahit River system hydrogeochemistry developed, that identifies and quantifies sources of elements to the environment, notably to the toxic Banyu Pahit River.

# 2. Site and hydrologic setting

Kawah Ijen volcano, located within the Ijen caldera in East Java, Indonesia  $(08^{\circ}03'S, 114^{\circ}14'E;$  elevation  $\approx 2,346$  m.a.s.l.), hosts the largest naturally occurring body of hyperacidic brine in the world in its crater (Fig.1). The primary source of water to this lake is precipitation, and magmatic input is dominated by the vapour phase (e.g. HCI, H<sub>2</sub>S, HF, etc), producing hyperacid water that builds up its cation concentrations from water-rock interaction (van Hinsberg et al. submitted). The pH of the lake water is between -0.1 and 0.3, and total concentration of dissolved solids is greater than 100

g/kg (Delmelle and Bernard, 1994, 2000; Takano et al., 2004; van Hinsberg et al., submitted). The last large volcanic eruption occurred in 1817 with more recent activity restricted to small-scale phreatic eruptions (Hengevald, 1920; Kemmerling, 1921; Delmelle et al., 2000). Volcanic activity is currently characterized by degassing from fumaroles on the southern lake shore.

Four sets of springs are present in the upstream Banyu Pahit River valley, which descends on the western side of the volcano: diffuse springs just below the lake (1AS), a single spring 200 m downstream emerging at the contact with an impermeable lahar deposit (NAS), a set of springs below this lahar (2AS) and a set of springs emerging from beneath a lava flow approximately 1500 m downstream of the lake (3AS). Water sampled from the spring near Paltuding (Fig. 1a) is used as the representative meteoric derived groundwater sample (Palmer et al. in preparation) because its pH, as well as high Ca and Mg concentrations (Table 2), are indicative of water of meteoric origin in equilibrium with volcanic host rock and soil (Mizota and van Reeuwijk, 1989).

Crater lake water produces the first set of acid springs on the upper western flank of the volcano ( $\approx$  2090 m.a.s.l.) (1AS; Figs. 1b, 2), and is characterized by a pH between 0.01 and 0.1, and a temperature of ~ 35°C. Cooling and evaporation of spring water upon outflow to the surface result in the extensive precipitation of gypsum terraces and minor precipitation of yellow sulphates including alunogen (Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·16H<sub>2</sub>O), pickeringite (MgAl<sub>2</sub>(SO<sup>4</sup>)<sub>4</sub>·22H<sub>2</sub>O), tamarugite (NaAl(SO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O) and kalinite (KAl(SO<sub>4</sub>)<sub>2</sub>·11H<sub>2</sub>O) (Delmelle and Bernard, 2000). Water from these springs

flows approximately 100 m downstream on the surface in the area of the gypsum formations, and gradually disappears into the sediment.

Observations made in July and August, 2009, suggests a significant seasonal component to flow from the crater lake to the outer volcanic flanks. July and August, 2009, were characterized by unseasonably high rainfall, particularly compared with the same period in 2008. Surface flow from the 1AS springs, during the 2009 period, extended several tens of meters further than was observed in 2008, with flow reaching a second, distinctively different set of acid springs (2AS; elevation ≈ 2075 m.a.s.l.) (Figure 1b, 2). An additional spring of crater lake seepage was observed in 2009 emerging at approximately the same elevation as the second acid springs, at the base of a scoria deposit that pinches out several meters further down the valley. This spring was not active during the 2008 field season, suggesting that the activity of some flow paths of crater lake seepage are ephemeral, due to variable discharge related to differences in rainfall and lake level.

The second set of acid springs (2AS) is located at a topographic low in a scoria deposit bounded on either side by impermeable lava and lahar flows. Minor gypsum and sulphate deposition is observed at this location. The average temperature of these springs is 23.3°C, and the average pH is 0.22. These springs have been determined to contain both crater lake water and hydrothermal fluid (Palmer et al., in preparation).

The composition of the third springs (3AS; Fig. 1b) has been reported by Palmer et al. (in preparation). These springs do not have a crater lake component (Fig. 2). The average temperature and pH are 25.3°C and 0.44, respectively. The discharge from

these springs forms the headwaters of the Banyu Pahit River (Palmer et al., in preparation), and is observed to emerge from below the same lava flow as the second acid springs, where the Banyu Pahit valley from Kawah Ijen meets a valley from the adjacent Widadaren volcano. River water subsequently flows over a waterfall into an incised valley, and then northwest through and out of the Ijen Caldera.

Approximately 17 km downstream from its headwaters, at the town of Blawan, the Banyu Pahit Riveer is joined by two major neutral tributaries, the Kali Sat and the Kali Senggon, and has a discharge of >1000 l/s (Delmelle and Bernard, 2000). At the confluence with the neutral tributaries a white precipitate forms, and the river name changes to Banyu Putih ("White River") (Kemmerling, 1921). Approximately 20 km further downstream from Blawan, the river water (pH  $\sim$  4) is used for agricultural irrigation. The remaining river flow discharges into the Strait of Madera (van Rotterdam-Los et al., 2008a).

## 3. Methods and approach

We modeled the hydrogeochemistry of the Kawah Ijen – Banyu Pahit system using four hydrgeochemical end members: crater lake fluid, hydrothermal fluid, meteoric groundwater, and the product of water-rock interaction. Crater lake and meteoric groundwater compositions are known directly from the analysis of samples and representative chemical signatures for hydrothermal fluid and water rock interaction at Kawah Ijen have also been determined (van Hinsberg et al., submitted and Palmer et al., in preparation respectively). These end member compositions have been combined

with composition and discharge measurements for each set of acid springs, and the Banyu Pahit River to determine the relative contribution of each end member to the total composition. The sources of the acid springs and the Banyu Pahit River were determined from this information and, in conjunction with relevant geological mapping of the area, were used to develop a conceptual model of the associated subsurface hydrogeologic-hydrothermal system.

#### 3.1 Sampling and analytical methods

A comprehensive sampling campaign was carried out during July and August 2008 and 2009. On site pH, air and water temperature, and electric conductivity measurements were made at the crater lake, the Banyu Pahit River and all springs referred to above. (Table 1). Total discharge of each group of springs, and that of the Banyu Pahit River was determined using the area-velocity method. A series of velocity measurements were made across the width of the river, with depth and distance from the bank measured at each velocity measurement point to the nearest cm. More than 50 samples of the Banyu Pahit River, the Kawah Ijen crater lake, and all observed acid and neutral springs on and around the volcano were collected in 2008 (Fig. 1). Samples were filtered on site to 0.45 $\mu$ m, and acidified with dilute nitric acid (HNO<sub>3</sub>) when necessary (resulting in a pH < 0.5). Redundancy in the data set was achieved through duplicate sampling and analysis of multiple springs from each site whenever possible (Table 2). More than 40 elements were analyzed in each sample.

Analyses of all major and trace element concentrations were carried out at McGill University. Samples were analysed at a range of dilution factors chosen to

accommodate the large spread in the concentration of any single element among samples and of different elements within the same sample, and to accommodate the detection range of the instrumentation. All standards and sample dilutions were prepared by mass to an accuracy of 10<sup>-5</sup> grams. Anions (CI, Br, SO₄, and F) were analyzed by ion chromatography at the Hydrogeology Laboratory of McGill University. Sample dilutions and standards were prepared for ion chromatography in distilled water. Cations (Si, Al, Ca, K, Li, Fe, Mg, and Na) were analyzed by flame atomic absorption spectrometry (AAS) using a Perkin Elmer AAnalyst 100 Flame AAS at the Trace Element Analytical Laboratory (TEAL) of McGill University. Sample dilutions and standards were prepared for in a 3% trace metal grade HNO<sub>3</sub> matrix. Trace elements were also analyzed at TEAL, by inductively-coupled plasma mass spectrometry using a Perkin Elmer Elan 6100 DRCplus, and these sample dilutions and standards were prepared in an analytical grade (Nanopure<sup>TM</sup> quality) HNO<sub>3</sub> matrix.

## 4. Results

The results of measurements of pH, temperature, electric conductivity, and discharge made in the field are reported in Table 1. The pH ranged from -0.01 for the crater lake water to 0.44 for the Banyu Pahit River; the springs returned intermediate values (1AS = 0.13; NAS = 0.15; 2AS = 0.22; 3AS = 0.43). Electrical conductivity (EC) was highest for the first set of acid springs ( $365.1 \text{ S m}^{-1}$ ), and reached a minimum of 150.1 S m<sup>-1</sup> for the Banyu Pahit water. The pH of meteoric groundwater, taken from the Paltunding spring sample, was 8.17, and EC was 0.1 S m<sup>-1</sup>. The results of all laboratory analyses described in the previous section are found in Table 2. For all acid waters,

SO<sub>4</sub> concentrations vary from 61,202 ppm to 51,464 ppm, CI from 20,550 ppm to 15,990 ppm, and F from 1266 ppm to 965.4 ppm. In the hyperacidic waters, concentrations of anions are highest in crater lake water and lowest in the Banyu Pahit River water, as are concentrations of Mg, AI, and Na. The opposite is true for Si, Ca, and Fe, which have higher concentrations in the springs and Banyu Pahit River than in the crater lake water. In neutral, meteoric derived groundwater, the concentration of SO<sub>4</sub> is 31.50 ppm, CI is 3.616 ppm, and F is 0.771 ppm.

Less than 5% statistical error is associated with standard and duplicate analyses of all major elements, by both atomic absorption and ion chromatography. Statistical error is less than 10% for trace element analyses by ICP-MS, except in the cases of Be (19%) and Sb (34%). Slight variations in composition due to dilution by neutral groundwater and analytical uncertainty were corrected for by normalizing to the most concentrated spring using measured chloride concentrations (Palmer et al., in preparation). This was done to obtain the most representative sample for each set of springs for use in all further interpretation.

## 5. Interpretation and discussion

## 5.1 Hydrogeochemistry

In the following sub-sections, SO<sub>4</sub>, CI, and F, are used in mixing models of the hyperacid springs and Banyu Pahit River to reconstruct the proportions of hydrothermal, crater lake, and meteoric groundwater that make up spring and river waters. The conservative nature of these components is indicated by the fact that their
concentrations are four orders of magnitude higher in fluid of magmatic origin than in meteoric groundwater, and that they are not involved in fluid-rock interaction (van Hinsberg et al., submitted). Furthermore, as these anion concentrations are negligible in the groundwater, and water-rock interaction cannot change anion ratios (SO<sub>4</sub>/Cl, SO<sub>4</sub>/F), differences in these ratios between crater lake water, the different springs, and the Banyu Pahit River must reflect a magmatic fluid source in addition to the crater lake. Such differences in anion ratios were established in a companion study (Palmer et al., in preparation).

Palmer et al. (in preparation) assessed the influence of water-rock interaction on the spring fluid chemistry using the rock flux composition of completely altered Kawah ljen andesite established by van Hinsberg et al. (submitted). The water-rock ratio, which is the mass of rock dissolved per mass of water, was determined using a least squares approach, obtaining a line of best fit consistent over six orders of magnitude for the measured element concentrations in the spring water and the previously established flux of each element to the water during total andesite alteration (van Hinsberg et al., submitted).

#### 5.1.1 First acid springs

The first acid springs, i.e., those at the highest elevation on the western flanks of the Kawah Ijen volcano (Fig. 1b) are derived predominantly from crater lake fluid seeping out of the flank of the crater (Fig. 2), as shown by the anion ratios of the spring water, SO<sub>4</sub>/Cl and SO<sub>4</sub>/F ratios, which are indistinguishable from those of the crater lake directly (Palmer et al., in preparation). The bulk chemical signature of the first acid

springs is a mixture of three hydrogeochemical end members: crater lake fluid, the products of water-rock interaction, and neutral groundwater of meteoric origin, which dilutes the crater lake fluid signature. A mass-balance mixing model was used to determine the mass proportions of meteoric groundwater and crater lake fluid in the first acid springs based on the following equation:

$$Q_{\underline{AS1}}C_{\underline{AS1}} = Q_{\underline{gw}}C_{\underline{gw}} + Q_{\underline{lake}}C_{\underline{lake}}$$
(1)

where *C* represents the concentrations of SO<sub>4</sub>, CI, and F in the acid spring fluid (<u>AS1</u>), groundwater (<u>gw</u>), and crater lake fluid (<u>lake</u>), and *Q* represents the proportion (%) of each fluid type. Results of this mixing model indicate that on average the spring waters comprise 94.9( $\pm$ 0.8)% crater lake water, and that meteoric groundwater constitutes a relatively minor proportion of the spring water at this location, approximately 5.1( $\pm$ 0.8)% (Fig. 3).

Approximately 48.9 (±1.1) grams of rock are dissolved in each kilogram of the first acid spring water. The calculated total flux of elements to the springs is well within the error of that of the in situ crater lake fluid in proportion to its contribution to the spring water. Any differences between the composition of the lake water and the first acid springs can be attributed to dilution by meteoric groundwater. After removing the effect of dilution by neutral groundwater, it was determined that, within analytical error, no elements were added to the first spring waters by water-rock interaction other than those introduced to the crater lake. In situ crater lake water is not saturated with respect to most elements added through water-rock interaction, suggesting that host rock

encountered by the crater lake water along seepage flow paths is fully altered and does not contribute further to the spring water chemistry.

As there is no additional contribution to the spring water chemistry from waterrock interaction, a separate term for the latter was not included in the final mixing model. Formations of gypsum extend from the location of the first springs over an area of 50 by 100 meters, and have a thickness of 10 to 40 cm. Much less abundant and very soluble yellow precipitates, comprised of alunogen ( $AI_2(SO_4)_3 \cdot 16H_2O$ ), pickeringite ( $MgAI_2(SO^4)_4 \cdot 22H_2O$ ), tamarugite ( $NaAI(SO_4)_2 \cdot 6H_2O$ ) and kalinite ( $KAI(SO_4)_2 \cdot 11H_2O$ ) also appear near the springs (Delmelle and Bernard, 2000). However, mineral precipitation was observed only to take place several meters from the outflow locations of the springs, and did so due to cooling and evaporation. It therefore does not influence spring water chemistry at outflow.

# 5.1.2 Second acid springs

Ratios of SO<sub>4</sub>/CI and SO<sub>4</sub>/F measured in the waters of the second set of acid springs emerging on the western flanks of Kawah Ijen volcano indicate that the magmatic component of is a mixture of the two magmatic water types: crater lake water, also found in the first acid springs, and hydrothermal fluid from at depth in the system, which dominates the third acid springs (Palmer et al., in preparation). Crater lake water is characterized by significantly lower SO<sub>4</sub>/CI and SO<sub>4</sub>/F ratios than the third set of acid springs, indicating that distinct magmatic fluid types influence the chemistry of each spring set, linked to unequal partitioning of SO<sub>4</sub>, F, and Cl in magmatic vapour and brine. This is typical of the distribution of water types for volcanic-magmatic-

hydrothermal systems (Giggenbach and Corrales-Soto, 1992; Stimac et al., 2003). As the second group of acid springs has  $SO_4/CI$  and  $SO_4/F$  ratios that are between those of the crater lake water and the third group of acid springs, they are interpreted to be fed by a mixture of these two water types.

The proportions (Q) of crater lake fluid and hydrothermal fluid in the magmatic component of the second set of acid springs was determined using a mixing model incorporating the anion ratios (C) of the previously constrained hydrothermal fluid, the (Palmer et al., in preparation), and the crater lake water (Eqn. 2).

$$Q_{\underline{AS2(mag)}}C_{\underline{AS2(mag)}} = Q_{\underline{lake}}C_{\underline{lake}} + Q_{\underline{hydrotherm}}C_{\underline{hydrotherm}}$$
(2)

Results of this mixing model indicate that the proportions of the two volcanic end members in the second acid springs are approximately 45% crater lake fluid and 55% magmatic-hydrothermal fluid. Using the concentrations of SO<sub>4</sub>, Cl, and F in mixing models to determine the proportions of groundwater and magmatic fluid end members in the second acid springs (Equation 3), we calculated that approximately 34% of the spring water is of meteoric groundwater origin, and 66% of magmatic origin. By combining the results of Equation 2 and Equation 3 into Equation 4 we determined that, by mass, the second acid springs comprise 34% meteoric groundwater, 29% crater lake fluid, and 36% fluid from the deep magmatic-hydrothermal system (Fig. 3; Table 3).

$$Q_{\underline{AS2}}C_{\underline{AS2}} = Q_{\underline{gw}}C_{\underline{gw}} + Q_{\underline{mag}}C_{\underline{mag}}$$
(3)

$$Q_{\underline{AS2}}C_{\underline{AS2}} = Q_{\underline{gw}}C_{\underline{gw}} + (Q_{\underline{lake}}C_{\underline{lake}} + Q_{\underline{hydrotherm}}C_{\underline{hydrotherm}})$$
(4)

The water-rock ratio determined for the hydrothermal component of the second acid spring fluid indicates that  $25.5(\pm 1.05)$  grams of Kawah Ijen andesite are dissolved in each kilogram of spring water ( $R^2 = 0.99$ ). After removing the concentrations of elements derived from water-rock interaction from their total concentrations in the spring water, we found that the residual concentrations of some elements are significantly higher than the concentrations actually measured in the spring fluid. For example, the calculated concentrations of Ba, Si, Ca, and Cu are several hundred to several thousand times higher than measured, as in the third set of acid springs (Palmer et al., in preparation). This is due to precipitation and removal of these elements from solution, which is consistent with field observations of gypsum, barite, and cristoballite precipitation near the source of the springs.

## 5.1.3 Third acid springs and Banyu Pahit River

The water of the third acid springs consists dominantly of hydrothermal fluid derived from the Kawah Ijen magmatic-hydrothermal system sensu stricto, rather than crater lake water as was previously assumed (Delmelle and Bernard, 2000; Heikens et al., 2005a, b, c; Löhr et al., 2005, 2006, 2007; van Rotterdam-Los et al., 2008 a, b), based on SO<sub>4</sub>/Cl and SO<sub>4</sub>/F ratios as well as structural and topographical constraints on the emergence of crater lake fluid at this location. The valley in which the third group of springs is located does not connect with the crater (Palmer et al., in preparation). The Banyu Pahit River has SO<sub>4</sub>/Cl and SO<sub>4</sub>/F ratios within error of those of the third acid springs, supporting its origin from these hydrothermal springs rather than from crater lake seepage (Palmer et al., in preparation). As no tributary streams or surface runoff is

observed along this reach, river hydrogeochemical end members used here were water from the third acid springs, the dissolved products of water-rock interaction, and meteoric groundwater.

Changes in the end member proportions and overall chemistry of the river were analyzed from samples taken at its headwaters (the third acid springs) and three locations 1 to 3 km from the headwaters. Table 3 reports the proportion of magmatichydrothermal fluid in the river water at each of these locations, based on the previously determined composition of the hydrothermal fluid , which makes up approximately 48% of the third acid spring water (Palmer et al., in preparation). The proportion of hydrothermal fluid in the Banyu Pahit River is estimated to range from 48% at its headwaters to 37% at location c (Table 3), indicating a dilution of 29.7% by meteoric derived groundwater over this ~3 km stretch of the river.

The calculated ratio of dissolved rock to water is reported in Table 3. A linear regression for the fluid composition and element flux from altered rock at each location was determined to have  $R^2 > 0.96$  for locations *a* through *c*. The corresponding rock/water ratio varied between  $30.05(\pm 1.11)$  grams of rock per kilogram of water at site *a* to  $34.11(\pm 1.10)$  grams of rock per kilogram of water at location *c*. These results are within the range reported for this river stretch by van Hinsberg et al. (in review). The residual compositions obtained after removing the calculated contribution of elements released from the rock from the total water composition, suggest that Si, Ca, Cu, and Ba precipitate. The concentrations of these elements are predicted to be several hundred times greater than measured in the river water, based on the application of a mixing

model involving water-rock interaction, hydrothermal fluid, and meteoric groundwater. Precipitation of these elements is also predicted by mixing models for acid springs 2AS and 3AS.

Banyu Pahit River water is estimated to be saturated to supersaturated along the reach sampled in the current study with respect to barite as well as amorphous silica, based on the equilibrium thermodynamic calculations of Delmelle and Bernard (2000). These estimates are consistent with the persistence of Si and Ba in the bulk rock during water-rock interaction and the progressive alteration of the rock (van Hinsberg et al., in review). Dispersed barite, enriched in Sr and Pb, has been observed to have precipitated extensively in the altered rock matrix of the Banyu Pahit River bed, further explaining the observed incongruence between the predicted flux of Ba and the measured bulk rock concentration in fully altered rock material (van Hinsberg et al., in review). Similar conclusions are reached from the compositions of suspended solids filtered from Banyu Pahit River water, which consist of amorphous and poorly sorted silica and some gypsum particles, in addition to rock clasts (Delmelle and Bernard, 2000), indicating saturation and precipitation of Ca and Si. The processes controlling Cu concentration in the Banyu Pahit are difficult to constrain, however mineral precipitation and adsorption onto suspended sediment in the water both likely take place and may explain why we do not measure as much Cu in the Banyu Pahit water as our mixing model predicts (Delmelle and Bernard, 2000).

## 5.2 Hydrogeologic constraints

The emergence of acid water in the upstream Banyu Pahit valley is directly linked to the local stratigraphy and this provides a means of understanding the flow of fluids from different sources through the subsurface. At the first set of springs, the valley is incised into the lavaflows and scoria of the Kawah Ijen cone. These deposits are covered with numerous more recent phreatic and phreato-magmatic deposits, mostly unconsolidated and consisting of a fine-grained matrix with abundant bombs of altered lava and pumice. The valley at this location is steep and its floor roughly follows the dip of the phreatic and phreato-magmatic deposits. Where it cuts these layers, flow of pale blueish acid water is observed. These layers are clearly excellent aquifers and facilitate dispersed outflow of acid spring water of crater lake origin over an area of at least 50 by 100 m. The uppermost of these springs is only 100m downstream of the dam and we therefore conclude that it is fed by direct seepage from the lake.

The local stratigraphy at the second set of acid springs consists of multiple layers of impermeable consolidated lahar and mud flows, porous phreatic deposits ranging from magmatic to phreato-magmatic, and fine-grained pyroclastic flow material. Three lavaflows occur within these deposits, the middle of which ends several tens of metres downstream of this location. All units dip down the valley and deposition appears to have been controlled by the valley topography. Spring water emerges from a scoraceous phreato-magmatic deposit bounded above and below by impermeable lahar deposits, with an additional lava flow above the upper lahar deposit. This scoraceous unit follows the palaeotopography, and spring outflow occurs at a local low point in the elevation of the unit, channelled due to gravity-driven water flow. In 2009, there was also flow of acid water from a scoria layer in between the lower and middle lavaflows

(above the outflow of the second acid springs). This water was blueish in colour rather than yellow-green water as is the case at the second springs, and outflow was accompanied by extensive gypsum precipitation. This new spring is therefore similar to the crater lake seepage observed at the first springs.

The stratigraphy at the third set of springs is similar to that at the second set of springs. Consolidated mud and lahar flows alternate with scoraceous magmatic and phreatomagmatic material, and this sequence is capped by a lavaflow that is several metres thick. On top of this is a sequence of lavaflows, poorly sorted mudflows, and pyroclastic material that is continuous with the outcrops at the rapids. The spring water appears from fractures in the capping lava flow at the contact with an underlying impermeable lahar unit. The lava flow unit overlying the third set of springs is identical to that overlying the second set (based on unpublished major and trace element bulk rock data). As both these sets of springs contain hydrothermal fluid, the overlying lava flow may serve as an impermeable cap to upward water flow of the hydrothermal system at the regional scale, and the second and third sets of springs may represent two outflow locations from the same aquifer. The third set of springs are located at the confluence of the Banyu Pahit valley and the valley separating Widadaren and Kawah Ijen volcanoes and the springs actually occur in the latter valley. As the valley topography reflects subsurface stratigraphy, it is therefore likely that the presence of springs at this location is controlled by this stratigraphy.

The second set of springs has been shown in this paper to contain a crater lake component in addition to its hydrothermal fluid component. The hydrostratigraphic units

of the second springs and the lowest outflow elevation of the first acid springs are separated by an impermeable lahar unit approximately 1 m in thickness. Therefore the crater lake component that is observed in the 2AS springs, but not in the 3AS springs, is likely due to fractures locally connecting the two hydrostraphigraphic units.

#### 6. Conclusions and implications

This study has developed a conceptual hydrogeologic model for the upstream Banyu Pahit River valley and has determined the contributions to surface hydrology from the Kawah ljen crater lake and hydrothermal system based on the hydrogeochemistry of three sets of acid springs in the river valley. Measurements made during the course of this study, as well as the previously established chemical signature of hydrothermal fluid in the Kawah ljen magmatic-hydrothermal system (Palmer et al., in preparation) have made it possible to estimate the relative contributions of hydrothermal fluid, crater lake water and groundwater of meteoric origin, in each of the sets of acid springs. The first set of springs has been shown to comprise 95% crater lake seepage and 5% meteoric groundwater by volume. By contrast, the third set of springs was shown to consist of approximately equal volumes of hydrothermal fluid and meteoric groundwater, with no crater lake component. The second set of springs, located between the other two sets of springs, consists of a mixture of all three fluid types, with approximately equal volumes of crater lake water, meteoric groundwater, and hydrothermal fluid. Owing to local stratigraphic controls, water from the crater lake is potentially entering the hydrothermal aquifer locally, rather than representing a widespread, separate fluid type with a distinct aquifer.

Previous investigations of downstream volcanogenic contamination from the Banyu Pahit River have assumed that the contamination was derived from crater lake seepage (Delmelle and Bernard, 2000; Heikens et al., 2005a, b, c; Löhr et al., 2005, 2006, 2007; van Rotterdam-Los et al., 2008 a, b). Our research shows that the headwaters of the Banyu Pahit River are the third set of acid springs which are sourced directly by the hydrothermal system, and have no significant crater lake component (Palmer et al., in preparation). Therefore the large-scale volcanogenic contamination, which reaches at least 45 km downstream before ultimately discharging into the Strait of Madura, comprises increasingly dilute hydrothermal fluid, and is not directly linked to the Kawah Ijen crater lake. Discharge from the first and second sets of acid springs, which both have significant crater lake water components, disappears underground after flowing several hundred meters on the surface. It is unclear what effects these waters ultimately have on local ecology, both on surface and in the subsurface, and on what scale, but given their small discharge compared to that of the third springs, their impact is likely to be minimal.

Understanding the composition of the hydrothermal and crater lake water types, and their relationship to the Banyu Pahit River water should make it possible to reliably use the composition of the river water to monitor volcanic activity. In particular, increased magmatic degassing and volcanic activity should be reflected by increased concentrations of magmatic anions such as SO<sub>4</sub>, F, and Cl. The crater lake is composed of rain water that dissolves gases from the magmatic-hydrothermal system and rock from the crater walls. As a body of water that sits on the surface, crater lake inevitably has a composition that is strongly influenced by surface meteorological conditions (e.g.,

pH and TDS fluctuations due to rainfall events and evaporation). Although changes in crater lake water chemistry have been noted as precursors to eruptive activity at several volcanoes (Sigurdsson, 1977; Ossaka et al., 1980; Takano and Watanuki, 1990; Rowe et al., 1992; Badrudin, 1994; Armienta et al., 2000; Christenson, 2000; Varekamp et al., 2001; Tassi et al., 2005), early stage, low-level volcanic activity has been found often to be masked or buffered in the crater lake water chemistry by water-rock interaction and atmospheric processes (Armienta et al., 2008). In contrast, the chemistry of the hydrothermal fluid is controlled more directly by variations in activity of the magmatic-hydrothermal system without direct influence of climatic conditions, as this fluid is not in contact with the surface environment. The water of the Banyu Pahit River has been shown to contain a large proportion of hydrothermal fluid. Consequently variations in concentrations of elements such as Cl, F, and SO<sub>4</sub> should reflect variations in volcanic activity rather than variations in local climate, and are expected to be more sensitive to the early stages of a volcanic eruptive event than would be the crater lake water.

By combining the contribution of crater lake and hydrothermal fluid with the discharge at each set of springs, we have been able to calculate the total fluxes of each element and each fluid type from all three sets of springs (Table 4). The estimated total discharge of crater lake seepage is 1.2 l/s, whereas that of hydrothermal fluid is 15.4 l/s, indicating that the proportion of hydrothermal fluid released directly to the local surface hydrology is at least an order of magnitude greater than that released by crater lake seepage. This contradicts the earlier conclusion that the crater lake is the principal source of acid water from the volcano (Delmelle and Bernard, 2000; Heikens et al., 2005a, b, c; Löhr et al., 2005, 2006, 2007; van Rotterdam-Los et al., 2008 a, b).

Many components of the Kawah Ijen hydrogeochemistry are highly toxic (e.g.,TI, F, Cd, and Al) and constitute an important local and downstream risk to environmental and human health. The flux of elements from the Kawah Ijen hydrothermal system and the various source components of the hydrothermal fluid through these springs to the local surface hydrology can be estimated by combining the results obtained through this study with river discharge measurements. Our estimate of the current discharge from the hydrothermal springs is 31 I/s, which corresponds to a flux to the Banyu Pahit River, of 35.2 ton/day Cl, 113.4 ton/day SO<sub>4</sub>, 2.02 ton/day F, 10.4 ton/day Al, 0.08 kg/day Cd, and 1.39 kg/day Tl. Concentrations of Al, Cr, Cl, F, Pb, Mn, Na, and SO<sub>4</sub> in the hydrothermal springs and upstream Banyu Pahit River greatly exceed health-based guidelines by the WHO (WHO Drinking Water Standards, 1993).

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# **Figure captions**

Figure 1a. Ijen volcanic complex, East Java, Indonesia

Figure 1b. Topographical map of the upper Banyu Pahit River valley, Kawah Ijen volcano, including crater lake (elevation  $\approx$  2,200 m.a.s.l.), three sets of hyperacidic springs (1AS, 2AS, 3AS), and the hyperacidic Banyu Pahit stream. Modified from van Hinsberg *et al* (*submitted*).

Figure 2. A schematic cross-section of the Kawah Ijen magmatic-hydrothermalgroundwater system, showing the following hydrological features, crater lake, fumaroles, three sets of acid springs (1AS, 2AS, and 3AS), and the Banyu Pahit River. Cross-section transect from Fig. 1b labelled A – D.

Figure 3. A schematic drawing of part of the surface hydrological system of Kawah Ijen volcano showing the relative contributions of different fluid end members (meteoric derived groundwater, crater lake seepage, and hydrothermal fluid) to the acid springs of the upper Banyu Pahit River valley. Cross section transect from Fig. 1b labelled A – D.

Figure 4. Relative fluxes of elements (grams/day) from Kawah Ijen crater lake seepage and Kawah Ijen hydrothermal fluid.



Figure 1a.



Figure 1b.





Figure 3.



Figure 4.

	<b>,</b>	,	
		Water temperature	Electric
Sample	рН	(°C)	(S⋅m <sup>-1</sup> )
Crater Lake	-0.01	35.4	312.6
Acid Springs 1 a	0.15	34.5	325.1
b	0.11	34.7	365.1
Acid Springs 2			
a a	0.19	26.4	295.1
b	0.14	27.0	317.6
С	0.21	23.5	275.1
d	0.28	22.2	265.1
е	0.30	17.6	257.1
Bonyu Dobit St	room		
anyu Fanil Sl	0.44	22.2	150.1
b	0.43	21.3	160.1
с	0.41	19.8	177.6

Table 1. Field measurements of pH, water temperature, and electric conductivity for the Kawah Ijen crater lake, the first and second set of acid springs of the upper Banyu Pahit River valley, and the Banyu Pahit River.

	Oraclasia	Acid S	prings 1	Averge Acid		Acid Springs 2				Averge Acid	Banyu Pahit Stream		
	Crater lake	а	b	Springs 1	Springs 1 a b c d	d	е	Springs 2	а	b	с		
Flame Atom	nic Absorption Spectrom	netry (ppm)											
Si	53.7	35.1	34.6	36.2	38.1	38.1	38.1	38.4	36.9	42.81	44.2	45.5	45.3
AI	5476	4959	4772	5052	4506	4912	4076	3946	4513	4921	2994	3191	3184
Fe	2477	2409	2432	2516	2537	2750	2386	2275	2322	2756	1876	1857	2004
Mg	584.6	557.1	566.5	584.0	529.0	566.6	491.3	487.4	479.1	573.7	355.34	383.11	392.13
Са	444.7	436.7	465.0	469.0	425.4	436.7	582.4	548.2	550.2	580.3	438.3	452.5	1057
Na	1028	941.1	915.9	964.3	874.2	958.0	799.1	764.7	868.9	956.1	917.2	976.2	992.5
к	1285	1062	1027	1085	942.6	1050	884.9	836.4	917.4	1039	1065	1138	1157
Li	0.635	0.576	0.593	0.608	0.589	0.596	0.543	0.517	0.551	0.628	0.635	0.644	0.677
Pb	0.635	4.06	3.91	4.14	3.06	3.28	3.00	2.83	2.86	3.38	2.89	3.12	3.18
Ion Chroma	atography (ppm)												
F	1266	1213	1110	1205	898.1	937.0	745.2	781.0	853.2	943.6	642.5	625.4	621.1
CI	20550.2093	19348	17943	19348	15497	15990	12460	13034	14516	15990	10505	10357	10180
Br	50.6821889	53.91	46.91	52.25	38.4	45.4	38.3	37.7	41.3	45.17	30.47	35.29	33.50
SO4	61202.1472	58918	54024	58585	47318	49138	39343	41211	44935	49700	33810	32881	32894
ICP-MS (pp	om)												
Mn	43.5036666	40.32	42.25	42.94	38.54	42.48	35.77	33.03	35.12	41.47	38.12	40.91	41.89
Со	0.56880176	0.638	0.609	0.647	0.613	0.676	0.566	0.531	0.626	0.675	0.790	0.630	0.637
Ni	0.38143684	0.327	0.293	0.322	0.303	0.339	0.297	0.249	0.297	0.333	0.284	0.299	0.317
Cu	<d.l.< td=""><td>0.15</td><td>0.14</td><td>0.15</td><td>0.50</td><td>0.53</td><td>0.39</td><td>0.37</td><td>0.46</td><td>0.501</td><td>0.396</td><td>0.525</td><td>0.346</td></d.l.<>	0.15	0.14	0.15	0.50	0.53	0.39	0.37	0.46	0.501	0.396	0.525	0.346
V	11.0496509	10.47	10.78	11.05	10.40	11.19	9.59	8.99	9.14	11.06	10.61	11.35	11.47
Cr	0.29843744	0.297	0.279	0.299	0.278	0.297	0.248	0.226	0.269	0.296	0.259	0.268	0.289
Ga	1.11743233	1.20	1.14	1.22	1.11	1.22	1.03	0.97	1.09	1.21	1.204	1.278	1.302

Table 2. Major and trace and element concentrations in the Kawah Ijen crater lake, the first and second sets of acid springs of the upper Banyu Pahit River valley, and the Banyu Pahit River.

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	Crotor Joko		orings 1	Averge Acid		Aci	d Springs	2		Averge Acid	Banyu Pahit Stream		
	Crater lake	а	b	Springs 1	а	b	С	d	е	Springs 2	а	b	С
Cs	0.1184797	0.109	0.105	0.111	0.096	0.106	0.089	0.084	0.094	0.105	0.100	0.104	0.105
Rb	3.85745369	3.39	3.25	3.45	2.95	3.17	2.73	2.61	2.59	3.15	2.984	3.174	3.198
Be	0.1116945	0.069	0.065	0.069	0.059	0.063	0.052	0.053	0.056	0.063	0.077	0.099	0.038
Sr	15.3331314	13.91	14.50	14.77	13.32	14.53	13.35	12.61	12.63	14.96	15.49	16.73	17.01
Zr	1.97778894	1.80	1.82	1.88	1.83	1.82	1.75	1.59	1.82	1.98	1.108	1.080	1.203
Hf	0.03748804	0.035	0.036	0.036	0.034	0.041	0.030	0.027	0.032	0.037	0.010	0.010	0.011
Cd	0.04772467	0.045	0.044	0.046	0.038	0.043	0.035	0.034	0.038	0.042	0.038	0.040	0.039
Sn	0.35126735	0.205	0.208	0.214	0.238	0.274	0.236	0.207	0.217	0.263	0.142	0.151	0.148
Sb	0.01578328	0.059	0.053	0.058	0.014	0.013	0.012	0.012	0.014	0.015	0.004	0.001	0.001
ті	0.80910693	0.707	0.702	0.732	0.615	0.676	0.583	0.553	0.605	0.681	0.609	0.651	0.655
Ва	0.18428791	0.051	0.043	0.049	0.086	0.084	0.114	0.065	0.062	0.093	0.045	0.071	0.0424
Y	1.02511858	0.948	0.908	0.964	0.857	0.944	0.791	0.745	0.848	0.938	0.850	0.904	0.922
La	0.66522628	0.619	0.597	0.631	0.529	0.573	0.507	0.479	0.528	0.588	0.581	0.609	0.624
Ce	1.47701306	1.38	1.33	1.40	1.21	1.33	1.17	1.11	1.23	1.36	1.353	1.433	1.459
Nd	0.81770442	0.762	0.735	0.777	0.680	0.751	0.652	0.625	0.693	0.764	0.844	0.813	0.825
Sm	0.15897236	0.172	0.163	0.174	0.155	0.171	0.146	0.142	0.156	0.173	0.167	0.179	0.184
Eu	0.0463297	0.050	0.047	0.050	0.045	0.050	0.042	0.041	0.046	0.050	0.049	0.053	0.053
Gd	0.17291218	0.182	0.174	0.185	0.163	0.181	0.156	0.148	0.166	0.183	0.175	0.186	0.188
Tb	0.02566751	0.028	0.026	0.028	0.025	0.028	0.024	0.022	0.026	0.028	0.028	0.028	0.029
Dy	0.13885237	0.161	0.154	0.163	0.146	0.161	0.136	0.130	0.148	0.162	0.153	0.164	0.166
Но	0.0280506	0.036	0.031	0.035	0.030	0.033	0.028	0.026	0.030	0.033	0.031	0.033	0.034
Er	0.08457969	0.099	0.095	0.101	0.089	0.098	0.084	0.080	0.089	0.099	0.094	0.100	0.102
Yb	0.08259009	0.092	0.089	0.094	0.084	0.091	0.077	0.074	0.084	0.092	0.086	0.091	0.095
Lu	0.01231673	0.015	0.014	0.015	0.013	0.014	0.012	0.011	0.013	0.014	0.014	0.014	0.014
Th	0.28148345	0.253	0.247	0.260	0.224	0.245	0.210	0.198	0.219	0.246	0.247	0.268	0.272
U	0.08792737	0.052	0.051	0.053	0.045	0.050	0.042	0.040	0.045	0.050	0.046	0.049	0.051

	-	Crater lake fluid Magmatic fluid		Meteoric groundwater			
Site	Estimated total discharge (I/s)	%	Estimated Discharge (I/s)	%	Estimated Discharge (I/s)	%	Estimated Discharge (I/s)
First acid springs	1	95	0.95	0	0	5	0.05
Second acid springs	0.9	29	0.26	36	0.3	34	0.3
Third acid springs	31	0	0	48.5 <sup>a</sup>	15	51.5 <sup>a</sup>	16
Total	32.9	-	1.21	-	15.3	-	16.4

Table 3. Total discharge, and relative and absolute fluxes of crater lake water, hydrothermal fluid, and meteoric derived groundwater from the three sets of upper Banyu Pahit River valley acid springs.

<sup>a</sup> Average calculated proportion

Table 4. Concentrations of selected elements in the Banyu Pahit River headwaters (third set of acid springs) compared with WHO health based guidelines, and concentrations reported to normally be found in fresh/ surface water/ groundwater.

	Normally found in fresh water/ surface water/ ground water	Health based guideline by the WHO <sup>a</sup>	Average normalized ljen hydrothermal spring
Aluminum (Al)	< 1 mg/kg <sup>b</sup>	0.2 mg/kg	3865 mg/kg
Antimony (Sb)	< 4 µg/kg <sup>a</sup>	0.005 mg/kg	0.003 mg/kg
Barium (Ba)	< 0.1 mg/kg <sup>b</sup>	0.3 mg/kg	0.081 mg/kg
Beryllium (Be)	< 1 µg/kg <sup>a</sup>		0.096 mg/kg
Cadmium (Cd)	< 1 µg/kg <sup>a</sup>		0.031 mg/kg
Chloride (Cl)	0.1 - 100 mg/kg <sup>b</sup>	250 mg/kg	13174 mg/kg
Chromium (Cr)	< 2 µg/kg <sup>a</sup>	0.05 mg/kg	0.219 mg/kg
Copper (Cu)	< 10 µg/kg <sup>b</sup>	2 mg/kg	0.333 mg/kg
Floride (F)	<1 mg/kg <sup>a</sup>	1.5 mg/kg	753.1 mg/kg
Iron (Fe)	0.5 - 50 mg/kg <sup>a</sup>		2329 mg/kg
Lead (Pb)	1 - 100 μg/kg <sup>b</sup>	0.01 mg/kg	2.87 mg/kg
Maganese (Mn)	<1 mg/kg <sup>b</sup>	0.5 mg/kg	30.49 mg/kg
Sodium (Na)	< 20 mg/kg <sup>a</sup>	200 mg/kg	771.2 mg/kg
Sulfate (SO <sub>4</sub> )	<3 mg/kg⁵	500 mg/kg	42344 mg/kg
Uranium (U)	< 10 µg/kg <sup>b</sup>	1.4 mg/kg	0.055 mg/kg

<sup>a</sup> WHO (1993)

<sup>b</sup> Hem (1985)

#### General summary and conclusions

The headwaters of the Banyu Pahit River were previously considered to be crater lake seepage that emerges at approximately the elevation of the Kawah lien crater lake itself (≈ 2100 m.a.s.l.). The western side of Kawah Ijen volcano, between approximately the elevations 1895 and 2090 m.a.s.l. had not recently been explored and hydrogeochemical analysis of the Banyu Pahit between these elevations had not previously been reported. The main objectives of my M.Sc. research were to asses and characterize the hydrochemistry and hydrologic sources of water to the Banyu Pahit. We found that water from the crater lake seepage springs mentioned above flows on the surface for approximately 100 m before gradually disappearing into the sediment of the stream bed. Further along the river valley at elevation  $\approx$  2075 m.a.s.l. we found a second set of acid springs emerging that also flows on the surface for approximately 50 to 100 m before also disappearing into the sediment. Further downstream at elevation  $\approx$  1995 m.a.s.l., a third set of acid springs was discovered, and their discharge is much higher than the other two sets of springs. Flow from this third set of springs combines and flows into an incised canyon and forms the true headwaters of the Banyu Pahit River.

A hydrogeochemical approach was used to improve our understanding of the composition, provenance, and potential connections between each of these sets of springs. All collected water samples (n = 21) taken from each individual spring, the crater lake, and several locations along the Banyu Pahit River were analyzed for a suite of 46 major and trace elements, as well as oxygen isotopic composition. Between all hydrological features found on the western side of the volcano, two distinct types of

volcanic fluid were recognized based on ratios of conservative anion concentrations  $(SO_4/CI \text{ and } SO_4/F \text{ ratios})$ . These ratios were found to be unaffected by water-rock interaction or dilution by neutral, meteoric derived groundwater, thus the different ratios were expected to represent different sources impacted by different processes. Cl and F tend to be more volatile than SO\_4, and as such different SO\_4/Cl and SO\_4/F ratios are associated different partitioning in fluids (Giggenbach, 1974; Rowe *et al.*, 1992). At Kawah Ijen, crater lake water samples have relatively low SO\_4/Cl and SO\_4/F ratios compared with some of the spring samples, particularly the third set of acid springs which have the highest measured SO\_4/Cl and SO\_4/F ratios.

Our interpretation of the anion ratios is that water from the crater lake is predominantly meteoric in origin, and that the magmatic fluid component is from predominantly the vapour phase condensing into the lake. Alternatively, the third acid springs, those furthest from the summit of Kawah Ijen, have the lowest SO<sub>4</sub>/CI and SO<sub>4</sub>/F ratios of all the springs, suggesting that their magmatic component is comparatively dominated by the liquid phase and is likely hydrothermal fluid directly from the magmatic system at depth. Using these ratios in a mass balance mixing model, the magmatic component of the first springs just below the lake elevation is crater lake water (>95%), that the second acid springs are a mixture of 45% crater lake water and 55% hydrothermal fluid, and that the third springs are hydrothermal fluid.

The presence of springs with a distinct hydrothermal signature provides insight as to the composition of the hydrothermal fluid at depth. The three hydrogeochemical end members of the hydrothermal acid spring water (third springs) are meteoric derived groundwater, rock flux from water-rock interaction, and hydrothermal fluid. The

composition of meteoric derived groundwater is known from samples analyzed as part of this research. The composition associated with water-rock interaction was determined using the flux from fully altered Ijen andesite based on van Hinsberg *et al.* (*in review*) combined with the acid spring water chemistry. It was determined that on average 33.4(±1.1) g of rock are dissolved in each kilogram of hydrothermal spring fluid. We were able to remove the known meteoric water and rock-flux end members to establish the composition of the third hydrogeochemical end member, the hydrothermal fluid at depth.

Magmatic fluid and meteoric groundwater proportions in the spring water were constrained with the range of possible  $\delta^{18}$ O values for andesitic waters reported by Taran *et al.* (1989) and Giggenbach (1992) (7 to 13 %), which were used to project the range of concentrationns of three other conservative natural tracers of the magmatic fluid, Cl, SO<sub>4</sub>, and F. The results of four independent mixing models using these tracers agree to within 3%, and show that the magmatic component of the hydrothermal acid spring water comprises 41(±2) to 56(±3)% of the spring water by mass.

Conservative tracers, CI, SO<sub>4</sub>, and F, were then also applied to mixing models of the first and second sets of springs and the upper-most stretch of the Banyu Pahit River. Magmatic and meteoric groundwater proportions were determined, and in the case of the second set of acid springs which is a mixture of hydrothermal fluid, crater lake water, and meteoric derived groundwater, results of mixing models using CI, SO<sub>4</sub>, and F independently were combined with results of mixing models that used the anion rations discussed above (SO<sub>4</sub>/CI and SO<sub>4</sub>/F) to determine the relative proportions of each fluid type in the spring water. The first acid springs consist of 94.9( $\pm$ 0.8)% water

from crater lake seepage, and 5.1(±0.8)% meteoric derived groundwater. The second acid springs consist of approximately 29% water from crater lake seepage, 34% meteoric derived groundwater, and 36% hydrothermal fluid.

Following are the discharge measurements for each set of springs: first acid springs are 1.8 l/s, second acid springs, 1.0 l/s, and third acid springs, 31.3 l/s. Combining total discharge of each set of springs with the proportions of each fluid type shows that the total flux of hydrothermal fluid (~15.4 l/s) is a full order of magnitude greater than the total flux of crater lake seepage (~1.2 l/s), as is the flux of many toxic elements. For example, 2.14 ton/day Cl, 6.35 ton/day SO<sub>4</sub>, 0.13 ton/day F, 0.57 ton/day Al, 0.005 kg/day Cd, and 0.08 kg/day Tl is transported to the surrounding environment in crater lake seepage compared with 36.4 ton/day Cl, 117.1 ton/day SO<sub>4</sub>, 2.08 ton/day F, 10.7 ton/day Al, 0.09 kg/day Cd, and 1.4 kg/day Tl from hydrothermal fluid. Furthermore, hydrothermal fluid represents environmental contamination on a much larger scale than crater lake seepage, being transported by the Banyu Pahit River more than 45 km to the Madura Strait and being used in its more dilute form (pH ≈ 4) for irrigation on the Asembagus Plains.

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