Crafer Lakes Reveal Volcanic Heat and Volatile Fluxes

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ABSTRACT

Aqueous lakes situated at the top of active, but quiet-volcano areas exist as gas condensers and calderas that provide long-term integrated release rates of volatiles and heat during passive degassing of sub-surface magma. Some crater lakes contain the most acidic natural water on Earth (pH <0). Analysis of hydrogeochemistry of the acid lake at Volcán Poás, Costa Rica, reveals volatile release rates into the hydroosphere of 0.78 Gg/yr fluorine, 15 Gg/yr chlorine, and 1.3 Gg/yr sulfur (1 Gg = 10⁹ g) and a power output of 200 MW during passive degassing in 1988-1989. An equivalent flux of sulfur may be precipitating as chemical sediments in the crater lake. After magma intrusion or hydrofracturing events in the subsurface, these fluxes were observed to double (E C) or even increase tenfold (E S) for shorter periods of time. At Grímsvötn volcano, Iceland, the database for flooding from the lake suggests volatile release rates of 0.58 Gg/yr fluorine, 6.8 Gg/yr chlorine, 3.1 Gg/yr sulfur, and 39 Gg/yr carbon integrated over 15, 32, 32, and 15 yr, respectively, and 4000-5000 MW power output. Volatile flux rates calculated over several years at Poás and over 15 yr at Grímsvötn are observed to be 0.87 and 0.71 (S/C) and 17 and 48 (S/F); the C/S flux ratio averaged 14 over 15 years at Grímsvötn. Power output for each volcano can also be used to calculate rate of magma cooling in the subsurface; the volatile release rate divided by the rate of magma cooling yields estimates for the decrease in volatile content of subsurface magma during cooling. For the shallowly buried calc-alkaline basaltic and andesite lakes at Poás, the magma lost 17.4 Gg 34 ppm, 13.4 ppb, and 3000 ppm S; for the deeply buried basaltic at Grímsvötn, the magma lost 1.6 Gg 34 ppm, 46 ppm, and 1650 ppm CO₂. Integrated estimates for release of E C, and S at Poás are roughly within an order of magnitude of published estimates for most actively degassing volcanoes. However, E C, S, and C fluxes at Grímsvötn are smaller than observed at noneruptive volcanoes. These low values suggest either that there are unaccounted sinks for the system or that other degassing estimates, based on short-term sampling, are overestimates. Only a few of the 80 or so crater lakes of the world have been analyzed; these lakes may reveal the long-term power and volatile release rates for these volcanoes.

INTRODUCTION

To assess the effects of anthropogenic input of critical components on the Earth system, we need to quantify the rates of natural release and cycling of these components into and within Earth’s hydrosphere, biosphere, geosphere, and atmosphere. For example, to model the geochemical carbon cycle, we need to quantify degassing rates of CO₂ from volcanoes. Similarly, degassing rates of E C, and S are needed to quantify the geochemical cycles of these elements. Most global volcanic budgets rely on short-term measurements of volcanic release at individual volcanoes, which are then extrapolated to longer time frames and multiplied by the number of passively degassing or actively erupting volcanoes (e.g., Stoiber et al., 1987). Gas emission rates and gas chemistry are measured by remote-sensing spectrometry, direct fumarole sampling, treated filter analysis, sublimation analysis, MIAR infrared spectrophotometry, Raman spectrometry, satellite remote sensing, incrustation sampling, ice-core-inclusion analysis, and melt-inclusion gas analysis. Most of these techniques do not provide for long-term emission rates, unless permanent monitoring stations have been established. However, for at least 12% of the 714 Holocene-age or younger volcanoes listed in the Catalog of Active Volcanoes of the World, aqueous lakes in the crater condense volcanic volatiles. These lakes also change in volume and temperature, reflecting the power output of the volcano. Acting as condensers and coolants, these crater lakes thus integrate the long-term volcanic and heat output of some active volcanoes.

Almost 40 crater lakes are reported to have above-ambient temperatures and to contain acidic, sulfur-rich water. Some of these lakes maintain the lowest pH of any natural waters on Earth (pH <0). A few of these lakes have been sampled and analyzed: e.g., El Chichón, Mexico; Kusatsu-Shirane, Japan; Mt. Ruapehu, New Zealand; Volcán Poás, Costa Rica; Rincon de la Vieja, Costa Rica. Other crater lakes contain neutral to basic water that represents condensed volcanic gases diluted by meteoric inflow. The pH of the lake water is determined by the rates of the natural titration reaction: acid volcanic gas + water + acid-neutralizing silicate rock. In many cases, these closed-basin lakes concentrate dissolved solutes until chemical sediments (e.g., gypsum) precipitate.

Estimation of the heat, mass, and/or solute budgets of a few crater lakes has revealed mechanisms of fluid flow and heat exchange above shallow magma chambers (Shepard and Sigurdsson, 1978; Bjornsson, 1988; Hunt et al., 1991; Brown et al., 1989; Brantley et al., 1992; Rowe et al., 1992a). We summarise the implications of the heat and mass balance studies at two volcanoes: Volcán Poás, a convergent-platonic volcano in Costa Rica, and Grímsvötn, a hot-spot volcano in Iceland.

VOLATILE AND HEAT BUDGETS

To estimate the volatile and heat budget of a volcanic crater lake, we define the outputs and inputs of the system (Fig. 1): R_{out} (evaporation), R_{in} (river or floodwater flow), R_{bottom} (bottom seepage), R_{up} (temperature influx), R_{geo} (geothermal influx as vapor), R_{geo} (geothermal influx as water). The flux, R_{geo}, can be computed dominantly from rain (R_{geo}) as in Volcán Poás.

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Editor's Note:
Each year the David and Lucile Packard Foundation awards 20 Fellowships for Science and Engineering in a national competition to promising young scientists and engineers working in fields that receive relatively less popular attention than high-energy physics, space, and medicine. Each Packard Fellowship provides $100,000 per year for five years to the Fellow's institution, $90,000 of which is for use of the Fellow to support his/her research work. These young researchers are truly among the "best and brightest" in the United States. The science article in this issue is one of several in which Packard Fellows in earth science report on research in their field.
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Poás, or dominantly of meltwater from ice (Rf) as in Grímsvötn.

Water mass balance is simply the balance between mass inputs, $R_{in} + R_{w} + R_{p}$, and outputs, $R_{w} + R_{p} + R_{out}$. Heat balance is simply the balance between heat inputs, $R_{in} + R_{w} + R_{p}$, and heat outputs, $R_{w} + R_{p} + R_{out}$. Hence, $L_{e}$ is the latent heat of condensation at the temperature ($T_{e}$) at which the geothermal vapor enters the lake; $L_{e}$ is the latent heat of melting of ice; $h_{o}$ is the specific enthalpy of water at $T_{o}$; $h_{g}$ is the specific enthalpy of water at $T_{g}$; and $h_{w}$ is the specific enthalpy of water at the temperature at which rain or meltwater enters the lake. We can also write a mass balance on a dissolved solute of concentration $c$ which is non-volatile and does not dissolve or precipitate in the lake. Solute mass balance equates the solute inputs due to low-temperature water (Rg, dowd), geothermal vapor (cRg), and geothermal water (cRw), to the solute outputs due to evaporation (cRvap), seepage (cRf), and river or flood output (cQsurf).

Slightly modifying the approach of Björnsson (1988), we define the ratio of geothermal input to meteoric input as $k = (R_{in} + R_{w} + R_{p})/R_{out}$. Noting that seepage or river output is chemically identical to lake water, $c_{i} = c_{o}$, we can solve the heat and mass balance equations and constrain $k$ by noting that either $R_{in}$ or $R_{w}$ can equal zero:

$$k = \frac{R_{in}}{R_{out}} \text{ or } \frac{R_{w}}{R_{out}}$$

In this equation, $k = (R_{in} + R_{w} + R_{p})/R_{out}$. To total water influx, $k(1 + k)$. A further constraint can be placed on $k$ by estimating $c_{in}$, the concentration of solute in the liquid component of geothermal influx (see Björnsson, 1988).

HEAT AND WATER BUDGET OF VOLCÁN POÁS

Volcán Poás, along with adjacent volcanic centers, forms the Cordillera Central of Costa Rica. The northern half of the main crater is occupied by a pit crater, which contains an acidic lake (Fig. 2). The southern edge of the Poás lake consists of a 30-m-high pyroclastic cone that formed during the last phreatomagmatic eruption (1953-1954), and which represents the locus of sub-aerial fumarolic activity. The lake varied between 38 and 91°C and had pH values of 0.9 to 0.5 between 1978 and 1991. Gravity measurements suggest that the top of the cooling magma body lies at a depth of ~500 m (Rymer and Brown, 1987).

Inputs and outputs of the summit hydrothermal system, including ground-water seepage to the watersheds of the Agrio River to the northwest, are summarized in Figure 3. Rowe et al. (1992) analyzed all available data over the period 1978-1990 and concluded that the baseline power output of the volcano was 200 MW, with fluctuations to 800 MW. Using appropriate values summarized by Rowe et al. (1992a) for Poás for the period March 22, 1978, to January 1, 1980, we calculate that $k$ must lie between 0.77 (all vapor geo- thermal influx) and 8.5 (all liquid geothermal influx). Noting that lake and rain water at Poás contained 1400 ppm and 4 ppm Na, respectively, geothermal fluid must have had a concentration of dissolved Na at least 4 times higher than the lake water. Rowe et al. (1992) concluded that the lake thus represents the upper manifestation of a liquid-dominated convection cell (Fig. 3) and that virtually no vapor enters the lake: $k = 8.45$. Calculations for other periods of lake stability during the past decade yielded similar conclusions. A value of $k = 8.45$ suggests that 90% of the lake's water mass is geothermal input.

HEAT AND WATER BUDGET OF GRÍMSVÖTN VOLCANO

Grímsvötn, the most active volcano in Iceland (more than 50 eruptions over the past 1100 years) is located in the interior of the Vatnajökull ice cap. Grímsvötn consists of evolved quartz- rich tholeiites, and it hosts a dilute, neutral-pH crater lake. The bottom of the lake is at 1050 m above sea level, and precipitation; the lake bottom varies from 3.5 MPa when the top of the lake surface is 3330-3350 m above sea level, to 4 MPa when the top of the lake reaches 1425 to 1450 m (Björnsson, 1988). At this critical level, the water lifts the 7-km-wide ice barrier lying in the saddlepoint at the south-eastern edge of the caldera, and lake water floods for 50 km beneath the ice (probably through tunnels), and continues over 30 km of the Icelandic coast to the sea. These periodic floods, termed jökulhlaup, drain water from the bottom of the lake at maximum discharge rates since 1938 of 9000-10000 m³/s (Björnsson, 1988). Jökulhlaup are closely monitored; discharge, river chemistry, and ice cap elevation data are available back to 1945. From 1974, jökulhlaup water samples were collected from the river Skjálfand a few km from where the jökulhlaup water emerges beneath the glacier.

Using these data, Björnsson (1988) estimated the rate of ice melting into the lake (Rf) at 400 Tg/yr (1 Tg = 10¹² g), and the rate of ablation at the surface of the glacier (Rg) at 80 Tg/yr. Total water input, Rg, thus amounts 480 Tg/yr. Assuming that the lake temperature ($T_{l}$) averages 0.1 °C, the melting temperature ($T_{m}$) is 0°C, and the temperature at which the geothermal fluid enters the lake ($T_{l}$) is 235 °C (boiling temperature at 3 MPa), Björnsson (1988) concluded that the power output of the volcano has decreased from about 5000 to 4000 MW since 1860.

Between jökulhlaup, we can follow Björnsson (1988) and solve for $k < 0.3$ to $< 0.28$. Assuming that silica is a conservative component introduced to lake only by geothermal input, we can use our observed value for lake, $c_{i} = 18$ ppm (see data below), and again following Björnsson and Kristmannsdottir (1984), we note that the upper limit for silica concentration in liquid geothermal waters is 700 ppm, which, assuming mass balance on silica, puts a lower constraint on $k$. The liquid fraction of the geothermal influx must therefore be greater than 65%. These calculations, first completed by Björnsson and Kristmannsdottir (1984) reveal that the lake at Grímsvötn, like Poás, is primarily receiving liquid geothermal input. The ratio of geothermal to total water input is less than 22%, explaining the wide difference in chemistry between Grímsvötn and Poás.

VOLATILE BUDGET OF VOLCÁN POÁS

Rowe et al. (1992a) summarized several periods of relative constancy in lake chemistry from 1978-1990. During these periods, the only volatile losses from the system consisted of gases lost in geothermal outflow. The liquid-dominated convection cell at the top of the volcano, the cinder-cone fuma- role flux, and volatilization from the
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lake (Fig. 3). Quantification of these fluxes reveals overall volcanic flux from the volcano. No attempt was made to assess CO2 flux.

Numerical modeling of the summit craters suggests that seepage from the crater lake, constrained by a high water table associated with the north-south and east-west flow dominated by the Rio Agrio watershed to the northwest, is also important. These craters have shown that acid seepage causes dissolution around the volcano to form a large magma chamber along the north-south flank aquifer is approximately 6.7 g/yr (Rower et al., 1992b). Observed fluxes of the conservative elements Fe, Cl, and S in waters exiting the Rio Agrio watershed during 1988-1989 were 0.66, 14, and 11.4 g/yr, respectively, and the residence time of fluids in the aquifer is estimated to be between 3 and 17 yr (Rower et al., 1993).

The fluxes through the dome fumaroles fluctuated greatly: during the high temperature period of 1981-1984, observed Fe, Cl, and S fluxes were 0.72, 22, and 110 g/yr, respectively; fluxes during the low temperature period of 1985-1989 were on the order of 0.036, 0.22, and 0.36 g/yr (Rower et al., 1992a; see Table 2). The observations of Titon et al. (1992a) argued that these heat and volcanic bursts were caused by heating of the magma chamber, increasing magma caprace, or by influx of magma in the subarca. Analyses of lake chemistry reveal that some HCl gas escapes from the lake, especially when the lake temperature increases, increased chloride concentrations in the vapor phase during high temperature periods were monitored by the increased chloride concentrations in acid rain falling downwind (Rower et al., 1992b). On the other hand, the concentration of sulfur in acid rain collected during periods of low fumora emission was generally low, and high and significant volatilization of HF from the lake was also not observed (Rower et al., 1992b).

To quantify the loss of components such as CH4 by volatilization from the lake during moderate-temperature periods (e.g., 1978-1988), we can calculate the flux of these components in flake rivers affected by acid rain (Ammons, Despain, Galán, Escan, Pozo Aníl, Angel; Fig. 4). By first correcting these compositions by subtracting concentrations of a nonacalcified river (Gnón), and then multiplying corrected concentrations by flow rates measured in 1988 and 1990, we can calculate the average rate of release of F, Fe, and FeCl3 for the two jökulhlaups associated with eruptions (1953 and 1983) is 0.04. Similarly, the ratios of release rates of S and Cl for noneruptive vs. eruptive periods is 0.53 and 1.4, respectively.

The lake water is undersaturated with respect to all oxidized gas phases (CH4, H2S, HS, HS-, and CH2S), the closest gaseous components is expected. However, some degassing of HS occurs at the edge of the lake where there is ephemeral exposure (area of ice hole in summer 1991 was only 20 m²). HS degassing is probably also significantly influenced by the lake.

Calculations of chemical speciation in the lake suggest that there is no precipitation of volatile-containing minerals is likely to occur, with the exception of aluminite [KAl2Si3O10(OH)2]. However, no alunitc was detected in sediments.

We have also assumed that contributions from snow melt and dissolution of bedrock or sediment are minimal. The concentrated dissolved inorganic volatiles in glacial snow from Vatnajökull are well below 1 ppm. Correction of the volcanic fluxes for calculated contribution from dissolution of basal decreases the fluxes only slightly (Agústsdóttir, 1993).

We expect little degassing to occur during the several-hour transport time into ice tunnels 50 km to the edge of the glacier, but some degassing must occur in the 8 km between ice and sampling sites, especially for CO2 and H2S. We can compare concentrations of the relevant components in lake water sampled in June 1991 and jökulhlaup river water sampled in November 1991 (Agústsdóttir, 1993). Because lake chemistry as a function of distance to Grímsfjall is impossible to predict average lake concentration or predicted jökulhlaup concentration if no degassing occurred—from just three sampling locations. For three components: hydrogen fluoride, sulfuric acid, and total carbonate as the observed jökulhlaup concentrations (0.14, 1.10, and 0.61 mol/L, respectively) were less than the observed highest concentrations in the lake water (1.05, 35, and 1160 mol/L, respectively). All the components (except Ca) were observed to be identical between jökulhlaup and most concentrated lake waters. This suggests that, in the worst case, errors could be as large a factor of 7.5, 4.9, and 2.5, respectively for S, Cl, and C, respectively (Fig. 5).

VOLATILE RELEASE VS. POWER OUTPUT

Bjornsson (1988) calculated the rate of magma cooling in the subarca Grímsvötn jökulhlaups and the heat released per kilogram of cooled magma: the specific heat of crystallization (419 kJ/kg) plus the specific heat capacity (1.046 kJ/kg°C -1) multiplied by the drop in temperature (3.00 to 200°C). The power output of the volcano divided by the heat release per kilogram of magma reveals the rate of magma cooling in the subarca at Grímsvötn and power requires 9 x 109 kg/yr. Using the same thermo-
Grimsvötn may indicate that our esti-
mates for magmatic volcanoes are too low. Small vol-
canologic bias may also emphasize volca-
noes with large volatile release rates.

CONCLUSIONS

At 200 MW, Volcán Poás is compa-
rable to a moderately small coal-fired power
plant. The United States' 4000-5000 MW, Grimsvötn is much
larger than the average coal-burning power
plant (1000 MW). However, we note that only 102 volcanoes were
known to be degassing in 1981-1982 (Stolper et al., 1987), and if the power
output for these volcanoes is between 200 and 5000 MW (see also Glaze et
al., 1989), we calculate a rough global power output between 2 x 10^13 and
5 x 10^14 MW for nonrupturing volcanoes. This global power output is small com-
pared to the overall heat flow of Earth (4 x 10^14 MW) or commercial power
consumption by humankind worldwide
(1 x 10^14 MW, according to the
Worldwatch Institute).

At 13 Gt yr^-1, Poás is comparable to a 200 MW coal-fired power plant
burning coal that has 2 W/m^2. The
local effect of this volcanic S release were documented by Brantley
et al. (1992). Storage of S at the top of the atmosphere would have important
implications for a large-scale explosive eruption released the S. Globally, re-
lease of S to the atmosphere from pass-
pively degassing volcanoes amounts to about 3.4 Gt yr^-1 (Stolper et al., 1987).
This is a very small flux compared with the total anthropogenic emission
(approximately 100 Gt yr^-1).

Ratios of S2^- and S3^-/Si release integrated over several years at Poás
(0.87 and 17), and integrated over 35 yr at Grimsvötn (0.71 and 48), are
within the range 0.5 to 0.5 estimated by Symonds et al. (1988) for most active
volcanoes. Symonds et al. (1988) used such ratios to calculate global release
rates of F and Cl based on a assumed global release of 3.4 Gt S/yr. Our long-
term integrated ratios may be especially useful in predicting global volatile
release rates by this method; however, more long-term estimates of volatile
ratios are needed. The two long-term estimates summarized here would
suggest global passive release rates of approximately 0.07 to 0.2 Gt yr^-1 for
3.9 to 4.8 Gt yr^-1, comparable to the anthropogenic fluxes due to
burning and industrial production of halocarbons: 0.4 Gt yr^-1 for F and
4.0 Gt yr^-1 for Cl (Symonds et al., 1988).
The ratio of S2^- release at
Grimsvötn is quite large, possibly because of the depth and magnitude
of the body. The average global C/S ratio lies between the estimated minimum
of 2.3 (Gerlach, 1991) and the value at Grimsvötn (14), then the global
C/S flux would lie between 7.8 and 44 Gt yr^-1, much smaller than the
global anthropogenic flux (approxi-
ately 6000 Gt yr^-1). However, more
such long-term estimates, based on crater lakes or spectrophotometric
monitoring, are needed to determine more accurately the global flux of all
the volatile elements.

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GSA Officer and Councilor Nominees for 1994

Council announces the following officer and councilor candidates. Biographical information on all candidates will be mailed to the ballot to all voting members in August.

For Councilor (1994-1995) and President (1994)
William R. Dickerson: Tucson, Arizona

For Councilor and Vice-President (1994)
David A. Stephens: Scottsdale, Arizona

For Councilor and Treasurer (1994)
David E. Dunn: Richardson, Texas

For Councilor (1994-1996)—Position 1
Charles G. Groce: Baton Rouge, Louisiana
John A. Cherry: Waterloo, Ontario, Canada

For Councilor (1994-1996)—Position 2
Grand Garven: Baltimore, Maryland
Lynn L. Cambridge: Cambridge, Massachusetts

For Councilor (1994-1996)—Position 3
Keris Cartwright: Champaign, Illinois
C. Blaine Cecil: L.essburg, Virginia

For Councilor (1994-1996)—Position 4
George H. Davis: Tucson, Arizona
H. Catherine W. Skinner: New Haven, Connecticut

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