Poás volcano crater lake acts as a condenser for acid metal-rich brine

Susan L. Brantley*, Andrea Borgia†‡, Gary Rowe*, Jose F. Fernandez§ & Jennifer R. Reynolds‡||

* Department of Geosciences, Penn State University, University Park, Pennsylvania 16802, USA
† Department of Geological and Geophysical Sciences, Princeton University, Princeton, New Jersey 08544, USA
§ Instituto Costarricense de Electricidad, San Jose, Costa Rica
|| Department of Earth Sciences, Dartmouth College, Hanover, New Hampshire 03755, USA

Models of formation of volcanic-hosted metal deposits hypothesize that subsurface brines transport metals to sites of deposition. Laguna Caliente, in the active crater of Poás volcano, central Costa Rica, consists of acid–sulphate–chloride brine with extreme *p*H (0.0). Lake water sampled between 9 and 12 January 1987 at eight sites within the 40-m deep, 210-m wide lake revealed temperatures between 58 and 64 °C, and densities (measured in the laboratory at 60 °C) of $1.0575 \pm 0.0015\ \mathrm{g\ cm^{-3}}$. The water's extreme acidity reflects the dominating input of acid fumaroles. The presence of precipitated silica, gypsum and sulphur as sediments reflects lake-water equilibrium with those phases. Mass balance considerations require that dense brines percolate downwards from the lake into the volcano. These may act as a source of metal-rich brine feeding an underground ore-forming hydrothermal system.

Of the approximately 40 active volcanoes in Central America, roughly one fifth host acidic crater lakes (M. Carr, personal communication). Laguna Caliente, situated in a small pit crater within the main crater of Poás Volcano, Costa Rica, is the most acid and sulphur-rich lake reported[1]. The most recent lava eruption at Poás occurred in 1953, at which time the crater lake totally disappeared, not to reappear until after 1965. Phreatic explosions, consisting of frequent irregularly timed geyser-like mud plumes erupting from the lake, resumed in June of this year after eight years of inactivity[2].

To investigate the chemical homogeneity of the lake, we designed a sampling raft to collect water and measure temperature at depth (Fig. 2*a*). Our water samples complement earlier near-shore samples which we also summarize[3] (Table 1). Chemical compositions for near-shore samples from March 1985 and filtered mid-lake samples from January 1987 showed similar chemical compositions (see examples in Table 1). Unfiltered lake water showed consistent density at all depths at mid-lake, and slightly lower densities along the eastern shoreline (Fig. 2*b*). Measurements of temperature variation with depth showed 1.2 °C warmer temperatures at mid-depths in the centre of the lake (Fig. 2*c*). Sediments (predominantly chemical precipitates of amorphous silica, elemental sulphur and gypsum) at the eastern shoreline measured 6 °C cooler than overlying water.

Our temperature data show the same patterns as reported for the lake in 1984 (X. Neshyba *et al.*, in preparation). At that time, bottom sediments at the centre of the lake were 1.6 °C hotter than bottom waters. These data indicate that the lake is heated predominantly by fumaroles passing through bottom sediments and through the rocks of the dome on the southern side. The observed discoloration at lake centre and the site of observed phreatic activity in the southern section (Fig. 1) may be major sites of convective upwelling. Convection explains the density, temperature and chemical homogeneity. Lower density values and sediment temperature along the eastern shore may indicate input from groundwater associated with the ephemeral stream (Fig. 1).

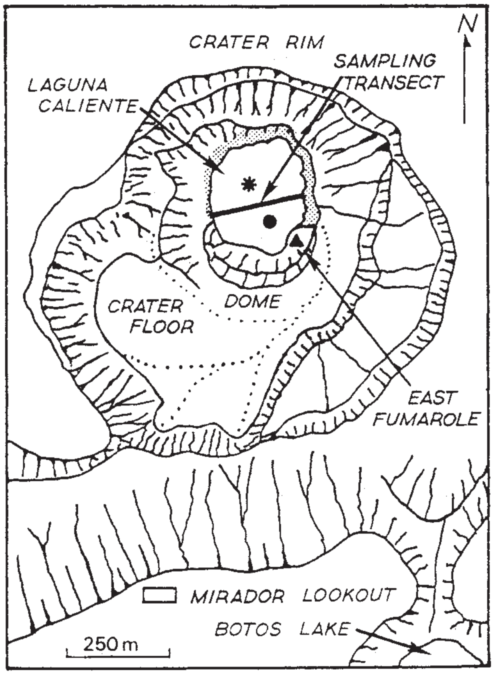

Fig. 1 Map of main crater of Poás Volcano, indicating location of Laguna Caliente, the eastern fumarole, and location of our sampling transect. A site of occasional lake-water discolouration (*) and the site of phreatic explosions (●) are also noted. Dotted lines represent the bed of the intracrater ephemeral river. Sketched lake area is approximately as observed in January 1987, when the level was approximately 7 m lower than January 1985. Between 7 and 10 January 1987, no rain fell and we observed that the lake-water depth fell at the shoreline by about $12\ \mathrm{cm\ d^{-1}}$. During this period, the lake level had reached the lowest level of the past ten years (J. Barquero, personal communication), revealing extensive layered lake sediments (stippled area) and occasional hollow yellow tubes, approximately 3 cm in diameter and 20 cm in length, composed of radiating, orthorhombic sulphur crystals.

Charge balance in the brine can be approximated to first order as $[\mathrm{H_3O^+}] = [\mathrm{Cl^-}] + [\mathrm{HSO_4^-}]$, where the most highly concentrated species in the lake is the hydronium ion. The extremely low *p*H of the water results from the continual condensation of fumarolic acid vapors; acidity is enhanced by continual evaporation of water, producing isotopically heavy acid-sulphate-chloride brine (Fig. 3). Because lake water has maintained consistently low *p*H since at least 1979, *p*H-buffering crater rock dissolution reactions must proceed at slow rates compared with the rate of fumarole input. Banding in precipitated lake sediments reflects fluctuations in saturation index of gypsum and silica related to short- or long-term variations in temperature, rainfall or volcanic activity.

To quantify lake inputs and outputs (Fig. 3), we calculate a water mass, heat and chloride mass balance between 1985 and 1987. The net rate of water loss, R_t, is determined by the rates of water loss through evaporation (R_e) and subsurface outflow (R_{of}), and rates of water addition from rainfall (R_r) and fumaroles (R_f):

$$R_t = -R_e - R_{of} + R_r + R_f \qquad (1)$$

If conduction of heat between lake and wall rocks, loss of heat from the lake through air convection and radiation of heat from the lake are minimal (as found for the crater lake of Soufriere)[4], the rate of heat change, Q, will also be determined by the rates of heat loss through evaporation, outflow and rainfall, and the

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‡ Present addresses: Smithsonian Institution, Department of Mineral Science, NMNH, Washington DC, 20560, USA (A.B.) and Lamont-Doherty Geological Observatory, Palisades, New York 10964, USA (J.R.R.).

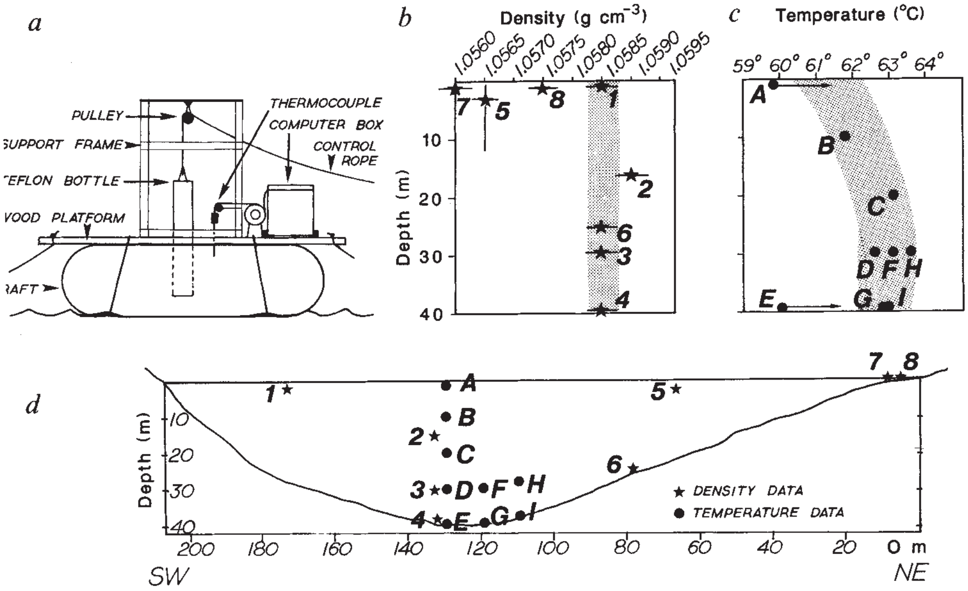

Fig. 2 *a*, The sampler consisted of a small rubber raft with a wood and metal frame rigged with pulleys. The raft was manipulated from opposite shores, using two polypropylene ropes strung across the lake. A third line was used to lower a weighted Teflon bottle to the desired depth where the bottle was triggered to fill. Lake depth was determined at points noted by measuring when the sampler weight hit bottom. In independent measurements, temperature was recorded with a Type-K thermocouple (accurate to ±0.25 °C) suspended from the raft and attached to an onboard computer. All undiluted samples formed a silica precipitate upon cooling, so samples were diluted in the field for subsequent chemical analysis. *b*, Density data for lake samples. All densities were measured on unfiltered samples in the laboratory at 60 °C. Stippled area shows density profile at mid-lake. *c*, Temperature data for mid-lake as measured 9 January 1987. Where no definite temperature is noted (sites A and E), the thermocouple never fully equilibrated. Stippled area shows estimated temperature profile at mid-lake. *d*, Locations of temperature measurements and sample locations along the 210-m transect.

Table 1 Chemical composition of lake system components

	Lake water* (p.p.m.)	Lake water† (p.p.m.)	Lake water‡ (p.p.m.)	Fumarole condensate§ (p.p.m.)	Rio Agrio‖ (p.p.m.)	Rain water¶ (p.p.m.)	Crater lavas# (wt. %)	Lake sediments** (wt. %)
Date	24 Jan. 85	8 Jan. 87	8 Jan. 87	1 Mar. 85	14 Feb. 87	—	—	—
T	~44 °C	~60 °C	~60 °C	584 °C	NA	NA	NA	NA
*p*H	0.0	0.0	0.0	NA	2.2	4.3	NA	NA
F	1,390	1,460	1,420	410	24.1	0.5	NA	NA
Cl	25,400	30,000	31,300	13,600	670	7.1	NA	0.04
SO_4	49,500	64,400	64,800	3,420	1,660	11.4	NA	16.5 ($\sum S$)
Na	770	504	500	7	66.4	NA	2.15	0.05
K	300	236	234	5	24.0	NA	1.25	0.06
Ca	1,200	2,860	2,400	31	125	NA	5.50	14.3
Mg	790	529	536	2	82.1	NA	2.39	0.1
Al	3,000	2,000	2,040	19	218	NA	8.95	0.7
Si	50	164	190	60	47	NA	25.0	16.4
Fe	1,400	978	971	10	64.7	NA	6.28	0.16
Unfiltered density (g cm^{-3} at 60 °C)	NA	1.0590	1.0585	NA	1.0025 (at 25 °C)	NA	NA	NA
δO^{18}	+5.5	12.3	NA	+3.0	NA	+2 to −4 (est.)††	NA	NA

NA, not analysed.
* SE lake shore, surface[3].
† Mid-lake, 15 m depth (sample 2 on Fig. 2*d*).
‡ Mid-lake, 40 m depth (sample 4 on Fig. 2*d*).
§ Sampled from eastern fumarole[3], 1 Mar. 1985.
‖ Sampled 14 Feb. 87, NW flank of volcano, flow $>100 \text{ l s}^{-1}$.
¶ Sampled at Mirador, average value for 17 samples Nov. 1984–Mar. 1985[11].
\# Average of 14 summit lava flows[12].
** Sampled from SE shore, 1985.
†† Values for rainfall for similar latitude (Barbados)[13].

rate of heat input from fumaroles:

$$Q = -\Delta H_e R_e - h_{of} R_{of} - \Delta H_r R_r + \Delta H_f R_f \qquad (2)$$

where ΔH_e is heat of vaporization, h_{of} is specific enthalpy of lake water, ΔH_r is heat loss in warming rainwater to lake temperature and ΔH_f is the heat of condensation of fumarolic water vapour to liquid at lake temperature. This calculation assumes that all transfer of heat from fumaroles to the lake occurs as condensation; if heat is also transferred conductively, this assumption will tend to overestimate water input from fumaroles. From January 1985 to January 1987, the lake decreased in depth from approximately 47 m to 40 m, and increased in average temperature from 44 °C to 60 °C, indicating that $Q = -2 \times 10^6$ *W* and $R_t = -4 \text{ kg s}^{-1}$. This calculation is based on a lake volume modelled as a cone of depth 40 m and diameter 210 m capped by a cylinder of variable height.

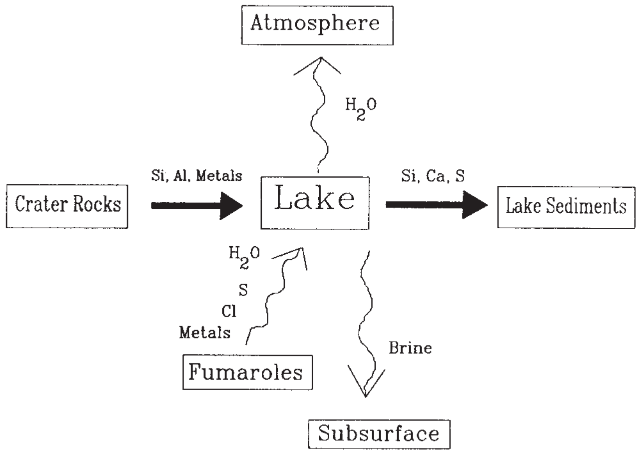

Fig. 3 Simplified box model of Laguna Caliente inputs and outputs. The lake acts as a condenser system, in which H_2O-S-Cl fumarolic fluid enters, condenses and then concentrates through evaporation of water to the atmosphere (vertical arrows show net direction of fluid fluxes). Crater rocks erode into the lake by rain-fed rivers, dissolve and cause supersaturation with respect to gypsum and silica (horizontal arrows). Net result is accumulation of rock- and fumarole-derived metals and anions in lake-water brine, which we hypothesize then seeps downwards into the volcano. Chemical analyses of lake water reveal concentrations between 100 and 3,000 p.p.b. of Cr, Co, Ni, Cu, Zn, Cd and Pb, and concentrations between 10 and 2,000 p.p.m. of Ti, V, Mn and Fe. Note that oxygen isotope values of lakewaters are significantly heavier than fumaroles and estimated rainfall values, (Table 1), indicating that downward-flowing brines provide a source of isotopically-heavy waters to the subsurface groundwater system.

Data from Table 1 for lake chloride concentrations for samples in 1985 and 1987 show that lake chloride concentration $[\mathrm{Cl}]_l$, remained approximately steady at 0.03 kg (Cl) per kg (H_2O), despite fumarolic input ($[\mathrm{Cl}]_f = 0.01$ kg (Cl) per kg (H_2O)) and overall decrease in lake volume. We postulate that brine outflow occurs as seepage through the sediments into the underlying crater rocks as recently suggested for other crater lakes[5]. Mass balance on chloride requires that the net rate of change in total lake chloride ($=[\mathrm{Cl}]_l R_t$) represents a balance between fumarole input and brine outflow as seepage:

$$[\mathrm{Cl}]_l R_t = [\mathrm{Cl}]_f R_f - [\mathrm{Cl}]_l R_{of} \qquad (3)$$

The hypothesis of brine seepage is a necessary consequence of the fact that, despite continual inputs, no outlets from the lake have been observed for dissolved species other than Si, S and Ca (Fig. 3). The steady lake chemistry and low pH observed over the last six years[1,3] require an outlet for the brines.

Solving equations (1)-(3) using appropriate enthalpy values and $R_r = 60\ \mathrm{kg\ s^{-1}}$ (based on an average rainfall of $4\ \mathrm{m\ yr^{-1}}$ over a catchment area estimated from aerial photographs to be twelve times the lake area[6]), we calculate $R_e \approx 100\ \mathrm{kg\ s^{-1}}$, $R_{of} \approx 40\ \mathrm{kg\ s^{-1}}$, and $R_f \approx 80\ \mathrm{kg\ s^{-1}}$. Our estimate of brine outflow from the lake is approximate, since we have overestimated contribution of fumarolic condensation, and neglected both vaporization of HCl at the lake surface and temporal and spatial variations in fumarolic chloride content. However, recasting the rates as lake level drop per day, we can calculate drop during periods of no rain ($R_r \approx 0$, neglecting groundwater input): ~10 cm per day. This calculated rate of drop compares well with the drop of 12 cm per day observed during the rainless period of 9-12 January 1987.

Similarities between Poás lake and the well-described lakes of Ruapehu and Chichón, including similar water and sediment chemistries, complete water mixing and layered sediments, suggest that such crater lakes commonly evolve along the same chemical lines[7,8]. Evidence from Poás suggests that such lakes act as condensers to produce acid, metalliferous and isotopically heavy brine which then percolates downward into the volcano (Fig. 3). Downward-percolating brine must either vaporize and re-rise as fumaroles, remain stored as groundwater, or reissue from the flanks of the volcano as a low-pH high-salinity spring (for example, Río Agrio, Table 1). The downward percolation plays an important part in the mass balance and should provide a significant input of metals (for example, tens of grams of Fe per second) into the local groundwater system. Indeed, circulation of hot, dense metal-rich brine is a necessary component of the accepted models for generation of metal deposits within volcanic stockworks[9]. We expect that downward-flowing brines at Poás may be causing subsurface acid-sulphate alteration and possibly contributing to the generation of heavy metal ore deposits[10].

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Late-glacial mammoth skeletons from Condover, Shropshire, England

G. R. Coope* & A. M. Lister†

* Department of Geological Sciences, University of Birmingham, Birmingham B15 2TT, UK
† Department of Zoology, University of Cambridge, Downing Street, Cambridge CB2 3EJ, UK

We report the discovery of abundant skeletal remains of mammoth, *Mammuthus primigenius* (Blumenbach) from late-glacial sediments filling a kettle-hole near Shrewsbury, Shropshire in England. Radiocarbon dated to ~12,800 yr BP, they are by far the latest dated remains of mammoth from Britain, extending its known occurrence there by around 5,000 yr. They provide clear evidence that the full-glacial episode of the last cold stage did not bring about the final extinction of the mammoth in western Europe, but that the species returned in the late glacial before its ultimate demise. The finds represent the most complete mammoths found in Britain, and include the largely complete skeleton of an adult together with partial skeletons of at least three juveniles.

During removal of superficial deposits at the ARC (Western) gravel pit at Norton Farm, Condover (5 km south of Shrewsbury; map ref. SJ498075) in September 1986, numerous mammoth bones were thrown onto spoil heaps. Bone associations suggest that articulated skeletons had occurred *in situ*, but unfortunately their taphonomic relationships were largely destroyed during excavation. Systematic sorting of the spoil heaps by teams of volunteers organized by Shropshire County Museums Service