Geochemical Journal, Vol. 28, pp. 243 to 262, 1994

The geochemistry of the Keli Mutu crater lakes, Flores, Indonesia

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(*Received June 23, 1993; Accepted March 18, 1994*)

Three crater lakes occur on top of the dormant stratovolcano Keli Mutu in Flores (Indonesia). The lakes contain cool (20–30°C) acid-sulfate-chloride brines and have high TDS with relatively high Zn and Pb contents. Two lakes show plume-like upwellings, probably fed by subaqueous fumaroles. A river on the mountain slope contains fluids that escaped from the lakes through seepage. The fluid compositions have varied strongly over time for S and the halogens (the volcanic-gas derived elements), whereas many of the major cations (rock-derived elements) show a net increase in the lakes over this century. Speciation and mineral saturation modeling, bulk sediment analyses, and micro-probe sediment analyses indicate that the lakes are reducing at depth, and all three lakes are close to saturation with gypsum/anhydrite. One lake is also saturated with Fe-oxides, while the other two are thought to be saturated with a suite of Cu and As minerals. The most acid lake is also saturated with native sulfur and possibly pyrite. Mass balance estimates based on fresh volcanic rocks and ashes, the dissolved element load and the lake sediment chemistry strongly suggest that the lakes are partly fed by underlying geothermal circulation systems. The lakes are thus not closed reaction vessels with dissolution of local rock debris by fluids acidified by volcanic gases, but they draw a rock-derived element flux from deeper levels. Mass transfer is large in these dynamic systems, including the transport of tonnes of ore metals over a period of centuries.

INTRODUCTION

Crater lakes serve as natural condensers of volcanic gases and hydrothermal fluids, and some accumulate extremely acidic, concentrated fluids. Such lakes are transient phenomena, their existence in volcanic zones of high heat flux dependent on adequate cooling through evaporation of meteoric inflow waters. Interest in crater lakes exists because of their potential danger as storage reservoirs for pressurized CO_2 (e.g., Kling *et al.*, 1987; Sigurdsson *et al.*, 1987; Kusakabe *et al.*, 1989) and their possible use for volcano monitoring (e.g., Giggenbach and Glover, 1975; Takano, 1987; Brown *et al.*, 1991; Rowe *et al.*, 1992). The acid fluids also may be modern analogs of ore brines (Brantley *et al.*, 1987; Hedenquist and Aoki, 1991; Hedenquist *et al.*, 1993). Detailed chemical studies of crater lakes may thus aid in volcano monitoring, provide data on volcanic element fluxes and may enhance our understanding of the formation of shallow ore bodies. We present new analytical data from the three Keli Mutu crater lakes (Flores, Indonesia), compare these with earlier water analyses, and assess the variations in Keli Mutu lake water compositions over time. We try to constrain the geochemical processes in the lakes, including the stability of new mineral phases and the nature of water-rock interaction in and possibly below the lakes.

Keli Mutu is a large stratovolcano (8°46′ 24″ S; 121°49′ 12″ E) on Flores, an island in the Lesser Sunda chain of Indonesia (Fig. 1a). The summit region of the volcano (highest point 1639 m above mean sea level) contains three crater lakes, each sitting deep inside steep craters (Fig. 1b). The walls consist of bedded ashes and lapillis, some of it highly altered, which may have been deposited during phreatic explosions of the lakes in the past. All of the lakes are older than the

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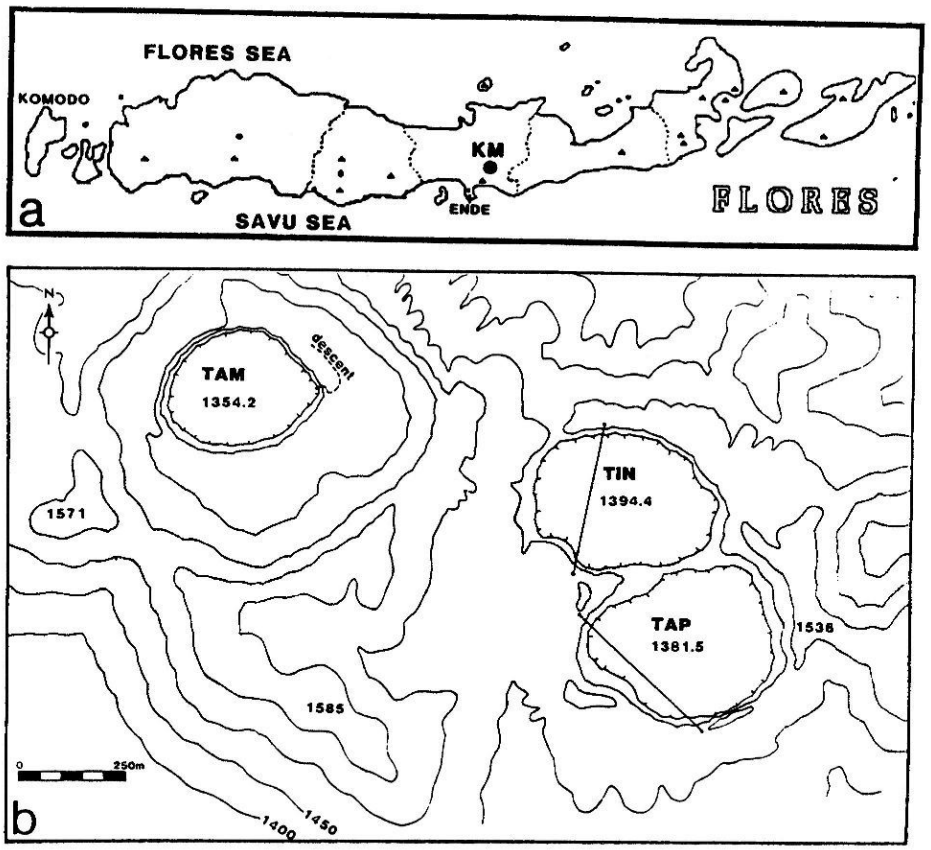
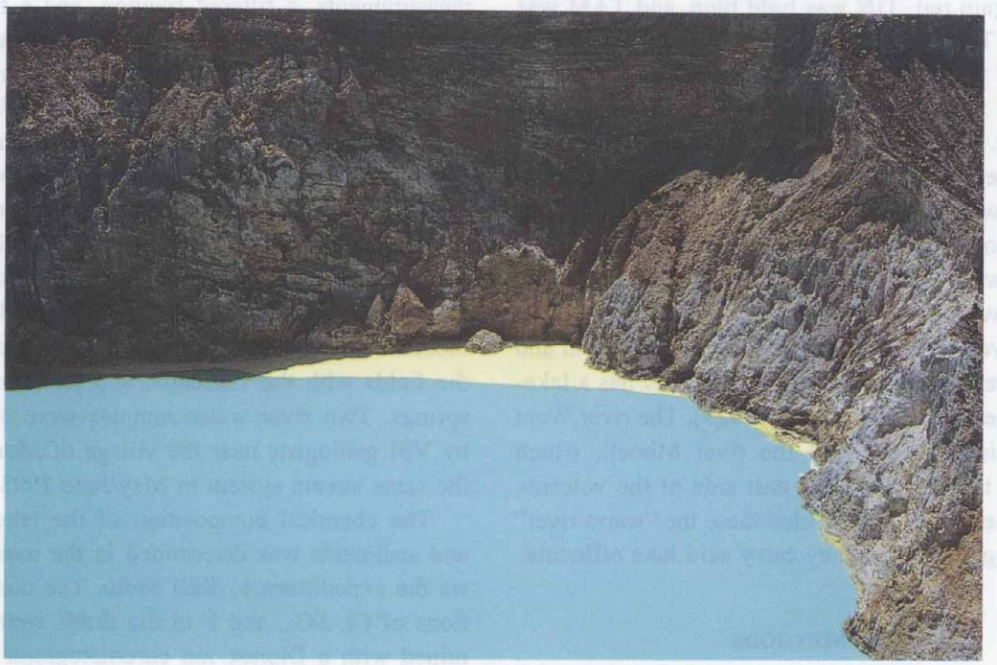


Fig. 1. a. Location of Keli Mutu (KM) on Flores, Nusu Tengara, Indonesia. b. Topography of the Keli Mutu summit, showing the lakes, the sampling transects across TAP and TiN, and the descent trail for TAM.

memory of the oral tradition of the local people. Large hydrothermal eruptions may have occurred between 1860 and 1870 (Kemmerling, 1929). Basic geomorphic data are given in Table 1, partly after Kemmerling (1929) and from a 1993 VSI map, simplified in Fig. 1b. The lakes are not in hydrostatic equilibrium, with 13 and 40 meters difference in water level. The 1929 map from Kemmerling has altitudes that are overall about 30–35 m higher than the 1993 map. Taking that into account, it seems that the absolute lake water levels today are not substantially different from those in 1929.

Tiwu Ata Polo (TAP), the "enchanted lake", is the southeastern-most of the three lakes. Subaqueous fumarolic or hydrothermal activity in TAP is indicated by a large upwelling in the northwest part of the lake, marked by a white froth and large gas bubbles (Fig. 2). Tiwu Nua Muri Koohi Fah (TiN), the "lake of young men and maidens", is the central lake. A large dip in the western wall was the location of a pre-1929 overflow, and the eastern crater walls formerly had fumaroles (Kemmerling, 1929). The surface waters of TiN are continuously in motion, presumably the result of a large upwelling at the lake's center which drives a yellow froth toward the crater walls (Fig. 2). "Hydrothermal blasts" of TiN in 1938 and 1965 lasted longer than a month but were confined to the crater (Simkin *et al.*, 1981). TAP and TiN are separated by a narrow partition that arcs down to a minimum height of ~35 m above the surface level of the lakes. Tiwu Ata Mbupu (TAM), the "lake of elders", fills a pit crater located inside a

(a)



(b)

Fig. 2. a. View of TAP (with zone of upwelling) and TiN in the background. b. TiN with floating sulfur.

Table 1. Physical parameters of the Keli Mutu lakes

Physical parameter	TAP	TiN	TAM	TAM rim
Maximum lake depth*	64	127	67	
Diameter (Max/Min)**	400/330	430/306	357/260	600/550
Crater rim diameter (Max/Min)**	580/375	520/375	400/360	900/850
Waterlevel in crater**	1382	1394	1354	
Surface area (m^2)*	81700	91700	60400	
Volume ($\times 10^6$ m^3)	5.3	6.4	4.2	
Catchment area (10^5 m^2)*	1.7	2.3	4.1	

*Dimensions in meters, *after Kemmerling (1929), **after VSI map, 1993.*

larger crater. Kemmerling (1929) reported fumarolic activity in the TAM crater, but none is currently observable. TAM's shoreline is coated with fine red/yellow incrustations and gypsum crystals.

Each Keli Mutu lake has a vibrant color that periodically changes. In 1929 TAP was red, TiN was light green, and TAM was green. In 1938 TiN turned white and its surface water temperature may have reached 65°C. During the 1970's TAP was again red, TiN was light blue, and TAM was white. TAP's color changes frequently from "dark green" to "deep red/brown" and back, which correlates with the cyclical change from dry to wet season. TAP's color change is said to occur rapidly, beginning along the crater walls and enclosing inward in a matter of days (VSI geologists, pers. comm.). During May 1989 and August 1992, TAP was dark green, TiN was light blue, and TAM was black.

Several rivers drain the flank of Keli Mutu and the river Ai Bai (south flank) possibly has a lake-seepage input (Kemmerling, 1929). The river Watu Gana is a tributary of the river Mboeli, which drains the northeast and east side of the volcano. Kemmerling (1929) labeled these the "warm river" and suggested that they carry acid lake effluents.

METHODS

Three surface water samples were collected in May, 1989, and 30 water samples were recovered from various depths during an expedition in August 1992. Water and sediment sampling of TAP and TiN required the use of a remote sampling system because of the more than 100 meter high, vertical crater walls that separate the lake waters from the crater rim. Water samplers modified for the highly corrosive environment were ferried out over TAP and TiN via a 400 m long cable strung across the craters (Fig. 1b). TAM was sampled directly by climbing down to its shoreline. The water samples were split into a test fraction for temperature, pH, and dissolved oxygen content measurements, a filtered fraction, and a filtered/1000× diluted fraction. Temperature, pH and dissolved O_2 were measured in the field with digital equipment. The % O_2 saturation was calculated later, taking into account the salinity and temperature (but not the barometric pressure), after Riley and Skirrow (1965). Bottom sediments from TAP (22 m-depth) and TAM (~10 m-depth) were scooped up remotely with rubber cups. The river Mboeli was sampled along the paved road up the mountain between the km 3–4 markers, close to the fields with the Liasembe and Kolorongo hot springs. Two river water samples were obtained by VSI geologists near the village of Moni from the same stream system in May/June 1993.

The chemical composition of the lake fluids and sediments was determined in the months after the expeditions to Keli Mutu. The concentrations of Cl, SO_4, and F in the fluids were determined with a Dionex ion chromatograph (model QIC) and a Dionex five anion standard solution. Cation concentrations in fluids were determined using Inductively Coupled Plasma/Optical Emission Spectroscopy (ICP/OES) for the 1992 data

set and ICP-mass spectrometry and ICP/OES for the 1989 data set. Standard errors for Cl^-, F^- and SO_4^{2-} are 2.7%, 0.9% and 0.4%, respectively. The relative error for Si analyses by ICP/OES is large (up to 25%) whereas errors for major elements are a few % (Pasternack, 1993). Polythionate species ($S_xO_6^{2-}$, where x = 4, 5, or 6) were determined by Prof. Takano according to methods detailed by Takano and Watanuki (1988). Bulk sediment analyses were done by ICP/OES and ICP-MS after total digestion with a multi-acid mixture of $HF/HNO_3/HClO_4$. Some sediment samples were fused and then dissolved for silica analyses and S was determined after combustion in a furnace. Bottom sediments and suspended sediment particles were individually analyzed using a Scanning Electron Microscope with an Energy Dispersive System (SEM/EDS).

Analytical Results

The three Keli Mutu lakes differ in temperature and chemical composition, but all contain acid-sulfate-chloride fluids undersaturated in O_2

Table 2. Chemical composition of TAP

	1992 data				1989 data
	0 m	10 m	15 m	20 m	0 m
Temp (°C)	20.4	21.4	21.6	22.4	22.5
pH	1.8	1.7	1.8	1.9	1.75
TDS	16.63	17.22	17.71	16.58	14.88
O_2	5.4	3.9	4.3	3.8	7.8
O_2 % sat.	68	50	55	49	100
Cl	2670	2880	3400	2650	2630
SO_4	9780	9920	9960	9660	8600
F	238	220	242	242	160
B	21.1	21.8	20.8	21.6	12.4
Be	<.1	<.1	<.1	<.1	0.03
Li	0.3	0.3	0.3	0.3	0.3
As	0.6	0.9	0.7	0.9	1.3
Sb	<.5	<.5	<.5	<.5	0.07
Ca	599	632	618	606	607
Mg	242	257	251	247	217
Fe	1190	1270	1240	1210	1020
Mn	8.4	8.9	8.7	8.5	7.7
K	53	55	53	53	43
Na	229	247	241	237	213
Al	1500	1600	1570	1540	1260
Si	91	97	95	92	94
P	4	4	4	4	3.3
Sc	0.2	0.2	0.2	0.2	0.2
Ti	<1	<1	<1	<1	0.4
V	2.9	3.0	2.9	2.9	1.8
Cr	0.2	0.2	0.1	0.2	0.2
Ga	0.2	0.2	0.2	0.1	0.1
Sr	2.0	2.2	2.1	2.1	1.5
Y	0.3	0.3	0.3	0.3	0.2
Zr	0.2	<.1	<.1	<.1	0.06
Ba	<.1	<.1	<.1	<.1	0.02
Zn	1.8	2.0	1.9	1.7	1.7
Cu	0.7	0.3	0.2	0.1	0.2
Pb	<.3	<.3	<.3	<.3	<.3

Units: ppm; TDS in ‰; polythionates are below detection.

with respect to the atmosphere. The TAP waters are strongly acidic, with high concentrations of Cl, S, and major cations (Table 2). The short depth trajectory of four samples shows the highest concentrations for most major cations at 10 m depth, whereas the highest S and Cl concentrations occur at 15 m depth; Cu concentrations decrease with depth. No detectable concentrations of polythionates exist in either the surface waters or those from 20 m depth. The surface water has a temperature similar to the ambient air and the temperature increases at 1° per 10 meters.

The TiN waters are significantly more concentrated acids than the TAP waters (Table 3). The lake's center was warmer, more depleted in O_2, and more concentrated in S and Cl compared to waters collected near-shore. Sulfur occurs in various dissolved species and as a floating el-

Table 3. Chemical composition of TiN

	1992 data			1989 data
	0 m near-shore	0 m lake center	10 m near-shore	0 m near-shore
Temp (°C)	28.2	31.4	29.3	32.7
pH	0.4	0.4	0.5	0.3
TDS	93.74	97.04	96.93	90.01
O_2	1.9	1.3	1.8	3.6
O_2 % sat.	49	39	50	60
Cl	25100	26700	25250	25600
SO_4	48900	49350	47250	47000
S_4O_6	603	641	632	285
S_5O_6	545	570	575	100
S_6O_6	224	230	238	28
F	2840	2460	2750	2450
B	230	224	229	135
Be	0.1	0.1	0.1	0.02
Li	1.4	1.4	1.5	1.5
As	5.3	5.4	5.1	7.2
Sb	<.5	<.5	<.5	0.2
Ca	869	899	911	1032
Mg	1280	1280	1270	1194
Fe	2620	2620	2595	2180
Mn	38.1	38.0	37.7	35.6
K	542	545	539	630
Na	939	942	937	1042
Al	8630	8610	8590	8460
Si	66	66	61	83
P	51	51	50	51
Sc	2.3	2.3	2.3	1.9
Ti	7	7	7	60
V	21	21	21	15
Cr	1.2	1.4	1.3	0.9
Ga	1.7	1.8	1.8	2.4
Sr	11	11	11	10
Y	0.9	0.9	0.9	0.8
Zr	0.3	0.3	0.4	0.4
Ba	0.2	0.2	0.2	0.3
Zn	8.8	9.3	9.6	7.5
Cu	0.2	0.1	0.3	0.05
Pb	3.5	4.0	3.5	3.7

Units: ppm; TDS in ‰.

emental sulfur froth. The tetrathionate ($S_4O_6^{2-}$) and pentathionate ($S_5O_6^{2-}$) concentrations are also higher at the lake's center; the hexathionate ($S_6O_6^{2-}$) concentrations are everywhere much lower than those of the other polythionates. Most major cations and trace metals show no significant variation in concentration between the samples. Apparently, the surface layer of TiN is well-mixed except for the higher S and Cl concentrations in the warm area of upwelling.

The waters from TAM are much more dilute than those from TiN and TAP (Table 4). No significant variations in concentration were found in the TAM samples, but the surface waters are slightly warmer and more-oxidizing than the waters from below the surface. Polythionates were found in trace quantities in the surface water sample. A spring trickling into TAM appears to be slightly diluted lake water, although it is depleted in Al and has much lower dissolved O_2 contents at its head. Downstream, the water is more oxidizing and iron-oxides coat the rocks over which the spring water flows.

Sediment data for the Keli Mutu lakes

Small quantities of sediment were recovered from TAP and TAM during water sampling. The chemical analyses from TAP are duplicates of the same sample (Table 5, 1a–1b); a red clay (TAM sed 1a–1b) and a blue clay (TAM sed 2) were

Table 4. Chemical composition of TAM

	1992 data				1989 data
	0 m	~3 m	~10 m	spring	0 m
Temp (°C)	20.45	19.3	19	18.4	18
pH	3.2	3.1	3.2	4	2.9
TDS	2.36	2.37	2.35	2.06	2.22
O_2	7.5	5.9	6.0	0.9*	9.1
O_2 % sat.	87	66	67	10	78
Cl	88	98	86	13	100
SO_4	1585	1593	1590	1405	1475
S_4O_6	0.8	NA	BD	NA	BD
S_5O_6	0.1	NA	BD	NA	BD
S_6O_6	BD	NA	BD	NA	BD
F	16	16	16	5	10
B	0.9	0.8	0.8	0.5	0.6
Be	<.1	<.1	<.1	<.1	0.01
Li	<.1	<.1	<.1	<.1	0.03
Ca	437	437	428	470	434
Mg	34	34	33	32	32
Fe	21	18	20	<1	10
Mn	1.4	1.4	1.3	0.9	1.3
K	5	6	5	5	4
Na	53	52	51	56	43
Al	69	67	66	14	68
Si	50	50	51	56	44
P	<1	<1	<1	<1	0.2
Sc	<.1	<.1	<.1	<.1	0.01
Cr	<.1	<.1	<.1	<.1	0.06
Ga	<.1	0.1	<.1	<.1	0.04
Sr	0.6	0.6	0.6	0.5	0.5
Y	<.1	<.1	<.1	<.1	0.03
Zn	0.2	0.2	0.3	0.1	0.14
Cu	0.2	0.2	0.2	0.3	0.15

*NA = Not analyzed; BD = below detection; in ppm; TDS in ‰. *Downstream: 6.15 ppm O_2.*

Table 5. Chemical composition of Keli Mutu lake sediments and volcanic rocks

	TAP sed-1a	TAP sed-1b	TAM sed-1a	TAM sed-1b	TAM sed-2	TAM ash-f	TAM ash	KM scoria
Na*	0.41	0.61	0.26	0.24	0.42	0.31	0.44	1.88
Mg*	0.28	0.23	0.20	0.15	0.15	0.12	0.15	2.64
Si*	18.1	NA	7.3	NA	20.8	30.4	NA	25.2
S*	20	NA	2.6	NA	11.1	2.1	NA	NA
Al*	5.76	5.63	2.20	1.84	6.77	2.84	0.65	9.90
Ca*	0.32	0.21	0.45	0.36	2.48	0.39	4.30	6.07
K*	0.40	0.54	0.32	0.27	0.58	0.54	0.62	0.33
P*	0.05	0.07	0.05	0.06	0.05	0.05	0.06	0.06
Ti*	0.39	0.34	0.17	0.12	0.49	0.65	0.46	0.61
Fe*	1.09	0.87	31.60	39.80	3.42	2.40	4.53	7.07
Mn	72		120		54	97		1380
Li		5		2			4	13
Be							0.9	3
Sc	47	54	6	4	15	13	14	30
Cr	16	16	14	16	16	10	7	20
V	140	145	244	239	161	110	137	240
Co				4	11		14	
Ni		4					9	
Cu	154	148	144	167	89	47	93	91
Zn	23	25	21	7	11	11	14	101
Ag		0.1		0.9			0.4	
As	1350	618	185	178	96	70	78	4
Sr	187	214	85	73	268	160	271	335
Y	10	5	3	3	5	8	5	51
Zr	53	46	23	14	66	88	50	89
Sb		33						
Ba	253	284	101	92	272	333	294	299
Pb		27		14		74	28	
Bi		18		52			21	
Mo		4					9	

*Units: *%, rest in ppm; NA = not analyzed; space = below detection.*

analyzed from TAM. Also analysed were a fresh scoria sample from the flanks of Keli Mutu and fine ashes (TAM ash-f) and coarse ashes (TAM ash) from the crater walls of TAM. These ashes were deposited during phreatic blasts of the lakes in the past and thus may carry a large "old lake sediment" component. The Keli Mutu lake bottom and suspended sediments have major element compositions that are broadly comparable to the ashes from the crater walls, except that the TAP sediment is strongly enriched in S and the TAM sediment in Fe. The TAP sediments are slightly depleted in Si and Fe, but enriched in Al with respect to the ash. TAM sediment 1a–1b is strongly enriched in Fe and sed 2 is rich in Ca and S, possibly the result of the presence of gypsum. The TAP sediment is strongly enriched in As and Cu, and the TAM sediments show milder enrichments in As and Cu. Gold levels in all the analyzed sediment samples are below 1 ppm.

Particulate analyses of sediment and filtrate crystal grains by SEM/EDS suggest one grain type common to all lakes and others unique to each lake. TAP bottom sediments have two types of grains with distinct compositions: 1) a Si-Al dominated grain, probably glassy-rock detritus, which is sometimes coated with sulfur and 2) anhydrite/gypsum crystals. Suspended sediments from TiN consist of Si-Al bearing grains, anhydrite/gypsum crystals, and heterogeneous crystal aggregates rich in S, Si, Ti, Ca, Al, Fe, and K. TAM bottom sediments contain Fe-rich grains with

Table 6. Chemical composition of spring and river waters from Keli Mutu

	hot spring Kolorongo	hot spring Liasembe	am-6-93 Ai Mutu	am-1-92 Mboeli	wg-6-93 WatuGana
Temp (°C)	36	42	NA	18	NA
pH	6.8	7.8	2.0	2.1	3.2
TDS*	0.17	0.13	8.76	14.51	1.22
O_2	3.8	1.1	NA	NA	NA
O_2 % sat.	54	17	—	—	—
Cl	8	3	1334	3740	352
SO_4	29	7	4859	7120	514
F	<2.5	<2.5	4.7	396	10
B	0.2	0.2	23.7	27.7	2.3
Li	<.1	<.1	<.1	0.3	<.1
As	<.3	<.3	0.9	0.9	<.3
Ca	34	33	331	495	82
Mg	11	8	191	265	31
Fe	<1	<1	293	297	<1
Mn	0.1	<.1	8.8	9.2	1.5
K	7	6	77	72	13
Na	27	23	180	240	36
Al	2	<1	1370	1770	130
Si	51	51	78	69	50
P	<1	<1	4	4	<1
Sc	<.1	<.1	<.1	0.4	<.1
V	<.1	<.1	2.3	2.8	<.1
Cr	<.1	<.1	<.1	0.3	<.1
Ga	<.1	<.1	<.1	0.3	<.1
Sr	0.2	0.1	2.0	2.8	0.4
Y	<.1	<.1	0.2	0.3	<.1
Zr	<.1	<.1	<.1	<.1	<.1
Ba	<.1	<.1	NA	<.1	NA
Zn	<.1	<.1	1.4	1.6	0.4
Cu	0.1	<.1	0.3	0.1	0.2

NA = not analyzed; Units: ppm; TDS: ‰.

a sulfur coating. Suspended particles from TAM are Fe-rich grains with easily volatilized S (presumably Fe oxides with an S^0 coating), anhydrite/gypsum crystals, and Ca-Si dominated grains (photographs and analyses in Pasternack, 1993).

Keli Mutu flank springs and rivers

Water samples were collected from the flank of Keli Mutu to search for evidence of leakage from the lake systems. The springs and river fluids differ strongly in composition: the river system Mboeli, Watu Gana and Ai Mutu has an acid-chloride-sulfate discharge, whereas the Kolorongo and Liasembe warm springs have neutral, dilute waters (Table 6). The Mboeli river water sample has some similarities with TAP fluids but the volcanic element ratios are almost identical to TiN. The waters from Kolorongo and Liasembe have no direct relationship with the crater lakes. Even though they are only a few hundred meters apart, they strongly differ in their relative concentrations of S, Cl, Na, and Mg. The only detectable trace elements in either spring are Cu and Sr (Table 6).

Discussion

Secular trends in Keli Mutu lake water chemistries

We first compare the 1989 and 1992 data sets because these data were all collected and analyzed by us with similar methods. Because we only have two sets of observations for a 3 year period, we

can not regard the compositional variations as true secular trends: strong compositional fluctuations may have occurred during this sampling interval. For several elements, the 1989 TAP data (Table 2) are outside the compositional range of the 1992 TAP samples: Mg, Fe, Mn, K, Na, Al, F, and SO_4 all increased, by factors from 1.08 to 1.38, but the 1989 Cl concentration was in the range of the 1992 concentration. The increased concentrations cannot be accounted for by evaporation alone because of the different magnitude of increases in element concentrations. The data sets for TiN (Table 3) show a strong increase in the B concentration (1.66), moderate increases in the concentrations of Mg (1.06), Fe (1.19), and Al (1.02), whereas Ca (0.88), K (0.87) and Na (0.90) decreased in concentration; the Cl and total S concentrations did not vary much. The two TAM data sets (Table 4) only show small differences between 1989 and 1992 concentrations and the lake waters thus remained almost constant in composition for the three year period.

The 1989 TiN samples were analyzed in 1992 for polythionates and the smaller concentrations in the 1989 samples may be partly related to degradation during storage. Bulk ICP sulfur analyses of the 1989 samples in 1989 gave similar concentrations as the 1989 SO_4 analyses with ion chromatography, suggesting that low concentrations of polythionates in the 1989 samples already occurred before storage.

The 1929, 1971, 1978, 1989 and 1992 data for

Table 7. Historic chemical composition of the Keli Mutu lakes

	1929	1971	1978	1989	1992
TAP					
Cl	533	1180	11008	2630	2670
SO_4	3166	1033	2765	8600	9780
Ca	265	484	648	607	599
Mg	51	140	165	217	242
Fe	356	NA	713	1020	1190
Na	NA	136	114	213	229
Al	392	NA	NA	1260	1500
Si	56	83	482	94	91
TiN					
Cl	5298	28150	29888	25600	25100
SO_4	10286	10160	9812	47000	49100
Ca	261	280	1022	1032	869
Mg	203	1420	520	1194	1280
Fe	546	NA	857	2180	2620
Na	NA	1164	1044	1042	939
Al	1624	NA	NA	8460	8630
Si	50	40	1137	83	66
TAM					
Cl	4154	630	1907	100	88
SO_4	4039	318	1892	1475	1585
Ca	808	376	399	434	437
Mg	206	55	129	32	34
Fe	378	NA	77	10	21
Na	NA	74	60	43	53
Al	NA	759	NA	68	69
Si	42	NA	81	44	50

NA = not analyzed; Units: ppm; 1929 data: Kemmerling (1929); 1971 data: Krafft and Krafft (pers. comm.); 1978 data: Badrudin and Sriwana (VSI) (pers. comm.).

some elements are given in Table 7. These data were collected and analyzed many years ago with different methods and so are not completely comparable to our data. The search for a long term secular trend is even more uncertain than that just attempted with the 1989 and 1992 data. Nevertheless, we observe an overall increase in major cations (especially Mg), halogens, and S in TAP, with a peak event in Cl around 1978. Waters from TAM show a strongly fluctuating S content and an overall decrease in halogens. Also, most major cations in TAM are now present in much lower concentrations than in 1929. Kemmerling (1929) described extensive fumarolic activity around TAM which is not present today, consistent with a waning volcanic/hydrothermal fluid input in TAM, but possibly with an increased fluid input during 1978. The data from TiN are incomplete and show strong variations of S and a strong increase of Mg, Fe, and Al during this century.

Aqueous Speciation and Mineral Saturation Modeling

The ionic speciation and mineral saturation in each Keli Mutu lake was assessed using SOLVEQ, a computer program that calculates water-mineral-gas equilibria (Reed, 1982). A requisite for this modeling is a calculated charge balance in the solution, which depends on the analytical precision and redox conditions (e.g., Fe^{2+}/Fe^{3+}). The extreme acidity and high ionic strength of the fluids make pH measurements better than ±0.05 difficult, and this uncertainty may be one source of charge imbalance. The SOLVEQ routine modifies the analytical chlorine concentration to achieve charge balance. We tried to constrain the lakes' redox conditions, which could not be measured *in-situ*, by varying the input Eh value and searching for solutions with the smallest calculated charge imbalance. All analyzed 1992 surface water samples were undersaturated with respect to atmospheric oxygen (Tables 2, 3 and 4). The convective overturn continuously mixes the surface waters with deeper waters that have not yet been exposed to atmospheric oxygen, and so these deeper waters must have Eh values below those measured at the surface. Calculated Eh values are low (<0.5), in agreement with the measurements. We compared the mineral stabilities predicted by SOLVEQ with the chemical composition of the sediments and evaluated the obtained speciation model.

SOLVEQ modeling of TAP showed that trials with Eh < 0.5 required 22% change in Cl concentration, whereas higher Eh scenarios required up to 47% Cl modification. The cations in TAP occur primarily as free cations and cation-sulfate pairs. The dominant S species are HSO_4^- and SO_4^{2-}; the Al speciation is dominated by the charged complexes $AlSO_4^+$, $Al(SO_4)_2^-$, and AlF^{2+}. Most F occurs in Al-F complexes instead of free F , comparable to findings at Poás (Rowe *et al.*, 1991).

The stability of most Fe-, Cu-, and As-bearing phases is redox sensitive and an Eh > 0.6 gives saturation with respect to hematite (Fig. 3). Between Eh = 0.21 and 0.6 the surface waters of TAP are not saturated with respect to any Fe mineral. When the fluid is modeled with Eh = 0.21 the minerals tennantite, enargite, chalcocite, bornite, covellite, pyrite and chalcopyrite are saturated. No Cu-mineral phases are near saturation unless the Eh is below 0.29. Native sulfur and pyrite are only saturated when Eh < 0.205 and Eh < 0.21, respectively. The silica minerals (except for amorphous silica) are saturated in the TAP solution, and gypsum/anhydrite and celestite are close to saturation (Table 8).

The lack of native S accumulations on the lake's surface and the absence of an H_2S odor (both present in TiN) suggest that TAP has low dissolved H_2S contents. TAP sediments are strongly enriched in Cu and As, but not in Fe relative to local ash and average andesitic rock (Table 5), which is even more obvious when the analyses are normalized on a S-free basis. These sediment data suggest that Cu-As bearing phases precipitated from the fluids but no Fe-rich phases. The best approximation for the redox conditions in TAP according to the SOLVEQ output and in agreement with the chemical composition of the

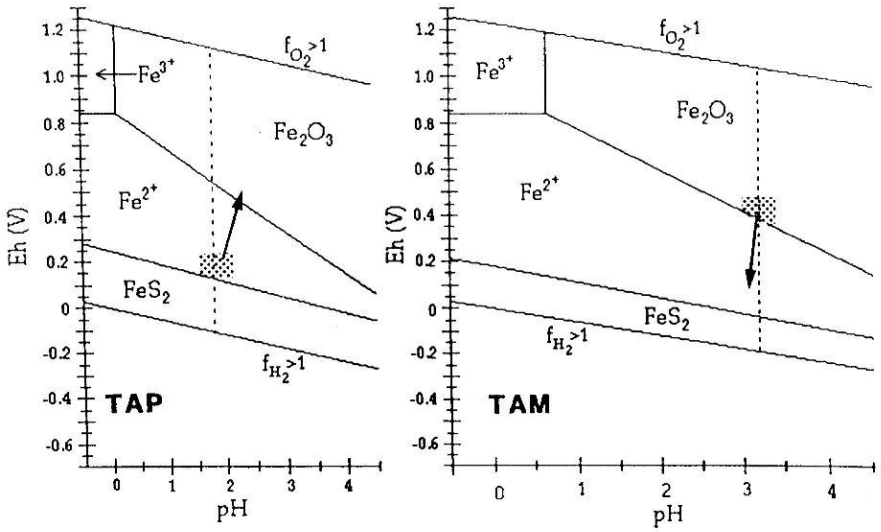


Fig. 3. Eh-pH diagrams for TAP and TAM, with aFe and $aHSO_4^- + aSO_4$ = from SOLVEQ output. Probable 1992 redox conditions are shaded. Arrow for TAP towards conditions for the "red stage"; for TAM, arrow points to more reducing conditions indicated by some of the sediments.

Table 8. Results of SOLVEQ modelling

Mineral	Formula	Mineral saturation index* at the relevant Eh. TAP 0.2352	TiN 0.2894	TAM 0.4431
quartz	SiO_2	1.52	1.27	1.25
chalcedony	SiO_2	1.32	1.05	1.05
a-cristobalite	SiO_2	1.03	0.77	0.76
barite	$BaSO_4$	—	0.78	BS
b-cristobalite	SiO_2	0.58	0.35	0.31
am. silica	SiO_2	0.27	0.07	0.01
hematite	Fe_2O_3	BS	BS	0
native sulfur	S	BS	0.91	BS
tennantite	$Cu_{12}As_4S_{13}$	0.1	4.96	BS
enargite	Cu_3AsS_4	0.04	4.97	BS
chalcocite	Cu_2S	2.21	1.31	BS
bornite	Cu_5FeS_4	0.83	0.52	BS
covellite	CuS	0.91	2.75	BS
chalcopyrite	$CuFeS_2$	−5.05	−0.44	BS
pyrite	FeS_2	BS	1.98	BS
orpiment	As_2S_3	BS	2.96	BS
gypsum	$CaSO_4$-$2H_2O$	−0.17	−0.42	−0.3
anhydrite	$CaSO_4$	−0.38	−0.46	−0.52
celestite	$SrSO_4$	−0.94	−0.39	−1.48
pyrophyllite	$Al_2Si_4O_{10}(OH)_2$	BS	BS	−0.93
kaolinite	$Al_2Si_2O_5(OH)_4$	BS	BS	−1.91
alunite	$KAl_3(SO_4)_2(OH)_6$	BS	BS	−2.29

BS = far below saturation.
**Index is log (ion activity product/solubility product).*

sediment is an Eh value of ~0.24, where the minerals tennantite, enargite, chalcocite, bornite and covellite are saturated, but the Fe-rich minerals chalcopyrite, pyrite, and orpiment are not saturated; also native S is not saturated at this Eh and H_2S activities are small.

Modeling of the TiN water composition demanded the smallest Cl adjustments for calculated charge balance at Eh = 0.3–0.5. The HSO_4^- activity is 45× greater than SO_4^{2-} because of the extremely low pH in TiN, and this paucity of free sulfate causes the predominance of metal chloride complexes, comparable to data from Poás (Rowe *et al.*, 1991). The non-amorphous silica minerals are saturated in TiN, and celestite and gypsum/anhydrite are close to saturation. Pyrite and native sulfur become saturated at Eh < 0.298. At Eh < 0.282 the minerals tennantite, enargite, covellite, chalcocite, bornite, chalcopyrite, and orpiment are all saturated.

No TiN bottom sediments are available for verification of the modeling, but the yellow froth on the surface of TiN is native sulfur. SEM/EDS analysis of suspended grains from TiN were also found to be coated with a veneer of native S. The TiN bottom sediments probably carry pyrite, silica, and Cu-As minerals if the Eh in TiN is less than the upper limit for S^0 saturation. Extraction of Cu minerals from TiN water is suggested by its low Cu concentrations. The TiN fluids probably have Eh < 0.28, as also suggested by the copious emissions of H_2S from this lake.

SOLVEQ modeling of TAM suggests that the lake water has Eh < 0.5 (best charge balance scenario). Many ions occur in uncomplexed form, except for Al which occurs predominantly as Al-sulfate complexes. Sulfur is principally present as sulfate. The non-amorphous silica minerals are saturated in TAM and gypsum/anhydrite and pyrophyllite are close to saturation. Hematite is saturated at Eh > 0.44 (Fig. 3) and FeOOH and $Fe(OH)_3$ are saturated at higher Eh values.

The red TAM sediments (sed 1a) are strongly enriched in Fe, suggesting precipitation of an Fe-oxide. The Cu and As enrichments in the sediments as well as the S coatings on some grains cannot be explained at an Eh > 0.44. TAM was not visibly in a convective state, so the lake may be stratified with respect to redox conditions, with precipitation of an Fe-oxide in the upper water body and more reducing conditions in the bottom waters.

None of the lakes is saturated with alunite, a mineral described from other sulfate-rich crater lakes (e.g., Zotov, 1967), which is probably a result of the strong complexation of Al and SO_4. The changes in color of TAP, and possibly TAM, from red to green and back seem to correlate with the alternation of dry and wet seasons (Pasternack, 1993). They may be caused both by Eh (e.g., enhanced influx of atmospheric O_2 with rain input) and pH (dilution effect) changes, which will move the fluids in or out of the hematite (or goethite/limonite) stability fields (arrows, Fig. 3).

Origin of the Keli Mutu Lake Fluids

Volcanic element fluxes

Crater lakes are mixtures of endogene and exogene fluids. The origin and composition of the endogene fluid can usually only be inferred because it cannot be sampled directly. The input fluid at Keli Mutu has the chemical signature of a volcanic gas: rich in S, Cl, and F and to a lesser degree B and Li, and extremely acidic. Most hydrothermal fluids of meteoric origin are not highly acidic, except when shallow-level boiling of H_2S-bearing fluids occurs, but then the resulting fluids tend to be poor in Cl. Most likely, the volcanic input at Keli Mutu is either a volcanic gas that is absorbed directly by the lake waters or was already absorbed by fluids deeper in the volcanic system which are then injected into the lakes. The release of large gas bubbles (probably CO_2) at the surface of TAP is as expected for a volcanic gas input into the lakes. The temperature of the TiN lake waters above local ambient temperatures indicates the input of a hot fluid, presumably a vapor, because the enthalpy of condensation is needed to keep the lake water at the elevated temperature (Brown *et al.*, 1991). The presence of the polythionates in two lakes is also evidence for

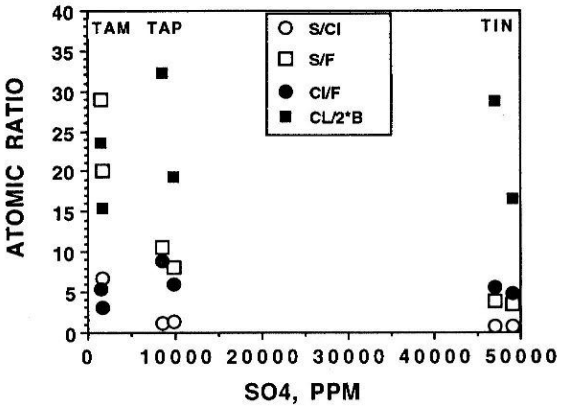


Fig. 4. Volcanic element ratios for the three lakes. The S/F and S/Cl ratios decline from TAM to TAP to TiN, whereas the Cl/F and Cl/B ratios show much less variation and have their maximum in TAP.

an active volcanic gas input (Takano, 1987).

The element ratios of the volcanic/hydrothermal input vary in the three lakes, with S/Cl and S/F ratios decreasing with increasing S content of the lakes (Fig. 4). This is probably largely the result of the precipitation of native sulfur and S-bearing minerals in the more concentrated lakes. The Cl/F and Cl/B ratios show much less variation and have their maximum value in TAP. The F/B ratios are close to constant. Volcanic crater fumaroles with a low mass output commonly also have a relatively low temperature (about 100–200°C) and may be vapors escaping from a hydrothermal system at depth. The species HF and HCl are depleted in such low temperature fumaroles because they remain largely behind in the fluid, and HF also tends to be depleted in cooler fumaroles, possibly as a result of extensive wall-rock interaction during cooling of the gases (e.g., Poorter *et al.*, 1991). The three lakes may be ultimately fed by a common volcanic gas phase, but TAM may be fed by small and cool fumaroles with a fractionated composition rich in H_2S (oxidized to SO_4 in the lake waters) and probably CO_2. TiN is fed by fumaroles with a high mass flux and a higher temperature; this would represent the least fractionated volcanic gas that possibly carries both SO_2 and H_2S as suggested by the abundance of the polythionates in TiN (Takano, 1987). TAP would be fed by an intermediately fractionated source. The atomic S/Cl of about 1.3 of TAP is in the common range of volcanic arc gases (e.g., Varekamp *et al.*, 1984; Poorter *et al.*, 1991), whereas the value of 0.6 of TiN is in the low part of that range. The relative sulfur depletion of TiN is most likely linked to its precipitation of native sulfur.

We calculated the sulfur budget for each lake over the periods 1989–1992 and 1978–1992 (Table 9). These values represent the differences in surface water concentrations over that period (Table 7) multiplied by their lake masses (from Table 1). These calculations are for static lake systems, that is, without element loss through seepage and mineral precipitation, and thus provide *minimum flux* values. These spot measurements carry uncertainties with regard to true secular trends, and there may have been other periodic fluctuations in composition related to evaporation and other physical processes. The S fluxes for TiN are significant and fall in the lower range of values measured at active volcanoes (Casadevall *et al.*,

Table 9. Net changes of dissolved elements: changes in sulfur concentration expressed as sulfur fluxes (tonnes SO_2/day) for the three lakes over the periods 1989–1992 and 1978–1992; the total change in dissolved cation masses for 1989–1992 is expressed in tonnes. Estimates of the dissolved equivalent rock mass over that period (in kilotonnes) are based on quantitative Ma transfer from rocks with the KM scoria composition in Table 5.

	TAP	TiN	TAM
S (1989–1992)	3.8	8	0.3
S (1978–1992)	4.8	32	−0.3
Ca	−42	−1043	12
Mg	133	550	8
Fe	901	2816	46
Mn	3.7	13	0.4
K	53	−563	2
Na	85	−660	40
Al	1272	1088	4
Eq. rock mass	5	20	0.3

1984). The fluxes for TAM are small and well within the margin of analytical error, whereas those for TAP are ten times larger and apparently consistent over time. Both TAP and TiN were building up towards higher S concentrations during the 1980's whereas TiN and TAM may be now close to reaching a chemical steady state for S. If there is a consistent input, there must also be an output of fluids from these systems, most likely a seepage flux (as indicated by the acid rivers on the Keli Mutu mountain flank) and a significant sulfur precipitation flux, especially for TiN.

The nature of water-rock interaction processes

Conceptual models of crater lakes may invoke input of a hyperacid volcanic-hydrothermal component, rich both in volcanic elements and cations, as e.g., found in Sirung, Indonesia (Poorter *et al.*, 1989a, 1989b). Alternately, a volcanic gas input may acidify the lake waters, which then react with rock debris in the lake and build up an inventory of cations until saturation and precipitation of new mineral phases occurs (e.g., Sigurdsson, 1977). A more complex model invokes an input of a volcanic/hydrothermal gas phase into the lake and the acidified lake waters circulate through the mountain, react with volcanic rocks and the resulting brines are partly reinjected into the lake and partly lost from the crater lake system. In this section we try to constrain the nature and location (inside or outside the lake) of the water-rock interaction processes.

High temperature volcanic gases transport heavy metals like Zn, Pb and Cu as volatile chlorides, Al and Ca as volatile F-compounds, and Na and K as volatile chlorides (e.g., Symonds *et al.*, 1987, 1992; Varekamp *et al.*, 1986; Thomas *et al.*, 1982). A volcanic gas input may thus well be associated with a substantial cation input. Rock digestion within the lake may be important too, because rainstorms carry large amounts of fine-grained material into the lakes.

A comparison of the three lake systems shows approximately linear increases for Na, K, Al and Mg from TAM to TAP to TiN when plotted against B. Other cation ratios differ considerably between the lakes (Fig. 5; Tables 2–4), including elements not present in minerals saturated in the lakes. Strong deviations from a linear trend are found for Ca and Fe and TiN is depleted in these elements relative to the other lakes, possibly a result of precipitation of pyrite and gypsum. The roughly linear compositional trends for several elements in the three lakes either suggest an approximately common fluid input for cations and anions (a volcanic/hydrothermal fluid) or the more strongly acidified lake waters dissolved a proportionately larger mass of rock.

The SOLVEQ modeling indicates that no common alteration products (clays or micas) are stable in the lake waters (except the approximate pyrophyllite stability in TAM). Possibly, primary rock minerals dissolved only slightly and congruently in the hyper-acid fluids. Alternatively, hydrothermal fluids that were produced by water-

Table 10. Rock-to-fluid element transfer ratios (ETR, in %)

	TAP	TiN	TAM
Mg	100	100	100
Li	244	258	189
B	30200	60000	10500
As	4388	4400	—
Zn	204	164	114
Na	138	123	188
K	157	420	100
Ca	122	38	586
Al	155	189	56
Fe	175	68	12
Si	4.5	0.7	15
Ba	0.8	2	—
Ti	0.8	22	—
Zr	8	9	—
Cu	25	1.3	136
Sr	55	67	117
P	66	185	27
Mn	68	57	78
Cr	98	102	250
Co	100	17	570
Ge	100	295	—
Ni	115	55	193

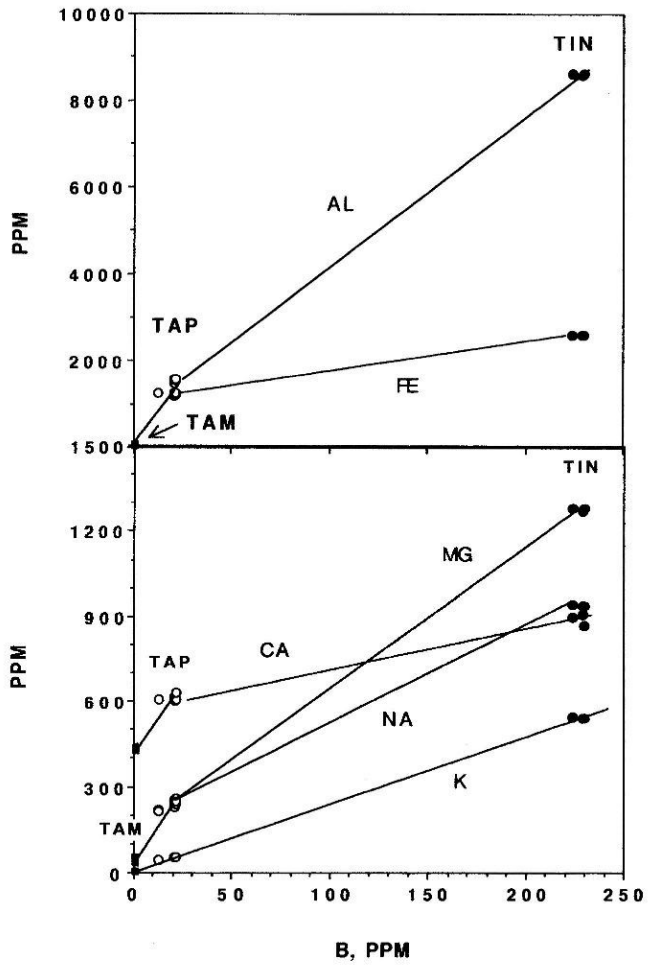


Fig. 5. Cation versus B relations for the three lakes. The elements Na, K, Mg, and Al show approximately linear relations whereas Fe and Ca show strongly kinked curves.

rock interaction outside the lake system may have become diluted by the lake waters and so produced fluids undersaturated in common secondary phases.

We can use a qualitative element mass balance expression if water-rock interaction takes place predominantly inside the lake system:

sediment + cations-in-lake-fluids ⇒ original rocks.

The lake sediments are made up of altered rock debris and minor amounts of newly precipitated phases. The scoria sample and ashes from the TAM crater walls serve as possible rock protoliths for dissolution and water-rock interaction (Table 5). We normalized the rock and sediment analyses on a S-free basis for these mass balance considerations.

One endmember model is to consider congruent rock dissolution in the acid lake fluids. Cation concentrations in the fluids can be predicted for congruent rock dissolution using "element transfer ratios" or "ETR" (Table 10). The ETR values are the measured concentrations in the fluid divided by those predicted from congruent rock dissolution assuming that Mg is quantitatively transferred from the rock into the fluid (see e.g., Giggenbach, 1974). Elements with an ETR of 100% are quan-

titatively transferred into the fluid; elements with an ETR > 100% may have been contributed by the volcanic gas phase or through non-congruent rock-dissolution that left Mg behind, whereas ETR < 100% suggest precipitation of a mineral phase with that element or water-rock interaction with incomplete element transfer.

The elements Li, B, As, Pb, and Zn have very high ETR's and may be largely derived from a high-temperature volcanic gas component, together with S and the halogens (Symonds *et al.*, 1987, 1992; Thomas *et al.*, 1982). Cu is depleted in the TAP and TiN lake fluids, although it is also enriched in volcanic gases (Symonds *et al.*, 1992; Rose *et al.*, 1982; Varekamp *et al.*, 1986; Lowenstern *et al.*, 1991). The TAP and TiN sediments are enriched in Cu compared to the andesitic scoria and SOLVEQ modeling predicts the saturation of Cu minerals at low Eh. Probably, Cu is extracted from the lake fluids through mineral precipitation. The TAM fluids have low ETR for Fe and the SOLVEQ output predicts saturation with Fe-bearing phases; the TAM sediments have indeed a strong Fe enrichment. Only 0.7 to 4.5 percent of the expected Si and Ba and half the expected amount of Sr is found in solution in the two most acidic lakes. Precipitation of silica minerals, barite and strontianite, as predicted by the SOLVEQ calculations, may be the cause of these depletions, but TAP sediments are not enriched in Sr, Ba and Si with respect to the scoria and the ashes (Table 5) and the SEM/EDS analyses show little evidence for the presence of pure silica phases. Use of the fine ash as a protolith provides ETRs < 100 for all elements, but it is unlikely that this fine ash is the only protolith in the system. The ETR approach thus shows that congruent dissolution, if occurring, is not the only process operating.

Cation ratios in the sediments, protoliths and fluids show that both the sediments and fluids are relatively enriched in Al compared with the protoliths, suggesting an "external" element source. The sediments and ashes are poor in Mg compared with the TAP and TiN fluids and the scoria sample (Fig. 6). Silica is depleted in the fluids and shows no enrichments in the sediments relative to the protoliths. The Si concentrations in the three lakes are higher than equilibrium saturation values with crystalline silica phases (but unsaturated with respect to amorphous silica), and possibly the fluids interacted outside the lakes with crystalline silica minerals at a higher temperature. The Na/K temperatures of the lake fluids (Fournier and Truesdell, 1973) are >150°C, much higher than measured lake temperatures, but it is unclear if this geothermometer can be used in these hyperacid systems. Taken all this evidence together, it seems that the lakes draw a cation flux from outside the lake system.

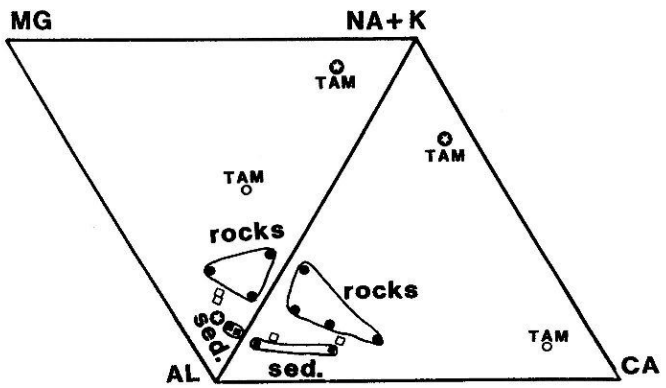


Fig. 6. Na+K–Al–Mg and Na+K–Al–Ca relationships between rock protoliths (dots, including a feldspar and a volcanic glass analysis), lake fluids (open circles and open squares), lake sediments (filled squares) and dissolved cations over the period 1989–1992 (stars).

We calculated the total dissolved element quantities from the differences in cation concentrations over 1989–1992 (Table 9). We also calculated equivalent digested rock masses, again based on quantitative Mg transfer from rocks, similar to the ETR approach, but now based on the amount of dissolved rock over a 3 year period instead of the instantaneous dissolved cation concentrations. The total amount of Mg dissolved in three years obtained from the difference in concentration multiplied by lake volume was recalculated as a mass of rock with Mg contents of the scoria sample. Comparison of the dissolved rock component with the rock protoliths shows severe misfits: TAM has a strong excess demand for Na and Fe, whereas TAP has an excess demand for Al and Fe. The compositions of these dissolved rock masses are shown as stars in Fig. 6, indicating that over the period 1989–1992 no congruent dissolution of the common rock types occurred. We saw earlier that the TAP sediments are also relatively enriched in Al, confirming the lack of internal mass balance for Al in TAP. TiN shows evidence for loss of Na, Ca and K over the period 1989–1992, whereas Fe, Al, and Mg were gained.

We conclude that the cation contents of the lakes are not simply derived from *in-situ* dissolution of the rock protoliths, although we cannot exclude that small degrees of *in-situ* congruent solution of a mixture of ashes and more mafic rock particles (scoria) contributed to the cation contents. Some elements must have been derived from an external source (e.g., Al) and part of the silica may be "missing", that is, not in the sediments and not in the fluid. We suggest that the lakes are not closed systems, but derive part of their cation load from a deeper geothermal system in the mountain. Possibly, the lake fluids circulate through the mountain, react with rocks and leave silica-rich precipitates behind, and acquire other elements which are then circulated back into the lakes or escape on the flanks. The acid fluids in the river system may be diluted TiN fluids (about 14%) but then have too high cation contents and a pH that is too high. Possibly, the acid fluids reacted with rocks during their subterranean travel, which raised the pH and increased the major cation loading. The Ai Mutu fluids were sampled further downhill and may be a mixture of several acid source fluids.

Conclusions

The above perusal of the available data on the three Keli Mutu lakes provides us with some constraints on the origin of the Keli Mutu fluids and the hydrology of the crater system. The three lakes have waters of dramatically different composition and thus fluid exchange between the lakes has to be extremely limited. During this century, TAM has seen an overall decrease in ion concentrations, TAP has seen a build-up in concentrations (with fluctuations), and TiN's composition has fluctuated more widely. The dilution of TAM was accompanied by the disappearance of subaerial fumaroles, pointing to a waning input of volcanic-hydrothermal fluids into that section of the Keli Mutu crater system. It also indicates that the lake fluids gradually seep out of the lakes and are replaced by rainwater. The presence of acid-chloride-sulfate fluids in a river on the mountain flank suggests leakage from the lakes, although fluid escape from an acid system that is also feeding the lakes cannot be excluded. TiN and TAP are convectively stirred, but TAM seems quiet at present and may be stratified. As such, TAM may have the greatest potential for accumulated CO_2 in the bottom layer of water.

The data suggest an input of a hot volcanic fluid rich in S and the halogens in TiN, a smaller, possibly compositionally different input in TAP and a very small input (if any) in TAM. The influx of Cu, possibly from these volcanic fluids, may be trapped in the lakes and Cu is precipitated with As in the sediments, but no strong Au enrichments were observed. The lakes may be modern analogs of systems that deposited shallow Cu ores in the past, similar to the periferal zones of the White Island volcano-hydrothermal system (Hedenquist *et al.*, 1993).

The minimum volcanic element flux of about 30–50 tons SO_2/day is in the lower range for ac-

tive, passively degassing arc volcanoes (Casadevall *et al.*, 1984), but the true mass fluxes are larger because these estimates are based on static lake systems. Sinks for sulfur may be seepage and precipitation of native sulfur and gypsum/anhydrite.

Various indications (e.g., element ratios in water, lack of closure in mass balance modeling of sediments and fluids versus dissolved rocks) suggest that the lakes receive a cation input from below the lake in addition to their cation loading from rock dissolution within the lake. The total element inventories in the lakes are substantial and may represent mass transfer on the order of 10^9–10^{10} grams/year. Such acid brine systems can alter a large part of a volcanic mountain within 10,000 years and transport tonnes of metals within a few centuries.

Acknowledgments—This work was made possible by financial support from NSF, grant # INT8713836 to JCV and support from Wesleyan University through the McKenna fund to GBP and the Smith Fund to JCV. We appreciated the cooperation with staff and geologists from the Volcanological Survey of Indonesia (VSI) in Bandung. We also thank David Hilton, Terry Sriwana and Rob Kreulen for their help during the 1989 field campaign and the help of Petros Tiba, Agus Da Silva, and Usman from VSI and Daniel Curewitz and Stephen Scholand from Wesleyan University during the 1992 campaign. We gratefully acknowledge the work of Professor B. Takano (University of Tokyo), who carried out the polythionate analyses. Reviews by Dr. Shinohara and Dr. Kusakabe improved the original manuscript.

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