Chemical characters of crater lakes in the Azores and Italy: the anomaly of Lake Albano

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(Received April 23, 1993; Accepted January 10, 1994)

Investigations have been carried out on crater lakes in areas of recent volcanism in the Azores and in Italy, with the aim of detecting possible evidence of residual anomalies associated with past volcanic activities; data from crater lakes of Cameroon have been considered for comparison. Among the physical-chemical characters taken into account, the increases of temperature, ammonium and dissolved carbon dioxide with depth are interpreted as providing information about the contribution of endogene fluids to the lake water budgets. The greater extent of such evidence at Lakes Monoun and Nyos (Cameroon) appears associated with the disasters that occurred there during the last decade; some similarities observed at Lake Albano (Italy) suggest a potential instability also for this crater lake.

INTRODUCTION

Crater lakes in active volcanic systems have been investigated with reference to changes occurring in water chemistry in response to different stages of activity, and interesting information is available about Ruapehu (Giggenbach, 1974), Kusatsu-Shirane (Ossaka *et al.*, 1980), Chichón (Casadevall *et al.*, 1984), Poàs (Casertano *et al.*, 1985), and Maly Semyachik (Fazlullin, pers. comm.). Much of the attention of scientists and public officials, however, has been recently captured by crater lakes not influenced by active volcanism; in fact, the events in Cameroon, at Lakes Monoun (Sigurdsson *et al.*, 1987) and Nyos (Sigvaldason, 1989), represent the consequences of a rather uncommon type of geologic hazard. Crater lakes appear thus to deserve serious attention as potential sources of disasters significantly affecting the populations in the surrounding areas.

Systematic investigations of water chemistry have been carried out at crater lakes in areas of recent volcanism in Italy and in the Azores; other results from Cameroon have been used for com-

parison. With reference to the data collected so far and considering the possibility that the actual chemical characters of crater lakes are influenced by residual thermal anomalies in the hosting volcanic systems, an effort has been made to verify whether and to what extent these anomalies can be revealed by simple observations.

Be this procedure sufficiently correct, monitoring a large number of crater lakes would become a viable program even where high-level technology is not available and a wealth of information could be easily collected. According to the intensity of thermal and chemical anomalies, possibly related to past volcanic activities, different levels of probability could be estimated for potentially hazardous events.

VOLCANOLOGICAL SETTINGS

Given the general aim of this investigation, main attention was paid to the location of lakes within volcanic systems, and the difference between craters representing the whole structure or pertaining to larger calderas is not supposed to

Fig. 1. Location of the crater lakes in the Azores.

Fig. 2. Location of the crater lakes in Italy.

affect to a significant extent the chemical characters under consideration.

Significant volcanic activity is reported for the Azores, crossed in a north-south direction by the axis of the Mid-Atlantic ridge (Fig. 1); besides the last surtseyan eruption of Capelinhos at Faial in 1957–58 (Machado *et al.*, 1962), strombolian activity with lava flows occurred in 1761 at Terceira, and four explosive eruptions are recorded for S. Miguel in 1563, 1638, 1640, and 1811 (Booth *et al.*, 1983). Fogo lake fills the summit depression of Agua de Pau volcano, about 3 km wide; its present morphology results from cratering, volcano-tectonic collapse, and landslides. Sete Cidades lake is located inside a polygenetic caldera, 5 km in diameter, produced during a long series of plinian events, the last probably occurred in 1444. Furnas lake occupies the summit of the easternmost active stratovolcano, truncated by a large polygenetic collapse caldera, about 6 km wide. A well documented historical eruption is reported in 1640; intense thermal activity is at present occurring inside the caldera.

With reference to Italian lakes (Fig. 2) Bolsena lake is a large volcano-tectonic depression, about 13 km in diameter, probably produced by a series of huge ignimbrite forming eruptions during the period 0.60–0.35 m.y. b.p. (Varekamp, 1980; Gillot *et al.*, 1991). The volcanic activity continued in the western Vulsini area probably up to 0.125 m.y. ago, where the well shaped polygenetic Latera caldera developed (Nappi *et al.*, 1991; Turbeville, 1993).

The activity of Vico volcano occurred from 0.40 to 0.09 m.y. b.p.; its summit appears as truncated by a polygenetic collapse caldera, about 8 km wide (Bertagnini and Sbrana, 1986), and half of the caldera floor is occupied by the lake, probably established after a giant ignimbritic eruption dated at about 0.15 m.y. (Locardi, 1965). Explosive paroxysmal eruption with subordinate effusive episodes characterized the Sabatini area during a period of 0.60 m.y., and the development of the volcano-tectonic depression of Bracciano lake followed the exhaustion of the eruptive activity about 40,000 years ago (De Rita, pers.

comm.). Martignano lake pertains to the same structure. The activity of Alban Hills volcanic complex occurred during the period 0.70–0.036 m.y. b.p. with hydromagmatic explosions from eccentric craters in its final phase; Nemi and Albano lakes are filling two of these craters (De Rita *et al.*, 1991). Phlegrean Fields are located inside a large caldera possibly produced during a giant ignimbrite eruption about 0.035 m.y. ago (Rosi *et al.*, 1983). The crater hosting Lake Averno is considered as a monogenetic tuff ring formed during the recent subaerial period; it is dated at about 3.800 y.b.p. The last eruptive event in the area occurred in 1538 with the build up of a 140 m high tuff cone.

SAMPLING AND ANALYTICAL PROCEDURES

Water sampling has been carried out along a vertical profile above the deepest point of lake bottom; the position of the boat was constantly checked by means of a portable GPS (Sony IPS-360). Samples from depth have been collected in closed containers. Temperature was measured *in situ*, pH at the surface, at the same time of the collection of samples for dissolved CO₂ determination, in 100 ml glass bottles containing 10 ml of a 1 M Na₂CO₃ solution. The CO₃²⁻ excess subsequent to the reaction: H₂O + CO₂ + CO₃²⁻ ⇒ 2HCO₃⁻ allows then the calculation of dissolved CO₂.

The analytical methods used are as follows. Anions and dissolved CO₂ ⇒ Automatic titration with a Titroprocessor Metrohm 636 equipped with ion selective electrodes. Cations and Boron ⇒ Ion-chromatography with a Dionex DX100. NH₄ ⇒ Potentiometric determination. Li ⇒ Atomic absorption spectrophotometry.

OBSERVATION DATA AND DISCUSSION

The analytical results of major components for the samples collected from crater lakes at the surface and at approximately the maximum depth are given in Table 1.

Our attention has been mainly focussed on an-

Table 1. Chemical composition of the crater lakes; values in ppm

Sample	Depth (m)	Temp. (°C)	pH	Na	K	Ca	Mg	HCO ₃ +CO ₃	SO ₄	Cl	CO ₂
Lake Fogo	0	11	8.46	10	1.2	0.6	0.6	13	2.0	8.2	—
Lake Furnas	0	13	7.34	18	6.2	3.0	1.8	51	3.3	18	116
Lake Sete Cid.	-10	13	7.10	18	6.6	3.4	1.9	27	3.4	17	21
	0	13	7.86	15	3.1	2.6	1.4	24	2.4	22	90
	-27	13	7.93	15	2.7	2.2	1.3	25	2.3	17	35
Lake Bolsena	0	24	8.76	35	46	27	15	268	19	30	58
	-140	8	8.25	41	45	24	15	270	20	30	21
Lake Vico	0	21	8.69	18	24	23	13	150	41	17	21
	-40	10	8.48	22	25	23	12	156	41	18	13
Lake Bracciano	0	28	8.87	41	40	34	12	289	28	43	8
	-162	11	7.62	40	39	37	12	269	32	43	75
Lake Martignano	0	8	7.53	29	11	22	11	154	9.0	37	41
	-50	7	8.04	28	11	22	15	150	10	37	35
Lake Albano	0	19	8.72	33	47	22	17	265	2.9	21	32
	-160	9	5.55	32	48	40	17	262	2.9	21	222
Lake Nemi	0	17	8.35	22	22	21	11	186	3.4	17	9
	-28	9	7.81	21	23	22	12	187	3.6	20	30
Lake Averno	0	25	8.62	644	67	13	13	335	217	725	36
	-39	18	7.17	655	75	34	16	684	136	669	68
Lake Wum	0	25*	8.10*	1.4	1.5	1.9	2.1	24	0.05	0.47	— ^a
	-100	22	n.d.	1.6	1.7	2.2	2.5	36	0.08	0.77	— ^a
Lake Nyos	0	30*	6.75*	3.5	2.3	6.7	9.0	108	0.10	0.20	450 ^a
	-200	23	n.d.	17	6.5	31	64	622	0.03	0.59	6120 ^{a*}
Lake Monoun	0	23	6.90**	11	3.0	4.3	4.2	57	0.10	0.39	18 ^a
	-95	23	5.90**	22	7.2	19	23	1660	0.15	2.6	2920 ^a

^aFrom Kusakabe *et al.* (1989).^{a*}The value for CO₂ refers to the depth of 130 m.^{*}From Barberi *et al.* (1989).^{**}From Sigurdsson *et al.* (1987).

ions and CO_2 distribution, which appear to provide the best information. Figure 3 allows us to observe, besides the minor contribution of sulfur species, a trend along a Cl-HCO_3 line, possibly resulting from varying extents of chloride or of carbon dioxide.

The contribution of marine spray to the chloride concentration can be important for the lakes located near coastlines (Fogo, Sete Cidades, Furnas, Averno), and CO_2 inputs can be inferred for the lakes whose representative points lie near the bicarbonate corner; further information, however, can be obtained from the data of Table 2.

The contribution of CO_2 to natural solutions gives rise to a series of reactions, producing HCO_3 or CO_3 depending on pH conditions; these latter species represent the stable forms, unless a continuous input of CO_2 takes place. Accordingly, the values of the ratio $\text{CO}_2/(\text{CO}_3 + \text{HCO}_3)$ can allow an estimation of the persisting importance of CO_2 contributions. The discrepancies with respect to the theoretical balance between pH and distribu-

tion of carbon species, observed in most of the samples investigated, appear to reconfirm a perturbed situation which does not allow the attainment of a physico-chemical equilibrium. Anomalous values of CO_2 input can be derived for Nyos,

Table 2. Values of the ratio $\text{CO}_2/\text{HCO}_3 + \text{CO}_3$ for the samples from crater lakes (see text)

Sample	$\text{CO}_2/\text{HCO}_3 + \text{CO}_3$	
	Surface	Maximum depth
Lake Furnas	2.3	0.78
Lake Sete Cidades	2.7	1.4
Lake Bolsena	0.21	0.078
Lake Vico	0.14	0.083
Lake Bracciano	0.028	0.28
Lake Martignano	0.27	0.23
Lake Albano	0.12	0.85
Lake Nemi	0.048	0.16
Lake Averno	0.11	0.10
Lake Nyos	4.2	13.6 ^a
Lake Monoun	0.31	1.8 ^a

^aFrom Kusakabe et al. (1989).

Fig. 3. Diagram $\text{HCO}_3\text{-Cl-SO}_4$ for the samples from the surface of crater lakes. Mo (Monoun), Ny (Nyos), W (Wum), SC (Sete Cidades), Fo (Fogo), Fu (Furnas), Bo (Bolsena), V (Vico), Ne (Nemi), Br (Bracciano), Ma (Martignano), Al (Albano), Av (Averno).

Monoun, Furnas, Sete Cidades, and Albano; at Furnas and Sete Cidades the main contribution appears to occur at or near the surface, while at Nyos, Monoun, and Albano, significant increases are observed at maximum depths.

The distributions of NH_4 , B, and Li in natural waters pertaining to volcanic systems appeared useful in investigating the contributions of different processes (Martini *et al.*, 1984). Ammonia gas, giving rise to NH_4 when dissolved in aqueous solutions, can migrate at relatively low temperatures; the migration of boron in natural environments is mainly associated to vapour phases, which require a significant extent of heat contribution; not negligible concentrations of lithium in natural solutions always derive from prolonged leaching of country rocks, enhanced by higher temperatures.

The ratios among the above mentioned components, accordingly, can be related to the prevailing processes operating in the areas, possibly associated to different extents of thermal anomalies.

According to this interpretation, the data reported in Table 3 and Fig. 4 can suggest a seepage of gases through substantially closed systems for Cameroon and the Azores, while thermal anomalies of greater extent appear to characterize most of the Italian lakes.

The significant differences in ammonium and dissolved carbon dioxide observed for samples collected at the surface or at maximum depth, however, seem especially to deserve further consideration. Natural contributions of ammonium to the environment derive largely from degradation of organic material, sometimes in association with

Table 3. Distribution of NH_4 , Li and B in the samples from crater lakes

Sample	Depth (m)	NH_4	B	Li
Lake Fogo	0	0.32	0.010	0.002
Lake Furnas	0	0.31	0.010	0.003
	-10	0.25	0.010	0.003
Lake Sete Cidades	0	0.29	0.010	0.001
	-27	0.38	0.010	0.002
Lake Bolsena	0	0.17	0.44	0.020
	-140	0.10	0.38	0.018
Lake Vico	0	0.18	0.22	0.020
	-40	0.31	0.22	0.020
Lake Bracciano	0	0.063	0.33	0.011
	-162	0.036	0.32	0.014
Lake Martignano	0	0.14	0.001	0.001
	-50	0.16	0.001	0.001
Lake Albano	0	0.014	0.55	0.001
	-160	0.31	0.22	0.001
Lake Nemi	0	0.27	0.29	0.001
	-28	0.56	0.29	0.001
Lake Averno	0	0.090	1.2	0.38
	-39	16	1.2	0.37
Lake Wum	0	0.85	0.080	— ^a
	-100	0.76	n.d.	n.d. ^b
Lake Nyos	0	2.5	0.044	— ^a
	-200	7.9	n.d.	n.d. ^b
Lake Monoun	0	0.1	n.d.	n.d. ^c
	-90	12	n.d.	n.d. ^c

^aFrom Barberi *et al.* (1989).

^bFrom Kusakabe *et al.* (1989).

^cFrom Sigurdsson *et al.* (1987).

Fig. 4. Diagram $\text{NH}_4\text{-Li-B}$ for the samples from the surface of crater lakes. Ny (Nyos), W (Wum), SC (Sete Cidades), Fo (Fogo), Fu (Furnas), Bo (Bolsena), V (Vico), Br (Bracciano), Ma (Martignano), Al (Albano), Ne (Nemi), Av (Averno).

important thermal anomalies; leakage of ammonium is in fact an effective indicator of geothermal processes. With reference to lake bottoms, the degradation can occur inside the lake or fluids derived from similar processes can be fed from outside.

Carbon dioxide can also be considered as the product of decay of organic matter, but significant increases in its concentrations with depth, without corresponding increases in ammonium, appear better justified by contributions of fluids from an external source. At Averno, where only ammonium anomalies are detected in the deep sample, a degradation of organic material occurring inside the lake appears as a sufficient explanation; at Monoun, Nyos, and Albano, some extent of fluid contribution from outside seems to fit the chemical composition better.

Figures 5, 6, and 7 show vertical profiles of temperature, pH, and dissolved CO_2 for the Italian lakes. The B and Li concentrations in these lakes appear as related to thermal anomalies, but the constant patterns for temperature values at

depth allows to rule out important thermal anomalies near the lake bottoms, as observed at Lakes Nyos and Monoun (Kusakabe and Sano, 1992). A similar homogeneity can be derived also for pH values and dissolved CO_2 , with the exception of Lake Albano.

In addition to chemical evidences, the morphology of crater lakes in areas of recent and quiescent volcanism can provide information about residual phenomena associated to past activities. A detailed investigation by means of Video Scan Sounder revealed the shapes of the ancient craters where the Italian lakes are hosted (Figs. 8–10).

Besides minor particulars, Lakes Bolsena, Vico, Bracciano, Martignano, Nemi, and Averno, appear as characterized by substantially flat bottoms, possibly produced by continuous sedimentary re-filling, while a funnel shape pertains to Lake Albano. A quiet sedimentation can be thus regarded as a normal stage for most of the lakes considered; at Albano, on the contrary, a “cleaning” by circulating fluids can be inferred.

Fig. 5. Bathymetric profile of temperatures for Italian lakes.

Fig. 6. Bathymetric profile of pH-values of Italian lakes.

Fig. 7. Bathymetric profiles of dissolved CO_2 for Italian lakes.

Fig. 8. Reconstruction of the shapes of Bolsena and Bracciano lakes.

Fig. 9. Reconstruction of the shapes of Martignano, Nemi, and Averno lakes.

Fig. 10. Reconstruction of the shapes of Albano and Vico lakes.

CONCLUSIONS

According to the data collected during this investigation, in comparison with observations carried out at Cameroonian crater lakes, the variations with depth of temperature, pH, and chemical composition provide useful information about the persistence of anomalies possibly connected to past activities of the volcanic systems. Among chemical components, carbon dioxide and ammonium seem to reflect the contribution of endogene fluids to a greater extent.

From these data, besides Lakes Monoun and Nyos for which convincing evidence is available, some kind of the above mentioned anomalies can be inferred for Lake Albano. The reconstruction of the shapes, carried out for the Italian lakes, appears again to differentiate Albano with respect to the other systems. These differences cannot allow a sufficient evidence of residual phenomena associated to past volcanic activity; information from historical records, however, seems to provide further hints about.

Titus Livius, whose "Ab Urbe Condita Libri CXLII" represent the most important source of Roman history during the first eight centuries, reports the following: "Many wonders happened ... one in particular caught people's attention; the rising level of the waters of Lake Albano, not because of rainfall or of any other natural reason ... the water flooded out of the lake ...". These events occurred in the year 364 of Roman calendar, corresponding to 390 b.c., cannot be interpreted in a simple way; some instability, however, appears to have characterized Lake Albano at that time and an emission of fluids at depth may have been responsible.

On the basis of the information about physico-chemical characters of crater lakes, it appears thus possible to distinguish areas for which residual influences of the volcanic systems can be hypothesized; some even minor degree of hazard because of potential instabilities can be estimated accordingly.

Acknowledgments—We thank Prof. V. H. Forjaz of Universidade dos Azores for the assistance in collect-

ing samples in the Azores. This work was financially supported by Gruppo Nazionale di Vulcanologia and C.N.R. Centro di Studio per la Minerogenesi e la Geochimica Applicata.

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