Chemistry of Crater Lake Waters Prior to the 1992 Eruptions of Crater Peak, Mount Spurr Volcano, Alaska

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ABSTRACT

Waters sampled from the shallow lake in the Crater Peak vent of Mount Spurr volcano during June of 1992 were much higher in SO₄ and lower in Cl than waters sampled at the same locality in August of 1970. The major change in water composition is an effect of the degassing of shallow magma into the volcanohydrothermal system prior to the June 27, 1992, eruption. Though the timing of the chemical change is unknown, it may have been concurrent with a change in the lake observed in early June of 1992. At that time the lake changed from clear, blue-green to turbid, battleship gray. Volcanic unrest was also accompanied by upwellings and bubbling in the lake prior to its disappearance owing to evaporation and (or) draining.

INTRODUCTION

A nearly circular lake, approximately 100 m long, developed in the bottom of the satellitic Crater Peak vent on the south flank of Mount Spurr at an unknown time following the eruption of July 9, 1953. Air photos taken in September 1952 show ice filling the crater (Motyka and Nye, 1993) 10 months prior to its first known historical eruption. Careful study of tephras from Mount Spurr volcano show that the Crater Peak vent has erupted 35 times in the past 6,000 years, including 15 times within the past 500 years (Riehle, 1985). The lake in Crater Peak was visited

and its water sampled by Bruce Reed and Marvin Lanphere during U.S. Geological Survey (USGS) mapping in the region during the Summer of 1970. Fumaroles at Crater Peak were sampled in 1982 and also visited in 1985, but in 1985 they were too diffuse to sample (Motyka and Nye, 1993). No further sampling of the lake water or fumaroles was done until 2 weeks prior to the June 27, 1992, eruption.

Thermal springs low on the west flanks of Mount Spurr volcano below Crater Peak were discovered and sampled in 1985 by Motyka and Nye (1993). Unfortunately, other priorities precluded sampling these springs during the 1991–92 period of unrest and eruption of the volcano. They were resampled on June 2–3, 1993 (R. Motyka, unpub. data, 1993).

OBSERVATIONS AND SAMPLING OF CRATER LAKE WATERS

1970 SAMPLING AND OBSERVATIONS

Reed and Lanphere visited the Crater Peak lake on August 9, 1970, and collected two water samples for analysis (table 1). They were not equipped to measure temperature or pH. Reed's field notes (unpub. data) state that "both samples from approximately 6 inches depth; 2.5 to 3.5 ft from shore; water is milky gray, too hot to hold hand in; had difficulty collecting the samples because of the temperature-could hold hand in for 1–2 seconds, very hot, water is being diluted by snow meltwater . . ." These observations suggest temperatures in the range 55 to 65°C.

1992 SAMPLING AND OBSERVATIONS

Observations and photographs from fixed-wing aircraft overflights in May and the first week of June 1992 recorded the lake color as a clear blue-green, as had been observed during previous years. On the observation flight of June 8, however, the lake was reported as being a gray color with several small areas of upwelling or bubbling, the most prominent of which

occurred on the northeast side of the lake. During this flight, the usual scattered, wispy fumarolic activity was noted, and the most vigorous fumarole was emitting a strong steam plume from a talus pile adjacent to the lake on the west side of the crater floor.

On June 11, a descent was made into the Crater Peak vent for general observations. The lake was a murky, battleship gray color. Continued small upwellings were observed; the measured temperature of the lake water (49°C) indicated that the upwellings were caused by rising noncondensible gases, rather than

Table 1. Chemical and isotopic analyses of Crater Peak (Mount Spurr) lake waters, Alaska.

	*CP92-1	*CP92-2		
Conditions				
T°C	49 2.5	49 2.5		
field pH	2.5	2.5		
lab pH	2.48	2.49		
conductance	3130	3120		
Chemical species, in milligrams per liter				
SiO ₂	263	312		
Al	41.8	50		
Fe	33.2	31.6		
Mn	2.95	2.94		
As	0.16	0.26		
H	7.21	8.18		
Ca	184	187		
Mg	40.5	41.3		
Na	56.0	55.1		
K	3.51	3.69		
Li	0.034	0.035		
HCO3	0	0		
SO ₄	1450	1490		
C1	53.2	54.5		
F΄	0.42	0.42		
В	3.36	3.18		
SO ₄ :Cl ratio				
SO ₄ :Cl	27.3	27.3		
Isotopic hydrogen and oxygen composition				
**dD	-116	-113.5		
**d180	-7.2	-7.2		
***70AR-201 ***70AR-202				
	(south edge)	(north edge)		
	(south edge)	(norm edge)		

	***70AR-201	* <u>**70AR-202</u>		
	(south edge)	(north edge)		
Conditions				
T°C	nd	nd		
field pH	nd	nd		
lab pH	2.17	2.30		
Chemical species, in milligrams per liter				
Ca	192	182		
Mg	71	70		
Na	75	75		
K	7.5	7.3		
HCO3	Ü	0		
SO ₄	442	315		
Cl	1180	1100		
B	<u>?</u> A,	24		
SO ₄ :Cl ratio				
SO4:Cl	0.4	0.3		

^{*}analyst: J. Michael Thompson, USGS, **Menlo Park**, CA **analyst: L.D. White, USGS, **Menlo** Park, CA; values relative to SMOW

boiling. Geyser activity, previously unreported, was observed in the talus pile adjacent to the north edge of the lake where the most vigorous fumarole in the Crater Peak vent had been active for at least several months. Motyka and Nye (1993) reported the most vigorous fumarolic activity as being on the east side of the lake in 1982 and on the north side in 1985. The fairly rapid migration of active fumarolic vents suggests redirection of fumarolic channels by shallow seismic disturbances; local self-sealing of fumarolic channels by hydrothermal alteration must have occurred to some extent but probably was not the controlling factor in this case.

On the June 11 trip, two whole-water samples were taken from the lake. One sample (CP-1) was taken adjacent to the shore and the other (CP-2) was taken about 0.5 m out from shore. The samples were brought back to Anchorage approximately 4 hours following collection. Half of each sample was filtered and acidified. Chemical and isotopic analyses (table 1) were made following the procedures of Thompson (1990).

The pale gray, very fine-grained filtrate was analyzed for mineral phases using X-ray diffraction. Phases identified were poorly crystalline sulfur, alunite, pyrite, and kaolinite. Following the mineral analysis, the same filtrate was chemically analyzed using **semi**quantitative emission spectrographic methods to determine minor-element concentrations (table 2).

Two weeks later, on the afternoon of June 26, geologists from the Alaska Division of Geological and Geophysical Surveys who were returning from fieldwork by helicopter passed by Crater Peak and observed that the shallow crater lake had "drained." Gray mud covered the crater floor, and a substantial steam cloud rose from the crater. Lake waters evaporated when heated by the rising magma in addition to lake water draining into the subsurface along fractures caused by seismic disturbances in the volcanic edifice.

ISOTOPES

Oxygen and deuterium isotopic analyses were obtained only on the 1992 lake water samples (table 1). Comparison of these data to the World Meteoric Water Line (Craig, 1961) and to data presented by Motyka and Nye (1993) for meteoric waters from Spurr and Augustine volcanoes show that the Crater Peak lake waters of June 8, 1992, fall well off the meteoric water line (fig. 1). In a hydrothermal system, only oxygen shifts to heavier values during water-rock interaction but deuterium remains stable (Craig, 1966). Evaporation shifts both δD and $\delta^{18}O$ to heavier values. Thus, isotopic values for the Crater Peak lake waters indicate that evaporation dominated any water-rock interaction. The isotope values for the Crater Peak lake waters could also be interpreted to be a

^{***}unpublished analyses of water samples collected by Marvin Lanphere and Bruce Reed (USGS) on 8/9/70 were provided by Bruce Reed; analyst: Roberta Barnes, USGS, Menlo Park, CA; nd, not determined

Table 2 Semiquantitative emission spectrographic chemical analysis of minor elements in filtrate from Crater Peak (Mount Spurr, Alaska) lake waters of June 11,1992.

[Analyst, E.A. Bailey; ppm, parts per million]

element, in weight percent				
Ca	1.			
Fe	5.			
Mg	1.			
Na	1.5			
P	0.2			
Ti	0.7			
element, in ppm				
Ag	1.5			
As	<200			
Au	<10			
В	50			
Ba	>5,000			
Be	<l< td=""></l<>			
Bi	<10			
Cd	~20			
Co	20			
Cr	70			
Cu	150			
Ga	30			
Ge	<10			
La	50			
Mn	300			
Mo	<5			
Nb	<20			
Ni	50			
Pb	20			
Sb	<100			
Sc	50			
Sn	20			
Sr	1000			
Th	<100			
V	200			
W	<20			
Y	10			
Zn	<200			
Zr	70			

result of meteoric (hydrothermal) waters mixing with magmatic waters, using the field of Sheppard and others (1969).

SOLID PHASES

Crater Peak vent andesitic rocks, in contact for years with warm, acidic lake waters of the 1970 composition (table 1) and vent fumaroles (Motyka and Nye, 1993), must have altered somewhat to common acid-sulfate products such as alunite, kaolinite, pyrite, Fe oxides and hydroxides, as well as residual noncrystalline to poorly crystalline silica phases. The fine-grained gray mud of the filtrate is similar in appearance and mineralogy to that in areas of characteristic acid-sulfate alteration, including mudpots of Yellowstone National Park (White and others, 1988), acid altered andesite at White Island, New Zealand (Giggenbach, 1987), and the gray muds in the Ruapehu volcano crater lake (Christenson and Wood, 1993). Upwelling disturbance of the lake waters in Crater

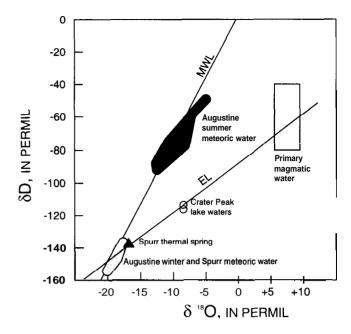


Figure 1. Plot of $\delta^{18}O$ versus 6D of waters from Mount Spurr and Augustine volcanoes compared to the World Meteoric Water Line (MWL) of Craig (1961) and an evaporation line (EL) for the Crater Peak (Mount Spurr) lake waters. Data for Augustine summer meteoric waters, Mount Spurr meteoric waters (including a cold stream, snowmelt), and Augustine winter meteoric waters, and the triangle representing the thermal spring on the lower south flank of Mount Spurr below Crater Peak from Motyka and Nye (1993). Data for primary magmatic waters from Sheppard and others (1969). Open circles, Crater Peak thermal lake waters of June 11, 1992.

Peak suspended the fine-grained alteration products in the water. Thus the poorly crystalline filtrate minerals (alunite, pyrite, kaolinite) identified by X-ray diffraction are residual rock alteration products, and the sulfur is from the oxidation of increased magmatic H_2S in the lake water. Although silica phases were not detected by X-ray diffraction and the amount of filtrate was too small to analyze for silica, some form of silica was probably present because the lake waters contained substantial dissolved silica.

DISCUSSION

The striking difference in chemical composition between the two sets of water samples is the high SO_4 :Cl ratio in samples taken in 1992 relative to those taken in 1970. The increased SO_4 in water sampled in June 1992 is most likely a result of increased sulfur species degassing from rising magma in the Crater Peak vent and disproportionation of magmatic SO_2 in the hydrothermal system and lake waters to form

aqueous H_2S and sulfate, which are much more stable in water than SO_2 (Giggenbach, 1987; Doukas and Gerlach, this volume). The Cl concentration in the crater lake water decreased in 1992 relative to 1970. The 1992 decrease in Cl was apparently simultaneous with increased sulfur degassing from the magma. Generally, the concentration of dissolved Cl in the volcano-hydrothermal system and (or) the overlying shallow lake water would be expected to increase as a result of magma degassing into water.

The relevant question may be why Cl was so high in 1970 rather than why Cl was so low in 1992. One possibility is that the subsurface hydrothermal system was not well developed in 1970 following the 1953 eruption, and so Cl from degassing magma could reach the surface waters, although the large amount of precipitation in the area should have reestablished the hydrothermal system very quickly. The relatively high concentration of B in the 1970 lake waters supports the hypothesis of a well-developed hydrothermal system at that time. High Mg concentrations of the lake waters in both years suggest substantial water-rock interaction between the acidic lake water and the andesitic host rock of the volcanic edifice. Perhaps Cl was more concentrated in the August 1970 lake waters because of evaporation of thermal water (where Cl remained dissolved) accompanied by the precipitation of sulfate as mineral phases, thus being removed from the lake water.

The volcano-hydrothermal system within the south flank of Mount Spurr volcano and beneath the Crater Peak vent was undoubtedly disturbed by the intrusion of magma leading to the June 27, 1992, eruption. As the magma began its ascent, the water of the hydrothermal system was further heated and boiling increased; these processes released H₂O, O₂, and H₂S, which condensed in the lake and surface waters. Accordingly, the lake waters sampled 16 days prior to eruption in 1992, are probably a mixture of pre-existing lake, magmatic, hydrothermal, and meteoric waters as well as some component of dissolved magmatic gases including sulfur species, Cl, and F. The volcano-hydrothermal system has since been severely disrupted by the three 1992 eruptions and the noneruptive intrusions in late 1992 (Eichelberger and others, this volume).

The changes in character of the lake in the Crater Peak vent prior to the June 27, 1992, eruption are probably a result of major disturbances within the shallow part of the volcano. Similar changes were reported in 1985 at Ruapehu volcano, New Zealand (Scott, 1987; Christenson and Wood, 1993) during heating episodes, some of which resulted in eruption. Crater lake disturbances such as color change and upwellings are frequently associated with increased heating by rising magma.

The fact that ice occupied the Crater Peak vent during September 1952 prior to the July 1953 eruption has interesting implications for monitoring Mount Spurr volcano. The Crater Peak vent has a frequent eruptive pattern. Riehle (1985) has documented 16 eruptions during the past 500 years, and this is a minimum of events because small eruptions that left no tephra records could also have occurred. Observations on the status of the ice in the crater or the development of a lake prior to the 1953 eruption are not known to exist. The development and maintenance of a warm crater lake in the vent between the 1953 and 1992 eruptions suggests that the volcano did not return to the level of inactivity that existed prior to the 1953 eruption, which was cool enough to permit ice to form in the crater. The presence or absence of ice in the crater and the characteristics and chemistry of any crater lake are important indicators of the future status of unrest. Sampling of flank thermal springs during periods of unrest and eruptions might indicate how well they are connected to the hydrothermal system near the vent.

CONCLUSIONS

The presence of a warm lake in the Crater Peak vent between its 1953 and 1992 eruptions indicates that the volcano had not returned to its pre-1953 state of inactivity when conditions were cold enough that ice occupied the crater only 10 months prior to eruption. Variations in crater lake appearance (color and turbidity) and chemical composition, especially the SO₄:Cl ratio, can be an indicator of volcanic unrest. Such variations may signal the intrusion of new magma. At Crater Peak, the lake disturbances could indicate imminent potential for magmatic or phreatic eruption. Although sampling of the lake waters in the crater may be useful, safety factors often preclude it.

REFERENCES CITED

Christenson, B.W., and Wood, C.P., 1993, Evolution of a vent-hosted hydrothermal system beneath Ruapehu Crater Lake, New Zealand: Bulletin of Volcanology, v. 55, p. 547–565.

Craig, H., 1961, Isotopic variations in meteoric waters: Science, v. 133, p. 1702–1703.

Craig, H., 1966, Isotopic composition and origin of the Red Sea and Salton Sea geothermal brines: Science, v. 154, p. 1544–1548.

Giggenbach, W.F., 1987, Redox processes governing the chemistry of fumarolic gas discharges from White Island, New Zealand: Applied Geochemistry, v. 2, p. 143–161.

Motyka, R.J., and Nye, C.J., 1993, Fumarolic gas chemistry (1982) and thermal spring water chemistry, Crater Peak (1985), Mount Spurr, Alaska, in Solie, D.N., and Tannian, F., eds., Short Notes on Alaskan Geology 1993: Alaska Department

- of Natural Resources, Division of Geological and Geophysical Surveys Professional Report 113, p. 31-40.
- Riehle, J.R., 1985, A reconnaissance of the major Holocene tephra deposits in the upper Cook Inlet region, Alaska: Journal of Volcanology and Geothermal Research, v. 26, p. 37–74.
- Scott, B.J., 1987, Ruapehu observations and inspections, Volcano and Geothermal Observations 1985 & 1986: New Zealand Volcanological Record No. 15, compiled by New Zealand Geological Survey, DSIR, p. 34.
- Sheppard, S.M.F., Nielsen, R.L., and Taylor, H.P., Jr., 1969, Oxygen

- and hydrogen isotope ratios of clay minerals from porphyry copper deposits: Economic Geology, v. 64, p. 755–777.
- Thompson, J.M., 1990, Chemical data from thermal and nonthermal springs in the vicinity of Mount St. Helens National Monument: U.S. Geological Survey Open-File Report 90-690A, 16 p.
- White, D.E., Hutchinson, R.A., and **Keith, T.E.C.**, **1988, The** geology and remarkable thermal activity of Noms Geyser Basin, Yellowstone National Park: U.S. Geological Survey Professional Paper 1456, 84 p.