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Analytical laboratory comparison of major and minor constituents in an active crater lake

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Abstract

The crater lake water from Maly Semiachik volcano in Kamchatka was used for the international analytical laboratory comparison of major and minor elements, and hydrogen, sulfur, and oxygen isotope data. Eight institutions participated in this program, giving analytical results of 9 major and 20 minor elements mainly by using ICP-AES for cations and IC for anions. Among the major elements, Na, Mg and Si showed coefficients of variation (CV) of 10% or more, whereas B, Al, Fe, Mn had coefficients less than 7%. The CV% of the minor elements Co, Cu, P, Cr, Pb was much greater (>30%) while the V analyses agreed well (<10%). Ti, Sr, Zn, and F were intermediate (between 10 and 20 CV%). The errors observed for these constituents are inherent to the methods applied: large dilutions and spectrometric interferences. Even the major anions such as Cl (>2000 ppm) and SO_4 (>5000 ppm) gave considerable ranges (5.1 and 8.8 CV%, respectively) as did the obtained pH values (22 CV%). The measured δ^{18}O of the water samples and δ^{34}S of sulfate are in excellent agreement but the δD values had CV% of 8. Technical recommendations are presented to improve the analytical results for these elements with significant deviations from the mean values. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: analytical intercalibration; crater lake water; atomic emission spectrometry; ion chromatography

1. Introduction

Detailed and reliable analytical results of major and minor chemical species are indispensable for understanding the physical and chemical dynamics of active crater lakes or their underlying environments, especially with respect to mineral transport. Saturation or undersaturation of a given mineral in these extreme aquatic environments has been assessed in terms of the saturation index (Rowe et al., 1992; Christenson and Wood, 1993; Delmelle and Bernard, 1994) computed with a variety of computer software packages developed for the chemical modeling of natural waters (e.g. Bethke, 1996). Another important aim of obtaining reliable analytical data of the active crater lakes is to construct an effective geochemical framework for the monitoring of hazardous crater lakes, as carried out on Tangiwai and Nyos (O'Shea, 1954; Beardsley, 1986). Without precise chemical data, no detailed discussion on the stability of gas-evolving lakes would be possible.

Thus we proposed to the Commission on Volcanic Lakes (CVL) of the International Association of Volcanology and Chemistry of the Earth's Interior (IAVCEI) that the sample preparation and performance of each institution's analytical *weapons* should be checked using a typical crater lake water as a reference material. The crater lake water from Maly Semiachik volcano in Kamchatka, sampled

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during the Field Workshop and the Third Meeting of the CVL in August 1995, was selected as the reference material, mainly because the chemical composition of this lake was not widely known. Eight institutions participated in this analytical cross-check program: The University of Tokyo, Japan; Brussels Free University, Belgium; Institute of Volcanology, Russia; Institute of Geological and Nuclear Sciences, New Zealand; Institute for Studies of the Earth's Interior, Japan; Kusatsu-Shirane Observatory, Japan; Geological Survey, USA; Wesleyan University, USA.

In this paper, we discuss the analytical precision of acid crater lake waters, and provide a basis for identifying the deficiencies and possible remedies.

2. Maly Semiachik volcano

Maly Semiachik volcano occurs in the central part of the eastern volcanic belt of Kamchatka (54°07′N, 159°53′E). This largely basaltic stratovolcano contains a strongly acidic crater lake at the southmost summit cone, Troitsky Crater (Selyangin and Braitseva, 1991). The circular lake was 550 m in diameter, 117 m in depth in 1993 and the elevation of the lake surface was 1170 m above mean sea level (data from the 1993 observations). Only one historic eruption has been recorded (1805), which may be doubtful because of its remote location in Kamchatka. Scientific observation of this volcano started in 1946 and has been conducted rather sporadically since then. A chemical study of the lake water in 1965 showed that the water was very acidic (pH 0.7; total dissolved solid 32 g/l) and the water temperature was 30–34°C. Increased volcanic activity was observed during 1965–1973, but it has been decreasing since then (Gavrilenko et al., 1993).

3. Sample preparation for the reference material

Twenty liters of Maly Semiachik crater lake water were collected by Fazlullin and Takano on 19 August 1992 at the upwelling point of the lake surface using a rubber boat. Another 20 l of the lake water was sampled by them at the same point of the lake surface during the workshop on 22 August 1995. In order to avoid contamination, filtration was neither carried out in the field nor in the laboratory. Aliquots of the 1992 sample (500 ml each) were taken in Takano's laboratory into polyethylene bottles which were carefully washed with the 0.1 M solution of ultrapure nitric acid (Cica–Merck), followed by rinsing with ultrapure water purified from a MilliQ® system and then rinsed with a small portion of the sample water. The 1995 sample was subdivided in the field into polyethylene bottles cleaned by the same procedure as described above, and these were directly distributed among the contributors that participated in the workshop or were shipped with the 1992 sample to the other contributors.

4. Analytical methods

The analytical methods applied by the various contributors were: atomic absorption spectrometry (flame: F-AAS or graphite furnace: GF-AAS) for alkali and trace metals; atomic emission spectrometry (Inductively Coupled Plasma Spectroscopy: ICP-AES or Direct Coupled Plasma spectroscopy: DCP-AES) for alkali and major/minor metals; mass spectrometry (ICP-MS) for trace metals; ion chromatography (IC) for most anions; high performance liquid chromatography (HPLC) for polythionates; colorimetry (C) for boron and sulfate; and titrimetry (T) for chloride. The last two methods has been applied in one institution to monitor their analytical consistency for more than 30 years.

5. Results and evaluation

The analytical results of the 1995 and 1992 Maly Semiachik waters reported by these institutions are listed together with the analytical methods in Tables 1 and 2. The data are plotted in Figs. 1 and 2, which are similar to those, used by Giggenback and Matsuo (1991) for volcanic gas intercalibration at Usu, Vulcano and White Island. We used the mean value of each composition instead of the median value to construct these figures. This kind of analytical cross checks should use as many different analytical methods as possible to illustrate their advantages or disadvantages (Kiba et al., 1977). Most geochemical institutions are equipped with analytical instruments that can provide as many analytical data as possible in a single run. ICP-AES or DCP-AES and IC are

Table 1
Analytical results of the Maly Semiachik water sampled in 1995 (mg/l)

Institution[a]	IGNS	Inst. Volcan.	U. Tokyo	B. F. U.	USGS	Tokyo I. Tech.	Wesleyan U.	Okayama U.
PH	1.22	0.74		1.05	1.4	1.23		
Temp						10.1		
Na	104 C[b]	82 C	102 D	76.5 A	100 A	93.2 A	107	
K	24.6 C	22.2 C	22.1 D	24 A	21.5 A	23.9 A	24	
Mg	104 A	97.3 L	93 D	94 E	107 D	113 D	119	
Ca	306 C	280.6 L	305 D	274 E	312 D	312 D	334	
Sr			1.25 D	0.97 E	1.3 D		1.5	
Ba			0.029 I	0.02 E	< 0.16 D			
B	6.8 G		6.9 D	7.3 E	8.2 D	7.2 D	7.4	
Al	380 A	351 G	369 D	369 E	367 D	387 D	415	
Ti			2 D	2.1 E	1.92 D		2.19	
Si	63.6 A		41 D	32.4 E	68.3 D	66.4 D		
Fe	310 A	279.2 G	279 D	272 E	288 D	296 D	308	
Co			0.078 I		0.2 D		< 100	
Ni			0.091 I				0.13	
Cr			0.019 I				0.178	
Mn			5.6 D	5.4 E	5.8 D	5.96 D	6.19	
Cu			0.066 I		0.063 B		0.117	
Zn			0.48 I		0.48 D		0.647	
Cd			0.018 I		< 89 D			
V			1.16 D		1.2 D		1.29	
Pb			0.020 I		0.025 B		< 300	
P			8.73 D				3.73	
As							< 300	
Sc							0.173	
Y							0.114	
Zr							< 100	
F		123.8 K		86 F	133 ± 6	105 F		
Cl	2096 H	2123 M	1880 F	2044 F	2050 ± 50	1860 F		
SO_4	5580 G	4803 N	6050 F	6085 F	5900 ± 100	5650 F		
S_4O_6			< 0.2 J					
S_5O_6			< 0.1 J					
S_6O_6			< 0.1 J					
δD (H_2O)						-73	-77	-79.5
δO (H_2O)						-8.2	-8.3	-8.17
δO (SO_4)								10.2
δS (SO_4)					13.6 ± 0.2			13.4

[a] IGNS: Institute of Geological and Nuclear Sciences, New Zealand; I. Volcanol.: Institute of Volcanology, Russia; U. Tokyo: The University of Tokyo, Japan; B. F. U.: Brussels Free University, Belgium; Tokyo I. Tech.: Tokyo Institute of Technology, Japan; USGS: The United States Geological Survey; Wesleyan U.: Wesleyan University, USA; Okayama U.: Okayama University, Japan.

[b] Alphabetical in each cell represents the method used to determine each element: A, flame atomic absorption spectrometry; B, graphite furnace atomic absorption spectrometry; C, flame atomic emission spectrometry; D, inductively coupled plusma atomic emission spectrometry; E, direct coupled plusma spectrometry; F, Ion chromatography; G, colorimetry; H, potentiometric titration; I, inductively coupled plusma mass spectrometry; J, high performance liquid chromatography; K, ion-selective electrode; L, EDTA titration; M, argentmetry; and N, lead nitrate titration.

therefore the most popular time-saving techniques for the determination of major/trace elements, and anions, respectively. The reported major- and trace-element data should have therefore similar precision. The comparison of the reported data is thus rather straightforward, but it is difficult to detect systematic errors inherent to these techniques. Further, the number of reported data for each element are critical

Table 2
Analytical results of Maly Semiachik water sampled in 1992 (mg/l)

Institution[a]	IGNS	U. Tokyo	B.F.U.	Tokyo I. Tech.	Wesleyan U.	Okayama U.
pH	0.96		1.01	1.02		
Temp						
Na	168 C[b]	166 D	120 A	161 A	169	
K		37 D	35 A	36.2 A	38	
Mg	166 C	155 D	159 E	175 D	186	
Ca	450 C	457 D	430 E	453 D	470	
Sr		2.1 D, I			2.31	
Ba		0.023 I	0.02 E			
B	11.7 G	11.6 D	11.9 E	12.4 D	12.3	
Al	590 A	598 D	555 E	600 D	639	
Ti		3 D	2.6 E		3.27	
Si	105 A	53.2 D	113.6 E	101 D		
Fe	440 A	440 D	447 E	453 D	471	
Co		0.114 I			0.243	
Ni		0.138 I			< 100	
Cr		0.033 I			0.257	
Mn		8.9 D	8 E	9.41 D	9.66	
Cu		0.080 I			0.17	
Ga		0.12 I				
As		0.026 I			< 300	
Rb		0.064 I				
Mo		0.001 I				
Ag		0.001 I				
Cd		0.033 I				
In		0.042 I				
Cs		0.001 I				
Sc					0.218	
Y					0.164	
Zr					0.161	
Sm		0.022 I				
Eu		0.008 I				
Hg		0.008 I				
Tl		0.081 I				
Pb		0.047 I			< 300	
Bi		0.012 I				
Zn		0.65 I			0.691	
V		2.0 I			2.03	
P		14.3 D			6.17	
F			179 F	188 F		
Cl	3547 H	3510 F	3262 F	3370 F		
SO_4	10200 G	9470 F	9373 F	9450 F		
S_4O_6		223 J				
S_5O_6		296 J				
S_6O_6		154 J				
δD (H_2O)				−61	−68	−71.4
δO (H_2O)				−5.8	−5.9	−5.85

[a] Institutions as in Table 1.

[b] Alphabetical in each cell represents the method used to determine each element: A, flame atomic absorption spectrometry; B, graphite furnace atomic absorption spectrometry; C, flame atomic emission spectrometry; D, inductively coupled plusma atomic emission spectrometry; E, direct coupled plusma spectrometry; F, Ion chromatography; G, colorimetry; H, potentiometric titration; I, inductively coupled plusma mass spectrometry; and J, high performance liquid chromatography.

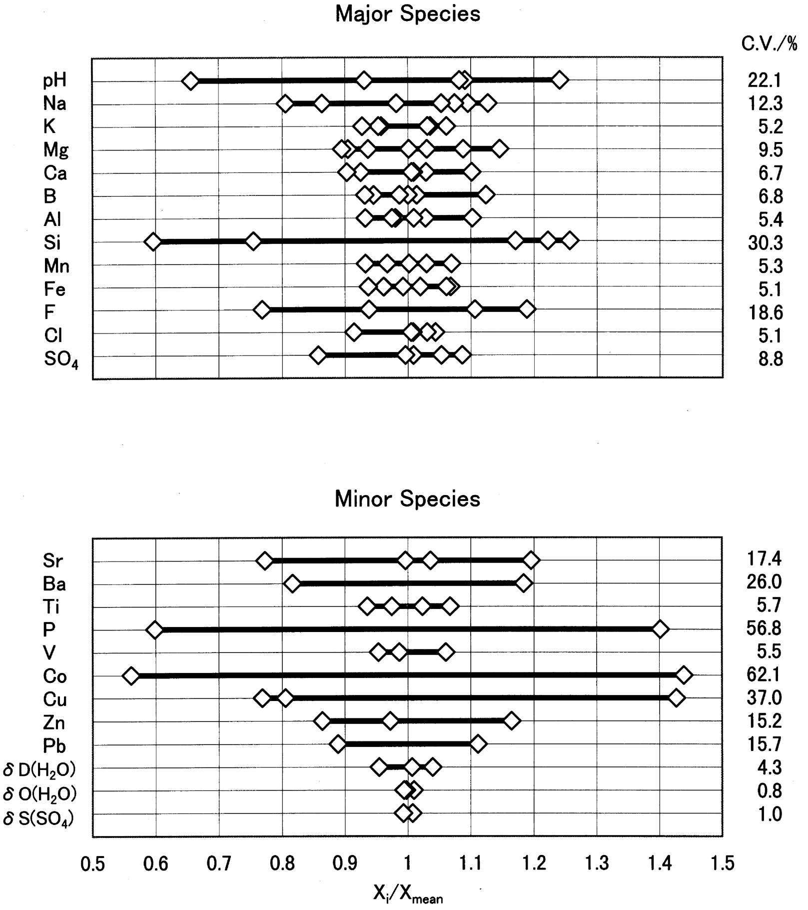

Fig. 1. Coefficients of variation in the analytical data for the major and minor species (mg/l) of the Maly Semiachik crater lake water (Kamchatska) sampled in 1995. X_i/X_{mean} represents the concentration of the *i*th species divided by its average concentration.

in order to determine the spread of these data. In this cross check study at most eight analytical data for one element have been obtained. Although this limits our discussion on the quality of the data, we can extract several analytical problems from the data discussed in the following groups of elements.

5.1. Sodium, potassium, magnesium, and calcium

Analytical data of these elements reported by four to seven institutions showed considerable scatter. Major elements with concentrations in excess of 100 ppm should be relatively easy to be determined by the spectroscopic methods described above, because the concentration ranges of the elements to be determined are far beyond their formal detection limits. However, Na showed unexpectedly large coefficients of variation (CV%) >10%, and those of Mg are >5%. Errors in the spectrometry are usually less than 5% for these elements at the concentration ranges of the lake waters. Not only magnesium but also other metallic elements can suffer serious interferences from Al, Si and Ti, because these elements may form refractory minerals in the various flames used for spectroscopic emission or absorption. Therefore, the standard solutions of elements for ICP-AES or AAS analysis are prepared without Si. The Si standard solution is in some cases mixed with As, B, Cr, Ag and P.

As far as we know, no special attention except for adding 1000 ppm of Li as $LiNO_3$ or Cs as CsCl was given to avoid this chemical interferences. A large amount of these alkali elements are effective in

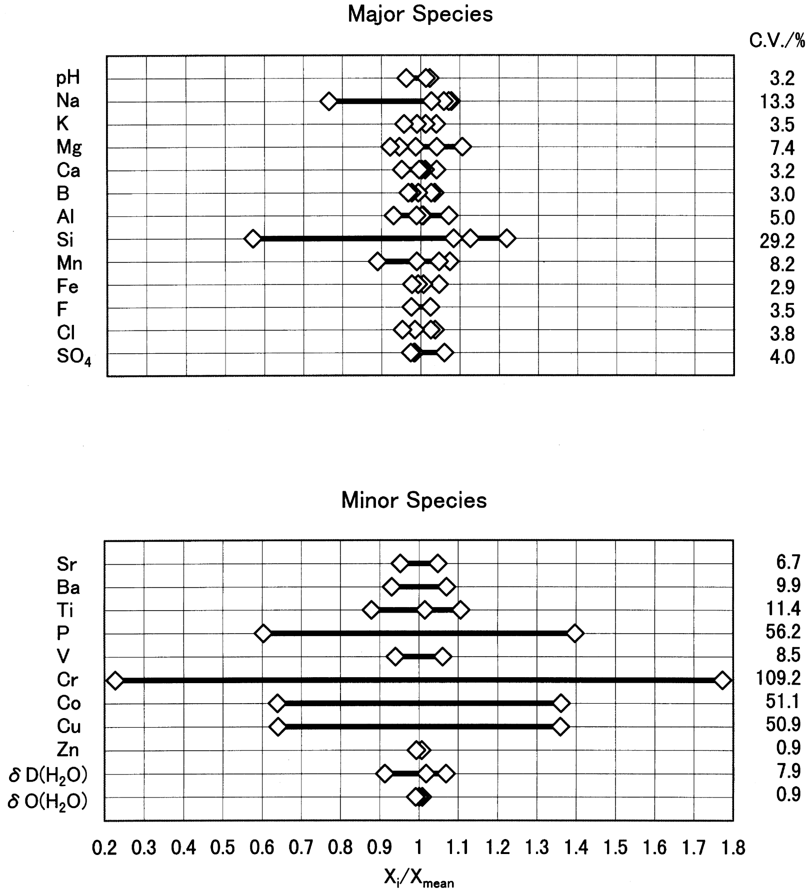

Fig. 2. Coefficients of variation in the analytical data for the major and minor species (mg/l) of the Maly Semiachik crater lake water (Kamchatka) sampled in 1992. X_i/X_{mean} represents the concentration of the *i*th species divided by its average concentration.

suppressing the ionization of Na and K in the air–acetylene flame of AAS as well as to avoid the formation of refractory substances such as $CaSO_4$. Such an analyte with a lot of Li or Cs has a large salinity which may affect the viscosity of the solution (Greenfield et al., 1976), when its acidity is not adjusted to that of the standard solution. This may bring a considerable decrease in both the absorption and emission intensities of the alkali and the alkaline earth elements. Two of the seven institutions gave relatively small Na values. One of them used $LaCl_3$ for suppressing the chemical interference in AAS, but this substance is questionable for suppressing ionization of Na, because La has a higher ionization potential. All institutions, however, are in an excellent agreement with each other in the K data. Sodium and Ca (CV 6.7%) are usually affected more by the acidity of solutions than K (Tada and Mizuike, 1971). Therefore, we speculate that the large disagreement in the Na data is because of the difference in acidity between the analytes and the standard solution, although information on the sample and standard solution treatment is quite limited.

5.2. Boron, aluminum, silica, iron, and manganese

These elements are in the concentration range of 5–400 ppm. Boron, Fe and Mn are the elements that are easily determined by AAS or AES. As expected, B, Fe and Mn data showed an excellent agreement between the laboratories. Aluminum and Si are usually major elements in acid crater lake waters, and tend to form refractory minerals in the low-temperature air–C_2H_2 flame of an AAS. A high-temperature (N_2O)—C_2H_2 flame is commonly used for the determination of Al and Si by AAS and the high temperature of the ICP-torch also accelerates the dissociation of refractory minerals in the plasma. As a result, the Al data are in good agreement with each other.

The Si data show considerable scatter, however, exhibiting a CV $>10\%$. Most of the study participants applied a similar procedure for the Si determination, and the disagreement must have come from different sources. As far as we know, one of the two participants that gave low Si levels filtered the subdivided crater lake water in situ with 0.45 μm membranes, followed by dilution with MilliQ® water; and the other filtered it in the laboratory before the analysis. If suspended silica existed in the water, it would produce the higher analytical result.

5.3. Sulfate, fluoride and chloride

The main anionic components in the Maly Semiachik crater lake water are chloride and sulfate which are almost equimolar in 1992 and 1995, although their concentrations decreased drastically from 0.1 to 0.06 mM. In addition, polythionate concentrations decreased more drastically from 673 ppm to less than their detection limits. The CV of Cl and SO_4 are 5.1 and 8.8%, respectively, and are significantly larger than expected ($\sim 2\%$) for anions at >1000 ppm level. Both anions were mainly determined by IC except for the data from an institution where Cl was determined by potentiometric titration and SO_4 by colorimetry using barium chromate. The latter two methods are much more appropriate in principle than IC to obtain more significant figures for Cl, because IC cannot avoid errors of $\sim 5\%$ or more as well as errors stemming from the great dilution factors. However, the titration is time-consuming in order to avoid significant interferences from coexisting ions (Br, I, H_2S, polythionates) in the lake water. Accordingly, almost all institutions use IC for the Cl and SO_4 determinations, resulting in the analytical errors $>5\%$ probably on account of high dilution. The IC has a great advantage over the classical methods mentioned above: it is almost free from interference from other halides and oxyanions as well as from the degradation of polythionates which releases sulfate and elemental sulfur in classical chemical treatments (heating, neutralization, argentmetry, etc.) of the sample solution (see Sections 5.4 and 5.5).

As for F, the advantage of IC is considerably lost, because of the so-called “water dip” which typically appears at the F-peak front when an $NaHCO_3$–Na_2CO_3 solution is used as an eluent. In order to reduce this water dip as much as possible, one of the contributor who gave the lowest F value diluted both the sample waters and the standard with the eluent. This procedure, however, raises the pH of the test solution that may accelerate the formation of Al, Si, Ti, Fe–fluoride complexes (O’Donnell, 1973; Delmelle, 1995). The IC only determine the free fluoride ion; thus unless any procedures such as separation of F by distillation (Horton, 1961), or addition of cyclohexanediamine tetraacetate (CyDTA, Orion Research, 1982) or methanol solution of 8-oxyquinolinol (Yokogawa Analytical Systems, 1995) for leaving all fluoride free are applied, a smaller value will be obtained. In addition, a part of the F forms tetrafluoroborate BF_4^-, which is rather stable in acid solutions. Onishi (1969) reported that BF_4^- in an acidic (pH 1.1) hot spring water is stable for at least one year at room temperature. According to the same authors, 22% of total F and 90% of total B at a high temperature (200°C), very acidic, fumarolic condensate forms BF_4^-. If these data are applied to the Maly Semiachik water, the contribution of BF_4^- to the analytical F results could not be ignored. Unfortunately no convenient method other than the distillation method has been found in the literature for liberating F from BF_4^-. Therefore, for the determination of F in volcanic crater lake water, BF_4^- should be independently determined by a method outlined by Pasztor and Bode (1960), or after separation by distillation of F. As far as we know, no such analytical procedures were applied for the Maly Semiachik waters among the participants of this program. Consequently it is difficult to say which F values in Tables 1 and 2 are close to the *true* value.

5.4. Minor elements

The concentration levels of the minor elements Co, Cu and Pb in the lake water are <0.1 ppm and are less than 300 times the detection limits for these elements by ICP-AES (0.4, 0.3 and 10 ppb, respectively; Winge et al., 1979; Boumans, 1981). Errors in their determination are probably substantial when the lake water has to be diluted to at most 100 times to avoid chemical interferences. The same is true for Ni, Cr, Cd and probably Ba, although their data are given by only one or two institutions. In order to monitor instability in instrumental and/or light-emitting conditions, yttrium is often used as an internal standard (American Society for Testing Materials, 1971). At least one institution applied this technique to this program. Because no other institutions reported using this technique, however, we cannot assess how it may improve the analytical results. According to Tao et al. (1983), Ca (~300 ppm), Fe (~300 ppm) and Mg (~100 ppm) in the lake water may give large spectroscopic interference to these minor elements up to as much as 75% of the determined values (Ba 7, Co 75, Cr 9.5, Cu 15, Cd 55, Ni 72, P 20%). Under the same conditions, Pb may suffer serious interferences from Fe and Mg, resulting in 6.5 times greater than a true value. Thus, as for Cr, Ni, Pb and P, three institutions presented the analytical data. The concentrations of Co, Ni, Cr and Cu in the 1992 sample determined by ICP-MS are systematically lower than those determined by ICP-AES. This fact suggests that the ICP-AES values of these elements are more or less influenced by the main constituents such as Fe, Ca, Mg, Si or sulfate which give numerous overlapping spectral lines. Phosphorus typically shows a systematic discrepancy between ICP-AES and ICP-MS: the concentration ratios obtained by the two institutions for the 1992 and 1995 waters are almost equal (0.61, 0.60, cf. Tables 1 and 2). In addition, the elemental sulfur that may be formed through the degradation of polythionates:

$$S_xO_6^{2-} + 0.5O_2 + H_2O = (x-2)S + 2SO_4^{2-} + 2H^+ \qquad (1)$$

has active surface sites and adsorbs heavy metal ions on its surface, resulting in gradual decrease in their concentrations (Ichikuni, personal communication). In order to avoid the trace metal adsorption, an aliquot of the trace metal determination should be treated with an oxidizing reagent described in Section 5.5.

Considering the polymetallic composition of the Maly Semiachik crater lake water, it remains difficult to carefully characterize the mutual spectroscopic interferences of these trace elements in the sample water. In order to minimize this problem, partial separation of the metallic ions using a chelating resin like Chelex® 100 may be effective (Uchida et al., 1977). Recent development in ICP-MS may give us a more simplified procedure for the polymetallic trace metal determination. Although ICP-MS has its own intrinsic problems such as isobaric interferences, it may provide more reliable analytical results than ICP-AES, because the former shows simpler spectrograms and has generally a higher sensitivity resulting in a reduced matrix effect after dilution. These analytical advantages in analysis lead to the successful analyses of thermal waters from France (Veldeman et al., 1991) and of semiconductor-grade sulfuric acid (Walsh et al., 1991). Unfortunately only one participant gave the data by ICP-MS; therefore we could not compare in detail the results obtained by both methods. Recent technical improvements in ICP-MS effectively suppress isobaric interferences due to the formation of molecular ions. Trace element analysis of natural waters will shift gradually toward ICP-MS in the near future. Consequently, these trace elements Co, Cr, Cu, Ni, Pb, Zn have only one analytically significant figure, while V, Mn, Ti and B may have two or more significant figures, because they have relatively lower detection limits and higher concentrations in the lake water.

5.5. Polythionates

One of the difficult problems encountered in the analysis of active crater lake waters is the determination of polythionates, which often occur at levels >1000 ppm, and in some cases >4000 ppm (e.g. Kawah Putih, Indonesia, Takano, 1987; Selyangin and Braitseva, 1991; Sriwana et al., 2000 – this volume). Thus polythionates are one of the major anions in some active crater lakes, and must be taken into consideration in the analysis. Takano (1987) and Takano and Watanuki (1988) presented a liquid chromatographical method for the determination of these anions and an indirect method was reported by Webster (1989). The 1995 lake water did not contain polythionates, but when high levels of polythionates occur, the interference due to the elemental sulfur formed from its degradation (Eq.

(1)) can not be ignored in both major and minor element determinations. Also high polythionate levels in crater lake waters, if not determined, cause a serious charge imbalance between cations and anions, resulting in an unexpected error in geochemical computer modelling of the crater lake waters. Sriwana et al. (2000 – this volume) initially applied the SOLVEQ computercode to the raw analytical data from Kawah Putih, which does not take polythionates into consideration. The saturation and speciation results were later based on the measured SO_4^{2-} data instead of total S data. The SOLVEQ chemical modeling program should be modified to incorporate the polythionate species. From a reference material point of view, the crater lake water selected for intercalibration should be analyzed for polythionates first, and then must be oxidized using an oxidizing reagent such as hydrogen peroxide (Makhija and Hitchen, 1979) before going on to major and minor elements analysis. For the determination of polythionates, crater lake waters should be filtered with 0.45 μm membrane filter to remove sulfur-oxidizing bacteria which use polythionates as a nutrient (Takano et al., 1997).

5.6. pH

A large discrepancy in pH has been observed for the 1995 water, ranging from 0.74 to 1.4. The pH measured in situ was 1.2, equivalent to the averaged value. No detailed information about the calibration of the pH meters that the participants used was given. We suspect that this large distribution of pH values may come from the pH-buffers used for the calibration: a combination of pH 4.01 phthalic acid–pH 6.86 phosphate buffer or of pH 1.0 HCl + KCl–pH 4.01 phthalate buffer. The former may give a lower pH value than the latter and the latter is recommended. In principle the accurate determination of pH value is rather difficult, especially in the case of $pH < 1$. Values of pH have been defined as those determined with a glass electrode using the reference buffer solutions of which pH values are given by the official institution in each country. The pH values of these buffers are from 3.5 to 9.2 at 25°C (USA). Usually the pH of a test solution should be measured using at least two pH calibration buffers of which pHs are closer but smaller or larger than that of the test solution.

Unfortunately we have no officially recommended buffer solutions to measure pH less than 1 which is commonly encountered in volcanic crater lakes. Conventionally, KCl–HCl solutions were used for calibration of pH from 1.0 to 2.2 (Bower and Bates, 1955). Potassium tetraoxalate solution (pH 1.679 at 25°C) is convenient for calibration at various temperature of lower than 95°C (Bates, 1962). If we want to give a semiquantitative meaning in chemical equilibrium calculation of the crater lake water, we should have a standard procedure for in situ measuring pH of the lake water, or at least should give data about temperature, and the buffer for calibration of a pH-meter. An approach developed by Nordstrom et al. (1996) for hyper-saline fluids ($pH < 1$) indicates a way of measuring pH of highly acidic crater lake waters. They used sulfuric acid of 10^{-4}–10 M as a standard for pH of -4 to 2 which were calculated with the program PHRQPITZ (Plummer et al., 1988). According to Nordstrom et al. (1996), a commercially available glass electrode potential showed a linear relationship to the calculated pH on the Pitzer ion-interaction theory (Pitzer, 1973; Pitzer and Mayorga, 1973). Some crater lake waters such as Kawah Ijen (pH 0.3) contain sulfuric acid as a main acid component; thus it seems convenient for the field pH measurement to use 0.1 to several molal sulfuric acid solutions as a pH standard to which a glass electrode potential is calibrated on the Pitzer approach.

5.7. Isotopes

Hydrogen, oxygen and sulfur isotope values were only determined by a few laboratories. However, $\delta^{18}O$ and $\delta^{34}S$ are in an excellent agreement within 1.2, and 0.74 CV%, respectively, while δD values show more scatter (4.6–8 CV%). According to one of the participants, errors in repetitive measurements were 0.6, 0.7 and 1.3% for $\delta^{18}O$, $\delta^{34}S$ and δD, respectively. Therefore the oxygen and sulfur isotope data are within the errors in measurement. The deuterium data, however, are far beyond the errors in repetitive measurements, seemingly due to systematic deviation between different laboratories. The international cross check of stable isotope measurements conducted by International Atomic Energy Agency (Gonfiantini, 1984) showed that the deviation of the δD values of Greenland Ice Sheet Precipitation (GISP) from the mean value (−188.4) is 3.2%, if some outliers (2σ) are excluded, and 6% if not excluded. Thus the δD values in the present cross check are not that much out of line.

6. Concluding remarks and recommendations

In the above comparison of analytical data of the crater lake water, we found that considerable discrepancies may occur even in the major component determinations as well as in the minor elements:

(1) Major elements Na, Mg and Si have CV values close to 10%.

(2)Minor elements Co, Cu, P and Pb may deviate >30% from the corresponding mean values.

(3) Fluorine shows a considerable discrepancies (4–19 CV%)) as does SO_4^{2-} (4–9 CV%) although it is one of the major anions.

(4) δD values show a 5–8% deviation from the mean value.

The very acidic waters from active volcanic crater lakes dissolve a variety of elements in a wide range of concentrations. Especially, high levels of Fe and Al as well as sulfate in the water are a great obstacle to the conventional spectroscopic determination of trace elements. In order to avoid the interference of these major components, dilution of the sample (up to 10 times) was often adopted. This procedure, however, often results in serious errors in the analytical data, because some trace elements are then closer to their detection limits, and even the dilution can not be fully effective to avoid the spectroscopic interference. As far as we employ ICP-AES for the determination of major and minor metal ions, the inherent problems described above will remain more or less unsolved. In this analytical comparison, no recovery test for each trace element was conducted or reported. Consequently we can not say which data are best under the present situation, but we can say at least that the quality of the analytical trace element data reported here are sufficient to discuss hydrothermal mass transfer in the active crater lake system, although almost all of them have only one significant figure at best and much room for technical improvement. The followings are recommendations in the analysis of active crater lake waters:

(a) Crater lake water should be filtered with 0.45 μm membrane filter and diluted in situ to avoid excess silica dissolution, precipitation of minerals, the trace metal adsorption to elemental sulfur, and proliferation of sulfur-oxidizing bacteria.

(b) The lake water should be checked if it carries polythionates or not. If it does, the water should be oxidized with H_2O_2 before major and trace element determination.

(c) For the F determination, fluoro-metal complexes should be breached by adding strongly complexing agents, and BF_4^- must be separately determined, if not by separating F by distillation.

(d) The acidity of the Na, K analyte mixed with $LiNO_3$ or $CsNO_3$ should be the same as the standard solution. This should also be the case for the determination of Mg, Ca, Sr and Ba when $La(NO_3)_3$ is added to avoid chemical interference in AAS and ICP.

(e) Polythionates are to be determined because these anions are very likely to be major anions in active crater lake water.

(f) For trace heavy metal analysis at low levels, a preliminary heavy metal group separation is recommended to avoid spectroscopic and chemical interferences in ICP-AES and ICP-MS.

(g) In situ measurements of $pH < 1$ is recommended using a glass electrode calibrated to the KCl–HCl ($pH = 1$) or more precisely to the sulfuric acid solution of which pH is calibrated based on the Pitzer approach.

The recommendation (b) should not be done if sulfur isotope measurement is planned, because high polythionate solutions may give different ^{34}S values for SO_4^{2-} from those of unoxidized solutions (Sriwana et al., 2000 – this volume).

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