

# Evolution of water chemistry in natural acidic environments in Yangmingshan, Taiwan

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In Yangmingshan National Park, located in the northern part of the Taiwan Island, there is a very rare area where fish (*Channa asiatica*) live in spite of acid environments. The origin of the acid in local acid ponds and rivers and the evolution of the water chemistry are discussed on the basis of sulfur stable isotope ratios and chemical equilibria. One of the sources of the acid is sulfuric acid, which is derived from the oxidation of hydrogen sulfide in volcanic gas gushing out from fumaroles around the area and from acid deposition supplied from Taipei City. It is also derived from the oxidation of pyrite: the sulfur stable isotope ratios of  $\delta^{34}\text{S}$  of +1‰ to +4‰ (relative to CDT) of sulfate in acid pond waters (pH 3–4) could be related to those of hydrogen sulfide in volcanic gas, pyrite in local pond sediments and soils, and sulfate in rain water. One acid source is sulfuric and hydrochloric acids arising in springs from geothermal activity: the  $\delta^{34}\text{S}$  values were characterised by +13‰ to +17‰ sulfate-S, which was provided by a disproportionation reaction of sulfur dioxide in the depths. Another acid source could be the oxidation of iron(II). Under acidic conditions, the water–rock reaction gives rise to high concentrations of aluminium and iron. While flowing down surface streams, iron(II) is oxidised to iron(III) and then hydrolysed to cause further acidification under oxic conditions. The concentrations of iron and aluminium are controlled by redox and dissolution equilibria.

## 1 Introduction

Since the beginning of the last century, acid deposition has resulted in the consumption of lake-water buffering capacities, leading to low alkalinity and subsequent acidification, especially in areas of Scandinavia and North America with thin soil cover. In contrast to lakes and rivers that have recently become acidified by acid deposition related to industrialisation, most of the lakes and rivers in volcanic areas in Japan and on Taiwan Island have been acidified by sulfuric and hydrochloric acids of volcanic origin.<sup>1,2</sup> Naturally acidified lakes and rivers, such as Lake Yugama (Kusatsu Shirane, Japan, pH 1.0),<sup>3</sup> Lake Fudo-ike (Kirishima, Japan, pH 3.8),<sup>4</sup> the Sukawa River (Fukushima, Japan, pH 2.8)<sup>5</sup> and Lake Usoriko (Aomori, Japan, pH 3.2)<sup>6</sup> usually have a longer history of acidification than those that have recently been acidified by acidic deposition, making them suitable for investigations of the long-term influence of acidification on environments. There have been investigations into the leakage of brine from active crater lakes and its implication for crater collapse,<sup>7</sup> seasonal changes in the water quality of rivers flowing from crater lakes,<sup>8</sup> and the heat, water, and chloride budgets of crater lakes,<sup>9</sup> but there have been few reports on the evolution of water quality in these areas.

In Taiwan, there are many lakes and reservoirs in which acidification is now progressing.<sup>10</sup> However, in Yangmingshan

National Park in the northern part of the island, there is a very unusual area where the Chinese snakehead fish (*Channa asiatica*) lives despite the acidity of the environment. We obtained permission to collect these extremely precious fish with the aim of clarifying the distribution of elements in their tissues and organs. Some of our results have already been reported in the proceedings of the IUPAC International Congress on Analytical Sciences 2001, held in Tokyo,<sup>11</sup> and the detailed results on this topic will be presented elsewhere. Here, to elucidate the environment in which the fish live, we investigated the origin of the acid in the local acid lakes and rivers and the evolution of the water chemistry in terms of sulfur isotope ratios and chemical equilibria.

## 2 Study areas and locations of sampling points

The study areas were Hsiao-yukeng, Lake Menghuan and Lengshuikeng, in Yangmingshan National Park in the northern part of Taipei City, Taiwan (Fig. 1). On Taiwan Island, volcanic rocks are distributed together with many hot springs only in this area, which is largely composed of different kinds of andesites with small quantities of basaltic rocks.<sup>12</sup>

In Hsiao-yukeng, there are many fumaroles from which water vapour and hydrogen sulfide gas gush out. Around the fumaroles, native sulfur is formed by the proportionation reaction of sulfur dioxide and hydrogen sulfide. Lake Menghuan (850 m above sea level (a.s.l.)) is a shallow crater lake located at the side of Mt. Chihsing (1120 m a.s.l.) (Fig. 2). This lake is known for a rare and unique type of submerged water fern (*Isoetes*

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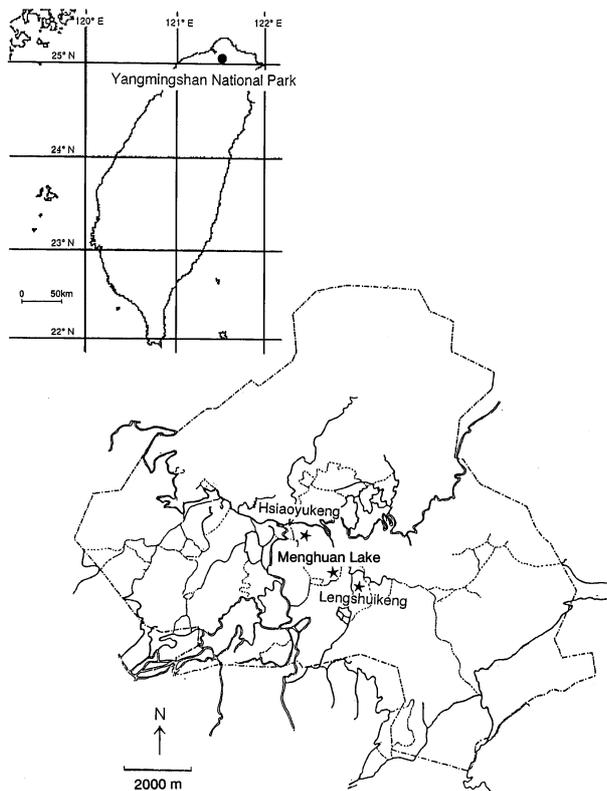


Fig. 1 Locality map of Yangmingshan National Park.

*taiwanensis*), which is one of Taiwan's special natural treasures. Although the lake is shallow and acidic, its floor is filled with aquatic plants. From local anecdotal knowledge it is claimed that until 1998 fish were living in this lake, but the details of this claim are unclear. Lengshuikeng is a much larger crater than

Lake Menghuan. This shallow depression is covered with tuff breccia together with hypersthene hornblende andesite, and has a zone of hydrothermal alteration. The area is a marsh in which nearly neutral hot spring waters (No. 23 in Fig. 2), nearly neutral surface and underground waters (Nos. 6, 8 and 9 in Fig. 2), and acid spring waters mainly supplied from an abandoned sulfur mine (No. 10 in Fig. 2) are mixed. A stream issues from the marsh. The discharges of water at sampling points No. 9, 10 and 23 were similar, and those at other sampling points were relatively small. Lengshuikeng pond was made by the damming of one of the tributaries of the stream. The Chinese snakehead *Channa asiatica* (*Limmaeus*), order *Channiformes*, family *Channidae*, lives in the pond. The pond used to be a small marsh and was developed in March 1999 by enclosing the middle reaches of the stream. It is said that *C. asiatica* also lives in the marsh. The area is very unusual in that fish are able to live in the water despite its high acidity.

The localities surveyed are shown in Fig. 2, and the analytical results for the water samples collected are shown in Table 1. Further samples for analysis of sulfur stable isotope ratios were collected at Hsiaoyukeng and in Taipei City.

### 3 Description of the experimental procedures

Field surveys were done in March, April, August and September 1999, February and March 2000, and March 2001. Water samples for analysis of major components were filtered through 0.45  $\mu\text{m}$  membrane filters (Millipore, Bedford, USA) and collected in polypropylene bottles. For analysis of trace elements, PTFE bottles and 0.20  $\mu\text{m}$  filters were used, and the water samples were preserved in 1.0 mol  $\text{dm}^{-3}$  nitric acid (Cica-Merck Ultrapur; Kanto Chemical, Tokyo). Water samples were stored in a refrigerator at 5  $^{\circ}\text{C}$  until analysis. Water temperature ( $T_w$ ) and pH, redox potential ( $Eh$ ) were measured on site with an HM-14P meter with a glass electrode,

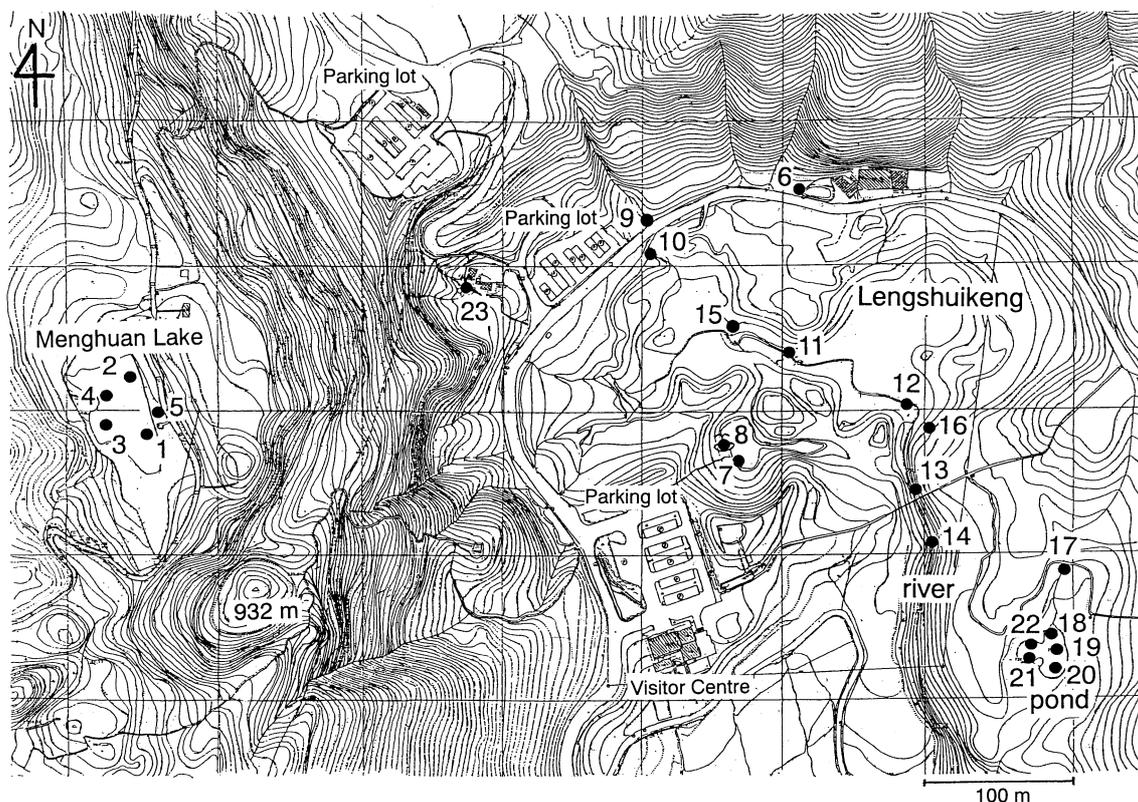


Fig. 2 Detailed map of Yangmingshan National Park, showing the locations of the sampling sites.

**Table 1** Analytical data of natural water in the Yangmingshan National Park in Taiwan

Sampling point	No.	$T_w/^\circ\text{C}$	pH	$Eh/\text{mV}$	$\text{Na}^+$ (ppm)	$\text{K}^+$ (ppm)	$\text{Mg}^{2+}$ (ppm)	$\text{Ca}^{2+}$ (ppm)	$\text{Al}^{3+}$ (ppm)	Total Fe (ppm)	$\text{Fe}^{2+}$ (ppm)	$\text{SiO}_2$ (ppm)	$\text{Cl}^-$ (ppm)	$\text{NO}_3^-$ (ppm)	$\text{SO}_4^{2-}$ (ppm)	CBE <sup>a</sup> (%)	Sampling date
Menghuan Lake	1	11.5	3.89	465	3.1	0.39	0.38	0.78	0.13	0.09		0.2	4.6	0.65	6.4	14.0	Mar. 30 '99
	2	11.9	3.84	477	3.4	0.36	0.40	0.84	0.16	0.11		0.6	4.6	0.70	7.0	16.0	Mar. 30 '99
	3	20.6	4.34	461	3.6	0.26	0.43	0.74	0.17	0.09		0.1	5.1	0.89	6.8	0.8	Mar. 31 '99
	4	22.3	3.77	366	3.9	0.43	0.45	0.84	0.15	0.17		0.3	5.1	0.58	7.8	18.0	Mar. 31 '99
Rain	5	26.1	4.65	—	0.24	0.12	0.06	0.78	n.d. <sup>b</sup>	n.d. <sup>c</sup>		n.d. <sup>c</sup>	0.51	1.3	1.4	11.0	Aug. 26 '99
	5	—	4.80	—	0.31	0.09	0.02	0.54	n.d. <sup>b</sup>	n.d. <sup>c</sup>		n.d. <sup>c</sup>	0.62	1.5	1.5	-9.5	Aug. 22 '99
	5	—	—	—	0.27	0.08	0.02	0.67	n.d. <sup>b</sup>	n.d. <sup>c</sup>		n.d. <sup>c</sup>	0.51	1.4	1.7	—	Aug. 22 '99
Well water	5	—	3.50	—	2.8	0.30	0.30	1.1	n.d. <sup>b</sup>	n.d. <sup>c</sup>		n.d. <sup>c</sup>	3.2	14.9	7.2	4.4	Aug. 23 '99
	5	7.7	4.62	—	1.0	0.08	0.13	0.60	n.d. <sup>b</sup>	n.d. <sup>c</sup>		0.07	2.2	1.0	3.1	-12.0	Feb. 1 '00
	6	16.8	6.47	355	6.7	1.4	2.1	8.0	0.001	n.d. <sup>c</sup>		36.0	6.6	1.3	11	0.3 <sup>d</sup>	Aug. 23 '99
Milk Pond (small crater lake)	7	20.0	3.83	119	6.9	1.3	4.4	12.4	2.6	2.7		25.0	9.4	0.09	109	-15.0	April 2 '99
	8	16.8	5.42	54	5.7	1.1	2.8	6.2	0.023	0.10		23.6	6.7	0.78	34	-4.7	April 2 '99
Water issuing from the soil	9	24.0	4.87	471	30.3	6.0	22.3	94.1	1.0	0.33		105	77.7	0.88	273	1.6	Aug. 26 '99
	10	24.1	3.21	111	20.0	4.9	19.5	125	31.0	11.7	11.7 <sup>e</sup>	101	49.8	0.26	596	1.6	Mar. 19 '00
Lengshuikeng River	11	24.4	3.59	634	27.7	6.0	19.5	54.7	0.18	4.7	1.1 <sup>e</sup>	51.3	66.3	1.1	198	1.8	Aug. 26 '99
	12	17.3	4.46	302	12.9	2.8	9.6	31.9	1.1	0.82	0.69	50.8	39.3	1.2	110	-3.0	Mar. 16 '00
Tributaries of the river	13	17.0	4.27	328	12.1	2.7	9.2	30.2	1.2	0.67	0.57	49.1	35.3	1.2	111	-3.9	Mar. 16 '00
	14	17.0	4.24	342	12.0	2.8	9.1	29.7	0.97	0.75	0.60	49.3	34.9	1.1	112	-4.9	Mar. 16 '00
Lengshuikeng Pond	15	24.2	5.53	261	27.7	5.8	20.4	67.8	0.11	5.6		175	64.7	0.32	213	3.7	Aug. 26 '99
	16	15.0	3.41	652	7.7	1.6	5.0	16.1	1.7	0.51	0.22	34.0	16.7	0.80	78	1.9	Mar. 16 '00
Hot Spring	17	21.2	3.40	602	5.2	1.2	1.4	4.8	1.0	0.25		14.9	6.7	1.7	43	0.8	Sep. 3 '99
	18	23.4	3.03	724	5.5	10.7	3.1	7.7	2.8	4.2		25.5	10.1	0.51	113	-0.6	Sep. 3 '99
Lengshuikeng Pond	19	23.4	3.10	742	5.4	11.0	3.1	7.7	2.5	5.8		26.0	10.2	0.54	112	-1.7	Sep. 3 '99
	20	23.4	2.85	683	5.5	11.2	3.2	6.1	2.4	4.3		26.1	10.1	0.70	115	5.3	Sep. 3 '99
Lengshuikeng Hot Spring	21	23.4	2.85	734	5.4	10.6	3.1	6.1	2.5	3.9		25.4	10.3	0.62	114	5.1	Sep. 3 '99
	22	23.4	3.15	729	5.4	10.7	3.1	7.4	2.3	3.7		25.2	8.7	0.37	96	0.8	Sep. 3 '99
	23	41.4	5.74	165	49.8	12.1	52.5	137	0.001	12.5		142	159	n.d. <sup>f</sup>	275	0.4 <sup>g</sup>	Mar. 28 '01

<sup>a</sup>Charge balance error =  $\{[(\text{total cation in mequiv dm}^{-3}) - (\text{total anion in mequiv dm}^{-3})] / [(\text{total cation in mequiv dm}^{-3}) + (\text{total anion in mequiv dm}^{-3})] \} \times 100$ . <sup>b</sup>n.d., <10 ppb. <sup>c</sup>n.d., <1 ppb. <sup>d</sup>HCO<sub>3</sub><sup>-</sup> concentration, 28 ppm. <sup>e</sup>Calculated value using eqn. (2). <sup>f</sup>n.d., <5 ppb. <sup>g</sup>HCO<sub>3</sub><sup>-</sup> concentration, 243 ppm.

an RM-12P meter, and a CM-1K meter (TOA, Tokyo), respectively.<sup>13</sup>

Sulfate ions in the water were recovered as barium sulfate by adding barium chloride, and the precipitate was provided for analysis of the <sup>34</sup>S/<sup>32</sup>S isotope ratio. Sulfur dioxide and hydrogen sulfide in fumarolic gas were oxidised at the site with hydrogen peroxide solution, and then finally collected as barium sulfate as mentioned above. The hydrogen sulfide in the fumarolic gas was collected as cadmium sulfide. Cadmium sulfide and pyrite (FeS<sub>2</sub>) in sediments were oxidised with an aqueous bromine solution in our laboratory, and then collected as barium sulfate.

The major cation components (Ca<sup>2+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup> and total-Fe) were analysed by flame atomic absorption spectrometer (Model AA8500, Nippon Jarrell-Ash, Kyoto). The detection limits (3s) were less than 0.1 mg kg<sup>-1</sup>. The ionisation and chemical interferences were suppressed by adding calcium chloride and lanthanum chloride to the sample solution.<sup>13</sup> The concentrations of the major anion components (Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup>) were determined by ion chromatography (pump: Sanuki DM2M-1024; separation column: Toso TSK IC-Anion PW; detector: Toso CM-8000).<sup>13</sup> The concentrations of silica and iron(II) ions were absorptiometrically determined by the Molybdenum Yellow and 1,10-phenanthroline methods, respectively, with a spectrophotometer (Model Ubest 35, JASCO, Tokyo). In the latter case, diammonium citrate was used as a masking agent for coexisting iron(III) ions.<sup>14</sup>

The concentration of trace levels of aluminium was determined by inductively coupled plasma mass spectroscopy (ICP-MS) with a spectrometer (Model PMS2000, Yokogawa, Tokyo; Centre of Advanced Instrumental Analysis, Kyushu University) by a standard additions method. The analytical results for the certified reference materials DORM-2 and DOLT-2 (NRCC, Canada) agreed well with the certified values, and the recoveries were 101% and 99.3%, respectively.

The sulfur stable isotope ratios of the barium sulfate samples were analysed by mass spectroscopy with a SIRA 10 spectrometer (VG Isogas, UK). The sulfur stable isotope ratio is shown as a permillage deviation by eqn. (1), relative to the reference material of FeS (troilite) in the Canyon Diablo meteorite.

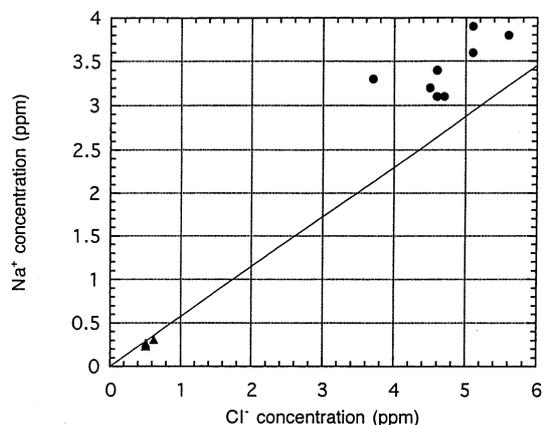
$$\delta^{34}\text{S} (\text{‰}) = \left\{ \frac{(^{34}\text{S}/^{32}\text{S})_{\text{sample}}}{(^{34}\text{S}/^{32}\text{S})_{\text{reference}}} - 1 \right\} \times 1000 \quad (1)$$

The activities of the dissolved chemical species and the saturation indices for some minerals were estimated by using the chemical equilibrium calculation program PHREEQ.<sup>15</sup>

## 4 Water quality formation in the acidic environments at Yangmingshan

### 4.1 Origin of acid in the water

**Acidic water in Lake Menghuan.** The ionic balance of the analytical results for each sample was tabulated and a reasonably high reliability for the data was obtained (Table 1). The pH of Lake Menghuan was in the range of 3.77–4.34 (Table 1). To determine the source of the acidity, an acid–base titration was done. The titration curve of a water sample from Lake Menghuan with a sodium hydroxide solution agreed well with that of strong acid and showed no inflection points that might have indicated the presence of weak acids. Correlation between the sodium and chloride concentrations of the waters of Lake Menghuan showed that the source of sodium chloride in Lake Menghuan is sea salt, because the contents of sodium chloride in the rain collected at the lake were almost on the dilution line for seawater (Fig. 3). If the rain is concentrated 10 times by evaporation, the pH is expected to be 3.7, and this agrees reasonably well with that of the lake water. In other words, the rain was considered as a source of hydrogen ions



**Fig. 3** Relationship between the concentrations of Na<sup>+</sup> and Cl<sup>-</sup> in Lake Menghuan. The line: equivalent line relating to the sea salt. ●, Lake Menghuan (some of the points are not listed in Table 1, although collections were made at the same time). ▲, rain water.

and other dissolved components in the lake. The small excess of sodium concentration in the lake water may be due to the interaction between the lake water and the sediments. The residence time of this lake water was short: the response of the water level of this lake was rapid after rainfall, and the increased water level was lowered within several days. Even in the rainy season, the greatest depth was less than 2 m. The concentrations of Ca<sup>2+</sup>, K<sup>+</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> in rain water were lower than those predicted by the simple concentration of rain, suggesting that these ions are taken up by aquatic plants. The concentration of nitrate in the rain was much higher than expected. The rain may contain acids derived from the combustion of fossil fuels in Taipei City; this hypothesis is later examined by sulfur isotope ratio analysis.

**Acidic water of Lengshuikeng.** In volcanic areas, acid sulfate–chloride waters may originate when high-temperature volcanic gas containing hydrogen chloride and sulfur dioxide condenses in the depths of volcanoes and then enters geothermal waters. Sulfate in these acid waters is formed by the disproportionation reaction of sulfur dioxide.<sup>16,17</sup> The pH at the Lengshuikeng sampling sites was in the range of 2.85–5.53 (Table 1). The concentrations of dissolved components were higher than those of Lake Menghuan (Table 1), because the water–rock interactions proceeded sufficiently at higher temperatures. At Lengshuikeng, the presence of hydrogen sulfide and sulfur dioxide related to the above reaction was supported by the presence of flowers of sulfur in the stream. The results of analysis of the water (Table 1) show the sources of acidity to be hydrochloric acid and sulfuric acid.

**Sulfur stable isotope ratio.** Since the 1960s, various reports have used analysis of sulfur stable isotope ratios to give information on the origin of sulfate ions contained in acidic precipitation. For example, Nagamine *et al.*,<sup>18</sup> by using sulfur stable isotope ratios corrected for the ratio of sea salts, reported that the contribution of sulfate ions supplied from sea salt to rain was small in Nagoya City, Japan. Kasasaku *et al.*<sup>19</sup> clarified the effects of volcanic gas from Mt. Sakurajima on the rain water chemistry of Mt. Shibi, 50 km away. It is also known that the sulfur stable isotope ratios of crater lakes gradually become smaller as volcanic activity declines.<sup>20</sup> These reports suggest that analysis of sulfur stable isotope ratios can be used to monitor volcanic activity.

The sulfur stable isotope ratios of the samples collected in Yangmingshan National Park were measured. Sulfate ions were separated into two groups on the basis of their sulfur isotope ratios:  $\delta^{34}\text{S} = +1.4\text{‰} \text{--} +4.0\text{‰}$ , and  $\delta^{34}\text{S} = +13.1\text{‰} \text{--} +16.8\text{‰}$  (Fig. 4). Two different origins of sulfate ions became

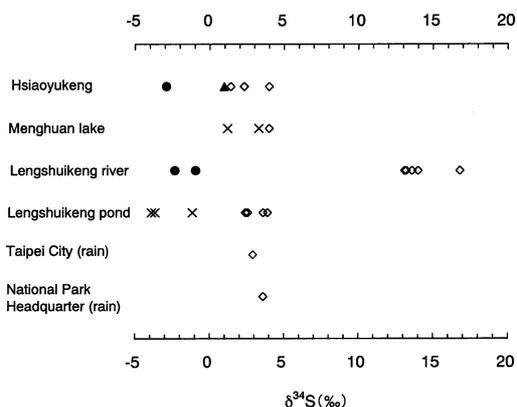


Fig. 4 Stable isotope ratios of sulfur species in Yangmingshan National Park. ●, elementary S; ◇,  $\text{SO}_4^{2-}$ ; ×,  $\text{FeS}_2$ ; and ▲,  $\text{H}_2\text{S}$  (fumarolic gas).

apparent. The sulfur dioxide dissolved in the depths of the geothermal waters is unstable and decomposes into sulfuric acid and hydrogen sulfide by a disproportionation reaction.<sup>21</sup> Additionally, the sulfate ions in the condensed waters of a volcano concentrate  $^{34}\text{S}$  against hydrogen sulfide (the isotope ratio of  $^{34}\text{S}$  in sulfate ions is 30‰ larger than that of hydrogen sulfide at 100 °C), so that their sulfur stable isotope ratio increases.<sup>17</sup>

The sulfur isotope ratios at Hsiaoyukeng ( $\delta^{34}\text{S} = +1.4\text{‰}$  and  $+2.3\text{‰}$ ), in rain water at Yangmingshan National Park Headquarters ( $\delta^{34}\text{S} = +3.6\text{‰}$ ), and at Lake Menghuan ( $\delta^{34}\text{S} = +4.0\text{‰}$ ) were small. This suggests that the source of sulfate in these areas is hydrogen sulfide vented from fumaroles, as represented by the hydrogen sulfide samples of Hsiaoyukeng ( $\delta^{34}\text{S} = +1.0\text{‰}$ ), and oxidised quantitatively to sulfuric acid. The sulfate represents complete or partial oxidation of hydrogen sulfide without any isotopic fractionation; for example, Ketetahi Hot Springs at Mt. Tongariro, New Zealand, have  $\delta^{34}\text{S}$  values of  $+2.6 \pm 0.7\text{‰}$  for sulfate, which represents complete oxidation of hydrogen sulfide.<sup>22</sup> The waters of the acid pond (Lengshuikeng pond) in which *C. asiatica* were caught, and of the tributary stream (No. 17) also showed small values for  $\delta^{34}\text{S}$ . Their sulfur source was presumed to be the fumarolic gases. However, the concentrations of dissolved components at these sample sites were too high for the water chemistry to be explained by evaporation and concentration of water alone, unlike those of rain water and Lake Menghuan water. In the soil and pond sediments at these sampling sites, pyrite, probably stored in this area during a period of high fumarolic activity, was abundant and was oxidised to sulfuric acid by micro-organisms such as sulfur bacteria. The  $\delta^{34}\text{S}$  values of the pyrite in the pond sediments were small ( $\delta^{34}\text{S} = -3.9\text{‰}$ – $-0.1\text{‰}$ ), and this fact supports the above description (Fig. 4). Judging from the nitrate concentrations in rain water samples taken in Yangmingshan (No. 5 in Table 1), acid generated from fossil fuels in Taipei City did affect the sample values: the  $\delta^{34}\text{S}$  of sulfate in rain water in Taipei City was  $+2.9\text{‰}$ . Therefore, the contribution of fossil fuels in Taipei City to acidification in Yangmingshan National Park cannot be ignored.

The larger sulfur isotope ratios ( $\delta^{34}\text{S} = +13.1\text{‰}$ – $+16.8\text{‰}$ ; Fig. 4) were considered to reveal the origin of the sulfuric acid provided by a disproportionation reaction of volcanic gas with larger isotope fractionation in the liquid layer. Similar fractionation occurred between crater-lake brine ( $\delta^{34}\text{S} = +12.3\text{‰}$ – $+15.5\text{‰}$ ) and hydrogen sulfide from fumaroles ( $\delta^{34}\text{S} = -10.2\text{‰}$ – $-8.0\text{‰}$ ) at the Poas volcano (Costa Rica).<sup>23</sup>

#### 4.2 Water quality formation at Lengshuikeng

A number of researchers have analysed the concentrations of the major cations and anions in an effort to understand the

water quality formation of acidic environments. Chiba<sup>24</sup> determined the concentrations of dissolved components in Lake Inawashiroko (pH 4.9, Fukushima, Japan), particularly of iron and aluminium, and compared the development of water quality in the lake with that in other Japanese freshwater lakes. He found that the water quality of Lake Inawashiroko is mainly controlled by the water quality of acidic rivers that flow into the lake. In volcanic areas where there are acidic springs, such as at Lake Usoriko<sup>25</sup> and the crater lake of the Kawah Ijen volcano, Indonesia,<sup>26</sup> the concentrations of iron and aluminium are much higher than those of other trace elements because of water–rock interactions. The solubilities of iron and aluminium minerals are high in acid environments, but they vary compared with those of other major elements according to changes in chemical environments (e.g., oxygen partial pressure and pH changes). In Yangmingshan National Park, we analysed the concentrations of the major components, iron and aluminium, in the Lengshuikeng River, where changes in water quality with time could easily be traced, and in the pond where the fish live.

**In the Lengshuikeng River.** Analysis of the concentrations of four major cations (calcium, magnesium, potassium and sodium) in the river water basically showed linear relations with silicic acid, chloride and sulfate concentrations (Fig. 5). This suggests that the concentrations of major components in the river water could be the result of the mixing of two kinds of source waters in high and low concentrations of dissolved

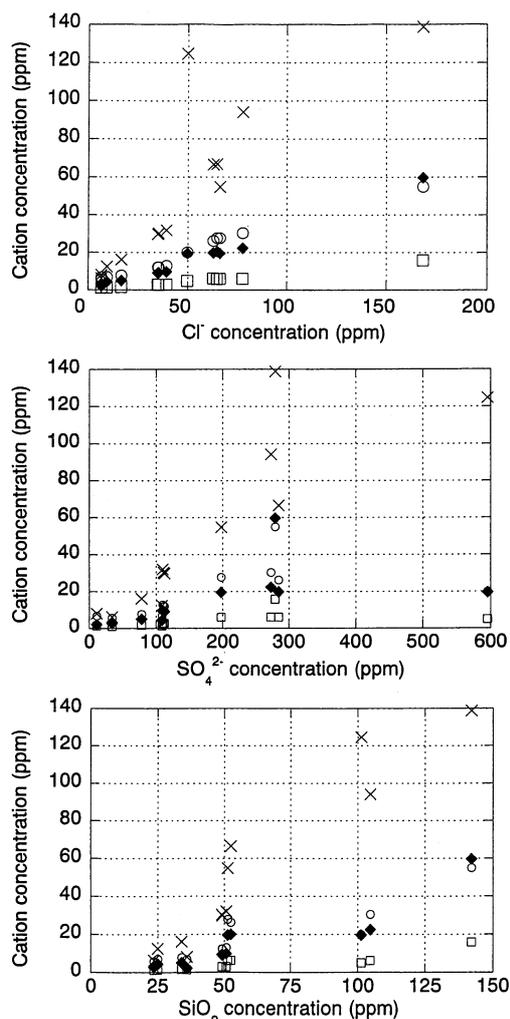


Fig. 5 Relationship between cation concentrations and  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  and  $\text{SiO}_2$ . ○, Na; □, K; ◆, Mg; ×, Ca.

components: the water issuing from the abandoned sulfur mine (No. 10 in Fig. 2) and that from the hot spring of Lengshuikeng (No. 23 in Fig. 2). Because of the high concentrations of geothermal-origin sulfuric acid and hydrochloric acid, the water dissolves the rocks to some extent. The other source waters, such as the well water and the water issuing from the soil layer (Nos. 6 and 8, respectively, in Fig. 2) are nearly neutral.

Principal component analysis identified 2 major components. The first (component 1) was characterised by  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ , total-Fe,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  and  $\text{SiO}_2$ , and the second (component 2) by  $\text{H}^+$  and  $\text{Al}^{3+}$ . The percentage contribution ratio accounted for by component 1 was 56.5%, and that by component 2 was 37.6%. Component 1 may originate from the mixing of two kinds of source waters in high and low concentrations of the dissolved components, implying that the acids in high concentrations in water were almost neutralised as a result of water-rock interaction. In nearly neutral solution, the solubilities of Al-containing minerals are low. In contrast, those of Fe-containing minerals can be fairly high under anoxic conditions.<sup>27</sup> The presence of component 2 may be related to the slow reaction of the acids with the rocks at a low water temperature.

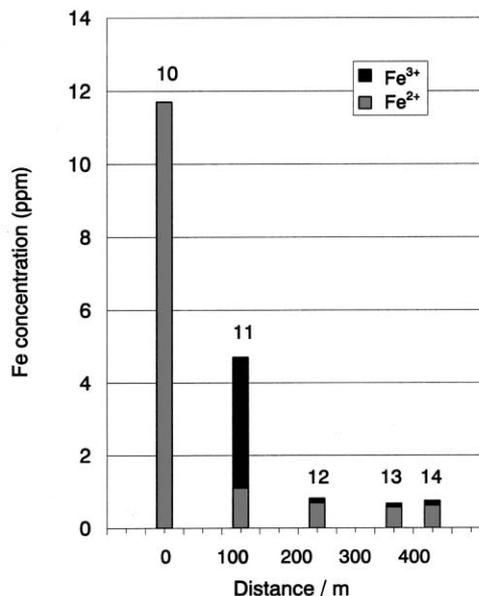
In the river, both dissolved iron and aluminium were supplied from water issuing from the abandoned sulfur mine (No. 10 in Fig. 2). There were no minerals at dissolution equilibrium or supersaturation, and the water at site No. 10 provided large amounts of iron and aluminium to the river. The concentration of iron was related to both the oxidation-reduction (redox) reaction and the dissolution equilibrium reaction, and its behaviour is much more complicated than that of aluminium.

There were yellow-brown precipitates without obvious diffraction patterns on powder X-ray diffractometry in the river. Additional observation with a polarisation microscope indicated that they were amorphous iron hydroxide. The concentration of iron showed no correlation with the concentration of major components, suggesting that the concentration of iron was not controlled by simple mixing of the two kinds of water, but that chemical reactions occurred as the river flowed further down. The concentrations of total iron were plotted against the distance from sites No. 9 to No. 14 along the river (No. 15 was not on the main stream), and the concentration of iron decreased with distance from site No. 9; for example, it was 12 ppm at site No. 10 and 0.75 ppm at site No. 14 (Fig. 6).

On the basis of the analytical results for differentiation of the dissolved iron oxidation states, the activities of dissolved chemical species and saturation indices for iron were estimated by using the chemical equilibrium calculation program PHREEQ.<sup>15</sup> The relationship between the logarithms of the activity ratios of iron(II) and iron(III) against the redox potentials observed at the sites was empirically expressed as follows:

$$E/V = 0.81 - 0.148 \log(a_{\text{Fe}^{2+}}/a_{\text{Fe}^{3+}}) \quad (\text{correlation coefficient, } r = 0.995) \quad (2)$$

where  $a_{\text{Fe}^{2+}}$  and  $a_{\text{Fe}^{3+}}$  are the activities of the respective free iron species. Although the slope was somewhat different from the Nernst one, it can be applicable for estimating the concentration ratios of iron(II) and iron(III) at other points with the redox potentials observed and the concentrations of total iron. The activity ratios of iron(II) to iron(III) in the upper stream were high owing to the inflow from site No. 10, they became small in the middle part of the marsh, and then increased because of the supply of iron(II) from other inflows (Fig. 6). When the concentration of iron(II) became low, it can be considered that iron(II) was oxidised into iron(III) and removed as iron hydroxide, produced by eqn. (3).



**Fig. 6** Relationship between distance and concentration of iron. Each bar shows the total concentration of dissolved iron and the fractions of  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$ . Distances were measured from site No. 10. The numbers above the bars show the sampling point numbers.



As shown in Table 2, calculation of the saturation indices for iron(III) hydroxide clarified the fact that the water was nearly at equilibrium with amorphous iron(III) hydroxide upstream of No. 11. The dissolved iron(II) seemed to be oxidised to iron(III) between sites No. 10 and No. 11. The dissolved iron then became supersaturated for amorphous iron(III) hydroxide and was removed as precipitation. This agreed well with the observation that large amounts of iron(III) hydroxide were precipitated in the marsh around site No. 11. The discharge at No. 10 was about  $10 \text{ dm}^3 \text{ s}^{-1}$ , and the residence time of the stream water was estimated to be about 18 h at sites No. 10 and No. 11. Under the pH condition of 3.5, the pseudo-first-order reaction rate constant of the oxidation reaction from iron(II) to iron(III) was about  $0.1 \text{ day}^{-1}$ .<sup>27</sup> Therefore, the half-life was about 7 days. It is hard to explain how the quantitative oxidation was progressing inorganically when the river flowed down to site No. 11. Probably, catalytic reactions by microorganisms, for example, iron bacteria such as *Ferrobacillus ferrooxidans* and *Thiobacillus ferrooxidans*, were involved.<sup>28</sup> The oxidation reaction progressed rapidly, and the  $\text{H}^+$  produced from the hydrolysis of iron(III) decreased the pH to below 4. Further precipitation of iron occurred downstream. The concentration of dissolved iron decreased and most of the iron existed as iron(II) at sites No. 12, No. 13 and No. 14. The

**Table 2** Saturation indices (SI) with respect to three minerals in natural waters in the Yangmingshan National Park in Taiwan

Sampling point	No.	$\text{SI}_{\text{Fe}(\text{OH})_3}^a$	$\text{SI}_{\text{Gibbsite}}$	$\text{SI}_{\text{Kaolinite}}$
Milk Pond	7	-2.2	-1.6	-1.0
Lengshuikeng River	9	-0.1	1.1	5.4
	10	-4.0	-2.6	-1.9
	11	-0.3	-3.4	-4.1
	12	-0.2	-0.2	2.4
	13	-0.5	-0.8	1.3
	14	-0.4	-0.9	-1.0
	16	-1.3	-3.2	-3.8
Lengshuikeng Pond	20	-1.9	-4.3	-6.6

<sup>a</sup>SI =  $\log \{(\text{activity product of species concerned})/(\text{solubility product})\}$ .

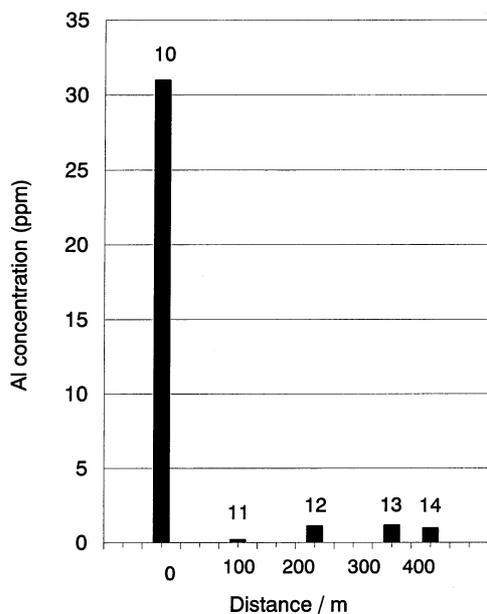


Fig. 7 Relationship between distance and concentration of aluminium. Distances were measured from site No. 10. The numbers above the bars show the sampling point numbers.

redox potentials of these waters were low, because of another inflow from a small crater lake (Milk Pond, No. 7 in Fig. 2) at the point between sites No. 12 and No. 13. It has been reported that most of the iron exists as iron(II) at the bottom of crater lakes, where the oxygen partial pressure is low.<sup>26</sup> In Lake Inawashiroko, in the presence of sufficient dissolved oxygen, the iron(II) is easily oxidised to insoluble iron(III) hydroxide and precipitated, and, therefore, the concentration of iron is low (0.02–0.1 ppm).<sup>24</sup>

The concentration of aluminium rose owing to the dissolution of aluminosilicate when the pH dropped. As well as iron, aluminium was also supplied from the abandoned mine (No. 10) in the upper stream, but the concentration of aluminium decreased to 1/180 in the area between sites No. 10 and No. 11 (Fig. 7), suggesting that the aluminium was removed there in the course of the mixing of the abandoned mine water and the waters of mainly the hot spring (No. 23) and the surface stream (No. 9). Unlike the case with iron, the water at No. 11 was not saturated with any aluminium-containing minerals (Table 2). This is because  $H^+$  was produced by the hydrolysis of iron(III), as mentioned above. The sediments found downstream in the river (at site No. 14) were analysed by powder X-ray diffractometry. The diffraction patterns did not indicate gibbsite, but kaolinite, the clay mineral that forms by chemical weathering in acid environments.<sup>29</sup> As expected, the river water was supersaturated with kaolinite at sites No. 12 and No. 13 (Table 2). Above all, the concentrations of aluminium in river water were controlled by chemical equilibria.

**In Lengshuikeng Pond.** The concentrations of major components in the pond were smaller than those in the river water. The concentrations of the dissolved components, except potassium, iron and sulfuric acid, in a stream flowing into the pond (site No. 17 in Fig. 2) were almost the same as those of the pond. Therefore, the water chemistry of the pond appeared to reflect the concentrations of the major components of the stream. The concentration ratios of sulfate to chloride in the pond water were much higher than those in the river water, indicating that sulfuric acid may be supplied from the oxidation of pyrite. The sediments of the pond were analysed by powder X-ray diffractometry and the diffractogram indicated the presence of pyrite. When pyrite is oxidised, 1 mol of iron(III) and 2 mol of sulfuric acid are produced.<sup>25</sup>

The pond water was not saturated with any minerals, including iron and aluminium, probably because of the short residence time. The concentration of iron and aluminium in the pond was almost the same at the five sampling points. The concentration of iron was higher than that of the river flowing into the pond and also higher than that downstream in the Lengshuikeng River, because the pyrite in the pond sediments may now be under somewhat oxic conditions since the construction of the pond in March 1999.

## 5 Conclusions

In Yangmingshan National Park, Taiwan, the concentrations of the major components in the river in the Lengshuikeng crater marsh are mainly controlled by the mixing of acid and neutral waters. The concentration of iron is controlled by redox reactions under oxic conditions and the dissolution equilibria for amorphous iron(III) hydroxide, and the concentration of aluminium by the dissolution equilibrium for kaolinite in water flowing down the stream. In the cases of Lake Menghuan and Lengshuikeng Pond, the sources of sulfuric acid may be mainly hydrogen sulfide in volcanic gas from fumaroles around the area and that accumulated in the soil and pond sediments as pyrite. In the case of the Lengshuikeng River, the origin of the acid is acidic springs containing sulfuric acid, provided by the disproportionation reaction of sulfur dioxide and hydrochloric acid. Analysis of the sulfur stable isotope ratios was an effective method of elucidating the origin of the acidity related to the sulfuric acid. The other source of acid is the oxidation of iron(II). Among metal ions that easily move in acid environments, iron(II) is oxidised to iron(III) and hydrolysed to cause further acidification under oxic conditions.

These results provide information that will help to understand water quality formation in natural waters where there is acidification of the environment.

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