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SHORT SCIENTIFIC COMMUNICATION

# Brownish discoloration of the summit crater lake of Mt. Shinmoe-dake, Kirishima Volcano, Japan: volcanic–microbial coupled origin

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**Abstract** A drastic change in lake water color from blue-green to brown was observed in the summit crater lake of Mt. Shinmoe-dake, Kirishima Volcano about 8 months after its 2008 eruption. The color change lasted for about 2 months (April–June 2009). The discoloration was attributed to a brownish color suspension that had formed in the lake water. X-ray fluorescence and Fourier transform infrared analyses of a sample of the suspension identified schwertmannite ($Fe_8O_8(OH)_6(SO_4)$). A cultivation test of iron-oxidizing bacteria for the sampled lake water with lakebed sediment revealed that the crater lake hosts iron-oxidizing bacteria, which likely participated in schwertmannite formation. We suggest that pyrite ($FeS_2$) provided an energy source for the iron-oxidizing bacteria since the mineral was identified in hydrothermally altered tephra ejected by the August 2008 eruption. From consideration of these and other factors, the brownish discoloration of the summit crater lake of Mt. Shinmoe-dake was inferred to have resulted from a combined volcanic–microbial process.

**Keywords** Crater lake · Color change · Ferric mineral · Volcanic ash · Bacteria

## Introduction

Active crater lakes at Holocene volcanoes display various colors resulting from absorption and scattering of sunlight by materials dissolved or suspended in the lake water (Oppenheimer 1997; Delmelle and Bernard 2000; Onda et al. 2003). Moreover, convective circulation, particle size, and chemical precipitation in crater lakes possibly enhance color changes in the water bodies. For example, at Crater Lake of Ruapehu Volcano, New Zealand, a transition in the lake

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color from blue-green to pale gray indicates the remobilization of lakebed sediments caused by vent activity (Christenson and Wood 1993; Christenson 1994). The crater lake of Poás Volcano (Laguna Caliente), Costa Rica, has changed from a greenish lake to a rapidly convecting and geysering pond, then to a sulfur-rich boiling mud pool. It then reverted to its former state as a blue-green colored lake (Rymer et al. 2005). During periods of phreatic activity (1987–1988), the crater lake water color changed drastically to yellow. Ohsawa (1992) attributed the color change to increased $Fe^{3+}$/total Fe ($Fe^{2+}$+ $Fe^{3+}$) in the lake water. Ephemeral color changes from blue-green to green were observed at Yudamari crater lake of Aso Volcano, Japan. Disappearance of the blue tint was interpreted as a result of a decrease in the content of colloidal sulfur, which is produced by the reaction of $SO_2$ and $H_2S$ emitted from subaqueous fumaroles (Ohsawa et al. 2010). At Voui crater lake of Aoba Volcano, Vanuatu, a spectacular color change from light blue to red, attributed to jarosite precipitation in the lake water, occurred following a phreatomagmatic eruption with injection of hot fresh primitive basalt into the lake and the construction of a cinder cone (Bani et al. 2009).

Color changes in lake waters to red or brown were also reported at the Kusatsu-Shirane Volcano, Japan (Ossaka and Kikawada 2009) and at Keli Mutu Volcano, Indonesia (Pasternack and Varekamp 1994). Recently, pronounced changes in lake water color from blue-green to brown were observed at the summit crater lake of Mt. Shinmoe-dake, called Shinmoe-ike, Kirishima Volcano in southern Kyushu, Japan (Fig. 1). Our aim here is to evaluate the factors leading to the brown discoloration of the lake water body through an interpretation of geochemical and microbiological analyses of samples collected from lake.

## Volcanic activity and summit crater lake of Mt. Shinmoe-dake

Kirishima Volcano is a Quaternary andesitic composite volcano occupying an area of about 20×30 km. It is elongated NW to SE and contains more than 20 eruptive centers, which have been repeatedly active. Mt. Shinmoe-dake is a small stratovolcano in the center of Kirishima Volcano. More than 50 eruptions of Kirishima Volcano have been documented since A.D. 742. They all occurred at Mt. Shinmoe-dake and Mt. Ohachi, with the exception of one at Mt. Iwoyama, which issued a small lava flow in 1768 (Imura 1992). Fumarolic activity at the crater of Mt. Shinmoe-dake, which was reported following the 1959 eruption, has been sustained (e.g., Kagiyama et al. 1979). The geochemistry of fumarolic gases was studied by Hedenquist and Aoki (1992), Ohsawa et al. (1995), Ohba et al. (1997), and Sato et al. (1999). During an eruption on 22 August 2008 (Table 1), an E–W trending, 0.8-km-long eruptive fissure opened, stretching 800 m from the interior of the summit crater of Mt. Shinmoe-dake to its upper western slope. Ash drifted to the NE and covered an area extending more than 30 km from the volcano (Geshi et al. 2010). Crater lake water discoloration occurred about 8 months after the 2008 eruption and continued for about 2 months (from the end of April to the beginning of July, 2009). Brownish discoloration also occurred from early June 2010 immediately after a small eruption on 27 May (Table 1), in contrast to the 2009 incidence. It persisted for 2 or 3 weeks.

The crater lake of Mt. Shinmoe-dake, whose diameter is about 200 m but whose depth is unknown, has no regular surface inlet or outlet (Fig. 1). Ohsawa (1992) reported that the lake water (on 24 July 1988) was acid-$SO_4$ type ($[SO_4^{2-}]$=144 mg/L, $[Cl^-]$= 0.7 mg/L) and that its pH was 3.1. This pH falls within the range recorded between April 1979 and May 2006 by the Kagoshima Local Meteorological Observatory (mean value=3.1, max=3.9, min=1.6; 74 samples). The observatory also routinely records lake temperature at the surface (Fig. 2a).

Figure 2b presents monthly water and air temperature data measured at an elevation of 1,200 m (Kusumoto 1984). The comparable trends in water and air temperatures suggest that the crater lake of Mt. Shinmoe-dake is a holomictic lake and that during this period there was at most only minor fumarolic activity at the lake bottom. The latter conclusion is consistent with self-potential observations made at the lake (Hashimoto et al. 1994).

Since the beginning of 2011, Mt. Shinmoe-dake has been the site of magmatic eruptions. The crater lake disappeared completely in January 2011 when lava filled the crater (Fig. 1d).

## Sampling and methods

Water samples for chemical analyses were collected from the crater lake three times: on 14 May and 16 July 2009 and on 25 April 2010. Water temperature measurements were conducted at the site with photographs of the lake taken using a digital camera. In addition, lakebed sediment samples were collected on 14 May and 16 July 2009. Colors of the crater lake waters, described in terms of the chromaticities x and y of the Yxy standard color system established by the Commission Internationale d'Eclairage (CIE) in 1931, were converted from numeric data of RGB values taken from digital photographs of the crater lake using a Photoshop histogram function (Adobe® Photoshop Elements; Adobe Systems Inc.). Digital photographs for 1988 were prepared using a flatbed scanner from a photographic print obtained using a still camera.

Major dissolved chemical components were determined using ion chromatography. The pH was measured using a digital pH meter. Total Fe [sum of ferrous and ferric ions ($Fe^{2+}$+$Fe^{3+}$)] was analyzed using spectrophotometry with the 1,10-phenanthroline method after reducing $Fe^{3+}$ with

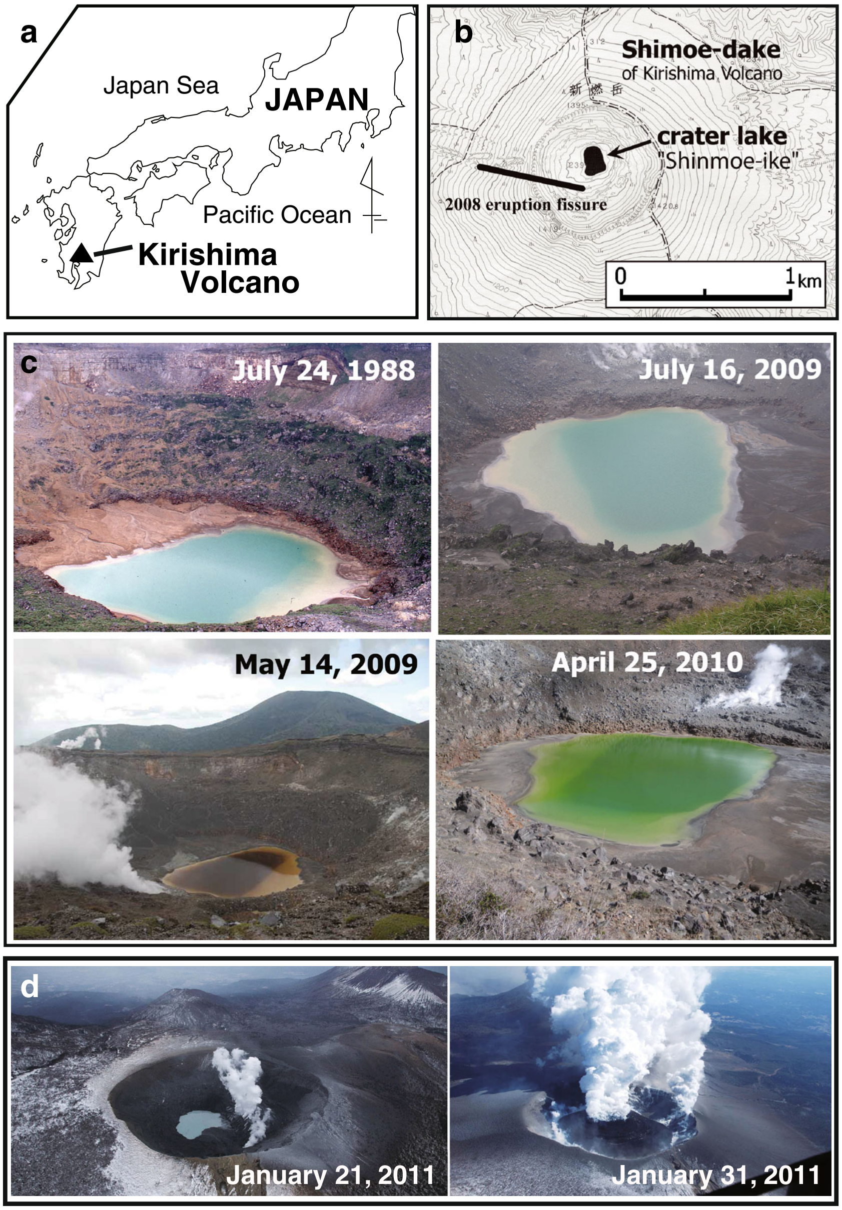

**Fig. 1** Location maps of Kirishima volcano (**a**) and of the crater lake of Mt. Shinmoe-dake [Shinmoe-ike] (**b**), photographs of the crater lake taken on the occasion of lake water sampling (**c**), and photographs of Mt. Shinmoe-dake taken immediately before and immediately after the magmatic eruption which began in early 2011 (**d**)

hydroxylamine hydrochloride. Then, $Fe^{2+}$ was determined without $Fe^{3+}$ reduction using the spectrophotometric method. The $Fe^{3+}$ concentration was obtained by subtracting the concentration of $Fe^{2+}$ from that of total Fe. X-ray fluorescence (XRF) and Fourier transform infrared (FT-IR) analyses were conducted for a filtered suspension of the lake water sample (ca. 7 mg from 340 mL) obtained on 14 May 2009 using a 0.45-μm pore-size membrane filter. The XRF analysis was conducted using an energy-dispersive X-ray spectrometer (JSX3220; JEOL) with a rhodium X-ray tube target (Rh). The FT-IR spectrum of the suspension sample was recorded using a FT-IR spectrometer (6700; Nicolet Biomedical Inc.) with an attached horizontal ATR accessory and a diamond crystal as a reflective element. Color measurements of the filtered suspension sample were conducted using a colorimeter (CM-503i; Konica Minolta Holdings Inc.). Powder X-ray diffraction (XRD) analysis of a fine part of the lakebed sediments sample was achieved using an X-ray diffractometer (Miniflex; Rigaku Corp.) with an X-ray tube of copper target (Cu) after desiccation at an ambient temperature.

Two culture media were prepared for cultivating sulfur-oxidizing bacteria (M-1) and iron-oxidizing bacteria (M-2). Following addition of 10 vol.% of the samples mixed in test tubes (see Fig. 7a), each was then incubated under aerobic conditions at 30 °C. In both cultivation experiments, control solutions (without samples) were prepared. Moreover, in both cultivations, subculturing was conducted several times for propagation of the bacteria.

**Table 1** Chronology of recent eruptions and discolorations of the crater lake of Mt. Shinmoe-dake

| Year | Month (day) | Eruption and discoloration of crater lake at Mt. Shinmoe-dake |
|---|---|---|
| 2008 | Aug 22 | Small phreatic eruption with ash fall after 17 years' quiescence |
| 2009 | Late Apr to early July | Discoloration of lake water |
| 2010 | Mar 30 | Very small eruption with ash fall |
| | Apr 17 | Very small eruption |
| | May 27 | Small (phreatic) eruption with ash fall |
| | Early June | Discoloration of lake water for 2 or 3 weeks |
| | June 27 and 28 | Very small eruptions |
| | July 5 | Very small eruption |
| | July 10 | Small eruption with cock's tail jet |
| 2011 | Jan 19 | Small eruption |
| | Jan 26 | Magmatic eruption, from that time down to this day |

*M-1* The W Medium was used for cultivation of sulfur-oxidizing bacteria (e.g., Takano et al. 1997). The composition of the basal salts solution used for the cultivation was as follows: $K_2HPO_4$, 3.0 g; $(NH_4)_2SO_4$, 0.2 g; $MgSO_4 \cdot 7H_2O$, 0.5 g; $FeSO_4 \cdot 7H_2O$, 10.0 mg; $CaCl_2 \cdot 2H_2O$, 250.0 mg; and distilled water, 1,000 mL. This salt solution was adjusted to a pH of 3.0 by addition of sulfuric acid, and it was sterilized by autoclaving at 121 °C for 20 min. Sulfur powder (10.0 g) was sterilized by autoclaving at 105 °C for 30 min and added to the basal salts solution as an energy source for this cultivation.

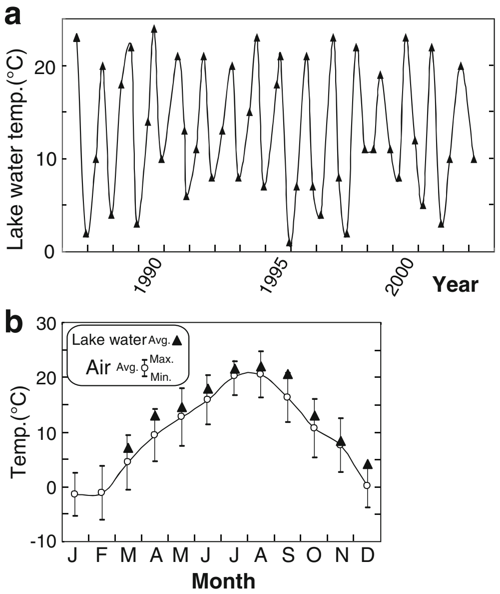

**Fig. 2** Temporal variation of surface water temperature of the crater lake observed by Kagoshima Local Meteorological Observatory (**a**). Water temperature data presented as monthly variation with air temperature data obtained at a nearby place of the same elevation reported in Kusumoto (1984) (**b**)

*M-2* The 9 K medium (e.g., Silverman and Lundgren 1959) was used for cultivation of iron-oxidizing bacteria. The composition of the basal salt solution for this cultivation was as follows: $K_2HPO_4$, 0.5 g; $(NH_4)_2SO_4$, 3.0 g; KCl, 0.1 g; $MgSO_4 \cdot 7H_2O$, 0.5 g; $FeSO_4 \cdot 7H_2O$, 50.0 g; $Ca(NO_3)_2$, 10.0 mg; and distilled water, 1,000 mL, and the solution was adjusted for pH 2.5 with sulfuric acid. This culture medium was also sterilized by autoclaving at 121 °C for 20 min.

Following cultivations, Gram staining was applied. The stained organisms were observed using phase contrast microscopy. Furthermore, XRF analyses of brown precipitations caused by the cultivations of the iron-oxidizing bacteria were made in the same way as those for the lake water suspension.

## Results and discussion

### Matter causing discoloration of Shinmoe-dake crater lake

Figure 3 shows that the hue of the brown discolored lake water is compatible with that of the brown suspension collected simultaneously from the water sample, demonstrating objectively that the brown discoloration was attributable to the brown suspension. Therefore, identification for the suspension implies the cause of the discoloration. Moreover, the brown suspension is likely to include various ferric hydroxide minerals such as goethite (FeOOH) and jarosite-K ($KFe_3(SO_4)_2(OH)_6$), as inferred from its color, and considering the pH and the chemical composition of the lake water.

Running the PHREEQ model with a mineral database, wateq4f (Saini-Eidukat and Yahin 1999) for the discolored lake water on 14 May 2009 shows that goethite and hematite ($Fe_2O_3$) are largely supersaturated, jarosite-K and maghemite ($Fe_2O_3$) are slightly supersaturated, and jarosite-Na ($NaFe_3(SO_4)_2(OH)_6$) and hydronium-jarosite ($(H_3O)Fe_3(SO_4)_2(OH)_6$) are not saturated (undersaturation). From this thermodynamic evaluation, it is difficult to determine which mineral is the main cause of the brownish precipitation. Furthermore, slow kinetics for precipitation reactions at the low temperature of the Shinmoe-dake crater lake is likely to preclude formation of minerals such as hematite and maghemite. Nevertheless, we deduce that at least some minerals, for example goethite and jarosite-K, were able to precipitate from the crater lake water on 14 May 2009.

The result of the XRF analysis of the suspension sample (Fig. 4 a) shows that it contains Fe, S, and Si. However, K and Na, which are usually included as the major monovalent cation components of jarosite, were not detected. Semi-quantitative analysis shows that Fe is clearly a major component and that S and Si are minor components but are likely to be present at concentrations of several percent or so. It is therefore inferred that the brownish suspension will be neither

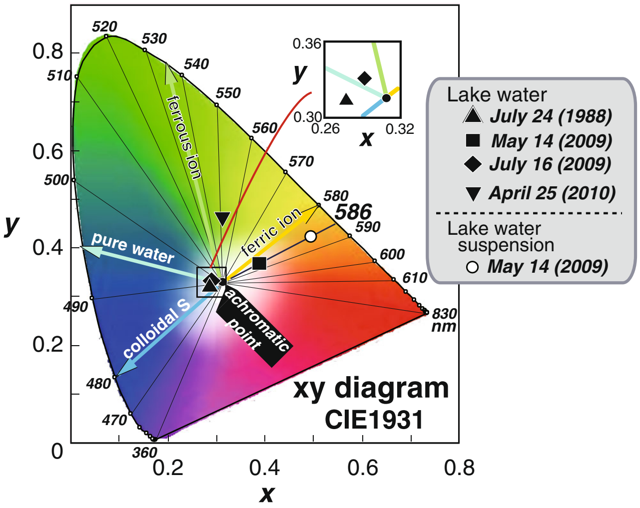

**Fig. 3** Colorimetric data of filtered lake water suspension using a colorimeter and of lake waters extracted from digital photographs presented in Fig. 1c on a xy-chromaticity diagram established by the Commission Internationale d'Eclairage (CIE) in 1931. *Colored vectors expressing hues* related to coloration of crater lakes on active volcanoes are cited from Ohsawa et al. (2010) for colloidal sulfur, and ferrous and ferric ions and Ohsawa et al. (2003) for pure water

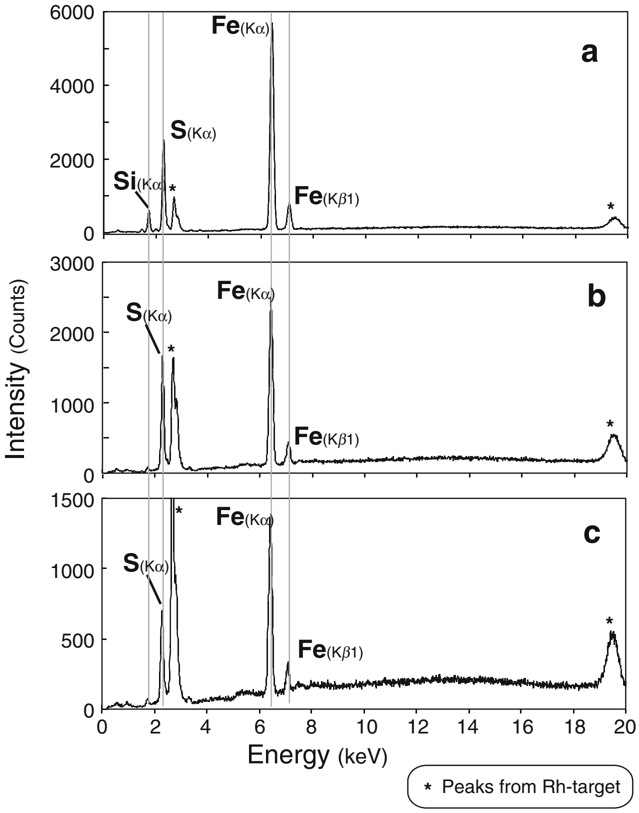

**Fig. 4** Results of X-ray fluorescence analysis of the brown suspension sample collected on 14 May 2009 (*a*) and brownish deposits following cultivations of iron-oxidizing bacteria using samples of 14 May 2009 and 16 July 2009 (*b* and *c*, respectively)

jarosite-K nor goethite if the S signal of Fig. 4 a is not from elemental sulfur ($S^0$) but is derived from sulfate ($SO_4$). Another possible mineral is schwertmannite ($Fe_8O_8(OH)_{8-2x}(SO_4)x$ [$1 \le x \le 1.75$]), which has been identified frequently in acid mine drainage (AMD) waters.

The FT-IR analysis yields persuasive evidence for the validity of the suggestion presented above for minerals in the brownish suspension sample. First, as shown in the IR spectrum pattern (Fig. 5), absorption peaks from elemental sulfur ($S^0$) are not detected. Therefore, sulfur in the sample exists as sulfate. Based on this observation and the lack of evidence for IR peaks below 1,000 cm$^{-1}$ characteristic of goethite, this mineral cannot be present in the brownish precipitate. Further, neither hematite nor maghemite were identified in the IR spectrum. The IR absorption spectrum of the sample does suggest the presence of jarosite and schwertmannite with a strong broad absorption at about 3,380 cm$^{-1}$ consistent with jarosite and another feature at 3,250 cm$^{-1}$ consistent with schwertmannite. A strong absorption at >1,000 cm$^{-1}$ is also consistent with schwertmannite. The geochemical speciation, XRF analysis, and the FT-IR spectra all point to schwertmannite as the origin of the brown suspension causing the discoloration of Shinmoe-dake crater lake from the end of April to the beginning of July 2009.

Figure 6 shows a stability diagram for schwertmannite precipitation of the discolored lake water drawn using the function of the PHREEQ model to derive activities of dissolved chemical species using thermodynamic data cited in Majzlan et al. (2004). Schwertmannite is shown to be oversaturated under the crater lake conditions of 14 May 2009, consistent with our analytical identification of the species.

## Origin of schwertmannite in Shinmoe-dake crater lake

A marked characteristic of the chemistry of the brownish-colored lake water on 14 May 2009 is the high concentration of $Fe^{3+}$ (Table 2). Unfortunately, we lack measurements of the $Fe^{3+}$ concentration in the lake water prior to the discoloration. However, its abundance can be inferred to some degree from the chemical data of the lake water on 16 July 2009, when it reverted to its former greenish-blue color. In this case, we see that the brownish-colored lake water is richer in $Fe^{3+}$ and $SO_4^{2-}$ and has a lower pH than the greenish-blue water, but otherwise the composition is similar. Before discussing the schwertmannite appearance, it is necessary to explain this unique supply of the chemical constituents into the lake water. The water temperature of 22 °C is too low to suggest an increase in hydrothermal input into the lake. This is corroborated by the lack of change in contents of rock-forming cations such as Mg and Ca (but excluding $Fe^{3+}$) in the lake water. In addition, an increased hydrothermal input should have increased $Fe^{2+}$ in the lake water. We therefore cannot explain

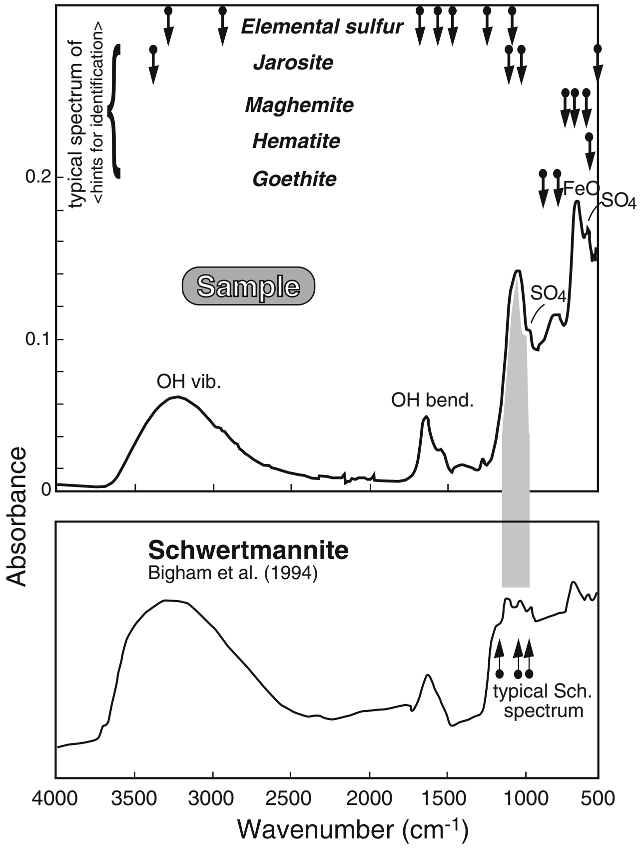

**Fig. 5** Result of FT-IR analysis of the brown suspension sample collected on 14 May 2009 with a FT-IR spectrum of schwertmannite (Bigham et al. 1994) and some hints for the mineral identification cited from Choo and Lee (2002), Regenspurg et al. (2004), Bishop and Murad (2005), Zhang et al. (2009), and Equeenuddin et al. (2009)

the increased $Fe^{3+}$, $SO_4^{2-}$, and protons ($H^+$) in the lake water by magmatic–hydrothermal processes. In contrast, a biotic process as described below can account for the schwertmannite ($Fe_8O_8(OH)_6(SO_4)$) precipitation from the crater lake water simultaneously with supply to the lake of water of $Fe^{3+}$ and $SO_4^{2-}$.

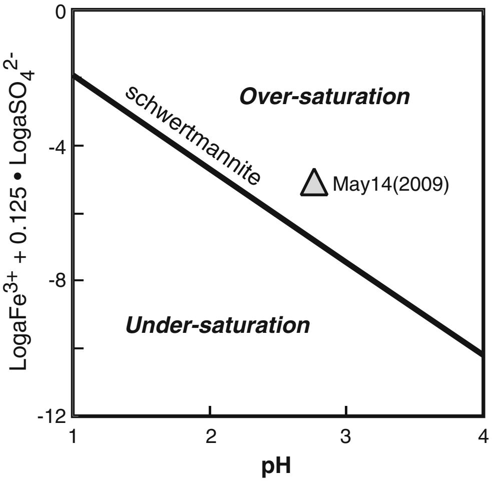

**Fig. 6** Plot of logarithm of the $Fe^{3+}$ and $SO_4^{2-}$ activities versus pH for the lake water sample on 14 May 2009. The solubility line of schwertmannite was calculated using thermodynamic data cited from Majzlan et al. (2004). Activities for plotting on this diagram are calculated using an aqueous geochemical modeling program: Web-phreeq (Saini-Eidukat and Yahin 1999)

Schwertmannite is typically found as a secondary iron mineral in pyrite-oxidizing environments. Iron-oxidizing bacteria are often associated with its formation, although it has been synthesized abiotically in the laboratory (e.g., Singer and Stumm 1970; Bigham et al. 1996; Childs et al. 1998; Kawano and Tomita 2001; Schroth and Parnell 2005; Hedrich et al. 2011). The reactions leading from pyrite oxidation to schwertmannite precipitation are:

$$4\cdot FeS_2[\mathbf{pyrite}] + 3.5\cdot O_2 + H_2O = Fe^{2+} + 2\cdot SO_4^{2-} + 2\cdot H^+ \quad (1)$$

$$4\cdot Fe^{2+} + O_2 + 4\cdot H^+ = 4\cdot Fe^{3+} + 2\cdot H_2O \quad (2)$$

$$8\cdot Fe^{3+} + SO_4^{2-} + 14\cdot H_2O = Fe_8O_8(OH)_6(SO_4)[\mathbf{schwertmannite}] + 22\cdot H^+ \quad (3)$$

The rate-determining step for the pyrite dissolution reactions corresponds to Eq. (2) (Singer and Stumm 1970). This slow chemical reaction is accelerated, together with reaction (1), by iron-oxidizing bacteria (Silvermann 1967). Although the oxidation of $Fe^{2+}$ to $Fe^{3+}$ by aqueous oxygen is hindered in strongly acidic conditions, acidophilic iron-oxidizing bacteria such as *Acidithiobacillus ferrooxidans* reportedly increase the rate of this oxidation reaction $10^6$-fold. The bacteria are enzymatically able to form $Fe^{3+}$ with ease (Lacey and Lawson 1970).

At Yugama crater lake of Kusatsu-Shirane Volcano, Japan, an iron-oxidizing bacterium (*A. ferrooxidans*) was isolated from acid-$SO_4$ streams with water temperature in the range 16.4–22.2 °C and pH from 2.0–2.9 (Takano et al. 1997). The aquatic environment of the Yugama streams closely resembles that of Shinmoe-dake crater lake (see Table 2). This tends to corroborate the likely involvement of bacteria in schwertmannite formation in Shinmoe-dake crater lake.

Figure 7a shows a photograph of culture solutions after iron-oxidizing bacteria cultivation using samples of lake waters with lakebed sediments sampled on 14 May and 16 July 2009. Brownish precipitates were clearly formed in both culture solutions except for the control solution (Fig. 7a-3); thus, we regard both samples a-1 and a-2 as having tested positive for the iron-oxidizing bacteria. Both precipitates have the same XRF spectrum pattern (Fig. 4 b, c) as the brownish suspension in the crater lake water sample taken on 14 May

**Table 2** Chemical data of Shinmoe-dake lake water samples with surface temperature

| Date | Tw (°C) | pH | Cl (mg/L) | $SO_4$ (mg/L) | Na (mg/L) | K (mg/L) | Mg (mg/L) | Ca (mg/L) | $Fe^{3+}$ (mg/L) | $Fe^{2+}$ (mg/L) |
|---|---|---|---|---|---|---|---|---|---|---|
| May 14, 2009 | 22 | 2.76 | 2.0 | 343 | 4.0 | 1.0 | 4.0 | 63.0 | 32.2 | n.d. |
| July 16, 2009 | n.m. | 2.97 | 1.7 | 276 | 3.1 | 0.4 | 3.7 | 55.2 | 4.6 | n.d. |
| April 25, 2010 | 14.7 | 3.15 | 56.6 | 685 | 46.4 | 9.3 | 37.0 | 183 | 5.5 | 5.8 |

*n.d.* not detected, *n.a.* not analyzed, *n.m.* not measured

2009 (Fig. 4 a). Although it was difficult to stain them with Gram staining, it was recognized that organisms of about 1 μm long growing in the culture solutions are thought to be an iron-oxidizing bacteria. Therefore, we can infer that Shinmoe-dake crater lake is a habitat of iron-oxidizing bacteria and that the schwertmannite formation is consistent with the presence of microbial Fe oxidizing activity.

In the culture solutions for the sulfur oxidizing bacteria, milky clouding around elemental sulfur from the medium was recognized as bacteria, just as observed in previous works (e.g., Schaeffer et al. 1963; Weiss 1973). Figure 7b shows a photomicrograph of the stained samples after cultivation of the sulfur-oxidizing bacteria. Many organisms of about 1 μm long isolated from the milky part in the culture solution, which are negative in Gram staining, are thought to be sulfur-oxidizing bacteria. This suggests strongly that the sulfur-oxidizing bacteria in the crater lake participate in the origin of the high concentrations of sulfate and protons as follows (Takano et al. 1997):

$$2\,S + 3\,O_2 + 2\,H_2O \rightarrow 2\,H_2SO_4 \left(= 2\,H^+ + 2\,HSO_4{}^- = 4\,H^+ + 2\,SO_4{}^{2-}\right) \tag{4}$$

in the period before the onset of phreatic activity such as that reported by Ohsawa (1992). Moreover, the existence of the sulfur-oxidizing bacteria consumes elemental sulfur ($S^0$). The energy source implies that the Shinmoe-dake crater lake will have bluish color because of the suspended colloidal sulfur similar to the active crater lakes of Aso and Kusatu-Shirane volcanoes (Onda et al. 2003; Ohsawa et al. 2010). The next important problem to examine is the origin of pyrite ($FeS_2$) that participated in the schwertmannite formation. Judging from the sudden appearance of schwertmannite in the lake water, the lake does not always have pyrite in it. As described previously, the brownish discoloration of the crater lake water in April 2009 occurred 8 months after the 22 August 2008 eruption. Clay-rich tephra consisting of non-juvenile lithic fragments with various degrees of hydrothermal alteration include many fine crystals of pyrite (Geshi et al. 2010). Based on the distribution of tephra fall (Geshi et al. 2010), we infer that pyrite bearing tephra fell into Shinmoe-dake crater lake. This is corroborated indirectly by the presence of pyrite peaks in the XRD pattern of the lakebed sediments sampled on 14 May 2009 (Fig. 8). Pyrite ($FeS_2$) detected with schwertmannite ($Fe_8O_8(OH)_6(SO_4)$) in this sediment sample is not precipitated directly from an anoxic bottom lake water but is instead accumulated onto the bottom with schwertmannite. Therefore, this pyrite could be derived from the tephra fall.

If pyrite ($FeS_2$) in the tephra ejected by the 2008 eruption is the substrate for the growth of the iron-oxidizing bacteria as described above, then we still must explain why the brownish discoloration of the crater lake water occurred about 8 months after the eruption (from the end of April to the beginning of July 2009). Excluding thermophiles, most iron-oxidizing bacteria have optimal growth temperatures at around 30 °C (Daoud and Karamanev 2006; Kim et al. 2008), but they can grow slowly at temperatures below the optimal value (e.g., 4 °C; Ahonen and Tuovinen 1989). Because the water temperature of Shinmoe-dake crater lake in the cold season (December–February) is lower than such a minimal growth temperature, extrapolating from the monthly variation of water temperature of the crater lake presented in Fig. 2b, bacterial growth in such a severe cold environment will be delayed. Regarding discoloration after the eruption on 22 August 2008, we suggest that the iron-oxidizing bacteria resumed their activity in the following spring (end of April 2009). This resumption of activity caused the formation of the brownish ferric mineral schwertmannite. At the time of tephra fall onto Shinmoe-dake crater lake during the eruption on 27 March 2010 (see Table 1), the lake water, whose temperature at on 25 April was 14.7 °C, changed immediately to a brown color after only about 1 week.

Finally, the chemical properties of the Shinmoe-dake crater lake water sampled on 25 April 2010 (see Table 2) must be discussed. They are markedly different from data obtained from samples taken on 14 May and 16 July 2009. Compared with these, concentrations of main chemical constituents, especially $Ca^{2+}$ and $SO_4{}^{2-}$, had increased remarkably. Ferrous ion ($Fe^{2+}$) appeared, but the water temperature and acidity did not increase markedly. Consequently, subaqueous input of underground thermal water, as discussed before, is difficult to infer. Here, we suggest the involvement of a leachate of water-soluble components of ejected volcanic ash.

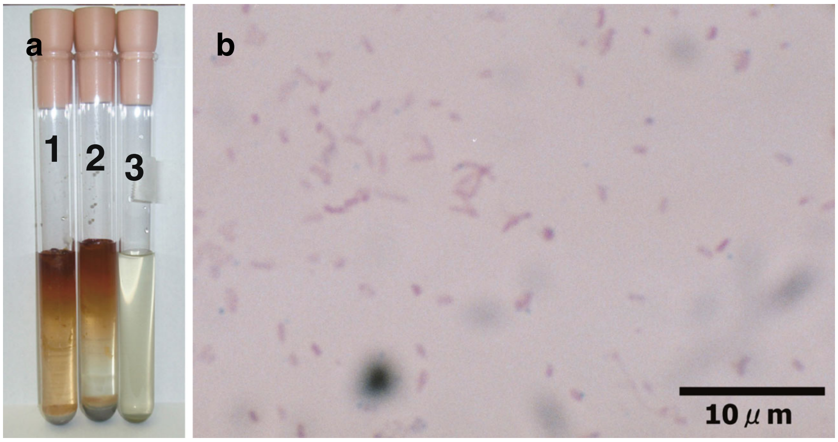

**Fig. 7** Test solutions of iron-oxidizing bacteria cultivation using samples of lakebed sediments with lake water collected on 14 May and 16 July 2009 (**a**-*1* and **a**-*2*, respectively; **a**-*3* is the control solution). Photomicrograph observed using phase-contrast microscopy for a stained sample (14 May 2009) of sulfur-oxidizing bacteria cultivation (**b**)

Water-soluble material is known to adhere generally to particle surfaces of volcanic ash (e.g., Taylor and Stoiber 1973; Smith et al. 1983; Nogami et al. 2001). At Mt. Shinmoe-dake, Geshi et al. (2010) reported that a gypsum ($CaSO_4 \cdot 2H_2O$)-like precipitate was crystallized from water that had washed hydrothermally altered tephra ejected by the 2008 eruption. Because an ash fall occurred on 30 March 2010 (see Table 1), about 1 month before the water sampling on 25 April 2010, it is possible that water-soluble components of the discharged ash were dissolved into rainfall.

## Conclusions

A drastic change in lake water color from blue-green to brown was observed at the summit crater lake of Mt. Shinmoe-dake, Kirishima Volcano about 8 months after the 2008 eruption. It continued for about 2 months from the end of April to the beginning of July 2009. We have assessed the factors leading to the brown discoloration of the lake water body using geochemical and microbiological analyses of samples collected from the crater lake. Based on the results we obtained, we arrived at the following conclusions:

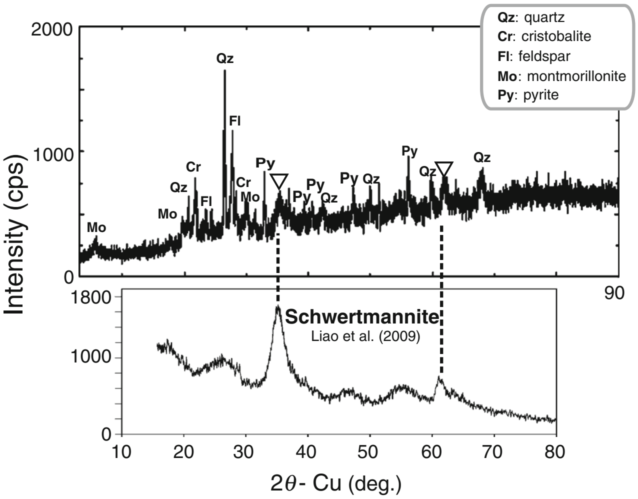

**Fig. 8** Result of powder X-ray diffraction (XRD) analysis of a fine fraction of lakebed sediment sampled on 14 May with an XRD pattern of schwertmannite (Liao et al. 2009)

1. The discoloration was attributed to a brownish color suspension that had formed in the lake water. This matter was identified as schwertmannite ($Fe_8O_8(OH)_6(SO_4)$) using XRF and FT-IR analyses of the suspension sample and a thermodynamic calculation based on chemical analyses of the lake water.
2. A cultivation test of iron-oxidizing bacteria for the sampled lake water with lakebed sediment and XRF analysis of its brownish products showed that Shinmoe-dake crater lake is the habitat of iron-oxidizing bacteria. These bacteria likely participated in the schwertmannite formation.
3. The mineral that served as an energy source for the iron-oxidizing bacteria was inferred to be pyrite ($FeS_2$) sourced from hydrothermally altered tephra that was ejected and fell into the lake during the 2008 eruption. The 8-month delay of the discoloration from the pyrite-including ash fall is explained by low bacterial activity during the winter when water temperatures were low.

We thus view the brownish discoloration of the summit crater lake of Mt. Shinmoe-dake as the result of a coupled volcanogenic–microbial process.

Results further suggest that the usual greenish-blue color of the Shinmoe-dake crater lake water occurred because of the presence of suspended colloidal elemental sulfur ($S^0$) as observed also at the crater lakes of Aso and Kusatsu-Shirane volcanoes. The other cultivation test for sulfur-oxidizing bacteria suggested that a sulfur-oxidizing bacterium inhabiting the crater lake produces sulfate and protons from elemental sulfur. Consequently, pH and water temperature can be somewhat decoupled in that low pH does not necessarily connote increased hydrothermal input into the lake.

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