

Temporal variation in the chemical composition (HCl/SO₂) of volcanic gas associated with the volcanic activity of Aso Volcano, Japan

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Continuous monitoring of volcanic gas at Aso volcano using volatile traps from 2002 to 2011 revealed that higher HCl/SO₂ ratios are associated with increasing volcanic activities. The HCl/SO₂ ratios obtained during the observation period can be categorized into three levels: high (≥ 0.2), intermediate (0.1~0.2), and low (≤ 0.1). From March 2003 to August 2005, and from December 2008 to August 2011, the HCl/SO₂ ratios were generally at intermediate levels, with sporadic high HCl/SO₂ ratios associated with small ash emissions. During other periods with no ash emission, the HCl/SO₂ ratios were constantly low (~ 0.02 in average). The HCl/SO₂ ratio and the water level in the crater lake are correlated; the lower the water level in the crater lake, the higher the HCl/SO₂ ratio. The reduced scrubbing effect of HCl from the intensely-emitted volcanic gas by a smaller amount of water is likely to generate high HCl/SO₂ ratios of volcanic gas. In addition, evaporation of HCl from the water of the crater lake with extreme acidity may contribute to high HCl/SO₂ ratios.

Key words: Volcanic gas, volatile trap, ash emission, chloride, sulfate.

1. Introduction

The chemical composition of volcanic gases is known to vary depending on the volcanic activity. Among the various chemical compositions, the ratio of HCl/SO₂ or Cl/S is often used as an indicator of volcanic activity. However, the variation of these ratios with volcanic activity differs among volcanoes: increases (e.g., Hirabayashi *et al.*, 1982; Aiuppa *et al.*, 2004) and decreases (e.g., Noguchi and Kamiya, 1963; Taran *et al.*, 2002; Duffel *et al.*, 2003) of these ratios are reported to be associated with increasing volcanic activity. In the case of Aso volcano, high HCl/SO₂ ratios were observed soon after intense eruptive activities, and subsequently decreased after the activities ceased (Iwasaki *et al.*, 1962; Ohsaka *et al.*, 1978, 1984). Although these observations described sporadically the relation between the HCl/SO₂ ratio and volcanic activity, continuous and longer observation is needed to further understand this relation.

We have monitored the HCl/SO₂ ratio of Aso volcano by a volatile trap method (Noguchi and Kamiya, 1963; Goff *et al.*, 1998; Witter *et al.*, 2004), for nine years, during which time ash emissions occurred repeatedly. This method has the advantage that continuous data of the HCl/SO₂ ratio can be obtained compared with sporadic data obtained by spectroscopic methods such as Fourier transform infrared (FT-IR) spectroscopy (e.g., Mori and Notsu, 2008).

2. Aso Volcano

Aso volcano (Fig. 1) is an active volcano with a huge caldera in the central part of Kyushu Island, southwest Japan. At the summit of Mt. Nakadake, which is one of the post caldera cones, seven craters are formed. Among these craters, recent activities of Aso volcano have occurred at the northernmost crater (first crater). The bottom of this crater is filled with hot water, forming a crater lake. The crater has some intense fumaroles on its southern crater wall. Fumarolic activity is also observed at the bottom of the crater lake when its water almost dries up.

Mt. Nakadake is one of the most active volcanoes in Japan. Recent significant eruptive activities have taken place in 1974 to 1980, 1985, and 1988 to 1995. After an inactive period from 1996 to 2003, ash emissions occurred in the first crater on July 10, 2003, and January 14, 2004 (Miyabuchi *et al.*, 2008). Small ash emissions were frequently observed between April and August 2005 (Miyabuchi *et al.*, 2008), and relatively large ones among them were observed on April 14, June 10–12, June 21, and July 25 in 2005. A small ash deposit was observed on February 18, 2008 (Miyabuchi and Ikebe, 2008). According to reports by the Japan Meteorological Agency (hereafter, JMA), small ash emissions were recently observed on February 4, 2009, and on May 16, 2011.

Terada *et al.* (2008) monitored the water level in the crater lake precisely and described that although the water level in the crater lake increases due to heavy precipitation during the rainy and typhoon seasons, the water level fluctuation in other seasons does not depend on precipitation directly. They speculated that the water is mainly supplied by the hydrothermal system.

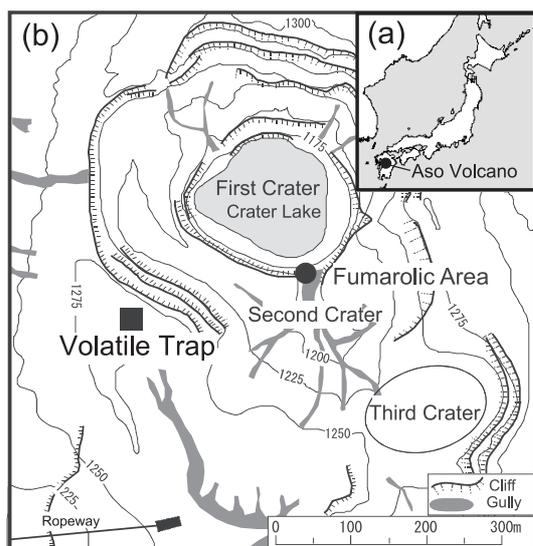


Fig. 1. Location of Aso volcano (a), and the observation point (b).

3. Measurement

To monitor the relative concentration of chemical components (SO_2 and Cl) in volcanic gas, we used a volatile trap (alkaline trap) method. The trap contains a solution of 1N KOH that absorbs the acidic components of volcanic gas. We put traps in a dome built as a volcano shelter at the southwest rim of the first crater of Mt. Nakadake (Fig. 1), from November 2002 to August 2011. To avoid ash contamination, we put the traps in a box that allowed air circulation only through slits in the side of the box. The traps were sampled at intervals ranging from one to two months until 2007; they were then subsequently sampled every three months. At the beginning, we placed one trap for each period, and later we placed a set of three traps for each period after July 2003.

The concentrations of chloride ion (Cl^-) and sulfate ion (SO_4^{2-}) in the volatile trap solutions were measured using an ion chromatograph (Dionex, DX-100) at Kyushu University, after the following treatments. First, the volatile trap solutions were filtered with a $0.45 \mu\text{m}$ DISMIC-25cs cellulose filter. Second, the solutions were filtered with a Dionex On Guard II H filter to neutralize the highly alkaline solution. The concentration of trapped components ranged between $10^2 \sim 10^4$ ppm for SO_4^{2-} and $10^0 \sim 10^3$ ppm for Cl^- , respectively.

The major sources of gas reaching the trap are likely to be the fumaroles at the southern crater wall and the lake surface. Fumarole gases have higher HCl/SO_2 ratios than the lake gases (Shinohara *et al.*, 2010). A fluctuation in the mixing ratio of gases from these sources may cause a short-term fluctuation of the composition of gas reaching the trap. However, since each observation period is long enough to average out this short-term fluctuation, we consider that the HCl/SO_2 ratio in each observation period represents the HCl/SO_2 ratio of volcanic gases emitted at the summit area of Mt. Nakadake, averaged in time and space. Consequently, we cannot distinguish if the observed changes in the HCl/SO_2 ratio are due to changes in the ratio of fumarole gases, lake gases, or both.

4. Results

The HCl/SO_2 molar ratios, measured as the $\text{Cl}^-/\text{SO}_4^{2-}$ ratios of the solution in the volatile traps, are tabulated in Table 1. The average ratio during each period ranges between 0.01 and 0.7, which are within the values of high-temperature ($>500^\circ\text{C}$) volcanic gases from arc volcanoes (Fischer, 2008).

The temporal variation of the HCl/SO_2 ratios of the volcanic gas from November 2002 to August 2011 is divided into three periods (Fig. 2): March 2003 to August 2005 (Period A), September 2005 to December 2008 (Period B), and December 2008 to August 2011 (Period C). During Period B, significantly low HCl/SO_2 ratios with an average of 0.02 were observed. In contrast, during Periods A and C, the HCl/SO_2 ratios were generally between 0.1 and 0.2, which we refer to as an intermediate ratio. In addition, high HCl/SO_2 ratios (≥ 0.2) were observed to be associated with all the ash emissions during Periods A and C. Such high ratios were also observed subsequently after ash emissions during Periods A and C. The HCl/SO_2 ratio remained low for the ash emission on February 2008 during Period B.

5. Discussion

The observed range of the HCl/SO_2 ratio (0.01–0.7) is consistent with preceding observations of volcanic gas at Aso volcano by direct sampling, a volatile trap method, and FT-IR spectroscopy. High HCl/SO_2 ratios of the volcanic gas up to 0.6 were reported after the intense volcanic activities in 1958 (Iwasaki *et al.*, 1962) and 1977 (Ossaka *et al.*, 1978). Subsequent monitoring during six months after the eruption in 1977 gave HCl/SO_2 ratios of 0.1–0.2 (Ossaka *et al.*, 1978). More than a year after the eruptive activity in January 1980, the HCl/SO_2 ratios observed by volatile traps were generally decreasing and were between 0.02–0.3 from May to December 1981 (Ossaka *et al.*, 1984). Ossaka *et al.* (1984) assumed that the composition of volcanic gas changed since part of its chemical composition dissolved in the water of the crater lake that appeared during this period. In addition, after the eruptive activity from 1988 to 1995 ceased, several low HCl/SO_2 ratios less than 0.1 were reported between 1996 and 2003 (Mori and Notsu, 1997, 2008; Ono *et al.*, 1999; Hirao *et al.*, 2001).

The result of the temporal variation in the HCl/SO_2 ratios, together with those of volcanic gas by FT-IR spectroscopy since 1996, are compared to the variation in the “water amount of the crater lake” in Fig. 2; JMA reports the proportion of the lake surface area relative to the maximum lake surface area as the “water amount of the crater lake”. High and intermediate HCl/SO_2 ratios are observed during the periods of low water level, while low HCl/SO_2 ratios are observed during the periods of high water level. In addition, high HCl/SO_2 ratios, except for those in 2005, roughly correlate with a high fumarole temperature represented by the temperature of the southern crater wall, which is considered to reflect largely the volcanic heat transfer to the summit area. These relations can be explained by the interaction of volcanic gas emission with the hydrothermal system beneath the crater, assuming that the water level in the crater is an indicator of the amount of water in the hydrothermal system. Mori and Notsu (2008) reported that the low HCl/SO_2

Table 1. The molar ratios of $\text{Cl}^-/\text{SO}_4^{2-}$ of solutions in the volatile trap samples.

Start	End	N^*	$\text{Cl}^-/\text{SO}_4^{2-}$ (mol/mol)		
11/28/2002	1/7/2003	1	0.050		
11/28/2002	3/11/2003	1	0.083		
1/7/2003	4/16/2003	1	0.089		
3/11/2003	5/15/2003	1	0.15		
4/16/2003	7/31/2003	1	0.18		
5/15/2003	7/31/2003	1	0.14		
7/31/2003	8/29/2003	3	0.046	0.067	0.083
8/29/2003	10/15/2003	3	0.19	0.20	0.20
10/15/2003	2/8/2004	3	0.45	0.46	0.52
2/8/2004	2/24/2004	3	0.36	0.44	0.48
2/24/2004	4/28/2004	3	0.36	0.42	0.48
4/28/2004	6/11/2004	3	0.11	0.12	0.12
6/11/2004	7/27/2004	3	0.47	0.47	0.48
7/27/2004	9/13/2004	3	0.15	0.16	0.17
9/13/2004	12/1/2004	3	0.025	0.027	0.028
12/1/2004	2/15/2005	3	0.061	0.067	0.078
2/15/2005	5/10/2005	3	0.35	0.36	0.45
4/18/2005	5/10/2005	3	0.084	0.099	0.14
5/10/2005	6/13/2005	3	0.22	0.22	0.22
5/10/2005	7/14/2005	3	0.19	0.21	0.22
6/13/2005	8/25/2005	3	0.16	0.18	0.18
7/14/2005	8/25/2005	3	0.20	0.20	0.22
8/25/2005	10/28/2005	3	0.034	0.035	0.037
10/28/2005	11/28/2005	3	0.0069	0.0069	0.0070
11/28/2005	1/17/2006	2	0.0084	0.010	
1/17/2006	3/7/2006	3	0.010	0.011	0.014
3/7/2006	4/18/2006	3	0.017	0.020	0.021
4/18/2006	6/5/2006	3	0.022	0.023	0.046
6/5/2006	7/26/2006	3	0.057	0.074	0.078
7/26/2006	9/20/2006	3	0.0053	0.0060	0.0077
9/20/2006	11/15/2006	2	0.012	0.014	
11/15/2006	1/14/2007	3	0.032	0.035	0.040
1/14/2007	3/12/2007	3	0.011	0.015	0.015
3/12/2007	6/2/2007	3	0.025	n.d.	n.d.
6/2/2007	8/10/2007	3	0.013	0.018	0.019
6/2/2007	9/11/2007	3	0.011	0.012	0.013
8/10/2007	12/20/2007	3	0.021	0.023	0.023
9/11/2007	12/20/2007	3	0.019	0.022	0.023
12/20/2007	3/27/2008	3	0.019	0.020	0.020
3/27/2008	6/28/2008	3	0.046	0.048	0.053
6/28/2008	9/29/2008	3	0.044	0.045	0.055
9/29/2008	12/15/2008	3	0.018	0.022	0.038
12/15/2008	3/10/2009	3	0.59	0.71	0.80
3/10/2009	6/30/2009	3	0.13	0.14	0.18
6/30/2009	10/8/2009	3	0.082	0.10	0.19
10/8/2009	1/19/2010	3	0.13	0.14	0.15
1/19/2010	4/8/2010	3	0.20	0.22	0.23
4/8/2010	7/8/2010	3	0.21	0.21	0.22
7/8/2010	10/5/2010	3	0.072	0.078	0.080
10/5/2010	12/20/2010	3	0.30	0.31	0.33
12/20/2010	3/1/2011	3	0.068	0.076	0.078
3/1/2011	5/20/2011	3	0.26	0.29	0.33
5/20/2011	8/19/2011	3	0.068	0.11	0.11

*Number of samples.

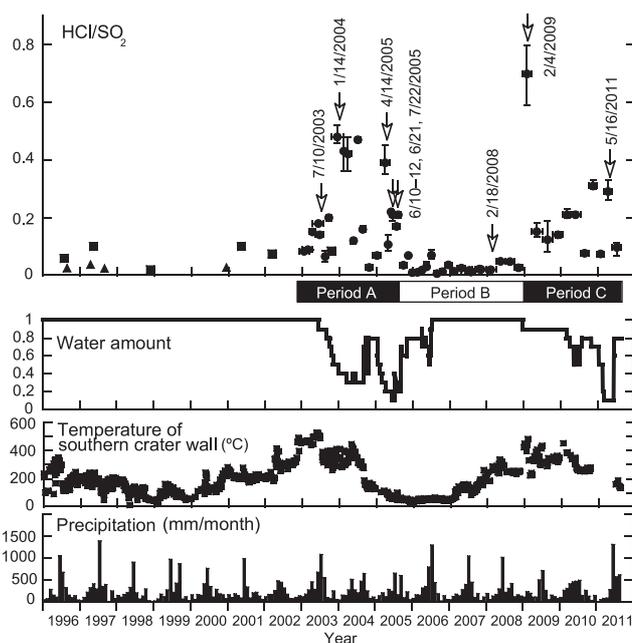


Fig. 2. The uppermost diagram shows the temporal variation of the HCl/SO_2 ratio. Circles are the results in this study; horizontal error bars indicate the observation period, and vertical error bars indicate the maximum and minimum values for each period. Triangles (Ono *et al.*, 1999; Hirao *et al.*, 2001) and squares (Mori and Notsu, 1997, 2008) are those by FT-IR spectroscopy. The arrows indicate ash emissions. The temporal variation of HCl/SO_2 ratio was divided into three periods (Periods A, B, and C) (see text). The other diagrams show the water amount in the first crater, the temperature of the southern crater wall, and the precipitation at Mt. Aso, respectively, reported by the Japan Meteorological Agency.

ratio during the period of high water level is explained by the scrubbing of HCl off the volcanic gas in the hydrothermal system, because HCl is more soluble in water compared with SO_2 . The scrubbing effect of HCl depends on the amount of water interacting with the volcanic gas and the intensity of volcanic gas emission (i.e. the total flux of volcanic gas supplied to the summit area). Either a decreasing amount of water, or an intensification of gas emission, or both, decrease the scrubbing effect by shortening the interaction time of bubbling gas and water. In a shorter interaction time, the gas passing through the water loses less HCl by dissolution into the water. That is, during inactive periods, in which gas emission is weak with less heat transfer and enough water remains, HCl is mostly scrubbed off the volcanic gas and the residual gas with a low HCl/SO_2 ratio is emitted into the air. On the contrary, during active periods, in which an intense gas emission occurs accompanied by much heat transfer, and the amount of water decreases due to the heat, volcanic gas with a high HCl/SO_2 ratio is emitted into the air because little HCl is scrubbed off. This interpretation is consistent with the variation in SO_2 flux by JMA (<http://www.seisvol.kishou.go.jp/tokyo/volcano.html>) which started in March, 2007. The SO_2 flux showed an increasing trend from 2007 to 2011, corresponding to the increasing trend in the HCl/SO_2 ratio, although the short-term correlation between them is not clear, partly due to the difference in the observation methods.

Although the general trend of a higher HCl/SO_2 ratio

which corresponds to a lower water level in the crater is obvious, each peak of high HCl/SO₂ ratio tends to precede a minimum water level by several months. Sudden increases in the HCl/SO₂ ratio were observed with the small eruptions of January 2004, April 2005 and February 2009. Following the increasing peak of the HCl/SO₂ ratio, the water level in the crater reached a minimum delayed by several months after the eruptions in January 2004 and April 2005. A high water level was maintained after the eruption in February 2009. The delay can be explained by the following. The water needs time to decrease in response to the heat accompanying an intensification of volcanic activity, whereas the HCl/SO₂ ratio of the observed gas reflects the intensification of gas emission immediately by a reduction of the scrubbing of HCl off the gas as described earlier. In contrast, when the water level rose suddenly due to heavy precipitation, such as in September 2004 and September 2005, the HCl/SO₂ ratio decreased rapidly. This is in agreement with the intense scrubbing of HCl off the volcanic gas by fresh water supplied by the heavy precipitation.

In addition to the mechanism discussed above, evaporation of HCl from the water of the crater lake may contribute to an increase of HCl/SO₂ ratio, according to the study by Rowe *et al.* (1992) at Poás volcano. Rowe *et al.* (1992) suggested that extreme acidity causes HCl vapors to be released from the lake surface at a relatively low temperature (<90°C) on the basis of vapor pressure for HCl solutions, which increases with higher acidity and higher temperature. At Aso volcano, Shinohara *et al.* (2010) suggested evaporation of HCl from the crater lake. Here, we compare the observed HCl/SO₂ ratio of the volcanic gas with the acidity and temperature of the water of the crater lake (Ohsawa *et al.*, 2010) in April and August 2003, which is in Period A, and in March and July 2007, which is in Period B. Although the water in both periods has an extreme acidity (pH < 0.4), the water during Period A is characterized by a higher acidity and higher temperature compared with that in Period B (Ohsawa *et al.*, 2010); this implies, following Rowe *et al.* (1992), that more active HCl evaporation is expected during Period A than Period B. Since the observed HCl/SO₂ ratio is higher in Period A than that in Period B, the relation of the observed HCl/SO₂ ratio with the acidity and temperature of the water of the crater lake, agrees qualitatively with Rowe's hypothesis. However, we cannot estimate the contribution of HCl evaporation quantitatively at present, and further investigation of this hypothesis is needed.

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References

Aiuppa, A., S. Bellomo, W. D'Alessandro, C. Federico, M. Ferri, M., and M. Valenza, Volcanic plume monitoring at Mount Etna by diffusive (passive) sampling, *J. Geophys. Res.*, **109**, D21308, doi:10.1029/2003JD004481, 2004.

Duffel, H. J., C. Oppenheimer, D. M. Pyle, Bo Galle, A. J. S. McGonigle,

and M. R. Burton, Changes in gas composition prior to a minor explosive eruption at Masaya volcano, Nicaragua, *J. Volcanol. Geotherm. Res.*, **126**, 327–339, 2003.

Fischer, T. P. Fluxes of volatiles (H₂O, CO₂, N₂, Cl, F) from arc volcanoes, *Geochem. J.*, **42**, 21–38, 2008.

Goff, F., C. J. Janik, H. Delgado, C. Werner, D. Counce, J. A. Stimac, C. Siebe, S. P. Love, S. N. Williams, T. Fischer, and L. Johnson, Geochemical surveillance of magmatic volatiles at Popocatepetl volcano, Mexico, *Geol. Soc. Am. Bull.*, **110**, 695–710, 1998.

Hirabayashi, J., J. Ohsaka, and T. Ozawa, Relationship between volcanic activity and chemical composition of volcanic gases—A case study on the Sakurajima Volcano, *Geochem. J.*, **16**, 11–21, 1982.

Hirao, T., Y. Fujimitsu, J. Nishijima, and S. Ehara, Remote observation of volcanic gases by FT-IR at Aso volcano, *Geotherm. Volcanol. Res. Rep. Kyushu Univ.*, **10**, 116–121, 2001 (in Japanese with English abstract).

Iwasaki, I., T. Ozawa, M. Yoshida, T. Katsura, B. Iwasaki, and M. Kamada, Chemical composition of volcanic gases in Japan, *Bull. Volcanol.*, **24**, 23–48, 1962.

Miyabuchi, Y. and S. Ikebe, The February 2008 ash deposit from the Nakadake crater, Aso volcano, Japan, *Bull. Volcanol. Soc. Jpn.*, **53**, 201–206, 2008 (in Japanese with English abstract).

Miyabuchi, Y., S. Ikebe, and K. Watanabe, Geological constraints on the 2003–2005 ash emissions from the Nakadake crater lake, Aso Volcano, Japan, *J. Volcanol. Geotherm. Res.*, **178**, 169–183, 2008.

Mori, T. and K. Notsu, Remote CO, COS, CO₂, SO₂, HCl detection and temperature estimation of volcanic gas, *Geophys. Res. Lett.*, **24**, 2047–2050, 1997.

Mori, T. and K. Notsu, Temporal variation in chemical composition of the volcanic plume from Aso volcano, Japan, measured by remote FT-IR spectroscopy, *Geochem. J.*, **42**, 133–140, 2008.

Noguchi, K. and H. Kamiya, Prediction of volcanic eruption by measuring the chemical composition and amounts of gasses, *Bull. Volcanol.*, **26**, 367–378, 1963.

Ohsawa, S., T. Saito, S. Yoshikawa, H. Mawatari, M. Yamada, K. Amita, N. Takamatsu, Y. Sudo, and T. Kagiyama, Color change of lake water at the active crater lake of Aso volcano, Yudamari, Japan: is it in response to change in water quality induced by volcanic activity?, *Limnology*, **11**, 207–215, 2010.

Ono, A., M. Koya, Y. Fujimitsu, and S. Ehara, Remote observation of volcanic gases by Fourier transform infrared spectroscopy (FT-IR) at Aso volcano, *Bull. Volcanol. Soc. Jpn.*, **44**, 123–130, 1999 (in Japanese with English abstract).

Ossaka, J., J. Hirabayashi, T. Ozawa, and K. Kimishima, The observation of volcanic gases at Aso volcano, *Rept. Joint Geophysical and Geochemical Observations of Aso Volcano August-December (1977)*, 64–68, 1978 (in Japanese).

Ossaka, J., J. Hirabayashi, and T. Ozawa, The geochemical observation at Aso volcano, *Rept. Joint Geophysical and Geochemical Observations of Aso Volcano August-December (1981)*, 82–84, 1984 (in Japanese).

Rowe, G. L., S. Ohsawa, B. Takano, S. L. Brantley, J. F. Fernandez, and J. Barquero, Using crater lake chemistry to predict volcanic activity at Poás Volcano, *Costa Rica. Bull. Volcanol.*, **54**, 494–503, 1992.

Shinohara, H., S. Yoshikawa, and Y. Miyabuchi, Degassing of Aso volcano, Japan through an acid crater lake: Differentiation of volcanic gas-hydrothermal fluids deduced from volcanic plume chemistry, Abstract V23A-2387 presented at 2010 Fall Meeting, AGU, San Francisco, Calif., 13–17 Dec, 2010.

Taran, Y., J. C. Gavilanes, and A. Cortés, Chemical and isotopic composition of fumarolic gases and the SO₂ flux from Volcán de Colima, México, between the 1994 and 1998 eruptions, *J. Volcanol. Geotherm. Res.*, **107**, 105–119, 2002.

Terada, A., T. Hashimoto, T. Kagiyama, and H. Sasaki, Precise remote-monitoring technique of water volume and temperature of a crater lake in Aso volcano, Japan: implications for a sensitive window of a volcanic hydrothermal system, *Earth Planets Space*, **60**, 705–710, 2008.

Witter, J. B., V. C. Kress, P. Delmelle, and J. Stix, Volatile degassing, petrology, and magma dynamics of the Villarrica Lava Lake, Southern Chile, *J. Volcanol. Geotherm. Res.*, **134**, 303–337, 2004.

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