Carbon dioxide emission from Katanuma volcanic lake, Japan

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We report herein the first results of a CO_2 efflux survey carried out at Katanuma volcanic lake, Japan. A total of 110 CO_2 efflux measurements were undertaken at the lake by means of the floating accumulation chamber method during August 2010 to estimate the total CO_2 output from the studied area. Two different mechanisms of degassing were observed during the survey; (1) diffusion through the water-air interface and (2) bubbling. CO_2 efflux values ranged from 0.5 up to 322 g m^{-2} d^{-1}. In addition, the probability graph was used to distinguish the existence of different geochemical populations in the measured values. Sequential Gaussian Simulation was used to construct a map of CO_2 efflux from 200 simulations and to compute the total CO_2 diffuse emission at the studied area, i.e., 17 ± 0.6 t d^{-1}.

Key words: Diffuse CO_2 degassing, volcanic lake, Katanuma, Naruko.

1. Introduction

During the last two decades, studies of the spatial distribution of soil CO_2 efflux has become an ideal geochemical tool for monitoring volcanic activity (Hernández *et al.*, 2001a, b, 2006; Granieri *et al.*, 2006; Pérez *et al.*, 2011). Several authors have demonstrated that continuous monitoring of CO_2 efflux provides important information for volcanic surveillance and seismotectonic monitoring (Salazar *et al.*, 2002; Carapezza *et al.*, 2004; Pérez *et al.*, 2006). Other studies have shown that diffuse CO_2 emissions from active volcanoes are of the same order of magnitude as the CO_2 released by visible emanations (plumes, fumaroles, etc), pointing out the importance of estimating the total diffuse CO_2 output from volcanic areas (Baubron *et al.*, 1990; Allard *et al.*, 1991; Hernández *et al.*, 1998, 2001a; Salazar *et al.*, 2001). Since the rate of diffuse CO_2 emission can increase greatly before the occurrence of a volcanic eruption (Hernández *et al.*, 2001a; Carapezza *et al.*, 2004), it is very important to map surface CO_2 efflux anomalies and to estimate the total output of this gas regularly in order to have a better understanding of on-going volcanic processes (Salazar *et al.*, 2001).

During the last years, several studies have focused on CO_2 emission from volcanic lakes. Volcanic lakes are generally formed by one of three mechanisms: 1) explosive excavation (crater lakes), 2) collapse of volcanic edifices (caldera lakes), and 3) blockage of common waterways (rivers, streams) by mudflows, lava flows or ash (http://www.wesleyan.edu/ees/JCV/vloverview.html). After the gas disasters at lakes Monoun (1984) and Nyos

(1986), both in Cameroon (Sigurdsson *et al.*, 1987; Sigvaldason, 1989), accumulation of CO_2 in these lakes has been well known by the scientific community. This led to the recognition that volcanic lakes are hazardous (Le Guern and Sigvaldason, 1989, 1990; Evans *et al.*, 1994; Kling *et al.*, 2005; Kusakabe *et al.*, 2008). Since a large amount of magmatic gases is dissolved in water, CO_2 degassing from volcanic lakes should be a process to be taken into account (Pérez *et al.*, 2011). Degassing through the lake surface occurs by bubbles (convective/advective degassing) or by diffusion through the water/air interface (Mazot and Taran, 2009). In order to measure the gas flux from crater lakes, it may be the only way to measure fluxes at the lake surface.

This work presents the first results of a CO_2 efflux measurement carried out in August 2010 at Katanuma lake, Japan. The main goals of this work are: 1) to study the spatial distribution of diffuse CO_2 degassing from this volcanic lake; 2) to discriminate diffusive degassing from degassing by bubbling); 3) to estimate the total output of CO_2 emitted to the atmosphere from the study area.

2. Geological Setting

The lake Katanuma, located in northwestern Miyagi prefecture, Japan ($38°44'$N, $140°43'$E; 306 m above sea level) belongs to the Narugo volcanic system (Fig. 1), which is one of the 44 Holocene volcanoes in the northeastern Japan arc. According to Sakaguchi and Yamada (1988) and Soda and Yagi (1991), the activity of the Narugo volcano began with pyroclastic activity; the Nizaka pyroclastic flow (73 ka) and the Yanagizawa pyroclastic flow (45 ka). A large caldera, of about 5 km in diameter was formed by these paroxysmal eruptions. Lake deposits found in the caldera indicate that water filled the caldera after 45 ka. Afterwards, lava flows and lava domes were formed in the inner part of the caldera. The youngest lavas, Toyagamori,
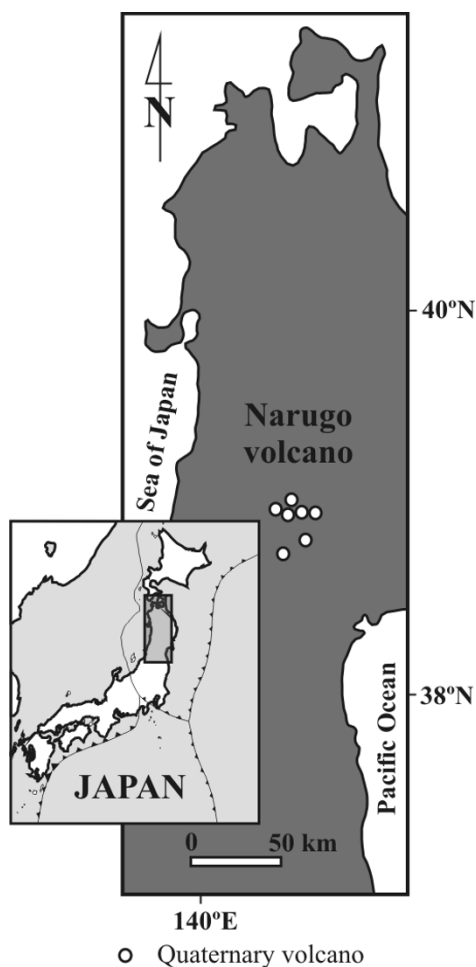
Fig. 1. Location map of Naruko volcano in Tohoku area, Japan (modified from Ban *et al.*, 2005).
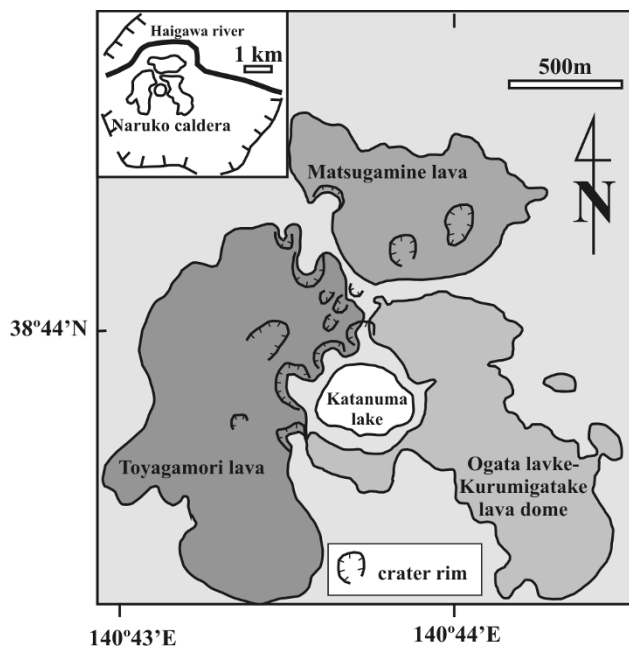

Fig. 2. Simplified geological sketch map of Naruko volcano, Japan (modified from Ban *et al.*, 2005). Grey colors indicate different lava units.
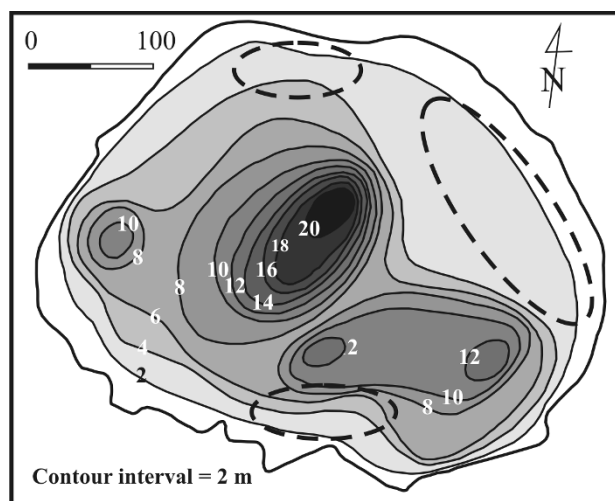

Fig. 3. Bathymetric map of Katanuma lake, Japan (modified from Takagi *et al.*, 2005). Dashed lines indicate areas of strong bubbling gas activity.

have been ^{14}C dated to be 11830±555 years BP (Omoto, 1993) (Fig. 2). Observed craters were formed in the lava surface by phreatic eruptions. The only known historical eruption at Narugo occurred in 837 AD.

Katanuma is a crater lake with strong acid water (pH: 2.0–2.2) influenced by the volcanic fluids. The lake forms an ellipse of 462 m E-W length and 326 m N-S breadth, with a 1380 m of shore line it has neither inflowing nor outflowing streams. The surface area is 1.26×10^5 m^2 with a maximum depth of 21.3 m with an approximately volume of 7.48×10^5 m^3. In the bottom of the lake there are some high temperature zones where hot springs flow out (Sato, 1995). These zones are located at the south and northeast basins of the lake's deepest area (Fig. 3). Volcanic gases emanating at the bottom and along the shore line of the lake dissolve in the shallow part and acidify the water by redox reactions of H$_2$SO$_3$, with heat supplied at the same time at a rate of 372×10^{-6} cal cm^{-2} s^{-1} (Sato, 1995).

Lake Katanuma is dimictic and covered by ice from January to mid-March. Inverse stratification occurs under the ice cover. After turnover in March, weak stratification develops with a thermocline at a depth of 3–5 m. Stratification is generally observed from April to late August. The circulation period is from late August to December (Takagi *et al.*, 2005).

3. Procedures and Methods

The CO$_2$ efflux survey was performed during August 2010 under stable weather conditions (no wind and sunny). 110 sampling sites were selected at the surface of Katanuma lake to obtain an even distribution of the sampling points over the area of 0.14 m^2 (Fig. 4). The GPS positioning of each measurement point was recorded with a resolution ±5 m. The accumulation chamber method (Parkinson, 1981; Chiodini *et al.*, 1998) was modified in order to work on a lake by using a floating chamber (Fig. 5). Measurements of CO$_2$ were performed in-situ by means of a portable non dispersive infrared (NDIR) CO$_2$ analyzer (LICOR-800 system). The LICOR analyzer was interfaced to a hand size computer that runs data acquisition software. At each sampling site, water temperature, conductivity and pH were
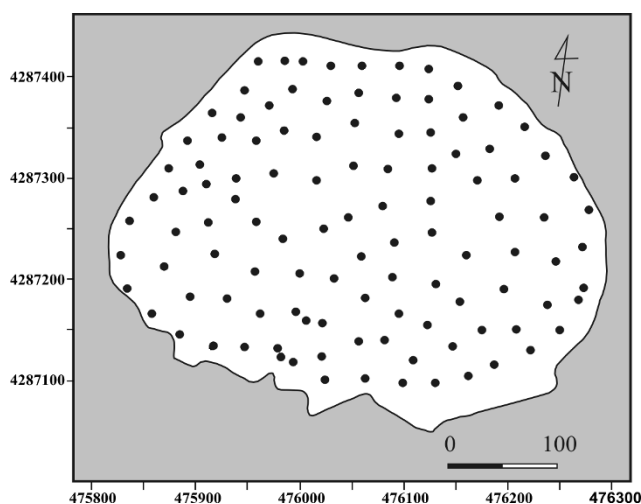
Fig. 4. Measurement sites during the study at Katanuma lake, August 2010.

Fig. 5. Picture showing the modified accumulation chamber for CO_2 efflux measurement at the Katanuma lake, Japan.

measured at a depth of 40 cm bellow the surface by means of a thermocouple and a portable pH meter. The pH meter was calibrated on site before the start of the survey.

Surface CO_2 efflux, water temperature and water pH maps for Katanuma lake were constructed using Conditional sequential Gaussian simulations (sGs) provided by the *sgsim* program (Deutsch and Journel, 1998; Cardellini *et al.*, 2003). In order to characterize the chemical and isotopic composition of the bubbling gas from Katanuma lake, gas samples were collected and gas composition was analyzed later in the laboratory. Gas composition was analyzed by combining a Varian CP-3800 gas chromatograph with Ar as the carrier gas and a Quadrupole Mass Spectrometer (QMS) model Pfeiffer Omnistar 422. The $^{13}C/^{12}C$ ratio of CO_2 (expressed as $\delta^{13}C$-CO_2‰ vs. V-PDB) was determined with a Thermo-Finnigan MAT 253 mass spectrometer at the ITER laboratory. The analytical error for $\delta^{13}C$ values is ±0.1‰. Elemental abundances of He and Ne, and He isotope composition of the gas samples collected in a 50 cm³ lead glass bottle with high vacuum stopcocks were analyzed in the laboratory of the Geochemical Research Center, The University of Tokyo. A magnetic-sector mass spectrometer VG 5400 was used for the analysis following the methodology described by Sumino *et al.* (2001).

4. Results and Discussion

CO_2 efflux values ranged between bellow the detection limit of 0.5 and 322 g m⁻² d⁻¹. Water temperature and pH ranged from 28.1 to 30.6 and 2.00 to 2.19, respectively. Figure 6(a) shows the histogram of log CO_2 efflux values (in g m⁻² d⁻¹) versus their frequency. The distribution of CO_2 efflux differs from a log-normal distribution indicating that there are at least two different mechanisms of degassing through the lake surface. Following the methodology described by Sinclair (1974), a Log-normal probability graph was constructed with the CO_2 efflux data (cumulative percentile frequencies against class intervals) to distinguish the presence of overlapped Log-normal geochemical populations that are recognizable by the inflection point on the curve (Fig. 6(b)). The inflection point of the curve allows us to distinguish the threshold value between the populations. The resulting probability graphs allowed to separate three geochemical populations: population I showing a mean of 21.1 g m⁻² d⁻¹ and represented 24.3% of the total data; population II, showing a mean of 98.2 g m⁻² d⁻¹ and represented 29.63% of the total data, and population III, showing a mean of 292.5 g m⁻² d⁻¹ and represented 3.3% of the total data. Rest of the cumulative probability corresponds to the mixing between the three identified populations. Pop-
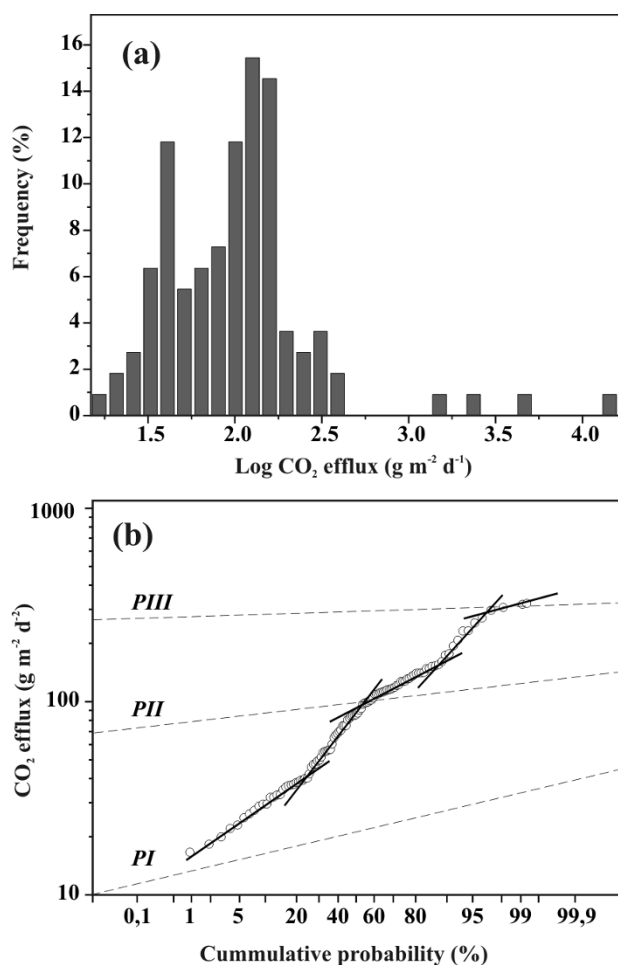

Fig. 6. Histogram (a) and probability-plot (b) of the CO_2 efflux data measured at Katanuma lake. Open circles indicate the original data. Dashed lines indicate separated geochemical populations.
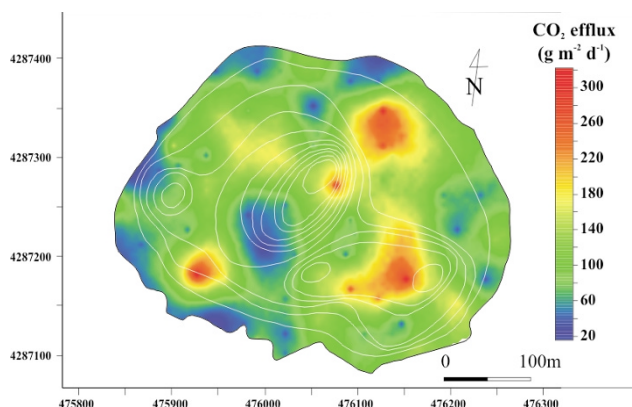
Fig. 7. Surface CO$_2$ efflux map of Katanuma lake as a mean of 200 sequential Gaussian simulations. Bathimetric lines (white lines) are also shown in the figure. *X* and *Y* axis are in UTM coordinates.
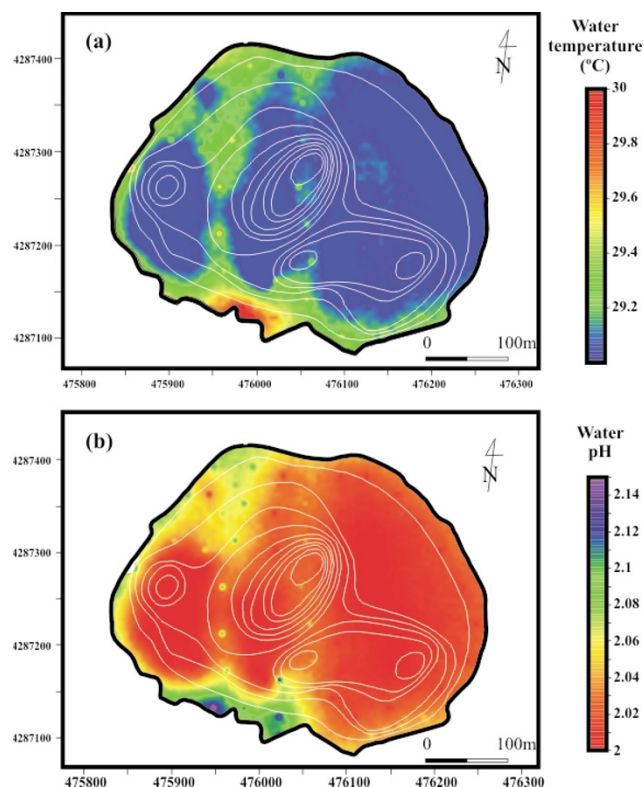

Fig. 8. (a) Surface water temperature map and (b) surface water pH map of Katanuma lake, both as a mean of 200 sequential Gaussian simulations for explanation). Bathimetric lines (white lines) are also shown in both figures. *X* and *Y* axis are in UTM coordinates.

ulation I represents the background values due to CO$_2$ degassing by diffusion through the water-air interface as has been proposed by Mazot and Taran (2009) for El Chichón lake, México, and checked using the thin boundary layer model (Liss and Slater, 1974). Population II represents the CO$_2$ efflux values from a deep source of a magmatic origin and Population III may represent gases resulting from mixing of diffuse and bubbling degassing. The existence of three different geochemical populations indicates that there are at least two different mechanisms of degassing through the lake surface, and supports the hypothesis of a deep contribution at Katanuma lake.

A total of 200 simulations were performed over a grid of 5696 squared cells (5 m × 5 m) following the variogram model to construct a spatial distribution map for CO$_2$ efflux (Fig. 7), water temperature (Fig. 8(a)) and pH (Fig. 8(b)). The experimental variograms were fitted with a spherical model with the following parameters: nugget of 0.15 and range of 45 m. An average map was then constructed using the average of the different values simulated at each cell. Since quantification of the uncertainty of the total CO$_2$ is an important task, the mean and standard deviation of the 200 simulated values of total CO$_2$ output were assumed to be characteristics of the CO$_2$ efflux and its uncertainty (Cardellini *et al.*, 2003). Figure 7 shows the CO$_2$ efflux distribution map at Katanuma lake based on the mean simulated total CO$_2$ output values.

Inspection of the CO$_2$ efflux contour map for Katanuma lake (Fig. 7) shows the existence of three anomalous areas of CO$_2$ degassing through the lake surface without a clear emission trend. High CO$_2$ efflux values were always measured nearby visible gas bubbling emanations and located above the deepest areas of the lake, south and northeast basins of the lake, where hot springs are thought to issue. Figure 8(a) shows water temperature contour map for Katanuma lake together with bathymetric contour lines. Even when there is a homogeneous distribution of temperature at the surface of the lake, some slight increase in temperature was observed at the southern most part of the lake. To estimate the total output of diffuse CO$_2$ released from Katanuma lake, we considered the contribution of each cell obtained after SGS and the average of the 200 simulations

to estimate the total output with one standard deviation as the uncertainty. The result was 17±0.6 t d^{-1} for diffuse CO$_2$. This value is smaller than the emission rates reported for other volcanic lakes (Pérez *et al.*, 2011). However, in order to compare individual CO$_2$ emission of various volcanic lakes, it is important to consider the lake-type and the area. Figure 8(b) shows water pH contour map for Katanuma lake together with bathymetric contour lines. Most of the surface water showed an almost homogeneous acidic pH (∼2.0) distribution. Katanuma, as an acid lake with an area of 1.26 × 10^5 m^2, would have a normalized CO$_2$ emission of 136 t d^{-1} km^{-2}, a value close to that from other acid volcanic lakes in the world (Pérez *et al.*, 2011).

As reported by Takagi *et al.* (2005), Katanuma lake circulates from late August to December and stratifies from April to late August. Our survey was carried out at the beginning of the monomictic circulation period (August), which significantly reduces accumulation of CO$_2$ in the deepest part of the lake, and maximizes CO$_2$ emission to the atmosphere. During the overturn period, when the present study was carried out, the emission of CO$_2$ is mainly diffusive, advective and convective, showing the maximum CO$_2$ emission in the year. In order to evaluate the CO$_2$ emission from the bubbling spots, we measured the CO$_2$ flux from 10 spots using the same method. We visually counted approximately 100 bubbling spots and assumed an average CO$_2$ emission rate per bubbling spot of 14 kg d^{-1}. Under the above assumption we estimated a total CO$_2$ emission of 1.4 t d^{-1} from bubbling degassing. As a whole, adding diffuse and visible

bubbling degassing, the total CO$_2$ emission from Katanuma is estimated to be 18.4 t d^{-1}.

Since water from Katanuma lake is acidic (pH ~2.0), almost all CO$_2$ is present as dissolved CO$_2$ and will diffuse out of the water, allowing volcanic gas fluxes to be channeled through the acid lake. Therefore, 18.4 t d^{-1} of CO$_2$ can be considered as a deep-seated CO$_2$ emission from Katanuma lake, because relatively high CO$_2$ efflux values were measured during this survey including data from all geochemical populations (16.6–322 g m^{-2} d^{-1}).

Chemical and isotopic compositions of bubbling gases were analyzed to constrain the origin of the gases emitted through the water of Katanuma lake. Bubbling gases are clearly CO$_2$-dominated (72.6%V) and contain He (10 ppmV), O$_2$ (4.6%V), N$_2$ (22.5%V), Ar (0.2%V) and CH$_4$ (477 ppmV) in minor amounts. N$_2$/Ar ratio at the Katanuma bubbling gases (112.5) is notably higher than the air ratio (83.6) and air-saturated water (ASW; ~36.8), indicating an additional non-atmospheric N$_2$ source, typical for arc volcanoes. Measured δ^{13}C-CO$_2$ value for Katanuma bubbling gases (-1.59 ± 0.03‰) is heavier than MORB values of -6.5 ± 2.5‰ (Pineau and Javoy, 1983; Taylor, 1986). The measured value indicates a typical isotopic composition for gases from volcanic arcs (e.g. Taylor, 1986; Marty *et al.*, 1989; Sano and Marty, 1995; Sano and Williams, 1996; Pedroni *et al.*, 1999; Shaw *et al.*, 2003).

The ^{3}He/^{4}He ratio was also measured at 3.46$\pm$0.06 Ra, where Ra denotes the atmospheric ^{3}He/^{4}He ratio (1.4 × 10^{-6}, Mamyrin *et al.*, 1970). The relatively low ^{4}He/^{20}Ne ratio of the sample (3.73) is higher than that of the atmosphere (0.318), but still suggests atmospheric contamination of the sample. The measured ^{3}He/^{4}He ratio is similar to the value of 4.86$\pm$0.17 Ra reported by Asamori *et al.* (2010) from the hot spring nearest to Naruko volcano. The value supports the existence of a hydrothermal system which supplies materials from underlying magma. In general, He in natural gases is composed of three components: atmospheric He, crustal or radiogenic He, and primordial He derived from the upper mantle. In order to estimate the mixing ratio of these components using the observed ^{3}He/^{4}He and ^{20}Ne/^{4}He ratios, we followed the methodology proposed by Sano *et al.* (1982). The calculated contribution for each component was 35.9%, 55.6% and 8.5% for MOR-type (upper mantle), crustal and air, respectively. The large contribution of the upper mantle He in Katanuma gas sample confirms active magmatic activity beneath the Naruko-Katanuma volcanic system.

Bubbling springs with lower gas/water ratios generally show higher ^{3}He/^{4}He ratios and consequently lower CO$_2$/^{3}He ratios (Rouwet *et al.*, 2009). As He is less soluble in water than CO$_2$ (Stephen and Stephen, 1963), and ^{3}He is lighter than ^{4}He, gases liberated from a weakly bubbling spring tend to be enriched in ^{3}He during near-surface degassing processes and vapour separation in an aqueous hydrothermal system. This has been observed in the other volcanic areas, e.g. Tacaná volcano in Guatelama (Rouwet *et al.*, 2009).

In order to detail deep magmatic and near-surface physical degassing processes at Katanuma lake, we have calculated the CO$_2$/^{3}He ratio of the bubbling gas. The CO$_2$/^{3}He ratio is 1.54 × 10^{10}, a value that fits well with the average value established for worldwide arcs (1.5 $\pm$ 1.1 × 10^{10}; Sano and Williams, 1996). The three-component mixing model reported by Sano and Marty (1995) to calculate relative proportions of carbon sources contributing to arc magmas; MORB (M), marine limestones (L) and organic sediments (S) was used to estimate the fraction of each C source for Katanuma gas sample. L source contributes 53.6%, S source 3.6% and the M source 42.8%. These values are in the same order than the reported by Sano and Marty (1995) for bubbling gas and fumarolic gas samples from Japanese volcanic areas, with limestones as the main C component followed by the MORB-type C. Organic sedimentary C fraction is relatively low (3.6%), suggesting that the fumarolic feeding system beneath Katanuma lake corresponds to high temperature fumaroles.

5. Conclusions

CO$_2$ efflux measurements were performed at the surface of Katanuma, a volcanic lake in Japan, by using the floating accumulation chamber method. This study allowed an estimation of 17$\pm$0.6 t d^{-1} as total diffuse CO$_2$ emission and ~1.4 t d^{-1} as CO$_2$ emitted from bubbling spots. Chemical and isotopic analyses of bubbling gas samples from the Katanuma lake indicate a strong magmatic contribution to the gases with CO$_2$ as the dominating gas species. To perform regular diffuse CO$_2$ emission surveys at Katanuma lake would be important for detecting possible changes in the activity of the volcano.

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