

# Carbon Dioxide Degassing by Advective Flow from Usu Volcano, Japan

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Magmatic carbon dioxide (CO<sub>2</sub>) degassing has been documented before the 31 March 2000 eruption of Usu volcano, Hokkaido, Japan. Six months before the eruption, an increase in CO<sub>2</sub> flux was detected on the summit caldera, from 120 (September 1998) to 340 metric tons per day (September 1999), followed by a sudden decrease to 39 metric tons per day in June 2000, 3 months after the eruption. The change in CO<sub>2</sub> flux and seismic observations suggests that before the eruption, advective processes controlled gas migration toward the surface. The decrease in flux after the eruption at the summit caldera could be due to a rapid release of CO<sub>2</sub> during the eruption from ascending dacitic dikes spreading away from the magma chamber beneath the caldera.

Usu volcano is one of the most active volcanoes in Japan, with seven major historic eruptions recorded since 1663. It is located on the northern coast of Funka-wan (Bay of Volcano) in the southwestern part of Hokkaido (Fig. 1) and consists of a basaltic edifice (49 to 53% SiO<sub>2</sub>) with a small summit caldera and several dacitic lava domes and cryptodomes (68 to 73% SiO<sub>2</sub>) on the summit and on its northern slope (1). The volcano is a postcaldera cone of Toya caldera, which is a nearly circular depression ~10 km in diameter, filled with Lake Toya. Boundaries of Lake Toya correspond to the Toya caldera rim. The summit of Usu consists of a small caldera, 1.8 km in diameter and ~500 m in elevation, covering a circular area ~7 to 8 km across the base. Domes and cryptodomes, aligned in two parallel zones running NW-SE, are probably controlled by the structure of the southern wall of Toya caldera, which is overlaid by Usu volcano. Historic volcanic eruptions are assumed to originate from episodic shallow dacitic intrusions, ascending from a deeper rhyolitic magma reservoir hypothesized to be at a depth of 10 km (2). The last eruption began on 7 August 1977, after 32 years of dormancy, and stopped in October 1978, forming the Usu-Shinzan cryptodome. Inter-eruptive activity consists of both fumarolic emissions distributed on the summit caldera and diffuse gas emanations spread over the volcanic edifice, together with persistent earthquake swarms.

Seismicity data observed by the Japan Meteorological Agency show an increasing number of volcanic earthquakes around Usu volcano since 1995. However, clear premonitory seismicity appeared at Usu on 28 March 2000, 3 days before the eruption (3). On 30 March, the ground began to rise in the area northwest of Nishi-yama and the north slope of Kompira-yama cryptodomes (Fig. 1), forming a new cryptodome due to a dike intrusion spreading northwest, away from a shallow dacitic magma chamber located at a depth of ~4 km beneath the summit caldera (4). The Usu Volcano Observatory Global Positioning System network detected upheaval over 2 m at the summit of Usu a few days before the eruption. The new cryptodome attained a maximum height of ~85 m (over the original altitude) on 10 July, and more than 50 craters formed in the area of ground uplift. The first crater was related to a phreatomagmatic eruption, followed by several phreatic eruptions.

CO<sub>2</sub> is the second-most abundant gas species released (after water), and the gas is generated mostly by subsurface magma-degassing bodies. As CO<sub>2</sub> travels upward by advective-diffusive transport mechanisms and manifests itself at the ground surface, changes over time in its flux pattern provide information about subsurface magma movement (5–8). For this reason, during this period (1998 to 2000) of unrest, three soil gas surveys were carried out, which focused mainly on the study of soil CO<sub>2</sub> (Table 1). The first survey was initiated in September 1998 under ideal weather conditions (no wind or clouds). These conditions provided minimal soil gas variations, thus eliminating disturbances such as soil moisture during the measurements. Atmospheric pressure slightly changed from 1019 to 1031 hPa during the survey. About 150 soil gas samples were

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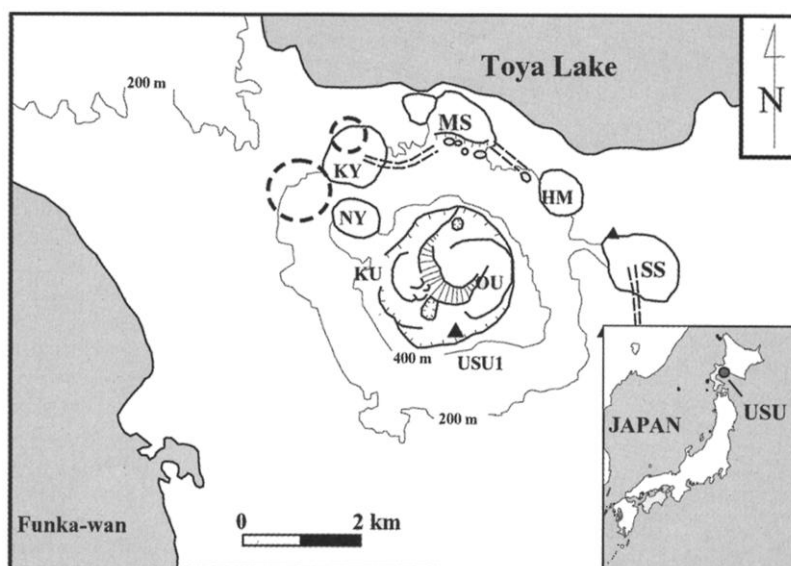
collected from a depth of 40 to 50 cm.  $\text{CO}_2$  concentration was then analyzed in the laboratory with a gas chromatograph, with  $\text{CO}_2$  concentration ranging from  $<0.1$  volume % at vegetated areas to  $>40$  volume % in arid areas affected by high diffuse degassing. Carbon isotope analyses were also performed on selected samples to determine the  $\delta^{13}\text{C}$  isotopic ratio [ $\pm 0.1$  per mil (‰)] with respect to the Vienna Pee Dee belemnite standard. At the same time, soil  $\text{CO}_2$  fluxes were determined in situ (210 sites) by means of the accumulation chamber method (9–11). The system consists of a cylindrical chamber that is open at the bottom and equipped with a fan in order to improve gas mixing and a nondispersive infrared spectrophotometer with an accuracy of  $\sim 5\%$ . The reproducibility for the range of 100 to  $10,000 \text{ g m}^{-2} \text{ day}^{-1}$  is 10%. This random error is based on the uncertainty calculated from the variability of the measurements carried out in the laboratory.

The  $\text{CO}_2$  flux data obtained in the survey of September 1998 were corrected for local atmospheric temperature and pressure conditions and then used to construct an efflux contour map of the summit and surrounding areas (Fig. 2). The kriging model was used because it produces better contour maps from irregularly spaced measurements (12, 13). Isotropic linear variograms with negligible nugget effect were fitted with log-transformed data for the three surveys. This procedure allows one to interpolate the soil  $\text{CO}_2$  flux at unsampled sites and assess the uncertainty of the total diffuse emission of  $\text{CO}_2$  estimated for the entire studied area. The map shows areas of high gas emissions, which follow two parallel zones running NW-SE through the summit and northern flank, a pattern controlled by the volcano-tectonic discontinuity of the southern wall of Toya caldera. In particular, the highest soil  $\text{CO}_2$  emissions were identified inside the summit caldera, outside the northwest and north flanks of the volcano, at Showa-Shinzan volcanic dome, and nearby the northwest flank in the proximity of the site of the March 2000 eruption. At the site of the eruption and the growing cryptodome, relatively high  $\text{CO}_2$  fluxes ( $>500 \text{ g m}^{-2} \text{ day}^{-1}$ ) were also found. This value is higher than the contribution of diffusive  $\text{CO}_2$  flux by biogenic activity estimated for most volcanoes [between 0.86 to

$2.63 \text{ g m}^{-2} \text{ day}^{-1}$ , at temperature  $T = 25^\circ\text{C}$  (14)], which can be considered negligible at Usu.

Using the same procedure as was used in the survey of September 1998, we carried out additional soil gas surveys in September 1999 and June 2000 at the summit of Usu volcano to detect possible changes in the spatial distribution of  $\text{CO}_2$  flux anomalies and its transient total output. Meteorological conditions were similar to those recorded in the first survey of September 1998, ruling out the influence of meteorological parameters on the pattern of soil gas changes over time (Table 1). The  $\text{CO}_2$  flux contour maps of the summit of Usu volcano for all three surveys are summarized in Fig. 3. The studied areas for the 1998 and 1999 surveys were of the same size ( $2.65 \text{ km}^2$ ), whereas for the 2000 survey, the area was smaller ( $2.00 \text{ km}^2$ ) because of inaccessibility to O-Usu dome. Inspection of the  $\text{CO}_2$  flux distribution showed the following features (Fig. 3): (i) Areas of high  $\text{CO}_2$  flux were characterized by high temperatures ( $>40^\circ\text{C}$ ) that increased closer to the fumaroles, whereas those of low  $\text{CO}_2$  flux corresponded to low soil temperatures

( $<25^\circ\text{C}$ ), as observed at other volcanoes (15, 16), and (ii) a close relation was observed between high soil  $\text{CO}_2$  flux values and the existence of fault or fractures, showing the importance of structural discontinuities in providing pathways for the ascent of deep gases toward the surface. Total  $\text{CO}_2$  outputs were estimated by multiplying the area of each class interval by the median value of two adjacent class intervals. The total  $\text{CO}_2$  flux emission on the summit of Usu volcano increased from 120 metric tons ( $\text{t day}^{-1}$ ) in September 1998 to  $340 \text{ t day}^{-1}$  in September 1999, just 6 months before the eruption, followed by a sudden decrease ( $39 \text{ t day}^{-1}$ ) 3 months after the eruption. The uncertainty based on the residual analysis approach is almost the same for the three surveys: 2.04, 3.16, and  $3.51 \text{ t day}^{-1}$ , respectively. According to these results, the differences in the  $\text{CO}_2$  outputs estimated for Usu volcano are of statistical significance. The analytical inspection of the residuals computed as differences between observations and model predictions yielded estimation errors of 1.7, 0.93, and 9.0% for the 1998, 1999, and 2000 surveys, respectively.



**Fig. 1.** The location of Usu volcano, together with the main domes and cryptodomes. Site abbreviations are as follows: HM, Higashi-Maruyama; KU, Ko-Usu; KY, Kompira-yama; MS, Meiji-Shinzan; NY, Nishi-yama; OU, O-Usu; and SS, Showa-Shinzan. Thick contours show lava domes. The two dashed circles indicate the location of the craters that opened during the recent eruption in March 2000. Double broken lines show the lateral extent of volcanic activity. The location of monitoring station USU1 ( $42^\circ31'57''\text{N}$ ,  $140^\circ50'07''\text{E}$ ) is indicated with a triangle.

**Table 1.** Gas characteristics of the soil gas samples for the three surveys. NM, not measured.

Date	Location	$\text{CO}_2$ (%)	$\text{CO}_2$ flux ( $\text{g m}^{-2} \text{ day}^{-1}$ )	$\delta^{13}\text{C}(\text{CO}_2)$ (‰)	Temperature ( $^\circ\text{C}$ )	Atmospheric pressure (hPa)	Wind speed ( $\text{m s}^{-1}$ )
1998	Usu	0.08 to 39.0	0.7 to 8,210	$-63.5$ to $-2.7$	16.3 to 101.0	1019 to 1031	NM
1998	Summit area	0.08 to 39.0	0.7 to 8,210	$-32.5$ to $-2.7$	16.6 to 101.1	1019 to 1031	NM
1999	Summit area	0.04 to 61.0	0.14 to 18,861	$-23.4$ to $-2.53$	18.3 to 99.8	1003 to 1022	0 to 9
2000	Summit area	NM	0.1 to 9,090	NM	11.5 to 100.0	1005 to 1017	0 to 5

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Furthermore, the CO<sub>2</sub> flux results for the 1998, 1999, and 2000 surveys were also statistically separated into three overlapping populations (17): background, peak, and intermediate or "threshold groups." The background and peak means for the three surveys were 37, 100, and 4 g m<sup>-2</sup> day<sup>-1</sup> and 2400, 7000, and 1800 g m<sup>-2</sup> day<sup>-1</sup>, respectively. Changes on the statistical parameters (background and peak means) are consistent with the temporal changes observed in the total CO<sub>2</sub> output for the summit of Usu volcano. The existence of several geochemical populations suggests that variations in the hydrothermal activity affected the measured CO<sub>2</sub> flux data, thus giving rise to such different populations. However, peak populations are related to the volcanic activity of Usu volcano. For this reason, in June 2000, a station to continuously monitor CO<sub>2</sub> was set up inside the summit caldera (USU1 in Fig. 1). Data of CO<sub>2</sub> flux, together with soil temperature (at a depth of 30 cm) and barometric pressure for the period of June to September 2000, show a

general decline in the diffuse degassing. Despite changes in atmospheric pressure, the soil CO<sub>2</sub> flux measured at this site was always low (<50 g m<sup>-2</sup> day<sup>-1</sup>, as measured in July 2000) compared to the higher flux (>1000 g m<sup>-2</sup> day<sup>-1</sup>) measured in September 1999.

In each survey, carbon isotopic analyses were also carried out with CO<sub>2</sub> from both the diffuse gas emanations and the fumaroles, and <sup>3</sup>He/<sup>4</sup>He and <sup>4</sup>He/<sup>20</sup>Ne ratios were measured in the fumaroles to determine possible sources of the emissions. Areas with high CO<sub>2</sub> flux at the summit showed δ<sup>13</sup>C of CO<sub>2</sub> [δ<sup>13</sup>C(CO<sub>2</sub>)] and CO<sub>2</sub> concentration values (−13.5 to −2.6‰ and 1.2 to 39 volume %, respectively) that were close to those of the fumaroles (−6.9 to −5.7‰ and 47.3 to 71.5 volume %, respectively) and in the same range as those reported by Giggenbach and Matsuo (18). These data indicate mantle-derived carbon, suggesting the existence of a common subsurface feeding source for all monitored emissions. Such a source is hypothesized to be linked to a dacitic magma chamber be-

neath the caldera. <sup>3</sup>He/<sup>4</sup>He ratios of the fumaroles [ $6.02 \times 10^{-6}$  to  $9.30 \times 10^{-6}$ ; 4.3 to 6.6  $R_A$ , where  $R_A$  is the atmospheric <sup>3</sup>He/<sup>4</sup>He ratio ( $1.4 \times 10^{-6}$ )] would support this hypothesis. On the basis of the observed <sup>3</sup>He/<sup>4</sup>He ratios and <sup>4</sup>He/<sup>20</sup>Ne (37.2 to 1.5) ratios, the fraction of mantle-derived helium in the total <sup>4</sup>He is estimated to be 45 to 71%, assuming a mixture of gases with three components (mantle, ~7 to 10  $R_A$ ; crust, <0.03  $R_A$ ; and atmosphere, 1  $R_A$ ) (19). Instead, for more peripheral areas with respect to the fumaroles, an increase of δ<sup>13</sup>C(CO<sub>2</sub>) was detected; this may be consistent with <sup>13</sup>C fractionation because it has been hypothesized for other volcanoes (20).

Moreover, the rapid increase of CO<sub>2</sub> flux before the eruption suggests that at the summit caldera, subsurface gases mostly rose by advection, bringing about the idea that surface CO<sub>2</sub> emission variation over time was controlled by Darcian flow rather than chemical diffusion, whose rate of matter transfer does not describe the observed flux changes. In fact, if we reasonably assume CO<sub>2</sub> diffusion coefficient ranging from 10<sup>-3</sup> to 10<sup>-5</sup> m<sup>2</sup> s<sup>-1</sup> (21, 22), diffuse magmatic CO<sub>2</sub> migration toward the surface during the three surveys would have required a magma chamber at a depth of ~100 to 200 m, which actually disagrees with the depth of ~4 km estimated from seismic data (4). Since the eruption of Usu, CO<sub>2</sub> flux anomalies have been focused in areas near fumarolic activity of the summit caldera, suggesting that gas flow is dominated by vent pathways (23). Nevertheless, this CO<sub>2</sub> flux decrease on the summit caldera can be explained by a CO<sub>2</sub>-depleted dacitic magma body beneath the caldera. In fact, the pre-eruptive CO<sub>2</sub> gas would have been drained off through the upward magma migration from underneath the summit caldera toward the northwest flank of the volcano, followed by phreatomagmatic eruption on 31 March 2000. CO<sub>2</sub>

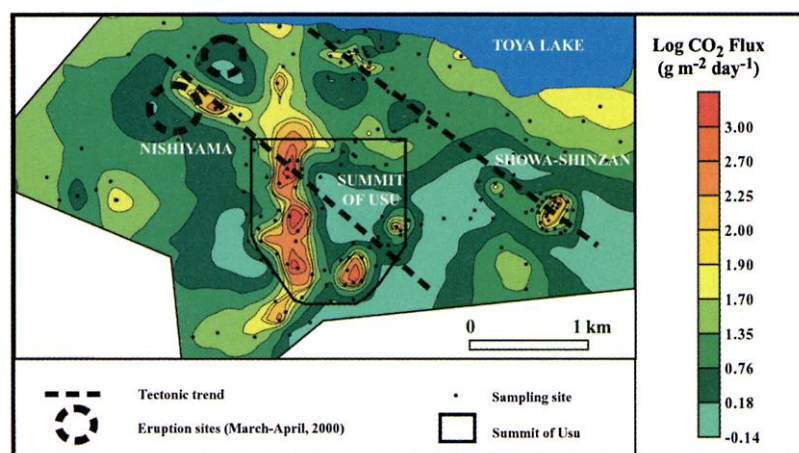


Fig. 2. CO<sub>2</sub> flux contour map at Usu volcano and surrounding areas in September 1998. The CO<sub>2</sub> flux values are expressed in g m<sup>-2</sup> day<sup>-1</sup>.

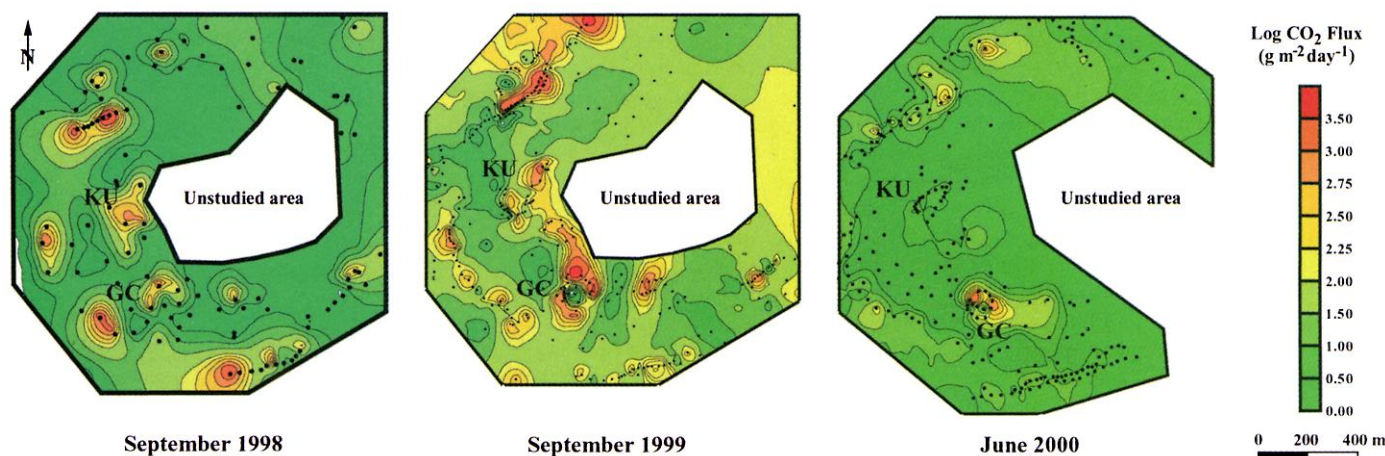


Fig. 3. CO<sub>2</sub> flux contour maps of the summit of Usu volcano based on 1998, 1999, and 2000 surveys. The thick black lines represent the survey boundaries and dots indicate the measurement sites.

thus escaped by being carried away rapidly to the surface during the northwest flank dike intrusion, causing the system to be partially degassed beneath the summit caldera. This mechanism is supported by geophysical observations of Usu during the eruption and post-eruption period (3, 4).

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## Control of Nitrogen Export from Watersheds by Headwater Streams

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A comparative <sup>15</sup>N-tracer study of nitrogen dynamics in headwater streams from biomes throughout North America demonstrates that streams exert control over nutrient exports to rivers, lakes, and estuaries. The most rapid uptake and transformation of inorganic nitrogen occurred in the smallest streams. Ammonium entering these streams was removed from the water within a few tens to hundreds of meters. Nitrate was also removed from stream water but traveled a distance 5 to 10 times as long, on average, as ammonium. Despite low ammonium concentration in stream water, nitrification rates were high, indicating that small streams are potentially important sources of atmospheric nitrous oxide. During seasons of high biological activity, the reaches of headwater streams typically export downstream less than half of the input of dissolved inorganic nitrogen from their watersheds.

Nitrogen (N) loading of terrestrial and aquatic ecosystems is increasing worldwide as a result of human activities such as fertilizer application, N fixation by legume crops, human and animal waste disposal, and fossil fuel combustion (1). As terrestrial ecosystems become saturated with N (2), excess N moves with surface runoff and groundwater flow to streams, lakes, rivers, and coastal oceans (3, 4). Because streams transport much of this N, quantitative information on N cycling in streams is needed to understand how N loading from watersheds will affect rivers, lakes, and estuaries where N availability can limit primary production (5, 6). Results from this cross-site tracer study of stream N cycling demonstrate how watershed-derived N is processed in stream chan-

nels and how these transformations affect the export of N to downstream ecosystems.

Headwater streams convey water and nutrients to larger streams and, despite their relatively small dimensions, play a disproportionately large role in N transformations on the landscape. Small streams (width 10 m or less) often constitute up to 85% of total stream length within a drainage network (7, 8) and collect most of the water and dissolved nutrients from adjacent terrestrial ecosystems. Nitrogen in small streams has been intensively monitored in watershed nutrient budget studies (9–12), and data on N transport in rivers suggest that the smaller streams and rivers are most effective in N processing and retention in large watersheds (13). However, the dynamics of N cycling within

stream channels have remained obscure because of a lack of techniques for tracing the fluxes of N at ambient concentrations.

Here, we report on rates of N uptake, storage, regeneration, and export in headwater streams. These processes were assessed via standardized protocols (14) in 12 headwater streams as part of the Lotic Intersite Nitrogen eXperiment (LINX). These streams and their watersheds (i.e., catchments) represent a diversity of biomes throughout the United States [Fig. 1; see Web table 1 (15)]. With only two exceptions, the streams had relatively low inorganic N levels (<10 μg NH<sub>4</sub>-N liter<sup>-1</sup>). Each experiment involved a 6-week continuous tracer-level addition of a stable N isotope as [<sup>15</sup>N]NH<sub>4</sub> to each stream (15). Sampling was designed to measure <sup>15</sup>N tracer movement through biotic and abiotic components of each stream during and for several weeks after tracer addition (15).

Cross-site comparison of NH<sub>4</sub> uptake lengths (16) revealed that the distance trav-

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