V. Geochemical Study

1. Monitoring of Active Volcanoes Before and After the Eruption

Usu volcano, Hokkaido, Japan erupted on March 31, 2000, after a dormancy of 22 years. Various geochemical studies have been reported related to the eruption. Prior to the 2000 eruption, several geochemical anomalies were identified. Soil CO_2 degassing from the summit area increased before and significantly decreased after the 2000 eruption (Hernandez *et al*., 2001b). Systematic water-level decreases were observed for a several month prior to the eruption at two wells (Shibata and Akita, 2001). Abrupt and large rises in well water levels were observed three days prior to the 2000 eruption (Matsumoto *et al*., 2002a). The constituents of the 2000 volcanic ashes were shown to be the alteration products of the volcaniclastics of the historic eruptions (Nogami *et al*., 2002a) and water-soluble components on volcanic ash are documented (Murayama and Ogino, 2002; Nogami *et al*., 2002b). Distribution maps for Boron and Ammonia concentration in the soil in 1999 showed anomalies at Nishiyama area where the 2000 eruption took place (Perez *et al*., 2002). Arsenic on ash and mudflow deposits is investigated (Yahata *et al*., 2001). Continuous soil CO_2 emission monitoring was carried out at the summit of Usu after the onset of the eruption and observed decreasing trend similar to the decreasing eruptive activity (Mori *et al*., 2002a). Satellite data are used for monitoring thermal activities (Kaneko *et al*., 2002) and ash fall distributions (Urai *et al*., 2001).

Miyakejima volcano started to erupt in June 2000; one of the eruptive activities that deserve special mention is continuous high SO_2 emission from the volcano. SO_2 flux as high as 230 ktons/day was observed using COSPEC and convective transport of magma model are proposed to explain the observed continuous high SO_2 flux (Kazahaya, 2001; Kazahaya *et al*., 2001; Uto *et al*., 2001). Sulfur dioxide and acid rain due to the Miyakejima eruption were observed and reported at many locations even on the Honshu Island, Japan (Yamakawa and Yamagami, 2001; Yokota, 2001; Katsuno *et al*., 2002; Matsumoto *et al*., 2002b), and dispersion of volcanic gas from the volcano is simulated (Chino, 2001). Reason for the high SO_2 emission of the Miyakejima 2000 eruption was discussed by analyzing sulfur, chloride, and fO_2 in melt inclusions inside phenocrysts (Yasuda *et al*., 2001; 2002). Soil CO_2 survey was performed in 1999 before the eruption (Hernandez *et al*., 2001c). Kinoshita (2001) reviewed geochemistry and effects of the volcanic gas.

Takahashi *et al*. (2000) reports on Koshimizu thermal spring formed in the 1986 eruption of Izu-Oshima volcano. Nogami *et al*. (2001) discussed the relationship between the chemical composition of volcanic ash and the contents of the water-soluble components adhering to it for the early stage of the 1990-1995 Unzen eruption. Related to the 1995 phreatic eruption of Kuju volcano, entrainment of atmospheric air into volcanic system was observed (Ohsawa *et al*., 2000a) and HCl emission rate variations are reported (Itoi *et al*., 2000). Hydrothermal processes of the 1997 phreatic eruption of Akita-Yakeyama volcano were revealed using geochemical data of fumarolic gases and ejecta of the eruption (Nogami *et al*., 2000).

2. Studies on Gas and Water Related to Volcanic Activity.

Special issue of "Earth, Planets and Space" (Vol. 54, No. 3) for Satsuma-Iwojima volcano, which is continuously degassing high temperature volcanic gas, is published in 2002. The issue has 15 manuscripts (12 by Japanese authors) on the volcano (Hamasaki, 2002; Iguchi *et al*., 2002; Kanda and Mori, 2002; Kawanabe and Saito, 2002; Kazahaya *et al*., 2002; Mori *et al*., 2002b; Saito *et al*., 2002b; Sato *et al*., 2002; Shimoike *et al*., 2002; Shinohara *et al*., 2002; Uchida and Sakai, 2002; Urai, 2002). Results from the fourth and fifth IAVCEI volcanic gas field workshop held respectively at Vulcano Island, Italy, and Java, Indonesia were evaluated (Giggenbach *et al*., 2001). Ossaka and Nogami (2001) reported the history and gas chemistry on Tyatya volcano as a result of Japan-Russia joint scientific study held in 1999. Ohba (2000) reviewed chemical approach for the prediction of volcanic eruptions.

Saito *et al*. (2002a) collected up to 15 fumarolic gas samples at Satsuma-Iwojima and Kuju volcanoes and showed that careful sampling and analyses provide reliable geochemical data. Trace gas species in fumarolic and volcanic gases are studied for light hydrocarbons (Igari *et al*., 2000) and halocarbons (Jordan *et al*., 2000). Sulfur isotope ratios of volcanic gases from Satsuma-Iwojima and Sakurajima volcanoes are obtained (Kasasaku *et al*., 1999).

Hydrothermal system and water chemistry and isotope compositions are discussed for crater lakes of Kusatsu-Shirane (Ohba *et al*., 2000a; Ohba *et al*., 2000b) and Patuha volcano, Indonesia (Sriwana *et al*., 2000), Kawah Lien volcano, Indonesia (Delmelle *et al*., 2000). Nishimura *et al*. (1999) surveyed crater lake, Lake Towada, for methane concentration and carbon isotopic composition profiles. An in-situ monitoring system for aqueous polythionate in Yugama crater lake, Kusatsu-Shirane volcano is developed (Takano *et al*., 2000b). The crater lake water from Mary Semiachik volcano was used for the analytical inter laboratory comparison for its chemistry (Takano *et al*., 2000a). Takano (2001) reviewed geosciences on active crater lakes. Geochemistry and/or disaster prevention at Lake Nyos, Cameroon is reported and discussed (Kusakabe *et al*., 2000b; Kusakabe, 2001a; Kusakabe, 2001b; Kusakabe, 2002). Sulfur isotope effects during the SO_2 disproportionation reaction were experimentally determined for hydrothermal conditions (Kusakabe *et al*., 2000a).

Lanthanoid abundances in hot spring waters are reported (Kikawada *et al*., 1999) and hydrothermal alternation of rocks by acidic hot spring water was reported and experimented (Kikawada *et al*., 2000a; Kikawada *et al*., 2001). Chemistry and/or isotope ratios of hot spring waters are studied at Manza area (Kikawada *et al*., 2002), Kagusa hot spring (Kikawada *et al*., 2000b), Tateyama-Jigokudani (Mizutani *et al*., 2000), Shimabara Peninsula (Ohsawa *et al*., 2002b), and Tamagawa hot spring (Muto and Matsubaya, 2002). Helium and/or carbon isotopic composition of hot spring gases are reported for Unzen volcano (Notsu *et al*., 2001), Kirishima volcano (Sato *et al*., 1999a), Tibet Plateau

(Yokoyama *et al*., 1999) and Tatun volcano (Yang *et al*., 1999). Chemical and isotopic compositions for water, CO_2 and noble gases in groundwater are reported for Bioko, Principe, Sao Tome and Annobon Islands off the western coast of Africa (Aka *et al*., 2001). Origin of CO_2 from Nagayu hot spring is discussed (Iwakura *et al*., 2000). Anomalously high $\delta^{13}C$ values up to +2.8‰ for CO_2 in fumarolic gases from Ogasawara-Iwojima is reported (Ohsawa and Yusa, 2001). Using chemistry and isotopic information of inorganic carbon in ground water system of Unzen volcano, Ohsawa *et al*. (2002c) showed that volcanic gas is escaping into ground water system.

Carbon dioxide emissions through ground surface of volcanic flanks have been measured at various volcanoes: Usu (Hernandez *et al*., 2001b; Mori *et al*., 2002a), Tarumae (Hernandez *et al*., 2001a), Miyakejima (Hernandez *et al*., 2001c), Satsuma Iwojima (Shimoike *et al*., 2002) volcanoes in Japan and Teide, Spain, (Hernandez *et al*., 2000) and Cerro Negro volcanoes, Nicaragua, (Salazar *et al*., 2001). Remote measurements on chemical composition of volcanic gas using FTIR spectral radiometer were carried out. The CO/CO_2 ratios were obtained at Aso volcano (Ono *et al*., 1999), and anomalously high SiF_4/HF ratio was identified at Satsuma-Iwojima volcano (Mori *et al*., 2002b). Urai *et al*. (1999) showed that it is possible to measure distributions of SO_2 emission from volcanoes using the ASTER launched on EOS AM-1 satellite. Gas or fluid velocity from boreholes were measured based on temperature data (Umeda *et al*., 1999; Igarashi *et al*., 2000). An in-situ method for CO_2 flux measurements from fumaroles using tracer gas is established (Mori *et al*., 2001). Natale *et al*. (2000) developed a system to measure pressure gradients in the soil at locations of ground gas emissions. A method for Carbon-isotope composition for extremely low concentration CH_4 was established and successfully applied to volcanic gases from Satsuma-Iwojima volcano (Sato *et al*., 1999b). A continuous monitoring system for measuring fumarolic gas composition was developed and applied to a steam-well at Izu-Ohsima volcano (Shimoike and Notsu, 2000). Colors of the waters or hot spring deposits are used to understand volcano-hydrothermal systems: Ohsawa *et al*. (2002a) showed that blue color of thermal waters are related to Rayleigh scattering by colloidal silica; Ossaka *et al*. (2000) reported discolor of sea water during the 1986 eruption of Izu-Oshima volcano; Oue *et al*. (2002) revealed the reason for the change in the color of the hot spring deposit at Chinoike-Jikoku in Beppu geothermal area.

Geochemistry and exploration of Geothermal and hydrothermal systems are studied at various locations: Kawayu spa (Suzuki *et al*., 2000), Matsukawa (Ozeki *et al*., 2001), Hachimantai (Kobayashi *et al*., 1999), Uenotai (Takeno, 2000), Kakkonda (Ehara *et al*., 2001), Hakone (Ohsawa *et al*., 2000b), Kusatsu-Shirane (Ohba *et al*., 2000b), Hachijojima (Matsuyama *et al*., 1999; Matsuyama *et al*., 2000), Fushime (Okada *et al*., 2000), Beppu (Yusa *et al*., 2000), Kirishima (Fujita *et al*., 2000; Fujita and Sakamoto, 2001a), Kagoshima city (Fujita and Sakamoto, 2001b), Sumikawa (Kato *et al*., 2001; Ueda *et al*., 2001). Polymerizations of silicic acids in geothermal and low temperature waters are discussed (Sugita and Yamamoto, 1999; Fujita and Sakamoto, 2001c). Yoshida (2000) reviewed and recommended procedures for chemical analyses of geothermal fluids.

Global volcanic fluxes of Nitrogen, Helium carbon are discussed based on elemental and isotopic compositions of the volatile species (Sano, 2001; Sano *et al*., 2001). Many studies on noble gas chemistry and isotope compositions in lavas or xenolithes were carried out to understand volcanism, and magma and mantle systems (Tedesco *et al*., 1998; Xu *et al*., 1998; Hanyu *et al*., 1999; Sumino *et al*., 2000; Sumino *et al*., 2001; Hanyu *et al*., 2001; Matsumoto *et al*., 2001; Orihashi *et al*., 2001; Yamamoto *et al*., 2001; Matsumoto *et al*., 2002c).

3. Geochemical Studies of Hydrothermal Activities on Oceanic Bottoms

Ishibashi and Gamo (1999) summarized the chemical aspects of submarine hydrothermal systems. A review article by Gamo (1999) focused on the behavior of methane gas associated with cold seepage from sediment of the Nankai Trough. New techniques for surveying trace amount of metals in seawater have been developed: Okamura *et al*. (1998, 2001) developed in-situ Mn analyzer using chemiluminescence and applied for hydrothermal plume observation; Obata *et al*. (2000) developed Al flow-through analysis method using fluorometric detection for collected samples from oceanic hydrothermal regime.

The chemical characteristics of hydrothermal fluids from the Indian Ocean have been revealed for the first time (Gamo *et al*., 2001). The concentration and stable carbon isotopic composition of methane in water related to seafloor hydrothermal venting of Myojin Knoll Caldera, Izu-Bonin arc, have been measured, and results showed the microbial methane oxidation in the effluent plume (Tsunogai *et al*., 2000). The hydrothermal petroleum has been investigated at the submarine Wakamiko caldera in northern Kagoshima Bay (Yamanaka *et al*., 2000). The pore fluids from Ocean Drilling Program (ODP) Leg 169 were analyzed for He and carbon gas geochemistry (Ishibashi *et al*., 2002), and the fluid was also compared with the fluid chemistry of ODP Leg 139 (Gieskes *et al*., 2002).

Various elements including rare earth element (REE), Yttorium, Tungsten and Molybdenum in hydrothermal fluids and deposits have been extensively studied (Douville *et al*., 1999; Hongo and Nozaki, 2001; Sohrin *et al*., 2002). Shikazono and Kusakebe compared the chemical and mineralogical characteristics of sulfate-sulfide chimney in backarc basin and mid-ocean ridge. Differentiated volcanic glasses dredged from the Manus Basin were analyzed for volatiles and Marty *et al*. (2001) suggest that most of the volatiles are lost continuously during the fractional crystallization.

(Toshiya Mori)

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