

## Secular variation of halogen concentrations in Yugama crater lake water, Kusatsu-Sirane Volcano

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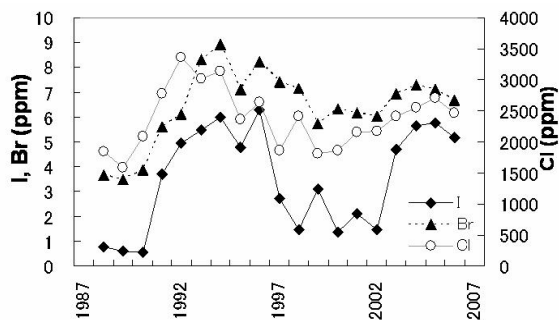
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Mt. Kusatsu-Sirane is an active volcano located along the volcanic front on Honshu Island, Japan. Crater lake water in Yugama, located at the top of Kusatsu-Sirane volcano, contains high concentration of chloride. It was observed that variation of chloride concentration in Yugama water reflected the volcanic activity (Ohba *et al.*, 2000). However, there are limited data on other halogens. In this study, concentrations of I and Br in Yugama water were determined to know their levels and their relationships to chloride.

54 water samples, which were collected from Yugama lake during 1988-2006 were used in this study. Some other samples collected surroundings of Yugama were also used. Concentrations of I and Br were measured by ICP/MS.

Concentration ranges of I, Br and Cl in Yugama water samples collected during this period were 0.3-6ppm, 2-9ppm and 1500-3500ppm, respectively (data for Cl; Ohba *et al.*, 2000). It is interesting to note that concentration of I in Yugama water is about 100 times higher than that of sea water. Secular variations of I and Br are similar to that of Cl. The concentrations of these three elements increased markedly during 1989-1992, with a special reference to I, which increased about 10 times. Relationships between the halogen concentrations and the volcanic activity (e.g. frequency of earthquakes) of Mt. Kusatsu-Sirane were observed, although the timing of I increase was 1-2 years later than that of Cl and Br.

In this area, there are some hot springs which are supposed to be originated from the same source as Yugama water. Variations of their halogen concentrations and also I/Cl ratios were found to be wide in those samples, while their Br/Cl ratios were relatively constant.



**Figure 1:** Secular variation of halogen concentrations in Yugama water

### Reference

T. Ohba *et al.*, (2000): *J. Volcanol. Geotherm. Res.* **97**, 329-346 (2000)

## Reconstruction of the past biogeochemical cycles based on compound-specific N and C isotopic analyses of sedimentary porphyrins

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Porphyrins are thought to have derived from biomolecules such as chlorophylls and heme, among which eoxophylloerythroetioporphyrins (DPEP) and its analogues are structurally related to chloropigments. These compounds thus preserve stable isotopic compositions of N and C of phototrophs of the past environment. We have developed methods for precise determinations of N and C isotopic compositions of individual sedimentary porphyrins and maleimides, which include isolation and purification of individual alkylporphyrins and porphyrin acids by dual-step HPLC preparation (Kashiyama *et al.*, 2007a). We have analyzed various alkylporphyrins and porphyrin acids from organic-rich Miocene sediments of the paleo-Japan Sea (Onnagawa Formation) as well as Cretaceous black shales (Livello Selli and Livello Bonarelli, Italy) deposited in the western Tethys during the Ocean Anoxic Events (OAEs). The N isotopic composition of DPEP, which should have derived in chlorophylls in general, ranged from -6.9 to -3.6‰ (n=7) in the Miocene shale and -6.6 to -3.9‰ (n=5) in the OAE black shales, indicating that the N<sub>2</sub> fixation was a major process for N assimilation hence the dominance of diazotrophic cyanobacteria in primary production in these paleo-oceans. Furthermore, DPEP were relatively enriched in <sup>13</sup>C in both environments (-17.9 to -15.6‰ in the Miocene shale and -20.5 to -17.9‰ in the OAE black shales), which suggests relatively small carbon isotopic fractionation during photosynthesis and supports significant contribution of cyanobacteria-derived chloropigments. We also determined isotopic compositions of *source-specific* porphyrins such as 17-nor-DPEP (derived from chlorophyll-*c*), 8-nor-DPEP (possibly derived from divinylchlorophylls; Kashiyama *et al.*, 2007b) as well as DPEP with extended alkyl side chains and their equivalents among porphyrin acids (derived from bacteriochlorophyll *c*, *d*, and *e*; analyzed as maleimides). The latter two porphyrins had variable and rather unique isotopic compositions compared to DPEP. Such an approach should allow reconstruction of community structures of phototrophs and associated biogeochemical processes associated with the photosynthesis in the past oceans.

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