

Volatile inventory of excess degassing

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Overview

Excess degassing is heterogeneous emission of volatiles and magma caused by gas-magma decoupling in the upper crust. There are two types of excess degassing caused by different mechanisms. Excess degassing by eruption is considered as the result of eruption of bubble accumulated magma [1] whereas excess degassing by non-erupting persistent degassing is driven by conduit magma convection [2]. Sulfur budgets of eruptions, in particular of silicic magmas at subduction zones, suggest that one to two orders of magnitude larger amount of sulfur than in the erupted magma was accumulated prior to the eruption. Composition of the accumulated gas phase can be estimated based on melt inclusion and solubility studies [1, 3], however, bulk volatile composition of the magma supplied to the shallow crust is hard to constrain based on those studies.

Persistent degassing emits about ten times larger amount of SO₂ than degassing by eruption at subduction zone and is the major source of crustal degassing [2]. Conduit magma convection continuously transports magmas stored at a deep chamber to a shallow vent and causes low-pressure degassing, resulting in almost complete magma degassing of volatile species with low solubility, such as H₂O, CO₂ and S. Therefore, compositions of the persistent degassing would be a good approximate of bulk volatile composition of original magmas and provided important constraints to volatile budget of the shallow crust.

Composition of Persistent Degassing

Quantitative estimates of Composition of persistent degassing became possible by application of FT-IR and Multi-GAS techniques to volcanic plume observation. Accumulation of such data for Japanese volcanoes suggests that magmas with a similar volatile composition are supplied to different volcanoes. One of the most intensively degassed volcano in this century, is Miyakejima volcano, Japan, which emitted about 24 Mt of SO₂. The intensive degassing of started in 2000 and the SO₂ flux decreased by almost 100 times during ten years but gas compositions remained similar; H₂O/CO₂ (mol ratio) = 50, CO₂/SO₂ = 0.7. Based on H₂O content of basalt melt inclusions, volatile contents in the original basaltic magma are estimated as H₂O=3.0, CO₂=0.15 and S=0.17 (wt.%) [4]. Other persistently degassing volcanoes in Japan have similar CO₂/SO₂ ratio of 0.5-2, indicating that subduction zone magmas are not always CO₂-rich. In contrast, there are some other subduction volcanoes, such as Stromboli, Masaya and Soufriere Hills, which persistently discharge gases with larger CO₂/SO₂ ratios of 6-10. If the CO₂-rich magma is necessary to cause bubble accumulation at a deep chamber resulting in the excess degassing by eruption, occurrence of the excess degassing might be coincident with the CO₂-rich persistent degassing. Further accumulation of the composition data of persistent degassing might reveal such coincidence, if any, and constrain the volatile budget in the upper crust.

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Characteristic of the long-term accumulation of lanthanides on *Saccharomyces cerevisiae*

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Interaction between actinides and fissiogenic rare earth elements (REEs) and microorganisms have attracted increasing attention due to the ubiquitous occurrence of microorganisms in the subsurface environment and to implication to the safety assessment of nuclear waste disposal. Although the post-adsorption nanomineralization process of individual REE was proposed by a recent study [1], the contaminating fluid may contain a series of actinides and fission products. Hence, the present study has investigated the post-adsorption process on microorganisms in the system containing a series of lanthanides (Ln) to understand the effect of coexisting Ln on the adsorption and post-adsorption process.

S. cerevisiae (yeast) was harvested in a YPD (P-rich) media prior to the experiment. The yeast was then contacted with a P-free solution containing 14 lanthanide elements (La-Lu) up to 72 h, in which the concentration of individual Ln was 0.0063 mM with the total Ln concentration of 0.085 mM. The experiment was conducted at three pHs, 3, 4, and 5, and at two different temperatures, 25 and 4 °C (no metabolism). The analytical techniques include ICP-MS -AES, FESEM-EDX, and TEM.

During exposure in the solution at 25 °C, all Ln were eliminated from the solution by 24 h at pH 4 and 5, while 50 % of the initial amount remained in the solution at pH 3 after 24 h. Particle at the size of ~100 nm precipitated on the cell surfaces at pH 3, while ~30 nm-sized nanoparticles were observed at pH 4 and 5. These nanoparticles are phosphate containing a series of Ln. The nanoparticles at pH 3 had monazite structure, while the particles forming at pH 4 and 5 were amorphous, indicating that crystallization took place only at pH 3. Deprotonation merely occurs at the functional group at pH 3 as evidenced by the other experiments at 4 °C, and the nanocrystallites possibly nucleated from the locally saturated solution adjacent to the cell surfaces. In contrast, Ln electrostatically adsorbed to the functional group was bound to P released from inside cell at pH 4 and 5. Most likely the geometry of Ln complex formation prevented the crystallization.

As for the Ln pattern, the greater amount of light REEs was removed from the solution than that of heavy REEs. The difference between the distribution coefficient, K_d (ml/g), of LREE and of HREE increased with time increasing. At 24 h, the K_d rate Nd to Tm ($K_{d, Nd}/K_{d, Tm}$) is 1.72, 4.61, and 6.86 at pH 3, 4, and 5, respectively. The K_d ratios greater than 1 indicate the preferential uptake of LREE by the microorganisms, which may be attributed to the lower solubility products of REE phosphate [2]. The present study demonstrated that the cell surfaces play a key role on kinetics and crystal formation in the post-adsorption biomineralization.

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