

## Complexation of REE and W in magmatic fluid coexisting with granitic magma based on thermodynamic calculation

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Generation of fluid from highly differentiated granitic magma is the most important process for the formation of magmatic hydrothermal ore deposits. The Yamaguchi W-Cu skarn deposit is located in the Northern Miyako granitoids in the W province of the outer zone of Northeast Japan. The scheelite ores occur in aplitic and pegmatitic veins and clinopyroxene skarn. The scheelite-bearing aplitic veins of the Yamaguchi deposit are composed of quartz, plagioclase (albite to andesine), K-feldspar, titanite and scheelite. Contents of major elements in the Miyako granitoids decrease from marginal to central zone, however, REE, Cu and W contents of granitic rocks decrease from marginal zone to central zone of Miyako granitoids. Moreover, concentrations of REE, Cu and W in the scheelite-bearing aplitic veins are also higher than those of the latest stage granitic rocks. REE concentration in scheelite in the mineralized aplitic veins is extremely higher than rock-forming minerals in the Miyako granitic rocks. Chondrite-normalized REE patterns of scheelite are LREE-rich with downward-sloping curve. The compositional data of scheelite with extremely high REE concentration suggest the removal of REE from residual melt by fluid. Fluid inclusions in scheelite-bearing aplitic veins have wide filling temperature ranges of 390-680°C (P = 1.5 - 2 kbar) with 4.0 - 19.0 wt.% NaCl equiv. and 3.0-5.5 wt.% CO<sub>2</sub>. Trapping conditions of these fluid inclusions are close to those of haplogranite solidus. These data also reveal that the fluid responsible to scheelite-mineralization should coexisted with late stage granitic melt. The speciation of REE and W in the fluid was estimated by EQBRM at T = 400, 500 and 600°C and P = 2 kbar. The speciation of REE and W complexes is carried out about chloride, hydroxide, carbonate and fluoride complexes in various pHs. The calculated results with the assumption for these of existence are as follows: (1) Cl- and OH-complexes are important for REE in neutral condition; (2) predominant species of W are probably Na-W hydroxide complexes such as NaHWO<sub>4</sub><sup>0</sup> and NaHWO<sub>4</sub><sup>-</sup>. The result of W speciation is consistent with mineral assemblages of scheelite-bearing aplitic veins. It is likely that the low REE, Cu and W contents in latest stage granite could have been caused which is responsible for the removal of those elements from the granitic melt.

## Isotopomer analysis of nitrous oxide emitted from burning of agricultural residue

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The intramolecular distribution of stable isotope composition in nitrous oxide in the burning plume was measured for analysis of behavior of nitrous oxide during the biomass burning. The biomass burning experiment was carried out for collecting the burning plume using a grate type test furnace. Dried rice straw was used as the biomass material for burning. It was confirmed that nitrous oxide was mainly formed in the flaming stage. Assuming the simple mixing of burning plume with background air, the isotopomer ratios of the end-member in burning plume were estimated. The nitrous oxide in the burning plume was depleted in <sup>15</sup>N relative to the nitrogen compounds bound in the rice straw, and was slightly enriched in <sup>18</sup>O relative to atmospheric oxygen. From the viewpoint of intramolecular distribution of nitrogen isotopes, the central nitrogen atom was slightly heavier than the end positioned one. The kinetic isotope effects for nitrous oxide during the thermal decomposition and hydrogen reduction were evaluated using a flow tube furnace at 1273K. The behavior of nitrous oxide with biomass burning was analyzed on the basis of the isotopomer signatures and the kinetic isotope effects during the destruction reaction at high temperature. The δ<sup>15</sup>N of the central nitrogen in nitrous oxide before destruction in the flame region was almost equivalent to that of the end positioned nitrogen. The extent of destruction reaction in the flame region was evaluated quantitatively.