

## Trace element behavior in hydrothermal processes: A geochemical study of skarn reaction zone from Hirao-dai, Fukuoka, Japan

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A reaction zone between a metamorphosed basic dyke (MB) and marble at Hirao-dai, north Kyushu, Japan, consists of well-organized sequential zones of diopside, garnet and wollastonite; textures are characteristic of diffusion-controlled structures. Each of the mineral zones consists dominantly of one mineral species except garnet zone. The modal composition of the garnet zone is garnet 67%, clinozoisite 17%, plagioclase 7%, diopside 4%, vesuvianite 3% and others 2% (titanite, apatite and K-feldspar). There is no compositional variation within individual mineral species in each mineral zone except vesuvianite. Oscillatory zoning is found in vesuvianite. The reaction zone was formed with H<sub>2</sub>O-rich fluid during contact metamorphism associated with intrusion of a Cretaceous granodiorite at about 300 MPa and 700°C (Fukuyama *et al.*, 2004; Fukuyama *et al.*, 2006). The MB consists of diopside, biotite and plagioclase ( $X_{Ab}=0.4-0.8$ ), whereas the marble is almost pure calcite. Nishiyama (1989) reported a composite vein derived from these reaction zones by hydrofracturing and mass transfer along the fracture. The composite vein consists of garnet, plagioclase and wollastonite. The vein is dominantly composed of garnet near the reaction zones and dominantly plagioclase at a distance of 2 m from the reaction zones.

We analyse REE and other trace elements in the reaction zone, marble and MB using ICP-MS, ICP-AES and LA-ICP-MS in order to examine the behaviors of trace elements during fluid-rock interaction. The chondrite-normalized REE pattern of garnet zone is similar to those of vesuvianite. Modal composition and trace element contents of minerals indicates that REE and trace elements in bulk garnet zone are contained in vesuvianite crystals, not in garnet crystals. The major and trace elements data indicate that sorption processes during fluid-rock interaction were controlled by the vesuvianites. The oscillatory zoning of major and trace elements in vesuvianite may be related to influxes of fluid due to rapid permeability changes with hydrofracturing. Based on the spatial variation of REE in the reaction zone, marble and MB, we can evaluate the mass transfer process of the H<sub>2</sub>O-rich fluids involved in the formation of the reaction zone.