

## Reaction zones and composite veins around the metamorphosed basic dykes in the Hirao limestone, Fukuoka, Japan.

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This paper describes petrography and mass transfer analysis of the reaction zones and composite veins around the basic dykes in the Hirao limestone both of which are thermally metamorphosed by the Hirao granodiorite (Cretaceous). Reactions between the basic dykes and the limestone due to the contact metamorphism lead to the development of the reaction zones between them and the composite veins which were derived from the reaction zones by hydrofracturing and mass transfer along the fracture (Nishiyama, 1989). The peak condition of the contact metamorphism is estimated as T=650-700 °C and P<500MPa, based on thermodynamic analysis of metamorphic reactions in the Tagawa metamorphic rocks underlying the Hirao limestone.

The reaction zones consist of three zones: diopside zone, garnet zone and wollastonite zone in this order from the metabasite dyke towards the crystalline limestone. Dominant mineral assemblages of the rocks are; metabasite: biotite + diopside + plagioclase, diopside zone: diopside + plagioclase, garnet zone: grossular + plagioclase, wollastonite zone : wollastonite, and crystalline limestone : calcite. In plagioclase albite lamellae are observed in the matrix of Ab<sub>62-76</sub> plagioclase, of which compositional gap corresponds to the peristerite gap, indicating the reequilibration at approximately 400 °C. The total reaction leading to the development of the reaction zones can be modeled as:

biotite + calcite + plagioclase =  
diopside+garnet+wollastonite+K<sub>2</sub>O+5Na<sub>2</sub>O+33CO<sub>2</sub>+2H<sub>2</sub>O

We employed the steady diffusion model (Joesten, 1979) to analyze the stability condition of the zonal sequence and to get exchange cycles, ignoring conservation of fluid species. As a result, the stability of the observed zonal sequence depends on  $L_{SiO_2SiO_2}/L_{Al_2O_3Al_2O_3}$  and  $L_{SiO_2SiO_2}/L_{CaOCaO}$  but not on  $L_{SiO_2SiO_2}/L_{MgOMgO}$ .

A composite vein consisting of garnet, plagioclase and wollastonite comes out from the reaction zones. The vein is rich in garnet near the reaction zones and rich in plagioclase at a distance of 2meters. This change in mode may reflect the relative magnitude of diffusivity of Al<sub>2</sub>O<sub>3</sub> against that of SiO<sub>2</sub>.

## The continuous growth of aqueous aluminum nanoclusters

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### Introduction

The geochemistry of aluminum in natural waters and soil has been debated for decades, mainly with respect to the formation of polynuclear species and hydroxide minerals. However, it is accepted now that the tridecameric molecule AlO<sub>4</sub>Al<sub>12</sub>(OH)<sub>24</sub>(H<sub>2</sub>O)<sub>12</sub><sup>7+</sup>(aq), known as Keggin Al<sub>13</sub>, can form spontaneously in acidic waters from acid-mine areas or poorly buffered soil receiving acid rain mixes with neutral surface waters (Casey et al., 2001). For many years it was thought that the tridecameric nanoclusters in aqueous solutions is decomposed rather fast and that in a first step amorphous and then crystalline aluminum hydroxide solids are formed.

### Discovery

Our new findings from long-term storage experiments confirmed these assumptions, however only partially. Five slightly acidic bulk solutions containing 7 mM Al<sub>13</sub> were stored on an office desk during 11 years at room temperature, gas tight but exposed to day light. In four glass containers the solutions were still fairly clear and about 95 % of the total Al(III) has been transformed into the larger nanocluster (AlO<sub>4</sub>)<sub>2</sub>Al<sub>28</sub>(OH)<sub>56</sub>(H<sub>2</sub>O)<sub>24</sub><sup>18+</sup>(aq) (Al<sub>30</sub>), which contains 30 Al(III) and bears an even higher charge (18+). In one glass container the solution became very milky; approximately 30 % of the total Al(III) has been transformed into crystalline gibbsite and the other 70 % into the Al<sub>30</sub> nanocluster. The chemical structure of the Al<sub>30</sub> nanocluster has just recently been resolved (Alloche et al., 2000; Rowsell et al., 2000).

### Conclusion

So far it was thought that elevated temperatures were necessary for the synthesis Al<sub>30</sub> molecule. Our finding shows that the Al<sub>30</sub> nanocluster forms spontaneously in aqueous solutions of Al<sub>13</sub> even at ambient conditions. Since this process seems to have a time constant of a couple of years, we might find even larger aluminum nanoclusters one day.

### References

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