

## 3.6.53

### Geochemical behavior of rare earth elements in altered rocks in Kuroko mining area

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Kuroko deposits are polymetallic sulfide-sulfate deposits occurring in Miocene altered volcanic region in Japan. The country rocks are suffered intense hydrothermal alterations. Previous studies on the hydrothermal alterations revealed that the systematic variations in oxygen isotopic compositions of altered rocks away from the ore body exist. The present study intended to obtain the REE data on hydrothermally altered dacite in the Kuroko mining area, Japan and compare these data with oxygen isotopic data. It was found that (1) altered footwall dacite exhibits Eu negative anomaly compared with fresh dacite, suggesting selective extraction of Eu(2+) by hydrothermal solution, (2) altered hanging wall dacite and dacite in deeper horizon exhibit Eu positive anomaly compared with fresh dacite, suggesting addition of Eu(2+) from the hydrothermal solution to the dacite, and (3) La/Yb ratio of altered dacite positively correlates with oxygen isotopic composition, suggesting that light rare earth elements added to the altered dacite from hydrothermal solution. The above features are

## 3.6.54

### Evolution of LREE-Y bearing fluoride-phosphate-hydrothermal system (thermodynamic model)

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Two versions of the model of physical-chemical behavior of REE in the process of post-magmatic evolution of the phosphate-fluoride ore-forming system elaborated on the base of both thermodynamic and mineralogical-geochemical data. The alkaline one corresponds to *carbonatites* with a clearly defined fluorite mineralization (e.g. Smith et al, 2000). The second version takes into account the *greisen* type of REE-bearing ore deposits (e.g. Kupriyanova et al, 1997). The general approach and the essence of the model were described recently in the relation to the more simple REE-fluorite system (Kolonin & Shironosova, 2001, 2002). Data base SUPCRT98 for REE and other aqueous species was adapted to the computer code "Hch" (Shvarov, 1999). Approximation of REE-fluorite and monazite as ideal solid solutions was used in numerical experiments under discussion.

*In the alkaline case* thermodynamic modeling has shown the high mobility of LREE at pH = 6-8 and temperatures of 500-350°C in chloride carbonate fluids containing 0.01-0.05m HF in equilibrium with calcite and fluorapatite. Concentrations of Ce, La and Nd, existing in the solutions as anion hydroxide complexes, first decrease at 350-200°C because of the formation of monazite and REE-fluorite and then return to the initial level at lower temperatures as a consequence of monazite dissolution. The high stability of monazite associated with fluorapatite in the fluid of the similar composition within 500-300°C and subsequent replacement of monazite by REE-fluorite was shown *in the acid version* with pH=3.1±0.1. In this case the initial low concentrations of LREE in the fluid are presented by halide complexes  $\text{LnF}^{++}$  and  $\text{LnCl}^{++}$ . They gradually increase up to the beginning of fluorite formation, especially after monazite dissolution.

Elucidation of predominant complex forms of REE in the fluid inclusions from natural quartz-fluorite veins with REE-mineralization (Banks et al., 1994) by the thermodynamic method is an important verification of the acid model.