

Fluid inclusion study on the ore-forming fluid of rutile occurring in eclogite from CCSD main hole

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Rutile is a major economic resource in the samples from Chinese Continental Scientific Drilling (CCSD) main hole, which located in Maobei, Donghai county, East China. Rutiles occur in UHP rocks, such as rutile eclogite, quartz-rutile eclogite, phengite - rutile eclogite, Kyanite - rutile eclogite etc. The formation of rutiles can be roughly divided into three stages corresponding to the metamorphic period. Fluid inclusion have been studied:

1. The rutiles formed in pre-peak metamorphism stage, which occurred as small inclusions in garnet and omphacite. Few fluid inclusions can be found in the rutiles of this stage. In fact, no valuable fluid inclusion information can be collected.

2. The rutiles formed in the peak metamorphism stage during progressive metamorphic process, which occurred as intercrystalline grains with garnets and omphacites. Three type fluid inclusions can be found in the rutiles of this stage, which are aqueous two phase fluid inclusion; pure CO₂ inclusions; CO₂-bearing three phase inclusion; These inclusions are similar to the fluid inclusions kept in other peak metamorphic period UHP minerals, such as garnet, zircon etc.

3. The rutile formed after peak metamorphism stage during retrograde metamorphic process, which occurred as rutile vein in the cleavage or fracture of garnet. Sometimes, the rutile veins associated with quartz vein. Several type fluid inclusions can be found in the rutiles of this stage, which are aqueous two phase fluid inclusion; CO₂-bearing two or three phase inclusion; solid-bearing multi-phase inclusions. These inclusions are similar to the inclusions formed in typical retrograde process of UHP rocks.

Fluid inclusions study indicate that the different stage of rutiles in eclogites formed in the specifically metamorphic period and fluid inclusion kept in rutiles provide a new and useful means to reveal not only the ore-forming fluid of rutile, but also fluid process related with the subduction and exhumation of UHP rocks.

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The structure of Gd³⁺ aqua and chloro complexes under hydrothermal conditions

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A greater understanding of the stability of REE complexes is needed in order to understand the transport of REEs in hydrothermal and metamorphic systems. As part of a broader study of REE in hydrothermal fluids, synchrotron x-ray spectroscopy experiments were made of the Gd³⁺ aqua and chloro complexes at elevated temperatures and pressures. Fluorescence Gd L₃-edge XAFS spectra were measured from 0.006M Gd/0.16M HNO₃ aqueous solutions in a hydrothermal diamond anvil cell at up to 500 °C and 260 MPa. The measurements were made on beamline 201D-B at the Advanced Photon Source, Argonne National Lab. Spectral analysis shows that the Gd-O distance of the Gd³⁺ aqua ion in a dilute nitrate solution exhibits a uniform reduction at a rate of ~0.007 Å/100 °C, whereas the number of coordinated H₂O oxygens decreases from 9.0 ± 0.5 to 7.0 ± 0.4, upon increasing temperature from 25 to 500 °C. The moderate loss of water molecules in the inner hydration shell over this temperature range (a 22% reduction) indicates a relatively stable Gd³⁺ aqua ion complex. Similar Gd L₃-edge XAFS measurements were made of 0.006M and 0.1M GdCl₃ aqueous solutions at up to 500 °C and 480 MPa. Results show that in the 25-150 °C range, association between Gd³⁺ and Cl⁻ ions is negligible and the Gd³⁺ exists predominantly as an aqua ion in both solutions. In the 300 to 500 °C range, stepwise complexes most likely of the type Gd(H₂O)_δ - nCl_n^{+3 - n} (δ ≈ 7) occur in these solutions. The number of chlorines (n) in these complexes increases steadily with temperature from 0.4 ± 0.2 to 1.5 ± 0.3 in the 0.006M aqueous solution whereas n increases from 0.9 ± 0.7 to 1.7 ± 0.8 in the 0.1M GdCl₃ aqueous solution in the 300 - 500 °C range. In going from 25 to 500 °C, the number of H₂O oxygens of Gd(H₂O)_δ - nCl_n^{+3 - n} complexes decreases uniformly from 8.9 ± 0.4 to 5.9 ± 0.7 and from 9.0 ± 0.5 to 5.0 ± 1.1 in the 0.006M and 0.1M GdCl₃ aqueous solutions, respectively, whereas the Gd-O bond of the Gd³⁺ chloro complexes exhibits slightly smaller rates of reduction (0.005-0.006 Å/100 °C) for both solutions. Our results have negligible pressure dependence up to 480 MPa.