

### Relics of samarskite structure in a metamict ABO<sub>4</sub> mineral and its high-temperature transformations

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A mineral predetermined as samarskite and originating from Beimyr, Iveland, Norway, was found to be amorphous to X-rays. The chemical analysis yielded the empirical formula  $(RE)_{0.381}Ca_{0.241}Fe_{0.297}U_{0.142}Zr_{0.971}(Nb_{0.764}Ta_{0.262}Ti_{0.065})_{2.1091}$  that fits quite well to the one of the assumed structural models for samarskite. Due to the metamict nature of the mineral, the structure recovery was induced by annealing experiments in air at 400, 500, 650, 800 and 1000°C. The sample portions were also heated in N<sub>2</sub> and in slightly reductive Ar/H<sub>2</sub> atmosphere at 600, 1000 and 1300°C. The annealing experiments in air showed the start of recrystallization at 650°C with crystallization of a pyrochlore phase and the occurrence of a new phase at 1000°C, which can be characterized as a proposed high-temperature samarskite phase with wolframite-type structure (s.g. P2/c, a=5.63(1) Å, b=9.93(2) Å, c=5.19(1) Å, β=93.6(2)°). The results of the annealing experiments in N<sub>2</sub> and Ar/H<sub>2</sub> atmosphere show similar recrystallization sequences like the experiments in air for 600 and 1000°C. At 1300°C, the phases that crystallized at lower temperatures are still present and there is no indication of new phases or phase transitions. Different atmospheric conditions during recrystallization seem to influence the heating products since the high-temperature samarskite phase is observed only for the mineral heated in air. For N<sub>2</sub> and Ar/H<sub>2</sub> atmosphere beta-fergusonite seems to be the most probable high-temperature phase along with pyrochlore. The variability of recrystallization of samarskite should be attributed to complex chemical composition, stability of the original structure, annealing conditions and heavily metamictized crystal structure, thus imparting the identification of the original structure in the thermally untreated sample. TEM micrographs of the unheated samarskite reveal the preservation of the original structure fragments in a predominantly amorphous mineral matrix. These crystalline domains show lattice fringes with d-values which could be assigned to a presumed low-temperature samarskite phase. SAED patterns obtained for the unheated sample confirmed these indications of the samarskite structure, which can be considered as the original one. The patterns might be indexed on an orthorhombic cell with Pbcn space group and calculated unit cell parameters a=5.69(2) Å, b=4.91(2) Å, c=5.21(2) Å. The low-temperature samarskite phase could be envisaged as a columbite-related structure assuming octahedral coordination for B-cations and octahedral or higher coordination for A-cations.

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### First in situ X-ray identification of coesite and retrogressed quartz on a glass thin section of ultrahigh-pressure metamorphic rock and their crystal structure details

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To ensure the presence of coesite and its transformed polymorph, quartz, in UHP rocks and to examine the relic of the phase transformation, crystal structures were analyzed by single crystal X-ray diffraction directly using the rock thin section mounted on a slide glass. The rock sample used is a coesite-bearing eclogite in the Sulu UHP terrain, eastern China. The crystal structures were successfully determined by this new method and the presence of coesite and quartz in UHP rocks are identified for the first time by X-ray diffraction. The R(F) converged to 0.046 for coesite and 0.087 for quartz. The displacement ellipsoids for coesite and quartz are larger than that previously reported for these two phases, and is consistent with expected effects of trapped strain due to the phase transformation from coesite to quartz during exhumation from the Earth's mantle.

This paper is the first report of single crystal X-ray diffraction of a rock thin section on a glass slide and establishes the technique, and provides proof-of-concept of the method. Although the mineral species included in a thin section can often be identified by other methods, such as Raman spectroscopy, an advantage of the reported method is that it can be applied to any mineral in a thin section, and not just to the UHP minerals. Moreover, it is applicable to an unknown or new mineral in a thin section, discarding the spots of known minerals and constructing a lattice from the residual spots to find the structure of the unknown phase.

### Reexamination of rengerite and strontio-orthojoaquinite from Ohmi-Itoigawa region, central Japan by TEM

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Varieties Sr-bearing minerals occur in tectonic block such as jadeite from serpentinite mélange exposed at Ohmi-Itoigawa region. Six Sr-bearing new minerals from this area have been reported. Crystal structure of rengerite and strontio-orthojoaquinite have been determined, however we carried out HRTEM observation and reexamined the structure. Rengerite crystals were very small, so HRTEM method is useful for these fine grained minerals.

Rengerite (Sr<sub>4</sub>ZrTi<sub>4</sub>(Si<sub>2</sub>O<sub>7</sub>)<sub>2</sub>O<sub>8</sub>) is Sr-Zr analogue of perrierite-(Ce)(Ce<sub>4</sub>MgTi<sub>5</sub>(Si<sub>2</sub>O<sub>7</sub>)<sub>2</sub>O<sub>8</sub>). We found orthorhombic polymorph of rengerite from mineral grain which was apparently rengerite-like. This mineral species has not been reported. The orthorhombic polymorph is over 5 μm in size and occur in parallel intergrowth with monoclinic rengerite.

Strontio-orthojoaquinite((Na,Fe)<sub>2</sub>Ba<sub>2</sub>Ti<sub>4</sub>(Sr,Ba,Nb,REE)(O,OH)<sub>4</sub>(Si<sub>4</sub>O<sub>12</sub>) · 2H<sub>2</sub>O) belongs to the joaquinite group. Strontiojoaquinite (monoclinic) is another polymorph. Only strontio-orthojoaquinite in joaquinite group mineral had been found in Japan. In this study, monoclinic structure was found in HRTEM examination. Monoclinic structure area is in parallel intergrowth with orthorhombic structure. HRTEM image shows that orthorhombic unit cell is composed of two monoclinic unit cells with twinning relation on (001). This structural property is based on the fact that orthorhombic joaquinite structure has pseudo mirror plane (Cannillo et al.,1972). Furthermore, we found another orthorhombic polymorph of 4O by HRTEM image. The orthorhombic joaquinite (Strontio-orthojoaquinite) is composed of two monoclinic unit cells, but this 4O orthorhombic structure is composed of four monoclinic cells with twinning-like relations.

These two minerals occur in different conditions in the same Ohmi-Itoigawa region: rengerite occurs as secondary veins in jadeite. Strontio-orthojoaquinite is spotted aggregate or lens-like in albite. Formation conditions of structure varieties of rengerite and strontio-orthojoaquinite are related to mother rock formation processes. We will discuss these formation conditions. Thus, HRTEM method is powerful tool even for descriptive mineralogy.

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### In situ high temperature single crystal X-ray diffraction study of natural heulandite at 150 °C

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In situ high-temperature crystal structure analysis of heulandite from Moharastra, India was conducted at 150°C to study the mechanism of dehydration to heat collapse phase. Both room temperature and high-temperature X-ray diffraction intensities of a single crystal (400 x 280 x 160 μm) were measured using Rigaku R-axis IV<sup>++</sup> diffractometer (MoKα radiation, 50kVx80mA) with imaging plate and the U-shaped furnace (Huber high temperature attachment:231).

The chemical composition of the specimen was determined by E.P.M.A. as (Na<sub>1.14</sub>K<sub>0.40</sub>Ca<sub>3.64</sub>Sr<sub>0.21</sub>)(Al<sub>9.21</sub>Si<sub>26.88</sub>)O<sub>72</sub>·25.86H<sub>2</sub>O (number of H<sub>2</sub>O molecules is from the result of structural refinement). At room temperature, the specimen has monoclinic, C2/m symmetry [a=17.761(3) Å, b=17.838(2) Å, c=7.431(1) Å and β=116.45(1)°]. Structural refinement of the data at room temperature yields the final R value 0.049 and Rw 0.123 for 1832 independent reflections, applying the weight w=1/[σ<sup>2</sup>(Fo<sup>2</sup>)+(0.0351p)<sup>2</sup>+23.740101p] where p=[2Fc<sup>2</sup>+Max(Fo<sup>2</sup>,0)]/3 for each reflection with anisotropic temperature factors. At 150 °C, the crystal has still monoclinic C2/m symmetry [a=17.762(3) Å, b=17.586(2) Å, c=7.452(1) Å, β=116.81(1)°]. Result of the structural refinement of the data at 150°C yields the R value 0.077 and Rw 0.206 for 1672 independent reflections, applying the weight w=1/[σ<sup>2</sup>(Fo<sup>2</sup>)+(0.0913p)<sup>2</sup>+36.4561p] where p=[2Fc<sup>2</sup>+Max(Fo<sup>2</sup>,0)]/3 for each reflection with anisotropic temperature factors.

The result of structural refinement at 150 °C showed that the size of the channels were compressed and elongated with the unit cell volume decrease of 1.4% compared with the room temperature data. Three cation sites found at room temperature were Na1, Ca2 and K3. The result of the crystal structure analysis at 150°C revealed that cations move towards the channel wall. Cation occupancy at Na1 site decreases more than at Ca2 site at 150°C, while the occupancy of K3 site increases.