

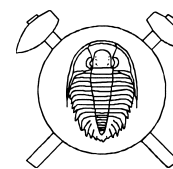
## Unraveling the history of high-grade rocks: What apatite may tell us?

(1 fig.)

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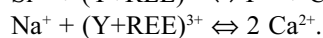
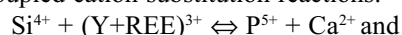
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Accessory minerals may provide important information on the history of metamorphic rocks. Minerals such as garnet, zircon, monazite, and xenotime have frequently been used to infer the T-P paths of the rocks and to unravel the chronology of metamorphic processes. The composition of apatite, which constitutes an abundant accessory phase in many metamorphic and igneous rocks, has been shown to be a function of temperature and portrays the activities of halogens (HF, HCl) in the fluids that finally equilibrated with the apatite.

In addition to estimates of T and halogen fugacities, the behavior of the lanthanides in REE-bearing apatite portrays the physico-chemical environment associated with fluid-mineral interaction. Depending on P-T-X of the infiltrating fluid, the lanthanides in the apatite may be unchanged, enriched or depleted. In nature, (REE+Y) depletion in apatite coupled with the formation of monazite and/or xenotime has been observed in variety of settings of fluid-rock interaction. Monazite/xenotime within or on the surface of fluorapatite typically occur in fluid-induced zones of dehydration (granulite-facies terranes) of amphibolite-facies rocks. Monazite has also been observed in fluorapatite thought to have interacted with late magmatic fluids. Both REE phosphate minerals have formed inside of igneous chlorapatite partially metasomatised under amphibolite-facies conditions.

To verify the conditions facilitating or suppressing the leaching of lanthanides from the apatite structure, a series of experiments have been conducted covering a wide range of temperature, pressure, fluid and apatite compositions. These experiments prove that monazite/xenotime, included in or grown on the crystal surface of the apatite, originates entirely from the apatite lanthanide budget available as the product of mass transfer during fluid-triggered metasomatic alteration, without the need of external REE sources. Initiation of mass transfer is primarily facilitated by two coupled cation substitution reactions:

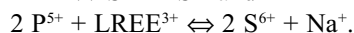
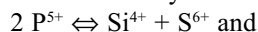


The ability of apatite to generate secondary REE phosphate minerals is a function of a series of factors: (1) the REE budget of the apatite itself, (2) the overall composition of the apatite, (3) temperature and pressure during fluid-mineral reaction, and (4) the composition of the metasomatising fluid.

Natural observations indicate, in accordance with the experimental data, that REE contents in the lower tenths of a weight-percent level are sufficient to produce REE

phosphate minerals under favourable conditions. Whether monazite or xenotime, or both, form is dependent on the LREE/HREE ratio of the parental apatite. Trace-element composition of the original apatite also determines the abundance of actinides accompanying the (Y+REE) in the reactant REE phosphate mineral(s). Because fluorapatite in nature usually contains Th and U in abundances much less than 100 ppm and displays Th/U ratios >1, resultant monazite typically is low in Th (<1 wt%) and U (<0.3 wt%) and can easily be distinguished from primary monazite in metamorphic and magmatic rocks for which Th contents exceeding 3 wt% are common. Experimental interaction of Th-rich fluorapatite (>400 ppm) as that from Durango, New Mexico, however, shows that a low Th abundance cannot be used as an unequivocal criterion for secondary monazite. Reaction of the Durango fluorapatite with water and KCl brines produced monazite containing up to 38 wt.% ThO<sub>2</sub>. Moreover, monazite inclusions have been observed in fluorapatite from dehydrated metamorphic rocks containing more than 2 wt% UO<sub>2</sub> and having Th/U ratios <1.

However, a high (Y+REE) content in the apatite does not necessarily guarantee its potential to nucleate REE phosphates. For example, monazite did not form in a LREE (7.7 wt.% REE<sub>2</sub>O<sub>3</sub>)-Si-S-rich fluorapatite, which was metasomatised in H<sub>2</sub>O under granulite-facies conditions. Instead, LREE-depleted and -enriched zones developed inside of the apatite in which two other cation substitution reactions came into operation in addition to the above two already described:



In this situation, the LREE removed from the depletion zone were, together with P, required to compensate the charge imbalance that resulted from the combined leaching of Si, S, and Na into the fluid. This observation addresses the importance of cations, other than the REE in the apatite, with respect to their ability in generating REE phosphates during metasomatism.

These experiments further demonstrate that apatite-related monazite/xenotime may form over a wide range of temperatures and pressures. Temperatures and pressures ranging between 300 and 900 °C and 500 and 1000 MPa, respectively, have been verified, but higher or lower T-P conditions may be suitable as well. This implies that REE phosphates associated with apatite could form in geological environments other than those already recognized so far. Furthermore, temperature

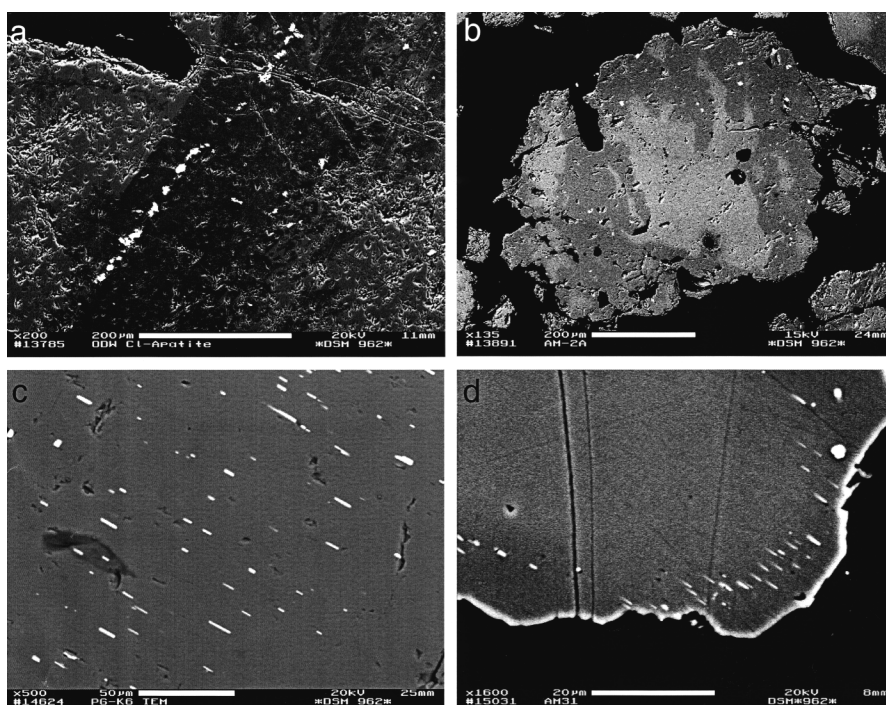


Fig. 1 (a) Chlorapatite (light) from the Ødegårdens Verk apatite mine, SE Norway, which has been metasomatically altered into hydroxy-fluorapatite under amphibolite-facies conditions. The dark alteration zone is depleted in (Y+REE) and contains a trail of monazite and xenotime grains along a cleavage fracture; (b) Experimentally metasomatised Cl-apatite from Ødegårdens Verk (900 °C, 1000 MPa, 7 days). The tiny bright grains in the dark alteration zones are monazite and xenotime; (c) Monazite rods in fluorapatite from the Kirunavaara magnetite-apatite ore, N Sweden, thought to be the product of metasomatism by late-stage residual magmatic fluids; (d) Fluorapatite from Durango, New Mexico, experimentally reacted with 1 M  $\text{H}_2\text{SO}_4$  (900 °C, 1000 MPa, 18 days). Note the presence of usually elongated monazite crystals in altered outer portions (dark) of the apatite.

seems to be one factor that determines the spatial position of the resultant REE phosphates with respect to the host apatite. The experiments suggest that higher T tend to favour nucleation of monazite/xenotime in the body of the apatite, whereas lower T facilitated their growth on the apatite grain surface.

The factor having the strongest impact on whether REE phosphate minerals form during fluid-rock interaction or not, is the composition of the fluid. Our experiments involved a great variety of fluids relevant to geological processes, which were brought into contact with the S-poor Durango fluorapatite: pure water,  $\text{H}_2\text{O}$ - $\text{CO}_2$  mixtures, Na-K-Ca chloride brines, as well as 1 and 2 M HCl and  $\text{H}_2\text{SO}_4$  solutions. Of these fluids, pure  $\text{H}_2\text{O}$ , diluted  $\text{H}_2\text{O}$ - $\text{CO}_2$  solutions, KCl brines, as well as 1 and 2 M HCl and  $\text{H}_2\text{SO}_4$  solutions partially depleted the apatite in (Y+REE) and caused monazite to form. These monazites have a variety of different compositions with respect to La/Ce ratio, Th-U content and the molecule in which the actinides were substituted into the structure (brabantite or huttonite). NaCl and  $\text{CaCl}_2$  brines did not induce monazite inclusions or rim grains to form.

Although considerable progress in understanding the basic principles of monazite/xenotime formation from REE-bearing apatite has been achieved over the past few years, we are just at the beginning. Many open questions demand further experimental work involving synthetic apatite. A selection of still unresolved problems include the

role of the geologic time scale, the influence of the anionic composition in the apatite and the reacting fluid as well as the significance of more complex fluids. Discovery of other occurrences of monazite/xenotime nucleated from apatite also will shed light into the question where and why these assemblages form in nature.

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