

An experimental study of apatite metasomatized by S-bearing fluid: the element redistribution and the formation of monazite and anhydrite (on the example of apatite from the Mushgai-Khudag complex, South Mongolia)

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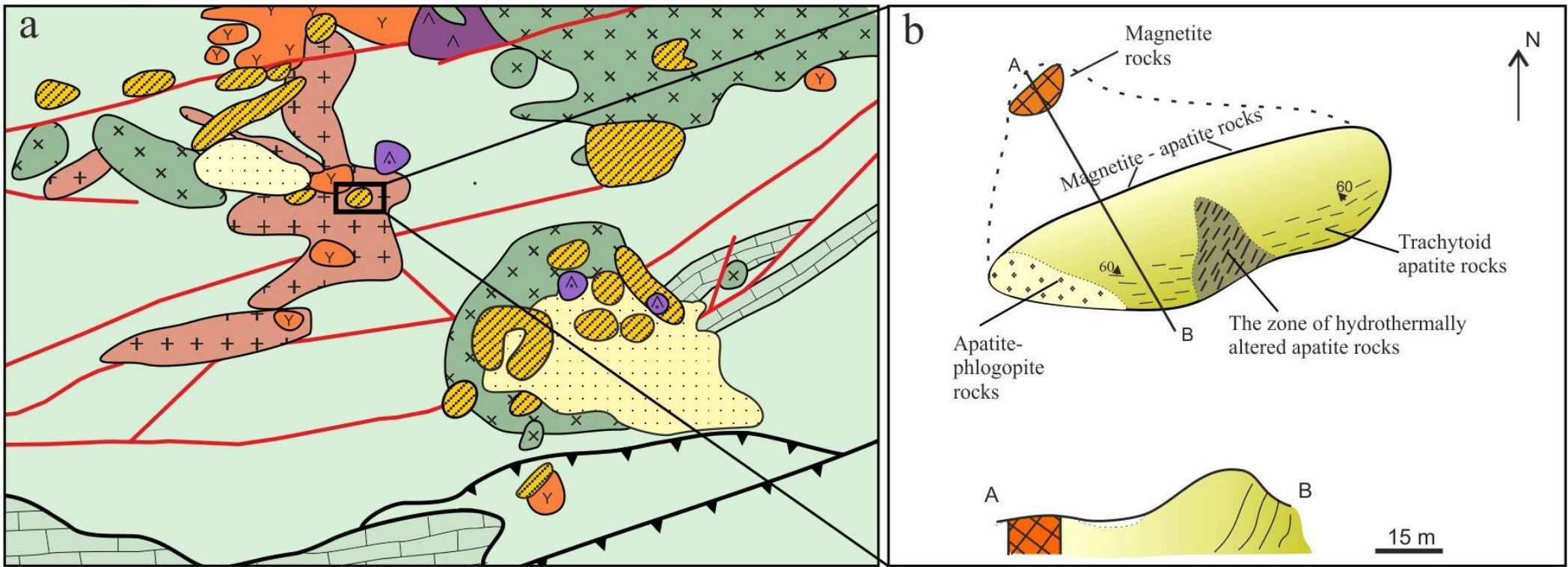
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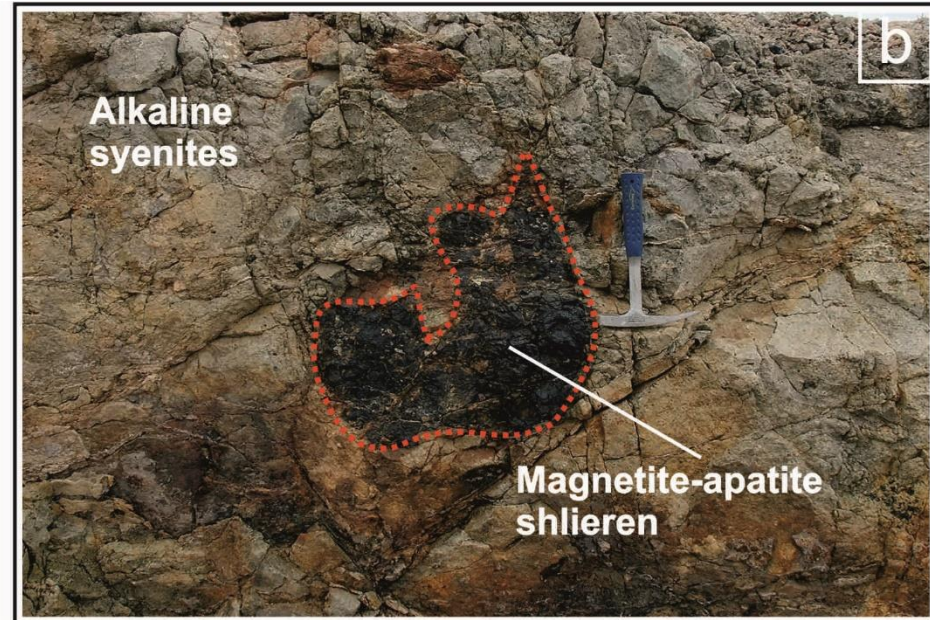
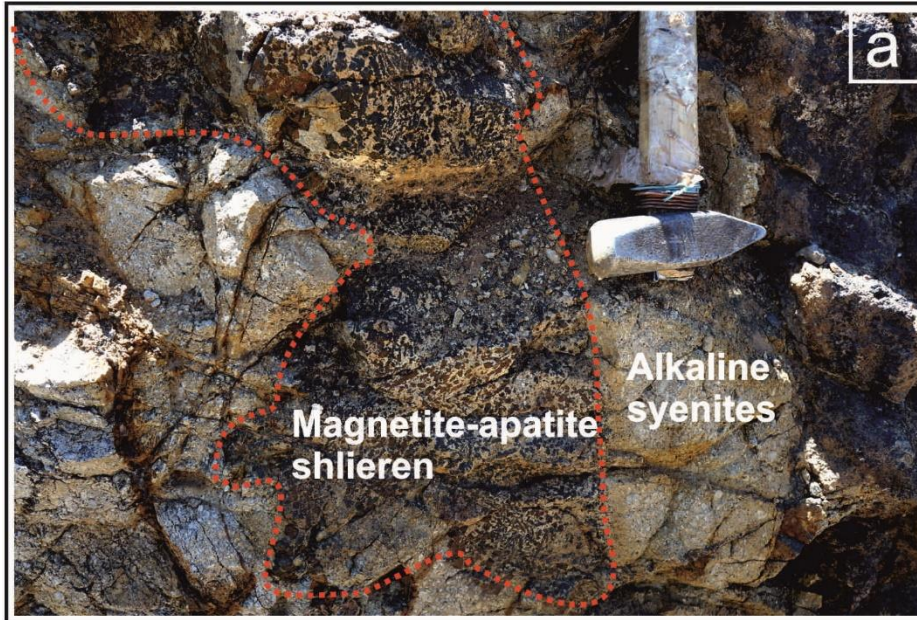
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Simplified geological map of the Mushgai-Khudag Complex (a) and geological scheme of the Apatite Hill (b) after (Samoilov and Kovalenko, 1983), with additions by the authors (Nikolenko et al., 2018).



The Mushgai-Khudag alkaline-carbonatite complex, located in southern Mongolia within the Central Asian Orogenic Belt (CAOB), comprises a broad range of volcanic and subvolcanic alkaline silicate rocks (melanephelinite-trachyte and shonkinite-alkaline syenite, accordingly) as well as magnetite-apatite rocks, carbonatites and fluorite mineralization.

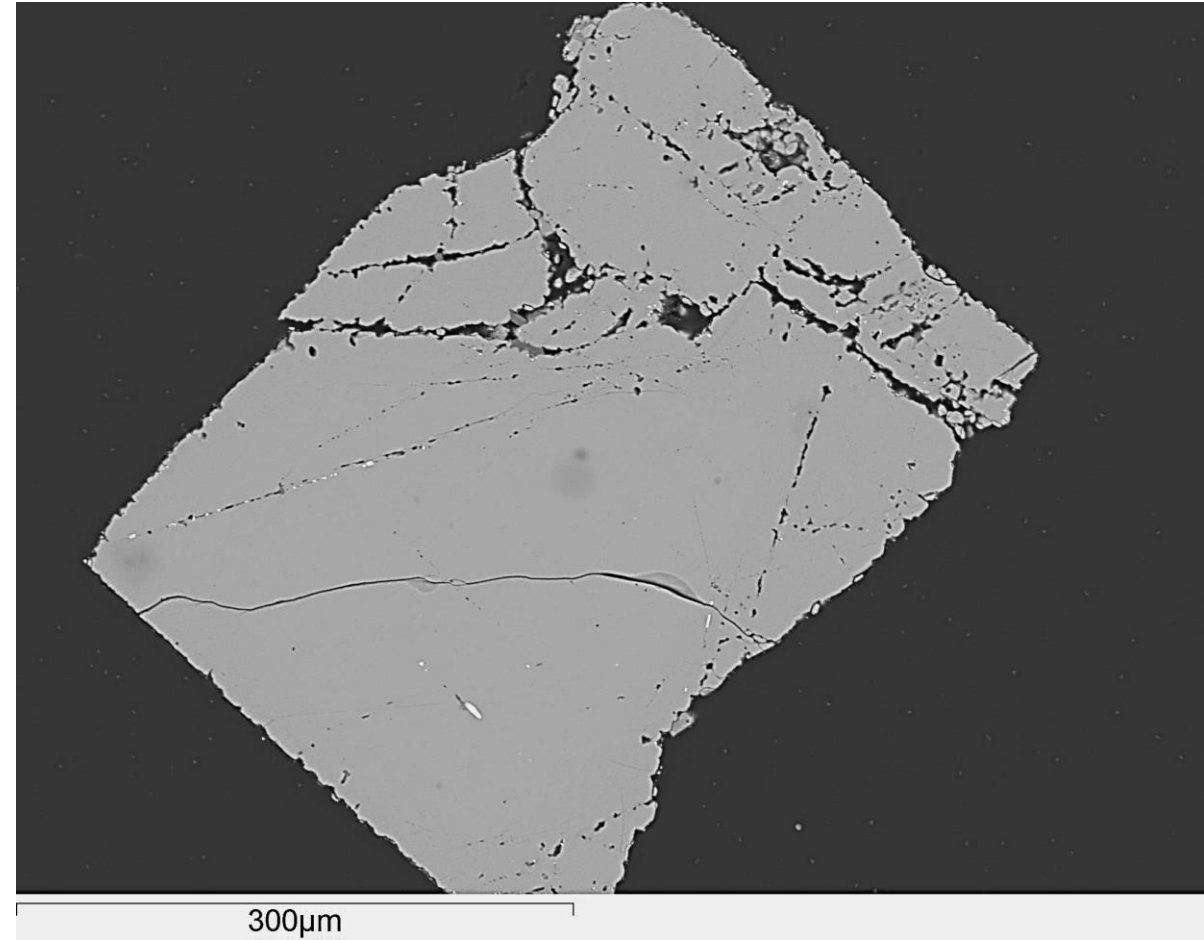
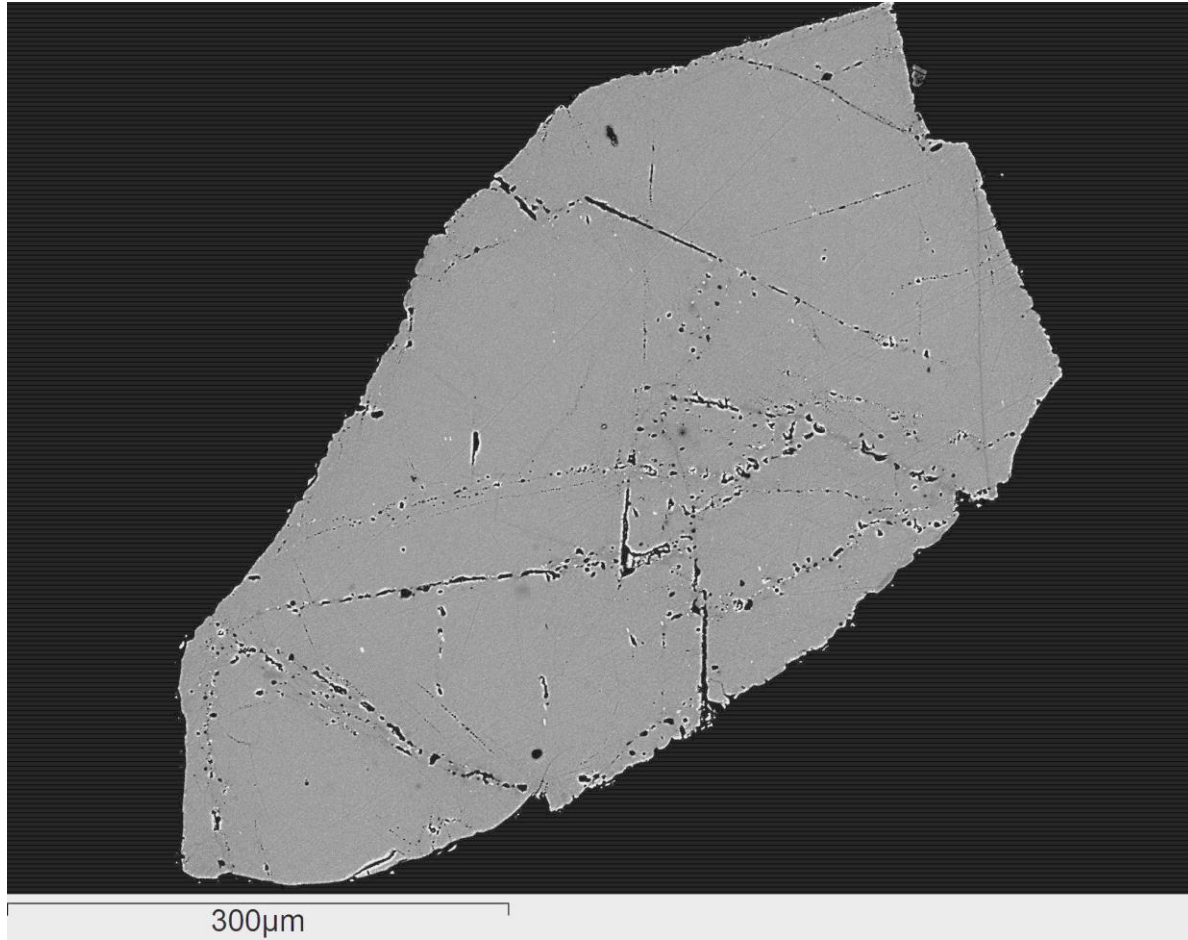
The zone of hydrothermally altered apatite rocks



The main minerals of magnetite-apatite rocks

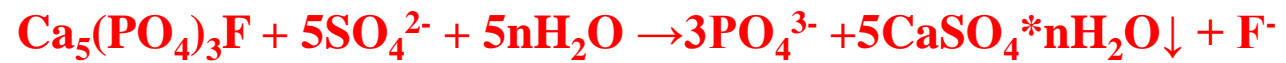
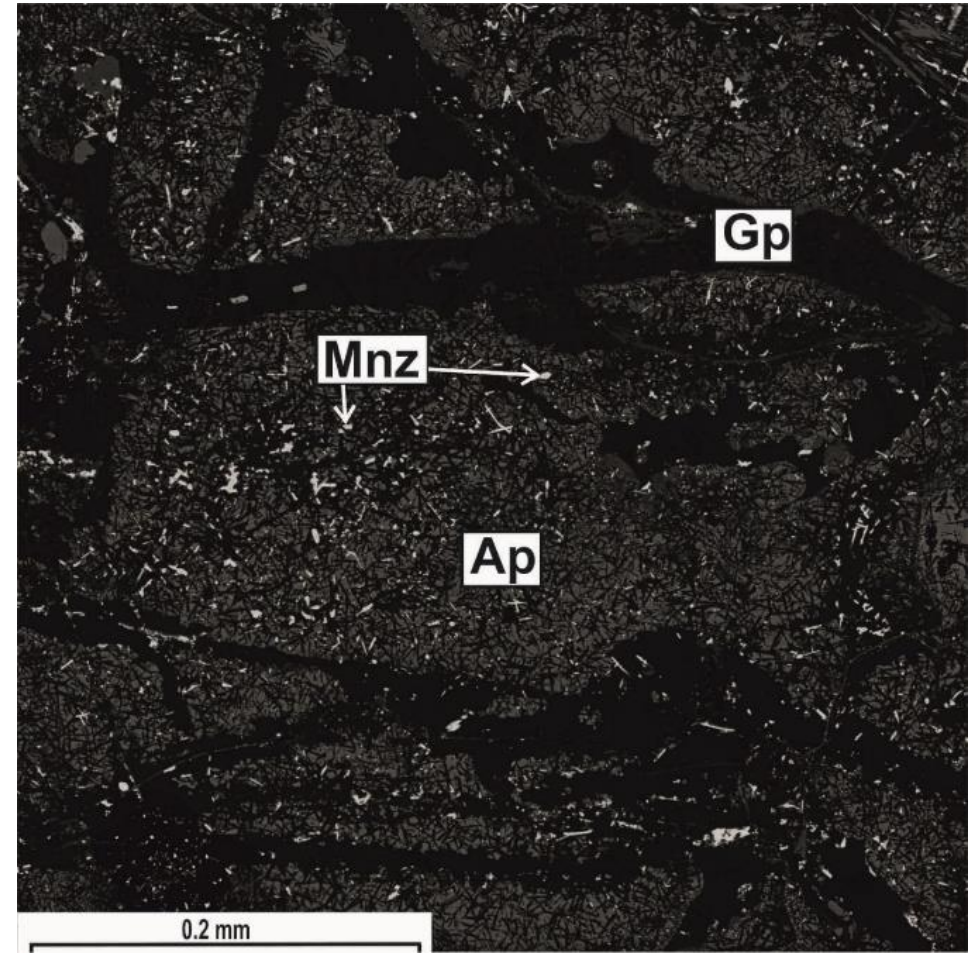
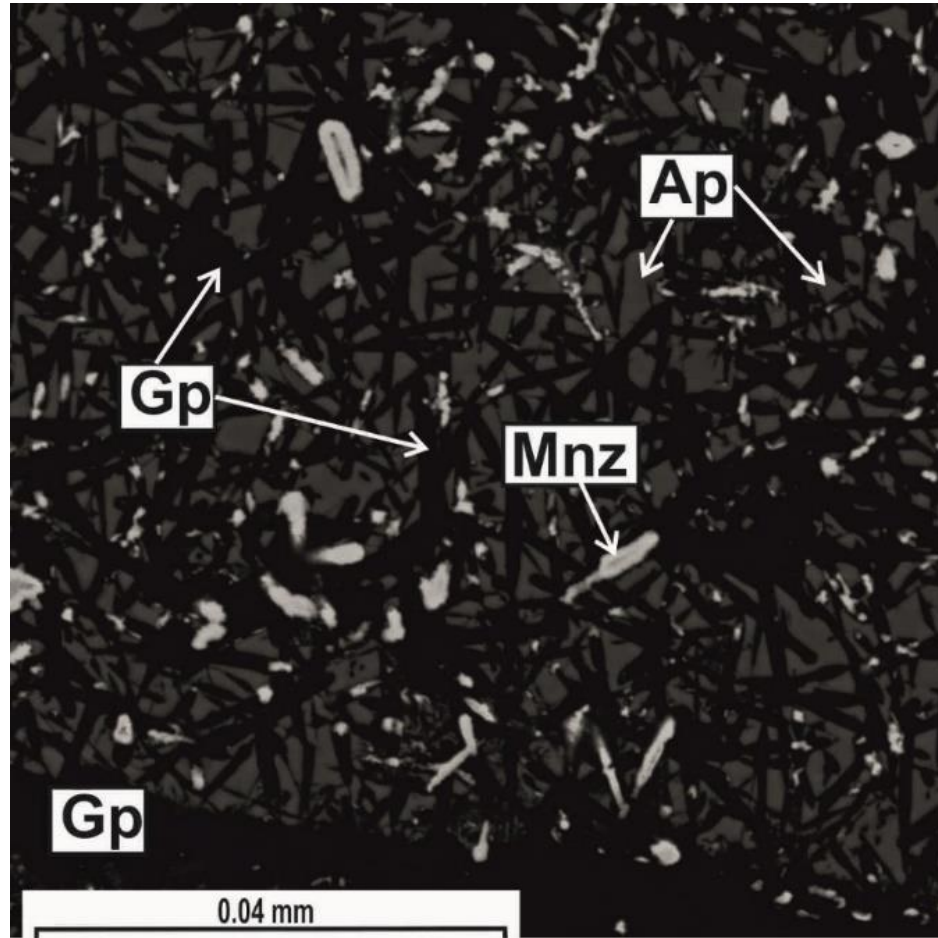
Main minerals of the magmatic association:	Minerals of the hydrothermal association:
Magnetite Apatite Phlogopite Ilmenite	Phosphosiderite Monazite-(Ce) Goethite Hematite Celestine Fluorite Barite Gypsum Fluellite Quartz Rutile (anatase?)

Unaltered apatite



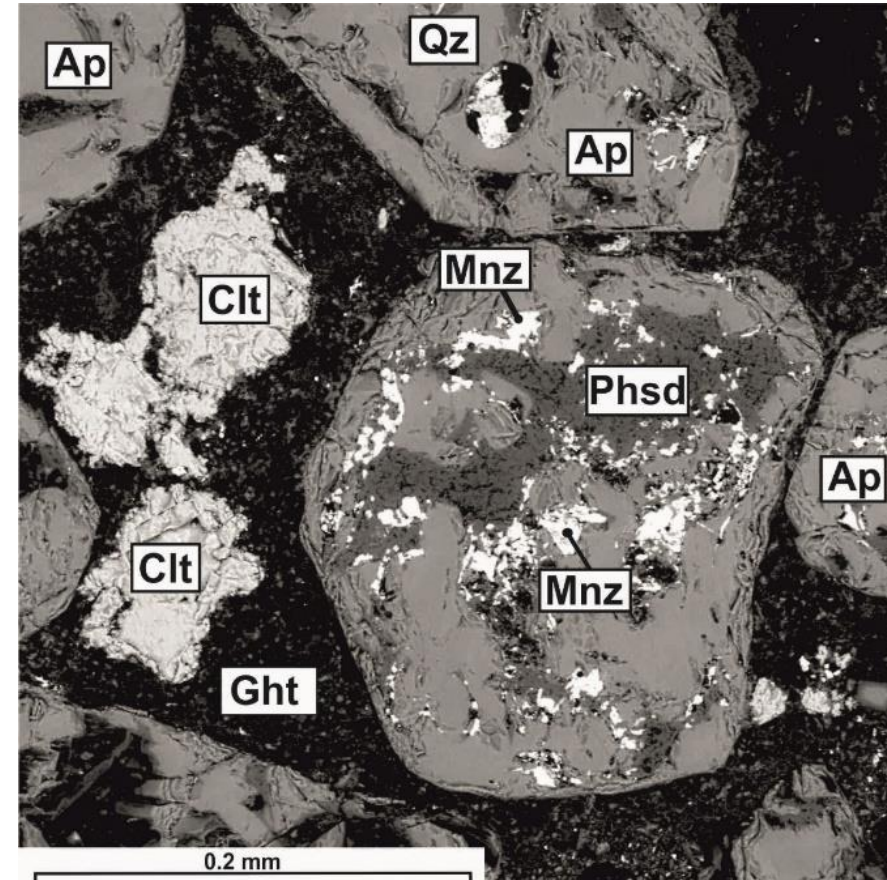
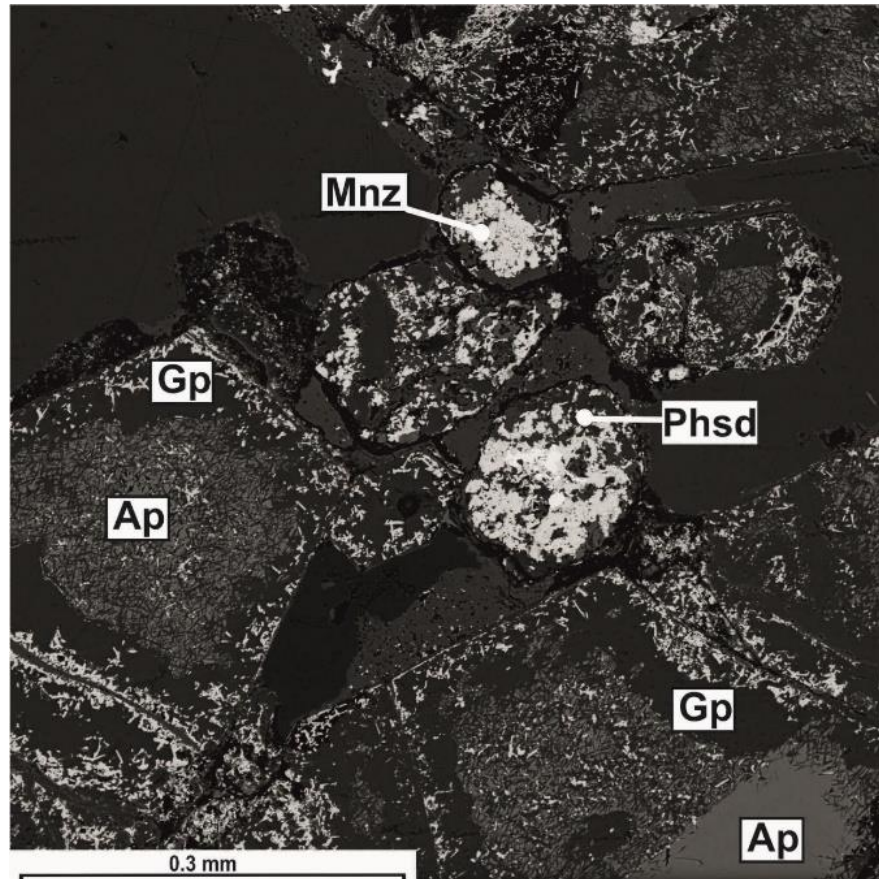
Unaltered apatite corresponds to fluorapatite (F up to 1.6 wt.%). It forms euhedral practically non-inclusion grains. Mineral contains SiO_2 (up to 2.1 wt.%), SO_3 (up to 1.8 wt.%) and Na_2O (up to 0.8 wt.%). The content of light rare earth elements (LREE) in unaltered apatite is up to 4.5 wt.%.

The first stage of the apatite alteration



The first hydrothermal-metasomatic alteration of the apatite crystals were characterized by the formation of gypsum and monazite-Ce (Nikolenko et al., 2018).

The second stage of the apatite alteration:



- $\text{Ca}_5(\text{PO}_4)_3\text{F} + 5\text{SO}_4^{2-} + 5\text{nH}_2\text{O} \rightarrow 3\text{PO}_4^{3-} + 5\text{CaSO}_4 \cdot \text{nH}_2\text{O} \downarrow + \text{F}^-$
- $\text{Fe}_2\text{O}_3 + 3\text{H}_2\text{SO}_4 = \text{Fe}_2(\text{SO}_4)_3 + 3\text{H}_2\text{O}$
- $\text{Fe}_2(\text{SO}_4)_3 + 2\text{PO}_4^{3-} + 2\text{H}_2\text{O} \rightarrow 2\text{FePO}_4 \cdot \text{H}_2\text{O} \downarrow + 3\text{SO}_4^{2-}$

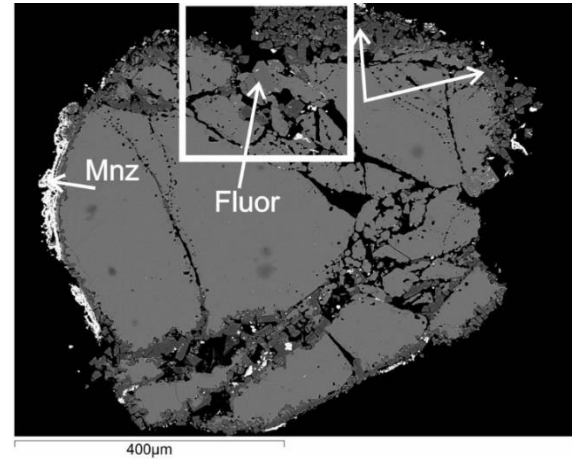
The strong hydrothermal-metasomatic alteration of the apatite crystals were characterized by the formation of gypsum, monazite-Ce, celectine and phosphosiderite (Nikolenko et al., 2018).

To recreate the natural conditions of Mushgai-Khudag apatite alterations, we have conducted a first series of hydrothermal experiments on the dissolution of fluorapatite in reactions with sulfate-bearing and saline fluids at post-magmatic P-T conditions.

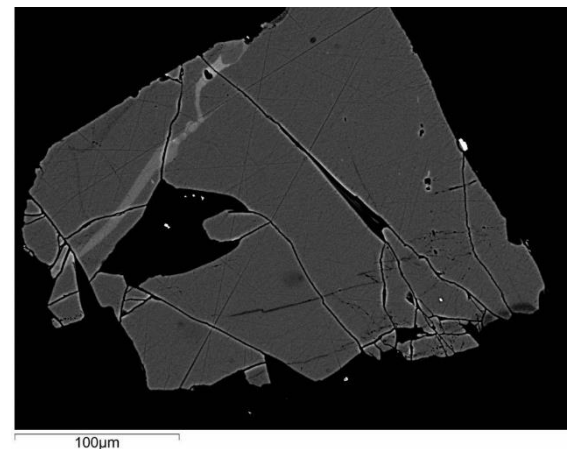
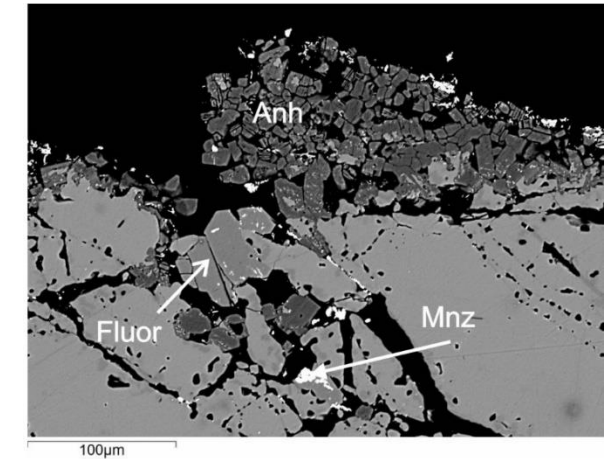
The fluids used include aqueous solutions:

- $\text{H}_2\text{SO}_4/\text{La}_2(\text{SO}_4)_3 = 50/50$
- $\text{FeCl}_3/\text{H}_2\text{O} = 50/50$
- $\text{Fe}_2\text{O}_3/\text{H}_2\text{SO}_4 = 50/50$
- $\text{La}_2\text{SO}_4/\text{H}_2\text{O} = 50/50$

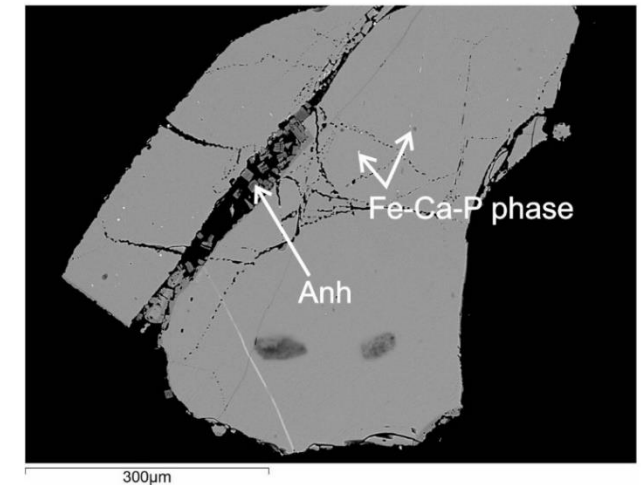
The solids + fluids were placed in 1 cm long/3mm wide Pt capsules and arc-welded shut. They were then placed in a cold-seal autoclave on a hydrothermal line at 200 MPa and 600 °C for a duration of about 3 weeks. The experiments were quenched using compressed air and the products were analyzed by SEM and EMP.



La2SO4/H2SO4 experiments



FeCl3/H2O experiments



Fe2O3/H2SO4 experiments

- In the $\text{La}_2(\text{SO}_4)_3/\text{H}_2\text{O}$ experiments, the fluorapatite did not show any changes in composition compared to the original fluorapatite. Monazite and anhydrite did not form.
- In the $\text{La}_2(\text{SO}_4)_3/\text{H}_2\text{SO}_4$ experiments, monazite and cubic crystals of anhydrite were formed along the cracks and rims of the fluorapatite grains. A single grain of fluorite was found associated with anhydrite and monazite.
- Fluorapatite metasomatized in a $\text{FeCl}_3/\text{H}_2\text{O}$ saline solution developed light trails across the grain surface. These trails are moderately depleted in Ca, P, Sr, and enriched in Si, S, and LREE as compared with the darker areas, which represent the original fluorapatite. Monazite and anhydrite did not form.
- In the $\text{Fe}_2\text{O}_3/1\text{N H}_2\text{SO}_4$ experiments, the fluorapatite developed a zonal structure where light zones are enriched in Si and LREE. Cubic crystals of anhydrite formed along the cracks and rims of the fluorapatite grains. Monazite did not form. A Fe-Ca-P phase was found as rounded or elongated grains within the fluorapatite.

Conclusions:

- **Our results indicate that H_2SO_4 in the fluid promotes the highest reactivity allowing for the formation of new mineral phases in the fluorapatite during the dissolution-reprecipitation process.**
- **Our experimental study reproduced the first stage of apatite alteration observed in the Mushugai-Khudag complex.**