Experimental high-grade alteration of zircon using alkali- and Ca-bearing solutions

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Natural alteration of zircon takes place either via partial dissolution coupled with overgrowth or via fluid-aided coupled dissolution-reprecipitation [1, 2]. Coupled dissolution-reprecipitation results in the zircon being partially to totally replaced by compositionally re-equilibrated zircon, a new mineral phase or both. In this study, fragments (50 - 200 µm) from an inclusion-free, relatively non-metamict euhedral zircon (nepheline syenite pegmatite, Seiland magmatic province, northern Norway) were experimentally reacted in 20 mg batches with a series of alkali- and Ca-bearing fluids plus 5 mg (ThO₂ + ThSiO₂ + SiO₂) in sealed Pt capsules at 900 °C and 1000 MPa for 6 to 11 days (piston cylinder press, CaF₂ setup, cylindrical graphite oven). Fluids included 5 mg 2 N NaOH, 5 mg 2 N KOH, 10 mg Na₂Si₂O₅ + 5 mg H₂O, 1 mg NaF + 5 mg H₂O, and 1 - 5 mg Ca(OH)₂ + 5 mg H₂O. In each experiment, the fluid reacted with the zircon. This reaction took the form of partial replacement of the zircon with compositionally altered zircon via coupled dissolutionreprecipitation plus varying amounts of overgrowth. The reacted zircon is characterized by a sharp compositional boundary between the altered and original zircon as well as, in some cases, by a micro-porosity and/or inclusions of ZrO₂ or ThSiO₄. SIMS analysis of the replaced zircon indicates that it is strongly enriched in Th + Si, heavily depleted in U, and heavily to moderately depleted in (Y+REE). If YPO₄ replaces (Th + Si) in the system, the altered zircon is enriched in YPO₄ and heavily depleted in Th and U. In all experiments radiogenic 206Pb (3 to 5 ppm in the unaltered zircon) is strongly depleted in the altered zircon. Hf concentrations in the altered zircon retain the same value as in the original zircon. The results from these experiments indicate that zircon can be compositionally altered via alkali- and Ca-bearing fluids via coupled dissolution-reprecipitation processes under high-grade conditions and that their internal geochronometer can be reset due to the massive loss of radiogenic Pb.

[1] Geisler *et al.*, (2007) *Elements* **3**, 43-50. [2] Putnis (2009) *Rev Mineral Geochem*, vol **70**, 87-124.

Pyrrhotite oxidative dissolution: A microstructural perspective by FIB-TEM and surface topometry

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Pyrrhotite is non-stoichiometric iron sulfide (Fe_{1-x}S with x < 0.125) and abundant in the Earth's crust. Due to variable Fe deficiency many structural variants arise from the ordering of Fe vacancies within the NiAs-based structure [1]. The resulting superstructures show different physicochemical and magnetic properties, bearing on pyrrhotite's contribution to rock magnetisation and many issues in geochemistry, petrology, and technical mineral processing (e.g., [2]). In the processing of Ni ores, pyrrhotite needs to be separated and is usually discarded to the tailings, where interaction with meteoric waters may lead to oxidation and formation of acid mine drainage.

In order to study differences in reactivity of pyrrhotite varieties, we conducted oxidative dissolution experiments on carefully polished pyrrhotite surfaces containing crystallographically coherent intergrowths of 4C- and NC-pyrrhotite (N = 4.81-4.87). The intergrowths, sharing the same crystallographic orientations, offer the possibility to eliminate the effect of crystal anisotropy, which is significant. Experiments were conducted at 30-50 °C using Fe³⁺ and H₂O₂ as oxidants in acidic solution of pH<3.0. From the reacted samples, surface cross sections in form of electron transparent lamellae were prepared using the FIB technique and studied using analytical TEM. The surface topography of the reacted pyrrhotites was recorded by vertical scanning confocal microscopy and used to deduce individual reaction rates of the intergrown pyrrhotite varieties.

Our results show, that reaction rates strongly and abruptly decrease as pH become larger than 2.65 (close to the isoelectric point [3]). At pH<2.65, NC-pyrrhotite oxidises and dissolves faster than 4C-pyrrhotite and abundant elemental sulfur precipitates. At pH>2.65, 4C-pyrrhotite reacts faster and sulfur appears to be absent. We are continuing to search for Senriched sulfides (e.g., FeS₂) at the reaction interface by TEM, but until now, no such phases have been found.

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