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Dissolution-reprecipitation in fluorapatite: Fluid infiltration and formation of metasomatic monazite

D.E. HARLOV, R. WIRTH AND H.-J. FÖRSTER

GeoForschungsZentrum, Telegrafenberg, D-14473 Potsdam,
FR Germany (dharlov@gfz-potsdam.de)

Monazite inclusions in fluorapatite have been demonstrated, both from nature as well as experimentally, to be derived from the host fluorapatite as the direct result of metasomatic alteration [1]. In this study, single crystals of Durango fluorapatite have been partially metasomatised using 1 M HCl solutions at $T = 300 - 900$ °C and $P = 500 - 1000$ MPa. Metasomatised regions are characterized by heavy depletion in (Y+REE) as well as monazite inclusions, which tend to be situated in the vicinity of the reaction (or infiltration) front between the metasomatised and unmetasomatised areas of the fluorapatite. Decrease in the number of monazite inclusions, with subsequent increase in the size of the remaining inclusions, as a function of either increased reaction time or increased T, suggest that fluid-aided Ostwald ripening is taking place within the metasomatised regions. These regions are interpreted as being the result of a replacement reaction, which proceeds via a moving interface or reaction front in the form of a simultaneous dissolution-reprecipitation process [2]. One outcome is the creation of pervasive, interconnected microvoids or pores throughout the metasomatised region which permit fluids to infiltrate thereby allowing for rapid element diffusion and subsequent mass transfer to take place, i.e. the growth of monazite inclusions. Microvoids also serve as nucleation sites for monazite. TEM investigation of foils cut across the reaction front between the original and metasomatised fluorapatite using FIB (30 kV Ga) has confirmed the presence of interconnected microvoids (which resemble worm trails) in the metasomatised areas. Clumps of monazite crystals are also seen growing in fluid-filled cavities surrounded by a high density of microvoid worm trails. As the reaction front migrates into the original fluorapatite, these voids preferentially move into regions of higher energy density, leaving behind irregular 10–20 nm wide worm trails of inter-connected microvoids. During this process, portions of the original fluorapatite are dissolved away, while (Y+REE)-depleted fluorapatite is simultaneously reprecipitated utilizing remnants of the original fluorapatite as a template. This allows for lattice parameters across the reaction front to be preserved such that both the metasomatised and original fluorapatite remain parts of the same single crystal.

References

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2.5.23

Making and filling space: Coupled hydrothermal karst genesis and sulfide/sulfate precipitation

M. CORBELLA¹, C. AYORA² AND E. CARDELLACH¹

¹Dept. Geologia, Universitat Autònoma de Barcelona, 08193-Bellaterra, Spain (merce.corbella@uab.es; esteve.cardellach@uab.es)

²Institut de Ciències de la Terra Jaume Almera, CSIC, 08028-Barcelona, Spain (cayora@ija.csic.es)

Filled porosity in carbonate rocks is a common feature of oil reservoirs and lead-zinc deposits. Fluid mixing is more effective in dissolving deep carbonates than hydrogen sulfide oxidation to sulfuric acid or metal sulfide precipitation [1].

The Rocabrana deposit (Eastern Pyrenees, NE Spain) consists of metric bodies, hosted in Cambrian dolostones, that preferentially developed along the intersection of strata and joints. These cavities are coated with a centimetric rim of sulfides, and filled by large barite crystals and sporadic blocks of host dolostone. Isotopic and fluid inclusion data suggest that precipitation of sulfate and sulfides was due to mixing of fluids at temperatures around 150°C [2]. Similar ore deposits occur in most of the European Hercynian domain and similar textures are found in Mississippi Valley type ore deposits.

Reactive transport simulations have been used to illustrate that the observed textures, cavity formation and mineral infilling may be part of the same overall process of warm fluid mixing in a carbonate host. Dissolution occurs because of the intrinsic effects of fluid mixing whenever two chemically different fluids (in terms of pH, [Cl], [Ca], pCO₂), independently saturated in carbonate, mix at a cross-fault intersection. Depending on the relative fluxes of the two mixing fluids, the cavities form at fracture intersections or along the fractures with the smallest flux. Sulfide and sulfate precipitation occurs independently of cavity formation when the mixing fluids carry enough sulfur and metals respectively. The small sulfide/cavity volumetric ratios present in Rocabrana are reconstructed in our simulations from metal concentrations around 10⁻⁵ mol/L in a brine. Precipitation of sulfide minerals occurs on one side of the cavity if the proportion of metal to sulfur in the mixture is close to 1. Otherwise (Me/S >> 1 or Me/S << 1 in the resulting mixture) sulfide precipitation takes place along the fractures. Finally, barite fills up most of the cavity when the metalliferous solution is very enriched in barium (~10⁻² mol/L). Thus the mineral textures, paragenesis and proportions observed in the deposit are reproduced.

References

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