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Pyrrhotite nano-inclusions in apatite from Les Guilleries lamprohyres (NE Iberian Peninsula)

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Apatite is ubiquitous in most types of rocks but in trace amounts, and can form by a variety of processes. Apatite is of great interest because it is an important carrier of volatiles (F, Cl, and OH) and rare-earth elements (REEs), and can be used to reconstruct petrogenetic processes in different environments (e.g., [1]). However, very few studies are dedicated to understanding apatite microstructures (e.g., [2]). Here, we explore apatite in Les Guilleries lamprophyre dykes to gain insights into the parental melt and potential processes of re-mobilization of REEs. The studied dykes are calc-alkaline and represent upwelling of deep lithospheric mantle material (least modified magmas) that emplaced at the end of the Hercynian orogeny in a variety of igneous rocks [3].

The texture and composition of apatites were examined in two thin sections of the least altered dykes, numbered GUI-40 and GUI-41, using SEM/EDS, EPMA, and FIB-TEM. Our results show that apatites in GUI-40 are REE-depleted, mostly rounded, subhedral, and range from ~5 to ~35 μm in size. Their average X-site occupancy is F=78, Cl=2, and OH=20 (mol%). Apatites in GUI-41 are highly acicular (~3-10 μm wide and up to ~120 μm long), REE-enriched compared to GUI-40, and their average X-site occupancy is F=64, Cl=5, and OH=31 (mol%). TEM work on an apatite grain in GUI-40 reveals the presence of abundant nano-inclusions, ~10-60 nm in size, with euhedral, hexagonal shapes in the apatite core (Fig. 1). The nano-inclusions are (i) fully occupied by pyrrhotite, (ii) half occupied by pyrrhotite, or (iii) completely empty.

The data suggest that apatites in GUI-40 are primary and their microstructure reflect immiscibility of liquids, interpreted as a characteristic inherited from the primary lamprophyre melt. The presence of Fe in the magma and/or the reducing conditions likely prevented S to form ellestadite domains within the apatite structure. This study also demonstrates that slight REE re-mobilization did occur during a secondary, hydrothermal event.

[1] Zirner et al. (2015), *Lithos* 228, 12-22.

[2] Martínez et al. (2023) American Mineralogist. Preprint. doi.org/10.2138/am-2022-8794

[3] Mellado et al. (2021) *Geologica Acta* 19, 1-23.

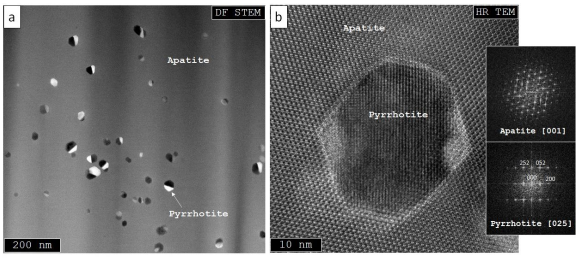

Figure 1. TEM images of a FIB section extracted from an apatite grain in Les Guilleries lamprophyres. a) Dark-field STEM image showing hexagonal nano-inclusions in the apatite. The inclusions can be partially or totally filled by pyrrhotite. b) High-resolution TEM image showing the hexagonal crystal structure of apatite down the [001] zone axis and a nano-inclusion consisting of pyrrhotite oriented parallel to the [025] zone axis.