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Rare earth elements as proxies of supergene alteration processes from the giant Imiter silver deposit (Morocco)

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Abstract. The giant Imiter silver mine located at the northern edge of the West African craton in Morocco is assumed to be a late Neoproterozoic epithermal deposit mainly characterized by a hypogene paragenesis of Ag-rich sulphides and sulfosalts, and Ag-Hg alloys occurring preferentially in quartz-rich veins. The secondary enrichment zone at Imiter reaches a thickness of 50 to 150 m below ground surface. The upper levels, famous because of giant native silver crystals, grade up to 300 kg/t. Metallographic observations, SEM-EDS and XRD analyses reveal the presence of a quite complex secondary paragenesis made of acanthite, cinnabar, imiterite, perrouditite, cerussite, mimetite, iron oxyhydroxides, synchisite and coronadite. Supergene alteration processes of the giant Imiter silver mine deposit consist of the remobilisation of the primary hypogene paragenesis by (i) deep and old basinal brines and (ii) downward infiltrations of surficial waters becoming progressively more reduced and F-enriched in response to fluid-rock interactions. Development of such a supergene mineralization strongly suggests prevalence of arid to semiarid conditions.

Keywords. Ag, secondary ore, sulfohalide, lanthanides.

1 Introduction and geological setting

The world-class Imiter mine is the 10th largest worldwide and the largest African deposit with ~210 metric tons of silver produced in 2009. Since 1960, the total production is estimated at ~4,300 t of Ag. The deposit's total reserves are approximately 8,000 t of Ag and a 30 year mine life is estimated. Ore grades range between 500 and 700 g/t. Mercury is exploited as a by-product of silver, but no production data are available regarding this metal. The deposit, located at the northern edge of the West African craton (Fig. 1A), belongs to the Moroccan Pan-African chain (Neoproterozoic orogeny: 750 to 540 Ma). The Imiter deposit is assumed to be a late Neoproterozoic epithermal vein deposit, formed during regional-scale strike slip faulting and is associated with felsic volcanism dated at 550 ± 3 Ma by ion-probe U/Pb on zircons (Cheilletz et al. 2002; Tuduri et al. 2006).

To date, the supergene enrichment of the silver-rich

Imiter deposit has been poorly documented, even though it is being exploited. Few details exist in mining reports but one can note interesting grades related to secondary enrichments that can reach 400 to 500 g/t with locally more than 300 kg/t. In this study, the processes of supergene alteration of the hypogene ore were evaluated, with an emphasis on the deeper part of the underground mine. Eventually, such supergene conditions have been modelled using rare earth elements (REE) as proxies of low temperature processes.

2 Geometry and paragenesis of hypogene mineralizations

The primary hypogene ore is mainly related to the E-W 10-km long Imiter fault system that separates Cryogenian black shales to the south from Ediacaran plutonic, volcanic and volcanoclastic rocks to the north (Fig. 1B).

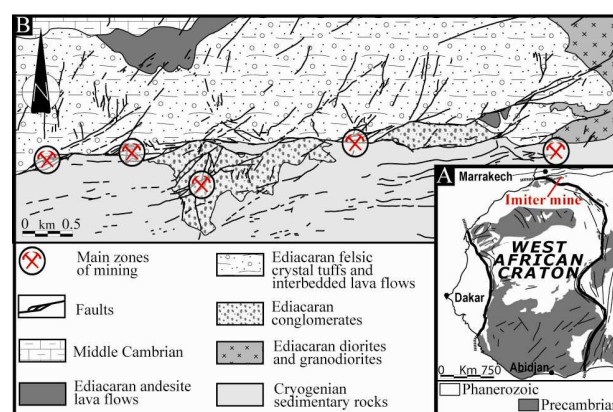


Figure 1. A) Simplified map of the West African Craton, B) Simplified geological map of the Imiter silver mine.

The Imiter fault consists of the association between N090°E and N060–070°E lineament arrays and defines a succession of apparent left-lateral pull-apart textures at district scale (Fig. 1B). According to Tuduri et al. (2006) a simplified two stage hypogene model is herein proposed. (i) Stage one would correspond to the silver-

rich low sulfidation epithermal deposit model. Quartz is the primary gangue, associated with minor dolomite, chlorite, sericite and scarce adularia. Metallic ore (Fig. 2) is mainly composed of Ag–Hg alloys, arsenopyrite, acanthite-argentite, Ag sulfosalts and imiterite (Ag_2HgS_2). Along N060–070°E structures, large open voids are observed, as a result of important dissolution of carbonates during hydrothermal alteration. (ii) Stage two corresponds to a reactivation of the Imiter fault system. As a consequence, this stage reopened and re-used stage 1 structures along the shear-zone. Structures correspond to veins filled with massive pink dolomite ($\Sigma_{\text{Fe+Mg}} \approx 0.1$ atoms per formula unit). Scarce quartz and a sulfide-rich paragenesis characterize this stage. Sulfides are mainly Ag-rich galena and sphalerite, pyrite, chalcopyrite, with minor amounts of argentite and arsenopyrite (Fig. 2).

Minerals	Stages		Secondary supergene ore	
	Primary hypogene ore Economic stage 1	Stage 2	Ag-rich type	Oxidic type
Acanthite	—	—	—	—
Adularia	—	—	—	—
Ag-Hg alloys	—	—	—	—
Ag-Hg arsenates	—	—	—	—
Ag-sulfosalts	—	—	—	—
Arsenopyrite	—	—	—	—
Cerussite	—	—	—	—
Chalcopyrite	—	—	—	—
Chlorite	—	—	—	—
Cinnabar	—	—	—	—
Coronadite	—	—	—	—
Dolomite	—	—	—	—
Galena	—	—	—	—
Goethite	—	—	—	—
Hematite	—	—	—	—
Illite	—	—	—	—
Imiterite	—	—	—	—
Kaolinite	—	—	—	—
Mimetite	—	—	—	—
Perroudite	—	—	—	—
Pyrite	—	—	—	—
Quartz	—	—	—	—
Sphalerite	—	—	—	—
Synchisite	—	—	—	—

Figure 2. Paragenetic diagram of Imiter hypogene vein filling and supergene alteration minerals, earliest formed minerals to the left.

3 Vertical zonation of supergene alteration

The supergene enrichment zone depth reaches 50 to 150 m below the surface and is vertically zoned. This supergene part has been intensively mined since the discovery of the deposit and is still exploited. The Imiter deposit is herein considered as a pyrite-poor deposit type (Sillitoe 2009) at least in the first 200 m of exploitation below the surface.

The main supergene alteration displays a generalized downward progression with (i) massive Ag^0 veins (up to 300 kg/t, from surface to 50–75 m depth), Ag-rich galena and Ag-rich sphalerite and related Mn oxides, and (ii) powdery black and rusty materials in the deeper part, from 50–75 m and up to 150 m below the surface (400–500 g/t). Such material was studied and determined by metallographic observations, SEM-EDS and XRD analyses. The alteration of the hypogene mineralization consists of cerussite, mimetite, acanthite, cinnabar, perroudite/imiterite and various Ag-Hg arsenates, coronadite ($\text{PbMn}_8\text{O}_{16}$), synchisite ($\text{Ca}(\text{Ce},\text{La})(\text{CO}_3)_2\text{F}$), hematite and goethite that can be attributed to two main alteration stages: (i) the former is characterized by the crystallization of supergene sulfides associated with

carbonates and arsenates; (ii) the latter is mainly oxidic (Fig. 2). According to XRD data, quartz, illite and kaolinite are predominant in the oxidized altered rocks. Dolomite occurs only in the least oxidized varieties.

4 Mineralogy of the deep supergene enrichment zone

The first alteration type (sulfidic) is defined by a redistribution and local enrichment by accumulation of secondary silver phases. Arsenopyrite, primary acanthite and Ag-Hg alloys are not preserved. Thus Ag, As, Hg and Pb are solubilized and further incorporated into new minerals depending on geochemical conditions (e.g., pe, pH). In such cases, galena may be replaced by acanthite and cerussite, or only by cerussite. According to SEM and XRD analysis, imiterite and perroudite ($\text{Hg}_5\text{Ag}_4\text{S}_5(\text{Cl},\text{I},\text{Br})_4$) are also present. Generally cerussite is well developed until formation fluids favor mimetite precipitation. At this moment, cerussite and mimetite may display complex intergrowths. Then mimetite occurs as the common crystal and free growth textures of euhedral prismatic to acicular crystals may be observed. Scarce inclusions of acanthite and cinnabar have also been observed within mimetite (Fig. 2).

The second alteration type occurs as overgrowths on the first alteration type of oxidized minerals such as iron oxyhydroxides, rare earth element fluorocarbonates and Pb-Mn oxides. It generally consists of syn-crystallization of a goethite-hematite mixture with synchisite overgrown by fibrous botryoidal aggregate textures of complex manganates such as coronadite (Fig. 3). Mimetite may also occur in the earlier oxidic processes associated with iron oxyhydroxides.

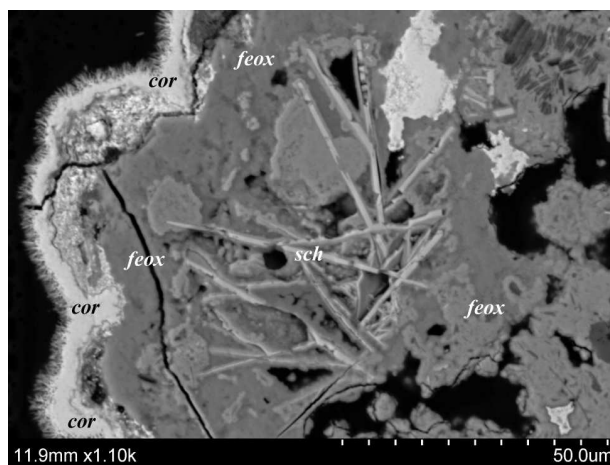


Figure 3. SEM backscattered electron image showing syn-crystallization of iron oxyhydroxide (feox), with synchisite (sch) overgrown by botryoidal coronadite (cor).

5 Supergene enrichment

Both alteration processes described above are mainly oxidizing phenomena (i.e., increasing $f(\text{O}_2)$ and decreasing $f(\text{S})$) that are superimposed on pre-existing primary mineralization. The oxidation of sulfide releases dissolved Ag, Hg, S and Pb into formation fluids. Subsequently, the dissolved species undergo

