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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 basal 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

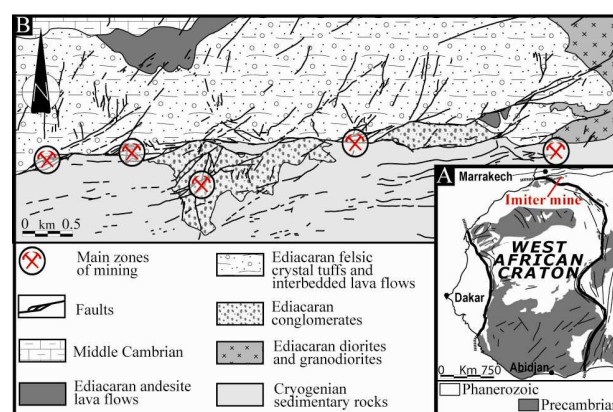
The world-class Imiter mine is the 10<sup>th</sup> largest worldwide and the largest African deposit with ~210 metric tons of silver produced in 2009. Since 1960, the total production is estimated at ~4,300 t of Ag. The deposit's total reserves are approximately 8,000 t of Ag and a 30 year mine life 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  $550 \pm 3$  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 ( $\text{Ag}_2\text{HgS}_2$ ). 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.

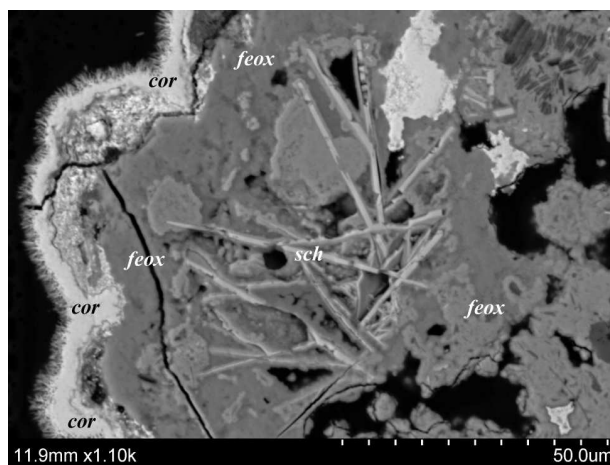
The main supergene alteration displays a generalized downward progression with (i) massive  $\text{Ag}^0$  veins (up to 300 kg/t, from surface to 50–75 m depth), Ag-rich galena and Ag-rich sphalerite and related Mn oxides, and (ii) powdery black and rusty materials in the deeper part, from 50–75 m and 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.



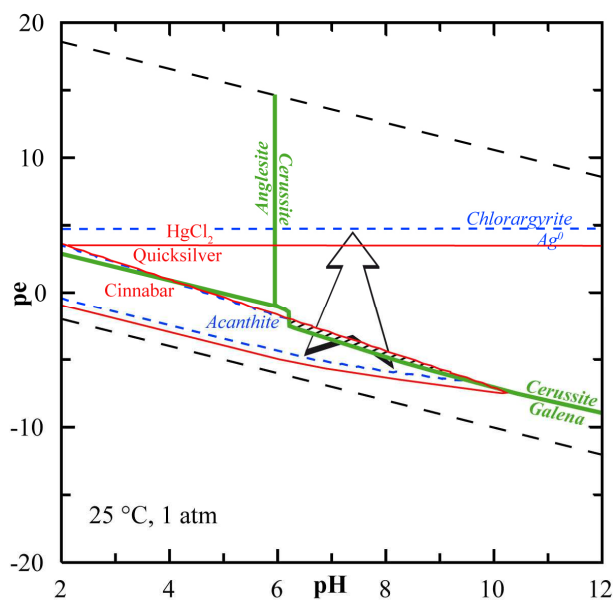
**Figure 3.** SEM backscattered electron image showing syn-crystallization of iron oxyhydroxide (feox), with synchisite (sch) overgrown by botryoidal coronadite (cor).

### 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

oxygenation and/or complexation by other ligands, which then concentrate them to form new insoluble phases. The secondary concentration observed in the first alteration type documented in this study, results in a zonation from sulfide to sulfohalide, probably in response to an increasing oxidation state (Gammons and Yu 1997).

Thus, the replacement of galena by acanthite suggests neutral to alkaline pH values, a relatively low oxidation state and high total sulfide (hatched area, Fig. 4). Moreover, release of S, Ag, Pb, As and Hg during sulfide alteration (i.e., acanthite and primary minerals), probably influenced by halide-rich solutions, provides the necessary ingredients for imiterite/perroudite crystallization.



**Figure 4.** pe-pH stability diagram for Ag, Hg, Pb minerals and dissolved species of Ag-Hg-Pb-Cl-S-C at 25°C. Arrow shows pe-pH trend for supergene alteration stages.

## 6 Rare earth elements as proxies of supergene processes

The weathering process has resulted in the mobilization and redistribution of the REE affected by the nature of secondary mineral formation (e.g., Mn oxides, fluorocarbonates). The presence of aqueous ligands, notably fluoride, carbonate or hydroxide in water strongly affects REE solubility. Indeed, formation of secondary REE-minerals (i.e., synchisite) can give some clues for deciphering the probable ligands present in the supergene ore-forming fluid. In order to establish the supergene conditions, REE speciation in two multi-ligand solutions (reduced seawater and F-rich groundwater) was calculated. Results show that (i) in the reduced seawater at near-neutral pH, lanthanides exist as free ionic, carbonate and chloride species; (ii) in F-enriched groundwater, lanthanides occur as free ionic, carbonate and fluoride complexes. While there is no indication for the presence of alkaline fluids, there is evidence for the presence of F-bearing fluids. Indeed, the precipitation of F-REE-bearing synchisite suggests the presence of F and CO<sub>2</sub> in the aqueous fluid.

Because the Ag enrichment zone occurs in response to chloride-rich, neutral to alkaline pH and reduced formation fluid circulation, two alternative ore-forming models are proposed below: (i) deep Phanerozoic basinal brines channelled within Precambrian basement fractures influence primary ore destabilization during the long and complex history of the south-Moroccan area; (ii) downward infiltration of surficial water such as modified rainwater are progressively reduced in response to fluid-rock interaction (F-rich groundwater resulting from interactions with volcano-sedimentary host-rocks). Organic matter encountered within black shales hosting the mineralization (Pašava 1994) would participate in redox processes. The paragenetic evolution from mimetite, Ln-fluoro-carbonate and iron oxyhydroxide to coronadite (Fig. 3), observed in the second alteration type, implies a drastic increase of the oxidation states with probable neutral to alkaline pH preservation conditions and reinforces a continuum model of supergene weathering (arrow on Fig. 4).

In conclusion, supergene processes provide Ag-rich sulfide concentration in response to saline groundwater circulations. This suggests that supergene enrichment processes of Ag deposits in the Imiter mine are dynamic in nature and do not exclusively require the presence of meteoric water. As compared to other ore deposits (e.g., Cu, Reich et al. 2008; Ag, Sillitoe 2009), development of such mineralization suggests prevalence of arid to semiarid conditions during the supergene enrichment. Processes controlling the supergene products of the giant Imiter silver deposit belong to the pyrite-poor deposit type and are controlled by neutral pH solutions (Sillitoe 2009).

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