REE geochemistry applied to the genetic study of fluorite in the mining district of El Hammam (Central Morocco)

Geoquímica de REE aplicada al estudio genético de la fluorita en el distrito minero de El Hammam (Marruecos Central)

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ABSTRACT

The macroscopic and geochemical investigations of REE in fluorites of the mining district of El Hammam reveal several types of fluorite: green massive fluorite (FV type A), green brecciated fluorite (FV type B), white fluorite (FBl) and blue fluorite shaded in yellow (FBj). All these fluorites seem crystallized into four stages that have occurred over time. Thinks to its high REE content, FV type A is the oldest. This is followed by FV type B, FBl, and finally FBj, which are inceasingly depleted in REE. The FV type A and FV type B are attributed to magmatic fluids, associated with lamprophyres and monzogranites respectively. The other fluorites (FBl and FBj) are generated mainly by the remobilization of the green fluorites (FV type A&B), and associated with interaction of magmatic and surficial fluids with the sedimentary and/or metamorphic host rocks. The footprint of basinal fluids becomes increasingly evident when comparing the FBl to FBj.

Key-words: *REE, fluorite, lamprophyre-monzogranite, El Hammam, Morocco.*

RESUMEN

La investigación macroscópica y geoquímica de REE en fluoritas del distrito minero de El Hammam revelan varios tipos de fluorita: fluorita verde masiva (FVtipoA), brechas verdes de fluorita (FVtipoB), blanco de fluorita (FBl) y fluorita azul sombreada en amarillo (FBj). Todas estas fluoritas aparecen cristalizadas en cuatro etapas que se han sucedido en el tiempo. Debido a su contenido de alta REE, FV tipo A puede interpretarse como la más antigua. Esta etapa se continúa con FV tipo B, FBl, y finalmente FBj progresivamente empobrecidas en REE. La FV tipo A y FV tipo B se atribuyen a los fluidos magmáticos, así como diques de lamprófido y monzogranito respectivamente. Las otras fluoritas (FBL y FBj) se generan principalmente por la removilización de las fluoritas verdes (FV tipo A y B), resultante de la interacción de fluidos magmáticos con agua meteórica en relación con las rocas sedimentarias y/o metamórficas del encajante. La impronta de estos fluidos de cuenca se hace cada vez más evidente cuando se compara FBl y FBj.

Palabras clave: *REE, fluorita, lamprófido-monzogranito, El Hammam, Marruecos.*

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Introduction

The mining district of El Hammam (Central Morocco), operated since 1974 by the Anonymous Society of mining companies (SAMINE certified ISO since 1997), is located in Central Morocco (56 km southwest of Meknes city). This district is counted among the largest producer of fluorite in the Hercynian chain in the world.

This paper studies fluorite mineralization in order to: i) distinguish between different types of fluorite in El Hammam mine; ii) chronologe their paragenetic succession; iii) and discuss their relationship with the occurrence of late-Hercynian magmatism, based on geochemical data.

Geological setting

The district of El Hammam includes sedimentary, metamorphic and igneous rocks (Fig. 1). Sedimentary and metamorphic formations are predominated by limestone, sandstone, shale, sandstone and quartzite, which range from Silurian to Namurian. The magmatic activity, dating from Viseo-Namurian to Autunian, begins with the establishment of a succession of dolerite dykes oriented NE-SW. In the south of the El Hammam district; geological and geophysical data indicate the presence of a buried batholith. In the center of the district, a monzogranite appears as a small hectometer outcrop at the level of the river Beht. Finally, the same shear band (NE-SW) connects the lamprophyre dykes, whose calc-alkaline/alkaline signature, announces the beginning of the Triassic distension (Chraibi, 2000). This extension will be fully realized by the introduction of tholeiitic basalts of the Late Triassic-Early Liassic. This magmatic activity, varied and irregular in the district of El Hammam, is accompanied by a variety of hydrothermal processes. The hydrothermal alteration, namely boron enrichments in tourmalines, seems to be the most important. This hydrothermal alteration is responsible for the genesis of fluorinated vein mineralization. The majority of veins is hosted in the Visean formation and shows two major directions, E-W and especially

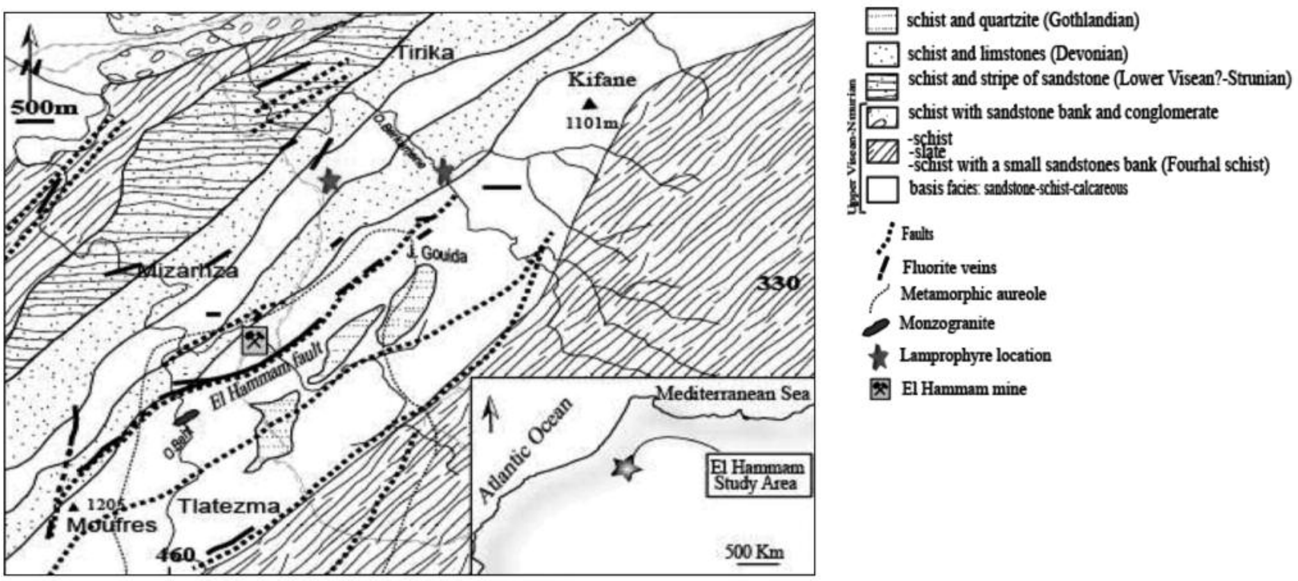


Fig. 1.- Location map and the simplified geological setting of El Hammam district (modified from Agard, 1966).

Fig. 1.- Mapa de situación geológica del distrito de El Hammam (modificado de Agard, 1966).

NE-SW (Fig.1). In the field, the detailed analysis of this fluoridated mineralization reveals the existence of four types of fluorite: green fluorites generally massive (FV type A), sometimes brecciated (FV type B); white fluorite (FBl), and finally blue fluorite shaded in yellow (FBj) and either brecciated or with geodes.

Geochemistry of REE

Methodology and Results

All the fluorite samples are collected from the primary El Hammam ore vein. A few samples of fluorite were taken from from Jebrak (1985) and Cheilletz *et al.* (2010). In this study, the samples of fluorite and magmatic rocks are analysed for their major oxide, trace and rare earth elements in the Analytical Laboratory at the University of the Basque Country in Spain by ICP-MS. The microprobe (Camebax) analysis was done by the Department of Lithospheric at the University of Vienna (Austria) and the fluorine contents in total rocks by HOLCIM (Oujda-Morocco). The observation of the morphological appearance of different types of fluorite and especially the scrutiny of their REE, allows to infer a polyphased fluorinated mineralization. In fact, at least four generations of fluorite appear in the El Hammam mine (Fig. 2A and Table I):

1) Massive green fluorite (FVtypeA) with an REE spectra significantly enriched in LREE and with a positive Eu anomaly. The values of the La/Yb and La/Lu ratios vary from 219.45 to 527.14 and 2110.00 to 3690.00 respectively.

2) Brecciated green fluorite (FVtypeB) relatively rich in LREE and showing a marked negative Eu anomaly. The La/Yb and La/Lu ratios range from 18.01 to 301.42 and 157.00 to 2110.00 respectively.

3) White fluorite (FBl) with flat REE curves. A ratio of La/Yb ranging from 0.57 to 1.42 and a ratio of La/Lu ranging from 4.80 to 13.28.

4) Blue fluorite shaded in yellow (FBj), highly depleted in LREE and with very low ratios of La/Yb and La/Lu (0.004 to 0.005 and 0.037 to 0.051 respectively).

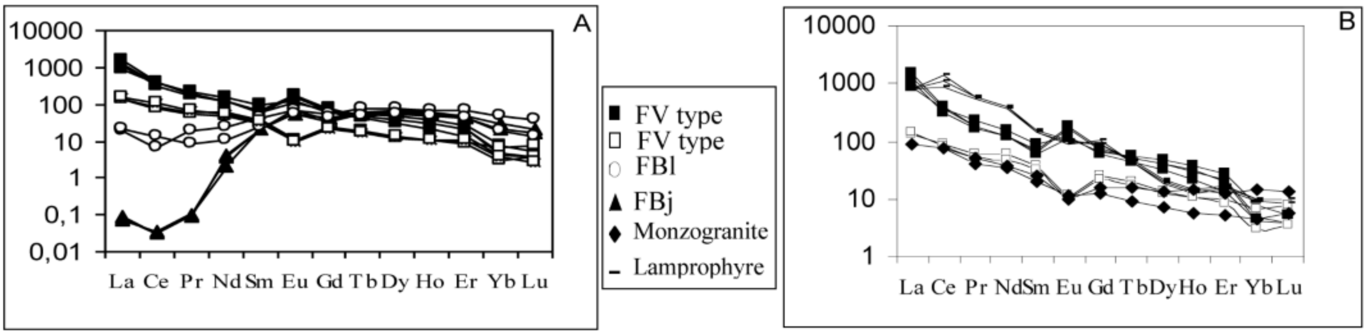
Discussion

FVtypeA fluorites, with a positive anomaly in Eu, are the most enriched in REE (REE > 579.50) (Fig. 2A and Table1). This feature attests to the genesis of these fluorites associated with fluids, which are largely magmatic in relation to lamprophyric activity (Fig. 2B).

The lamprophyres appear to play a dual role as of both heat engine and fluorine source. This is corroborated, firstly, by the relatively high homogenization temperatures of early fluorites in the range of 170-180°C (Jebrak, 1985) and, secondly by the high F levels in lamprophyres in both total-rock (≈ 9% F) and monomineralic apatite (≈ 3% in F). The diagram of Tb/La vs Tb/Ca (Fig. 2C) indicates that FVtypeA is plotted in the pegmatite field, presumably in connection with a boron-rich phase in tourmaline well expressed in the area (Jebrak, 1985; Chraibi, 2000).

The FV type B with a negative Eu anomaly is enriched in REE (125.67 < REE < 153.10) (Fig. 2A and Table I). The spectra of rare earth elements show a clear parallelism between the FVtypeB and monzogranite, which suggests a genetic relationship between both (Fig. 2B). Considering the REE spectra the origin of fluorine could be related to the monzogranites. The fluorine content of these monzogranites is about 0.15%. Furthermore, high concentrations of F in the FVtypeB can be also related to remobilization of F from lamprophyres (Diagram of Möller *et al.*, 1976; Fig. 2C). The fact that FV type B sometimes shows a brecciated appearance and crystallizes at temperatures of homogenization (130-140°C; Jebrak, 1985), lower than FV type A, justifies its late character and its subsequent formation by remobilization more or less partial of the FV type A.

The FBl shows flat REE curves with LREE depletion (63.24 < REE < 89.92) (Fig. 2A). The rough draft in some samples with a negative anomaly in Ce and a positive anomaly in Eu, indicates a precipitation of the FBl at relatively low temperatures and under oxidizing conditions (high fO_2) (Santos *et al.*, 1996). This results in an oxidizing environment and hence, a significant contribution of surficial fluids and the possibil-



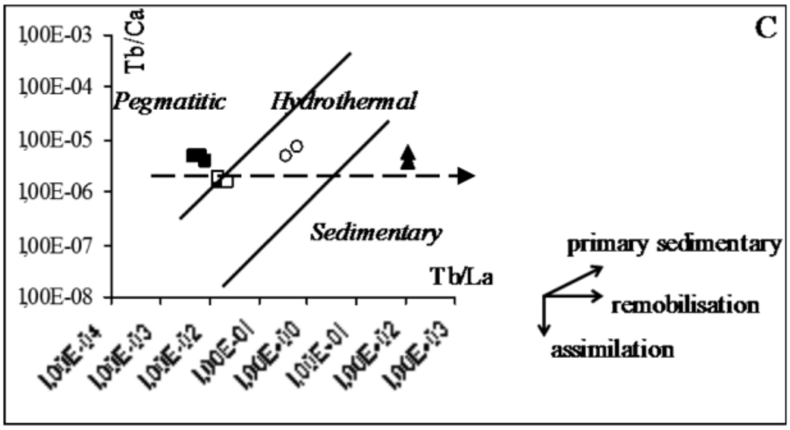


Fig. 2.- Chondrite-normalized (Sun and McDounough, 1989) REE patterns and Möller's Diagram of fluorites samples in El Hammam mine area. A: several type of fluorite; B: green fluorite (typeA-B) and magmatics rocks (lamprophyre and monzogranite);C: Plot of the El Hammam fluorites on a Tb/Ca versus Tb/La variation diagram (after Möller *et al.* 1976). Trends are taken from O'Conner *et al.* (1993).

Fig. 2.- Curvas de elementos de tierras raras (REE) y diagrama de Möller de muestras de fluorita en la zona minera de el Hammam. A: distintos tipos de fluorita. B: fluorita verde (tipo A.B) y rocas magmáticas (lamprófido y monzogranito). C: Tb/Ca frente a Tb/La en el diagrama de Möller et al. *(1976) en fluoritas de El Hammam. Líneas de tendencia a partir de O'Conner* et al. *(1993).*

REE	Green fluorite							White fluorite (FBl)		Blue fluorite (FBj)			Magmatic rocks				
	FVtypeA				FVtypeB								Monzogranite		Lamprophyre		
	Chr1	C1	C2	C3	J1	J2	J3	Chr2	J4	Chr3	Chr4	Chr5	Chr6	J5	Chr7	Chr8	Chr9
La	294.50	211.00	260.00	369.00	37.95	31.40	33.20	4.66	4.84	0.02	0.02	0.02	21.29	21.89	197.27	197.00	185.65
Ce	232.90	230.00	194.00	244.00	65.47	52.60	48.80	4.14	7.90	0.02	0.02	0.02	44.86	44.86	856.64	659.41	552.10
Pr	17.70	20.90	15.80	17.40	6.71	5.90	4.90	1.78	0.80	0.01	0.01	0.01	4.74	3.78	54.22	56.40	51.61
Nd	54.77	72.70	55.40	56.70	26.27	27.70	22.50	11.37	4.90	1.00	1.94	1.75	17.27	16.41	178.10	185.15	171.12
Sm	9.30	13.90	11.00	9.80	5.00	5.80	4.70	6.18	3.80	3.20	3.36	3.08	3.75	3.15	22.37	24.44	22.37
Eu	6.33	6.90	10.30	9.40	0.54	0.61	0.65	4.17	2.97	3.90	3.25	3.21	0.56	0.65	5.01	5.82	5.61
Gd	13.34	12.40	15.00	14.50	4.22	5.20	4.50	11.08	9.10	7.79	8.31	7.01	3.24	2.47	20.84	18.86	18.86
Tb	2.01	1.60	1.90	1.90	0.62	0.74	0.64	2.80	1.83	2.26	2.22	2.00	0.57	0.35	1.65	1.81	1.69
Dy	11.64	7.80	10.00	10.20	3.29	3.47	3.17	19.91	13.66	16.44	15.24	14.91	3.49	1.78	4.80	5.41	5.19
Ho	2.11	1.20	1.70	1.80	0.58	0.60	0.58	4.06	2.68	3.30	3.00	3.11	0.84	0.31	0.69	0.80	0.78
Er	4.49	2.30	3.50	3.40	1.77	1.61	1.41	10.71	7.00	8.27	7.13	8.03	2.02	0.87	2.50	2.75	2.64
Yb	1.34	0.70	0.80	0.70	0.61	1.11	0.53	8.08	3.41	5.03	3.82	5.05	2.48	0.76	1.54	1.73	1.68
Lu	0.13	0.10	0.10	0.10	0.07	0.20	0.09	0.97	0.35	0.57	0.41	0.57	0.34	0.14	0.22	0.25	0.24
∑REE	650.56	581.50	579.50	738.90	153.10	136.94	125.67	89.92	63.24	51.81	48.72	48.77	105.45	97.42	1345.85	1159.83	1019.54
La/Yb	219.45	301.43	325.00	527.14	62.21	28.29	62.64	0.58	1.42	0.00	0.01	0.00	8.58	28.80	128.10	113.87	110.51
La/Lu	2282.95	2110.00	2600.00	3690.00	542.14	157.00	368.89	4.80	13.83	0.04	0.05	0.03	62.62	156.36	896.68	788.00	773.54

Table I: REE contents (ppm) in fluorite samples from the El Hammam deposits.(J: from Jebrak, 1985; C: from Cheilletz *et al.*, 2010; Chr: this work).

Tabla I: Contenido en REE (ppm) en muestras de fluorita de los yacimientos de el Hamman (J: según Jebrak, 1985; C: según Cheilletz et al.*, 2010; Chr: este trabajo).*

ity of mixing with magmatic fluids which generate FV type A and FV type B. The placement of the FBl in the Hydrothermal field of the Möller diagram (Fig. 2C) and their evolution through remobilization of the green fluorites (FV type A and FV type B) confirms this hypothesis. Finally, FBj shows an REE spectrum, which is significantly depleted in LREE and relatively enriched in MREE (Fig. 2A). This configuration is typical of REE fluorites in relation with sedimentary fluids (Trinkler *et al.*, 2005). This proves that the fluids which given rise to the FBj undergo a significant interaction with host rocks, most probably as a result of the broad movement of meteoric fluids. The origin of the FBj could be linked to a remobilization of early fluorites (FV type A, FV type B, and FBl) under the effect of fluids that are mainly meteoric, as is evident in the Möller diagram (Fig. 2C). The position of the FBj in the field of sedimentary fluorite corroborates this hypothesis, putting extra emphasis on the clear involvement of sedimentary and/or metamorphic rocks. The low values of REE (48.72 < REE < 51.80) and the ratios (La/Lu) of FBj (Table I) are often interpreted as fluorites derived from a sedimentary environment (Ronchi *et al.*, 1993; Santos *et al.*, 1996; Hill *et al.*, 2000).

Conclusions

The study of the fluoridated mineralization in the mining district of El Hammam, coupled with geochemical investigations, reveals at least four types of fluorite: i) massive green fluorite (FV type A); ii) green fluorite which is often brecciated (FV type B); iii) white fluorite (FBl); iv) and blue fluorite shaded in yellow (FBj). Indeed, the total REE (REE) and the ratios of LREE/HREE (La/Yb, La/Lu, etc.) decreases progressively from FV type A to FV type B, FBl, and finally FBj. This shows that the precipitation of these varieties fluorite takes place at least four stages. FV type A, the most enriched in REE, seems to be the earliest and is the most associated with the hydrothermal boron phase. The genesis of FV type B is due to the intervention of hydrothermal fluids, mainly of magmatic nature, with the emplacement of monzogranites. The monzogranites deliver a portion of the F and the rest is remobilized from the FV type A (lamprophyres). The FBl, then the FBj are mainly the out come of the remobilization of previous fluorites by the phenomenon of mixing between meteoric and magmatic fluids. The degree of negative Ce anomalies and positive Eu anomalies indicates the participation rate of meteoric fluids (host rocks), which become more and more pronounced moving from FBl to FBj.

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