Multi-Technique characterization of fluorite from the Mining Districts of Asturias, Spain

Antonia Cepedal[1], Mercedes Fuertes-Fuente[1], Agustín Martin-Izard[1], José A. Marín-Barcáiztegui[2], Luis Villa[2]

[1] Department of Geology, Oviedo University, Asturias, Spain. mcepedal@uniovi.es.
[2] Minerales y Productos Derivados, S.A. (MINERSA), Asturias, Spain

INTRODUCTION & AIM

Asturias is the main producer of fluorite, currently mining in three districts -Villabona, La Collada and Berbes (Fig. 1)- with an annual production capacity of approximately 140,000 t. (https://www.minersa.com/mpd_fluorspar.php).

Mineralization shares characteristics with MVT deposits (Magotra et al., 2017) and mainly occurs along the margins of a Mesozoic basin which unconformably overlies the Palaeozoic basement. Fluorite is found as stratabound bodies and veins in Permo-Triassic rocks, and as veins hosted by Carboniferous limestones (Martínez García, 1983; Sánchez et al., 2009,2010; Symons et al., 2016, and references therein).

The aim of this work is to develop a protocol for quantifying major and trace elements in fluorite using fs-LA-ICP-TOFMS, and to study their variation during mineral formation.
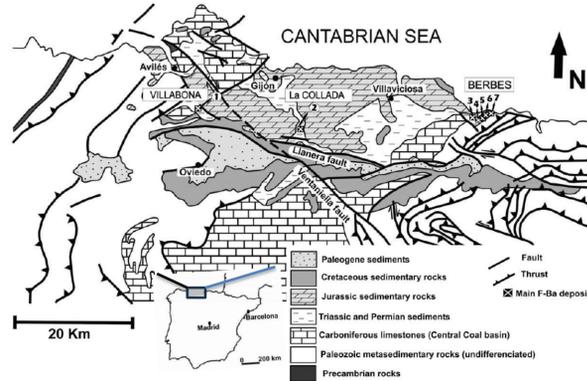

Fig. 1. Location of the fluorite mining in Asturias (modified from Sánchez et al., 2010).

METHOD

- Textural and mineralogical characterization of samples were done using **optical microscopy** and **scanning electron microscopy** (JEOL-6610LV with EDS).
- **Fluorescence** was texted using an Olympus Automatic Microscope BX61 equipped with a UV filter (BP 360-370).
- A Linkam THMSG 600 heating–freezing stage was use for **microthermometric analyses** of fluid inclusions.
- For the **fs-LA-ICP-TOFMS** analyses, A NWRFemto UltraCompact laser ablation system (*Elemental Scientific Lasers,* USA) was used, consisting of a diode-pumped Yb:KGW fs-laser (<290 fs, Pharos, Light Conversion) operated at λ ~257 nm. Detection was performed using a Vitesse ICP-TOFMS (*Nu Instruments Ltd.*, UK). Operating conditions are listed in Table 1. Data were processed using Iolite 4.8 (Paton, 2011).
All analyses were conducted at the University of Oviedo.

| Spot mode		Line mode		
Spot size	15 µm	Spot size	15 µm	NIST610, NIST612 external standard
Repetition rate	50 Hz	Repetition rate	50 Hz	%wt ^{44}Ca internal standard
Fluence	3 y 3.5 J/cm^2	Fluence	3 y 3.5 J/cm^2	% RSD (<5% up to 20%)
Time of measure	10 s (5s background)	Scan rate	50 µm/s	

RESULTS & DISCUSSION

Sample M47 (Moscona Mine, Villabona): euhedral of colourless, fluorite crystals showing concentric clear growth bands, with few inclusions, alternating with turbid bands rich in fluid inclusions. The last infill of the cavity is composed of calcite.
The crystals exhibit bands with light purple fluorescence in the inner zones, as well as a thin band showing yellow fluorescence. At the end of the crystals, several thin growth bands are present, one of which displays intense blue fluorescence. The white arrow indicates the direction and sense of the ablation line (Fig. 2D, Fig. 9).

Fig. 2
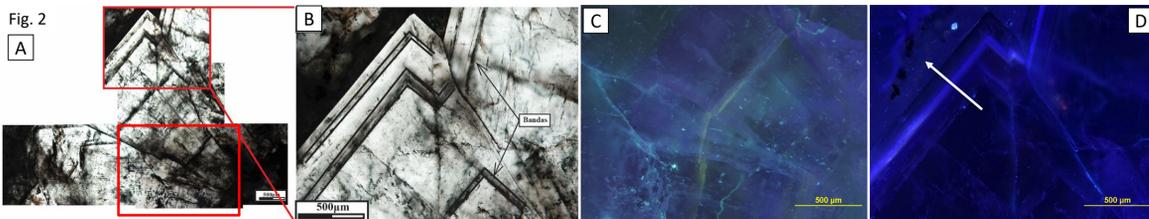
Sample E21 (Emilio Mine, Berbes) is also composed of colourless fluorite with alternating clear and turbid growth bands. In this case, the cavity is filled by barite. These fluorite crystals do not display fluorescence.
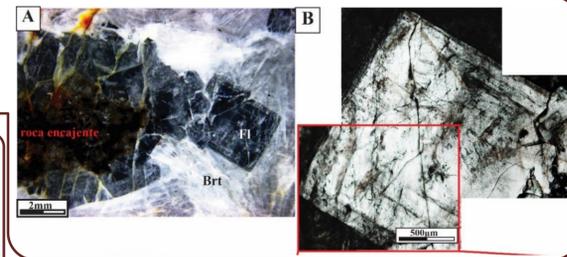
Fig. 4

The samples of yellow fluorite (M46 and M29, Moscona Mine, Villabona) consist of crystals with alternating yellowish and colorless growth bands (Fig. 4A). In M29, a later generation of fine-grained fluorite coats earlier crystals and is intergrown with sphalerite and chalcopyrite (Fig. 4B). The cavity is filled by calcite.
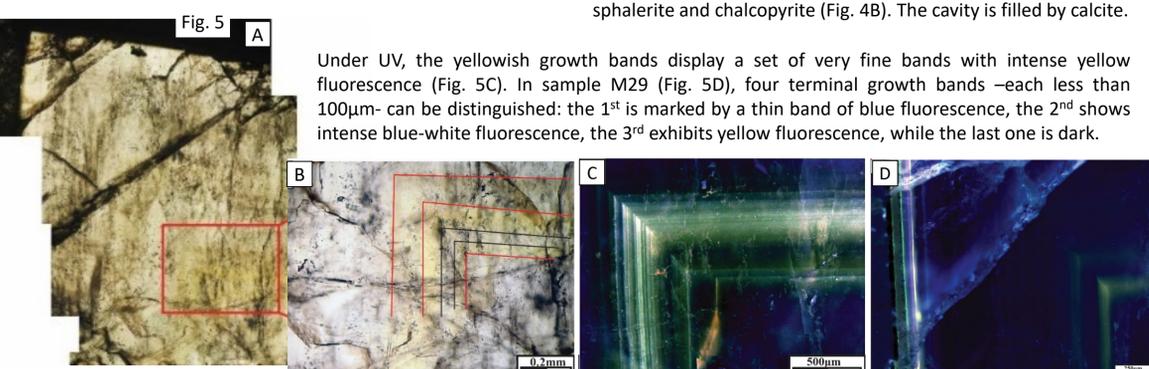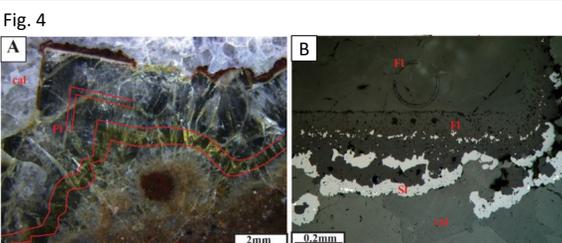
Fig. 5

Under UV, the yellowish growth bands display a set of very fine bands with intense yellow fluorescence (Fig. 5C). In sample M29 (Fig. 5D), four terminal growth bands –each less than 100µm- can be distinguished: the 1st is marked by a thin band of blue fluorescence, the 2nd shows intense blue-white fluorescence, the 3rd exhibits yellow fluorescence, while the last one is dark.
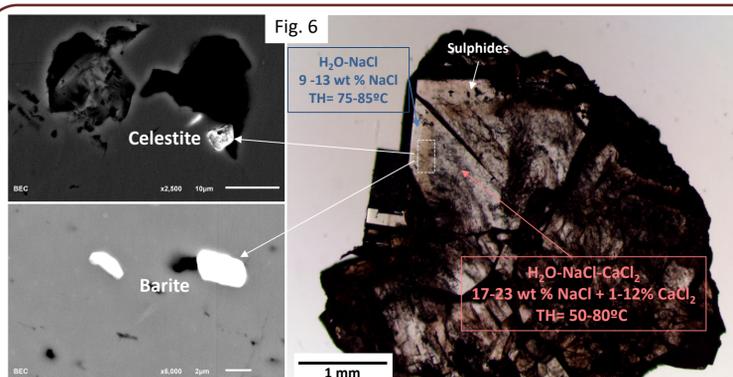

Fig. 6

Fluorite growth zoning and fluid/solid inclusions distribution (Fig. 6) support a fluid-mixing process that induced a local transition from oxidizing to reducing conditions, facilitating the shift from sulphate to sulphide precipitation.

Fig 6. Fluorite crystal showing an inner zone with primary H$_2$O–NaCl–CaCl$_2$ fluid inclusions (FIs) containing barite/celestine, a yellow band full of tiny barite/celestine inclusions and an outer band with primary H$_2$O–NaCl FIs and sulphides. Total Homogenization (TH) vs Salinity from the FIs of this crystal (right).
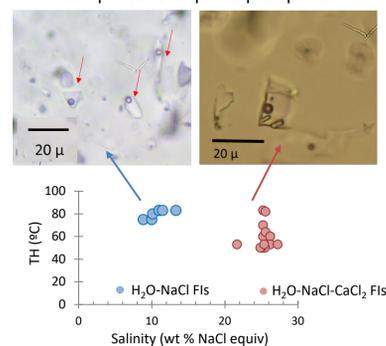
Fs-LA-ICP-TOFMS analyses

SPOT MODE: Around 130 analyses were performed. The main trace elements detected are Na (< ~1300 ppm), Sr (< ~560 ppm), Y (< ~150 ppm), Al (< ~120 ppm) and Mg (< ~60 ppm), with Si (< ~220 ppm) occurring less frequently. Minor amounts of Zr, Ba, Th, U, Fe and REE are also present. The REE distribution in fluorite shows convex-up patterns with a slight enrichment in the MREE (Fig. 6). The ΣREE is lower in fluorite from Berbes than in fluorite from Villabona, and in the latter, the higher ΣREE values correspond to the bands exhibiting stronger fluorescence. These concentrations are consistent with values reported by other authors using different analytical techniques (Table 2).
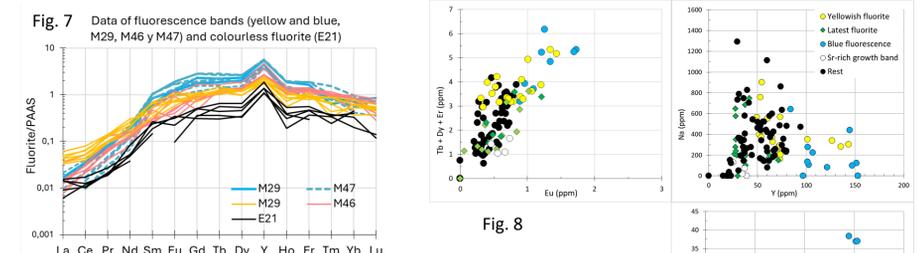

Fig. 7 Data of fluorescence bands (yellow and blue, M29, M46 y M47) and colourless fluorite (E21)

Fig. 8

Table 2: Normalized REE and Y values (PAAS, McLennan, 1989).

	Berbes	Villabona						Sánchez et al. (2010a)	
	E21	M29		M46		M47		Berbes	Villabona
Sample	ΣREE	ΣREY	ΣREE	ΣREY	ΣREE	ΣREY	ΣREE	ΣREY	ΣREE	ΣREE
Max	4.61	6.06	14.86	20.32	11.90	16.60	21.85	27.21	0.77	11.66
Min	2.30	3.15	3.30	4.23	5.66	7.67	2.41	3.22	0.1	9.53
Average	3.29	4.61	7.64	9.72	8.08	10.77	8.43	10.64	0.38	10.59

The activator of the blue fluorescence may be Eu^{2+}, whereas the yellow fluorescence might result from the lower Eu content and the presence of Tb, Dy and Er (Fig. 8) (Aierken et al., 2003).
Y enrichment is not correlated with the amount of Na (or Al, not shown), but it shows a strong positive correlation with middle and heavy REEs, suggesting a substitution type of Ca^{2+} = REY^{3+} + F$^-$.

LINE MODE: Lines were performed across selected areas (last growth bands, yellowish bands), allowing the quantitative observation of trace-elements variations (counts per second) along the line. For example, in sample M47 (Fig. 2D, Fig. 9) the ablation line shows rapid fluctuations in Sr and Y contents (associated with LREE and MREE+HREE, respectively) between the thin bands. A similar pattern was observed in sample M29 (Fig. 5D), suggesting mixing of fluids during crystal growth.

Fig. 9
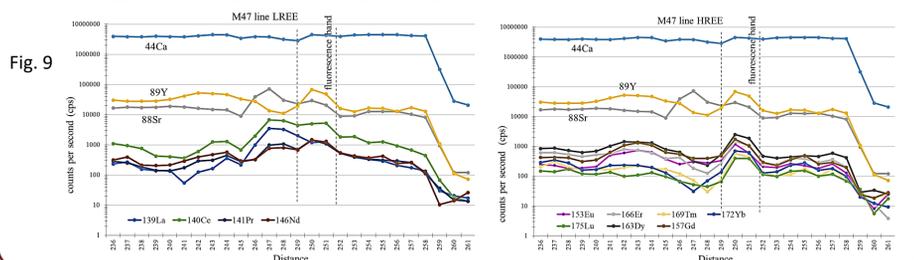
CONCLUSION

- The application of the fs-LA-ICP-TOFMS technique to the geochemical characterization of Asturian fluorites has produced results consistent with previously published data, while providing substantially higher spatial resolution at the crystal scale.
- The study of fluid inclusions in fluorite supports the occurrence of fluid mixing, as previously proposed by other authors (e.g., Sánchez et al., 2010). This process likely generated local shifts from oxidizing to reducing conditions, which may explain the observed variations in trace-element distributions

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