New data on Alpine type fluorite deposits: Case of Lújar mine in Betic Cordillera (SE Spain)

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INTRODUCTION.

Fluorite (CaF_2) is an essential fluorine ore for modern industry (e.g. metallurgical and chemical). There are two most common styles of mineralization for this mineral (included in the list of Critical Raw Materials for European Union): deposits in sedimentary rocks, mostly carbonates, and deposits related with igneous activity. The former is typically associated to Mississippi Valley-type (MVT) deposits, which suggest an epigenetic origin for the ores. However, there are some cases in which the characteristics of this style of mineralization are not totally compatible with the MVT model and are quoted in the literature as Alpine-type deposits until late 1990s. Since then, there is little focus on this peculiar ore deposit type.

GEOLOGY AND MINERALOGY OF THE DEPOSIT.

The Lújar mine is the only active F-Pb mining site in the Betic Cordillera. It is located near the town of Órgiva, province of Granada in the southern Spain (Fig. 1). The deposit has estimated current ore reserves of about 2 Mt of fluorite, which occurs as irregular stratabound replacive bodies and mantos, or as fault-related veins, mainly in two specific dolomite levels of the transit of Upper Ladinian–Lower Carnian of Lújar Nappe (Alpujarride Complex, Internal Betic Zones).

The mineralogy of the deposit is relatively simple consisting of fluorite, subordinate galena and gangue of dolomite. The host rock is mostly represented by dark massive dolomicrite and limestone, although it also might retain internal lamination. Rhythmic textures in host dolomites were also observed. This zebra texture consists of alternating black-white or geopetal white (footwall)-grey-black (hanging wall) centimetric bands, whose genesis was discussed by Merino and Canals (2011) and references therein. On some occasions the presence of saddle dolomite and ankerite were noticed, which is likely to be related to the last stage of dolomitization.

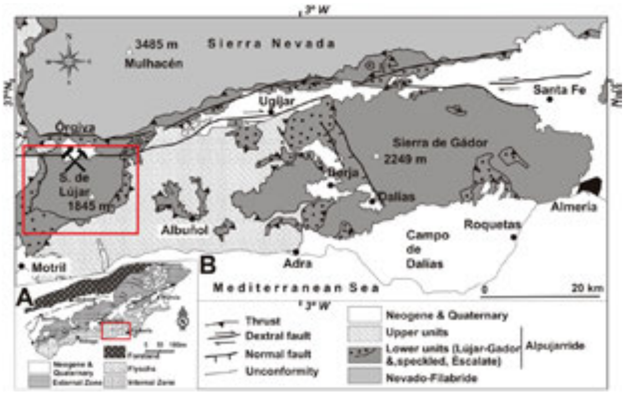

Fig 1. Geological map of Betic Cordillera with specified location of Lújar mine. Modified from Sanz de Galdeano and López (2014).

In the mine the fluorite typically occurs as dark and light (white or purple) crystals, being the latter larger in size and free of impurities. Also, those two varieties may grow in parallel (alternating), developing centimetric zebra patterns ("*piedra indiana*") similar to those found in the dolomite host rocks ("*piedra franciscana*"). In addition to galena, the ore minerals contain minor amounts of pyrite, chalcopyrite, sphalerite, barite, quartz and phyllosilicate (illite). Finally, as supergene minerals goethite, malachite, azurite, hemimorphite and cerussite were identified.

FLUID INCLUSION DATA.

The microthermometric measures were performed using a Chaixmeca stage. Most of the fluid inclusions (FI) in dolomite gangue showed so small sizes that made their study a really difficult or impossible task. Both monophasic and biphasic FI were explored with no success. Neither was possible to obtain any data from dark band of fluorite, due to low visibility by transmitted light. On the contrary, in the light fluorite bands a great number of FI with sizes in the range of 4-30 µm (average 10 µm) were observed. From a total of 118 fluid inclusion measurements (Fig. 2) we have distinguished four fluid inclusions assemblages (FIAs) of aqueous fluids in terms of homogenization temperature (Th), salinity and presence of CO_2. The first one (I) is represented by biphasic inclusions with 16-25 wt% NaCl eq. and Th of about 110-160ºC. The second population (II) clearly triphasic (liquid+vapour+halite), is characterized by both higher salinity (28-36 wt% NaCl eq.) and higher Th (180-250ºC). Ideally the composition of both FIAs could belong to the $NaCl+CaCl_2+H_2O$ system with traces of CO_2.

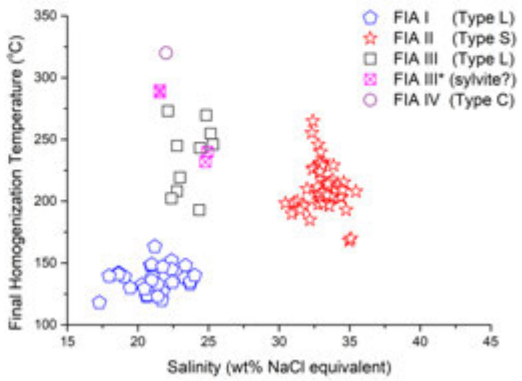

Fig 2. Th-salinity plot for fluid inclusions in fluorite from the Lújar deposits.

The third group (III) is similar to the first one, but has higher Th and salinity (193-290ºC and 21-25 wt% NaCl eq.) and higher amounts of CO_2 (gas-rich biphasic inclusions). Occasionally, in some of these FI an additional solid phase has been observed. The temperature of melting of these daughter crystals (Tm) is around 120-135ºC (in contrast to 180-250ºC measured in FIA II), which might suggest the presence of sylvite. Finally, the fourth group (IV) brings together all triphasic inclusions with abundant CO_2 phase, moderate salinity and relatively high Th (16-27 wt% NaCl and up to 320ºC). Those last two groups have an ideal composition typical of more complex systems, such as $NaCl+CO_2+H_2O\pm H_2S(\pm CH_4)$.

RAMAN SPECTROSCOPY.

The micro Raman spectroscopic study of the more complex fluids has revealed the presence of variable amounts of CO_2 in most of the analyzed samples. In the case of hipersaline fluid inclusions (II), and biphasic (I and III), the amount of CO_2 does not exceed the 5-10 molar percent. On the contrary, in gas-rich inclusions (IV) (Fig. 3) this amount reach 13-40 molar percent. Besides, in both III and IV groups trace amounts of CH_4 and N_2 have been detected. The concentration of methane in these fluids was estimated in 1.8 molal and 3.1 molal respectively. The presence of H_2S in the IV population of inclusions, was previously suggested by the intense smell of the samples and by microthermometric criterias.

DISCUSSION AND CONCLUSIONS.

On the base of the obtained data, the history of the deposit may be subdivided in four main phases: sedimentary, diagenetic, hydrothermal (dolomitization and ore deposition) and supergene.

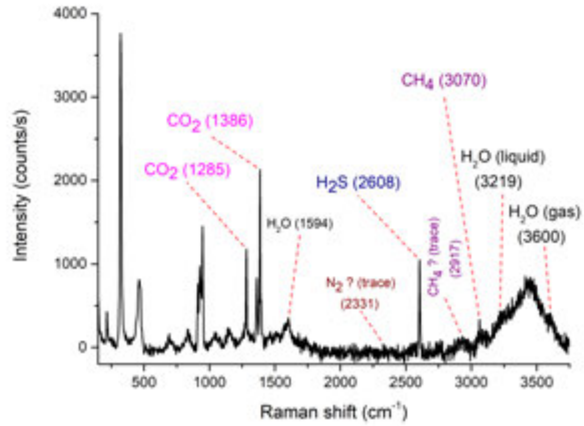

Fig 3. Micro-raman spectra of CO_2-H_2S-CH_4-N_2(?)-H_2O vapor phase of C-type fluid inclusion (population IV) from Lujar Mine.

In reference to the hydrothermal episode, it consists in an early dolomitization of the host rocks (including the formation of "franciscana"), followed by the mineralization. The latter event evidences at least two replacement stages that confirm the epigenetic origin of the fluorite deposit. The first one, of relatively lower temperature and higher salinity, includes fluids I and II. Either their mixing triggered precipitation or represent discrete stages. It was probably syn-/pre-Alpine, related to Late Cretaceous beginning of deformation(?) The second event was of higher temperature (fluids III and IV), with moderate salinity and influenced by metamorphic fluids (CO_2 enrichment, sylvite(?) and authigenic illite). This second post-Alpine stage, might be related to the development of extensional faults (18-14 M.a) coeval with the formation of the Alpujarride Corridor during the Late Serravallian (13-12 Ma) or Late Miocene concurrent with the active volcanism (12-7 Ma) in the region. Interestingly, the galena from various prospects through the Sierra de Lújar display annealing textures that indicate that ores undergone deformation and vey low-grade metamorphism and that temperature locally could have reached higher values (Ilin, 2018).

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