CECHITE, $PbFe^{2+}(VO_4)(OH)$: RAMAN SPECTROSCOPY OF THE HIGH-QUALITY OCCURRENCE OF ULLDEMOLINS (TARRAGONA, SPAIN)

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Abstract The Cechite is a rare lead and iron vanadate mineral, first described in samples from Alexander mine and the Posepny vein, at Vrancice, Bohemia, Czech Republic. Taking the finding of outstanding specimens from the "María Magdalena" mine (Ulldemolins, Tarragona, Spain), the first description of the Raman spectrum of the mineral is reported. The Raman and energy dispersive X-ray spectroscopy of the samples showed some samples are copper-rich and suggests the presence of a new mineral phase.

Keywords: Cechite, vanadate minerals, Ulldemolins, Raman, Descloizite group.

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1 Introduction

Cechite (Čechite) is a rare lead and iron vanadate with ideal formula $PbFe^{2+}(VO_4)(OH)$, member of the adelite-descloizite group of arsenate and vanadate minerals. This group have the general idealized formula $A^{2+}B(^{2+}/^{3+})(XO_4)(OH)$, where X=As, V and A,B=Ca, Mg, Pb, Zn, Co, Cu, Ni, Fe and Al (Palache et al., 1951; Basso et al., 1989; Đorđević et al., 2016). The group is divided in two crystallographic differenced subgroups: the adelite-type members, orthorhombic vanadates and arsenates with space group P212121, and the descloizite-type members of orthorhombic vanadates, with space group Pnma (Đorđević et al., 2016) The basic vanadates of the descloizite-type, with general formula $PbM(VO_4)(OH)$, includes to date the minerals mottramite (M=Cu), descloizite (M=Zn), pyrobelonite (M=Mn) and cechite (M=Fe) (Frost et al., 2014)

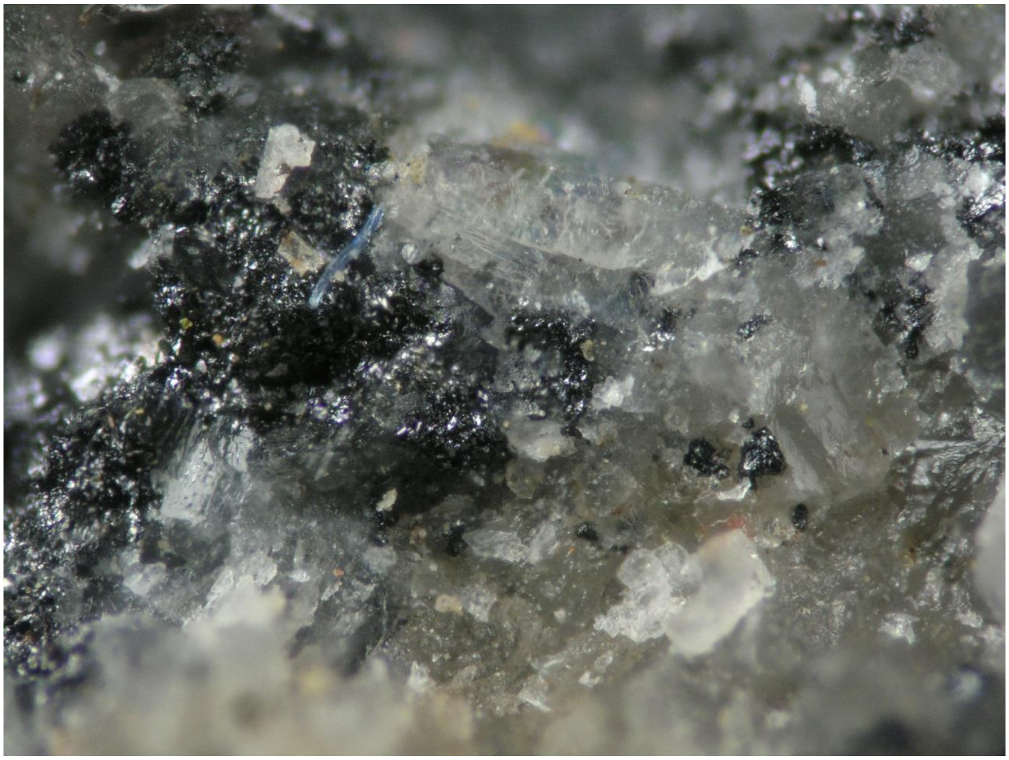

Figure 1. Cechite (black grains) from the type locality. Field of view 1mm.

Cechite was first described in samples from the old mine dumps of the Alexander mine and the Posepny vein, at Vrancice, Bohemia, Czech Republic, forming small (up to 3 cm, usually millimeter-size) black granular masses with submetallic to resinous luster (Fig. 1). Rarely, it forms small crystals, normally equant or rounded.

The empirical formula found for the type locality is $(Pb_{0.93}Ca_{0.02})(Fe^{2+}_{0.81}Mn_{0.25}Zn_{0.01})(V_{0.96}As_{0.01})O_{3.90}(OH)_{1.10}$ (Mrazek and Taborsky, 1981). Ideally, cechite is the lead and ferrous vanadate analog of pyrobelonite, and variable quantities of manganese are usually present. Sometimes, the analysis by EDS of the members of the descloizite group is not straightforward, due to the common occurrence of partial substitutions and solid solutions. Raman spectroscopy, instead, is the most useful technique for the fast and reliable identification of vanadate minerals of the adelite-descloizite group. The Raman spectra of mottramite and descloizite have been described in the literature (Frost et al., 2014; Frost et al., 2001) and a reference Raman spectrum of pyrobelonite is publicly accessible at the RRUFF database (Lafuente et al., 2015; http://rruff.info) Regarding cechite, just one reference for its Raman spectrum can be found in the literature, published in Tarcea et al. in 2009 and available in the database of the freeware Crystal Sleuth (Laetsch and Downs, 2006). The reported spectrum is questionable, as it show Raman shifts completely inconsistent with the structure and composition of cechite. The research presented here proved it definitely wrong and the published spectrum actually corresponds to goethite. Given the appearance of cechite, is an understandable confusion, if the sample used by the researchers for their study was acquired without proper analysis, a common problem with rare species in the specimen mineralogy market.

Recently, remarkable cechite specimens were found by mineralogy enthusiasts of the GMC (Grup Mineralògic Catalá) at the *María Magdalena* mine, in Ulldemolins, Tarragona, Catalonia, Spain (Fig. 2).

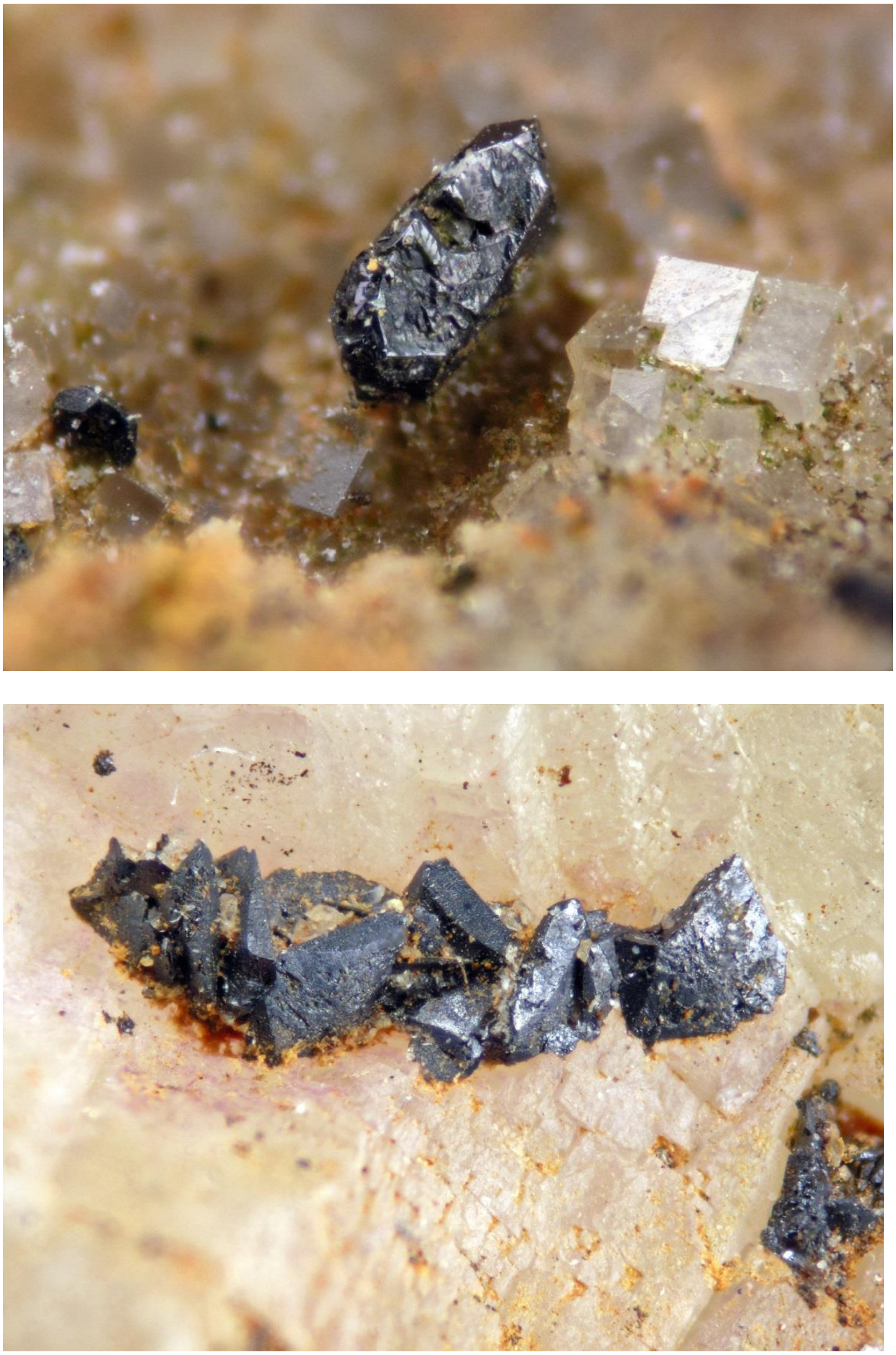

Figure 2. Cechite on fluorite from *María Magdalena* mine (Ulldemolins, Tarragona, Spain). Field of view 1.5 mm (above) and 4 mm (below).

The size and purity of the cechite crystals allow obtaining and confirming the Raman spectrum of the mineral. The objective of this paper is to report the first Raman spectroscopic study of the cechite from both the type locality and Ulldemolins mines, which could be useful for the fast identification of the possible cechite specimens by the mineralogical community. Also, an interesting feature on the chemical composition of the Ulldemolins' cechite is reported.

2 Samples and Methods

Two specimens of cechite from the type locality of Posepny vein, at Vrancice (Bohemia, Czech Republic), consisting in black grains of sizes < 1mm (Fig. 1), were used as reference. Cechite from Ulldemolins occurs as dark brown to black euhedral crystals grown on fluorite, with sizes ranging from sub-milimeter to 0.5 cm in the provided samples, usually millimeter-sized. The cechite from Ulldemolins could be easily confused with descloizite or mottramite, showing tabular habit, with predominance of pinacoid (100). The crystals appear rounded and the sharp, well-formed crystals, are less common. The disphenoid form {111}, which shows a bipyramidal shape, is uncommon. Also, the mineral occurs as black granular masses and equant crystals. The similarity in habit and shape of the cechite from Ulldemolins with those of descloizite and especially with mottramite, together with the lack of Raman spectrum references and the quality of crystals, which makes it preferable the non-destructive study, encouraged some collectors from the Spanish association GMC (Group Mineralogistes de Catalunya) to submit samples for analytical study. The analyses were performed by scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (EDS) and Raman microscopy at a laser excitation wavelength of 785 nm and with a resolution of 2 cm^{-1}. Spectra were processed using the software Spektwin32 (Dr. Friedrich Menges, Germany)

3 Results and Discussion

The EDS analysis of the cechite from Ulldemolins revealed two possible compositions (Fig. 3). First, a composition very close to the ideal formula was found, consisting in Pb: 50.8%; Fe: 16.4%; V: 13.5% and O: 19.2%, with no identifiable substitution by manganese, calcium or copper and only traces of arsenic (Fig. 3A). These crystals were used to describe its Raman spectrum for the first time in the literature (Fig. 4A). The resulting Raman spectrum, similar to those of descloizite and pyrobelonite, suggests the strong structural relation between the three minerals.

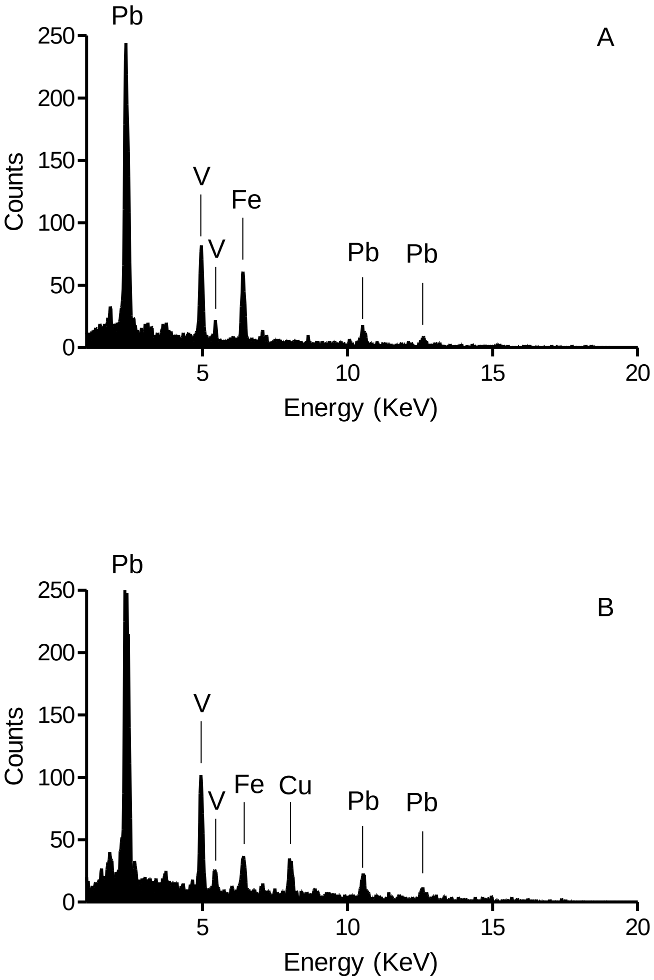

Figure 3. EDS analysis of the cechite from *María Magdalena* mine (Ulldemolins, Tarragona, Spain). A: Near-ideal composition of the crystals pictured in figure 2; B: Copper-rich cechite crystals (Figure 5).

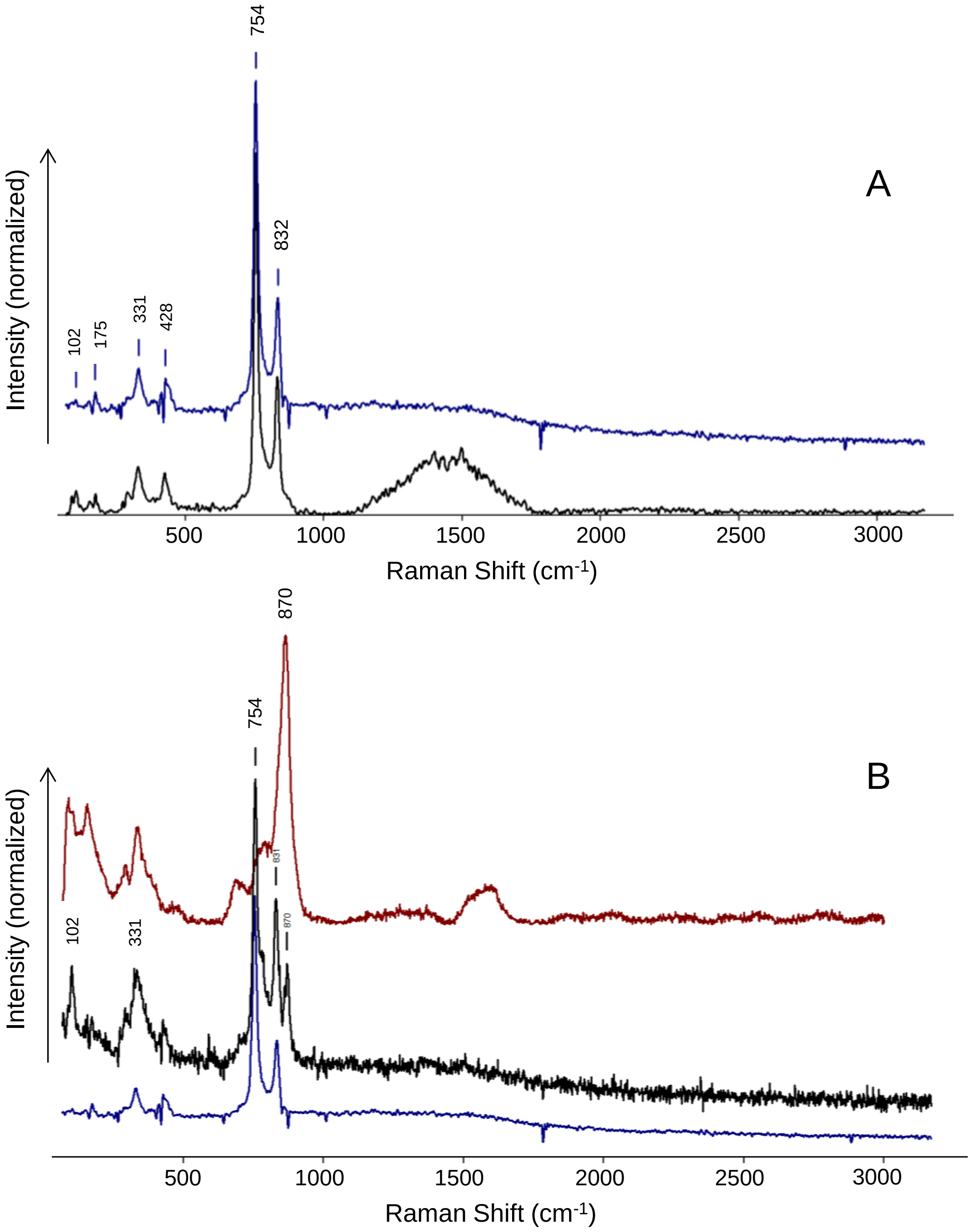

Figure 4: The Raman spectrum of cechite. A: Spectra of samples from type locality (black line) and Ulldemolins (blue line); B: Spectra of copper-rich crystals containing two phases (black line) or only the copper vanadate unidentified phase (red line) compared with pure cechite (blue line).

The spectrum is dominated by a very intense and narrow band at 754 cm^{-1}, interpreted as the antisymmetric vibration mode ν_3 of the VO_4^- units. The corresponding band in descloizite is observed at 777 cm^{-1} (Frost et al., 2001) and also at 754 cm^{-1} in pyrobelonite (RRUFF database). The intense symmetric ν_1 stretching mode of VO_4^- shifted at 832 cm^{-1} and, as in the case of pyrobelonite, its intensity is surprisingly lower than the antisymmetric vibration. The corresponding vibrations in descloizite, mottramite and pyrobelonite have been observed at 845, 821 and 859 cm^{-1} respectively (Frost et al., 2001). To validate these observations and the usefulness of this spectrum in the identification of cechite in mineral specimens, the Raman spectrum of confirmed cechite from the type locality is provided (Fig. 4A), showing the same shifts and confirming the identity.

Figure 5: Crystals of copper-rich cechite on fluorite from Ulldemolins. Field of view: 3.5 mm.

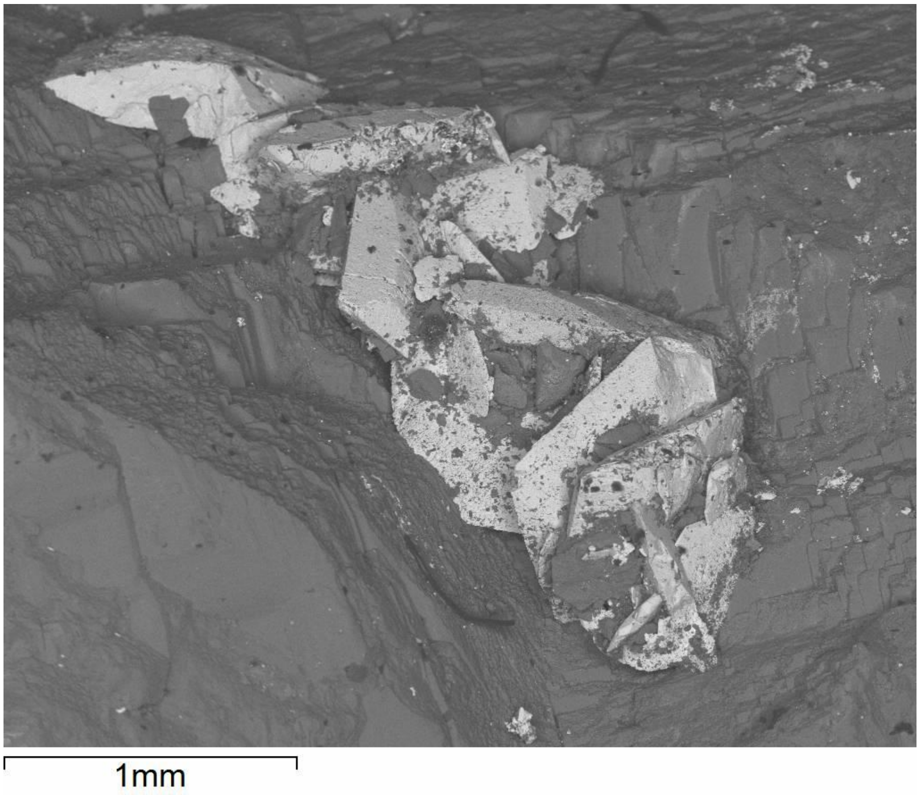

Figure 6: Electron microscope image (BSE detector) of copper-rich cechite crystals from Ulldemolins.

In the second compositional case, some crystals of the possible cechite from Ulldemolins moves away from the ideal composition, showing a significant presence of copper (Fig. 3B). The composition found is: Pb: 44.7%; Cu: 19.7%; Fe: 5.6%; V: 11.9%, and it is indistinguishable *de visu* from pure cechite in the Ulldemolins samples, albeit the copper-rich vanadate, according the observed samples, tends to form tabular crystals of bigger size and dark brown color (Fig. 5). The Raman spectrum of the copper-rich vanadate is dominated by an intense band at 870 cm^{-1}, interpreted as the symmetric ν_1 stretching mode of VO_4^- and equivalent to the 821 cm^{-1} band of mottramite (Fig. 4B). Unlike the case of cechite and descloizite, the antisymmetric ν_3 mode of vanadate does not appear as a narrow, intense band, but as broad, unresolved band at 789 cm^{-1}. The complexity of the chemical analysis is reflected in the multiple unresolved bands observed in the 500-1000 cm^{-1} region, suggesting overall a structural relationship with mottramite, reflecting the multiple bands the structural perturbations associated with copper-vanadate interactions (Frost et al., 2014). This opens a very interesting question regarding the substitution by copper and the possibilities of solid solutions, given the different bond order of Cu^{2+} and structural distortion by Jahn-Teller effect, which prevents the complete solid solutions among members of the group. Unlike in the case of mottramite-descloizite isomorphous series (Cooper and Hawthorne, 1995), in which the descloizite structure can accommodate copper, we do not expect a complete solid solution across cechite-mottramite. Instead, a double phase could be observed clearly on the Raman spectrum at lower copper content of the crystal (Fig. 4B), suggesting that the cechite structure cannot support the copper substitution, leading to a phase transition. As a result, we observe the vibrations of pure cechite together with the vibrations of the additional copper-rich vanadate phase in some crystals (Fig. 4B).

Figure 7: Cechite crystals with fluorite from Ulldemolins. Field of view: 5 mm.

The shifts found are reproducible, independently of the purity of cechite or its copper content, suggesting a mixture of phases or solid solution and not a cation substitution in the structure.

An open question is the nature of the lead-copper-iron vanadate showed in Fig. 6. There are, at least, two possibilities: first, an iron-containing mottramite, in which the partial replacement by iron causes a change in the interatomic interactions of vanadate groups. The vibrational selection rules are more relaxed, resulting in multiple overlapping bands, reflecting the different association of vanadate with either copper or iron, and the structural perturbation induced by iron could lead to a shift in the main symmetric stretching vibration of vanadate. The second possibility, given the strong Raman shift differences in the ν_1 stretching mode of VO_4^- between the lead-copper-iron vanadate and the mottramite, is that the former is a new, undescribed mineral species. From the Raman spectrum is possible to infer that this hypothetical new species could be related with the vanadates of the brackebuschite group. Unfortunately, the unavailability of disposable samples forced us to discuss only the hypothesis derived from the available data, obtained by means of non-destructive analysis, hoping that in the future will be elucidated whether or not a new species is present.

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