

The use of Raman spectroscopy in the characterization of variscite provenance: the Gavà case

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Abstract. The Gavà phosphate deposit, mined during the Neolithic, was produced by weathering processes affecting primary apatite beds. It exhibits a neat vertical zoning, related to chemical gradients during weathering. Strengite, yellowish Al-rich strengite and ferroan variscite are found at the top, pale-green variscite at the intermediate levels, and green variscite in depth. Fe values are very low in the greenish samples, as well as Cr and V. Raman spectrums of the Gavà variscite show differences with samples from other occurrences worldwide. Moreover, some spectral differences can also be observed in the Raman spectra of variscite coming from different depths in the deposit. Raman spectroscopy can be an efficient tool to discriminate not only samples from different geographical localities, but also from its original position in a given deposit.

Key-words: variscite, Raman, microprobe, veins, supergene.

Résumé. Le gîte de phosphates de Gavà, exploité au Néolithique, s'est formé par des processus de météorisation qui auraient affecté des strates primaires d'apatite. Ce gîte a une zonation chimique verticale, qui aurait été produite par des gradations chimiques lors de la météorisation. La partie haute du gîte contient de la strengite, de l'Al-strengite et de la Fe-variscite jaunâtres ; les niveaux intermédiaires contiennent de la variscite verdâtre et les niveaux plus profonds, de la variscite verte. Les teneurs en Fe sont très basses dans les variscites vertes, de même que les valeurs de Cr et de V. Les spectres Raman de la variscite de Gavà présentent de petites différences avec ceux des autres variscites du monde, mais dans le gîte de Gavà on trouve aussi des variations dans les spectres Raman de variscite de chaque couleur. Donc, si on peut avoir une bonne base de données, la spectroscopie Raman présente non seulement un intérêt pour la discrimination en terme de provenance géographique d'un échantillon de variscite, mais aussi pour en déterminer la position au sein d'un gîte donné.

Mots-clés : variscite, Raman, microsonde, filons, supergénétique.

Introduction

The use of variscite for the production of ornaments has been recorded in many countries (Herbaut and Querré, 2004). Variscite is a relatively uncommon phosphate mineral, and in spite of its enormous signification in Archaeology, it has not been enough studied by the mineralogists.

Ornaments carved with variscite are regularly found in many Neolithic tombs. From the archaeological point of view, one of the most important aspects in the study of these ornaments is to discern their provenance. This is not so obvious, because variscite mineralizations are spread worldwide, and are quite common in Western Europe, and this mineral has been found in a pleiad of archaeological sites (Domínguez-Bella, 2004).

Many techniques of analysis have been used to help to discriminate the possible origins of variscite. The most common are chemical, in particular, the study of trace elements (made generally by ICP-MS). However, this technique has serious concerns: a) it is destructive, b) it is difficult to explain the reason of the changes in trace elements' compositions among several possible sources, and c) there is not enough confidence about the homogeneity of the deposits in terms of the distribution of trace elements. Therefore, the scientific validity of the method is doubtful. In fact, a large diversity of variscite facies can

be found in a single variscite deposit as are the Neolithic mines of Gavà. A strong variation in chemical compositions in major and trace elements (and, hence, in color and other physical properties) is found in these deposits, largely depending on the depth of the variscite formation. Therefore, the use of chemical tools in this situation must be envisaged carefully.

Variscite ($\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$) is morphologically variable upon its formation. Euhedral rhombic crystals, with pseudotetragonal bipyramidal habit, are very scarce and small and have been found as a low-temperature hydrothermal mineral mainly as a late mineral filling vein cavities in pegmatite deposits. Some localities provide single crystals or spherulitic aggregates with strong vitreous luster and a diversity of colors: colorless (Beauvoir quarry, Échassières, Ébreuil, Allier, Auvergne, France), grass-green or dark green (Ribeirão Cascalheira, Mato Grosso, Brazil), or reddish (Boa Vista pegmatite, Conselheiro Pena, Doce valley, Minas Gerais, Brazil).

However, variscite is most commonly formed in supergene environments. In this case, it occurs as cryptocrystalline aggregates filling thin veins or as pseudomorphs of pre-existing minerals. It usually replaces members of the apatite group in diagenetic environments, and it can form beds or nodules. It has a waxy shine and a typical apple-green color, which can be more or less pale. All the variscite used in archaeological ornaments correspond to this second type of variscite (these varieties are also known as “*calaite*” or “*lucinite*”).

Metavariscite is a rarer polymorph of variscite. It is found in some diagenetic environments as microcrystalline crusts composed of monoclinic crystals of tabular habit, often grouped in botryoidal aggregates. The color of metavariscite is pale bluish green, and depending on the grain size these aggregates may have a vitreous or waxy luster. It is hardly distinguishable from variscite, and XRD or Raman should be necessary to discriminate between them.

Another dimension of the variscite problem is that this mineral is isostructural with strengite ($\text{Fe}^{3+}\text{PO}_4 \cdot 2\text{H}_2\text{O}$) and may form solid solutions. Strengite may occur as beautiful violaceous, purple or lilac crystals of vitreous shining in pegmatite environments, but it is more common as apatite pseudomorphs in sedimentary deposits. In this case, it is cryptocrystalline and thus waxy, and tends to have dark coloration. Intermediate terms of the variscite-strengite series have also intermediate properties: crystalline ferrian variscite is reddish, and crystalline aluminian strengite (the variety “*barrandite*”) may be dark green; the cryptocrystalline intermediate varieties tend to be yellowish or cream. Strengite has also a monoclinic polymorph, phosphosiderite, which may occur also in a diversity of colors when it is crystalline and like waxy black cryptocrystalline aggregates.

This contribution aims 1) to explore the use of Raman spectroscopy, coupled with chemical characterization, as a tool to discriminate the provenance of members of the variscite-strengite series among several possible deposits, and, 2) to check the possibility to determine approximatively the provenance of samples in the case of a single zoned deposit.

For the first objective we compared the color and the Raman spectra of variscite samples with diverse mineral properties obtained from a diversity of provenances worldwide. We used the samples from the Systematic Collection of the *Departament de Cristal·lografia, Mineralogia i Dipòsits Minerals of the Universitat de Barcelona*. Raman spectroscopy in variscite samples has been used in the study of soils, but in different thermal conditions (Frost *et al.*, 2004).

For the second objective, we used samples obtained from the Gavà Neolithic mines to check if possible variations occurred in the Raman spectra depending of the variscite colour, which is controlled by the depth of formation of the variscite.

1. Methodology

Precise color parameters of the samples were obtained using a CM-503i (Minolta) spectrophotometer. The mineral homogeneity of the samples was tested thanks to optical microscopy in transmitted and reflected light, SEM-EDS-BSE (using an ESEM Quanta 200 FEI Europe at 20 kV and 1nA) and XRD (using

a Panalytical X'Pert PRO MPD X-ray diffractometer with monochromatic Cu K α 1 radiation at 45 keV and 40 mA). Microprobe analyses were performed with a Cameca SX50 at the Centres Científics i Tecnològics (CCT) at the University of Barcelona.

Conditions of analysis were: 15 keV, 20 nA, beam diameter of 1 μ m, and a counting time of 10 s. We used the following standards: orthoclase (SiK α , AlK α , KK α), rutile (TiK α), chromium oxide (CrK α), V metal (VK α), hematite (FeK α), rhodonite (MnK α), wollastonite (CaK α), albite (NaK α).

Raman analyses were performed at the CCT of the *Universitat de Barcelona*, using a dispersive spectrometer HORIBA Jobin Yvon LabRam HR 800 coupled with an optical microscope Olympus BXFM. Raman spectra were obtained using a laser with a wavelength of 532nm (green laser with a beam of 2 μ m in diameter). Acquisition time was 10 s per spectrum. The resulting spectra were compared with the database RRUFF (Downs, 2006).

2. The Gavà Neolithic mines

The Gavà Neolithic mines are among the most important mining complexes exploited for variscite in western Europe (Blasco *et al.*, 1991; Bosch *et al.*, 1996; Villalba, 2002). The mining activity for variscite is recorded in these mines around 5200 BP (Villalba *et al.*, 1986; Blasco *et al.*, 1992; Borrell *et al.*, 2009; Borrell and Bosch, 2012). The Gavà Neolithic mines are found in the Gavà town, 20 km west from Barcelona in Catalonia. Other variscite occurrences have been identified in the Paleozoic basement of the Catalonian Coastal Ranges, but, no evidence for mining activity is provided has been found already (fig. 1).

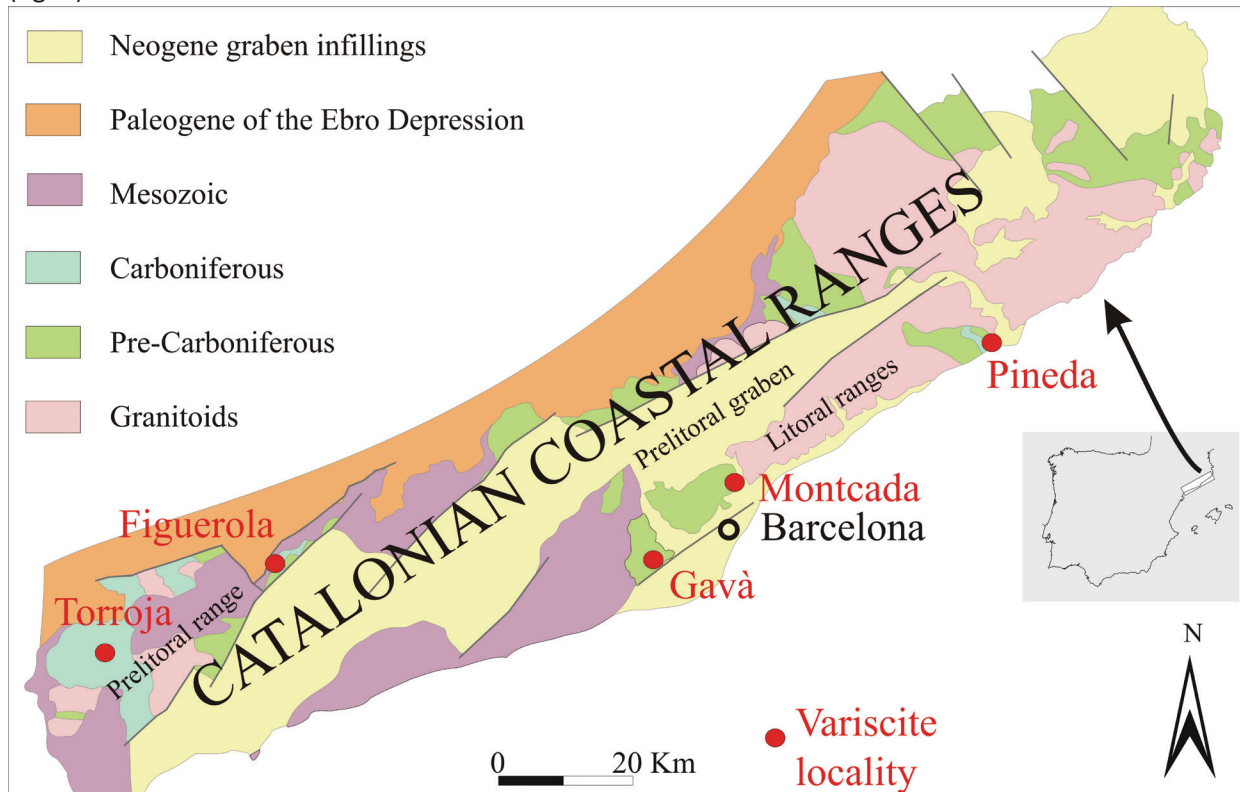


Fig. 1: Variscite showings in the Catalan Coastal Ranges.

Two main geological units can be distinguished in the Gavà area (Costa *et al.*, 1994): a Paleozoic metamorphic basement and an unconformable cover of Quaternary sediments. The Paleozoic basement in the mine area consists mainly of black shales of lower-middle Silurian age with minor beds

of chert or phosphate (apatite). These shales have abundant pyrite and other sulphides scattered as small crystals. In some parts of the area there are limestones, more or less dolomitized, of upper Silurian-lower Devonian age, and some brownish shales and sandstones of middle Devonian age. These materials are affected at a very low grade by Hercynian metamorphism, and have intensely folded by two generations of Hercynian folds that have associated thrusts in the flanks. The ensemble has an unconformable cover of Quaternary sediments, mainly reddish clays and creamy paleocaliches. The Silurian black shales, close to the unconformity, were strongly weathered and have lost their organic matter, becoming pale grayish. The weathering domain extends up to 10 m depth below the unconformity.

Phosphate mineralization occurs only in the basement (Mata-Perelló *et al.*, 1983; Gimeno *et al.*, 1995), and the following styles can be distinguished (Camprubí *et al.*, 1994; fig. 2):

a) Sedimentary beds and nodules. These are thin beds (1 mm up to 2 cm in thickness) or nodules (spherical or flattened bodies of 1-3 cm in diameter) made up by cryptocrystalline grayish to black fluorapatite. These strata are concordant with the Silurian shales and are affected by the same deformations as those. This mineralization is considered as primary mineralization and is found in the black shales and slightly altered shales. It may be accompanied by small pyrite cubes.

b) Diagenetic phosphates replacing the above deposits. The replacement starts with irregular veining of the beds and nodules and may pseudomorphize completely the older fluorapatite. The replacing minerals are black phosphosiderite or yellowish aluminian strengite together with jarosite in the uppermost domain (up to 4 m depth), yellowish green ferrian variscite in an intermediate domain (4-8 m depth) and gemmy green variscite in the deep domain (more than 8 m deep).

c) Phosphate veinlets cutting gray shales. These are generally vertical, thin (1 mm-2 cm) veinlets filling joints. The infilling minerals depend on the depth: the upper domain (up to 4 m depth) is infilled with alunite or jarosite, aluminian strengite and cuprian crandallite, the intermediate domain (4-8 m depth) is infilled by yellowish green ferrian variscite and the lower domain consists of green variscite. The phosphates disappear in depth, when the joints come to the unweathered black shales.

d) Secondary phosphates replacing limestones and marls. These may occur in veins, nodules and massive beds, and comprise Ca-Fe rich phosphates as tenticite, montgomeryite, hydroxilapatite, and dufrenite. These phosphates are associated with goethite, alunite, jarosite and secondary carbonates. These iron ores were mined during Iberian, Roman and Middle age times, and in the 19th century.

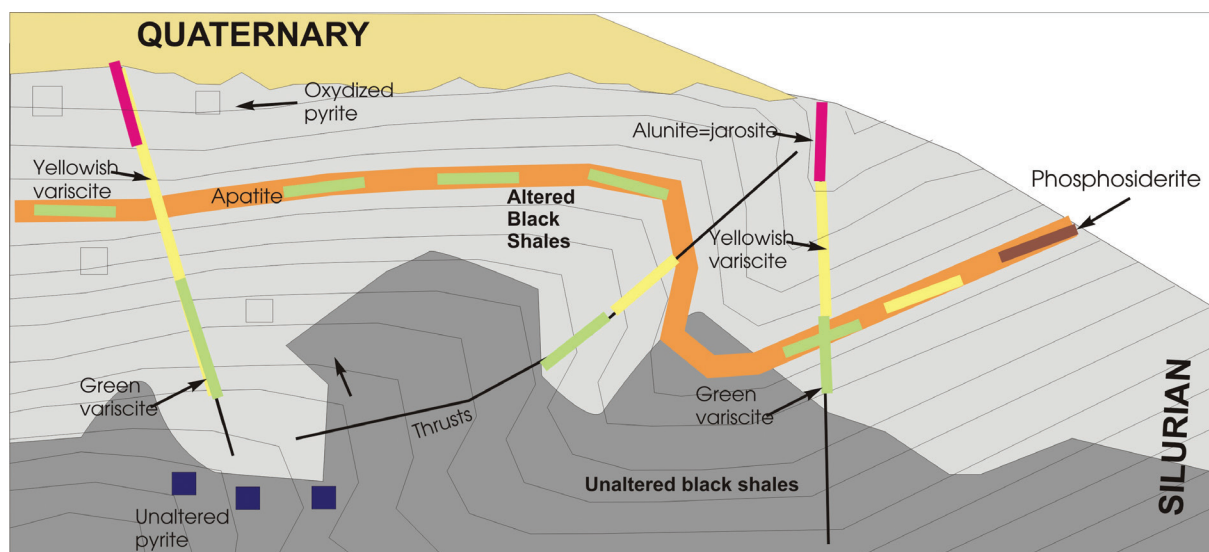


Fig. 2: Distribution of the different types of phosphate mineralization in the Gavà deposit. Note the changes in the color of variscite in depth. Drawing is not to scale.

The Neolithic mines exploited the phosphate deposits of types a) and b) by means of a complex system of galleries (Camprubí *et al.*, 2003).

As indicated above, the color of variscite changes in depth because of changes in its chemical composition: the uppermost domains, with independence of the shape of the deposit, contain Fe-rich members of the variscite-strengite series or phosphosiderite, and an increase of Al in depth which produces finally variscite and the change of color from greenish yellow to green. The change in the color is noteworthy, since the variscite with better green color is found in the deepest places, close to the contact with the unreplaced black shales.

Therefore, the origin of the variscite is related with supergene processes during the Quaternary. As indicated by Ar/Ar dating of alunite associated with the secondary phosphates, the age of the mineralization is Quaternary. In absence of hydrothermal activity in this period, the caolinitic-alunitic alteration of the black shales can be produced by the oxidation of the pyrite contained in the black shales. The resulting sulphuric acid was able to leach the shales and the primary phosphates contained in them, thus removing the phosphoric acid, aluminum and iron necessary for the precipitation of the members of the variscite-strengite series (Camprubí *et al.*, 2003). Similar process, when produced in the carbonatic units of the transit Silurian-Devonian, could produce the Fe-Ca-rich oxide and phosphate deposits (Costa *et al.*, 1993).

3. Comparison of colorimetry and Raman spectra between different deposits

Variscite may have a wide spectrum of colours depending on the locality of provenance. The results for the colorimetry analyses for variscite from different places worldwide are found in table I. The color diversity found in the Gavà deposit falls in the range in other localities. Therefore, the color of variscite in Gavà depends on the depth of formation of the variscite, and this problem can possibly be found also in other deposits. Hence, the color alone is not a precise tool to discriminate variscite from different provenances.

Locality	Color	Crystallinity	L	a	b	E
Gavà, Catalonia	greenish yellow	cryptocrystalline	-23,9	-0,9	26,5	32,6
Gavà, Catalonia	brownish yellow	cryptocrystalline	-31,0	0,2	24,3	35,0
Gavà, Catalonia	greenish yellow	cryptocrystalline	-13,3	-4,6	21,8	24,3
Gavà, Catalonia	greenish yellow	cryptocrystalline	-23,5	0,3	20,2	27,1
Gavà, Catalonia	greenish yellow	cryptocrystalline	-15,8	-0,2	24,3	26,8
Gavà, Catalonia	greenish yellow	cryptocrystalline	-10,9	-4,6	19,3	21,2
Gavà, Catalonia	greenish yellow	cryptocrystalline	-5,8	-12,2	2,6	9,9
Gavà, Catalonia	greenish yellow	cryptocrystalline	-14,4	-7,3	17,5	21,6
Gavà, Catalonia	greenish yellow	cryptocrystalline	-12,9	-6,4	16,7	20,1

Gavà, Catalonia	greenish yellow	cryptocrystalline	-33,3	-2,1	24,4	36,8
Gavà, Catalonia	pale green	cryptocrystalline	-7,1	-13,1	2,2	10,7
Gavà, Catalonia	pale green	cryptocrystalline	-12,5	-5,6	16,9	19,9
Gavà, Catalonia	pale green	cryptocrystalline	-22,0	-16,4	4,9	21,8
Gavà, Catalonia	pale green	cryptocrystalline	-9,6	-15,2	3,2	13,6
Gavà, Catalonia	pale green	cryptocrystalline	-9,0	-10,7	11,3	16,1
Gavà, Catalonia	pale green	cryptocrystalline	-20,1	-7,3	19,0	25,6
Gavà, Catalonia	pale green	cryptocrystalline	-11,4	-10,5	13,4	18,4
Gavà, Catalonia	pale green	cryptocrystalline	-18,4	-12,6	14,2	23,0
Gavà, Catalonia	pale green	cryptocrystalline	-9,2	-11,8	8,9	14,9
Gavà, Catalonia	pale green	cryptocrystalline	-3,2	-8,3	4,0	7,7
Gavà, Catalonia	green	cryptocrystalline	-35,8	-16,9	6,8	33,0
Gavà, Catalonia	green	cryptocrystalline	-31,8	-17,6	1,5	28,3
Gavà, Catalonia	green	cryptocrystalline	-24,4	-24,3	3,7	28,1
Sta. Coloma (Catalonia)	greenish yellow	cryptocrystalline	-28,8	-2,1	22,1	32,2
Sta. Coloma (Catalonia)	greenish yellow	cryptocrystalline	-38,3	-0,6	20,1	37,4
Pineda (Catalonia)	pale green	cryptocrystalline	-15,0	-4,2	8,3	13,7
Montcada (Catalonia)	pale green	cryptocrystalline	-23,4	-7,9	12,5	23,0
Montcada (Catalonia)	pale green	cryptocrystalline	-21,6	-11,9	10,3	22,0
Montcada (Catalonia)	pale green	cryptocrystalline	-12,0	-9,2	5,0	11,8
Montcada (Catalonia)	pale green	cryptocrystalline	-34,2	-11,6	11,3	31,5
Mato Grosso-Brazil	green	fanerocrystalline	-54,4	-10,4	10,1	48,1
Dug Hill, Arkansas, USA	green	microcrystalline	-49,4	-17,0	15,2	47,6
Dug Hill, Arkansas, USA	green	microcrystalline	-27,5	-19,5	14,3	31,9
Palazuelo , Zamora, Spain	green	cryptocrystalline	-34,3	-21,4	9,9	35,3
Palazuelo , Zamora, Spain	green	cryptocrystalline	-50,4	-14,9	5,9	44,4
Lucin, USA	green	cryptocrystalline	-22,7	-21,7	7,4	26,8
Figuerola (Catalonia)	green	cryptocrystalline	-30,0	-16,1	9,1	29,0

Table I: Color parameters for variscite samples from several localities.

Raman spectra were obtained from different localities and were compared with the spectra available in the RRUFF database. Samples with different crystallinity degrees and different colors were tested. The low frequency part of the spectra provides meaningful differences when comparing variscite samples from Gavà and samples from other deposits, in particular, some from Palazuelo de las Cuevas. For instance, samples from Palazuelo de las Cuevas have a well fit band at 400 cm^{-1} which is not so in the Gavà spectra (fig. 3).

The high frequencies part of the spectrums allow to observe noticeable changes in the behavior of the bands; these differences may be due to differences in crystallinity of the samples, since fanerocrystalline

samples (those generally reported in the bibliography) show sharp peaks, whereas cryptocrystalline samples have a broad band in similar positions or yielded a high background (fig. 4).

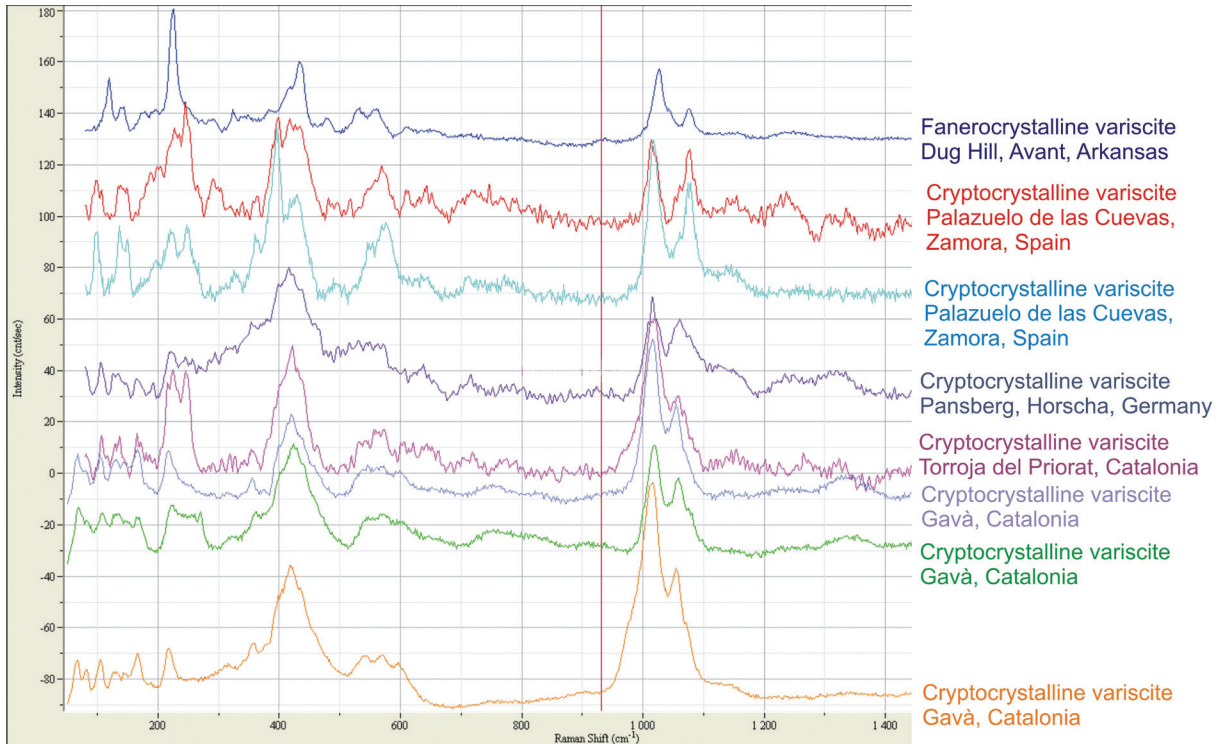


Fig. 3: Comparison of the low frequency domain of the Raman spectra of different samples from several localities. Note some differences in the position of the main bands.

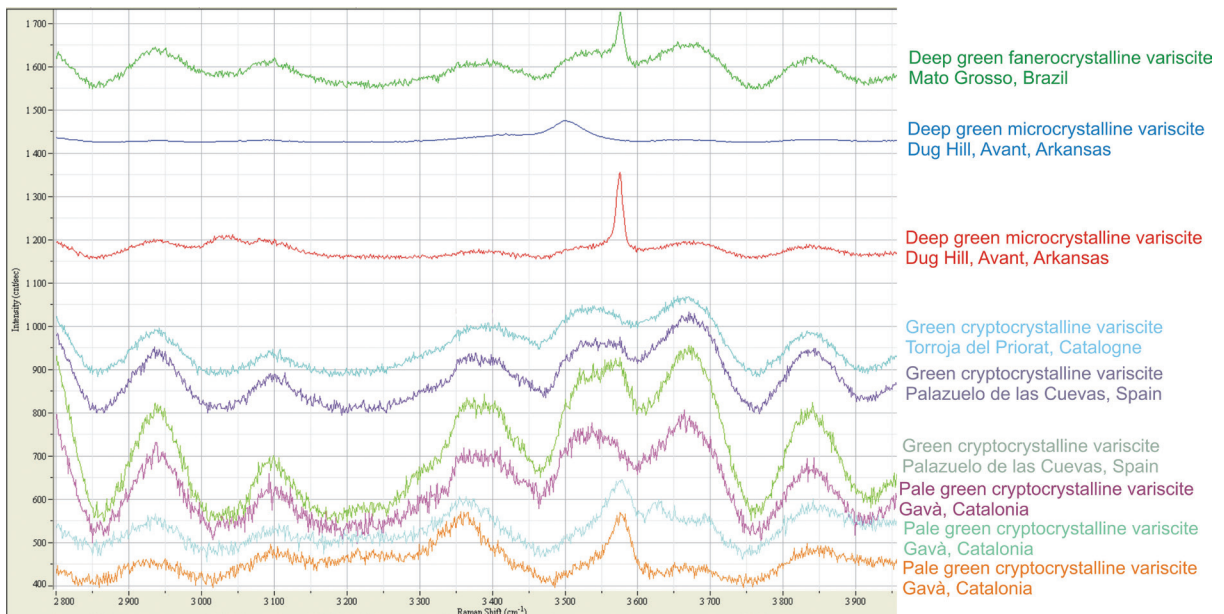


Fig. 4: Comparison of the high frequency domain of the Raman spectra of different samples from several localities. Note some differences. Unclear meaning of the H₂O band near 3575 cm⁻¹.

4. Comparison of colorimetry, microprobe data and Raman spectra between variscite from different levels in the Gavà mines

As indicated above, members of the variscite-strengite series exhibit color changes when deepening in the Gavà deposit. Microprobe analyses reveals that changes in color are partly related to changes in the ratio Al/(Fe+Al), which increases with depth. Therefore, shallow exposures have brownish or yellowish strengite (Al-poor), which becomes enriched in Al in depth and acquires a pale yellow hue. Samples from intermediate and deep exposures are enriched in Al and chemically close to the variscite end member (fig. 5). All these samples have different hues of green. However, those from intermediate exposures are pale green and those from the deepest ones are deep green. It can then be postulated that the chemical composition within the Al-Fe range is not the only parameter that controls changes in color. Microprobe analyses reveal that other possible chromophore elements such as V and Cr occur below the detection limits, and the deep green color can be probably a result of the simultaneous occurrence of Fe²⁺ and Fe³⁺ in the variscite structure, perhaps as a consequence of the variscite growth in a more reducing environment near the oxidation front.

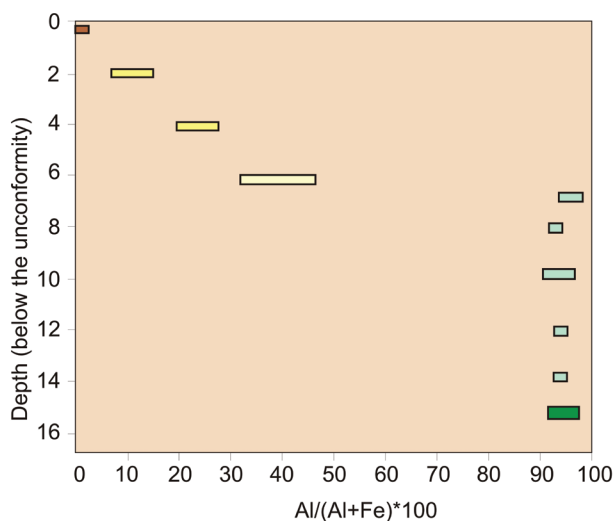


Fig. 5: Variations color and composition of the members of the strengite-variscite series in relation with the depth of formation at the Gavà deposit.

Comparison of the Raman spectra from variscite of different color sampled at different depths reveals significant differences (fig. 6). All these samples are cryptocrystalline and differences in the Raman spectra cannot be attributed to changes in the grain orientation. The most significant element is that a band near 980 cm⁻¹ occurs in the yellow variscite, which corresponds to a spectrum close to strengite. Pale green samples of intermediate and Al-rich compositions in the strengite-variscite series have a band near 1075 cm⁻¹ which is not found neither in the Fe-rich varieties nor in the green variscite. Green variscite samples from the deepest levels lack 980 cm⁻¹ nor the and 1075 cm⁻¹ bands.

5. Discussion

Many authors used Raman spectroscopy to characterize phosphates of the variscite group. However, all of them used as mineral standards fanerocrystalline samples, produced in most cases by hydrothermal processes or subject to strong recrystallization (*i.e.*, reddish ferroan variscite from Iron Monarch mine, Australia, and green variscite from Lavers Hill, Australia; Frost *et al.*, 2004). The Raman spectra of such standards material do not fit well with the cryptocrystalline or poorly crystalline samples typically found in the archaeological sites, which were produced under supergene conditions. The color of members within the variscite-strengite series strongly changes in depth along a few tens of meters. Green variscite has been attributed to the presence at low levels of octahedral Cr³⁺ (Calas *et al.*, 2005). It should be noted that in spite of the indication by these authors that Cr is in the range of %, the tables provided in this paper indicate values below %. In fact, Cr and V are below the detection limit of the microprobe in the Gavà samples. Moreover, the Gavà samples are among those having the lowest tenors of Cr and V found in the literature, ranging between 0 and 500 ppm (Querré *et al.*, 2008). In any case, it is important to note that the Gavà samples with similar Al/(Al+Fe) ratios may have different color. Therefore, it is likely that low Cr contents could be enough to provide critical changes in color, or that there is another factor that can influence the color in variscite.

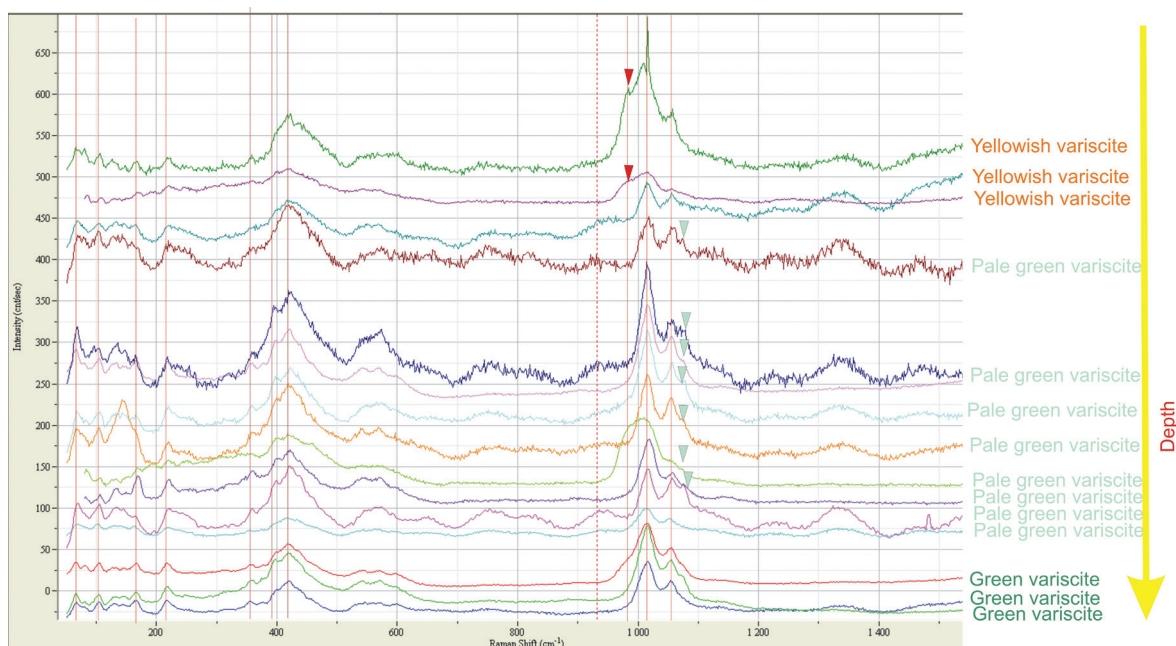


Fig. 6: Variation of the position of Raman bands in different variscite samples from the Gavà deposit in relation to the color changes alongside depth.

The irregular distribution of color and changes in the major elements in a single deposit is also a major problem to establish a regular methodology for the determination of variscite provenances. Major and trace element contents in variscite have been used for a long time to compare chemical data of variscite from different sources and obtain provenance data (*i.e.*, Fernández Turiel *et al.*; 1995, Querré *et al.*, 2008). These chemical analyses are destructive or non-routine techniques. As demonstrated in the current contribution, there are also strong uncertainties about the homogeneity in the distribution of the elements (major and, trace) in a given deposit. Similar problems have been found in other variscite deposits (*i.e.*, Linares, Odriozola, 2011; Odriozola, 2015), and poses a question about the real cause for the green color of variscite.

Alternatively to trace elements, P/Al atomic ratios have been used as a discriminative tool to determine variscite provenance (Odriozola *et al.*, 2013). However, in Gavà these values also show broad variations, between 0,8 and 1,2. The calculation of the structural formulas suggests that deficiencies in the P position could be compensated with the entrance of Si. X-ray diffraction does not provide evidence for the occurrence of mixtures of variscite with silicates, and some high Si contents (up to 0,2 apfu) could be explained by P substitution by Si in the variscite structure. Moreover, the highest Si values are found in the green variscites. However, the mechanism to achieve the charge balances remains obscure.

Hence, the changes in variscite color from yellowish to pale green alongside depth in the Gavà deposits are the result of high Fe contents in variscite-strengite **at the top and lower values in depth**. This can be explained by different elements mobility during the weathering processes and by the existence of redox fronts. However, the change in color from pale green to deep green is independent of the Fe proportions and its relation to the trace elements is not clear.

In any case, the Raman spectra provide noticeable differences among the different variscite samples representative of different depths of formation.

Conclusions

The use of the variscite color and chemistry are parameters that can be helpful in the studies of variscite provenance. However, color spectrophotometry and chemical characteristics of variscite must be used in parallel to other techniques. These properties may strongly change between different domains of

a single deposit, probably in relation to the changes of the oxidation state of Fe alongside depth and the occurrence of chemical fronts. Alternatively, a combination of the color parameters and the Raman spectra, as non-destructive techniques, can be applied successfully in the identification of the depth of extraction of variscite samples in a given deposit. Hence, it is important to enlarge the Raman databases with representative data of cryptocrystalline phosphates from archaeological and geological sites.

Also, the existence of slight differences in the Raman spectra from different localities suggests that Raman spectra can be used in some cases to discriminate the provenance of variscite samples if a database of variscite spectra from the archaeological sites is available.

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