

Vesuvianite from the metamorphic aureole of the Panticosa Pluton (Huesca, Spain)

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INTRODUCTION

Devonian marbles within the internal aureole of the Panticosa Pluton contain good examples of vesuvianite that were overlooked. The pluton emplacement provoked recrystallization of the regional low-grade organic matter-bearing limestones and the formation of skarnoids at the expenses of interbedded siliclastic layers. The latter contain large crystal of vesuvianite. Other minerals in addition to vesuvianite are clinopyroxene, wollastonite, and graphite, among others. Graphite is abundant in both marbles and skarnoids.

The subject of this work is the mineralogical and chemical description of vesuvianite, i.e., the more significant mineral of the skarnoid layers. Relevant variations in color, optical and textural features and mineral assemblages are confronted with EPMA compositional data.

GEOLOGICAL SETTING

The marble spot referred to here is located within the metamorphic aureole at the southern contact of the Panticosa Pluton on the road from the Panticosa Spa to the homonymous town (Fig. 1). The latter pluton is part of a complex formed by several granitic plutons between Caurel (France) and Panticosa (Spain) in the Variscan basement of the Pyrenees in the Axial Zone (Santana, 2002). The more recent radiometric age of the complex (using the U-Pb method), yielded ca. 301 My (Ternet et al., 2004). Host rocks to the pluton belong to the regional low-grade Larrue Black Limestones and to the detrital series Facies Sia. Both series are middle Devonian (Bresson, 1903).

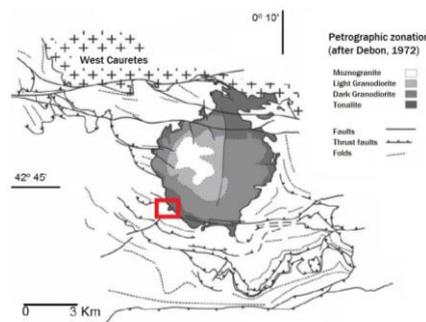
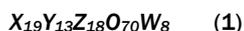


fig 1. Panticosa pluton geologic map, where the red square indicates the study area. Modified from Santana (2002).

VESUVIANITE

Vesuvianite or idocrase is a rare rock-forming or accessory silicate mineral mainly found in skarns, rodingites and altered alkali syenites. The vesuvianite crystalline structure was determined by Warren and Modell (1931), who found an arrangement similar to the structure of grossular structure, but including additional atoms on the fourfold axes. This resulted in a lower symmetry, which corresponds to space group P4/nnc. However, there still are some uncertainties related to the actual symmetry and complexity of the crystalline structure. Several crystal-chemical formulae have been proposed. The huge range of possible cationic substitutions generated the major difficulty to adequate a general formula for this mineral.

In order to generate a structural formula, the cations are assigned to three different coordination groups according to their charge and atomic ratio, following the schematic formula (1):

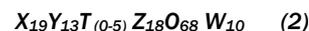


The Z sites are in tetrahedral coordination and are occupied by Si⁴⁺, with some minor substitutions by Al⁴⁺. The X locations show [8]- or [9]- fold

coordination and are mainly occupied by Ca²⁺, although possible substitutions by Na⁺, La³⁺ (REE), Pb²⁺, Bi³⁺ y Th⁴⁺ have been described (Groat et al., 1992). For the Y positions, the most relevant cation is Al³⁺, with some important amounts of others elements as Mg²⁺, Fe²⁺, Fe³⁺, sometimes Ti⁴⁺, and less frequently other metallic elements as Cr²⁺, Mn²⁺, Cu²⁺ or Zn²⁺.

The refined structure of the vesuvianite without B shows the presence of 78 anions (a.p.f.u), where 68 are unmistakably O²⁻, based on the joins valences (Groat et al., 1992). The W corresponds to O²⁻, (OH)⁻ or F⁻. Accordingly, the ionic charge range from 146- to 156-, depending on the number of OH⁻, from ten to zero, respectively.

It is relevant to point out that vesuvianite may contain a variable amount of B in the structure, thus producing a significant variation in the general formula (2):



Where the boron positions correspond to the T, from zero to five.

As mentioned above, vesuvianite is a mineral with a wide range of compositional variations, thus allowing the existence of crystals with differences in physical properties like color and optical behavior based on their chemistry, even if the mineral structure and symmetry are preserved.

Materials and Methods

X-ray diffraction (XRD) and optical microscopy was used to characterize the mineral assemblage in each sample. The textural relationships were established through a detailed petrographic study. The analytical methods used for the chemical

palabras clave: Vesubiana, Idocrasa, Panticosa, Química mineral.

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characterization were scanning electron microscopy (SEM) and electron microprobe analyses (EMPA). Due to the limitations of these techniques, it was not possible to measure the amount of structural water and light ions like B. All the iron measured was assumed as Fe²⁺, the sulfur as SO₃, and the H₂O content has been calculated according to the balanced charges for 78 a.p.f.u. anions.

The first proposed formula was calculated based on 78 oxygen atoms (Coda et al., 1970; Rucklidge et al., 1975). This is a preliminary useful method, but since the vesuvianite structural formula can contain F, Cl, and OH⁻ as additional anions substituting for O²⁻, an alternative properly formulation is based on the reduction to 50 cations, excluding the B (Hoisch, 1985). In the case of Panticosa, both methods have been proved and the resulting formulae show an excess on the ionic charges valence and of Ca²⁺ in the X cation positions, which cannot be fit in another place due to its large size. For this reason, the used method has been a normalization to ΣX (Ca²⁺) = 19 cation p.f.u. (Groat et al., 1992).

MINERAL PARAGENESIS

Vesuvianite dealt with here is found in two mineral paragenesis into the restricted area occupied by the aureole of the Panticosa pluton. In both cases the crystals morphology, size and setting are similar, i.e., isolated idiomorphic prisms 1 to 4 cm long with a perceptible zoning.

The most common paragenesis (MP1) consists of brown vesuvianite, diopside,

prehnite, calcite, wollastonite, graphite and minor amounts of quartz and pyrite (Fig. 2).



fig 2. Skarnoid sample with paragenesis MP1, with graphite patches around brown idiomorphic vesuvianite crystals.

The second paragenesis (MP2) is formed mainly by yellow to green vesuvianite and calcite (Fig. 3), together with fragmented clinopyroxene and prehnite crystals cemented by recrystallized calcite. It is remarkable the absence of graphite and the presence of pyrite crystals in this assemblage.



fig 3. Sample with Paragenesis MP2. Blackish marble (without graphite) in the upper half, and calcite veins and yellow vesuvianite prismatic crystals in the lower part.

Vesuvianite skarnoids formed at the expense of strongly folded competent beds within the Devonian marbles. Folding was in part older than the pluton

emplacement but flattening probably reactivated during intrusion provoking some deformation of the vesuvianite crystals. These competent beds can be further correlated with fine grained sandstones interbedded with marbles that outcrop on the same road outside the metamorphic aureole.

Mineral Chemistry

A comparison between the two different types of vesuvianite found inside the contact aureole has been performed. SEM and EPMA analyses have allowed determine the chemical differences in crystals with distinct colors.

The brown vesuvianite crystals show higher Fe contents (Fe-vesuvianite henceforth), however the green to yellow vesuvianite crystals contain lesser Fe and higher amounts of Mg (Mg-vesuvianite) Al, F and Cl. A relevant point is that the same chemical variation trend is shown by clinopyroxene from each paragenesis. Cpx from PM1 (Fe-vesuvianite) and PM2 (Mg-vesuvianite) show higher iron and magnesium contents, respectively.

Selected analyses from both types of vesuvianite are shown in Table 1. Briefly, the Fe-vesuvianite has a large variation range among the different measured crystals, being most remarkable in the following oxides: FeO (2.13-5.53 wt. %), MgO (1.15-2.57 wt. %), TiO₂ (0.14-2.21 wt. %), SO₃ (0.02-0.17 wt. %) y Cl (0.15-0.28 wt. %). In contrast, Mg-vesuvianite has a lower range of chemical variation with a lesser FeO content (0.41-0.67 wt. %) and higher MgO (2.59-2.89 wt. %), SO₃ (0.37-0.67 wt. %) and Cl (0.25-0.49 wt. %) values, variations in TiO₂ (0.07-2.12 wt. %) and F (1.31-1.89 wt. %) also remarkable.

	Fe-Vesuvianite* (MP1)	Mg-Vesuvianite** (MP2)
SiO ₂	36.2	36.17
Al ₂ O ₃	16.59	18.33
FeO	2.44	0.58
MnO	0	0.11
MgO	2.57	2.78
CaO	36.78	36.83
Na ₂ O	0.04	0.02
K ₂ O	0.01	0.01
TiO ₂	1.72	1.07
NiO	0.02	0
Cr ₂ O ₃	0.03	0.01
SO ₃	0.08	0.6
F	1.62	1.56
Cl	0.18	0.43
○≠ F,Cl	0.72	0.76
Total	97.55	97.73

*Ca_{19.00}(Al_{1.88}Mg_{1.88}Fe_{0.96}Ti_{0.62})Al_{0.55}Si_{17.45}O₆₈(OH)_{7.39}F_{2.47}Cl_{0.14}
 **Ca_{19.00}(Al_{1.92}Mg_{2.00}Fe_{0.23}Ti_{0.39})Al_{0.58}Si_{17.42}O₆₈(OH)_{7.28}F_{2.37}Cl_{0.35}

Table 1. Representative analyses and mineral formulae calculated for the both types of vesuvianite, based on 19X cations (without S).

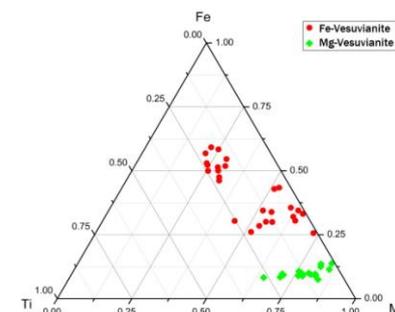


fig 4. Triangular plot with both vesuvianite populations, for the Fe-Mg-Ti elements (a.p.f.u).

Figure 4 shows a triangular plot of the Fe, Ti and Mg contents in both crystal populations, with distinguishable

patterns lined up depending on their Ti values.

Crystal Zonation

Zoning of vesuvianite is recognized on the naked eye and under the microscope. EMPA analyses were performed from core to rim to search for relations between zoning and chemical composition. Core to rim chemical profiles are shown in Fig. 5. In both types of vesuvianite zoning resulted from changes in the cations which occupy the Y positions, mainly from substitutions of Ti⁴⁺ relative to Al³⁺, Fe²⁺, Mg²⁺. Ti decreases from core to rim, i.e., during crystal growth. It is interesting to notice that while Mg-vesuvianite shows rather regular Mg/Fe ratios, Fe-vesuvianite displays some significant variations, the more remarkable being the increase of the Mg/Fe ratio at the rim, and the decrease in S content from core to rim (Fig. 5).

FORMATION CONDITIONS

Mg-vesuvianite stability field is constrained by the reaction (Valley et al., 1985): vesuvianite (Mg) + CO₂ ↔ silicates + calcite + H₂O. The latter implies a water-rich fluid (XH₂O>0.8) and correspondingly low CO₂ content (XC₂O<0.2) at P=1-4 kbar and T=600°C, i.e., values close to those estimated for the metamorphic aureole formation

(Debon, 1975). The different mineral assemblages and the variety of chemical composition of vesuvianites probably are a reflection of the sedimentary protolith. Moreover other causes such as local fO₂ differences constrained by the presence/absence of graphite probably also played a role.

CONCLUSIONS

The compositional differences in the host rock (detrital intercalations inside limestones) probably play an important role to explain the chemical variations in both mineral paragenesis. The mineralogical study has shown the main chemical differences of the vesuvianites found into the metamorphic aureole of the Panticosa Pluton. The color variations are associated to the Fe-Mg content, and the optical zonation might be related changes in the Ti content.

The precise role of sulfur within the vesuvianite structure remains uncertain, as well as the potential presence of Fe³⁺ and boron in the Panticosa vesuvianite.

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Fe-Vesuvianite

Mg-Vesuvianite

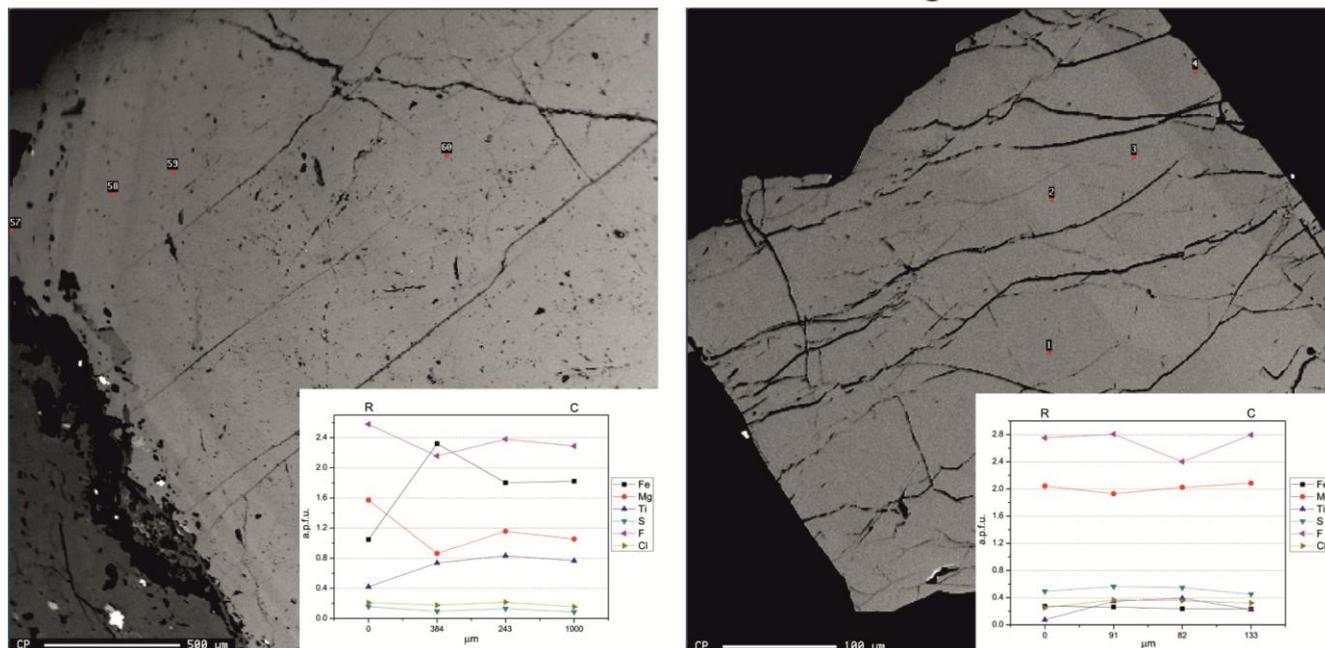


fig 5. BSI images of two vesuvianite crystals with spots selected for analysis. Chemical profiles are shown below in a.p.f.u. Fe-vesuvianite (left); Mg-vesuvianite right. Rim (R), core (C).