

Article

Cortesognoite, $\text{CaV}_2\text{Si}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$, a New Mineral from the Molinello Manganese Mine, Graveglia Valley, Italy

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Abstract: Cortesognoite (IMA 2014-029), $\text{CaV}_2\text{Si}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$, is a new vanadium silicate mineral that occurs within V-bearing lawsonite in association with vanadiocarpopholite, chalcocite, quartz, minor poppiite, roscoelite, vanadomalayaite and volborthite in a silicified wood hosted in Mn-ore-bearing metacherts from the Molinello manganese mine in the Graveglia Valley, Northern Apennines, Liguria, Italy. The mean chemical composition of type cortesognoite by electron probe microanalysis is (wt%) SiO_2 34.33, V_2O_5 31.38, CaO 15.80, Al_2O_3 7.69, MnO 0.14, FeO 0.09, MgO 0.06, TiO_2 0.02 and H_2O 10.29, totaling 99.80, giving rise to an empirical formula of $(\text{Ca}_{0.99}\text{Mn}_{0.01})(\text{V}_{1.47}\text{Al}_{0.53}\text{Mg}_{0.01})\text{Si}_{2.00}\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$. The end-member formula is $\text{CaV}_2\text{Si}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$. Cortesognoite has the *Cmcm* lawsonite structure with $a = 5.85(1) \text{ \AA}$, $b = 8.79(1) \text{ \AA}$, $c = 13.13(1) \text{ \AA}$, $V = 675(1) \text{ \AA}^3$ and $Z = 4$ as revealed by electron back-scatter diffraction. The calculated density using the measured composition is 3.44 g/cm^3 . Cortesognoite is a secondary alteration phase, formed with V-bearing lawsonite by multi-stage hydrothermal processes that occurred in the silicified fossil wood. The mineral name is in honor of Luciano Cortesogno, professor of petrography at University of Genova, Italy.

Keywords: cortesognoite; $\text{CaV}_2\text{Si}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$; new mineral; lawsonite–ilvaite group; the Molinello manganese mine; Graveglia Valley; Italy



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1. Introduction

During a nanomineralogy investigation of specimens from the Molinello manganese mine in the Graveglia Valley, Northern Apennines, Liguria, Italy, a new vanadium silicate mineral, ideally $\text{CaV}_2\text{Si}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$ with the lawsonite structure, named “cortesognoite” was identified within V-bearing lawsonite (Figures 1 and 2). Brownish V-bearing lawsonite aggregates fill mm-thick veins and patches within silicified wood hosted in red Jurassic metacherts.

Synthetic $\text{CaV}_2\text{Si}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$ has not been reported. The new mineral and its name have been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA 2014-029) [1]. The name cortesognoite is in honor of Luciano Cortesogno (1941–2005), an Italian petrographer, for his contributions to research on Ligurian ophiolites and the silicified-woods-associated Mn ore deposits of the Graveglia Valley, Eastern Liguria, Italy. The type specimen is deposited at Dipartimento di Scienze della Terra, Ambiente e Vita (DISTAV) of Università di Genova, Genova, Italy, registration number MO482.

An outstanding variety of rare and new minerals come from the ore deposits hosted in ophiolitic rocks of the Ligurian Alps and Apennines, both from high-pressure and low-grade metamorphic occurrences e.g., [2–7]. Among the seventeen mineral species having their type-locality in the manganese ores of Graveglia Valley, nearly 80 percent of them display vanadium as a major constituent in the chemical formula. On one hand, the primary manganese ore hosted in metacherts was previously investigated and well

characterized [2,8,9]; on the other hand, much less is known on the origin of Mn-As-V mineral associations in secondary hydrothermal veins, despite the fact they often display unusual or unique crystal-chemical features [10,11].

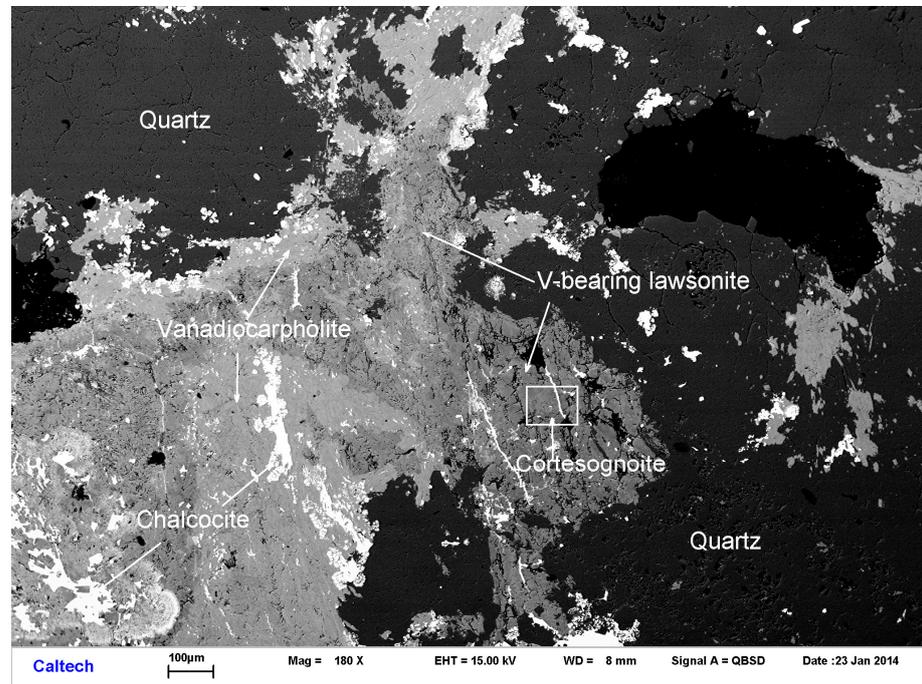


Figure 1. Back-scatter electron (BSE) image showing cortesognoite, V-bearing lawsonite, vanadocarpopholite, chalcocite and quartz in thin-section MO482. The location of cortesognoite is enclosed by the rectangle.

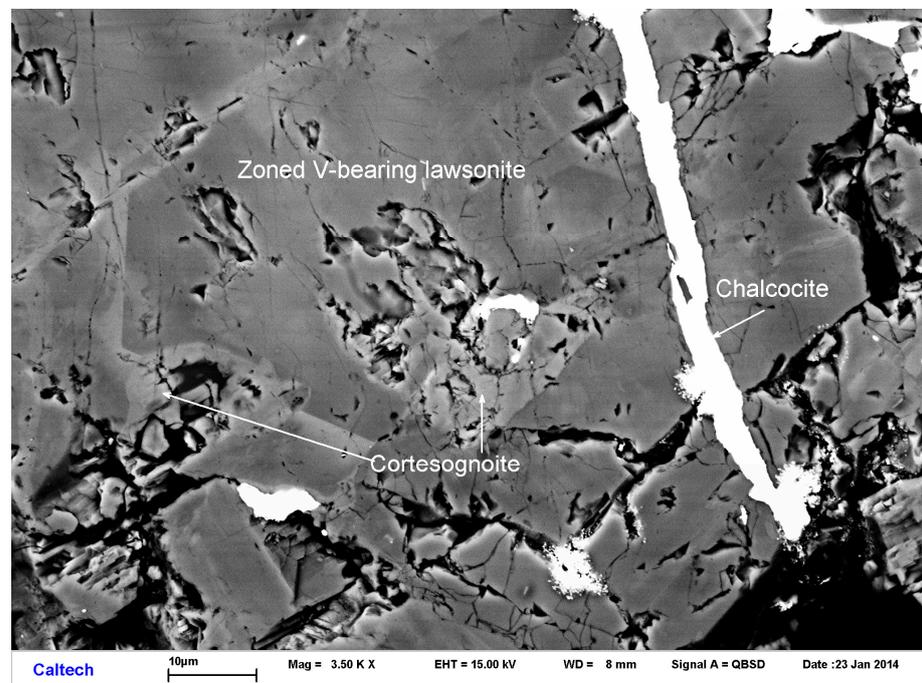


Figure 2. Enlarged BSE image showing type cortesognoite in zoned V-bearing lawsonite.

We describe here the first natural occurrence of cortesognoite, as a new mineral, and discuss its origin and significance for hydrothermal alteration processes that affected the silicified wood occurring at the Molinello mine.

2. Methods

Electron probe microanalysis (EPMA) with X-ray wavelength-dispersive spectroscopy (WDS) and scanning electron microscopy (SEM) with X-ray energy-dispersive spectroscopy (EDS) and electron back-scatter diffraction (EBSD) were used to in situ characterize the composition and structure of cortesognoite. A ZEISS 1550VP Field-Emission SEM with an Oxford X-Max EDS at Caltech was used for high-resolution back-scatter electron (BSE) imaging and fast elemental analysis at 10 and 15 kV. Quantitative elemental microanalysis was carried out using a JEOL 8200 electron microprobe at Caltech (WDS: 15 kV; 10 nA; beam in focused mode) interfaced with the Probe for EPMA program from Probe Software, Inc (Eugene, OR, USA). Analyses were processed with the CITZAF correction procedure [12]. Analytical results are provided in Table 1. No other elements with atomic number greater than 4 were detected by WDS scan at 15 kV and 25 nA.

Table 1. Analytical data for cortesognoite (average of 5 point analyses).

Constituent	wt%	Range	SD	Probe Standard
SiO ₂	34.33	34.05–34.65	0.23	anorthite
V ₂ O ₃	31.38	30.48–32.02	0.59	V ₂ O ₅
CaO	15.80	15.69–15.93	0.10	anorthite
Al ₂ O ₃	7.69	7.11–8.50	0.51	anorthite
MnO	0.14	0.09–0.21	0.05	Mn ₂ SiO ₄
FeO	0.09	0.06–0.11	0.02	fayalite
MgO	0.06	0.06–0.07	0.00	forsterite
TiO ₂	0.02	0.01–0.05	0.01	TiO ₂
H ₂ O *	10.29			
Total	99.80			

* H₂O concentration was calculated based on ideal (OH)₂·H₂O in the formula.

Conventional X-ray studies could not be carried out because of the small crystal size. Single-crystal EBSD analyses at a sub-micrometer scale were performed using an HKL EBSD system on the ZEISS 1550VP SEM, operated at 20 kV and 6 nA in focused beam mode with a 70° tilted stage and in a variable pressure mode (25 Pa), using the method described in [13,14]. The EBSD system was calibrated using a single-crystal silicon standard. The structure was verified and cell constants were obtained by matching the experimental EBSD patterns with structures of lawsonite e.g., [15].

3. Results

3.1. Occurrence and Physical Properties

Cortesognoite occurs within V-bearing lawsonite in a hydrothermally altered silicified wood fully enclosed within metacherts. Associated minerals are vanadiocarpolite, chalcocite, quartz, minor poppiite, roscoelite, vanadomalayaite and volborthite (Figure 1). Polyphase mineral assemblages occur in the Mn ore deposits within metacherts of the Northern Apennine ophiolitic units (“Diaspri di Monte Alpe” formation). The ore bodies of the Graveglia Valley, mainly constituted of braunite + quartz + Mn-silicates (e.g., rhodonite, tinzenite, ganophyllite, bementite) and carbonates (manganoan calcite, rhodochrosite, Ca-rich kutnohorite), underwent prehnite–pumpellyite facies metamorphism ($P = 0.25 \pm 0.05$ GPa and $T = 275 \pm 25$ °C) followed by hydrothermal mobilization along fractures under decreasing thermobaric conditions [9,16]. Circulation of fluids led to further concentration of dispersed elements such as As, V and Te in secondary veins, favoring the formation of rare minerals with peculiar compositions [17–21]. Silicified woods hosted in metacherts, which are quite common in the ophiolitic sequence [22], represent a particularly interesting case as, on some rare occasions, they display complex Cu-Mn-As-V mineral associations formed during different stages of hydrothermal alteration and low-grade metamorphic recrystallization processes.

For the most part, silicified woods are poorly mineralized, but sometimes they are characterized by relevant concentration of Cu-bearing mineral phases, mostly carbonates and vanadates (malachite, volborthite) [23]. In a single outstanding occurrence at the Molinello mine, pervasive mineralization of V-bearing phases occurs in the silicified wood, with vanadium in three different oxidation states (V^{3+} , V^{4+} and V^{5+}). V-bearing oxy-hydroxides, silicates and vanadates are commonly found here within mm-thick fractures and cavities in a *Araucarioid*-type fossil wood about $0.5\text{ m} \times 1\text{ m} \times 0.5\text{ m}$ in size [22].

The mineral occurs as subhedral crystals about $10\text{ }\mu\text{m}$ in size (Figure 2). It is brown and transparent. Luster, streak, hardness, tenacity, cleavage, fracture, density and optical properties are not determined because of the small grain size but may be similar to those of lawsonite. The calculated density is 3.44 g/cm^3 using the empirical formula.

3.2. Chemical Composition

The mean chemical composition of the type cortesognoite (Table 1) gives rise to an empirical formula (based on 10 oxygen atoms per formula) of $(\text{Ca}_{0.99}\text{Mn}_{0.01})(\text{V}_{1.47}\text{Al}_{0.53}\text{Mg}_{0.01})\text{Si}_{2.00}\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$. The general formula is $\text{Ca}(\text{V},\text{Al})_2\text{Si}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$. The end-member formula is $\text{CaV}_2\text{Si}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$, which requires V_2O_3 41.39, SiO_2 33.18, CaO 15.49 and H_2O 9.95, for a total of 100.01 wt%.

A range of chemical variability is observed along the ideal cortesognoite–lawsonite joint due to $\text{Al} \leftrightarrow \text{V}^{3+}$ substitutions in the octahedral sites of the structure (Figure 3). Cortesognoite and V-bearing lawsonite phases are always coexisting in the reducing spots of the silicified fossil woods at the Molinello mine and the latter often displays quite evident chemical zonations (cf. Figures 1 and 2). Although further studies are necessary to understand if a complete solid solution may occur along the $\text{CaV}_2\text{Si}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$ – $\text{CaAl}_2\text{Si}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$ join, it is worth mentioning that wide Al – V^{3+} chemical substitutions have already been reported in the literature for other phases occurring in the same mineral paragenesis as cortesognoite, as in the case of the carpholite–vanadicarpholite series [17] and in some vanadium-rich pumpellyite group minerals [24].

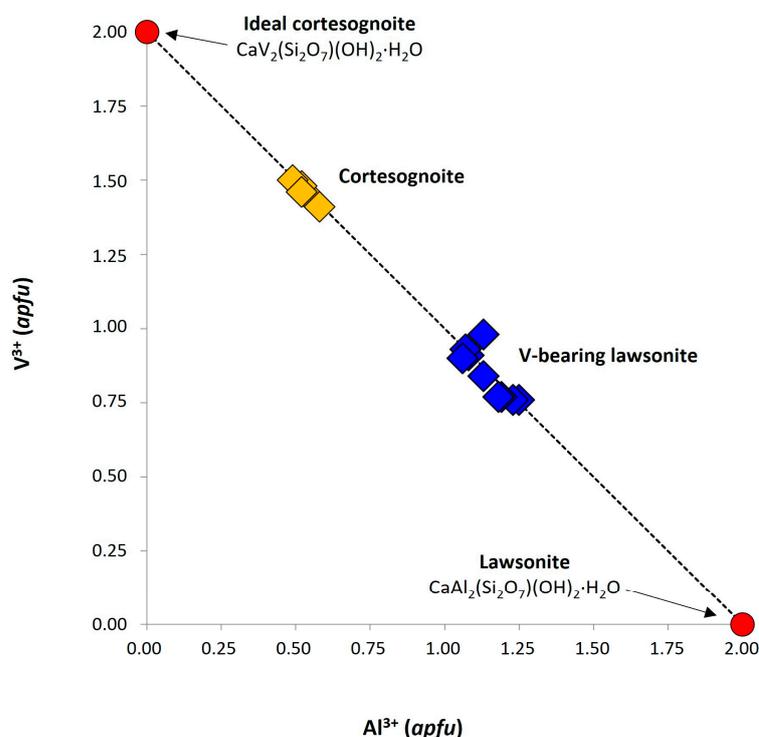


Figure 3. Al vs. V^{3+} diagram (atoms per formula units, *apfu*) showing the observed chemical range of the cortesognoite (orange diamonds)–V-bearing lawsonite (blue diamonds) samples in the silicified fossil wood at the Molinello mine. Ideal end-member compositions are also represented (red circles).

3.3. Crystallography

The EBSD patterns can only be indexed on the *Cmcm* lawsonite structure model and provide the best fit using the lawsonite structure from Libowitzky and Armbruster (1995) (Figure 4), with a mean angular deviation of 0.46° to 0.52° , showing the cell parameters $a = 5.85(1) \text{ \AA}$, $b = 8.79(1) \text{ \AA}$, $c = 13.13(1) \text{ \AA}$, $V = 675(1) \text{ \AA}^3$ and $Z = 4$.

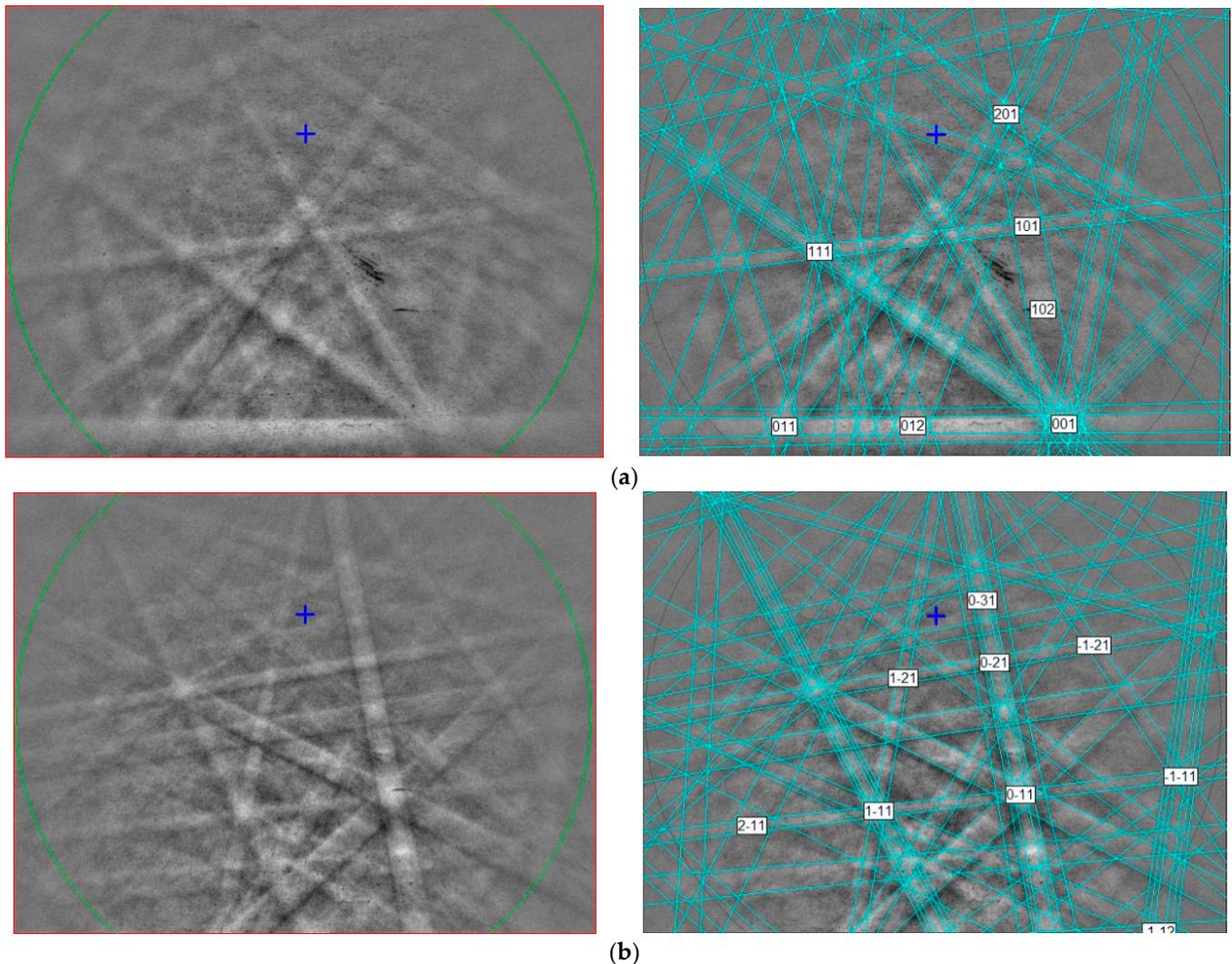


Figure 4. (a) EBSD pattern of one type cortosognoite crystal in Figure 2, indexed with the lawsonite structure; (b) EBSD pattern of a V-bearing lawsonite crystal in Figure 1, indexed with the lawsonite structure. The blue cross is pattern center. The diffraction bands in the green circle were used for indexing.

The structure of cortosognoite is shown in Figure 5, projected down [001]. X-ray powder diffraction data (in \AA for $\text{CuK}\alpha_1$, Bragg–Brentano geometry) are calculated from the unit cell parameters of [15] with the empirical formula using Powder Cell version 2.4. The strongest calculated lines are [d in \AA , intensity, I , scaled to 100 for the most intense peak, (hkl)] [2.630, 100, (024)], [3.652, 95, (022)], [1.549, 95, (244)], [6.565, 89, (002)], [2.722, 78, (114)], [2.672, 72, (202)], [2.435, 56, (220)], [2.128, 54, (223)], [2.620, 51, (130)].

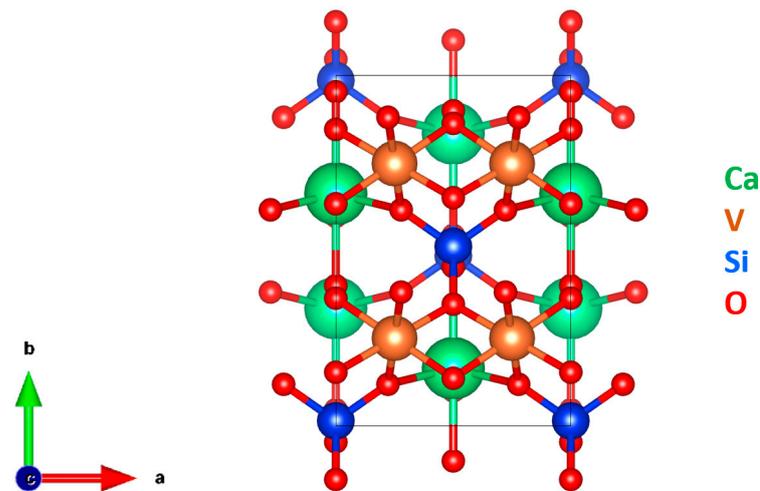


Figure 5. The structure of cortesoignoite, projected down [001].

4. Discussion

Cortesoignoite, $\text{CaV}_2\text{Si}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$, is the V analogue of lawsonite $\text{CaAl}_2\text{Si}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$. It is a new member of the lawsonite–ilvaite group.

Cortesoignoite is a hydrothermal alteration phase, formed in veins and patches with V-bearing lawsonite, vanadiocarpholite and chalcocite in a silicified wood hosted in red Jurassic cherts (Figure 6).



Figure 6. Cortesoignoite, brownish microcrystalline aggregate in hydrothermally altered silicified wood. Field of view: 3 mm. Molinello mine, Graveglia Valley, Northern Apennines, Liguria, Italy.

The geochemical mobility of elements like V, As and Mn in hydrothermal fluids of oceanic or sub-seafloor origin is well documented [25–27], as well as its close relationship to the origin of metalliferous ore deposits in Northern Apennine ophiolites e.g., [8]. In a realistic genetic scenario, the origin of cortesoignoite can be related to that of a complex suite of V-bearing minerals developed in the silicified woods of Val Graveglia by hydrothermal

mobilization and alteration processes. Mineral association in such an environment is exceedingly complex due to the geochemical behavior of vanadium species, which are highly redox-sensitive, display a marked amphoteric nature in the higher valence states and form multivalent aqueous complexes whose concentration in predominance diagrams is strongly dependent upon pH [27–29]. Previous geochemical studies demonstrate that vanadium could be transported by aqueous fluids in a soluble oxidized forms, hence being mobilized in hydrothermal environments mostly as V^{4+} or V^{5+} species [30,31]. Then, under the action of a chemically reducing agent, the oxidized vanadium aqueous complexes, which are strongly redox-sensitive, could be promptly reduced and precipitated in the form of V^{3+} or V^{4+} mineral phases (mostly oxy-hydroxides and silicates). The most likely reducing agent in the mineralization environment could be represented by the degradation and oxidation of the organic matter of the woods [32], which locally created small “reduction spots” that induced the selective concentration and uptake of elements like vanadium and copper in the mineral association of the fossil woods. Clear evidence of such processes is the occurrence of V^{3+} - and V^{4+} -rich minerals like poppiite, roscoelite, vanadiocoropholite, vanadomalayaite, lenoblite [17], duttonite and oxyvanite [33], often directly associated to cortesognoite and mainly concentrated in the core of silicified wood at the Molinello mine. Cortesognoite is actually a ubiquitous phase in the fossil wood, even though it displays the highest V^{3+} contents right within the inner parts of it (cf. Figure 3). The widespread occurrence of Cu sulfides (mostly chalcocite) in the mineral association also suggests that the presence of H_2S in the mineralizing environment could have acted as a further reductant cf. [31].

It seems likely that vanadium concentration processes occurred in the early stages of silicification and diagenesis of the wood since silicic acid, H_4SiO_4 , present in slightly acidic to neutral aqueous solutions along with vanadium solute species, displays a high affinity with the organic matter and promotes permineralization of the fossil wood cf. [34–36]. Silicification processes are then followed by the circulation of hydrothermal fluids under more oxidizing conditions, which probably extended until the latest orogenic stages and determined leaching and mobilization of elements like V, Cu, Mn, Ca, Na and K along fractures within the silicified wood. As a result, a complex suite of alteration minerals developed towards the outer shell of the fossil wood due to fluid–rock interaction at oxidizing and roughly neutral to alkaline conditions. V^{5+} -bearing mineral phases, mostly represented by complex oxides of the crichtonite group (i.e., paseroite and V-rich senaite [37]) and copper vanadates (like tangeite and volborthite [23]), formed during this later alteration stage along with copper oxides (e.g., cuprite), carbonates (malachite) and sulphates (brochantite, langite).

As to the possible source of vanadium in this kind of hydrothermal mineralization, a few considerations can be made. Accumulation of low-valence vanadium in clay minerals and micas has already been reported in a number of diagenetic to hydrothermal environments, such as in the altered uranium–vanadium ore deposits of the Colorado Plateau [38–40]. The fact that silicified woods hosting V-rich mineralization in the Val Graveglia ophiolitic sequence are enclosed within metacherts often rich in detrital components made of chlorite, illite and micas (cf. “Green detrital cherts”, “Varicolored cherts” and “Pelitic cherts” lithofacies in the “Diaspri di Monte Alpe” Formation, according to [41,42]) makes this scenario realistic. The widespread occurrence of roscoelite in the silicified wood could represent further evidence supporting the role of clay minerals as potential sources of vanadium. However, a hydrogenetic or exhalative–hydrothermal contribution (as defined in [43]) is equally plausible. For instance, geochemical data obtained on the “Diaspri di Monte Alpe” metacherts support the evidence that hydrothermal contribution is prominent in the stratigraphically lower part of the sequence, where silicified fossil woods are usually found [22,42]. Finally, it should be stressed that, in the oceanic environment where Ligurian Jurassic ophiolites hosting Mn ores originally form, elements like V may be easily fixed by sorption onto Mn–Fe oxides and hydroxides which constitute the primary ore deposits of Val Graveglia (see [44] and references therein for details on the subject).

Author Contributions: Conceptualization, C.M., C.C. and D.B.; Methodology, C.M.; Formal analysis, C.M.; Investigation, C.M., C.C. and D.B.; Writing—original draft, C.M. and D.B.; Writing—review & editing, C.M., C.C. and D.B.; All authors have read and agreed to the published version of the manuscript.

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