

Possible microbial mediated woodwardite precipitation in a circumneutral drainage (preliminary data)

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Short Note

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ABSTRACT

Along the stream bed of a tributary creek of Fiumara Allaro river (Calabria, Italy), which drains ore-rich terrains exploited for mining purposes in the past century, a light blue-greenish fine-grained precipitate occurs. Multiple analytical techniques, including optical microscopy, scanning electron microscopy (SEM), and Raman spectroscopy were employed to characterize the water and the solid phase. The drainage waters are circumneutral (pH 6.8) and characterised by a dominant Ca-SO₄ composition, while the dissolved metal load is mainly composed of Zn (15.3 mg/L), Mn (3.1 mg/L), and Cu (1 mg/L). The light blue-greenish precipitate is composed of woodwardite, a secondary hydrated copper-aluminum sulphate hydroxide, appearing with two nanostructures: fine tabular platelet crystals 1 to 5 µm in length consisting of clusters of smaller tabular mineral units, tens of nanometres thick and several micrometres in length, together with irregular aggregates of mineral nanospheres 200 nm in size. Both mineral phases commonly encrust organic structures and possibly substitute organic mucilages, likely produced by microbial bacterial communities. Among these, filamentous structures 2 µm to 10 µm wide and hundreds of micrometres long are particularly abundant and may play an active role in the biomineralisation process.

KEYWORDS: Woodwardite, copper, microstructure, biomineral.

INTRODUCTION

Secondary metal(loid)-bearing minerals have recently attracted increasing attention due to the control they exert to metal mobility in near-surface environments and to the direct influence they can have on the environmental fate of potentially

toxic elements, also thank to the mediation of microorganisms (De Giudici et al., 2014; Burton et al., 2021; Schoepfer & Burton 2021; Guerrieri et al., 2025). Among these secondary phases, minerals of the woodwardite group constitute a relevant class. This group belongs to the hydrotalcite supergroup, whose phases are characterised by pulverulent (fine-grained) light blue/greenish amorphous to poorly crystalline, phases (Ardau et al., 2007). One of these is the woodwardite, i.e. a secondary hydrated copper-aluminum sulphate hydroxide mineral that typically forms under near-surface oxidising conditions, related to the alteration of sulphide-bearing lithologies in aluminum-bearing host rocks, where water-rock interaction promotes metal mobilisation and secondary mineral formation (Barrese et al., 2006 and references therein). The idealised chemical formula of woodwardite is commonly expressed as CuAl₂(SO₄)(OH)₁₂·nH₂O, although its composition is variable due to cation substitutions and variable degrees of hydration, a characteristic feature of layered double hydroxides (Mills et al., 2012; Trujillano et al., 2023).

Woodwardite and all the layered double hydroxide minerals, have viewed a rise in the scientific community attention also because of their capacity to retain significant amount of rare earth (REE; Consani et al., 2018), but also to incorporate metal cations and to exchange sulphate and other anions within their layered structures (Miyata et al., 1983; Cavani et al., 1991). One typical substitution occurs with Cu and Zn due to the close similarity between the ionic radii of Cu²⁺ (0.73 Å) and Zn²⁺ (0.74 Å) that promotes the substitution, as Zn²⁺ can easily occupy Cu²⁺ lattice

sites with minimal structural distortion (Pudza et al., 2021). In addition, their layered structure allows efficient incorporation of the ion arsenate through anion exchange, feature that might be crucial in mining-impacted waters, enhancing the immobilisation of this toxic element (Ardau et al., 2013). Although this mineral group has been widely studied, very few works have addressed the possible microbial mediation in the woodwardite precipitation process, an aspect that we have begun to investigate.

GEOLOGICAL FRAMEWORK

The study area is located in the Mt. Granieri-Salincriti area, located along the western sector of Southeastern Calabria. From

a geological standpoint, the area is characterised by the presence of a well-developed high-temperature metamorphic aureole related to intrusive bodies of aplitic and pegmatitic composition, with a thickness ranging between ~ 20 and 50 m in this area. The site is included in a historically significant mining region, largely exploited during the past centuries, which has contributed significantly to the formation of numerous metal-contaminated drainage systems affecting this area. The studied system is represented by a small tributary creek on the right hydrographic side of the Fiumara Allaro.

Along most of the stream course the studied light blue/greenish fine-grained precipitate covers the streambed clasts and plants forming a mineral layer from few millimetres up to 1 cm in thickness (Fig. 1D).

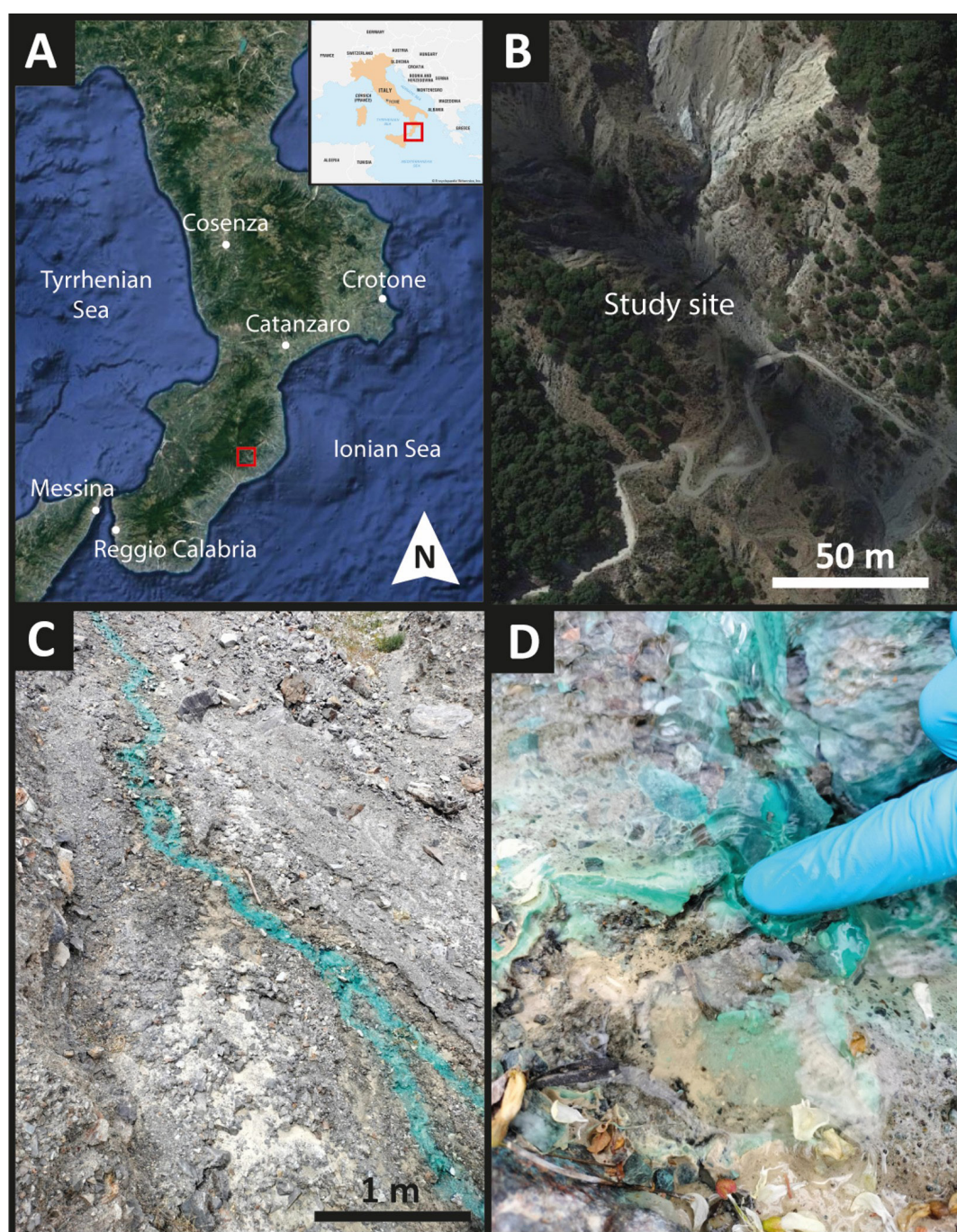


Fig. 1 - A. Location of the study area in Calabria, Southern Italy. Satellite image from Google Earth website. B Satellite image from Google Earth website showing the study area. C. Studied drainage system, where the solid sample was collected. D Field image showing the light blue precipitate.

METHODS

Micromorphological investigations were conducted using both optical and electron microscopy techniques. Observations were carried out with a Zeiss Axioscop-40 optical microscope, and with a ZEISS Crossbeam 350 scanning electron microscope (SEM), operated at accelerating voltages ranging from 5 to 20 kV and with working distances between 6 and 15 mm. Elemental composition of solid sample was determined using an EDAX OCTANE Elite Plus energy-dispersive X-ray spectroscopy (EDS) system coupled to the SEM. These analyses were performed on two untreated aliquots. Mineralogical characterisation was obtained by micro-Raman spectroscopy, conducted on wet and untreated aliquots using a Jasco NRS-5100 spectrometer equipped with a 532 nm laser (0.3 mW power) and a 100× objective. Raman spectra acquisition was intentionally limited to 1200 cm⁻¹ to capture the diagnostic vibrational range of copper sulphates while minimising spectral alterations related to sample hydration. Phase determination was achieved by comparison with reference data from the RRUFF database (R060762). In situ measurements of temperature, pH, oxidation-reduction potential (Eh), and electrical conductivity were collected at several locations along the stream using a waterproof multiparameter probe (HI98194, Hanna Instruments, Romania). A water sample was obtained approximately 1 m downstream of the uppermost weir (Fig. 1). Three filtered (0.45 µm) water aliquots were prepared: (i) one unacidified sample for the determination of major cations and anions by ion chromatography, and (ii) two samples acidified to 1% with suprapure HNO₃ for trace metal analysis. Metal concentrations were quantified using inductively coupled plasma optical emission spectrometry (ICP-OES; ARL Fisons ICP Analyzer 3520 B, Waltham, MA, USA) and inductively coupled plasma mass spectrometry (ICP-MS; Perkin-Elmer Elan DRC-e, USA). Analytical detection limits were calculated as ten times the standard deviation of blank solutions. Method accuracy (<5%) and precision (<5%), for trace elements, were verified using certified reference materials (EnviroMAT Drinking Water, High EP-H-3 and Low EP-L-3). Rhodium served as an internal standard during ICP-MS analyses to correct instrumental drift. Charge balance errors for the water chemistry consistently fell within ±10%.⁷

RESULTS

Water Chemistry

The water analysis collected from the studied stream is resumed in Table 1. The results show an approximately neutral pH value (6.8), and conductivity reaching 1.25 mS/cm. The stream water has a dominant Ca-SO₄ elemental composition, with Zn, Mn, and Cu as the most abundant metals.

Mineral characterisation

Several point-specific micro-Raman measurements were carried out to determine the mineralogy of the fine-grained light blue/greenish precipitate. An example of the Raman spectra obtained from one sample aliquot is presented in Fig. 2. It shows

Table 1 - Studied stream water geochemistry from ICP-OES and ICP-MS analyses.

<i>Water parameters</i>		<i>Minor elements (µg L⁻¹)</i>			
Temperature (°C)	16.5	Mn	3110	As	2
pH	6.8	Cu	1020	Be	1
Cond. (mS/cm)	1.25	NO ₃	900	Cr	1
TDS (mg L ⁻¹)	382	Ni	790	U	0.5
Eh (mV)	284.1	Sr	490	PO ₄	<100
<i>Major elements</i>	<i>mg L⁻¹</i>	Pb	116	Br	<100
		Co	380	NH ₄	<100
		Li	148	Fe	<17
		Cd	70	Se	<3
		Pb	60		
		B	51		
		Ba	21		
		Al	15		
		Rb	13		
		Mo	3		
SO ₄	670				
Ca	120				
Na	89				
Mg	53				
Alk	18				
Cl	16				
Zn	15.3				
K	9.1				

bands at approximately 295, 387, 506, 606, 675, 821, 974, 1055, and 1113 cm⁻¹. Peaks observed at 506, 606, and 974 cm⁻¹ closely align with used reference spectrum of woodwardite, acquired using a 532 nm excitation wavelength and reported in the RRUFF database (R060762).

Microscopical features and composition

The woodwardite deposit occur as subtle fine-grained and loosely consolidated precipitate that coat streambed clasts and river plants. The deposit is generally structureless, although rare millimetre-scale laminations are locally observed (Fig. 1D). The thickness of the deposit is typically a few millimetres and only rarely reaches the centimetre, mainly in sheltered niches. Under optical microscopy, the Mt. Granieri-Salincriti woodwardite is primarily characterised by irregular mineral aggregates with a mean width of ~20 µm (Fig. 3A, B).

Blue aggregates are formed by irregular crystals ranging in size from 1 to 5 µm, which commonly encrust, or are closely associated, with organic material often filamentous (Fig. 3A, B). Such filamentous structures are composed of slightly curved, solid, sometimes segmented tubes (Fig. 2E), whose diameter range from ~2 µm up to 10 µm. Woodwardite is also observed forming thin coatings on plant remains (Fig. 3C and 3D).

At the nanoscale the mineral is constituted by two crystalline structures:

- tabular platelets (tens of nanometres thick and several hundred nanometres long) that are arranged into irregular aggregates, or folded onto themselves, to form sponge-like structures (Fig. 3D).
- 200 nm in diameter nanospheres (Fig. 3D), that are commonly found in irregular aggregates.

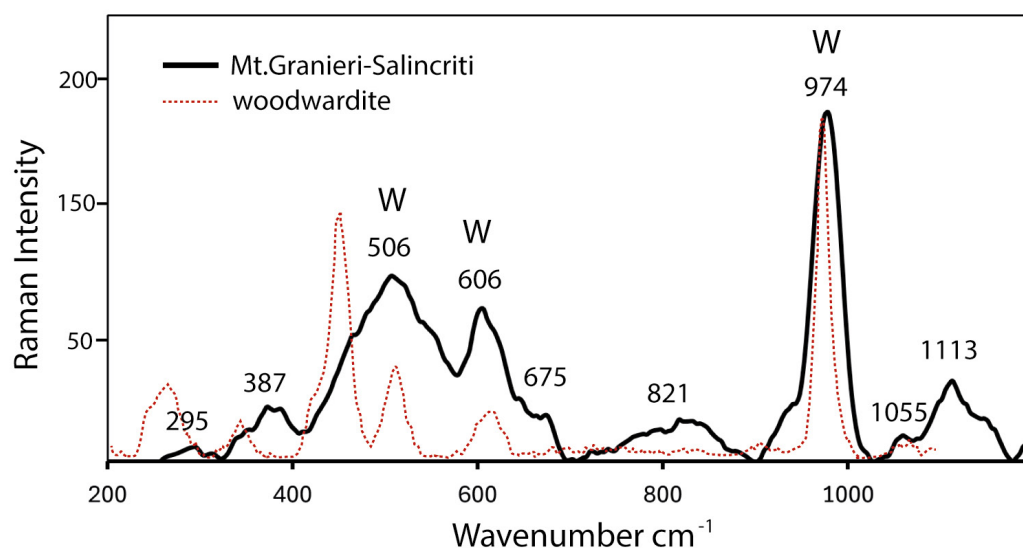


Fig. 2 - In black solid line Raman spectrum of the sample compared with the reference spectrum of woodwardite from RUFF database. With "W" are shown the peaks aligning with woodwardite.

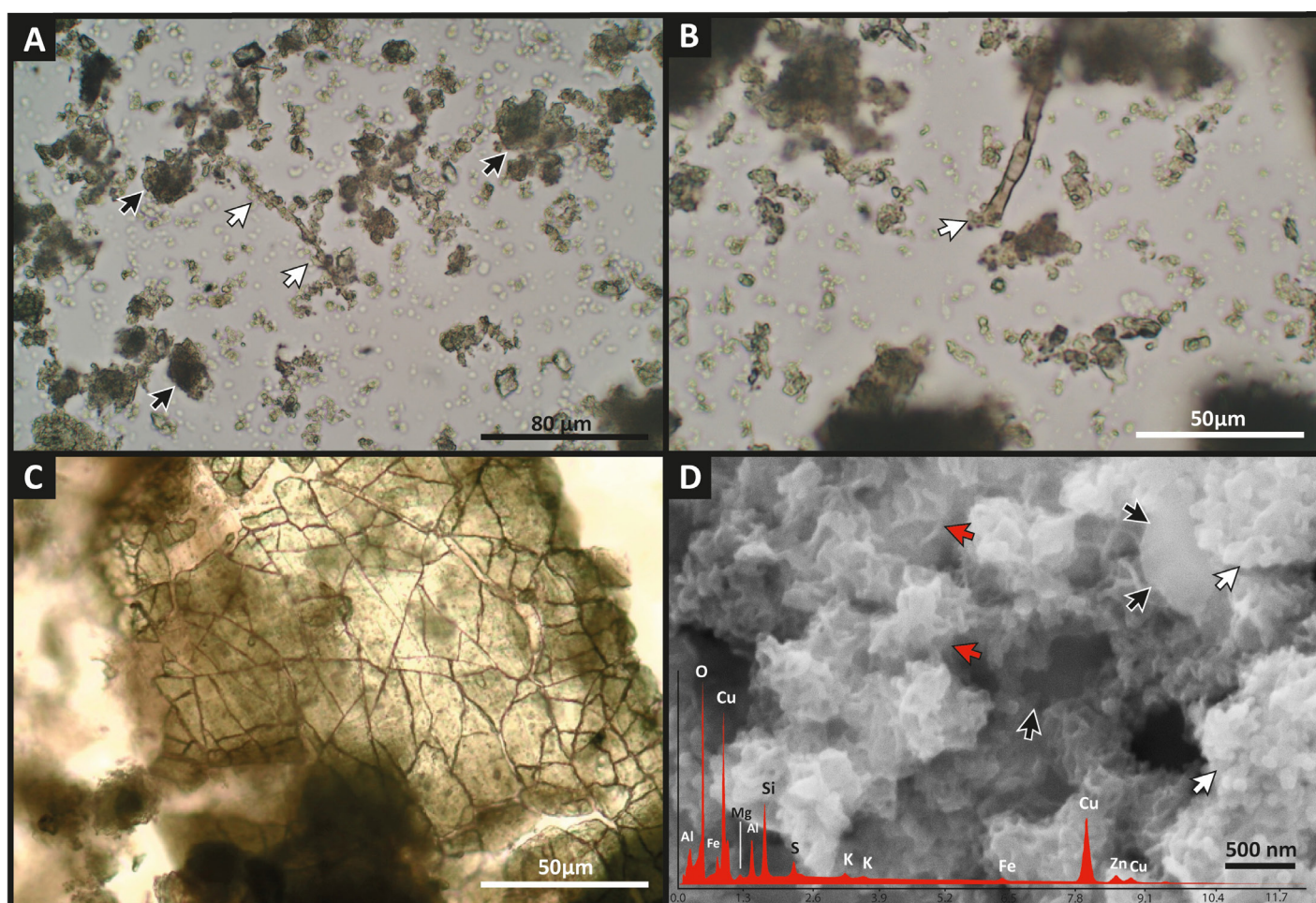


Fig. 3 - A-C. Optical microscopy image obtained using transmitted light microscopy with parallel polarizers. Woodwardite particles forming irregular aggregates (black arrows). White arrows indicate a microbial filament partially covered by the precipitate. B. Image highlighting a microbial filament partially encrusted by the precipitate (arrow). C. Mosaic of ~10 µm-sized mineral platelet-like crystal covering a plant remain. D. SEM image showing the general nanostructure of woodwardite. Red arrows indicate the sponge-like morphology, white arrows indicate aggregates of nanospheres and, black arrow indicates an organic structure. At the bottom of the image is shown the average EDS spectrum measured for this sample region. X-axis is expressed in KeV.

Both structures frequently encrust or occur along the surface of organic structures (Fig. 3D), possibly related to microbial cells and/or mucilaginous sheaths (e.g. exopolysaccharides). SEM-EDS

analyses provide insight into the chemical composition of the precipitate. The EDS spectrum (Fig. 3D) shows the main elemental constituents: Cu, O, Al, Si, Mg, Zn, and K.

DISCUSSION AND CONCLUSION

The measured Raman spectrum is generally consistent with the reference spectrum of woodwardite reported in the RRUFF database (R060762), although the second most prominent band in the reference spectrum, located at approximately 445 cm⁻¹, appears only as a shoulder on the main peak centered at 506 cm⁻¹ (Fig. 2). Additional bands observed at 675, 821, 1055, and 1113 cm⁻¹ are not characteristic of woodwardite and may be attributed to chemical contamination, e.g., Zn incorporation into the crystal lattice, or to the presence of organic compounds. The remaining bands of the reference spectrum are located below the measurement range of this study.

The studied light blue/greenish precipitate, interpreted as woodwardite in accordance with Barrese et al. (2006), displays distinctive compositional and microstructural features that could suggest at least a partial microbial mediated mineralisation: (i) the likely presence of organic filaments and mucilaginous sheaths partially to totally encrusted by the light green mineral particles (Fig. 3A, B); (ii) the presence of the nanospheres (rounded mineral particles with average diameter of ~ 200 nm - Fig. 3D), representing a typical biomineral nanostructure of Cu-bearing phases and other various biomineral groups (Borrelli et al., 2024; Borrelli et al., 2025; Fabbi et al., 2024; Guerrieri et al., 2024, 2025; Liu et al., 2021; Perri et al., 2024a, 2024b, 2025; Santagati et al., 2024; Slowakiewicz et al., 2016). EPS matrices, likely present in woodwardite samples, are produced by various microorganisms in variable amounts. These provide chemically reactive microenvironments that concentrate metal ions and serve as effective nucleation templates for Cu-, Zn-, and Al-bearing mineral phases (Braissant et al., 2007; Decho, 2010). In fact, numerous studies have shown that microorganisms inhabiting metal-rich environments possess efficient Cu-tolerance and positive charge attractor mechanisms, with consequent accumulation and successive precipitation within EPSs (Beveridge, 1989; Konhauser, 2007).

Based on such observations, we could infer that these processes may also have occurred in the studied woodwardite precipitation process at the studied site. On the other hand, the precipitate is widely characterised by aggregates of tabular platelets forming thin coatings or sponge-like structures. Such structures, have already been recognised in natural and synthesised glaucocerinite (a mineral belonging to the woodwardite group) samples, showing analogous morphology and size (Ardau et al., 2011a, 2011b), and were not associated with any biotic mediation.

In summary, while purely abiotic precipitation of studied woodwardite from Cu-Al-sulphate-rich waters cannot be excluded, microstructural and compositional evidence corroborates a model in which microbial processes potentially played also a significant role.

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