THE CU–NI–BEARING TODOROKITE FROM WESTERN PINDOS SERIES (PELOPONNESE, GREECE): ANALOGOUS TO TODOROKITE IN DEEP–SEA MANGANESE NODULES

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Abstract: The Mn mineralisation of Kato Figalia is associated with the Late Jurassic-Early Cretaceous chert of the Pindos series (Peloponnese). The Mn-oxides comprise pyrolusite, which is always replaced by todorokite. The latter mineral has a lamellar structure arranged into spherical shapes, and a chemical composition (rich in Mn and progressively enriched in Cu and Ni transition metals, and poor in Fe), which suggest similarities to present day marine todorokite in deep-sea manganese nodules.

Key words: Todorokite, SEM, IR spectrum, XRD, Chert, Pindos, Greece.

The manganese ore deposits of western Pindos isopic zone in Peloponnese are associated with Upper Jurassic to Lower Cretaceous thin-bedded radiolarian red chert (Fig.1). This Mn-bearing chert occurs at the footwall of imbricated thrust slices, which are overlain by the first flysch formation and the Upper Cretaceous thin-bedded limestone (Lalechos 1973; Papadopoulos 1997). This association of manganese-oxide mineralisation with chert is a dominant feature of western Pindos isopic zone. Their chemical composition comprises very small amounts of Fe, very low Fe/Mn, high Si/Al ratios, and very low concentrations of trace elements, such as Cu, Zn, Ni, Co and Pb (Varnavas & Panagos 1983). Their chemistry suggests a submarine hydrothermal origin with deposition of Mn in a deep-sea volcano-sedimentary environment.

The present study is focused on the characteristic features of todorokite, derived from the western part of Pindos chert slices (Lalechos 1973), outcropping at locality (x=37°27′ and y=21°47′), which is situated at 1,5 km in the SE part of Kato Figalia village (Fig. 1). In this area the chert thrust slices are characterised by recumbent west-facing folds gently dipping to the east, due to the overthrust onto the external isopic zone of Gavrovo-Tripolis during Oligocene. However, there is no direct association of Kato Figalia manganiferous chert with Jurassic pillow lavas of MORB affinity, except those that have been described from eastern localities (Gruszczyk et al. 1970; Pe-Piper & Piper 1991; Papadopoulos 1997). The manganese chert series is characterised by manganese horizons intercalated with red-brown bedded chert. Further, the same manganese horizons, when examined in detail, are also found to contain layers of manganiferous chert. Field observations show all transitional stages. However, this diagenetic chert succession also encloses bedded jasper and thin discontinuous m-sized lenticular Mn-mineralisation, which is parallel to the bedding plane and concentrated at its base.

The todorokite under study was collected from veinlets (few mm in size), crosscutting the laminae and thin beds of manganese-oxides (mainly pyrolusite with very low amount of cryptomelane) interstratified with red radiolarian chert and variable-coloured chalcedonic jasper. Numerous polished thin sections have been studied under reflected light, showing an intimate association of pyrolusite and todorokite, which is emphasised by a distinct contrast between the high reflection pyrolusite areas, and the low reflection anisotropic fine sheaf-like structure of todorokite. Todorokite seems to be replacing pyrolusite. These two manganese oxides occur as veinlets inside a silica mass, consisting of exclusively poorly crystallised chalcedony. Likewise, the todorokite appears in veinlets of well-crystallised carbonates, which also crosscut the chalcedony.

Scanning electron microscopy (SEM) indicates that the todorokite appears as a lamellar structure (Fig. 2). The todorokite impregnation within the siliceous rocks, takes the form of veinlets (Fig. 2a), where its lamellar structure is frequently developed into spherical arrangements (Fig. 2b and c). Moreover, it is worth mentioning that the lamellar structure of the studied todorokite approaches the morphology of Cuban todorokite, as well as the marine todorokite related to deep-sea manganese nodules (Burns & Burns 1978; Leclaire & Perseil 1979; Perseil & Jehanno 1981).

The X-ray diffraction studies reveal four typical reflections of todorokite: 9.70, 4.80, 2.40 and 2.30 Angstroms; the first two reflections have a strong intensity, whereas the latter two very weak. The infrared spectrum of the studied todorokite coincides with its known characteristic bands (Potter & Rossman 1979), i.e., $757cm^{-1}$, $635cm^{-1}$, $552cm^{-1}$, $515cm^{1}$ and $437cm^{-1}$ regions.

Microprobe analyses (Tables 1 & 2, each analysis represents an average of 30 analyses) show a large variation in the amount of manganese and transition metals. In general, no relation can be found between the concentration of manganese and the transition metals (Table 1). However, towards the periphery of veinlets high concentrations of transition metals (Ni, Co and Cu) within the high Mn-content analysed points have been observed (Table 2).

The features of Kato Figalia terrestrial todorokite are apparently similar to those of marine todorokite in deep-sea manganese nodules, i.e., besides being rich in manganese and poor in iron, contains also copper as well as nickel in equal proportions (Burns & Burns 1978; Leclaire & Perseil 1979; Perseil & Jehanno 1981). However, the marine todorokite is frequently associated with poorly crystalline birnessite, and always encloses transition metals, such as Co, Cu and Ni, which stabilise the todorokite structure in an oceanic environment (Burns & Burns 1978; Leclaire & Perseil 1979). Among the terrestrial todorokites, only two cases rich in transition metals are known, the first one is the copper-rich todorokite (>2% Cu) from Ambollas Eastern Pyrenees, France (Perseil & Giovanoli 1982), and the other is the Argolis nickel-rich todorokite (Ni>10 wt%) (Photiades et al. 1995).

Taking into account the morphological features of the studied todorokite, i.e., its lamellar structure arranged in spherical shapes and progressively enriched in transition metals, such as Cu and Ni (especially in the periphery of the veinlets) and its low Fe-content, suggest either an authigenic or post-depositional recrystallisation origin, but also a deuteric alteration may be postulated.

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Table 1. EMP analyses of Cu+Ni-Todorokite.

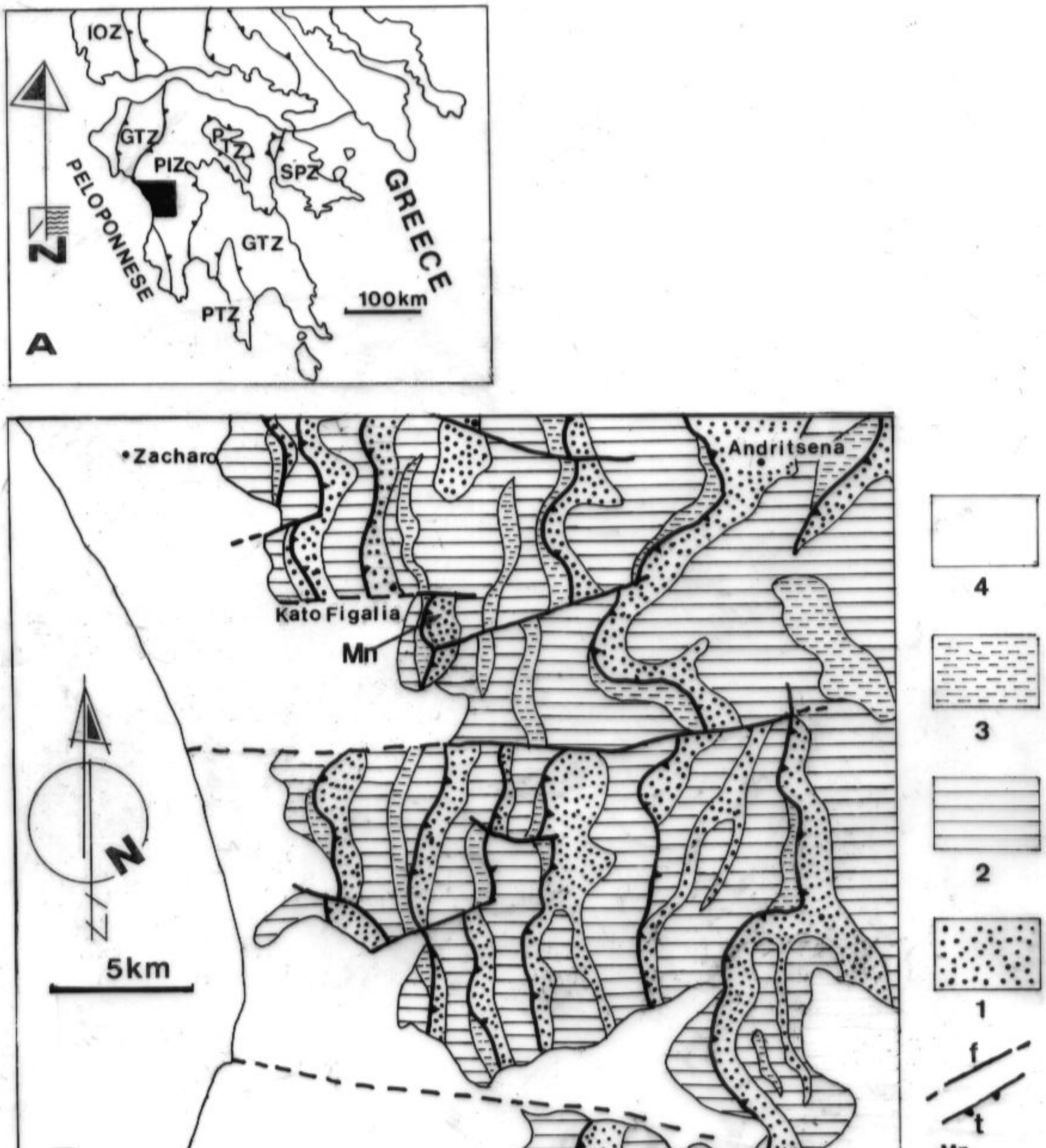
Table 2. EMP analyses of Cu+Ni-Todorokite.

Fig. 1. Geological position of Kato Figalia area in relation to tectono-stratigraphic isopic zones of southern Hellenides (**A**) and its geological map (**B**); Ionian zone (IOZ); Plattenkalk series (PLT); Gavrovo-Tripolis zone (GTZ); Pindos zone (PIZ); Subpelagonian zone (SPZ); Jurassic to Lower Cretaceous Mn-rich bedded red chert and sandstone (**1**); Upper Cretaceous bedded limestone (**2**); Palaeocene to Eocene flysch (**3**); Quaternary deposits (**4**); fault (**f**); thrust (**t**); **Kato Figalia Mn-occurrences (Mn).**

Fig. 2. BSE micrographs of todorokite from Kato Figalia crystallised in veinlet (**a**) and showing a lamellar structure (**b** and **c**).

Table 1	1	2	3	4	5	6	7
MnO2	61.38	64.27	66.21	70.58	78.81	78.85	79.11
Fe2O3	0.28	0.29	0.26	0.23	0.13	0.11	0.16
TiO2	0.00	0.02	0.05	0.02	0.02	0.00	0.02
Al2O3	6.43	0.40	0.39	0.46	1.06	0.38	0.27
NiO	2.94	0.64	0.92	0.71	0.06	0.02	0.09
CuO	3.02	0.85	2.74	1.54	0.11	0.11	0.02
CoO	0.00	0.04	0.04	0.15	0.04	0.03	0.11
CaO	4.50	8.10	9.93	4.84	2.61	3.29	2.99
K2O	0.21	0.09	0.05	0.07	0.73	0.52	0.49
Na2O	0.28	0.19	0.30	0.17	0.75	0.62	0.73
BaO	1.23	7.43	4.49	6.77	0.13	0.00	0.00
SrO	0.00	0.05	0.00	0.00	0.11	0.14	0.09
MgO	2.01	0.40	0.42	0.58	1.93	1.58	1.71
SiO2	4.02	4.52	2.32	3.04	2.10	0.86	1.43
Σ	86.30	87.29	88.12	89.16	88.59	86.51	87.22
H2O	11.78	11.25	11.33	11.54	12.22	11.84	11.98

Table 2	1	2	3	4
MnO2	67.46	66.90	57.12	68.67
Fe2O3	0.47	0.31	0.44	0.00
Al2O3	0.88	1.14	3.96	0.53
NiO	3.09	2.46	1.74	4.22
CuO	1.24	1.26	1.45	2.78
CoO	0.00	0.10	0.23	0.87
CaO	5.86	9.51	7.59	6.90
K2O	0.15	0.77	0.11	0.13
Na2O	0.33	0.11	0.23	0.44
BaO	4.81	0.49	7.01	3.03
MgO	0.55	0.49	1.41	0.37
SiO2	4.82	4.51	7.12	2.19
Σ	89.66	87.56	88.41	90.14
H2O	10.10	10.16	9.99	9.95



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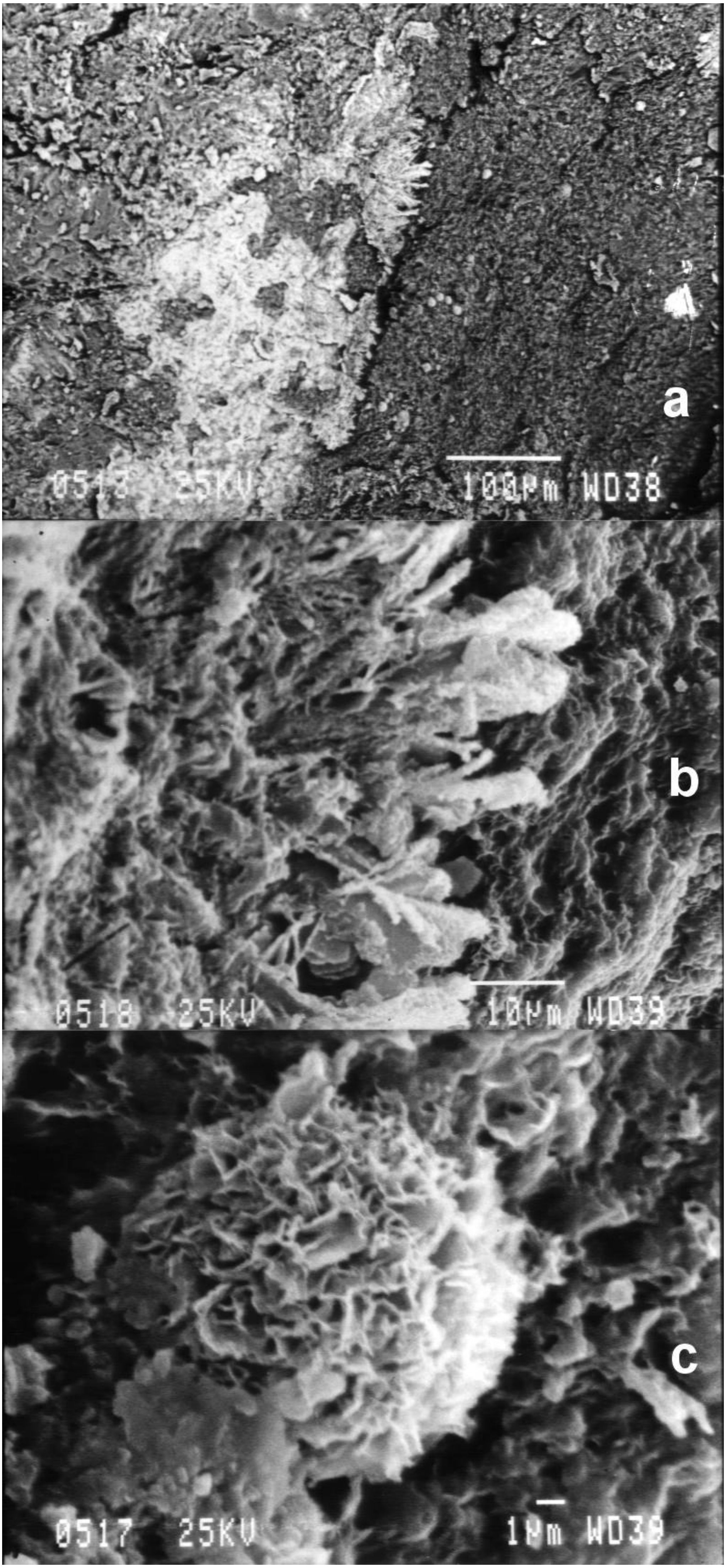
a
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c
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