Todorokite - a 10 Å manganate from the Jabuka Pit (Central Adriatic)

Todorokit – 10 Å manganat z Jabuške kotline (srednji Jadran)

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Abstract: Additional studies of ferromanganese crusts and coatings from the Jabuka Pit, a depression up to 275 m deep in the Central Adriatic, revealed the presence of todorokite. This mineral was recognized as the major constituent of an Fe-poor and Mg-rich 10 Å manganate phase, forming an up to 1 mm high stalactitic structures composed of about 4:m long plate-like crystals, as well as of collomorph-banded and botryoidal aggregates, found on shells and shell fragments of *Ostrea cochlear Poli* exposed to seawater. The exact mechanism of todorokite precipitation in the Jabuka Pit is still unknown. However, we hypothesized its hydrogenous precipitation at the sediment-water interface in oxygenated conditions at Eh ≈ 0.5 V and pH around 8.18.

Izvleček: V okviru nadaljnih raziskav feromanganovih prevlek in skorij, iz do 275 m globoke Jabučke kotline v srednjem Jadranu, smo ugotovili prisotnost todorokita. Gre za 10 Å manganat reven z Fe in obogaten z Mg, ki smo ga našli na lupinicah in odlomkih školjke *Ostrea cochlear Poli,* kjer v glavnem tvori do 1mm velike stalaktitom podobne tvorbe sestavljene iz okrog 4 μm velikih ploščic in kolomorfne oblike ter sferične aggregate. Njegov nastanek na območju Jabučke kotline še ni povsem jasen. Zaenkrat predpostavljamo, da se izloča pri oksidacijskih pogojih in sicer pri Eh ≈ 0,5 V ter pH okrog 8,18 na meji sediment - morska voda.

Key words: todorokite, XRD, SEM and EDS study, Jabuka Pit, Central Adriatic
Ključne besede: todorokit, XRD, SEM in EDS študij, Jabučka kotlina, srednji Jadran

Introduction

Todorokite is a 10 Å hydrated manganese oxide mineral first reported from the Todoroki mine, Hokkaido, Japan (Yoshimura, 1934). It was later found in manganese ores from many locations such as Cuba (Frondel et al., 1960; Levinson, 1960; Straczek et al., 1960), Portugal, Austria, the Saipan Islands, Brazil, New Jersey, France and Australia (Frondel et al., 1960; Perseil & Giovanoli, 1982; Ostwald, 1993). Todorokite was further identified in sea floor manganese nodules and crusts (Hewett et

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AL., 1963; BURNS & BURNS, 1978; CHUKHROV ET AL., 1978, 1979, 1981, 1983; TURNER ET AL., 1982; SIEGE & TURNER, 1983; PIPER ET AL., 1984; PATTAN AND MUDHOLKAR, 1990; NATH ET AL., 1994). In the Adriatic Sea todorokite was first recognized as the major manganese mineral of the ferromanganese coatings found in the Jabuka Pit of the Central Adriatic (DOLENEC & FAGANELI, 1996). Coated structures from the Jabuka Pit comprise a complex assemblage of materials, including 10 Å manganate, mostly todorokite, amorphous iron oxyhydroxides, as well as several detrital and authigenic minerals and hard parts of marine organisms (DOLENEC, 1999). Mollusc shells and other biogenic detritus appear to be essential for the nucleation and intimate intergrowth of hydrated Mn and Fe oxides, as already observed by BURNS AND BURNS (1975).

This paper presents the results of further mineralogical and geochemical studies of todorokite bearing ferromanganese coated structures from the Jabuka Pit and discusses the possible mechanism of its deposition on mollusc shells and on other biogenic detritus.

MATERIALS AND METHODS

Deep water molluscs shells and shell fragments with ferromanganese incrustations and coatings were collected during summer cruises in the years 1997 - 1999 by dredging the floor with fisherman's net in the central part of the Jabuka Pit (Fig. 1). For the present XRD and SEM - EDS study only stalactitic aggregates on *Ostrea cochlear* shells were chosen. In the laboratory the stalactitic aggregates were removed from 15 mollusc shells by a plastic knife and dried at ambient temperature and then homogenized by grinding in an agate mortar for X-ray diffraction analysis. For characterization of the microstructure and composition of the coated structures a Jeol JSM 5800 SEM instrument with Link ISIS 300 EDS was used. Quantitative analyses were performed using SEM Quand software and a virtual standard package library (VPS). Measured peak intensities in the spectra were corrected and quantified using a ZAF matrix correction programme. For oxygen, semi-quantitative estimation is possible only by comparison between the peak areas of the oxygen peaks in different spectra without exact quantification. The relative random errors of EDS were less than 6 % for the trace metals Ni, Co and Ba, and better than 3 % for major and selected minor oxides.

The mineralogy of the composite sample of stalactitic aggregates (TOD-1) was determined by X-ray powder diffractometry using a Philips PW 3710 diffractometer and Cu K" radiation. Powdered sample was scanned at a rate of 2° per minute, over the range of 2 - 70° (2Θ). The results were stored on a PC computer and analysed by PC-APD diffraction software. The manganese phases in the diffraction pattern were identified using the following minerals from the JCPDS system: todorokite (JCPDF card numbers: 38-475, 13-164, 18-1411), birnessite (JCPDF card numbers: 43-1456, 23-1046, 23-1239), buserite, a hydrous manganate from the 10 Å todorokite group with 10 Å spacing, but with a layered rather than a tunnel structure (JCPDF card number 32-1128), vernadite (JCPDF card number 15-604) and data for synthetic todorokite from BILINSKI ET AL. (2002).

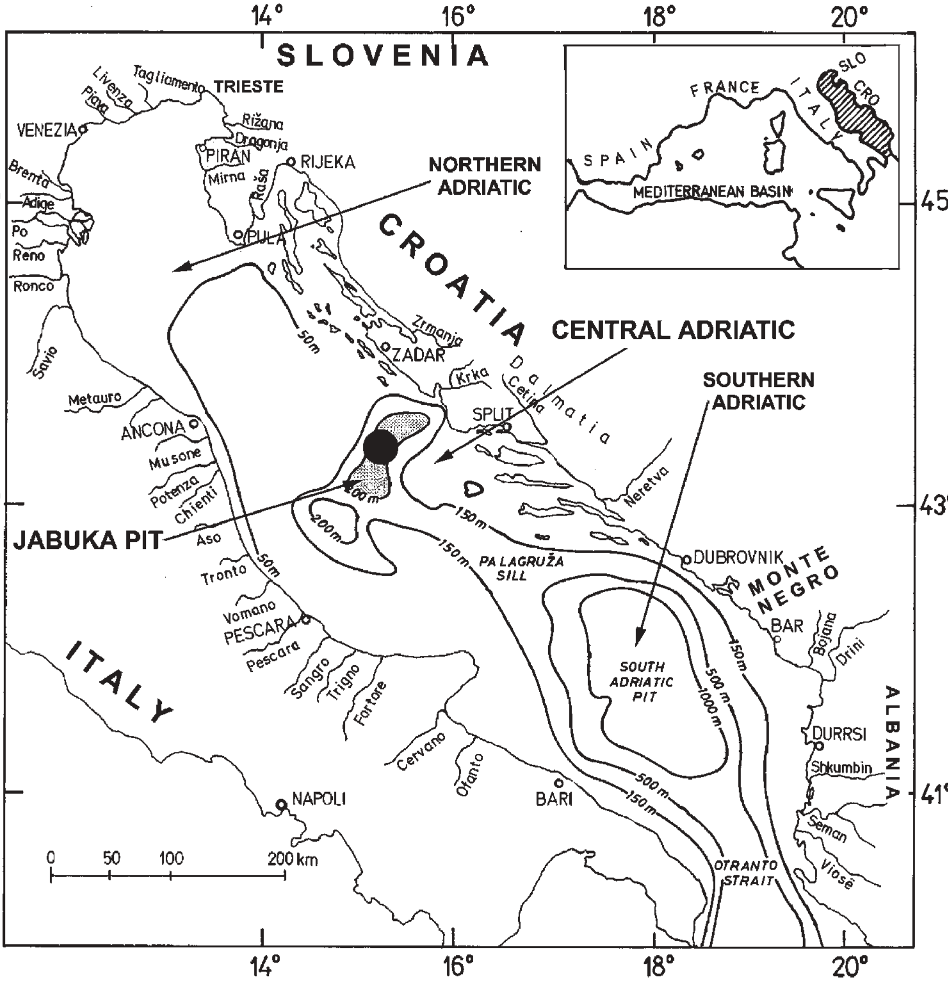


Figure 1. Map of the Adriatic Sea, showing the position of the Jabuka Pit and the sampling area (●).
Slika 1. Poenostavljena geografska karta Jadranskega morja s položajem Jabučke kotline in vzorčevanega območja (●).

Results

Phase analysis and microscopic investigations

The heterogeneity, cryptocrystallinity or very fine particle size of the crusts and ferromanganese coatings as well as of the stalactitic structures from the Jabuka Pit made identification of their mineralogy by means of X-ray diffraction difficult. The characteristic diagnostic peaks were frequently broad and indistinct and did not not serve as a satisfactory basis for identification. However, in our suite of stalactitic agregates selected for this study todorokite (sample TOD-1) was recognized by two relatively strong diagnostic peaks at 9.62 Å and 4.85 Å and weaker ones at 7.13 Å, 2.46 Å, 2.35 Å, 2.13 Å, 1.98 Å and 1.42 Å

(Fig. 2). These values correspond well to the similar reflections of the *d*-spacing of the reference todorokites (Table 1). Other authigenic and/or detrital minerals including calcite, dolomite, halite, aragonite, mixed layer clay minerals (illite / montmorilonite and chlorite / montmorilonite), quartz and feldspars were also detected in minor to trace amounts.

Examination under an optical microscope showed that the todorokite from the Jabuka Pit forms up to 1 mm long earthy black stalactitic structures growing directly on the surfaces of mollusc shells and shell fragments exposed to seawater. It also occurs as collomorph-banded and rare botryoidal aggregates, which are a few tenths of a millimetre or less in diameter.

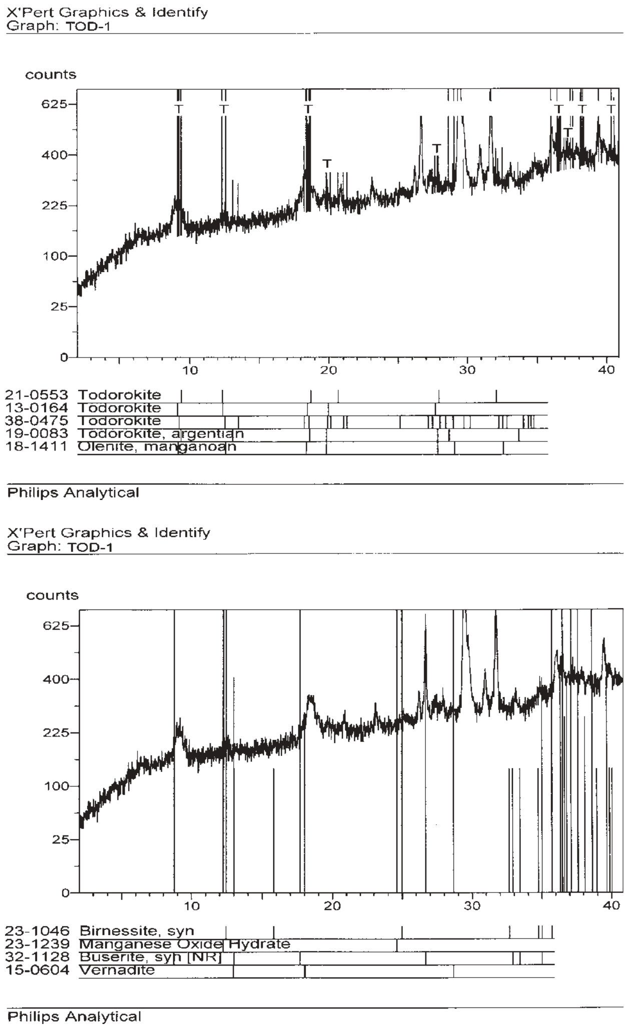


Figure 2. XRD pattern of composite sample (TOD-1) of stalactitic todorokite aggregates from *Ostrea cochlear Poli shells* (T - Todorokite).
Slika 2. Rentgenogram kompozitnega vzorca (TOD-1) todorokitovih stalaktitnih agregatov iz lupinic školjke *Ostrea cochlear Poli* (T - todorokit).

Table 1. Literature values of *d*-spacing in Å and intensity - *I* in % for todorokite, birnessite, buserite and vernadite used to identify the manganese phase in stalictitic aggregates from the Jabuka Pit.
Tabela 1. Literaturni podatki za *d*-vrednosti Å in intenziteto – *I* v % za todorokit, birnessit, buserit in vernadit uporabljeni za določitev manganove faze v stalaktitnih agregatih iz Jabučke kotline.

Todorokite South Africa (38-475)		Todorokite Japan (13-164)		Todorokite Cuba (18-1411)		Synthetic todorokite Bilinski et al. [8]		Sample TOD-1		Birnessite (43-1456)		Birnessite (23-1046)		Birnessite (23-1239)		Buserite (32-1128)		Vernardite (15-604)	
d	*I*	*d*	*I*	*d*	*I*	*d*	*I*	***d***	***I***	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*
-	-	-	-	-	-	-	-	**-**	**-**	-	-	-	-	-	-	10.1	100	-	-
9.555	100	9.68	100	9.65	100	9.54	100	**9.62**	**100**	-	-	-	-	-	-	-	-	-	-
7.061	5	7.15	2	7.05	40	7.15	50	**7.13**	**10**	7.144	100	7.09	100	7.21	100	-	-	6.81	30
6.554	9	-	-	-	-	-	-	**-**	**-**	-	-	-	-	-	-	6.79	10	-	-
-	-	-	-	-	-	-	-	**-**	**-**	-	-	5.60	10	-	-	-	-	-	-
-	-	-	-	-	-	-	-	**-**	**-**	-	-	-	-	-	-	5.01	70	-	-
4.860	17	-	-	-	-	-	-	**-**	**-**	-	-	-	-	-	-	-	-	4.92	20
4.773	24	4.80	80	4.82	70	4.79	80	**4.85**	**70**	-	-	-	-	-	-	-	-	-	-
4.462	7	4.45	5	4.48	70	-	-	**-**	**-**	-	-	-	-	-	-	-	-	-	-
4.410	10	-	-	-	-	-	-	**-**	**-**	-	-	-	-	-	-	-	-	-	-
4.220	10	-	-	-	-	-	-	**-**	**-**	-	-	-	-	-	-	-	-	-	-
4.170	11	-	-	-	-	-	-	**-**	**-**	-	-	-	-	-	-	-	-	-	-
3.540	2	-	-	-	-	-	-	**-**	**-**	3.572	27	3.56	80	3.61	80	-	-	-	-
3.283	2	-	-	-	-	-	-	**-**	**-**	-	-	-	-	-	-	3.34	50	-	-
3.254	2	3.22	15	3.20	10	-	-	**-**	**-**	-	-	-	-	-	-	-	-	-	-
3.181	3	-	-	-	-	-	-	**-**	**-**	-	-	-	-	-	-	-	-	-	-
3.173	1	-	-	-	-	-	-	**-**	**-**	-	-	-	-	-	-	-	-	-	-
3.081	7	-	-	3.07	40	-	-	**-**	**-**	-	-	-	-	-	-	-	-	3.11	60
3.003	8	-	-	-	-	-	-	**-**	**-**	-	-	-	-	-	-	-	-	-	-
2.958	2	-	-	-	-	-	-	**-**	**-**	-	-	-	-	-	-	-	-	-	-
2.777	7	-	-	-	-	-	-	**-**	**-**	-	-	-	-	-	-	-	-	-	-
2.752	7	-	-	2.75	10	-	-	**-**	**-**	-	-	2.74	10	-	-	2.72	10	-	-
2.727	2	-	-	-	-	-	-	**-**	**-**	-	-	-	-	-	-	2.68	10	-	-
2.634	1	-	-	-	-	-	-	**-**	**-**	-	-	-	-	-	-	-	-	-	-
2.609	2	-	-	-	-	-	-	**-**	**-**	-	-	-	-	-	-	-	-	-	-
2.595	3	-	-	-	-	-	-	**-**	**-**	-	-	-	-	-	-	-	-	-	-
2.581	3	-	-	-	-	-	-	**-**	**-**	2.519	14	2.58	10	-	-	-	-	-	-
-	-	-	-	-	-	-	-	**-**	**-**	-	-	2.56	10	-	-	2.56	30	-	-
-	-	-	-	-	-	-	-	**-**	**-**	-	-	2.51	70	-	-	-	-	-	-
2.453	16	2.46	20	2.46	40	2.47	20	**2.46**	**20**	2.480	2	2.47	10	2.46	100	2.47	30	2.45	20
2.443	17	-	-	-	-	-	-	**-**	**-**	-	-	-	-	-	-	2.44	30	-	-
2.429	10	-	-	2.42	10	-	-	**-**	**-**	2.429	13	2.42	60	-	-	-	-	-	-
2.399	36	-	-	-	-	-	-	**-**	**-**	-	-	-	-	-	-	-	-	2.39	100
2.388	25	2.39	40	-	-	2.40	50	**-**	**-**	-	-	-	-	-	-	-	-	-	-
2.355	24	-	-	-	-	-	-	**2.35**	**5**	-	-	-	-	-	-	2.36	20	-	-
2.345	25	2.34	15	2.35	40	2.33	10	**-**	**-**	-	-	-	-	-	-	-	-	-	-
2.320	4	-	-	-	-	-	-	**-**	**-**	2.324	2	2.31	10	2.33	100	-	-	-	-
2.280	5	-	-	2.28	10	-	-	**-**	**-**	-	-	2.26	10	-	-	2.27	30	-	-
-	-	-	-	-	-	-	-	**-**	**-**	-	-	2.25	10	-	-	-	-	-	-
2.217	7	2.22	20	-	-	2.21	10	**-**	**-**	2.222	5	2.21	40	-	-	-	-	-	-
2.206	5	-	-	2.20	5	-	-	**-**	**-**	-	-	-	-	-	-	-	-	-	-
2.194	2	-	-	-	-	-	-	**-**	**-**	-	-	-	-	-	-	-	-	2.19	20
2.151	2	2.15	5	-	-	-	-	**-**	**-**	2.154	7	2.15	40	-	-	2.15	10	2.15	60
2.120	2	-	-	2.13	10	-	-	**2.13**	**5**	-	-	2.14	40	-	-	-	-	-	-
2.106	3	-	-	-	-	-	-	**-**	**-**	-	-	-	-	-	-	-	-	-	-
2.090	3	-	-	-	-	-	-	**-**	**-**	-	-	2.09	10	2.04	80	2.06	10	-	-
1.993	5	-	-	-	-	-	-	**-**	**-**	-	-	-	-	-	-	2.02	10	-	-
1.986	6	1.98	20	1.98	10	1.97	10	**1.98**	**5**	-	-	1.97	10	-	-	-	-	-	-
-	-	-	-	-	-	-	-	**-**	**-**	-	-	1.94	10	-	-	-	-	-	-
-	-	-	-	-	-	-	-	**-**	**-**	-	-	1.86	40	-	-	-	-	-	-
-	-	1.92	5	1.91	5	-	-	**-**	**-**	1.823	4	1.82	40	-	-	1.83	10	1.827	40
-	-	-	-	-	-	-	-	**-**	**-**	-	-	1.81	40	1.802	10	-	-	-	-
1.765	5	-	-	1.77	10	-	-	**-**	**-**	-	-	1.77	20	-	-	-	-	-	-
1.755	5	1.75	10	-	-	-	-	**-**	**-**	-	-	1.75	10	-	-	-	-	-	-
1.742	8	-	-	-	-	1.74	10	**-**	**-**	-	-	-	-	-	-	-	-	-	-
1.738	6	-	-	-	-	-	-	**-**	**-**	-	-	-	-	1.723	80	1.69	5	-	-
-	-	-	-	-	-	-	-	**-**	**-**	-	-	1.66	20	-	-	1.68	5	-	-
-	-	-	-	-	-	-	-	**-**	**-**	-	-	1.63	20	-	-	1.62	5	1.649	30
1.550	4	1.54	5	1.54	10	-	-	**-**	**-**	-	-	-	-	-	-	-	-	1.537	40
-	-	-	-	-	-	-	-	**-**	**-**	-	-	-	-	1.454	20	1.46	50	-	-
1.423	16	1.42	30	1.42	5	-	-	**1.42**	**8**	1.425	3	-	-	1.422	60	-	-	1.422	40
1.408	9	1.39	10	1.406	5	-	-	**-**	**-**	-	-	-	-	-	-	-	-	-	-

(Numbers in parantheses indicate JCPDF card number)
(Številke v oklepajih označujejo številko JCPDF kartice)

Scanning electron microscope examination showed varied surface structures on the scale of a few micrometres, e.g., aggregates of botryoidal clusters and stalactite structures (Fig. 3), as well as up to 4 : long plate-like crystallites. In Fig. 4 at the highest magnification (7,500 x) one can see a part of an isolated todorokite stalactitic structure mostly composed of plates. Biogenic debris, represented by coccoliths is also common.

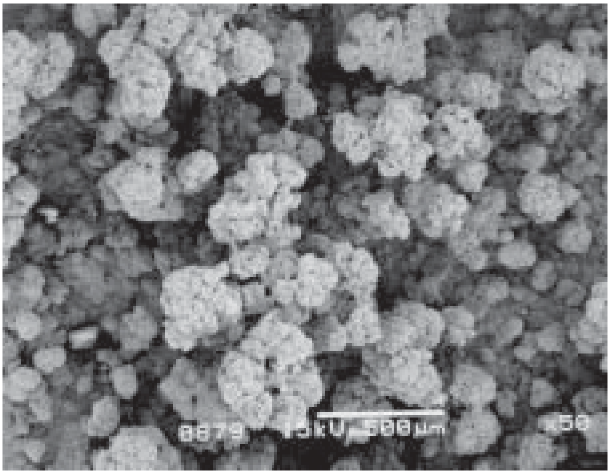


Figure 3. SEM photo of stalactitic todorokite aggregates on an *Ostrea cochlear Poli* shell.
Slika 3. Stalaktitne tvorbe todorokita na lupinici školjke *Ostrea cochlear Poli.* Elektronski mikroskop, sekundarni elektoni, povečava 50 x.

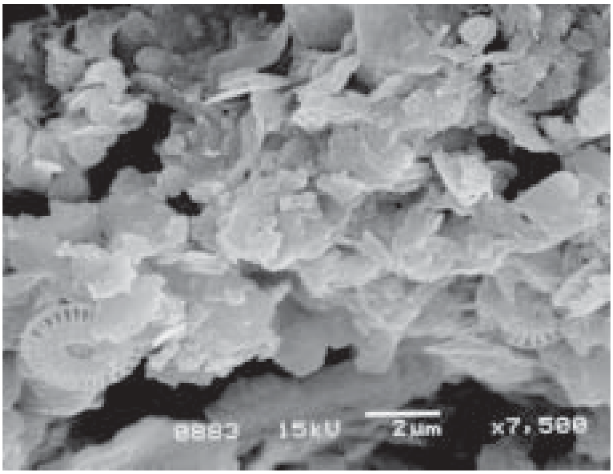
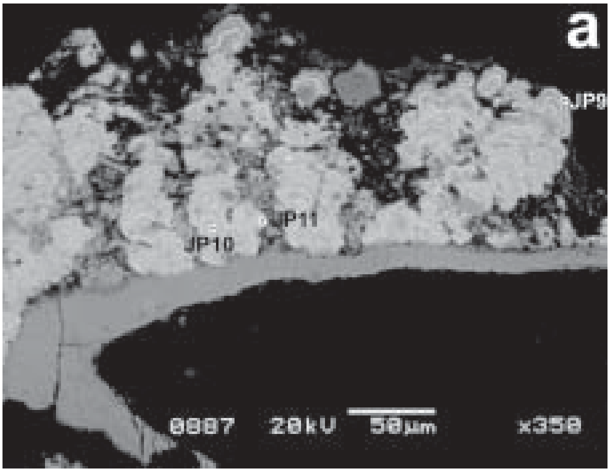


Figure 4. SEM photo of a part of an isolated stalactitic todorokite aggregate on an *Ostrea cochlear Poli* shell at the highest magnification (7 500 x) mostly composed of plates. Biogenic debris, represented by coccoliths, is also present.
Slika 4. Detajl stalaktitnega agregata todorokita iz lupinice školjke *Ostrea cochlear Poli* sestavljenega iz ploščic. Elektronski mikroskop, sekundarni elektoni, povečava 7.500 x.

Backscattered electron examination of polished sections of stalactitic aggregates (Fig. 5 **a** and **b**) revealed a laminated, more or less concentric banded pattern. Fragments of detrital minerals inside the stalactitic aggregates were also observed.

SEM – EDS investigation

Quantitative analysis of one sample of a stalactitic aggregate (Fig. 5 a) carried out by the SEM-EDS system revealed the following elemental contents in wt % (Table 2):



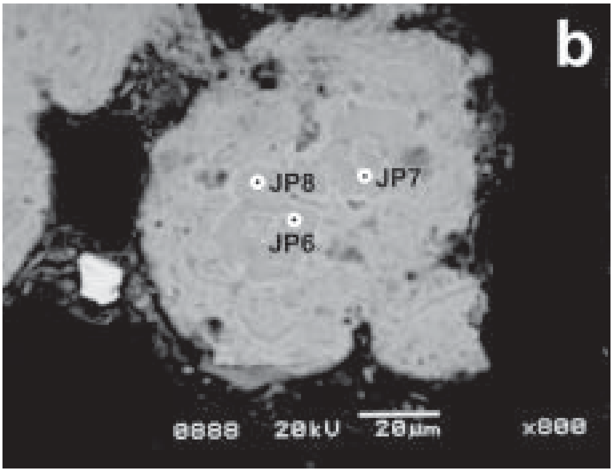


Figure 5. Backscattered electron micrographs of a polished section showing a vertical (a) and horizontal (b) cross-section of stalactitic aggregates of todorokite growing on an *Ostrea cochlear Poli* shell. Points JP-6 to JP-11 refer to the EDS point count analysis presented in Table 2.

Slika 5. Vertikalni (a) in horizontalni (b) presek poliranih todorokitovih stalaktitnih agregatov iz lupinice školjke *Ostrea cochlear Poli.* Točke JP-6 do JP-7 so mesta točkovne analize z EDS, katere rezultati so podani v tabeli 2. Elektronski mikroskop, odbiti elektroni, povečava 350 x in 800 x.

48.39 to 62.20 % Mn, 0 – 1.22 % Fe, 4.85 – 8.19 % Mg, 1.25 – 2.52 % Ca, 1.09 – 4.40 % Al, 0.82 – 6.05 % Si, 0.73 – 1.53 % K, 0.75 – 2.37 % Na, 0 – 0.72 % Ba, 0.32 – 1.10 % Cl, and 0 – 0.67 % Ni. Although the internal todorokite layers of the stalactitic structures showed variations in brightness (from dark grey to light grey), alternating layers did not not exhibit marked changes in the proportions of the major constituents. As no Fe phase was detected in the XRD scans of the todorokite samples, the bulk of the Fe must be absent and/or present in some amorphous compound. Some bright layers of the stalactitic structures observed in backscattered electron photographs (Fig. 5 **a** and **b**) are somewhat richer in Mn than darker ones. A comparison between the peak areas of manganese and oxygen in the EDS spectra shows that the darker layers exhibit a lower oxygen and manganese peak than the lighter ones (Fig. 6).

DISCUSSION AND CONCLUSIONS

The heterogeneity, cryptocrystallinity or very fine particle size of the stalactitic ferromanganese structures from the Jabuka Pit made identification of their mineralogy by means of X-ray diffraction difficult and often impossible. The occurrence of carbonates, mixed layer clay minerals, silicates and halite admixed with ferromanganese minerals in the stalactitic structures caused an additional complication, because their X-ray lines can sometimes be confused with those of manganese oxides. However, in the case of the stalactitic structures investigated during this study, the strongest peaks at 9.62 Å and 4.85 Å and the weaker ones at 7.13 Å, 2.46 Å, 2.35 Å, 2.13 Å, 1.98 Å and 1.42 Å suggest that the main constituents of the stalactitic aggregates is undoubtedly a 10 Å manganate mineral. The samples investigated show values of *d*-spacing in Å similar to natural and synthetic todorokite but not to any pattern of buserite, birnessite or vernadite (Table 1). According to the data presented we believe that the major observed 10 Å manganate mineral phase in the suite of stalactitic aggregates selected for this study is todorokite. BURNS ET AL. (1983) who summarized observations of tunnel structures of both marine 10 Å manganates and terrestrial todorokites, recommended that the name todorokite be universally adopted for the predominant marine 10 Å manganates.

However, we must to point out that due to the relatively low crystallinity of the ferromanganese coated structures and their admixture with other autigenic and detrital minerals we are unable to ascertain if the 7.13 Å reflection of sample TOD-1 corresponds only to a 10 Å manganate mineral phase, or also indicates the possible presence of the 7 Å layer-structured phyllomanganate birnessite (Table 1). A reflection at approximately 7 Å is usually attributed to birnessite (BURNS AND BURNS, 1979). In our set of XRD data relatively strong peaks of birnessite (i. e. those at 3.6 Å, 2.46 Å, 2.33 Å, 2.04 Å and 1.723 Å) are missing or masked by reflections of the 10 Å manganate phase, so we are not able to exclude the possible presence of birnessite. Because the diffraction lines of 10 Å manganates also overlap the characteristic X-ray diffraction lines at 2.40 – 2.45 Å and 1.40 – 1.45 Å of vernadite (BURNS AND BURNS, 1979) it is also impossible to determine the presence of this mineral in our samples. Therefore, for more precise identification of other manganese

Table 2. Chemical composition in wt. % of ferromanganese stalactitic aggregate (points JP6 - JP11) as determined by Energy Dispersive Spectroscopy (EDS) - point count analyses. The analyses correspond to points JP6 to JP11 plotted in Fig. 5.

Tabela 2. Kemična sestava stalaktitnega todorokitovega agregata (točke JP6 – JP11) določena s pomočjo energijsko disperzijskega sistema (EDS) – Točkovna analiza. Analizirane točke JP6 do JP11 so prikazane na sliki 5.

Sample point	Si	Al	Fe	Mn	Ti	Ca	Mg	Na	K	P	S	Ba	Ni	Co	V	Cl	O	Total %	Mn/Fe	Mg/Mn
JP6	1.76	4.40	n.d.	51.63	0.39	2.52	8.19	1.35	0.42	n.d.	n.d.	n.d.	0.67	n.d.	n.d.	0.32	28.35	100	-	0.16
JP7	2.21	2.83	n.d.	55.60	n.d.	1.25	6.56	1.85	0.78	n.d.	n.d.	0.72	0.56	n.d.	n.d.	0.58	27.08	100	-	0.12
JP8	6.05	3.63	n.d.	48.39	n.d.	2.30	5.30	1.03	1.53	n.d.	0.48	0.37	n.d.	n.d.	n.d.	0.87	30.05	100	-	0.11
JP9	1.90	1.40	n.d.	57.13	n.d.	2.17	6.71	2.37	0.73	n.d.	0.24	n.d.	n.d.	n.d.	n.d.	0.70	26.66	100	-	0.12
JP10	0.82	0.89	n.d.	62.20	n.d.	1.54	4.85	1.81	1.41	n.d.	n.d.	0.71	n.d.	n.d.	n.d.	1.10	24.65	100	-	0.08
JP11	1.39	1.09	1.22	60.63	n.d.	1.43	4.88	0.75	1.26	n.d.	0.16	0.59	0.33	n.d.	n.d.	0.83	25.44	100	49.70	0.08

n.d. – not detected

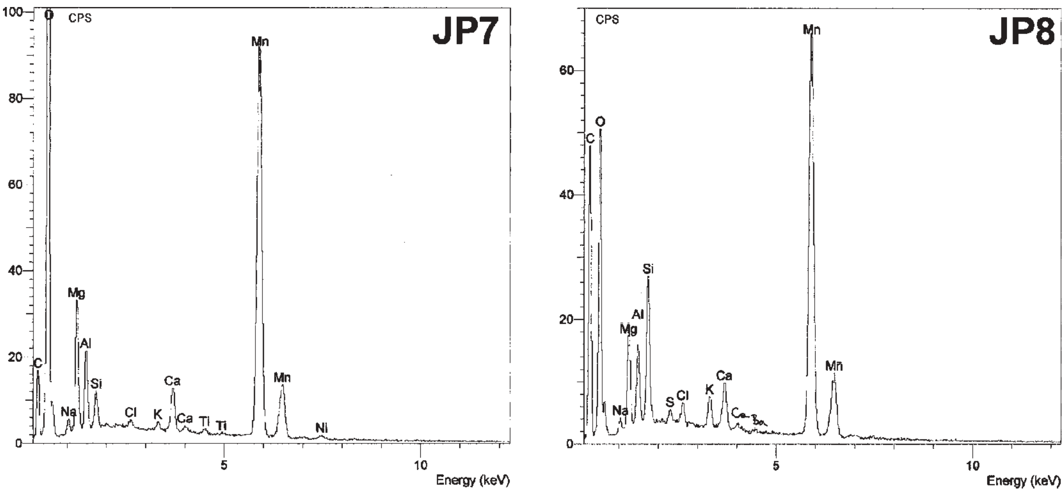


Figure 6. Energy Dispersive Spectroscopy (EDS) of the dark-grey (JP-8) and light-grey (JP-7) todorokite layer from Fig. 5 (b) showing differences in the height of the oxygen and manganese peaks between the dark and bright layers.

Slika 6. EDS diagram svetlosive (JP-8) in temnosive (JP-7) todorokitove plasti iz slike 5 (b) na katerem so vidne razlike v višini kisikovih in manganovih pikov. Elektronski mikroanalizator, energijski disperzijski system (EDS).

phases in stalactitic aggregates from the Jabuka Pit further studies such as the contraction and expansion test, differential scanning calorimetry (DSC) and Mössbauer spectroscopy are necessary.

The significant feature of the todorokite from the Jabuka Pit is its considerable enrichment in Mg from 4.85 to 8.19 %. This is often found to be the case with todorokites of different origin. Comparison of our analyses with those given by Frondel et al. (1960), Levinson (1960), Straczek et al. (1960), Lawrence et al. (1962) and Nath et al. (1992), however, indicates that the todorokite from the Jabuka Pit is much more enriched in Mg than the todorokites analysed by these authors. The magnesium content in their todorokite samples varied from 0.61 to 2.35 % (recalculated from MgO data). Concentrations of Mg (from 6.9 to 12.2 wt. %) similar to our samples have been reported only for the 10 Å manganate produced by bacterial spores of the marine Bacillus, strain SG-1 (MANDERNACK ET AL., 1995). Magnesium is believed to be an important structural cation for todorokite or for fixed 10 Å phyllomanganates (BURNS & BURNS, 1979). MANDERNACK ET AL. (1995) have suggested that replacement of Mn (II) by Mg stabilizes the 10 Å manganate structure. Thus the Mg-rich 10 Å manganates did not collapse to 7 Å manganates even on baking at 100 °C.

The Mg/Mn ratio (elemental wt. %) of the todorokite samples analyzed in this study varies from 0.08 to 0.16 (Table 1) and compares very well with Mg/Mn values in the range between 0.08 and 0.15 for 10 Å Mn (IV) manganates of microbial origin (MANDERNACK ET AL., 1995), as well as with values of 0.17 in todorokite-rich ferromanganese nodules (PIPER ET AL., 1984).

The origin of todorokite in the marine environment has been the topic of considerable discussion ever since this mineral was identified as one of major consistuent of deep-sea ferromanganese nodules. LYLE ET AL. (1977) explained the formation of todorokite by diagenetic reaction of Fe-Mn oxyhydroxides with biogenic silica, which should led to the formation of iron-rich smectite and pure todorokite. According to CALVERT AND PRICE (1977) todorokite is precipitated from interstitial water as a result of diagenetic remobilization of Mn. BEVERIDGE (1989) has reported that todorokite observed in marine sediments and nodules may be indicative of microbial origin. Arrhenius and TSAI (1981) have suggested that todorokite might also be formed from buserite by oxidative processes.

The exact mechanisms of formation of stalactitic todorokite aggregates in the Jabuka Pit are still unknown. Since they were found only on surfaces exposed to seawater, we believe that they are essentially hydrogenetic and most probably precipitate in connection with the activity of microorganisms. The relatively high content of Ce and a strong positive Ce anomaly observed in the previously investigated 10 Å manganate crust and coatings from the same location (DOLENEC, 2003) also suggests a highly oxidizing environment during the precipitation of todorokite aggregates. Oxidizing conditions in the Jabuka Pit were also indicated by BULJAN AND ZORE-ARMANDA (1979). For precipitation of manganese, especially at low concentrations, higher Eh values are required, otherwise it remains in solution. According to CHUKHROV ET AL. (1979) a sharp catalytic acceleration of Mn^{2+} oxidation to Mn^{4+} by microorganisms leads to an earlier deposition of manganese from solution than iron, and thus could be responsible of the formation of "Fe-poor" stalactitic todorokite structures such as those found in the Jabuka Pit. The Eh-pH diagram for Mn species in the Jabuka Pit (Fig. 7) shows that under highly oxygenated conditions pyrolusite (MnO_2) should ultimately be the most stable mineral followed by todorokite. Todorokite formation in the Jabuka Pit thus takes place in sufficiently oxygenated conditions at Eh ≈ 0.5 V and a pH around 8.18. Such conditions are expected to prevail in the Jabuka Pit. According to BULJAN AND ZORE-ARMANDA

(1979) the temperature of bottom seawater in the Jabuka Pit ranges from 9 to 12 °C, while the pH varies from 8.14 to 8.22. The average concentrations of O_2 are mostly in the range between 4.85 and 6.21 ml l^{-1}. The formation of stalactitic todorokite structures at the sediment-water interface is obviously caused by a supply of Mn and other trace metals from the near-bottom seawater, as well as from the upper part of the sediment during oxic diagenesis. Oxic diagenesis involving reactions in the oxidized topmost part of the surficial sediment is hypothesized to provide much higher fluxes of Mn and

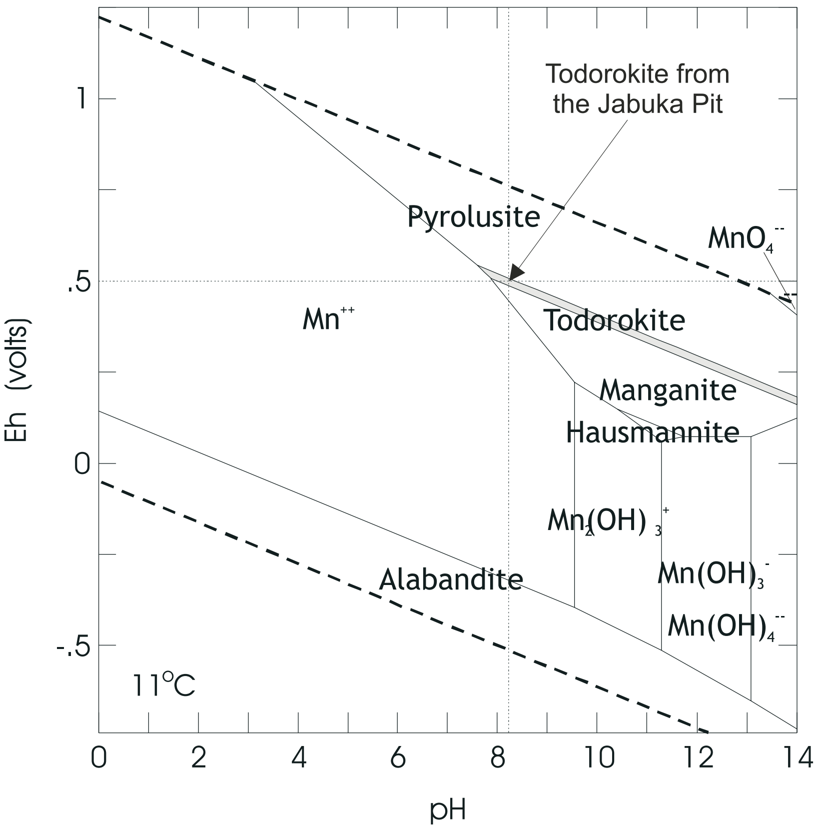


Figure 7. A simplified Eh-pH diagram for dominant Mn species showing the stability fields of common Mn minerals and the Eh-pH conditions of Todorokite precipitation in the Jabuka Pit. The diagram was calculated using the Geochemist Workbench Release 3 Software. The calculations assumed a temperature of 11 °C for bottom water and a pressure of 27 bars. The solubility of Mn species is calculated according to Martin and Knauer (1984) at approximate oxic concentrations of 10^{-8} m. Total concentrations of other components were chosen to be consistent with data for the major element composition of seawater published by Drever (1988).
Slika 7. Poenostavljen stabilnostni Eh – pH diagram za najpomembnejše manganove spojine in območjem izločanja todorokita v Jabučki kotlini. Diagram je napravljen z računalniškim programom Workbench Release 3 Software za temperaturo morske vode 11 °C in pritisk 27 barov. Topnost manganovih spojin je izračunana po Martinu in Knauerju (1984) pri približni koncentraciji mangana v oksičnem okolju (10^{-8} m). Koncentracije ostalih prvin, predvsem glavnih komponent v morski vodi se skladajo s podatki o njihovi vsebnosti, ki jih za morsko vodo navaja Drever (1988).

trace elements to the precipitating todorokite. The release of Mn from the surface sediment in the Jabuka Pit during oxic diagenesis is supported by the Mn enrichment within the upper 0-5 cm of the sediment and its decrease in the deeper parts, as noted by PAUL AND MEISHNER (1976) and KOSTA ET AL. (1978). The topmost part (0-5 cm) of the surficial sediment from the Jabuka Pit contains up to 4250 ppm of Mn, while the Mn concentrations in sediments from deeper sections (5 – 15 cm) are, according to KOSTA ET AL. (1978), considerably lower (up to 1300 ppm). In contrast, only slightly lower Fe concentrations within the upper 0-5 cm of the sediment (3.6 %) as compared to the values (3.9 %) in deeper sediments indicate that Fe remains more or less bound in the sediment (KOSTA ET AL., 1978).

POVZETEK

Todorokit – 10 Å manganat z Jabuške kotline (srednji Jadran)

Nadrobne raziskave feromanganovih prevlek in skorij, Jabučke kotline v srednjem Jadranu, so pokazale prisotnost 10 Å manganata - todorokita. Določili smo ga s pomočjo XRD analize in sicer na podlagi sledečih glavnih odbojev pri 9.62 Å in 4.85 Å ter ostalih odbojev pri 7.13 Å, 2.46 Å, 2.35 Å, 2.13 Å, 1.98 Å and 1.42 Å. Ti se skladajo z odboji za todorokit na JCPDF karticah št.: 38-475, 13-164 in 18-1411 ter odboji za sintetični todorokit, ki jih navajajo BILINSKI ET AL. (2002). Kljub temu, da kažejo rezultati rentgenske analize, da je raziskani mineral najverjetneje todorokit, so za njegovo potrditev in podrobnejšo identifikacijo potrebne še dodatne analize. Todorokit smo našli na lupinicah in odlomkih školjke *Ostrea cochlear Poli,* kjer v glavnem tvori do 1mm velike stalaktitom podobne tvorbe sestavljene iz okrog 4 μm velikih ploščic in kolomorfne oblike ter sferične aggregate. Kvantitativna analiza z SEM-EDS sistemom je pokazala, da je zelo reven z železom, vsebuje pa precej magnezija. Njegov nastanek na območju Jabučke kotline še ni povsem jasen. Zaenkrat predpostavljamo, da se izloča na meji sediment - morska voda. Njegova kristalizacija poteka pri oksidacijskih pogojih in sicer pri Eh ≈ 0.5 V ter pH okrog 8.18. Vir mangana predstavlja morska voda iz dna, ki se bogati s to prvino zaradi migracije mangana iz površinskega dela sedimenta zaradi oksične diageneze.

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