# Mn-crust todorokite mineralization on SW backshore Cretaceous limestones from the island of Dugi Otok (Central Adriatic, Croatia)

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*The southwest shore of the island of Dugi Otok is characterized by the unusual sample occurrence of Mn-hydrated oxide mineralization in the form of botryoidally and globular, fine-laminated concentric aggregates, crusting the Upper Cretaceous backshore limestones. The mineralization consists mainly of Fe impoverished 10-Å tecto-manganate todorokite (enriched in Mg and transition metals) accompanied by accessory MnO·OH. Todorokite chemical composition is typical of a hydrogenous origin in an oxic shallow marine environment. According to our model, Mn has been recurrently leached and mobilized from the Late Pleistocene sea floor sediments located around 50 nautical miles south of Dugi Otok. We propose a link between the Mn-geochemical anomaly of these sediments and the alteration of distinct, spatial close pre-Holocene tephra, dispersed over the entire recent Adriatic area.*

**Key words**: 10-Å manganates, todorokite, hydrogenous origin, pre-Holocene tephra, Dugi Otok island, Adriatic

## INTRODUCTION

The island of Dugi Otok is a part of the Adriatic carbonate platform and belongs to the Dinaridic orogenic mountain chain. The coastal outline of the orogenic topography was ultimately reshaped by extensive sea level rise during Holocene deglaciation (Fig. 1). The island consists entirely of gastropods fosiliferous Upper Cretaceous limestone and minor dolomite (MAMUŽIĆ *et al.,* 1967) showing various karstification morphology phenomena (DŽAJA, 2003). The Mn-mineralization presented by the predominant todorokite and accessory

MnO·OH occurs as fine-laminated films, crusts or small Mn-cretes onto the bedding planes of the host carbonate rocks whereby spatially adjacent goethite mineralization (ŠEGVIĆ et al., 2008) may be also coated by Mn-crusts (Fig. 2). Lithological and geochemical characteristics of Dugi Otok surface rocks preclude them as a potential source of Mn for mineralization.

Mn-(Fe) hydrated oxides are widespread and common marine precipitates. They occur in the oceans as nodules, micro-concretions, coatings and crusts (CRERAR & BARNES, 1974) representing the key to understanding marine geochemical cycles, submarine hydrothermal processes, location of oxygen minimum zones, etc. (e.g. DYMOND et al., 1984; HALBACH, 1986; ABOUCHAMI & GOLDSTEIN, 1995). They may be either hydrogenous precipitates from hydrothermal solutions and ambient sea-water or formed by diagenetic processes showing different respective chemical compositions and distinctive mineralogy (HEIN et al., 1992). In the Adriatic the presence of Mn is ubiquitous, especially in the north Adriatic sea-bottom mainly due to the inputs of the river Po (TANKÉRÉ et al., 2000). Ferromanganese coated structures are reported in the Jabuka pit, central Adriatic (DOLENEC, 2003) and Mn-anomalies were detected in the central Adriatic depression (DOLENEC et al., 1998).
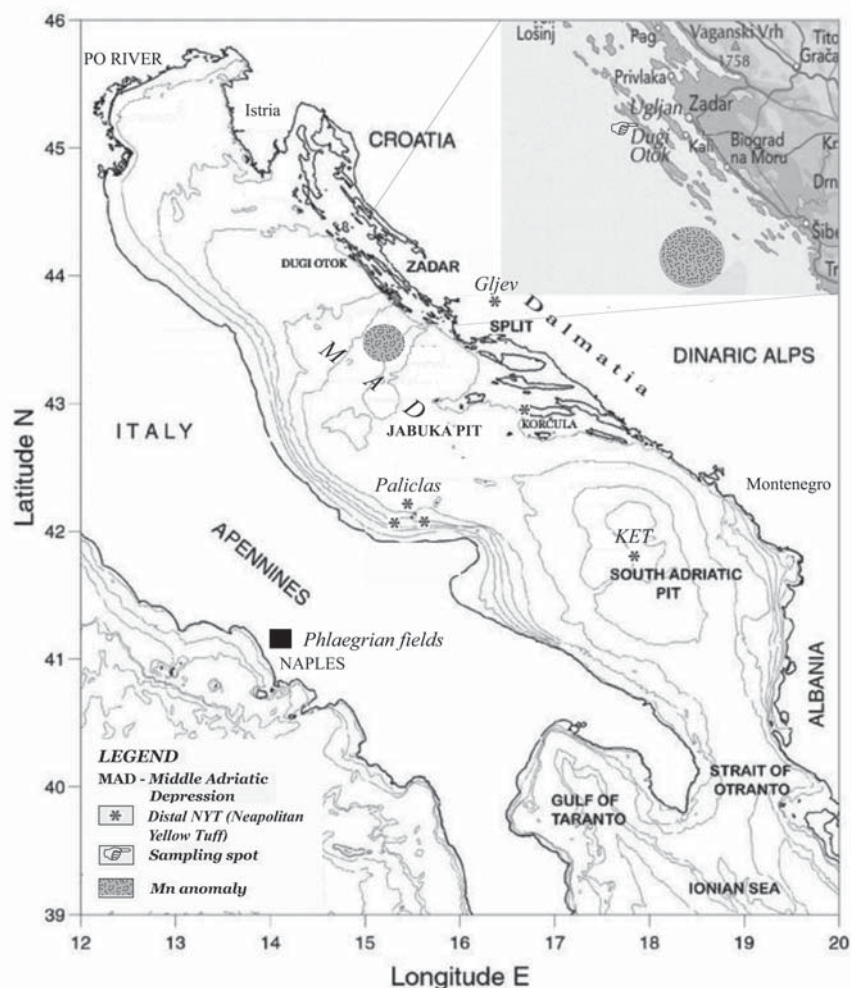


Fig. 1. Map of the Adriatic Sea and the surrounding mainland showing the location of Mn-mineralization on the island of Dugi Otok and the position of the related Mn-anomaly in the middle Adriatic Depression. The relevant sites of Neapolitan Yellow Tuff dispersed from the Campi Flegrei caldera near Naples are indicated as PALIKLAS (CALANCHI et al. 1998), KET (PATERNE et al. 1988), KORČULA and GLJEV

*Fig. 2. Photography of Mn-crete onto the bedding plane of host limestone. Note the sharp crevice infilled by genetically unrelated goethite partly coated by Mn-crete (pen bottom)*

In this work we present, for the first time, evidence of relatively abundant 10-Å Mn mineralization predominantly confined to the SW backshore zone of the island of Dugi Otok (Fig. 1). The aim of this research is to characterize mineralogical and geochemical characteristics of the Mn-mineralization and determine the origin and source of Mn.

## MATERIAL AND METHODS

Manganese crusts and films were manually separated from the host carbonate rocks. The remaining carbonates were dissolved with pH 4.5 buffer solution of $CH_3COONa$ (NaAc/HAc). Powdered samples were analyzed by X-ray diffraction (XRD) at the Faculty of Science, University of Zagreb using a Philips diffractometer 1820 and Cu$K\alpha$ radiation with a graphitic monochromator (V=40 kV, I=35 mA). The samples were scanned at a rate 2 °/min over the range of 4-63° 2Θ. The diffraction patterns were interpreted using the files from the International Centre for Diffraction Data (JCPDS-1996). The phases were identified as follows: todorokite-JCPDF card number 00-013-0164; MnO·OH-JCPDF card numbers 01-089-2354, 01-088-0648; quartz-JCPDF card number 01-086-1630; illite-JCPDF card number 00-002-0056.

The chemical composition of todorokite was measured by SEM EDS and EPMA at the Mineralogical Institute of Ruprecht - Karls University of Heidelberg using the CAMECA SX51 electron microprobe equipped with five wavelength-dispersive spectrometers. The operating parameters were 15 kV accelerating voltage, 20 nA beam current, ~1 μm beam size and 10 s counting time for all elements. Natural minerals, oxides (corundum, spinel, hematite and rutile) and silicates (albite, orthoclase, anorthite and wollastonite) were used for calibration. Raw data for all analyses were corrected for matrix

effects with the PAP algorithm (POUCHOU & PICHOIR, 1984; POUCHOU & PICHOIR, 1985) implemented by CAMECA. Formula calculations were done using a software package designed by Hans-Peter Meyer (Mineralogical Institute of Ruprecht-Karls University of Heidelberg, Germany).

The SEM imagery of the Mn crust was performed at the Geology Department of the Faculty of Science, University of Zagreb using TESCAN instrument equipped with Oxford Instruments INCA analyzing system.

## RESULTS

### Shape and size

The black to earthy colored Mn crust is 5 μm to 300 μm thick, forming aggregates of mostly tecto-manganates. The aggregates show botryoidal, dendritic and globular concentric textures and comprise predominantly of todorokite, accompanied by MnO·OH and very minor quartz and illite. Scanning electron microscope (SEM) imagery depicts manifold surface morphology comprising of aggregates of spherulites, plates and disks as may be clearly observed under different magnification (Fig. 3a, 3b, 3c, 3d).

### XRD mineralogy

Todorokite is identified as the principal mineral phase by the strongest diagnostic peaks of 9.8150 Å and 4,8350 Å corresponding to the reflection pattern of 10-Å manganates. A complete data pattern along with the reference data on the todorokite from the Todoroki mine in Japan is reported in Table 1. Other determined phases are MnO·OH, identified by peaks of
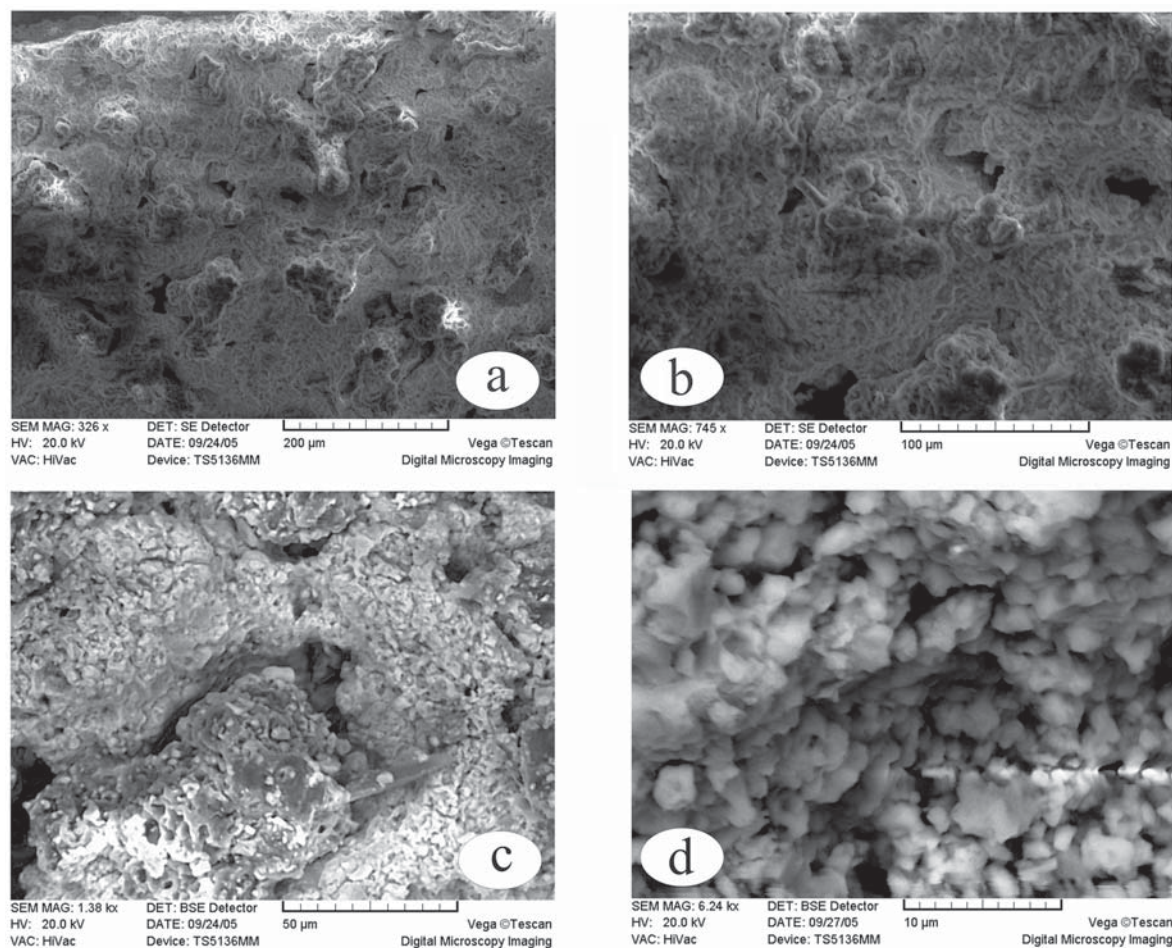


*Fig. 3. SEM imagery of Mn-mineralization showing manifold todorokite morphologies at four different magnifications. The highest magnification depicts mostly aggregated spherulites and minor plates and disks (3d)*

4.2136/4.1996 Å, 2.6972/2.6875 Å and 2.8080/ 2.8175 Å, minor quartz and illite.

## EPMA mineralogy and chemistry

Quantitative EPMA data for todorokite chemistry and calculated structural formulae are presented in Table 2. Mn is arbitrarily assumed to be $Mn^{4+}$. Besides Mn, the most abundant is Al (0.147-1.067 c.p.f.u.). A significant abundance of Mg (0.440-0.881 c.p.f.u.) suggests isomorphic substitution in the M2 position at the edges of the triple $MnO_6$ octahedra chain framework (BURNS & BURNS, 1978). Alkali elements (Na, K), alkali-earth elements (Ca, Ba), Ce, and transition metals (Cu, Co, Ni and Zn) enter the cell to balance the charge and stabilize the manganate structure (e.g. BURNS & BURNS, 1978; LECLAIRE & PERSEIL, 1978). The abundances of large cations K and Ba are highly positively correlated with Mn content (Figs. 4a and 4b) or show a weak

*Table 1. d-spacing (d/Å) and intensity (I/%) for the reference todorokite and todorokite from the Mn-crusts of Dugi Otok*

| Todoroki/Japan (00-13-164) | | Sample BZ-3 todorokite | |
|---|---|---|---|
| $d$ | $I$ | $d_{obs}$ | $I_{obs}$ |
| 9.68 | 100 | 9.82 | 100 |
| 7.15 | 2 | 7.38 | 42 |
| 4.80 | 80 | 4.84 | 65 |
| 3.22 | 15 | 3.23 | 28 |
| 2.46 | 20 | 2.44 | 56 |
| 2.22 | 20 | 2.21 | 7 |
| 1.75 | 10 | 1.72 | 26 |

In parentheses JCPDF card number.

correlation trend for Ca and Na (not shown) whilst the abundance of small cations Al and Mg (Figs 4c and 4d) as well as Si (not shown) are negatively correlated.
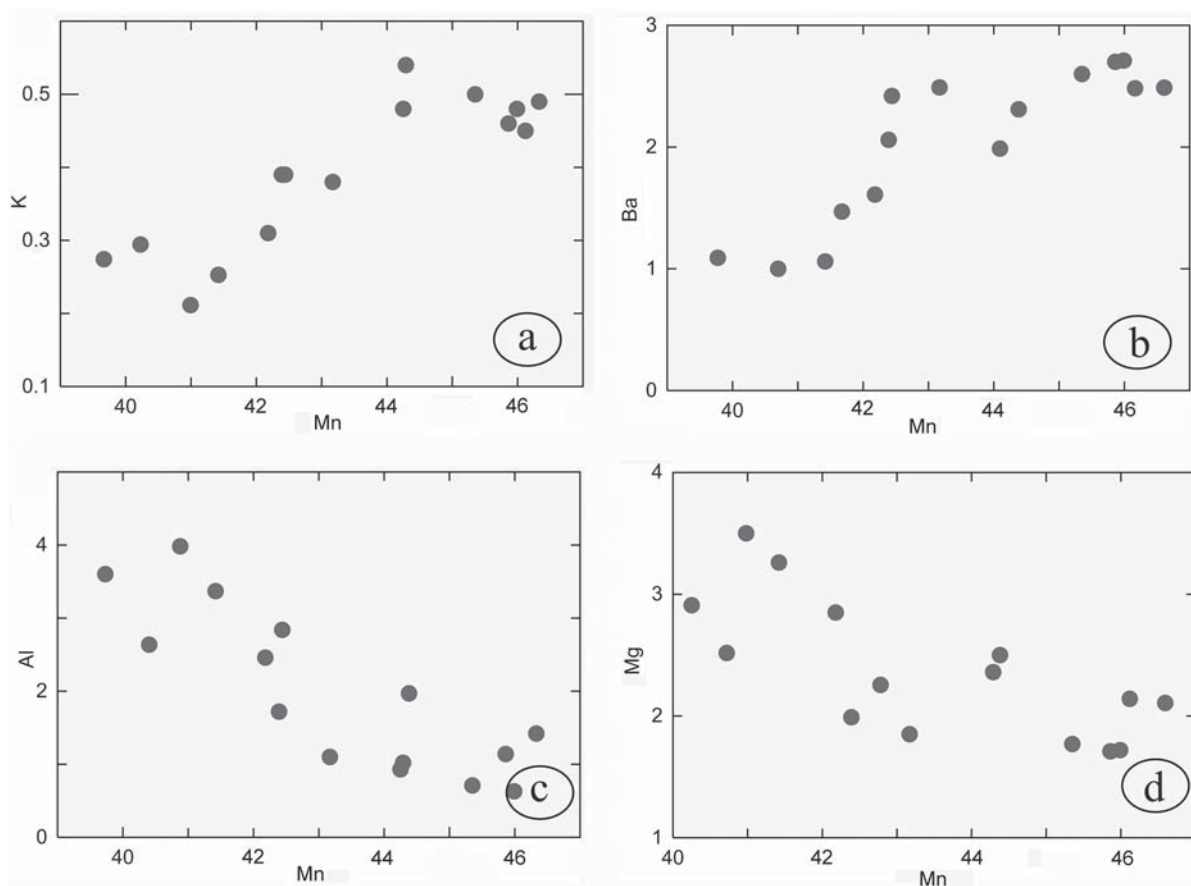


*Fig. 4. Plot of K, Ba, Al and Mg versus Mn (all elements in wt%) for todorokite from Dugi Otok Mn-mineralization*

*Table 2. Selected microprobe chemical analyses (in wt%) of todorokite from the Dugi Otok mineralization and calculated number of cations per formular unit (c.p.f.u.)*

| Analysis No. | bo-3 | bo-7 | bo-8 | bo-11 | bo-12 | bo-18 | bo-21 | bo-24 | bo-25 |
|---|---|---|---|---|---|---|---|---|---|
| $Na_2O$ | 0.75 | 0.95 | 1.05 | 0.95 | 1.06 | 0.97 | 1.36 | 1.32 | 1.14 |
| $Ce_2O_3$ | 0.41 | 0.98 | 0.72 | 0.73 | 1.01 | 0.17 | 0.67 | 0.66 | 0.71 |
| $BaO$ | 1.18 | 3.03 | 2.30 | 2.30 | 3.02 | 0.50 | 2.07 | 1.80 | 2.13 |
| $CoO$ | 0.12 | 0.05 | 0.07 | 0.09 | 0.08 | 2.99 | 1.97 | 1.52 | 0.07 |
| $NiO$ | 1.02 | 0.20 | 0.50 | 0.49 | 0.27 | 2.76 | 1.24 | 1.82 | 0.62 |
| $CuO$ | 0.21 | 0.25 | 0.24 | 0.23 | 0.23 | 0.34 | 0.17 | 0.23 | 0.32 |
| $MgO$ | 5.40 | 2.86 | 4.37 | 3.30 | 2.83 | 6.18 | 3.91 | 4.72 | 3.60 |
| $Al_2O_3$ | 6.37 | 1.19 | 2.69 | 3.25 | 2.15 | 8.58 | 1.92 | 4.64 | 2.82 |
| $SiO_2$ | 0.18 | 0.04 | 0.19 | 0.08 | 0.05 | 0.14 | 0.03 | 0.08 | 0.08 |
| $K_2O$ | 0.27 | 0.58 | 0.59 | 0.47 | 0.55 | 0.19 | 0.65 | 0.38 | 0.49 |
| $CaO$ | 6.12 | 5.01 | 3.29 | 7.33 | 3.77 | 2.23 | 2.24 | 2.72 | 7.82 |
| $MnO_2$ | 65.53 | 72.76 | 73.29 | 67.06 | 72.55 | 58.20 | 70.07 | 66.73 | 64.13 |
| $FeO$ | 0.07 | 0.00 | 0.00 | 0.17 | 0.00 | 0.01 | 0.00 | 0.00 | 0.00 |
| $TiO_2$ | 0.00 | 0.01 | 0.00 | 0.04 | 0.00 | 0.01 | 0.00 | 0.02 | 0.00 |
| $ZnO$ | 0.15 | 0.01 | 0.07 | 0.10 | 0.07 | 0.25 | 0.09 | 0.12 | 0.14 |
| Total[a] (wt%) | 87.97 | 89.46 | 89.60 | 86.71 | 87.83 | 83.72 | 86.55 | 86.93 | 84.16 |

Number of c.p.f.u. on the basis of 12 oxygens and all Mn as $Mn^{4+}$ and all Fe as divalent[b]

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $Na^+$ | 0.147 | 0.193 | 0.206 | 0.194 | 0.214 | 0.198 | 0.279 | 0.266 | 0.241 |
| $Ce^{3+}$ | 0.015 | 0.038 | 0.027 | 0.028 | 0.039 | 0.006 | 0.026 | 0.025 | 0.028 |
| $Ba^{2+}$ | 0.005 | 0.012 | 0.009 | 0.010 | 0.012 | 0.002 | 0.009 | 0.007 | 0.009 |
| $Co^{2+}$ | 0.010 | 0.004 | 0.006 | 0.007 | 0.007 | 0.253 | 0.167 | 0.127 | 0.006 |
| $Ni^{2+}$ | 0.083 | 0.017 | 0.040 | 0.041 | 0.023 | 0.234 | 0.106 | 0.152 | 0.054 |
| $Cu^{2+}$ | 0.017 | 0.020 | 0.018 | 0.018 | 0.018 | 0.027 | 0.013 | 0.018 | 0.026 |
| $Mg^{2+}$ | 0.811 | 0.445 | 0.657 | 0.518 | 0.440 | 0.972 | 0.617 | 0.732 | 0.584 |
| $Al^{3+}$ | 0.756 | 0.147 | 0.319 | 0.404 | 0.264 | 1.067 | 0.240 | 0.569 | 0.361 |
| $Si^{4+}$ | 0.018 | 0.004 | 0.019 | 0.008 | 0.005 | 0.014 | 0.003 | 0.005 | 0.009 |
| $K^+$ | 0.017 | 0.038 | 0.038 | 0.031 | 0.037 | 0.013 | 0.044 | 0.025 | 0.030 |
| $Ca^{2+}$ | 0.661 | 0.561 | 0.355 | 0.827 | 0.422 | 0.252 | 0.254 | 0.302 | 0.911 |
| $Mn^{4+}$ | 4.560 | 5.258 | 5.105 | 4.884 | 5.232 | 4.243 | 5.120 | 4.793 | 4.823 |
| $Fe^{2+}$ | 0.006 | 0.000 | 0.000 | 0.015 | 0.000 | 0.001 | 0.000 | 0.000 | 0.000 |
| $Ti^{4+}$ | 0.002 | 0.001 | 0.000 | 0.003 | 0.000 | 0.001 | 0.000 | 0.002 | 0.000 |
| $Zn^{2+}$ | 0.011 | 0.000 | 0.005 | 0.008 | 0.006 | 0.019 | 0.007 | 0.009 | 0.011 |
| Total[c] | 7.115 | 6.739 | 6.805 | 6.996 | 6.718 | 7.304 | 6.884 | 7.033 | 7.094 |

[a] Chlorine (0.14–0.23 wt%) is included in the totals. The deficiency from 100 wt% corresponds to 3.4–4.0 $H_2O$ p.f.u (approx. 9 wt% $H_2O$).

[b] Total Fe was arbitrarily assumed to be $Fe^{2+}$ to diminish the ion vacancies deficiency.

[c] Deficiency from the ideal total of 8 c.p.f.u is due to $Mn^{4+}$ ion vacancies expected to appear in the M2 positions at the edges of the triple $MnO_6$ octahedra chains framework (BURNS & BURNS, 1978)

## DISCUSSION

Todorokite is a 10-Å tecto-manganate with multidimensional zeolite like tunnels formed by walls of edge-shared $MnO_6$ octahedra (POST, 1999) and is consequently a very important host phase for strategic metals (such as Ni, Cu, Pb, Zn and Co) and large cations (Na, K, Ba, Ce) due to allocating them into the structural channels. The abundance of these elements in todorokite is primarily controlled by their content in seawater and oxygen fugacity of the environment as has been shown for deep sea todorokite occurrences in the Quaternary sediments from the Jabuka Pit in the Central Adriatic (DOLENEC, 2003).

Mn-mineralization at the island Dugi Otok is restricted to the Upper Cretaceous carbonates of SW backshore and adjacent submarine terraces of bedding carbonates. Mineralization is characterized by well-crystallized, low Fe todorokite and accessory MnO·OH. Todorokite is stable in the marine environment showing a well-ordered structure due to low Fe in the solution (MORGAN & STUMM, 1965; HALBACH *et al.,* 1975). Analyzed todorokite contains a high abundance of Ba, Ni, Co, Cu (Table 2) typical of hydrogenous 10-Å tecto-manganate formed by direct precipitation of colloidal particles from the seawater. In the ternary diagram discriminating genetically different todorokites on the basis of the relative abundances of Mn, Fe and (Ni + Cu + Zn) our samples fall in the field of todorokites formed by marine hydrogenous and diagenetic processes (Fig. 5), thus also corroborating the marine source of Mn for mineralization.

Most of the transition elements are very sensitive to the redox potential of seawater and their relative abundance in Mn-oxides is used to distinguish hydrogenous oxic and suboxic environments, respectively. Enrichment of Cu, Ni, Zn and Co found in seawater Mn-oxides from the oxic environments is caused by their higher solubility compared to Mn thus making these elements capable of allocating into one of the octahedral positions of Mn-precipitates (WINTER *et al.,* 1997). The high correlation of Cu/Al and Mn/Al ratios (Fig. 6) and comparative enrichment of Cu relative to Mn in Dugi Otok
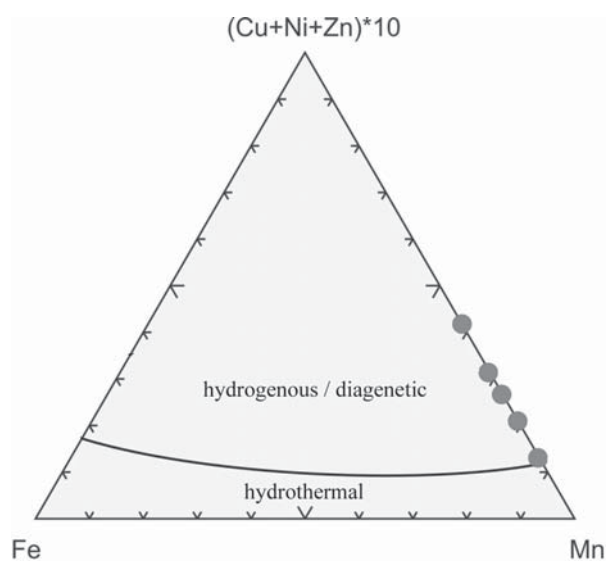


*Fig. 5. Fe – (Cu + Ni + Zn)∗10 – Mn diagram (BONATTI et al., 1972) discriminating hydrogeneous or diagenetic todorokite from hydrothermally precipitated todorokite. All elements are in wt%*

todorokite are diagnostic of hydrogenous oxic conditions.

Concerning the size of the investigated Mn-mineralization, the crucial question is from where the Mn for mineralization was derived? We believe that the most viable source is located some 50 nautical miles south of Dugi Otok Island (Fig. 1). There is a strong Mn-anomaly in the sea floor depression sediments attributed to the submarine weathering of gabbroic rocks from the islands of Jabuka and Brusnik (DOLENEC *et al.*, 1998).

However, we suggest another substratum as the parental source for this Mn-anomaly by linking it to the alteration of distal volcanic ash (tephra). We assume the Neapolitan Yellow Tuff (NYT) as the best candidate for the parental source. The NYT erupted 14.9 ka BP (DEINO *et al.*, 2004; SCHMIDT *et al.*, 2002) as the last pre-Holocene high-magnitude eruption from the Campi Flegrei near Naples in Italy. The NYT pumiceous ash was dispersed to the north over the entire ancient Adriatic mainland as we may conclude from known occurrences (Fig. 1) in the off-shore sediments (CALANCHI *et al.,* 1998; PATERNE *et al.*, 1988) and on-land deposits.
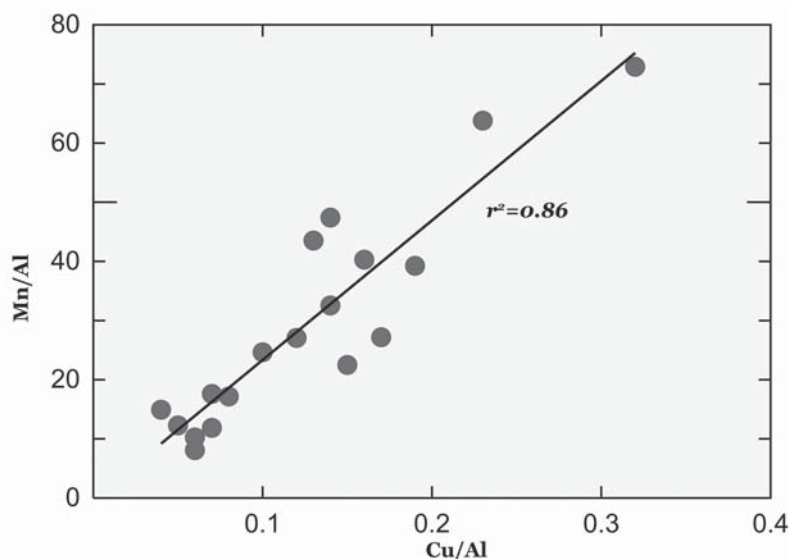
*Fig. 6. Mn/Al versus Cu/Al in Dugi Otok todorokite. All elements are in wt%*

Due to the onset of Holocene deglaciation and rapid sea level rise 10-8 ka BP (GIORGETTI & MOSETTI, 1969) tephra of a different alteration stage accumulated in the submerged Adriatic pits.

Since tephra has relatively low chemical stability during the post-depositional stage, cation leaching from the matrix may be very efficient (POLLARD et al., 2003). Adriatic on-land NYT tephra abundantly contains peculiar black, loose low-Fe todorokite nodules characteristic for decoupling of Fe and Mn even in the early stage of alteration. These nodules contain enhanced Ce and Ba abundances but are very low in transition heavy metals, typical of manganates from pedogenic and freshwater Fe-Mn nodules (PALUMBO et al., 2001). We suggest that similar processes might have been very common for all NYT tephra strewn over the Adriatic. However, the main alteration of the NYT took place after it had been marine redeposited. In the highly oxidizing environment Mn is readily leached from a volcano-sedimentary succession by interaction with seawater (KOSCHINSKY & HEIN, 2003) forming manganate nodules which, besides Ba and Ce, may characteristically adsorb a significant amount of many trace elements from

seawater (CHAUHAN et al., 1994; KOSCHINSKY & HALBACH, 1995).

Manganese of the investigated mineralization was being mobilized from the source located in the Dugi Otok depression by submarine currents during stormy weather characterized by strong stormy southerly winds (sirocco). It was followed by oxidation of manganese with self-sustaining growth of colloidal $MnO_2$ particles. A mesh of todorokite crystallites might have formed from $MnO_2$ particles by fixing large cations and heavy metal cations from circulating marine water inside the channel structure (BURNS & BROWN, 1972). Todorokite and $MnO \cdot OH$ have been successively precipitating onto higher and higher backshore carbonate terraces at the outward coast of the island of Dugi Otok consistent with the sea-level rise from the onset of Holocene to the Present.

The geochemical input of Mn from the river Po is confined to the north Adriatic and only one third of the total input is transported to the central Adriatic (TANKÉRÉ et al., 2000). Thus, neglecting unfavorable geographic and climatic parameters governing the possible input of Mn, the contribution of Mn from the river Po to the Adriatic appears insufficient to produce mineralization of such an extent.

## CONCLUSIONS

At the outward coast of the island of Dugi Otok a todorokite and MnO·OH crust has been successively precipitating during stormy weather characterized by southly winds from the onset of the Holocene to the Present. Manganese for mineralization was derived from the Mn-rich sediments located in the Dugi Otok depression. The Mn-anomaly of these sediments is believed to be caused by alteration of NYT tephra colluviated in the middle Adriatic pits at the beginning of Holocene.

## ACKNOWLEDGEMENTS

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# Manganska mineralizacija todorokitom po krednim vapnencima u zoni plime i oseke na jugozapadnoj strani Dugog otoka (središnji Jadran, Hrvatska)

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**SAŽETAK**

Na jugozapadnoj obali Dugog otoka prema otvorenom moru u zoni plime i oseke postoji neobična i obilna pojava mineralizacije manganom u formi hidratiziranih oksida. Javlja se kao ovojnica, kora, tanka presvlaka, odnosno kao grozdasti fino laminirani, koncentrični agregat na gornjokrednim vapnencima i dolomitima. Mineralizaciju čine željezom osiromašeni 10-Å tekto-manganati s prevladavajućim todorokitom. Kemijski sastav todorokita ukazuje na hidrogenetsko podrijetlo u oksičnom okolišu plitkog mora. Držimo da je mangan potrebit za mineralizaciju izlužen i mobiliziran iz pridnenih sedimenata smještenih nekih 50 nautičkih milja južno od mjesta mineralizacije. Mangan je bio izvorno vezan u prhkim piroklastičnim naslagama raspršenim vulkanskim erupcijama iz flegrejskih polja pored Napulja po cijelom jadranskom području neposredno pred početak holocena.

**Ključne riječi:** 10-Å manganati, todorokit, hidrogenetsko podrijetlo, pred holocenska tefra, Dugi Otok, Jadran