

# Si-P impure Al-goethite mineralization on the island of Dugi otok (Central Adriatic, Croatia)



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## Geologia Croatica

### ABSTRACT

*At the western seaward coast of the island of Dugi otok, unusual goethite mineralization occurs as the infilling of a system of thin crevices in the Upper Cretaceous limestones of the Adriatic carbonate platform. Goethite is exceptionally well ordered and shows a variety of chemical compositions ranging from almost pure FeO·OH to Al-substituted composition accompanied by high Si and P impurity. The most characteristic textural type assemblages are goethite and coarse grained calcite in composite aggregates. These aggregates contain Al-substituted goethite with metamorphic silicate minerals embedded in the core (black goethite), armoured by the XRD-pure, almost stoichiometric goethite (brown goethite). The geochemical and mineralogical features of the mineralization suggest an ascending solution from a hidden metamorphic source. We speculate that the source could have been activated by the thermal influx linked to the Pliocene intraplate magmatism in the eastern segment of Adria.*

**Keywords:** Al-goethite, stoichiometric goethite, crystalchemistry, endogenic origin, Dugi otok, Adriatic Sea, Adria microplate, Croatia

### 1. INTRODUCTION

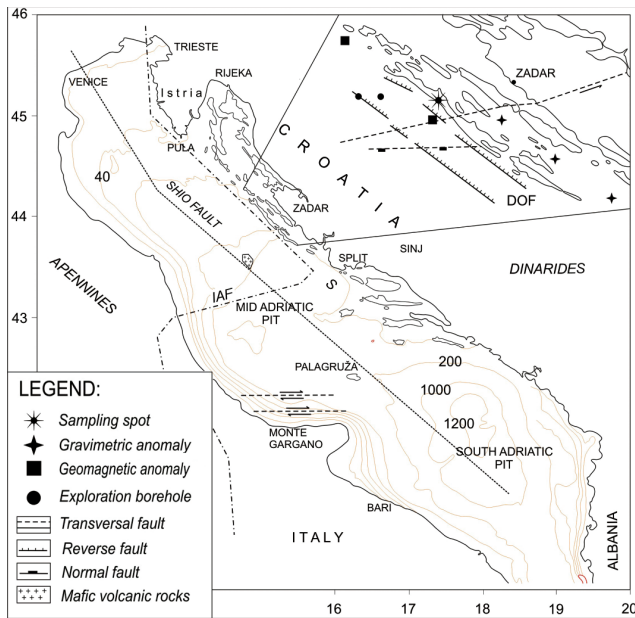
In carbonate terrains goethite is a common paragenetic mineral in soils, particularly in terra rossa, and is also found as principal constituent of Fe-cretes or it can be traced as the major phase in some mineral deposits in karstified areas. These kinds of goethite appearance are obviously controlled by weathering which cause an environment favouring formation of acidic solutions. The type and extent of goethite mineralization is dependent on the geochemical ability and amount of substrate available during the weathering processes. The mineralization has collomorph textures; goethite is low Al-substituted and poorly crystallized.

This work provides evidence of a completely different kind of goethite mineralization in the Adriatic segment of the Adriatic-Dinaride carbonate platform, with the type locality occurrence in the Brbinšćica cove on Dugi otok (Central Adriatic). Here, very fine aggregates of well crystallized, Al-substi-

tuted and stoichiometric goethite, accompanied by coarse grained calcite infill sharp tectonic crevices and inter-bedding planes in the Upper Cretaceous limestones. The mineralization suggests precipitation from a basic solution and a deep placed source, rich in Fe, Al, Si and P. Here, we present a set of X-ray diffraction (XRD), scanning electron microscope (SEM) and electron probe microanalyses (EPMA) mineralogical and geochemical data on the goethite mineralization. The origin of the mineralization is discussed and its significance on a regional scale is stressed in regard to the northern submerged segment of the Adria microplate.

### 2. GEOLOGICAL SETTING AND MINERALIZATION TEXTURES

Dugi otok, as part of the Adriatic carbonate platform, belongs to the Dinaridic orogenic mountain chain which was finally shaped by extensive sea level rise during the Holocene degla-



**Figure 1:** Map of the Adriatic Sea and surrounding mainland showing the location of goethite mineralization on Dugi otok. DOF = Dugi otok fault; IAF = Internal Adriatic fracture (Geophysical anomalies according to BRDAREVIĆ & OLUIĆ, 1979 and KOŠĆEC, 1986)

ciation (Fig. 1). The island consists entirely of Upper Cretaceous dolomites and limestones showing various karstification morphologies (DŽAJA, 2003).

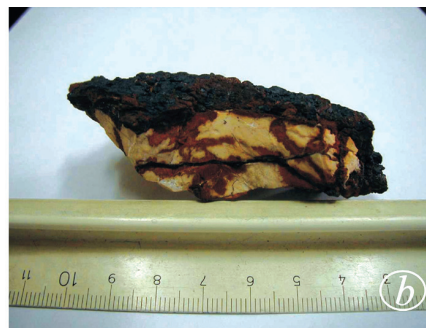
Goethite mineralization occurs exclusively along the western seaward coast of the island, as the infilling of interbedding planes (Fig. 2A) and subvertically, up to 10 cm thick tectonic crevices in the host limestones (Fig. 2B) which abundantly contain chondrodonts and rudists of the Cenomanian age.

Goethite mineralization shows three textural types. Mineralization of textural type 1 is confined to the veins inside the host limestones filled with a paragenetic assemblage consisting of aggregates of submicronic goethite and euhedral coarse grained calcite (Fig. 3A). Due to the microscopic to submicroscopic sized silicate mineral impurities, goethite aggregates show a black inner part (black goethite core), surrounded by the brown goethite without XRD detectable inclusions (brown goethite mantle).

The textural type 2 (Fig. 3B) comprises brown goethite aggregate [plus a minor quantity of submicroscopic quartz] fillings of micro fractures inside the host limestone. Although similar to the previous type 2, the textural type 3 (Fig. 3C) is characterised by an admixture of the virtual waxy quartz impregnations along the host limestone bedding planes.



**Figure 2:** Photography of an outcrop of goethite mineralization at Brbinšćica cove, infilling the system of interbedding planes (A) and subvertical tectonic crevices (B) in the host Upper Cretaceous limestone from the shallow sea and high-tidal zone. The occurrence comprises goethite mineralization of textural type 1.



**Figure 3:** Photographs of hand specimens of goethite mineralization of textural type 1 (A), textural type 2 (B) and textural type 3 (C). On textural type 3 completely genetic and temporal independent todorokite mineralisation is observed which is the subject of another paper (LUGOVIĆ et al., 2008). For goethite mineralization details see the text.



### 3. ANALYTICAL METHODS

Samples representing all three textural groups were treated with pH 4.5 buffered NaAc/HAc solution to dissolve calcite and disaggregate the goethite. Brown and black goethite of textural type 1 separated as virtually pure fractions by hand picking, using a binocular microscope after crushing the composite sample.

The XRD analyses of powdered separates from the goethite mineralization textural types 1 and 2 were performed at the Faculty of Mining, Geology and Petroleum Engineering, University of Zagreb, using a Phillips diffractometer 1820 and CuK $\alpha$  radiation, graphitic monochromator (U = 40 kV, I = 35 mA). The samples were scanned at a rate of 0.5°/min over the range of 2–70° 2 $\theta$ . The mineral phases were identified using the Powder Diffraction File (1996)<sup>(\*)</sup> data system (goethite – JCPDF cards number 00-029-0713; calcite – JCPDF cards number 00-005-0586; quartz – JCPDF cards number 00-005-0490). The XRD analyses of textural type 3 were done at the Faculty of Science, University of Zagreb using a Phillips diffractometer X'PERT PRO (U = 45 kV, I = 40 mA). The samples were scanned at the rate of 2°/min over the range of 4–64° 2 $\theta$  and the diffraction patterns were identified using the JCPDS system data base (quartz – JCPDF cards number 00-046-1045).

The chemical composition of goethite from textural types 1 and 2 was measured by SEM EDS and EPMA at the Mineralogical Institute of the Ruprecht-Karls University of Heidelberg using the CAMECA SX51 electron microprobe equipped with five wavelength-dispersive spectrometers. Operating parameters were 15 kV accelerating voltage, 20 nA beam current, ~1  $\mu$ m beam size and 10 s counting time for all elements. Natural minerals, oxides (corundum, spinel, haematite 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 & PICOIR, 1984, 1985) implemented by CAMECA. Formulae calculations were done using a software package designed by Hans-Peter Meyer (Mineralogical Institute of the Ruprecht-Karls University of Heidelberg).

## 4. RESULTS

### 4.1. XRD mineralogy

Goethite of textural type 1 characterizes strong peaks at 4.1698 Å, 2.4499 Å and 1.7195 Å for *black* aggregate, and 4.1730 Å, 2.4469 Å and 1.7166 Å for *brown* aggregate (Table 1). The XRD patterns of both aggregates suggest relatively high crystallinity, particularly that of the black variety. Quartz was identified as the mixing phase within the black aggregate, whereas the XRD pattern of the brown aggregate identified only goethite. Unit cell crystallographic parameters for brown and black goethite from the mineralization textural type 1 are displayed in Table 2. The *b* axis dimensions are almost identi-

**Table 1** Values for d-spacing (*d*/Å) and intensity (*I*/%) for the referent goethite and for brown and black goethite from the Dugi otok mineralization textural Type 1

Hindlow. UK (00-029-0713)		Sample Do-1d brown goethite		Sample Do-1c black goethite	
<i>d</i>	<i>I</i>	<i>d</i> <sub>hkl</sub>	<i>I</i> <sub>hkl</sub>	<i>d</i> <sub>hkl</sub>	<i>I</i> <sub>hkl</sub>
4.9800	12	4.9661	14	4.9599	12
4.1830	100	4.1730	100	4.1698	100
3.3830	10	3.3799	16	3.3749	9
2.6930	35	2.6900	40	2.6899	27
2.5270	4	2.5219	5	2.5212	8
2.4890	10	2.4857	8	2.4863	9
2.4500	50	2.4469	63	2.4449	39
2.2530	14	2.2498	14	2.2499	7
2.1900	18	2.1836	15	2.1876	14
2.0890	1	2.0078	3	2.0888	3
1.9200	5	1.9176	6	1.9172	3
1.7728	1	1.7166	21	1.7196	20
1.5637	10	1.5638	10	1.5649	10
1.4541	5	1.4536	11	1.4552	7

**Table 2** Crystallographic parameters of the brown and black goethite of the Dugi otok mineralization textural Type 1

Cell Parameters	brown (Do-1d)	black (Do-1c)
<i>a</i> (Å)	4.609(1)	4.616(2)
<i>b</i> (Å)	9.961(2)	9.963(3)
<i>c</i> (Å)	3.015(8)	3.022(1)
Volume	138.44(5)	138.99(6)

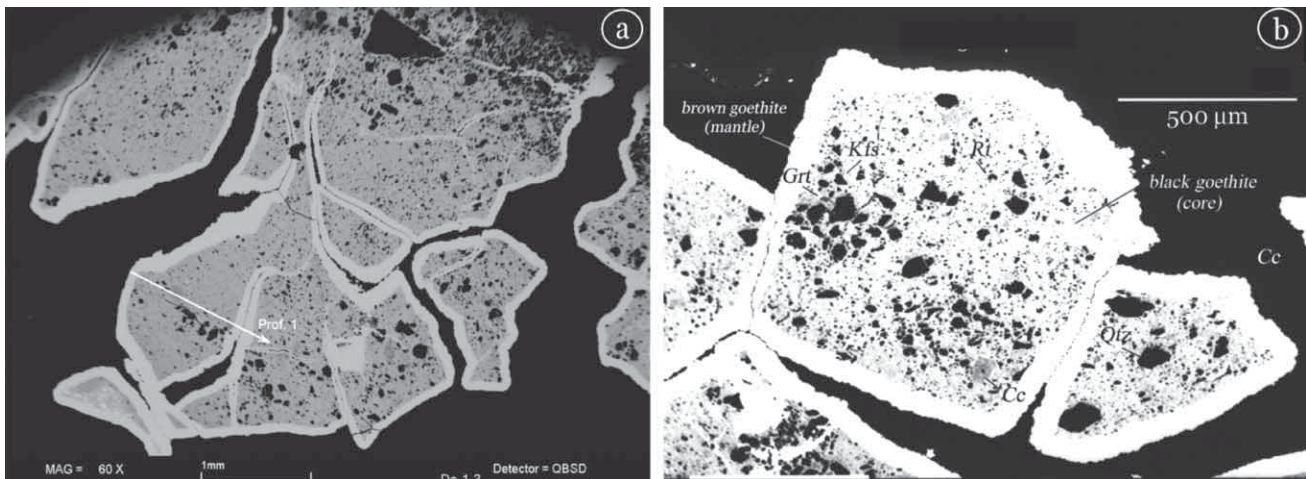
cal while the *a* and *c* axes of black goethite, i.e. Al-substituted variety (see below), are slightly larger resulting in its larger unit cell volume. Since Al<sup>3+</sup> is smaller than Fe<sup>3+</sup> these data appear crystallochemically illogical and will be revisited in the discussion.

Goethite of textural types 2 and 3 is characterized by strong peaks at 4.176 Å, 2.444 Å, 1.717 Å and 4.915 Å, 2.577 Å, 1.720 Å respectively. Quartz is a mixing phase in both types as well as MnO·OH in the textural type 3.

### 4.2. EPMA and SEM mineralogy and chemistry

Scanning electron microscope (SEM) observations (Figs 4A and 5) revealed that goethite mineralization of textural type 1 comprises a heterogeneous core, with various embedded petrogenetic minerals (*black goethite*), and a homogenous mantle consisting of goethite free of virtual inclusions (*brown goethite*). K-feldspar (Or<sub>91.4-94.9</sub>Ab<sub>5.1-8.4</sub>), almandine-rich metamorphic garnet (Py<sub>9.7</sub>Alm<sub>62.5</sub>Sp<sub>5.0</sub>And<sub>4.5</sub>Gro<sub>17.9</sub>), calcite, quartz and

(\*) JCPDF International center for diffraction data (1996)



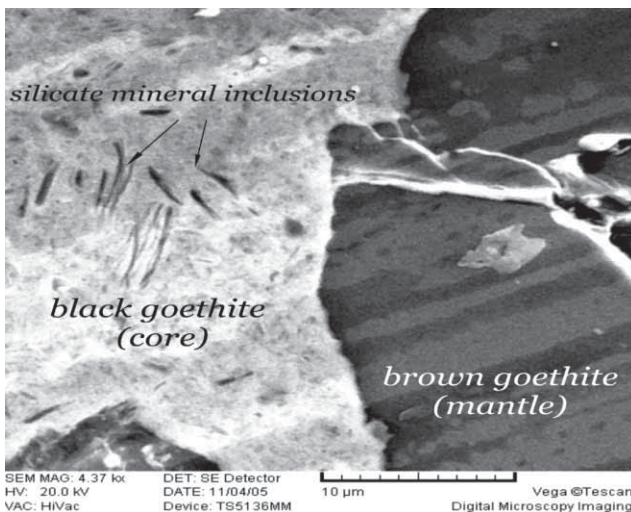
**Figure 4:** **A.** SEM imagery of goethite mineralization textural type 1 showing the location of the EPMA WDS measured compositional profile. Black goethite in the core (grey) includes various mineral impurities. Clean brown goethite (bright) forms a mantle around the black goethite. **B.** BSE imagery of goethite mineralization textural type 1. Kfs = K-feldspar, Grt = garnet, Rt = rutile, Qtz = quartz and Cc = calcite inclusions.

rutile were identified amongst the inclusions in the black goethite (Fig. 4B). Textural type 2 goethite showed no such regularities in the sense of structural and chemical disunity.

Although the EPMA measurements were performed using a highly focused beam ( $\sim 1 \mu\text{m}$ ), all goethite analyses appear to be contaminated by accessory phases, particularly quartz (Table 3). However, the measured chemical compositions from the black and brown segments of type 1 mineralization are clearly distinguished in the  $\text{Fe}_2\text{O}_3/(\text{Fe}_2\text{O}_3+\text{Al}_2\text{O}_3)$  vs.  $\text{Fe}_2\text{O}_3$  plot (Fig. 6). The majority of the analyses from the black segment form a narrow compositional field (70–76 wt %  $\text{Fe}_2\text{O}_3$ , Fe-Al ratio 0.91–0.94), and closely represent the composition of Al-substituted, i.e. black goethite. Brown mantle goethite shows comparatively low  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  (Table 3) and with the  $\text{Fe}_2\text{O}_3/(\text{Fe}_2\text{O}_3+\text{Al}_2\text{O}_3)$  ratio of  $\sim 1$  resembles the stoichiometric composition. The discrete knobby varieties itself

show similar polarized compositions independent of the textural position of the analyzed spots (Fig. 6).

Random SEM EDS analyses of goethite of textural type 1 are displayed in Fig. 7 as four major correlation trends. The correlation diagram  $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$  (Fig. 7A) depicts the positive correlation of silica with Al, i.e. it constrains silica exclusively along with the Al-goethite in the black cores ( $r^2=0.69$ ). The established  $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$  correlation is plotted against the  $\text{Fe}_2\text{O}_3$ , MgO and  $\text{P}_2\text{O}_5$  (Figs. 7B–7D) abundances. A negative  $\text{Fe}_2\text{O}_3$  correlation in respect to the  $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$  ( $r^2=0.52$ ) (Fig. 7B) amount shows the wane of goethite Fe content towards the mineral core. A positive MgO correlation in respect to the  $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$  amount ( $r^2=0.37$ ) (Fig. 7C) corroborates an amount of crypto-crystalline silicate phases in the goethite core. SEM EDS analyses revealed unusually high  $\text{P}_2\text{O}_5$  concentration in the analyzed goethite (up to 2.8 wt %, Fig. 7D). Higher phosphorus values are associated with high  $\text{Fe}_2\text{O}_3$  values (80–100 wt %) suggesting its compositional enrichment in the goethite black core aggregates.



**Figure 5:** SEM imagery of goethite mineralization type 1 showing in more detail the relationships from Figs. 4A and B. Black goethite (light grey) exhibits various silicate mineral inclusions (black spots). Clean brown goethite (dark) forms a rim around the black goethite.

## 5. DISCUSSION

### 5.1. Mineralization assemblage and goethite chemistry

Due to the slow goethite growth, the analysed mineralization consists of numerous medium to high crystallinity submicroscopic goethite crystallites. The mineralization is composed almost entirely of goethite. Impurities within goethite (especially black goethite of textural type 1), comprise silicate phases (quartz, K-feldspar, metamorphic garnet and rutile) and calcite. However, apart from coarse calcite and ubiquitous quartz, their amount is always below the XRD detection limit ( $\sim 5 \text{ wt } \%$ ).

It is known that quartz and P, (in the form of  $\text{PO}_4^{3-}$ ), bind to the reactive places of goethite terminal faces and do not enter the crystal structure (GLASAUER et al., 1999; PARFITT, 1979, 1989). In synthetic goethite, silica is constrained to be adsorbed on surfaces and located within the pores between structural domains (FISHER, 1999; GLASAUER et al., 1999).

**Table 3** Selected microprobe spot analyses (in wt.%) of the Dugi otok goethite mineralization

Mineralization type	I <sub>c</sub>	I <sub>c</sub>	I <sub>m</sub>	I <sub>m</sub>	II	II	III	III
Analyses no.	9a	27	02	17	01	04	04b	02a
SiO <sub>2</sub>	7.54	11.31	1.79	1.68	6.49	2.34	6.42	15.36
TiO <sub>2</sub>	0.17	0.31	0.00	0.00	0.05	0.02	0.09	0.35
Al <sub>2</sub> O <sub>3</sub>	5.97	11.46	0.04	0.05	4.77	0.00	4.59	9.12
Cr <sub>2</sub> O <sub>3</sub>	0.00	0.02	0.00	0.00	0.02	0.00	0.02	0.04
Fe <sub>2</sub> O <sub>3</sub>	71.22	60.59	81.12	81.08	71.57	78.26	72.59	58.36
MnO	0.00	0.06	0.08	0.03	0.06	0.03	0.14	0.12
MgO	0.55	0.48	0.12	0.18	0.99	0.09	0.76	1.46
CaO	0.25	0.21	0.33	0.36	0.38	0.34	0.52	0.82
Na <sub>2</sub> O	0.16	0.20	0.05	0.02	0.21	0.10	0.12	0.18
K <sub>2</sub> O	0.42	0.13	0.02	0.00	0.19	0.01	0.52	1.88
Total	86.29	84.77	83.55	83.40	84.73	81.19	85.77	87.69
Al subst. (mol. %)	13.10	29.60	0.10	0.10	10.40	0.00	9.90	24.50

- mineralization types I, II and III match different textural types (see text for detail information).
- c=core, m=mantle of the goethite appearance from the textural type 1.
- Al subst. (mol. %) corresponds to goethite formula calculated on the basis of 1.5 oxygen and 1.0 total cation after subtraction of SiO<sub>2</sub> and alkalis from the EPMA point analyses.

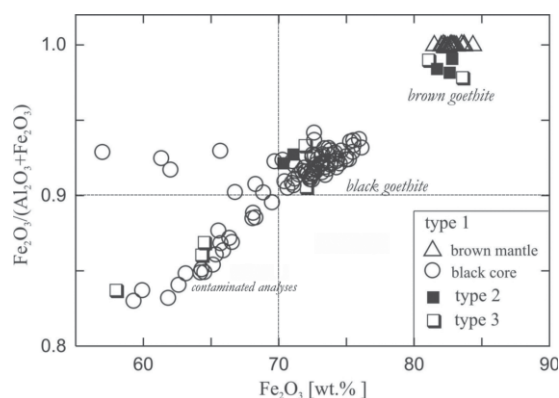
This variety is colloquially named Si-goethite. We propose to avoid this name since silica is not structured into the goethite cell. In the basic and slightly acid environment, phosphate willingly makes complexes with Fe<sup>3+</sup> depending on reactive surface FeO·OH groups and the crystallinity of the oxide. The reaction probably involves a rapid, strong ligand exchange, followed by weaker ligand exchange and phosphate penetration at defective sites and pores (PARFITT, 1989). Therefore, the random phosphorus content of analysed black goethite (Fig. 7D) reflects its complex porosity.

The measured goethite chemical composition was influenced by the chemistry of irradiated submicronic impurities, causing a significant number of analyses to be contaminated (Fig. 6, Fe<sub>2</sub>O<sub>3</sub> < 70 wt %). Results with Fe<sub>2</sub>O<sub>3</sub> > 70 wt % may be accepted as the least contaminated or even uncontaminated (Fe<sub>2</sub>O<sub>3</sub> > 80 wt %). The results between 70 and 76 wt % Fe<sub>2</sub>O<sub>3</sub> obtained for black goethite cores of textural type 1 show a high abundance of Al, (Table 3, Fig. 6) and Si, which is mostly allocated to quartz. The amount of Al cannot be stoichiometrically combined with other analyzed cations to yield any known (silicate) mineral phase. Since Al (oxy)hydroxides are excluded as possible paragenetic minerals, we presume that Al is substituted for Fe in the goethite aggregated black core of the textural type 1, (Fig. 6, Fe<sub>2</sub>O<sub>3</sub>/(Al<sub>2</sub>O<sub>3</sub>+Fe<sub>2</sub>O<sub>3</sub>) ratio varies from 0.90 to 0.95). Goethite from the brown mantle of the same textural type is Al poor (Fig. 6, Fe<sub>2</sub>O<sub>3</sub>/(Al<sub>2</sub>O<sub>3</sub>+Fe<sub>2</sub>O<sub>3</sub>) ratio ~1), and resembles a near stoichiometric composition.

In natural goethite, Fe<sup>3+</sup> is readily substituted by Al occasionally reaching up to 0.33 mole fraction (e.g. FITZPATRICK & SCHWERTMANN, 1982; TARDY & NAHON, 1985; FABRIS et al., 1986; CARLSON, 1995). The degree of substi-

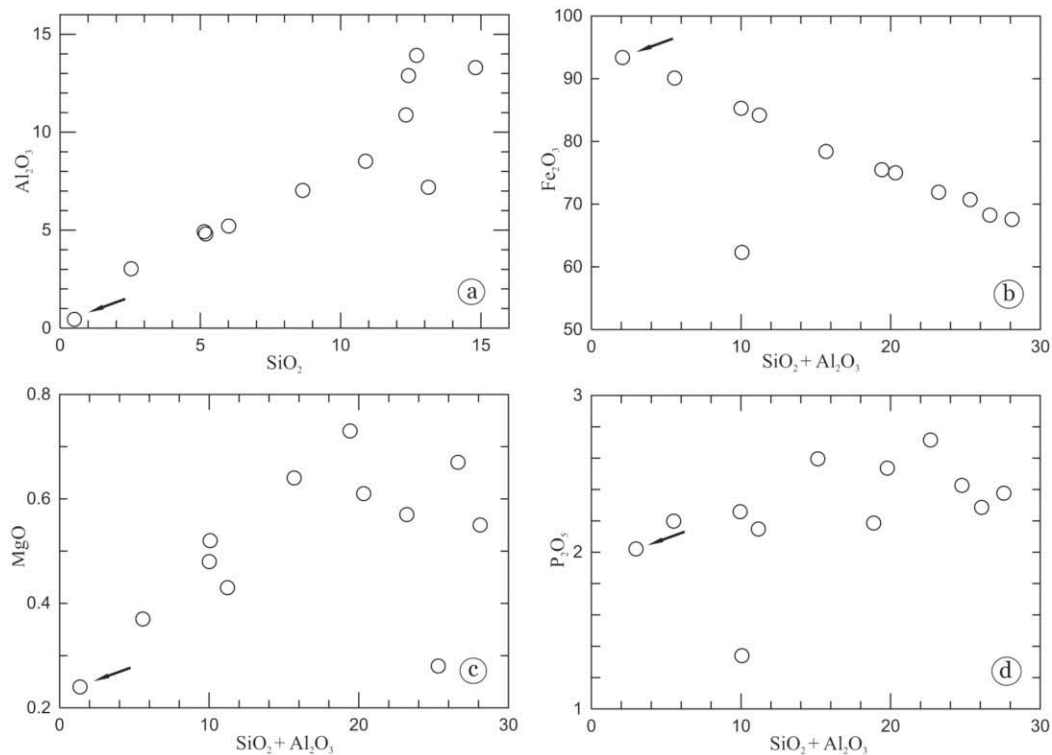
tution of Al for Fe is one of the parameters favouring high P abundance in goethite (AINSWORTH & SUMNER, 1985). Al substituted goethite from the analysed goethite mineralization strongly supports this statement by a positive correlation of P and Al abundances (Fig. 7D).

Referring to the unit cell parameter contradiction, i.e. larger cell volume of Al-substituted goethite (black goethite) compared to the stoichiometric goethite (brown goethite), the phenomenon can be explained with random Al-substitution as a plausible cause of this crystallochemical discrepancy. Investigations of Al-substituted goethite precipitated at relatively



**Figure 6:** Plot of Fe<sub>2</sub>O<sub>3</sub>/(Fe<sub>2</sub>O<sub>3</sub>+Al<sub>2</sub>O<sub>3</sub>) versus Fe<sub>2</sub>O<sub>3</sub> for EPMA WDS spot analyses of goethite mineralization from all three textural types. In the mineralization of textural type 1, three different compositions are clearly distinguished: SiO<sub>2</sub> + silica phases highly mixed composition and Al-substituted composition (virtually goethite) and near stoichiometric goethite (virtual brown goethite). The other two textural types show similar compositional relations.





**Figure 7:** Major element (all in wt.%) correlation diagrams of SEM EDS spot analyses from goethite mineralization type 1. Note the almost stoichiometric composition of goethite from the brown mantle (arrow). **A)**  $\text{Al}_2\text{O}_3$  vs.  $\text{SiO}_2$  diagram showing a positive correlation. **B)**  $\text{FeO}$  vs.  $(\text{SiO}_2 + \text{Al}_2\text{O}_3)$  diagram showing a negative correlation. **C)**  $\text{MgO}$  vs.  $(\text{SiO}_2 + \text{Al}_2\text{O}_3)$  showing a slight positive correlation. **D)**  $\text{P}_2\text{O}_5$  vs.  $(\text{SiO}_2 + \text{Al}_2\text{O}_3)$  showing a slight positive correlation.

low temperatures, also indicate that unit cell parameters increase with decreasing synthesis temperature (CORNELL & SCHWERTMANN, 2003). This relationship is attributed to the incorporation of structural OH in the goethite lattice which augments increasing Al-substitution (SCHWERTMANN et al., 1985).

## 5.2. Chemical constraints of goethite formation

Goethite is a common and abundant constituent of many secondary iron ore deposits and various types of soils, particularly of terra rossa (DURN et al., 1999). Formation of these products is strongly controlled by weathering, i.e. by descending solutions. Such goethite-bearing occurrences comprise leaching of Fe from a primary substrate and mobilisation in the form of ferrihydrite (SINGER et al., 1998). Later, goethite is formed directly by the transformation of ferrihydrite and/or eventually via haematite in an assemblage also consisting of Al-hydrated oxides and clay minerals as the products of incomplete lateritization (TARDY & NAHON, 1985). An assemblage formed following this genetic pattern shows typical collomorph-banded texture, poor crystallinity of all phases and purely Al-substituted goethite.

In contrast, goethite from the analysed mineralization is well crystallized and may show exceptionally coarse aggregates (Fig. 3A). Early crystallized Al-substituted goethite embeds K-feldspar, almandine-rich metamorphic garnet, calcite, quartz and rutile and is followed by almost pure goethite (Fig. 4). This natural case supports the results of thermodynamic experiments which show that the rate of Al-substitution in goethite

is strongly dependent on the availability of Al and the chemistry of associated minerals (TARDY & NAHON, 1985).

The Al-substituted goethite (black goethite) from Dugi otok is characterized by 13.1–29.6 mol % of Al (Table 3, Fig. 6), and high amounts of silica impurities and bonded phosphate. Silica binds to the goethite terminal faces suppressing the growth rate and consequently enhances its crystallinity (CORNELL & GIOVANOLI, 1990). The adsorption of silica is minimal at low pH due to formation of protonated or neutral silica polymers which make a stable  $\text{FeOSi}(\text{OH})_3^{2+}$  complex (WEBER & STUMM, 1965). At pH values between 8 and 11, goethite forms at the expense of hydrolyzed  $\text{Fe}(\text{OH})_4^-$ , whereas silica interferes either by hindering nucleation and crystal growth of goethite or by reacting with metastable ferrihydrite, thus retarding the supply to growing units (GLASAUER et al., 1999). Phosphate enrolls the goethite surface rapidly with strong ligand exchange both at the surface and at defect sites and pores. The rate of goethite formation is greatly reduced in the presence of phosphate, due to an increase in the entropic component of the free energy of activation. Analogous to the silica effect, the overall goethite crystallinity is enhanced due to the slower crystal growth (SHAW et al., 2005).

The enhanced crystallinity of goethite compositional types, the composition of Al-substituted goethite with silica sub-micro domains, the presence of P but lack of Fe-phosphate and stable, coarse grained calcite in the paragenesis strongly suggests alkaline conditions of formation. Therefore, formation of Dugi otok goethite mineralization directly linked to karstification could have been excluded since karstification

favours an acid environment. This statement is corroborated with the mode of mineralization occurrence observed at the outcrops.

### 5.3. Geotectonic environment of goethite mineralization

Similar goethite mineralization of post Eocene age was reported near Novi Vinodolski and on the islands of Krk and Cres situated some 125 km NNW from Dugi otok (Fig. 1) (MARKOVIĆ, 2002) suggesting that the investigated goethite mineralization should be considered on the regional scale of the North Adriatic.

The present surface lithology of Dugi otok does not offer any substratum from which Fe, Al, Si and P may have been derived. Hence, we postulate their source as being in the submerged Adriatic crust. There is a high positive gravimetric anomaly situated land-ward of Dugi otok, (KOŠČEC, 1986). Furthermore, several geomagnetic anomalies are located seaward of the island (BRDAREVIĆ & OLUIĆ, 1979). All could be assigned to igneous rocks, although igneous materials were not proven (Fig. 1). However, ultra-alkaline intraplate volcanic rocks dated to the Pliocene were recognized in several cores drilled in the depression of Dugi otok (MILETIĆ & LUGOVIĆ, 2000). The igneous occurrences trace the south eastern segment of the Schio fault system which continuously stretches NW-SE from Vicenza to Palagruža (GRANDIĆ et al., 1997). The Dugi otok fault (DOF), belongs to this fault system (Fig. 1), and traces a lithospheric fracture (Internal Adriatic fracture – IAF) within the Adria microplate (OLDOW et al., 2002). The Schio fault system caused major vertical displacements in the Adriatic crust and is transected by dextral strike slip W-E trending lithospheric faults (DI BUCCI & MAZZOLI, 2003). Both fault systems were reactivated during the Pliocene (5–2 Ma BP) on account of an ancient structural weakness in the Adriatic crust. Magmatic occurrences are located at or near the intersections of these fault systems (Fig. 1). We link the Dugi otok goethite mineralization to the Pliocene extensional tectonic activity which produced submarine magmatic activity during an extensive marine transgression after the Miocene emersion. The temperate ascendant parental solutions rich in Fe<sup>2+</sup>, Al, Si and P, yielded goethite mineralization, representing the aftermath of Pliocene magmatism.

## 6. CONCLUSIONS

In our model, goethite crystallized from ascendant solutions, probably slightly warmed due to increased heat flux caused by Pliocene igneous activity. The Fe<sup>2+</sup>, Al, Si and P rich solutions together were tectonically mobilized from a hidden Fe-enriched metamorphic silicate source, and rose up throughout the complex submerged crevices formed by Miocene karstification and Pliocene tectonic activity. It is likely that during the uplift, very small quantities of the metamorphic substrate were included in the solution represented by incomplete dissolved silicate minerals. Initial crystallization took place under high oxygen fugacity, and slightly basic pH, leading to the fast removal of Al, Si and P through the precipitation of mixtures comprising Al-substituted goethite and quartz with syntempo-

ral deposition of suspended metamorphic phases. Therefore, due to the complete removal of silica and Al, the residual solution crystallized as almost pure, stoichiometric goethite.

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