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Authigenic iron minerals as indicators of early-dolomitization in the Sandy Dolomites (uppermost Permian–Lower Triassic, Velebit Mt., Croatia)

Autigeni željezoviti minerali kao indikatori rane dolomitizacije u pjeskovitom dolomitu (najgornji dio perma i donji trijas, Velebit)

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Key words: Fe-authigenic minerals, early-dolomitization, Lower Triassic, Velebit Mt.

Ključne riječi: autigeni željezoviti minerali, rana dolomitizacija, donji trijas, Velebit

Sedimentation from the uppermost Permian to the Lower Triassic deposits in the Velebit Mt. area is continuous (SALOPEK, 1948), and occurs within the lowest part of the informal lithostratigraphic unit of Sandy Dolomite. Lower Triassic deposits are mostly represented by early-diagenetic dolomites characterized by scarce fossil findings and frequent siliciclastic grains. Their composition indicate shallow-water marine depositional environment strongly influenced by the hinterland. Authigenic Fe-mineral association present in these dolomites, mainly pyrite and siderite, can therefore help in reconstruction of diagenetic and geochemical conditions of the dolomitization environment.

Collected sediment samples were disintegrated, cut and polished, and analyzed by polarizing microscope, Scanning Electron Microscope (SEM), Energy Dispersive Spectroscopy (EDS), and X-ray Diffraction. Phase stability diagrams were constructed on the basis of mineral phases identified in the samples. The iron, calcium, magnesium and sulphide concentrations chosen for stability field calculations are variable, but within ranges considered normal for pore fluids in balance with carbonates. Up to four stability iterations with different activities per ion species were calculated and stability fields were overlaid. This approach enabled determination of trends in the mineral stability field change, minimizing errors in conclusions, due to unknown real ion activities in pore waters.

Due to the oxidation of authigenic sulphides and siderite their determination was sometimes possible only on the basis of crystal morphology examination under SEM. Pyrite was identified by distinctive crystal morphology – hexahedra with perfectly preserved striations and octahedra-hexahedra combinations, even though they were oxidized mainly into magnetite and goethite (Fig. 1). Siderite is present in the characteristic rhombohedral form (Fig. 2), rarely in

pseudo-hexagonal plates. Siderite is also oxidized to magnetite and goethite but in much lower extent compared to pyrite, and EDS show spectra characteristic for siderite. Siderite rhombohedral crystals are inter-grown with smaller dolomite or ankerite rhombohedra, in the form of crystal inclusions. Such aggregate formations indicate that dolomite and ankerite have been crystallized prior to the phase of siderite

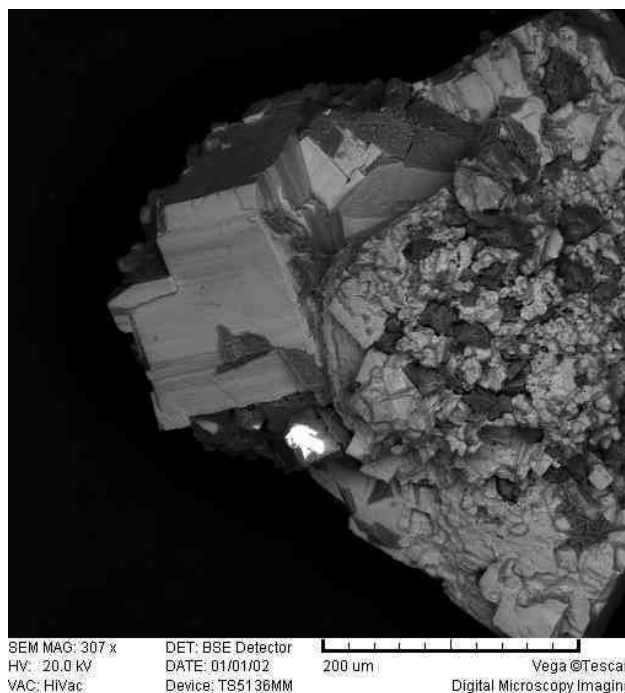


Figure 1. Pseudomorphosis of goethite after pyrite, hexahedra with preserved pyrite striations.

Slika 1. Pseudomorfoza goethita po piritu, heksaedri s očuvanim prutanjem karakterističnim za pirit.

rhombohedra formation. Host sediment containing described mineral association can be described as early-diagenetic dolomite, sometimes transitional to ankerite.

Authigenic iron minerals found in the carbonate sediments are typical for three very different geochemical environments: sulphidic, carbonate and oxic. Pyrite, siderite and magnetite are minerals stable under negative Eh and their stability fields are strongly influenced by the $p\text{CO}_2$ and $p\text{S}^2$ of the solution. In diagenetic environment described here siderite is found to be associated with pyrite. If there is lower activity of Fe^{2+} and higher Ca^{2+} and Mg^{2+} activity in the pore waters, then ankerite or ferroan calcite will form, as in studied deposits. Geochemical environment characterized by pyrite–siderite–ankerite–dolomite mineral association was the same diagenetic environment in which early-diagenetic dolomites were formed.

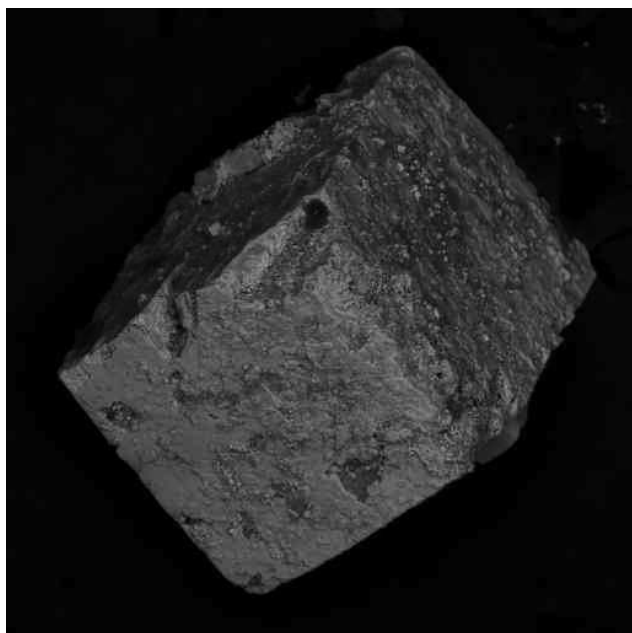


Figure 2. Siderite rhombohedron partially oxidized into goethite.
Slika 2. Romboedar siderita djelomično oksidiran u goethit.

The occurrence of siderite is characteristic for continental sediments with low concentration of dissolved sulphate (BERNER, 1981). In marine sediments siderite occur mostly as late-diagenetic cement, or may occasionally be precipitated during deposition or early diagenesis, if sulphate concentration is somehow lowered. Sulphate in marine environment is regularly reduced to sulphide by bacterial metabolic activity; sulphide concentration can be lowered by precipitation of iron sulphides, or by dilution with fresh water of meteoric or other non-marine origin. Siderite was therefore formed in the mixing zone of marine and fresh water due to significantly lower sulphate concentration in brackish waters. In such diagenetic environment iron sulphides were formed, which additionally lowered sulphide activity in sediment pore waters, resulting in relative Fe^{2+} concentration increase. These processes have moved diagenetic environment toward siderite stability area.

Dolomitization of the studied sediments containing characteristic mineral association of pyrite, siderite, ankerite and dolomite, occurred in the mixing zone of sea and fresh water. Such dolomitization model is typical for the transgressive sequences (e.g. WRIGHT et al., 1997), which is in line with the ongoing transgression recorded within the Sandy Dolomite unit and continuous siliciclastic input to the shallow-water environment during Early Triassic.

Fe-mineral associations and thermodynamic stability of authigenic iron minerals studied within uppermost Permian to Lower Triassic Sandy Dolomites of the Velebit Mt. provided a new tool to reveal diagenetic environment.

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