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Siliceous nodular concretions from Upper Cretaceous limestone near Vrgorac (Croatia)

Rožnjačke nodule iz gornjokrednih vapnenaca okolice Vrgorca (Hrvatska)

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Siliceous-carbonate nodular concretions – perfectly spheroid, in the form of oblate spheres and some of irregular shape – were found within Upper Cretaceous limestone near Vrgorac. Nodule is a mineral body that differs in composition from rock in which it is formed, commonly limestone and dolomite. Sediment surrounding the concretions is wackestone-packstone with abundant pelagic particles (pithonellas and calcispheres), echinoderm fragments and primitive planktic foraminifera. These deposits belong to the hemipelagic Cenomanian–Turonian Sveti Duh Fm (GUŠIĆ & JELASKA, 1990). Concretion outer surface and surrounding host sediment is often impregnated with bituminous material. The source of bituminous material was organic remains possibly giving opal (silica) material for concretion growth. Preservation of bituminous material in carbonates is connected with stagnant pore waters and rapid sea-level rise due to the Oceanic Anoxic Event (OAE) at the Cenomanian–Turonian transition (GUŠIĆ & JELASKA, 1990, and references therein).

Biogenic silica (opal-A) is amorphous, hydrated and the most unstable form of silica and its solubility greatly increase with temperature, pressure, solution under saturation and pH elevation. Typical early-diagenetic carbonate marine environment with elevated pH was under-saturated with silica, resulting in fast dissolution of biogenic opal remains. The dissolution-precipitation reaction of biogenic silica can be shown with the following expression: $SiO_2 + 2\ H_2O \leftrightarrow Si(OH)_4$. Fast dissolution of opal-A, and stagnant pore waters, yields solutions of relatively high silica content. In pore waters saturated with silica, open framework silica polymers form and flocculate to yield opal-CT. Once emplaced as a proto-concretion, such globular molecular cluster starts to grow in the direction of the new material supply. Highly spherical concretion shape indicates the same rate of the source material supply from all directions of the sphere envelope. Such conditions can be established in stagnant sediment pore waters where supply of the new material at the growth site goes only by molecular diffusion. Diffusion can be defined as molecular migration without pore fluid flow and at a constant temperature. The efficacy of diffusion is determined by the diffusion coefficient, the pore space path and geometry, and the concentration gradient. Diffusion is one of the most important processes acting during sediment diagenesis and especially concretion growth. With formation of the core, the growth starts, and source material concentration gradient is established. Concentration gradient results in ion flux from surrounding sediment toward growth site, which brings to ion depleted zone in the near concretion volume.

Spheroid concretions show extensive zonation of alternating zones with different carbonate and silicate content (Fig. 1). Oblate spheres are zoned in much less extent, while irregular mostly show no zonation and are composed entirely of silicate component. Alternating zonation of opal and carbonate rich zones derive from fast ”consummation” of silica material at the growth site.

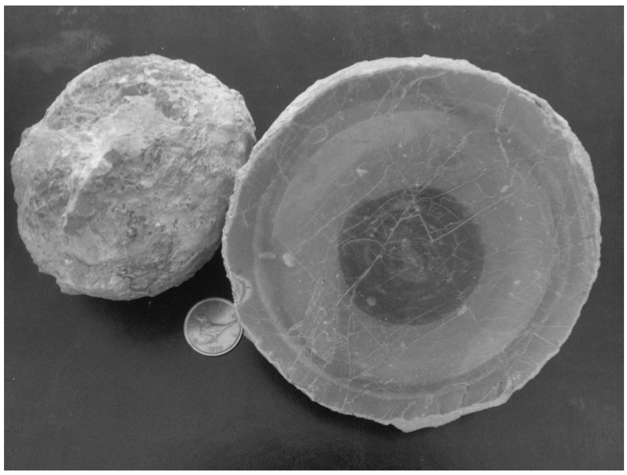

Figure 1. Nodular concretions from the Vrgorac area, with zonation of siliceous and carbonate material.

Slika 1. Nodula i presjek nodule iz okolice Vrgorca s vidljivom zonacijom između karbonatnog i silikatnog materijala.

Rhythmic carbonate-opal concentration variation can be explained with geometric relations of the sphere, and do not necessary reflect temporary variations in the environment. Sphere area increasing with square of its radius (4r^2Đ) and constant linear ion flux can not feed the rapidly increasing growth area, which results is concentration lowering. When silica becomes under-saturated, addition of new silica material to the concretion opal zone stops, and now carbonate zone precipitation begins with the same growth scenario described for the opal zone. Carbonate precipitation on the opal surface is strongly enhanced due to cation adsorption on dissociated silanol groups –SiOH. Silanol groups on biogenic silica surface are known excellent ligands for aluminium, calcium, iron and other cations existing in sediment pore waters. There are two different growth mechanisms for opal and carbonate, additionally enhancing zone formation acting during concretion formation and preferring different opal or carbonate content in one zone layer. Carbonate formation is result of crystallization process while silica gels forms by polymer flocculation, so carbonate precipitation could be slowed down, due to inhibition by adsorbed organic matter or sulphate on possible carbonate crystal nucleation sites.

Sediment partial consolidation and preferential orientation of platy shaped sediment particles would cause greater horizontal than vertical sediment permeability and a slight preferential transport horizontally, giving characteristic oblate sphere concretion shape. All apparently irregular concretion shapes are in fact typical for gel structures, resembling geometrical shapes of minimal surface tension (energy).

Described siliceous-carbonate concretions and mechanisms of their growth represent excellent and rare example where natural laws governing shaping and appearance of matter can be clearly seen and successfully used to explain the occurrence of geological phenomena. The Ministry of Culture started with the procedure of protecting the concretions as natural values by the Nature Protection Act.

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