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ARAGONITE PHASE IN RECENT SEDIMENTS FROM "MLJET'S LAKES" (ADRIATIC SEA, CROATIA)

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Unusual predominance of aragonite over calcite and other carbonate phases [1] is studied by electron microscopy, X-ray, and electron diffraction in recent sediments of Mljet's Lakes (Mljetska jezera), island Mljet, Adriatic sea, Croatia, Fig. 1. This is unusually high altitude for a location at which aragonite mud is detected in recent sedimentation.

Sediment chunks were collected by scuba diving in Mljet's Lakes, frozen and transported to the laboratory. Samples were prepared: by gold coating a piece of freeze-dry sediment - for SEM; by dropping a few drops of diluted slurry (dispersed by ultrasonic agitation) on a Formvar coated grid - for TEM; by scraping a sediment surface - for XRD study. The electron diffraction study was performed using goniometer tilt in a transmission microscope operating in SAD mode.

Analysis of the powder XRD pattern of Fig. 2. reveals prevailing fraction of aragonite phase over calcite and other carbonate phases in the most samples of collected sediments.

The needle-like particles are the most dominant morphology of the sediment's surface, as imaged in Fig. 3, as well as of the bulk of material, shown in Fig. 4. The size of "needles" ranges: 10^{-1} to 10^{0} μm -thickness; 10^{0} to 10^{1} μm -length. The plate-like particles are found next to "needles", with irregular shape and average size of 10^{0} μm (with more or less straight edges and angles close to 120° or 60°). Much smaller round-shape particles (size: $\leq 10^{-1}$ μm) are either spread around "needles" and "plates", or agglomerated in a sponge-like amorphous matrix between the larger particles, as indicated by arrows in Fig. 4. All types of particles display some kind of diffraction contrast. This is confirmed by electron diffraction on a cluster (see inset (a)), or on individual particles (inset (b)&(c)). The subset of rings in inset (a) belongs to aragonite powder pattern; the spot pattern of the encircled needle-like particle in inset (b) is assigned by aragonite lattice; the encircled area of a skeleton in Fig. 4, reveals the calcite pattern in inset (c). Spot patterns of single-grains with needle-like morphology are unambiguously indexed on the basis of orthorhombic aragonite lattice cell; plate-like grains usually reveal the [00.1] zone pattern of hexagonal calcite.

The abundance of aragonite $CaCO_3$ phase in surface sediments is quite unusual phenomenon for such high altitude (Fig. 1), in contrast to its presence in sedimentation mud at warm tropical climatic zone locations: Bahamas, Florida, Arabic Gulf, Red Sea [2]. "Mljet's lakes" are not real lakes, but rather a marine bay i.e. semi-enclosed depressions connected with open sea by a narrow shallow channel. Due to its scenic beauty, ecological peculiarities, and preserved environment the surrounding part of island Mljet was proclaimed a National Park in 1960. However, there is an ongoing debate on inorganic versus algal origin of the aragonite mud [3], so that the origin of this needle-like aragonite crystals in Mljet's Lakes recent sediments remains open.

Fig. 1 Schematic location of Mljet's Lakes at Croatian island Mljet (N:42°46'22", E:17°21'30") Adriatic Sea, Mediterranean basin.

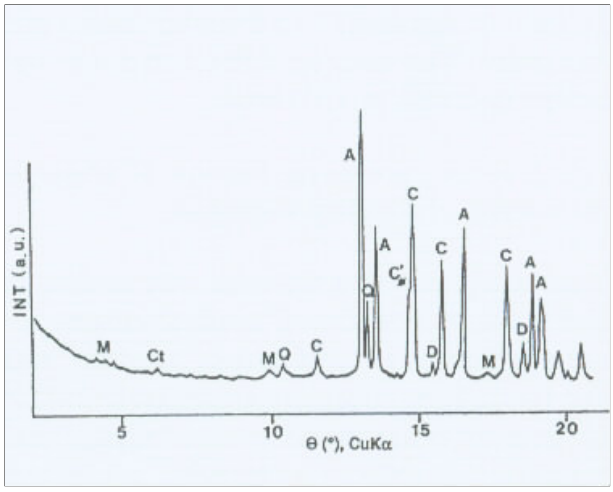

Fig. 2 Powder X-ray diffraction pattern of the recent sediment from Mljet's Lakes. The most prominent lines of a number of minerals are indicated:
A – aragonite; C – calcite; C' – Mg–calcite; Q – quartz; D – dolomite; Ct – chlorites; F – feldspar; M – micas.

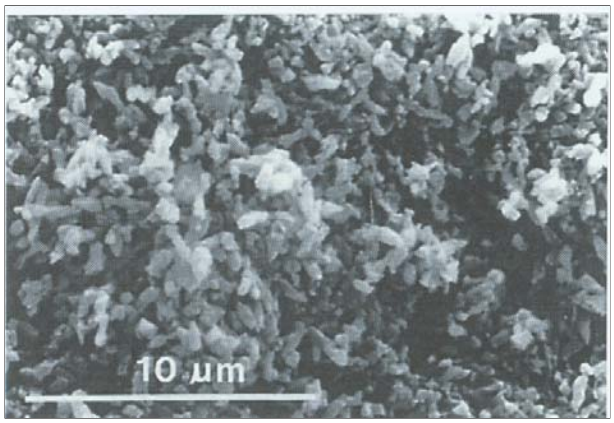

Fig. 3. Representative SEM image of a surface of Mljet's Lake recent sediment which reveals the needle-like grains as the most dominant surface morphology.

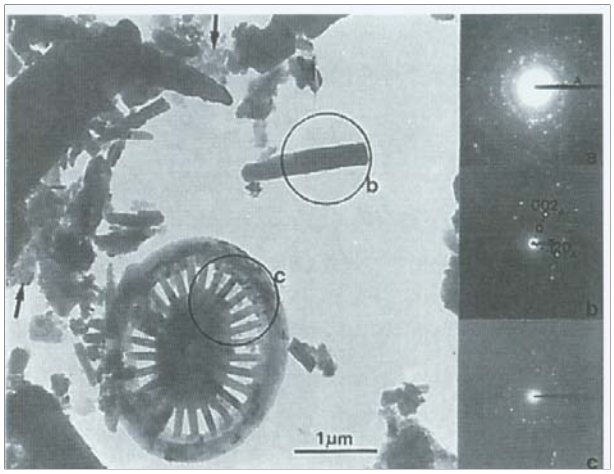

Fig. 4. TEM imaging and SAD patterns (insets) of particles constituting Mljet's Lakes recent sediment:
inset (a) – ED pattern of large cluster of different particles (see Fig. 2. for comparison);
inset (b) - ED pattern of a needle-like grain (encircled area - b) confirming its aragonite crystal structure;
inset (c) - ED pattern revealing calcite crystal structure of a skeleton (area marked by circle - c).

[1] Sondi I. et al., *Proc. Prirodne znacajke i drustvena valorizacija otoka Mljeta*, Zagreb (eds. P. Durbesic and A. Benovic), pp. 117-125, Ekoloske monografije 6, Hrvatsko ekološko društvo, Zagreb (1995)
[2] Tucker M.E. and Wrught V.P., *Carbonate Sedimentology*, p. 482, Blackwell Scientific Publ. Oxford (1990)
[3] Shin E.A. et al., *J. Sedimentary Petrology*, 59 (1989), 147-161