

**HARD TISSUES OF S-ELEMENTS OF LATE PALEOZOIC  
CONODONT: MICROSTRUCTURAL AND CRYSTALLOGRAPHIC  
ASPECTS**

*Frank-Kamenetskaya O.V.<sup>1</sup>, Rosseeva E.V.<sup>1,2</sup>, Zhuravlev A.V.<sup>3</sup>,  
Rozhdestvenskaya I.V.<sup>1</sup>, Banova I.I.<sup>1</sup>, Simon P.<sup>2</sup>, Buder J.<sup>2</sup>,  
Carrillo-Cabrera W.<sup>2</sup>, Kniep R.<sup>2</sup>*

<sup>1</sup>Saint Petersburg State University, Russia  
rosseev@mail.ru

<sup>2</sup>Max-Planck-Institut für Chemische Physik fester Stoffe, Dresden, Germany  
kniep@cpfs.mpg.de

<sup>3</sup>VNIGRI, Saint Petersburg, Russia  
stratigr@mail.wplus.net

Conodont elements are microscopic tooth-like fossilized skeletal remains of small, extinct, marine chordates inhabited a variety of environments in Paleozoic and Triassic seas. However, conodont affinity has been the subject of debate since their first discovery by C.H. Pander in 1859 (from clay near St. Petersburg, Russia), because the hard tissues of their fossilized skeletal remains are very special and not typical for known animal phylum. Previous investigation demonstrated that feeding apparatuses of conodonts composed by 15 or 19 discrete elements which structurally divided into three parts, so-called P-, S- and M –regions [1, 2]. The structure of conodont elements consists of two basic units: the crown and the underlying basal body. The crown typically comprises a combination of hyaline (or lamellar) tissue and albid (or white matter) tissue [1 - 4]. Recent results also showed that conodont hard tissues also contain trace amounts of organic matter, and may represent remnant proteinaceous material [5, 6]. However its exact architecture, arrangement and functions are still the matter of controversy. The main inorganic component of conodont elements is carbonated fluorapatite. The detailed analysis of chemical composition as well as the crystal structure of such bioapatite is a very difficult experimental problem. Furthermore the small size of conodont elements has been a limiting factor for their detail investigations. However modern microanalytical techniques now provides a lot of opportunity to analyze the specific of composition and structure of single conodont element, which is very important for understanding their organization and animal affinity.

The general purpose of our research is detail investigation of structure and composition of hard tissue of S-elements of Late Paleozoic conodonts. However present paper is especially focusing on characterization crystal chemistry of conodont apatite.

Samples of *Polygnathus* (*Ozarconidacla*) conodont elements were obtained from Late Devonian (Middle Frasnian ~ 380 millions years) deposits at south

coast of the Ilmen Lake (Novgorod region). According to the results of scanning electronic microscopy (ESEM FEI Quanta 200 FEGi system FEI company, Eindhoven, NL) the surface of all elements is covered with a very fine striate ornament which is typical for such types of elements and characterized as cell imprints [1-2]. Cusps of elements are slightly inner laterally curved, with smooth lateral faces. The internal structure in conodonts is clearly visible on fractured specimens showing the laminar structure of hyaline tissue and some parts of basal body. The crown tissues also exhibited internal irregular holes. The albid crown tissues composed by elongated crystallites with preferred crystallographic orientation and length up to several tens of microns. In contrast hyaline tissue composed by smaller (from 0.1 to 1 $\mu$ m) and less ordered crystallites. The basal body show significant porosity at the crystal boundaries and random arrangement of small nanocrystals (several nm). By means of high resolution transmission electron microscopy (CM 200 FEG/ST-Lorentz, FEI company, Eindhoven, NL) it was confirmed that albid crown conodont tissue composed by micrometer-sized crystallite subunits with preferable crystallographic orientation run parallel to the long axis of the conodont element. However some parts indicate the less ordering of crystallites, which can be also caused by damaging of sample during the cutting procedure or by existence of other hard tissue (hyaline or basal body). Additionally the significant porosity at the crystal boundaries (intracrystalline porosity) of albid crown tissue was demonstrated. The pores are varied in shape and size (from several nm- to  $\mu$ m-sized). The existence of mineralized organic fibrils also visualized as porosities or as region of less density which arranged in a row with varying diameters of 1.5-5.5 nm.. The HR-TEM micrograph exhibits the crystal lattice of apatite as demonstrated by the FFT inset. However, in some FFT images we also observed additional reflections with d-value which is not typical for apatite crystal structure. This finding can indicate the presence of trace amount of other mineral within the aggregate. Thus according to the results of electron microscopy study the conodont hard tissues can be characterized as apatite-organic nanocomposites. In addition within conodont elements the albid crown tissues structurally is the most ordered. According to X-ray diffraction study (four-circle autodiffractometers Nicolett R3, MoK $\alpha$ ) only albid crown hard tissue exhibits the scattering properties representative of a single crystal. The lattice parameters of albid crown tissue apatites:  $a = 9.374\text{-}9.376(2)$ ,  $c = 6.882\text{-}6.892(2)$  Å are very close to that of stoichiometric synthetic F-apatite ( $a = 9.367(1)$  Å,  $c = 6.884(1)$ Å, [7]). The EDX analysis (ESEM FEI Quanta 200 FEGi system, FEI company, Eindhoven, NL) of the most in details investigated apatite ( $a=9.374(2)$   $c =6.882(2)$  )Å ) shown that Ca/P molar ratio is 1.58(5), content of Ca = 38.4(8), Sr = 1.7(4) , Pb = 0.76(9), Pb = 0.76(9) , Na = 0.37(8), Mg = 0.14(8), Sn = 0.8(1), P = 18.7(6), Si = 0.31(6), F = 2.5(3), Cl = 0.19(6) wt.-%. The refinement of crystal structure of this apatite (3573 refl. with  $I > 2\sigma_I$ , S.G. P6<sub>3</sub>/m, R<sub>F</sub> =0.017, R<sub>w</sub> = 0.022) has been demonstrated that the bond length in the PO<sub>4</sub> tetrahedra is P-O1  $\approx$  P -O3 = 1.535(2) < P-O2 =1.543(2) Å. The

average P-O distance (1.537 Å) is similar to the value observed in stoichiometric fluorapatite (1.536 Å). The sites of all tetrahedral oxygens are partly vacant (the quota of vacancies = 0.03 - 0.01 at. un.). The splitting of F-site can be due to partial substitution of small F-ions by larger (Cl<sup>-</sup>, OH<sup>-</sup>) ions, or to formation of vacancies which can be filled by water molecules. The refined unit cell content of the biological carbonate apatite under consideration is (Ca<sub>9.30</sub> Sr<sub>0.19</sub> Na<sub>0.11</sub> Sn<sub>0.04</sub> Pb<sub>0.03</sub> K<sub>0.02</sub> Mg<sub>0.01</sub> □<sub>0.30</sub>)(PO<sub>4</sub>)<sub>5.86</sub> (SiO<sub>4</sub>)<sub>0.05</sub> (CO<sub>3</sub>)<sub>0.09</sub> (F<sub>1.29</sub> Cl<sub>0.04</sub> (□,OH, H<sub>2</sub>O)<sub>0.67</sub>).

The structure and organization of albid crown conodont hard tissue bears strong resemblance to the biomimetic fluorapatite-gelatine nanocomposite in the early state of morphogenesis [8]. These biomimetic aggregates can be characterized as inorganic-organic hybrid materials with apatite as inorganic component and gelatine as organic. The nano-structured collective is within composite aggregate represents a highly mosaic-controlled nanocomposite superstructure. This system is perfectly suited for obtaining information on processes of self-organisation, and may help in gaining insight into the essentials of the formation of inorganic-organic nanocomposites with biological relevance.

1. *Sweet W.C., Donoghue P.C.J.* Conodonts: past, present, future // *J. Paleont.*, 2001, 75(6), P. 1174-1184.

2. *Журавлев А.В.* Гистология и микроскульптура позднепалеозойских конодонтовых элементов. СПб: Геосервис Плюс. 2002. 94 с.

3. *Donoghue P.C.J.* Growth and patterning in the conodont skeleton // *Philosophical Transactions of the Royal Society of London, B*, 1998. № 353. P. 633-666.

4. *Trotter J. A., Fitz J. D., Kokkonen H., Barnes C.R.* New insights into the ultrastructure, permeability, and integrity of conodont apatite determined by transmission electron microscopy // *Lethaia*, 2007, 40, P. 97 – 110.

5. *Marshall C.P., Rose H.R., Lee G.S.H., Mar G.L., Willson M.A.* Structure of organic matter in conodonts with different colour alteration index // *Organ. Geochem.*, 1999, 30, P. 1339-1352.

6. *Kemp A.* Amino acid residues in conodont elements // *J. Paleont.*, 2002, 76(3), P. 518-528.

7. *Sudarsan K., Young R.A., Mackie P.E.* Composition of synthetic and mineral fluorapatite, Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>F, in crystallographic detail // *Materials research bulletin*. 1972, 7(11), P. 1331

8. *Kniep R., Simon P.* Fluorapatite-Gelatine-Nanocomposites: Self-Organized Morphogenesis, Real structure and Relations to Natural Hard Materials // *Top. Curr. Chem.* Springer. 2007. Vol. 270. P. 73-127