SHORT COMMUNICATION

Conodont bioapatite resembles vertebrate enamel by XRD properties

Jüri Nemliher and Toivo Kallaste

Institute of Geology at Tallinn University of Technology, Ehitajate tee 5, 19086 Tallinn, Estonia; nemliher@gi.ee, toivo.kallaste@gi.ee

Received 25 July 2012, accepted 6 August 2012

Abstract. XRD properties of Phanerozoic conodont apatite material were studied. It was found out that in terms of crystallinity the apatite resembles the enamel tissue of modern vertebrates. In terms of crystal lattice, apatite of conodonts is independent of taxa on the one hand and of chemistry of the surrounding rock type on the other hand.

Key words: Palaeozoic, conodont apatite, XRD.

The observable properties of conodont apparatus carry a variety of features permitting assignment of these higher taxa into different branches of Metazoa. Considering the information possibly saved into conodont apatite, the composition of conodonts was first recognized as calcium phosphate (Harley 1861), later as having the structure of apatite (Ellisson 1944) with lattice parameters $a = 9.37$ Å and $c = 6.91$ Å (Pietzner et al. 1968). Recent studies have revealed two apatite types of different composition in elements of euconodonts with different carbonate ion contents (Wright 1990; Trotter & Eggins 2006). Zhuravlev & Sapega (2007) showed that those chemical differences result in slightly different lattice parameter values for lamellar and white type tissues of conodont elements.

Based mostly on histological studies, researchers have suggested that conodonts might be homologous to odontodes (Smith et al. 1996) or true vertebrate teeth (Dzik 1986; Donoghue et al. 2000). In terms of classification, several criteria should be considered, among others the finest structure of mineralized tissue; the teeth (enameloid) of vertebrates, even fossil ones, always display a specific structure (Kallaste & Nemliher 2005). Fossils in the Baltic area are well preserved. Kirsimäe et al. (1999) noted that the Early Cambrian sediments in North Estonia were never affected by significant tectonic or thermal events after sedimentation 530 Ma ago and the clays still have a high water content. Our short note shows that XRD features of the studied conodont material resemble the properties of vertebrate enamel.

The conodont material studied comes from samples collected from the Lower Ordovician Kallavere Formation (Turjekelder outcrop, *Cordylodus angulatus* Biozone, weakly cemented sandstone, sample KONO3), the Lower Silurian Velise Formation (Velise outcrop, *Pterospathodus eopennatus* ssp. n. 1 Biozone, weakly cemented clay, sample KONO2) and the Upper Silurian Paadla Formation (Paadla outcrop, *Ozarkodina roopaensis* Biozone, limestone, sample KONO1).

Conodont apatite samples (at least 20 mg of conodont material) were picked out of originally ca 20–40 kg rock material; only euconodonts (CAI = 1) were analysed. A whole-pattern fitting procedure was applied to XRD patterns, according to the calculation model by Kallaste & Nemliher (2005). For both component phases, the strains varied independently in both directions, i.e. asymmetrically.

The following species were identified.

KONO1: *Ozarkodina roopaensis*, *Oulodus siluricus and Panderodus* sp. (Silurian, *Ozarkodina snajdri* Biozone, carbonate rock matrix).

KONO2: *Aspelundia flugeli*, *Ozarkodina polinclinata estonica*, *Pterospathodus eopennatus* ssp. n. 1 (*sensu* Männik 1998), *Astropentagnathus irregularis*, *Aulacognathus* cf. *kuehni*, *Distomodus staurognathoides*, *Walliserodus* sp., *Panderodus unicostatu*s, *P. recurvatus*, *P. greenlandensis*, *Oulodus* sp. and *Apsidognathu*s sp. (Silurian, *Pterospathodus eopennatus* ssp. n. 1 Biozone, clay rock matrix).

KONO3: *Cordylodus proavus*, *C. caseyi*, *C. intermedius*, *C. angulatus*, *C. lindstromi* and *Eoconodontus altus* (Lower Ordovician, *C. angulatus* Biozone, quartz sand matrix).

It appeared that conodont apatite is highly crystalline. The calculated lattice parameters, amount of finer-size-series apatite, crystallite dimensions and strain for finer series and large-size series (*sensu* Kallaste & Nemliher 2005) of the studied samples are presented in Table 1.

In spite of the multi-taxa composition of the studied samples, the high crystallinity of the XRD patterns allows us to conclude that inter-taxa variations of conodont bioapatite matter are minimal and close to the values reported earlier (Pietzner et al. 1968; Zhuravlev & Sapega 2007). At the same time, the values of lattice parameters significantly differ from those reported for both Recent and fossil bioapatite of other vertebrate enamel/dentine mineralized tissues (e.g. Wright 1990; Nemliher et al. 1997; Kallaste & Nemliher 2005). We interpret this phenomenon as similarity/homogeneity of the primary biomineralization product for Conodonta. Another conclusion is that the nature of the surrounding rock matrix has not affected the chemical composition of conodont apatite and its maturation during diagenesis is not time-dependent.

Table 1. Lattice parameters (*a* and *c*), amount of finer-size-series apatite (%D_f), its dimensions (D_{hk0} and D_{001}) and strains for finer series (εf_{hk0} and εf_{00l}) and large-size series (ε_{hk0} and ε_{00l}) of the studied samples and comparative material

Sample	*a*, Å	*c*, Å	%D_f	D_{hk0}, Å	D_{001}, Å	εf_{hk0} $\times 10^3$	εf_{00l} $\times 10^3$	ε_{hk0} $\times 10^3$	ε_{00l} $\times 10^3$
KONO1	9.373(3)	6.888(1)	26	157	100	6.4	0.0	1.2	1.5
KONO2	9.374(2)	6.889(5)	38	203	145	3.0	0.0	2.8	2.8
KONO3	9.369(5)	6.887(4)	33	154	120	3.1	10.2	2.2	2.2
hai03[1]	9.404(1)	6.877(9)	15	50	158	0.0	0.0	2.1	1.6
ELISH[1]	9.449(5)	6.883(6)	33	50	130	0.0	0.0	1.2	4.3

[1] Data from Kallaste & Nemliher (2005); hai03 – shark tooth; ELISH – human milk tooth enamel.

On the other hand, differences in the apatite lattice parameter values of various histological types of mineralized matter of conodont apparatus reported earlier (Zhuravlev & Sapega 2007) should be expressed as decrease in the crystallinity of the studied samples, causing the lowering of the lattice parameter *a* for a bulk sample of conodont elements. While this phenomenon was not recorded, we explain it by prevalence of enamel-type tissue in conodont material. It should be pointed out that the diagenetically altered conodont apatitic matter resembles rather enamel/enameloid than other types of phosphatic tissues (Nemliher et al. 2004). At the same time, it differs significantly from the analogue bioapatite of representatives of phylogenetically substantially younger taxa (Wright 1990; Nemliher & Kallaste 2005), revealing the possible difference of the original lattice of biomineralized tissue.

Calculation of crystallite dimensions and strain of conodont mineralized matter revealed that the larger elementary crystallite series had dimensions >3000 Å in both directions: in [hk0] as well as in [00l] for all studied samples. More exact determination of those dimensions appeared to be outside the limits of the method used for deconvolution of XRD patterns. It is assumed that this dimension series corresponds to a larger crystallite component in vertebrate enamel/enameloid, while the finer component is significantly diminished during diagenesis. The data in Table 1 show that although slightly elongated towards [00l], the crystallites of conodont apatite are significantly more plate-like than those of true vertebrates. However, as organization of the histology of enamel-type mineralized tissue on the finest level into two size-series components is intrinsic to vertebrates, most probably the conodont apatite organization is homologous with that of vertebrates.

In general, we conclude that although altered, the XRD properties of conodont apatite resemble those of Recent vertebrates.

Acknowledgements. The authors thank Viive Viira and Peep Männik for identification of conodont species. The study was supported by the Estonian Research Council (project SF0140016s09).

REFERENCES

Donoghue, P. C. J., Forey, P. L. & Aldridge, R. J. 2000. Conodont affinity and chordate phylogeny. *Biological Reviews*, **75**, 191–251.

Dzik, J. 1986. Chordate affinities of the conodonts. In *Problematic Fossil Taxa. Oxford* (Hoffman, A. & Nitecki, M. H., eds), *Monographs on Geology and Geophysics*, **5**, 240–254.

Ellisson, S. P. 1944. The composition of conodonts. *Journal of Paleontology*, **18**, 133–140.

Harley, J. 1861. On the Ludlow Bone-bed and its Crustacean remains. *Quarterly Journal of the Geological Society, London*, **17**, 542–552.

Kallaste, T. & Nemliher, J. 2005. Apatite varieties in extant and fossil vertebrate mineralized tissues. *Journal of Applied Crystallography*, **38**, 587–594.

Kirsimäe, K., Jørgensen, P. & Kalm, V. 1999. Low-temperature diagenetic illite-smectite in Lower Cambrian clays in North Estonia. *Clay Minerals*, **34**, 151–163.

Männik, P. 1998. Evolution and taxonomy of the Silurian conodont *Pterospathodus*. *Palaeontology*, **41**, 1001–1050.

Nemliher, J. & Kallaste, T. 2005. Thermal behaviour of bone apatite of Recent pike (*Esox lucius* L.). *Proceedings of the Estonian Academy of Sciences, Geology*, **54**, 112–118.

Nemliher, J., Kallaste, T. & Puura, I. 1997. Hydroxyapatite varieties in Recent fish scales. *Proceedings of the Estonian Academy of Sciences, Geology*, **46**, 187–196.

Nemliher, J. G., Baturin, G. N., Kallaste, T. E. & Murdmaa, I. O. 2004. Transition of hydroxyl-apatite of bony phosphate from the sea-floor during fossilization. *Lithology & Mineral Resources*, **39**, 539–551.

Pietzner, H., Vahl, J., Werner, H. & Ziegler, W. 1968. Zur chemischen Zuzammensetzung und Mikromorphologie der Conodonten. *Palaeontographica*, **128**, 115–152.

Smith, M. M., Sansom, I. J. & Smith, M. P. 1996. 'Teeth' before armour: the earliest vertebrate mineralized tissues. *Modern Geology*, **20**, 303–319.

Trotter, J. A. & Eggins, S. M. 2006. Chemical systematics of conodont apatite determined by laser ablation ICPMS. *Chemical Geology*, **233**, 196–216.

Wright, J. 1990. Conodont apatite: structure and geochemistry. In *Skeletal Biomineralization: Patterns, Processes and Evolutionary Trends* (Carter, J. G., ed.), pp. 445–459. V. Nostrand Reinhold, NY.

Zhuravlev, A. V. & Sapega, V. F. 2007. XRD data on composition of the hard tissues of the Late Palaeozoic conodonts. In *Bio-Inert Interactions: Life and Rocks. Materials of the 3rd International Symposium*, pp. 63–64. VSEGEI, St. Petersburg.