

# Isotope and chemical evidence for secondary phosphate mineralization of grasping spines of Lower Palaeozoic Chaetognatha

Hubert Wierzbowski <sup>1</sup>,

Hubert Szaniawski <sup>2</sup>,

Błażej Błażejowski <sup>2</sup>



<sup>1</sup> ***Polish Geological Institute – National Research Institute***

<sup>2</sup> ***Institute of Paleobiology, Polish Academy of Sciences***



POLSKA AKADEMIA NAUK  
**INSTYTUT PALEOBIOLOGII**  
im. Romana Kozłowskiego

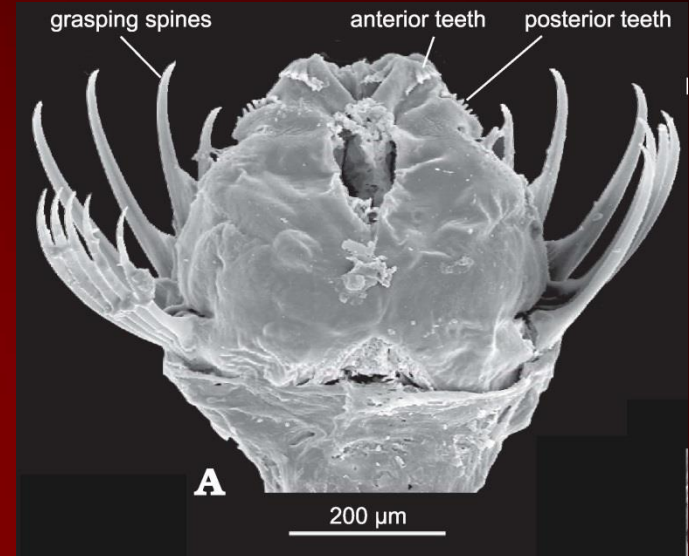
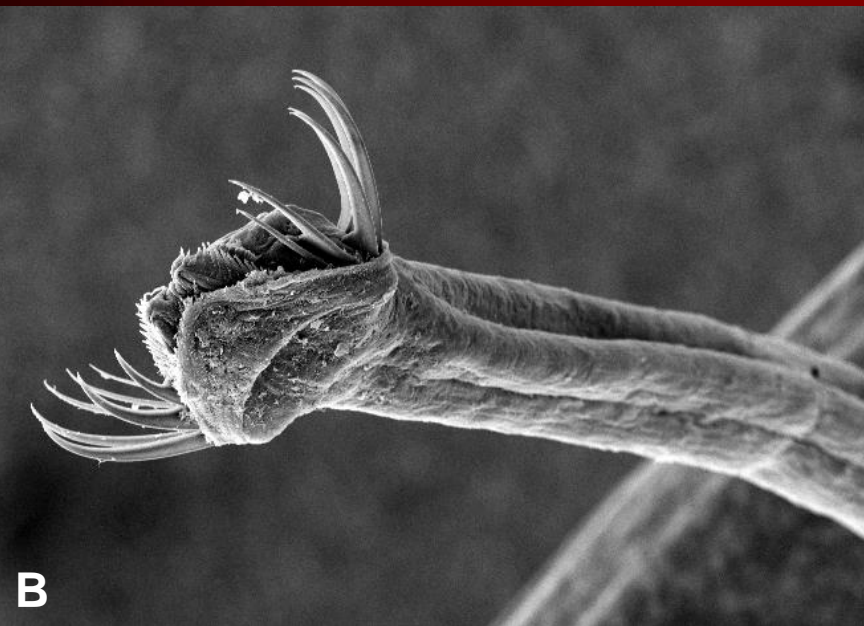
Öland Island, Sweden



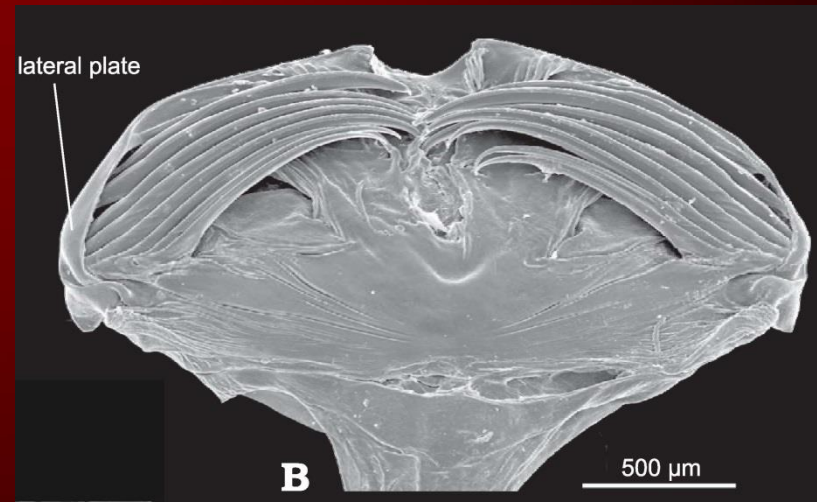
**Chaetognaths (arrow worms) are small marine, invertebrate creatures that possess a jaw organ with grasping spines**

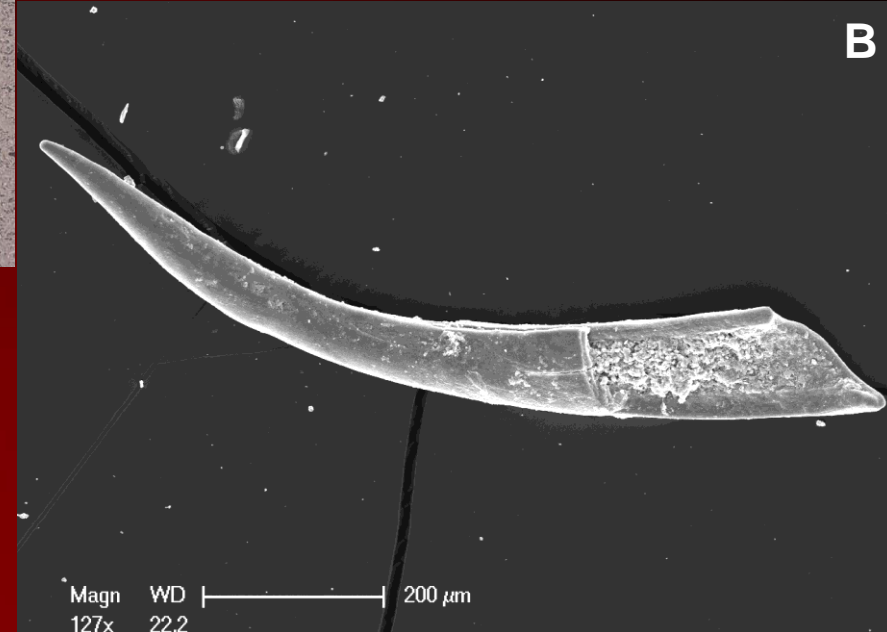


**A modern chaetognath - *Spadella cephaloptera* (A) and a head with grasping apparatus of modern *Sagitta* (B; after Wikipedia)**

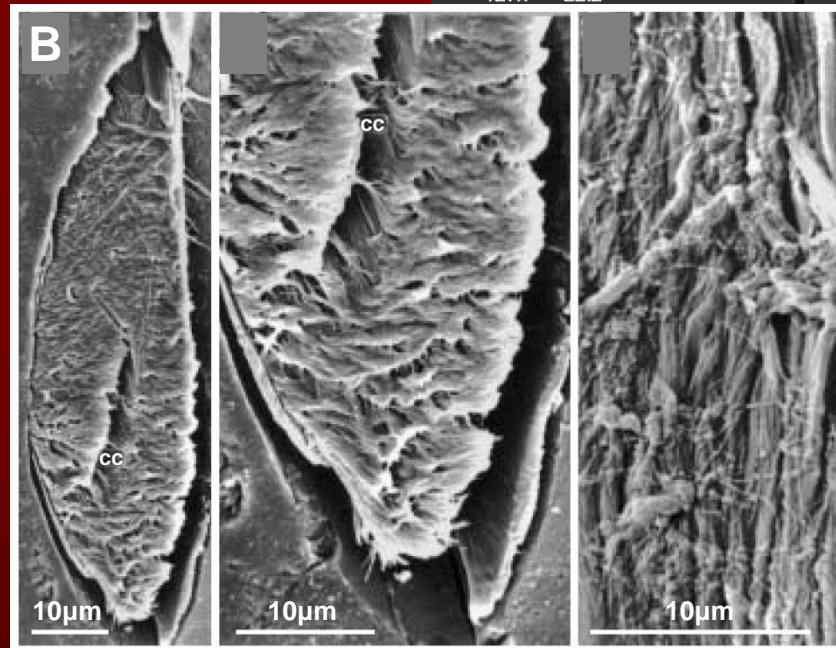
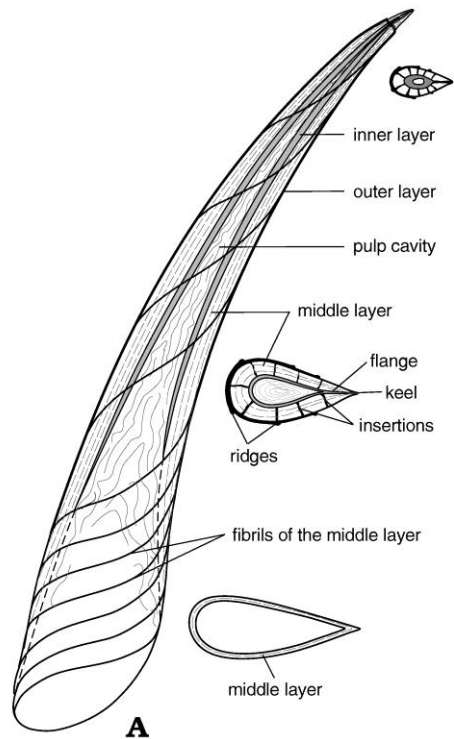


**Heads of modern chaetognaths with grasping apparatus in an open (A) and a resting (B) position (after Szaniawski, 2005)**



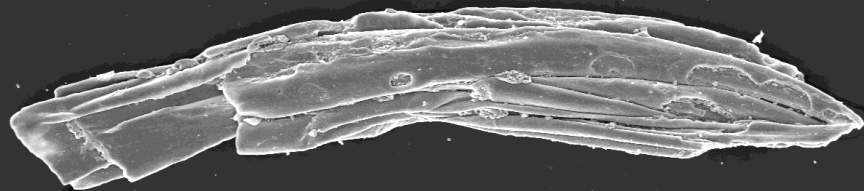


**A, B. Fossil grasping spines of chaetognaths (Cambrian-Ordovician boundary, Öland island, Sweden)**



**Construction of a grasping spine (A; after Szaniawski, 2002) and cross-sections through a modern (B; after Doguzhaeva et al. 2002) and a fossil spine (C)**

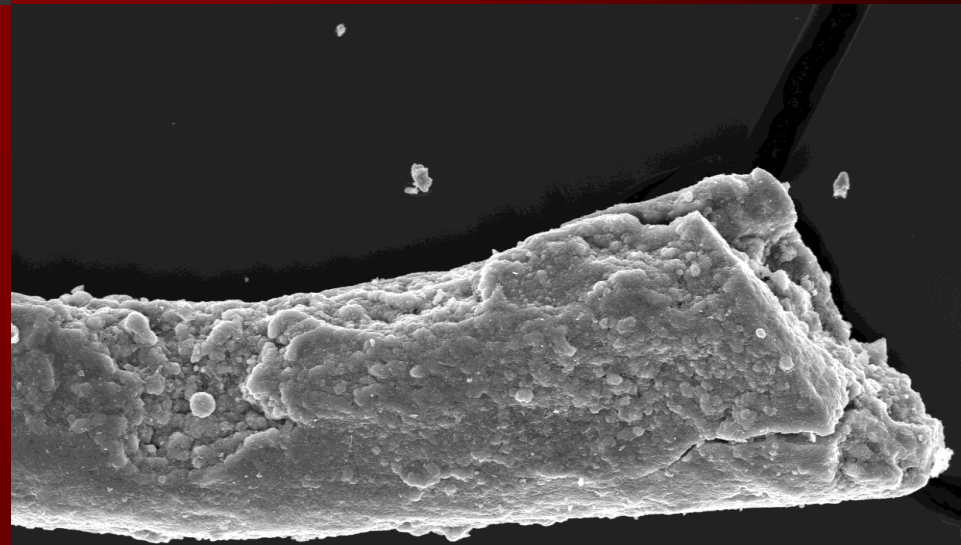




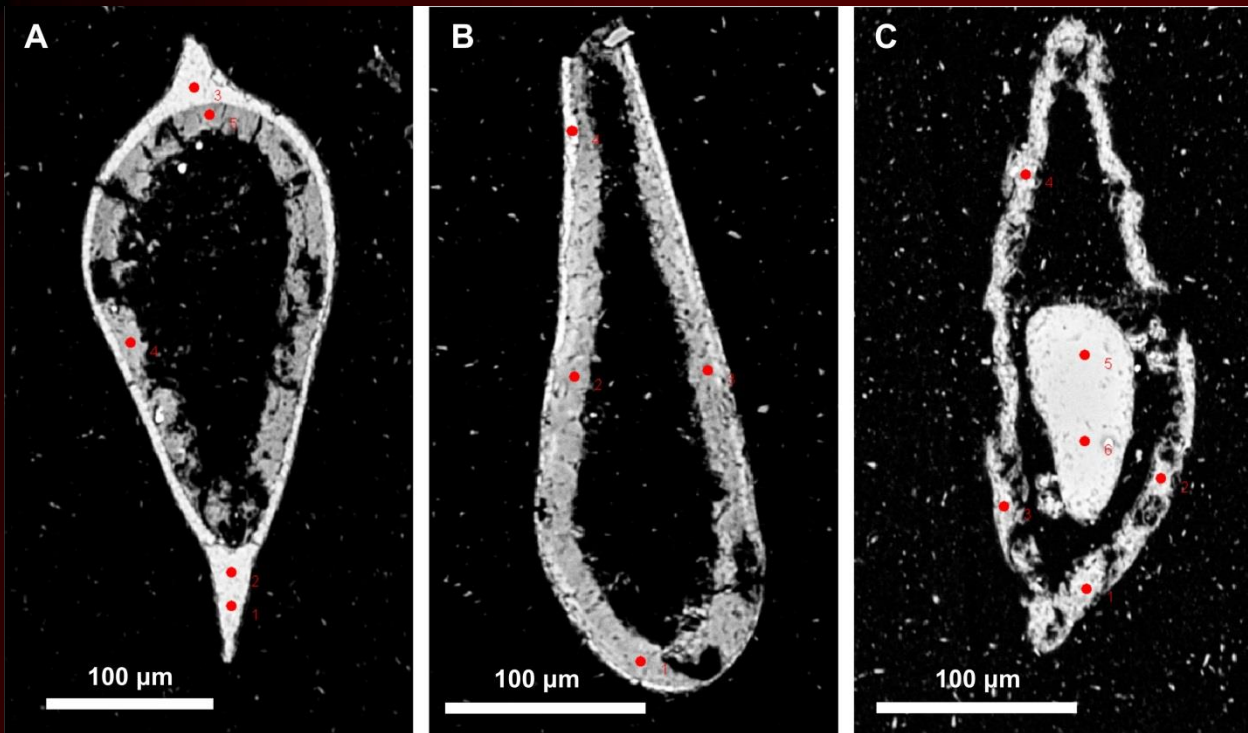
Magn 101x WD 22.0 200  $\mu$ m

Fragment of a *Phakelodus* grasping apparatus (Cambrian–Ordovician boundary, Öland island, Sweden).

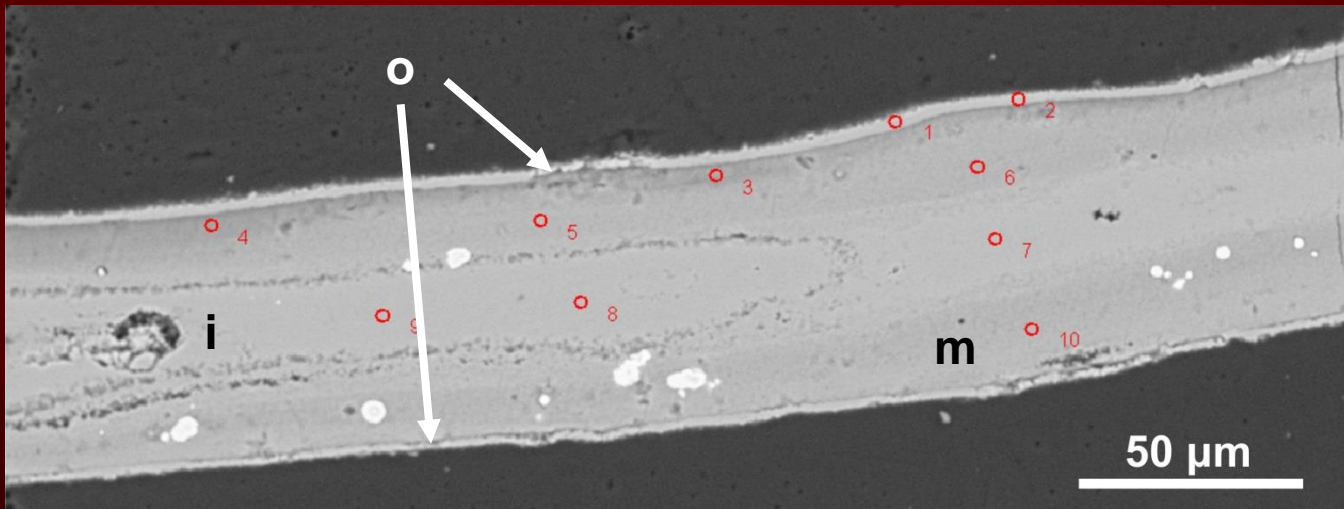
The root area of a grasping spine of *Phakelodus* with large apatite crystals of presumable diagenetic origin (Cambrian–Ordovician boundary, Öland island, Sweden).



Magn 377x WD 22.1 50  $\mu$ m

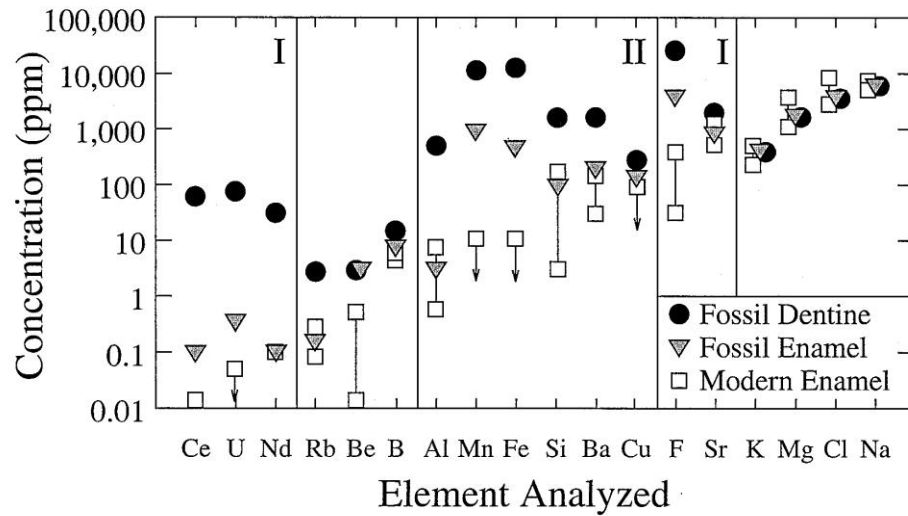


Backscattered electron images of cross-sections of fossil *Phakelodus* spines. (A, B) Outer and middle spine layers are visible. (C) Middle layer and diagenetic, empty space infilling. Red points – chemical analyses



Backscattered electron image of a longitudinal section of fossil a *Phakelodus* spine. Outer (o) and middle (m) spine layers as well as empty space infilling (i) are visible. Red points – chemical analyses

## Elemental concentrations



Concentrations of selected elements in well-preserved and altered mammal teeth (after Kohn et al. 1999).

Elemental concentrations in conodonts (*Cordylodus*, *Palmatolepsis*) and grasping spines of *Phakelodus*. Middle layer and diagenetic infillings of the spines show elevated F, S and decreased Ca, P and Sr contents (electron microprobe analyses – CAMECA SX100)

### Palmatolepsis\_summary

(wt. %)	Na	F	Si	Al	Ca	P	Fe	Mn	Ba	Sr	S	O	Total
---------	----	---	----	----	----	---	----	----	----	----	---	---	-------

#### Albid crown

Mean	0.3	2.9	0.0	0.0	38.9	18.2	0.0	0.0	0.0	0.6	0.1	39.3	100.4
------	-----	-----	-----	-----	------	------	-----	-----	-----	-----	-----	------	-------

#### Hyaline crown

Mean	0.4	3.1	0.0	0.0	37.9	15.5	0.2	0.0	0.1	0.2	0.4	35.6	93.4
------	-----	-----	-----	-----	------	------	-----	-----	-----	-----	-----	------	------

### Cordylodus\_summary

(wt. %)	Na	F	Si	Al	Ca	P	Fe	Mn	Ba	Sr	S	O	Total
---------	----	---	----	----	----	---	----	----	----	----	---	---	-------

#### Albid crown

Mean	0.4	3.0	0.0	0.2	38.8	17.4	0.0	0.0	0.0	0.7	0.0	38.4	98.9
------	-----	-----	-----	-----	------	------	-----	-----	-----	-----	-----	------	------

### Phakelodus\_summary

(wt. %)	Na	F	Si	Al	Ca	P	Fe	Mn	Ba	Sr	S	Cl	Mg	O	Total
---------	----	---	----	----	----	---	----	----	----	----	---	----	----	---	-------

#### Outer layer

Mean	0.3	2.4	0.0	0.0	39.2	17.1	0.1	0.0	0.0	0.2	0.2	0.1	0.0	38.3	97.9
------	-----	-----	-----	-----	------	------	-----	-----	-----	-----	-----	-----	-----	------	------

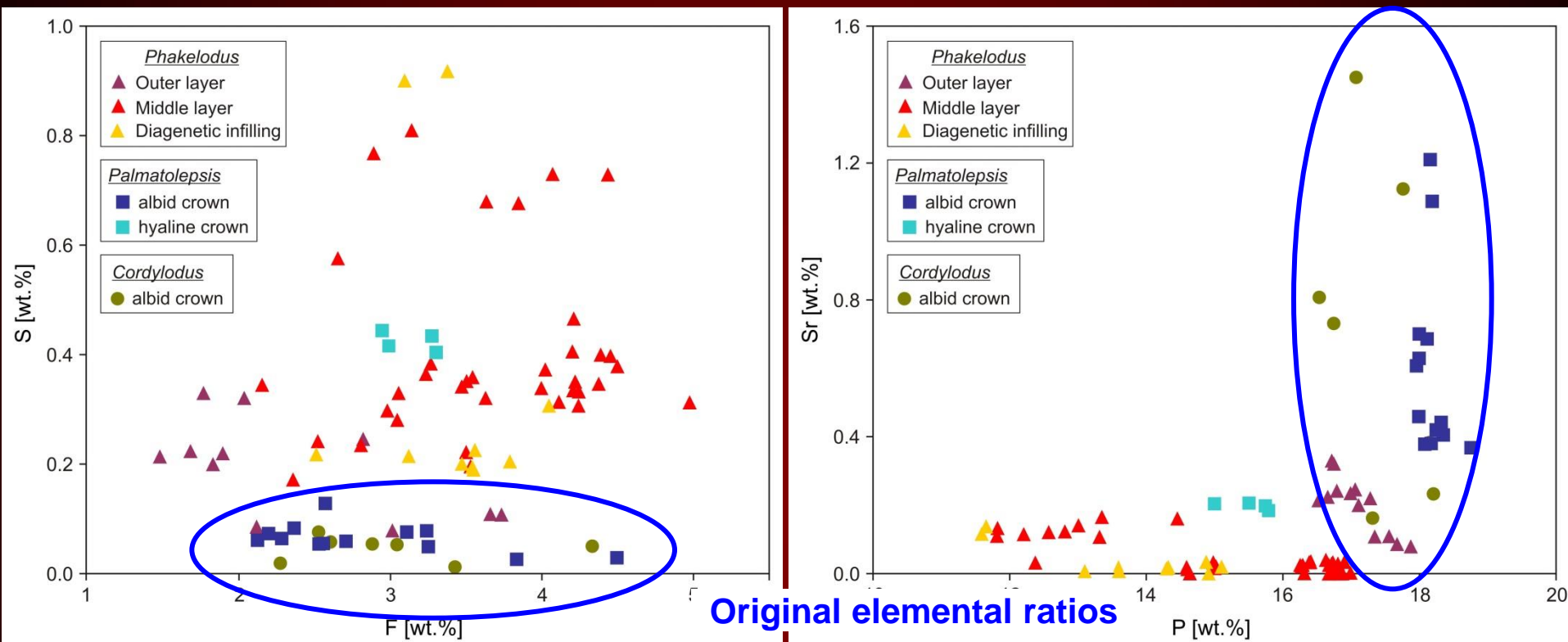
#### Middle layer

Mean	0.3	3.6	0.0	0.0	35.1	15.2	0.2	0.0	0.0	0.0	0.4	0.1	0.1	34.4	89.6
------	-----	-----	-----	-----	------	------	-----	-----	-----	-----	-----	-----	-----	------	------

#### Diagenetic infilling

Mean	0.2	3.4	0.1	0.1	36.6	13.7	0.1	0.0	0.0	0.0	0.4	0.0	0.0	33.0	87.8
------	-----	-----	-----	-----	------	------	-----	-----	-----	-----	-----	-----	-----	------	------

## Results of chemical analyses using an electron microprob (CAMECA SX100)



**Elemental concentrations in conodonts (*Cordylodus*, *Palmatolepsis*) and grasping spines of *Phakelodus*. Middle layer and diagenetic infillings of the spines show elevated S (and partly F) and decreased P and Sr contents. The outer layer of *Phakelodus* and albid crowns of conodonts have similar elemental concentrations (electron microprobe analyses –CAMECA SX100)**





**Cordylodus (€/O)**

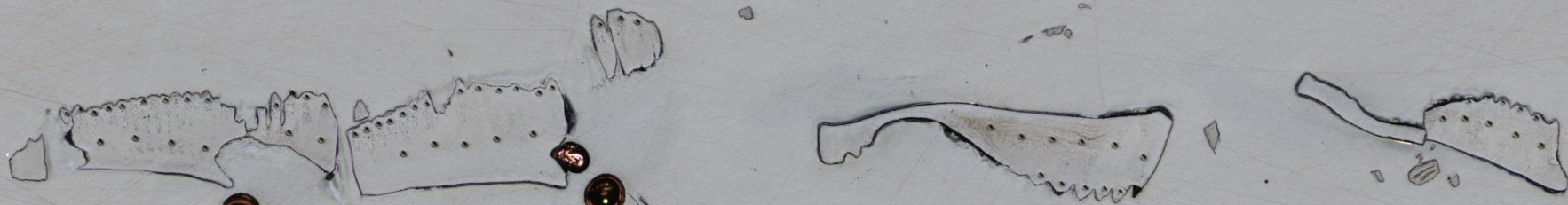
**A-2**

Measured  $^{18}\text{O}/^{16}\text{O}$  ratio was calibrated to Durango 3 ( $\delta^{18}\text{O} = 9.8\text{‰}$  VSMOW). S.E. of spot measurements was between 0.1 to 0.3‰. S.D. of analyses of the Durango 3 was 0.16‰ (n = 16).

**Durango**

**Phakelodus (€/O)**

**A-1**



**A-3**

**Palmatolepsis (D)**

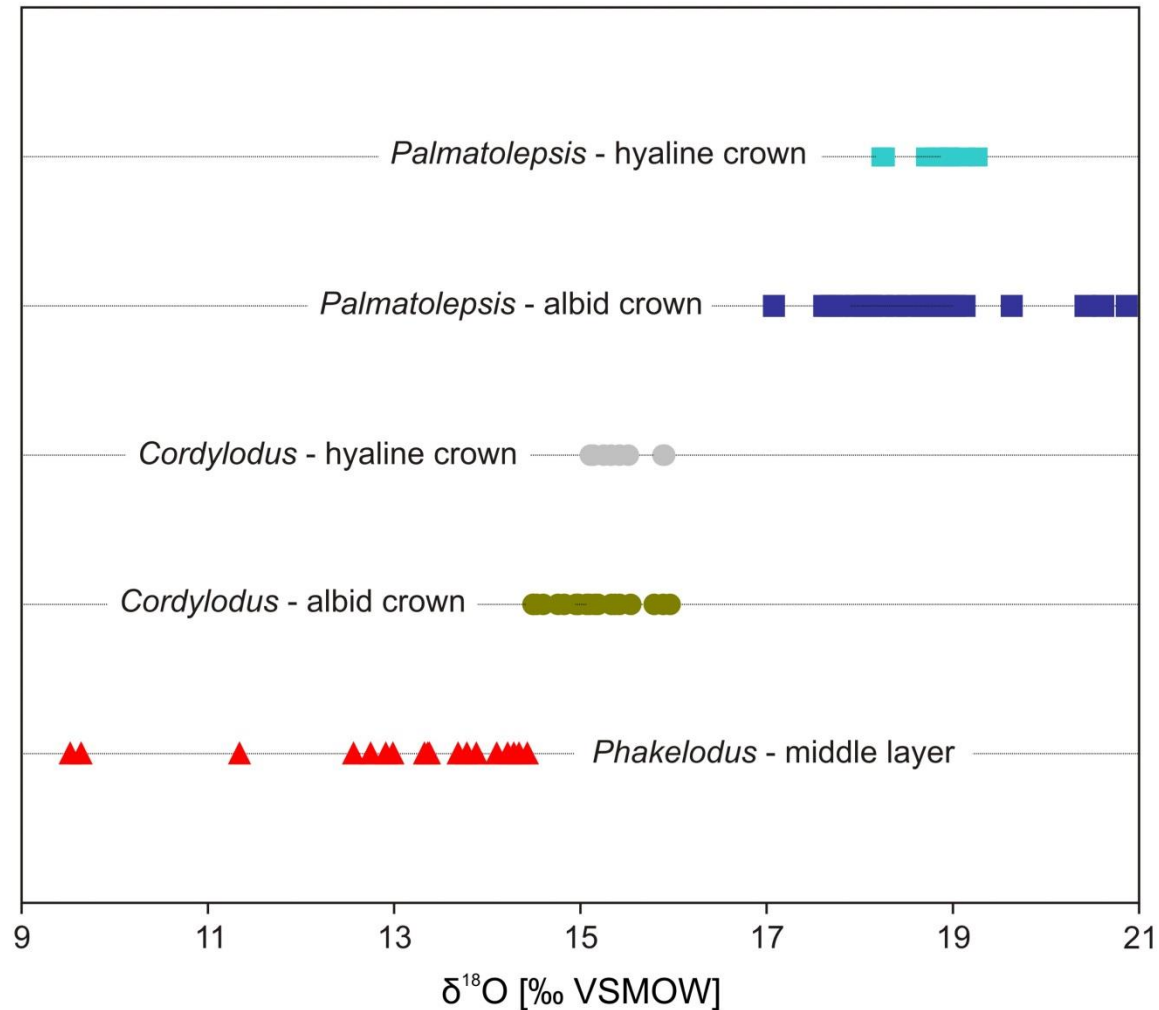
1 mm

**Reflected light image of chaetognath grasping spines (A1) and conodonts (A2, A3) analysed for  $\delta^{18}\text{O}$  values using a SHRIMP IIe/MC ion microprobe**



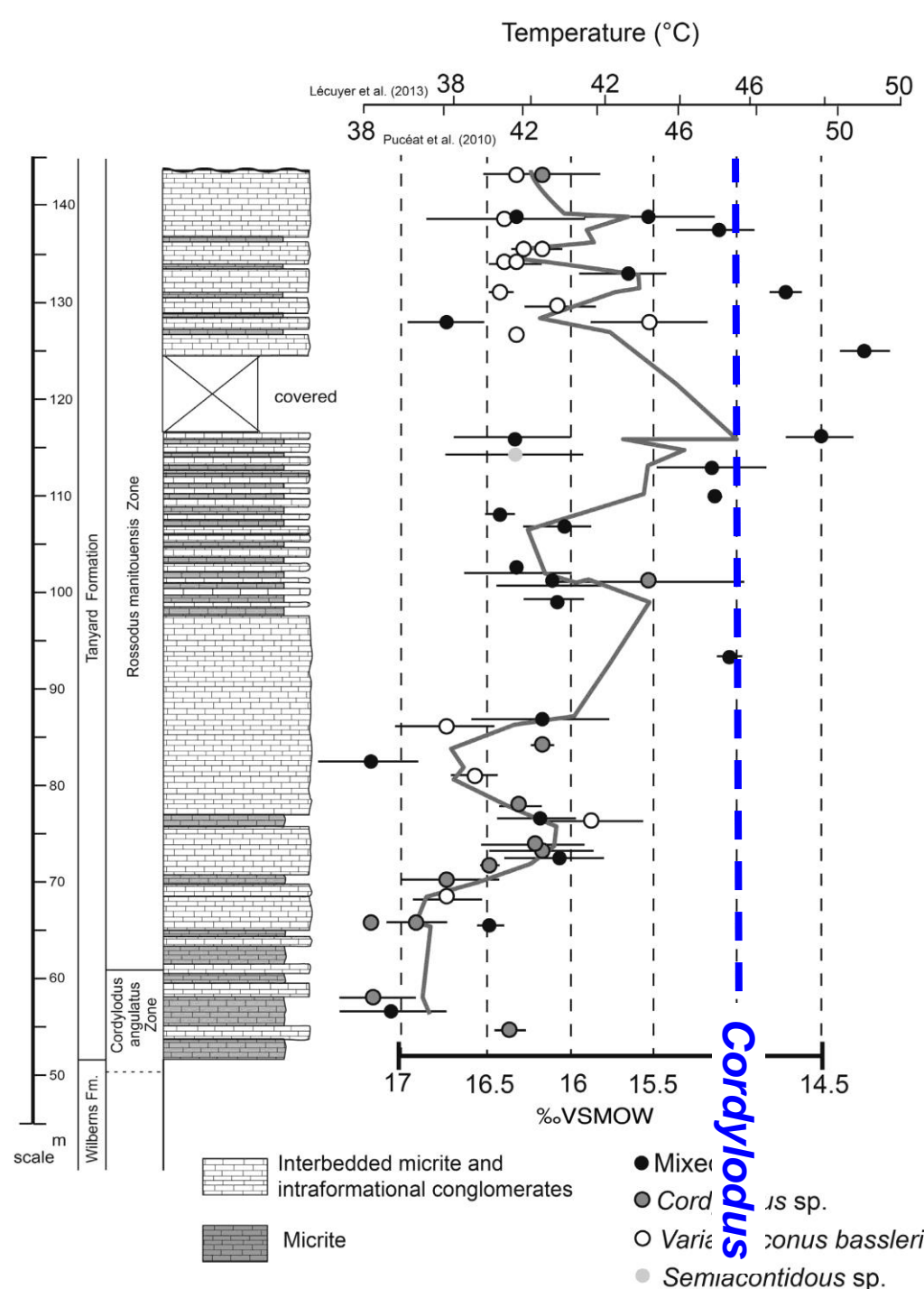
Phakelodus (€/O)		Cordylodus (€/O)				Palmatolepsis (D)			
Middle layer		Albid		Hyaline		Albid		Hyaline	
	$\delta^{18}\text{O}$ (‰VSMOW)		$\delta^{18}\text{O}$ (‰VSMOW)		$\delta^{18}\text{O}$ (‰VSMOW)		$\delta^{18}\text{O}$ (‰VSMOW)		$\delta^{18}\text{O}$ (‰VSMOW)
Min	9.5	Min	14.5	Min	15.1	Min	17.1	Min	18.2
Mean	13.0	Mean	15.1	Mean	15.4	Mean	18.7	Mean	18.8
Max	14.4	Max	16.0	Max	15.9	Max	20.9	Max	19.3

Ion microprobe (SHRIMP IIe/Mc) analyses have shown low  $\delta^{18}\text{O}$  values of the middle layer of *Phakelodus* grasping spines (ca. 13‰ VSMOW) which are much lower than those of coeval *Cordylodus* conodonts. This proves a diagenetic origin of *Phakelodus* oxygen isotope signal.



CAMBRIAN	EARLY ORDOVICIAN
	Tremadocian
	Skullrockian Stage
<i>C. lindstromi</i> - <i>C. proavus</i>	<i>R. manitouensis</i>
MooreHollow Group	Ellenberger Group
Wilberns Formation	Tanyard Formation
San Saba Member	Threadgill Member
	Study interval

Lower Ordovician conodont  $\delta^{18}\text{O}$  values from USA (after Quinton et al. 2018). The measured  $\delta^{18}\text{O}$  values of *Cordylodus* (ca. 15‰ VSMOW) match a part of the trend, whereas much lower *Phakelodus*  $\delta^{18}\text{O}$  values (ca. 13‰ VSMOW) are of clear diagenetic origin.





- ◆ **Apatite grasping spines of Lower Palaeozoic chaetognaths reveal major morphological and microstructural differences from conodonts and a resemblance to modern chaetognath spines built of chitin.**
- ◆ **Chemical analyses of the grasping spines conducted by an electron microprobe have shown diagenetic signatures of their middle layer and internal infillings. The outer layer of grasping spines has, in turn, elemental concentrations similar to those of conodonts.**
- ◆ **Results of microsampling of the grasping spines using a SHRIMP IIe/MC ion microprobe have shown low  $\delta^{18}\text{O}$  values (ca. 13‰ VSMOW) of their middle layer and confirmed its diagenetic origin.**
- ◆ **Although a thin, outer apatite layer of grasping spines of Palaeozoic chaetognaths, might have been precipitated during the animal growth or during very early submarine diagenetic processes it is too thin to form the sole structural support. The rest of the spines were presumable built of chitin or chitin-apatite complexes and underwent pervasive diagenetic phosphatization.**

**Thank you**  
**for your attention!**