Nd isotope composition of early Cambrian discrete basins

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Abstract – A Nd isotope map of early Cambrian epeiric basins has been inferred from the Nd isotopic signature recorded in phosphatic Small Shelly Fossils. The most radiogenic $\varepsilon_{Nd}(t)$ values characterize water reservoirs along the Avalonian and Cadomian belts, while $\varepsilon_{Nd}(t)$ values of –10 to –20 were obtained in Laurentia and East Gondwanan Australia and China. Such a distribution of Nd isotope signatures results from the different provenance of early Cambrian epeiric seas: juvenile magmatic arcs and/or cordilleran for Mongolia, Siberia, Iberia and adjacent terranes, and cratonic sources for Laurentia and East Gondwana. Biogenic apatite of Small Shelly Fossils may be a useful tool for mapping of Nd isotope composition and documenting water mass exchange between discrete basins.

1. Introduction

The Precambrian-Cambrian transition is a most dramatic period in the Earth's history. It is therefore crucial for the understanding of evolutionary changes in the Earth's external system including the biosphere. One of the most amazing events to take place at the beginning of the early Cambrian was the appearance and explosive diversification of Small Shelly Fossils (Conway Morris, 1989). Small Shelly Fossils are known from all continents and their wide geographic distribution and rapid evolution may facilitate the reconstruction of the spatio-temporal framework of major biotic and abiotic events (Gubanov, 2000). The almost instantaneous appearance of Small Shelly Fossils on all continents and their stable morphological features over all contemporaneous populations suggest the presence of closely related biotopes with extensive genetic exchanges. This surprising worldwide similarity of early Cambrian Small Shelly Fossils implies the occurrence of an immense shallow basin or a cluster of closely related basins. A reasonable explanation for this phenomenon is the existence of the early Cambrian supercontinent or, at least, a compact collage of continents separated by narrow seaways. However, existing palaeogeographic reconstructions tell us a different story. The presumed Proterozoic supercontinent Rodinia is supposed to have disintegrated around 750 Ma and Siberia, Baltica, Laurentia and Gondwana were far apart from each other at the beginning of Cambrian times (Torsvik et al. 1996 and references therein). In addition, the assumption that all early Cambrian organisms were pelagic or had planktonic larvae, which would enable them to reach any remote biotopes, seems implausible. Even

acritarch specialists, who are clearly dealing with planktonic organisms, are much more comfortable with narrow seaway reconstructions to explain taxonomic similarities (Moczydłowska, 1995, 1997).

The Nd isotopic composition of modern-day seawater is controlled by the provenance of radiogenic Nd released from source terranes surrounding ocean basins. The $\varepsilon_{Nd}(0)$ signature of recent oceans varies from -15.1 ± 3.4 in the northern Atlantic, through -8.3 ± 1.2 in the Indian Ocean, to -3.5 ± 1.7 in the Pacific, reflecting the prevalent Nd isotopic composition of bordering areas (Bertram & Elderfield, 1993). High values of $\varepsilon_{Nd}(0)$ characterize basins such as those of the Pacific Ocean which are surrounded by active continental margins with high proportions of young, mantle-derived volcanogenic rocks. In contrast, low values of $\varepsilon_{Nd}(0)$ occur in basins such as those of the Atlantic Ocean which are surrounded by old crystalline basements supplying low radiogenic Nd. Nd isotopic compositions of ancient seawater recorded in the $\varepsilon_{Nd}(t)$ values of fossil apatite (Bertram *et al.* 1992; Holmden et al. 1996; Stille, 1992; Stille, Steinmann & Riggs, 1996) deriving from stratigraphically welldefined levels, could be useful tools for reconstructing provenance, tracking changes in basinal configurations through time, and estimating ancient ocean circulation patterns. Strong local provenance controls on Nd isotope compositions in epeiric seawaters results in wide scatters of original $\boldsymbol{\epsilon}_{Nd}$ values recorded in biogenic apatite from different parts of any basin (Holmden et al. 1998) that correlate with the distribution of $\boldsymbol{\epsilon}_{_{Nd}}$ values in the surface water of modern-day oceans (Amakawa, Alibo & Nozaki, 2000). Regardless of such variations, both in recent seawater and in old biogenic apatite, the concept of discrete reservoir Nd isotopic signatures makes Nd systematics a useful tool in palaeoceanography (Keto & Jacobsen, 1987, 1988;

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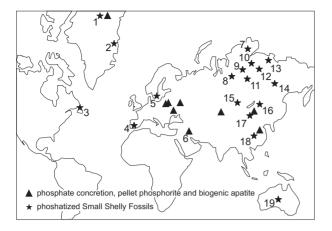


Figure 1. Location of studied latest Neoproterozoic–early Cambrian samples. 1 – northern Greenland; 2 – eastern Greenland; 3 – western Newfoundland; 4 – central Iberia; 5 – southern Sweden; 6 – Iran, Alborz Mountains; 7 – northern Siberia, Taimyr, Graviinaya River; 8 – northwestern Siberia, Sukharikha River; 9–12 – Northern Siberia; 13 – northeastern Siberia, Chekurovka village; 14 – eastern Siberia, Selinde River; 15 – Kuznetsky Alatau, Kiya River; 16 – Transbaikal, Georgievka village; 17 – western Mongolia, Zavkhan Basin; 18 – southern China, Meishucun village; 19 – South Australia, Flinders Ranges.

Holser, 1997). Decreased North Atlantic deep water flux to the Pacific during the last 80 ka (Rutberg, Hemming & Goldstein, 2000) as well as evolution of the palaeocurrents in the Mesozoic Atlantic and Tethys oceans (Stille, Steinmann & Riggs, 1996) were inferred from variations of Nd isotope ratios in marine precipitates. Using a similar approach, circulation patterns of water masses between discrete basins may be documented with Nd isotopic records in early Cambrian biogenic apatite.

Here we present new Nd isotope data on biogenic apatite from the earliest Small Shelly Fossils as the means to: (a) recognize the original Nd isotopic signatures of early Cambrian epeiric basins containing abundant fauna, and (b) integrate Nd isotope distribution data for relevant continental reconstruction. Forty-one samples of Small Shelly Fossils represented by the earliest helcionelloid molluscs with phosphatized (francolite) shells, as well as some problematic fossils, brachiopods with organo-phosphatic shells, phosphate nodules and pellet phosphorite, were studied from a variety of Lower Cambrian reference sections (Fig. 1). Molluscan shells of Aldanella, Anabarella, Watsonella, Oelandiella, Barskovia and the problematic Anabarites are abundant in early Tommotian strata; they were often used as reliable tools for global correlations (Brasier & Singh, 1987; Jiang, Brasier & Hamdi, 1989; Khomentovsky & Karlova, 1993; Gubanov, 2000) and palaeogeographic reconstructions (Gubanov, 1998, 2000) for the early Cambrian period. The basal Tommotian, as the most fossiliferous and stratigraphically well-defined level, was chosen to illustrate the spatial distribution of Nd isotopes for the Siberian Platform. Supplementary data are based on a study of brachiopod shells which are the dominant fossils in overlying Atdabanian to Toyonian strata.

2. Material and methods

The beginning of the Cambrian period was marked by the appearance and rapid diversification of the first Small Shelly Fossils, including molluscs. The first molluscs are usually small animals, a few millimetres in size, with a mineralized carbonate, cone-shaped or coiled shell (Fig. 2). Taxonomically, these molluscs are far from any modern mollusc and form the distinct Class Helcionelloida within the Mollusca (Peel, 1991). The first helcionelloid molluscs appeared in the earliest Cambrian (the late Nemakit-Daldynian of the Siberian time scale), experienced their acme in the early Cambrian (Tommotian-Atdabanian) and became extinct in the early Ordovician (Gubanov & Peel, 2001). The wide spatial distribution (Fig. 1) and explosive evolution of these molluscs were recently used to facilitate understanding of early Cambrian stratigraphy and palaeogeography (Gubanov, 2000). Most early Cambrian phosphatic Small Shelly Fossils and molluscs occur in shallow depositional facies representing platform or coastal environments.

Molluscs are usually preserved as phosphatized internal or external moulds with the shells replaced by phosphate. Phosphatization of soft tissue is an almost instantaneous (few hours) process in the milieu containing enhanced concentrations of phosphorus (Müller, 1983; Rozanov & Zhegallo, 1989; Gerasimenko et al. 1996). The phosphorus content in studied Small Shelly Fossils is usually as high as 12.2 ± 1.9 wt%, (n=27, microprobe data with LINK AN 10/85s; the whole surface of each sample was scanned to obtain the bulk concentration of major elements) with a Ca/P ratio (% wt) of 2.27 ± 0.18 . These values are compatible with a phosphorus content ranging from 9.2-14.0 wt % in pelletic phosphorite from Janytas mine field (early Cambrian, Maly Karatau, S. Kazakhstan), Doushantuo Formation (Sinian, Yangtze Gorges Region, S. China) and latest Neoproterozoic phosphorite of the Tsagaan Oloom Formation of the Salaany Gol Ridge section, Zavkhan Basin, western Mongolia. The Ca/P ratio in Small Shelly Fossils is slightly higher than in ideal carbonate-fluorapatite (2.15), in accordance with the mineral constituents in phosphatic moulds, a given deficit of phosphorus being expected for the collophane of marine phosphorite (Altschuler, 1973). Incorporation of REE and other elements into the phosphate debris in *post-mortem* stages is considered to occur within a 10^{1} – 10^{3} year time window (Holmden *et al.* 1996). All studied early Cambrian Small Shelly Fossils were deposited in a variety of epeiric seas where the

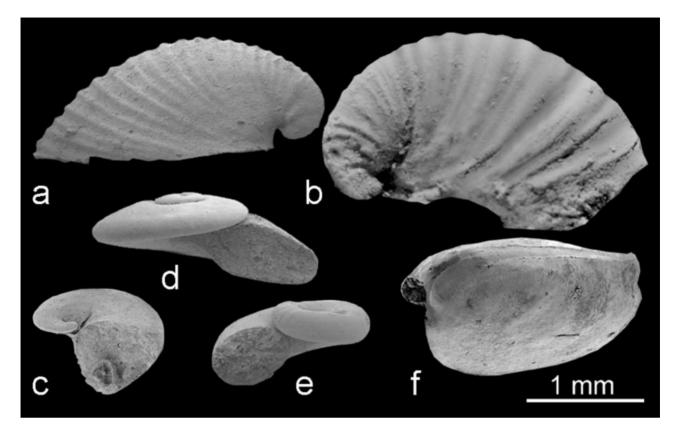


Figure 2. Phosphatized moulds of the early Cambrian helcionelloid molluscs. (a) *Oelandiella* sp. from the Dahai Member (Meisuchunian) of southern China. (b) *Anabarella* sp. *A*. cf. *plana* from the Upper Alcudian of south-central Spain. (c) *Pelagiella* sp. from the Bystraya Formation (Botomian) of Transbaikal (southern Siberia). (d) *Aldanella* sp. from the Graviinaya River Fm of Taimyr (northern Siberia). (e) *Barskovia* sp. from the Pestrotsvet Formation (Tommotian) of the Selinde River (southeastern Siberia). (f) *Watsonella sibirica* from the Medvezhinskaya Formation of the Rassokha River (northeastern Siberia).

sedimentation rate was 0.5-5.0 cm/1000 years (Kukal, 1983). Hence, the bottom layer of the water column was a source of elements trapped in cryptocrystalline biogenic apatite of the Small Shelly Fossil moulds and Nd isotope composition in Small Shelly Fossils should display the instant imprint of contemporaneous bottom water with an original Nd isotope signature. The old biogenic apatites with 'bell-' or 'hat-shaped' REE patterns were considered to be affected by a substitution mechanism of the REE incorporation at the late diagenetic stage (Reynard, Lécuyer & Grandjean, 1999) which could distort the Nd isotope signatures obtained on the rapid post-mortem phosphatization of the Small Shelly Fossils. Samples with pronounced middle REE enrichments (La/Sm_{sn} less than 0.4 and Sm/Yb_{sn} more than 2.0, 'sn' = shale-normalized values) are not presented in Table 1.

The thermal alteration of host rocks, that potentially could affect the original isotopic data, was very low; indices suggest that the rocks were heated primarily by burial, with negligible secondary heating from tectonism. The most altered host rocks of the Forteau Formation were buried no more than a few kilometres, with a thermal impact less than 200°C (Williams, Burden & Mukhopadhyay, 1998). The thermal impact on latest Neoproterozoic–early Cambrian sediments of the East European Platform does not even exceed 70°C (Felitsyn, Vidal & Moczydłowska, 1998). We therefore expect that the studied fossil apatite retained the Nd isotope compositions of seawater overlying the depositional sites, and that it provides a record of $\varepsilon_{Nd}(t)$ of the early Cambrian water masses.

The isotopic composition of Nd was measured using a Finnigan MAT-261 mass spectrometer at the Laboratory of Isotopic Geochronology and Geochemistry of the Institute of Precambrian Geology and Geochronology, St. Petersburg. The ¹⁴³Nd/¹⁴⁴Nd ratio was normalized within-run to ¹⁴⁸Nd/¹⁴⁴Nd = 0.241570. Seventy to ninety ratios for Nd were collected for adequate precision. Assigned errors (2 σ) for ¹⁴⁷Sm/¹⁴⁴Nd and ¹⁴³Nd/¹⁴⁴Nd were $\pm 0.3\%$ and ± 0.000015 according to results of multiple analyses of the La Jolla standard 0.511876±11 (21 measurements during the course of analysis). The 2σ errors cited in a table for ¹⁴³Nd/¹⁴⁴Nd reflect in-run precision and demonstrate the internal reproducibility of these analyses. The blank level for Sm was 0.01 ng and 0.05 ng for Nd. The data obtained for BCR-1 during the course of this analytical work are: Sm = 6.487 ppm, Nd = 28.45 ppm, 143 Nd/ 144 Nd = 0.512663 ± 9,

Table 1. Sm-Nd isotopic data for fossil apatite from a variety of early Cambrian reference successions

Material	Formation	Age	Sm (ppm)	Nd (ppm)	¹⁴⁷ Sm/ ¹⁴⁴ Nd	⁴³ Nd/ ¹⁴⁴ Nd±2σ measured	¹⁴³ Nd/ ¹⁴⁴ Nd initial		La/Yb _{s1}	Cr (ppm)
Siberia										
Aldanella sp.	Krasnyi Porog Fm	Tommotian	88.41	427.3	0.12547	0.512033 ± 21	0.511585	-6.5	3.1	24
<i>Aldanella</i> sp.	Emyaksa Fm	Tommotian	41.67	206.2	0.12258	0.512097 ± 17	0.511659	-5.6	3.5	23
<i>Aldanella</i> sp.	Emyaksa Fm	Tommotian	32.07	170.7	0.11392	0.512280 ± 13	0.511873	-1.5	3.0	9
*		Tommotian	70.68	364.5	0.11759		0.511637	-6.1	4.0	10
<i>Ildanella</i> sp.	Emyaksa Fm					0.512057±23				
<i>ldanella</i> sp.	Tyuser Fm	Tommotian	120.1	546.1	0.13331	0.512101 ± 22	0.511625	-6.1	2.2	54
<i>ldanella</i> sp.	Emyaksa Fm	Tommotian	37.61	188.9	0.12071	0.512092 ± 17	0.511661	-5.6	1.9	76
I <i>ldanella</i> sp.	Pestrotsvet Fm	Tommotian	37.48	163.2	0.13932	0.512129 ± 15	0.511632	-6.1	4.3	14
Vestern Mongolia										
Vatsonella sp.	Bayan Gol Fm	Tommotian	16.53	63.21	0.13812	0.512267 ± 16	0.511774	-2.9	2.1	27
nabarites sp.	Bayan Gol Fm	Tommotian	50.63	236.4	0.13451	0.512278±19	0.511798	-2.9	3.1	41
nabarites sp.	Bayan Gol Fm	Nemakit-Daldynian	8.855	38.93	0.13794	0.512259 ± 18	0.511766	-3.5	0.8	27
nabarites sp.	Bayan Gol Fm	Nemakit-Daldynian	29.24	146.2	0.13124	0.512178±21	0.511709	-4.1	1.3	92
nabarites sp.	Bayan Gol Fm	Nemakit-Daldynian		65.11	0.13361	0.512294±15	0.511817	-2.5	1.3	59
arskovia sp.	Bayan Gol Fm	Nemakit-Daldynian		67.23	0.13654	0.512287 ± 21	0.511799	-2.9	1.8	111
entral Iberia		The state of the s	120.6	500.0	0.15210	0.510141+11	0.511504	()	1.0	25
Anabarella sp.	Upper Alcudian Fm	Tommotian	128.6	509.3	0.15318	0.512141±11	0.511594	-6.3	1.3	35
altica										
Iickwitzia monilifera	Mickwitzia Sandstone	Atdabanian	327.4	1367	0.15388	0.512081 ± 16	0.511601	-8.3	1.9	18
hosphate concretion	Lezha Fm	Tommotian	95.4	542	0.12308	0.511915±9	0.511576	-9.1	1.6	10
hosphate concretion		Tommotian	108.4	606	0.13377	0.511985±4	0.511554	-8.6	1.5	11
hosphate concretion		Tommotian	169.8	450.2	0.22879	0.511905 ± 4 0.512410 ± 14	0.512002	-7.6	0.8	22
pper Silesia										
hosphate concretion	Goczałkowice Fm	Atdabanian	219.3	467.9	0.28329	0.512583±11	0.511571	-7.1	0.8	41
outhern Kazakhstan (Maly Karatau)									
ellet phosphorite	Chulaktau Fm	Tommotian	10.125	50.103	0.12224	0.512014±9	0.511582	-7.0	1.2	62
ellet phosphorite	Chulaktau Fm	Tommotian	10.452	51.533	0.12270	0.512009 ± 14	0.511575	-7.2	1.1	55
ustralia										
<i>licrina</i> sp.	Wilkawillina Fm	Atdabanian	24.56	94.42	0.15719	0.511804 ± 14	0.511243	_13.6	1.1	16
<i>licrina</i> sp.	Wilkawillina Fm	Atdabanian	53.84	177.9	0.18283	0.511983 ± 9	0.511245		1.2	18
outhern China										
	Valaria En	T	20.07	157 (0.11065	0.51170(+12	0.511201	10.7	1.0	22
<i>Iyolithes</i> sp.	Yuhucun Fm	Tommotian	29.97	157.6	0.11065	0.511786 ± 13		-10.7	1.0	23
<i>Delandiella</i> sp.	Yuhucun Fm	Tommotian	24.79	137.7	0.10883	0.511732±24	0.511343	-11.6	1.3	29
uznetski Alatau (Kiya	/									
<i>Barskovia</i> sp.	Ust'kundat Fm	Tommotian	29.99	136.9	0.13251	0.512113±13	0.511640	-5.9	1.0	41
ran										
Biogenic phosphate	Soltanieh Fm	Tommotian	71.06	352.7	0.12187	0.512024±11	0.511589	-6.9	6.4	11
ransbaikal										
Pelagiella sp.	Bystraya Fm	Botomian	12.34	57.91	0.12886	0.512201 ± 12	0.511741	-3.9	1.6	31
aimyr										
I <i>ldanella</i> sp.	Graviinaya R. Fm	Tommotian	43.26	213.6	0.12255	0.512098 ± 8	0.511660	-5.3	2.0	12
Vestern Newfoundland	l									
<i>ochelcionella</i> sp.	Forteau Fm	Botomian	105.9	375.3	0.17085	0.511744±9	0.511134	-157	1.6	7
<i>Iyolithes</i> sp.	Forteau Fm	Botomian	75.99	310.3	0.14814	0.511687 ± 12	0.511154		2.4	12
orthern Greenland										
iogenic phosphate,	Henson Gletscher Fm	Botomian	67.06	322.2	0.12589	0.511756±8	0.511306	-12.4	3.0	9
brachiopods										
iogenic phosphate, brachiopods	Henson Gletscher Fm	Botomian	69.92	310.4	0.13627	0.511874±13	0.511387	-11.0	1.7	41
iogenic phosphate,	Aftenstjernesø Fm	Botomian	60.1	455.0	0.07986	0.511724±11	0.511439	-9.9	4.3	20
brachiopods liogenic phosphate,	Henson Gletscher Fm	Botomian	110.0	432.8	0.15381	0.512235±10	0.511686	-5.0	1.6	19
brachiopods biogenic phosphate,	Aftenstjernesø Fm	Botomian	26.35	134.4	0.11859	0.511805±12	0.511382	-22.4	3.5	5
brachiopods	5									
hosphate concretion hosphate concretion	Aftenstjernesø Fm Portfjeld Fm	Botomian Atdabanian	147.2 57.66	626.0 228.9	0.14221 0.15239	0.511336±9 0.511434±11	0.510828 0.510890	-21.7 -20.5	4.0 5.0	4 6
	-									
astern Greenland									_	
iscinella micans	Ella Island Fm	Botomian	194.7	934.1	0.12612	0.511248 ± 16	0.510798		5.7	2
otsfordia caelata	Bastion Fm	Atdabanian-	168.2	765.9	0.13282	0.511644±13	0.511170	-15.1	4.4	14
		Botomian								
Eoobolus prisca	Bastion Fm	Atdabanian-	261.1	857.9	0.18412	0.511808 ± 7	0.511151	-15.4	2.1	8
20000ius priscu		Botomian								

 $^{147}\text{Sm}/^{144}\text{Nd}$ = 0.13829 (5 measurements). Nd isotopic compositions of the Small Shelly Fossils are also presented in epsilon notation: $\epsilon_{\rm Nd}(t)$ = $[(^{143}\text{Nd}/^{144}\text{Nd})_{\rm sample}$ (t)/ $^{143}\text{Nd}/^{144}\text{Nd}_{\rm CHUR}(t)-1]\times10^4$ where CHUR is the CHondritic Uniform Reservoir with a present-day $^{143}\text{Nd}/^{144}\text{Nd}$ = 0.512638 and $^{147}\text{Sm}/^{144}\text{Nd}$ = 0.19670.

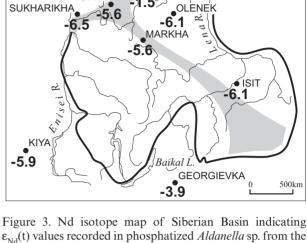
Rare earth elements and chromium contents were determined by neutron activation analysis (instrumental technique, INAA), with sample weight ranging from 0.3 to 12 mg, a density of neutron flux of $1.2*10^{14}$ n cm⁻²sec⁻¹, and a time of irradiation of 24 h. Measurements with Ge(Li) and High Purity Ge Low Energy Photon detectors after 7 and 30 days after irradiation, mean relative error is less than 3% for all elements with exception of Ho, Tb and Yb, for which the error is less than 6%.

3. Results

Each sample was analysed both by instrumental neutron activation analysis (INAA) and isotope dilution-mass-spectrometry (ID-MS) to obtain Sm and Nd concentrations. The data listed in Table 1 refer to Small Shelly Fossils and other biogenic apatites for which the divergence between the two methods was less than 10%. This was done to avoid possible contamination by detritus on the Nd isotope records, because the INAA samples were not chemically treated, whereas the ID-MS procedure includes acid dissolution. The close values of Sm and Nd abundance inferred from two methods may be interpreted as a dominant contribution of the phosphate phase in the determined Nd isotopic compositions.

The $\varepsilon_{Nd}(t)$ values of early Cambrian biogenic marine phosphorites (Table 1) display a wide scatter of values, from -26.2 recorded in the problematic Discinella micans from eastern Greenland to the most radiogenic ranging from -1.5 to -6.0 in Small Shelly Fossils occurring in the reference successions of the Zavkhan Basin in western Mongolia, the Siberian platform and adjacent terranes. The early Tommotian Aldanella from Siberian platform (Fig. 3) occurs in shallow-water archaeocyathan-microbial and openmarine carbonate facies, but the $\varepsilon_{Nd}(t)$ values over the entire platform are rather constant with the exception of $\varepsilon_{Nd}(t)$ value -1.5 in the deep part of the intraplatform basin facing the Taimyr palaeoseaway. Absolute ages accepted after Brasier & McIlroy (1998) are 543-534 Ma for the Nemakit-Daldynian, 534-530 Ma for the Tommotian, 530-526 Ma for the Atdabanian and 526-520 Ma for the Botomian.

Fairly homogeneous $\varepsilon_{Nd}(t)$ values close to -3 were recorded throughout the Nemakit Daldynian– Tommotian succession in the Saalany Gol Section of the Zavkhan Basin in western Mongolia. The $\varepsilon_{Nd}(t)$ in the early Cambrian, both from phosphate concretions and shells, has shown values of about -8.0 in the different parts of the Russian Platform, that characterize



KOTÙI

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5.3

PUTORAN

Figure 3. Nd isotope map of Siberian Basin indicating $\varepsilon_{Nd}(t)$ values recorded in phosphatized *Aldanella* sp. from the lowermost Tommotian strata, *Heraultipegma sibirica* Zone. Solid line shows the boundary of Siberian platform; shaded area is Anabar–Sinyaya (transitional) belt of the archaeocy-athan–microbial facies.

phosphatic brachiopods throughout the Cambrian in Baltoscandia (Felitsyn et al. 1998; Sturesson et al. 1999). The $\epsilon_{Nd}(t)$ of –15.5 inferred from the mollusc Yochelcionella americana and unidentified hyoliths of the Forteau Formation of western Newfoundland, is compatible with $\epsilon_{Nd}(t) = -18.7 (^{143}Nd/^{144}Nd_{measured} =$ 0.511281 ± 8) recorded in the middle Cambrian Dicellomus polita from the Dresbachian strata of Minnesota. Both values are consistent with low radiogenic Nd derived from a North American cratonic source in Cambrian time (Patchett, Ross & Gleason, 1999). The $\varepsilon_{Nd}(t)$ values are -10.6 and -11.7 in the earliest Cambrian Hyolithes and Oelandiella originating from the lowermost part of the basal Cambrian Yuhucun Formation of Meishucun in the Hunnan Province of Southern China. These values are perceptibly less radiogenic than the -8.0 value reported by Yang, Tao & Xue (1997) as recorded in sedimentary phosphate rocks of the Lower Cambrian Series in the Yangtze Region.

The Nd isotope map of early Cambrian discrete basins (Fig. 4) demonstrates clear geographic clustering in spatial distribution of the $\varepsilon_{Nd}(t)$ values. Nd isotope compositions in Small Shelly Fossils and biogenic apatite from Laurentia, Australia and South China point to old crust of more than 1.9 Ga provenance. Samples from the Eurasian continental blocks have original Nd signatures of Palaeozoic fold belts with juvenile volcanogenic complexes.

Nd isotopic compositions of the early Cambrian biogenic apatites display a lack of correlation with the REE patterns of the same samples, such as bulk REE

CHEKUROVKA

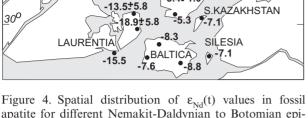
S.CHINA

-11.2

USTRALIA

-12.7

-6.3



GREENLAND

SIBERIA

 -5.4 ± 1.0

apatite for different Nemakit-Daldynian to Botomian epiplatform basins. Where the number of samples is greater than 5, an average value $\pm 1\sigma$ is shown. Continental reconstruction modified after Gubanov (1998).

content, presence or absence of Ce and Eu anomalies, LREE/MREE/HREE ratios, etc. The typical patterns of the REE distribution are shown in Figure 5, characterizing the REE patterns in all studied early Cambrian biogenic apatites. A given co-variation between Cr concentrations and Nd isotope compositions was found (Fig. 6). The samples with the lowest contents of Cr yield less radiogenic Nd compositions, with ¹⁴³Nd/¹⁴⁴Nd_{initial} less than 0.5112, whereas the Cr enrichment to 100 ppm accompanies the most radiogenic Nd compositions with ¹⁴³Nd/¹⁴⁴Nd_{initial} ratios above 0.5117. The estimation of the Pearson's correlation coefficient is +0.61 with the confidence level 99 %.

4. Discussion

4.a. Nd isotope map of the earliest Tommotian Siberian basin

The spatial distribution of the $\varepsilon_{Nd}(t)$ signature in the earliest Tommotian basin on the Siberian Platform (Fig. 3) corresponds to the Nochorocyathus sunnaginicus archaeocyath Zone (=Heraultipegma sibirica molluscan Zone) and spans a time interval of about 1 my (Bowring & Erwin, 1998). The time resolution of the earliest Cambrian biostratigraphic zonation can compete with those of the Silurian graptolitic zonation and the Mesozoic ammonitic scale. Original Nd isotope signatures of the early Tommotian Siberian Basin lack any obvious relation to the distribution of major facies belts. Helcionelloid molluscs from the shallow-water archaeocyathan-microbial facies belt (Sukharikha, Putoran, Markha and Chekurovka localities) have $\varepsilon_{Nd}(t)$ values ranging from -5.6 to -6.5, whereas similar molluses from the open marine carbonate facies (Isit, Olenek and Kotui localities) have $\varepsilon_{Nd}(t)$ of -1.5 to -6.1 (see Fig. 3). The latter values seem to be representative of the Taimyr seaway dividing Siberia and Baltica in the early Cambrian. Siberian $\varepsilon_{Nd}(t)$ values coincide with values obtained from

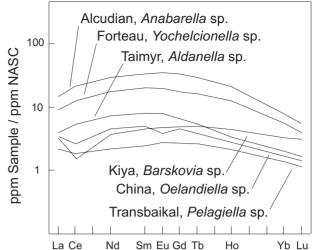


Figure 5. Typical rare earth element patterns in early Cambrian phosphatized Small Shelly Fossils. North American Shale Composite (NASC) after Gromet *et al.* (1984) was used for the normalization.

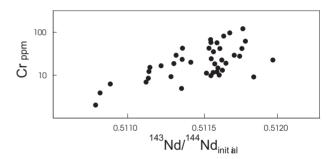


Figure 6. Relationship between original ¹⁴³Nd/¹⁴⁴Nd ratio and chromium in early Cambrian biogenic apatite.

areas adjacent to Siberia such as Taimyr, Kiya and Transbaikal. This proximity is also confirmed by the similar tropical molluscan assemblages (Gubanov, 1998, 2000; Pospelov *et al.* 1995). The $\varepsilon_{Nd}(t)$ value from Transbaikal is the most radiogenic for the Siberian platform region and appears to be transitional between Siberia and Mongolia. The middle subformation of the Bystraya Formation of Transbaikal is about 500 m thick and includes dark-grey limestone and dolomite with interbedded siliceous–argiilliceous shales containing layers of phosphorite (Astashkin *et al.* 1991). There is no volcanogenic sediment within the 2600 m thick Bystraya Formation.

The $\varepsilon_{Nd}(t)$ values of the Zavkhan Basin in western Mongolia stay fairly consistent throughout the early Cambrian succession from late Nemakit-Daldynian *Ilsanella compressa* Zone to early Tommotian *Watsonella crosbyi* Zone. All samples came from the Bayan Gol Formation which is up to 1300 m thick and comprises alternations of limestone and argillite, siltstone and sandstone (Khomentovky & Gibsher, 1996). High radiogenic Nd with $\varepsilon_{Nd}(t)$ values close to -3.0 is recorded in Small Shelly Fossils covering a 3-5 m.v. time span, according to the time table of Bowring & Erwin (1998). Such a Nd isotope composition in phosphatized shells of the Zavkhan rift basin could point to an Nd isotopic ratio in the adjacent seawater masses either originating from drainage of the bordering Darib-Khantayshir island-arc belt and/or from calcalkaline volcanic rocks of the Baydrik-Tarbagatay microcontinent. The highly diversified molluscan assemblage (Esakova & Zhegallo, 1996) suggests a low latitude close to the equatorial geographic position of Mongolia during early Cambrian times. It has been agreed that all continents occupied the southern hemisphere at that time, with Mongolia and other small terranes surrounding Siberia framing the Panthalassa Ocean that occupied the entire northern hemisphere.

4.b. Provenance control for Nd isotope compositions and Cr contents

Chromium contents in juvenile magmatic arc volcanics and orogenic andesites are about 60–100 ppm, at least two times higher than in the upper continental crust; Cr concentrations of the oceanic crust are 200-300 ppm (e.g. Taylor & McLennan, 1985). The main Cr mineral is chromite FeCrO₄ which produces chromate-ions during oxidization in the hypergenesis zone that are mobile in a wide interval of pH and E_{H} conditions (Bartlett & Kimble, 1976). In marine water, Cr contents are near 10^{-10} g/g with a residence time of about 103 years (Broecker & Peng, 1982). In authigenic phosphates, chromate-ion substitutes for PO_4^{2-} in the crystalline lattice, which suggests that marine phosphorites may be considered as a sink for Cr; the Cr concentrations in so-called 'geosyncline' phosphorites are significantly higher than in 'platform' equivalent varieties (Altschuler, 1973). This is why elemental compositions of marine phosphorites (including Cr and rare earth elements) are often considered to mirror the compositions of drained source areas (Scherbina, 1972). Consequently, the correlation between Cr contents and Nd isotopic records is a provenance control: the most radiogenic Nd was derived from eroded juvenile crust, whereas the source area also supplied enhanced Cr fluxes into the sedimentary basin. This type of provenance dominated in the Zavkhan Basin, the Maly Karatau, the terranes of Cadomian fold belts, and possibly in the Siberian platform (Şengör, Natal'in & Burtman, 1993). On the contrary, the lowest Cr concentrations up to 1 ppm were found in early Cambrian basins where neighbouring shield areas are dominated by Archaean (Innuitian Province) or Proterozoic cratonic basement (western Newfoundland, South China and Adeladian basins of Australia). The strong regional control on the Nd isotopic composition of conodonts derived from various aquafacies in the 454 Ma Mohawkian Sea in Eastern

Laurentia revealed by Holmden et al. (1998). On the other hand, occurrence of biogenic apatites with distinct geochemical signatures in the same stratigraphic level and uniform depositional setting means that the expanding water masses retained signatures of different provenances. The origin of such tracer signatures (adjacent source area or open marine reservoir) is speculative, but the comparison of Nd isotope signatures recorded in biogenic apatite and the geological framework seems to be pertinent. Thus, variation of the $\varepsilon_{Nd}(t)$ values in Botomian biogenic apatite and remnants of organo-phosphatic brachiopods (see Table 1), taken together with palaeogeographic evolution of northern Greenland during the Cambrian times (Ineson & Peel, 1997) favours the conclusion that periodic supplies of water masses containing juvenile Nd are more to be expected than abrupt appearances of juvenile Nd in the different parts of the Franklinian Basin. The contribution of cratonic sources with 3.0-2.5 Ga old crust was decisive during the whole Cambrian period for the Early Palaeozoic Franklinian basin of northern Greenland (Patchett, Ross & Gleason, 1999), and the $\varepsilon_{Nd}(t)$ values ranging from -21 to -26 display this provenance. However, $\epsilon_{Nd}(t)$ values from -5 to -10 which were recorded in biogenic phosphate from Peary Land, as well as in phosphatic problematic fossils from eastern Greenland, are too radiogenic for the Innuitian Province. The easiest way to explain the observed variation in original ε_{Nd} values in Greenlandian biogenic apatite is to postulate the expansion of water masses with distinct Nd isotope compositions, such as an embryonic Iapetus ocean with a Nd isotopic signature of -8.0. A relatively high Th/REE or Th/Sm ratio in old biogenic apatites reflects the enhanced influence of riverine input in shallow facies (Laenen, Hertogen & Vandenberghe, 1997). The Th/Sm ratios range from 0.006 to 0.08 with an average 0.07 in biogenic apatite and with radiogenic Nd occurring in Botomian strata in northern Greenland, while the Th/Sm ratio is 0.17-0.20 for biogenic phosphate and brachiopod shells with $\varepsilon_{Nd}(t)$ varying -21 to -26 (Felitsyn & Morad, unpub. data). The depositional setting of these strata is slope apron-deep shelf (Ineson & Peel, 1997) without a change in local provenance during early-middle Cambrian times. The occurrence of biogenic apatite at the same stratigraphic level with distinct geochemical records may result from periodic spreading of water masses with juvenile Nd far across a shelf, rather than changes in composition of eroded Precambrian basement. Therefore, a number of tracers point to open marine reservoir-supplied water masses with distinct geochemical signatures in shelf depositional settings in northern Greenland during the Botomian, rather than local provenance control. The lack of decoupling of such different geochemical tracers as $\epsilon_{\rm Nd}(t),$ Cr and Th/Sm suggests that the location of a reservoir with distinctive hydrochemistry was Phosphorite hardgrounds from the uppermost part of the Ekspedition Bræ Formation, Middle Cambrian, Peary Land, northern Greenland, have typical Franklinian $\varepsilon_{\rm Nd}(t)$ with ¹⁴³Nd/¹⁴⁴Nd_{measured} = 0.511392 ± 10 (Sm = 26.68 ppm, Nd = 147.9 ppm, ¹⁴⁷Sm/¹⁴⁴Nd = 0.10507, $\varepsilon_{\rm Nd}(520 \text{ Ma}) = -18.1$) reflecting the erosion of Archaean crust areas. At the same time, phosphorite hardgrounds from the Holm Dal Formation (late middle Cambrian, *Lejopyge laevigata* Zone) have shown a fairly homogeneous original Nd isotope composition, with $\varepsilon_{\rm Nd}(t)$ values ranging from -7.7 to -8.0 (Felitsyn *et al.* 1998). Both formations were deposited in the same environment of deep shelf (Ineson & Peel, 1997) and no changes in local provenance have been proposed.

4.c. Nd isotope map of early Cambrian basins

Original ε_{Nd} values inferred from early Cambrian biogenic apatites display three clusters corresponding to the Nd isotope composition of modern-day oceanic water masses. The first cluster includes Laurentia, Australia and South China with the lowest $\varepsilon_{Nd}(t)$ values up to -25 that are similar to recent Atlantic seawater. Transbaikal, Mongolia and the deepest part of the Siberian intraplatform basin with $\varepsilon_{Nd}(t)$ values of -1.5 to -6 are comparable to the modern Pacific Ocean waters, whereas Baltica, Iberia, Silesia, Kiya, Kazakhstan and Iran show intermediate $\varepsilon_{Nd}(t)$ values of -6 to -8, like the waters of the modern Indian Ocean. Holser (1997) reported Nd isotopic variations of Phanerozoic water masses obtained from various substrates (cherts, carbonates, phosphates, Fe-Mn coatings). Herein we extend the existence of water reservoirs with distinct Nd isotope signatures, at least to the beginning of the Phanerozoic. Pioneering work by Keto & Jacobsen (1987, 1988) provides scarce data for this period of time in support of this conclusion.

The early Cambrian Nd isotope map (Fig. 4) is combined with a continental reconstruction modified after McKerrow, Scotese & Brasier (1992), Vidal & Moczydłowska (1996) and Gubanov (1998), to show the original spatial distribution of basins with distinct Nd isotope compositions for contemporaneous seawater. The Nd isotope composition of Baltica was rather constant (about -8.0) during the entire Cambrian period (Sturesson *et al.* 1999), as were the Innuitian province and the North American Craton before the onset of the Caledonian Appalachian Orogeny at 450 Ma (Patchett, Ross & Gleason, 1999).

The Maly Karatau terrane of Kazakhstan was placed close to Siberia within the Cadomian belt according to the Siberian proxy of the early Cambrian fauna (McKerrow, Scotese & Brasier, 1992; Missarzhevsky & Mambetov, 1981), although there are not enough data. The $\varepsilon_{Nd}(t)$ value of Taimyr is the same as that of the Siberian region, and is in strong

agreement with the existence of an entire Siberian Small Shelly Fossils assemblage (Bezzubtsev *et al.* 1979) in the lower Tommotian Taimyrian strata.

The spreading Iapetus and Palaeotethys oceans separated Rodinia into several blocks (Hoffman, 1991), but the estimated dimension of these oceans varied from the size of the modern-day Atlantic to rather narrow seaways (Scotese & McKerrow, 1990; McKerrow et al. 1992). A recent study of late Nemakit-Daldynian-early Tommotian molluscs supports a palaeogeographic reconstruction with narrow seaways and with the main continental blocks remaining close to each other after the break-up of Rodinia (Gubanov, 1998). Furthermore, the evolution of the earliest molluscs reflects mastering of new ecological niches (Gubanov & Peel, 1999) that led to sympatric rather than allopatric speciation (Gubanov, 2000). The morphological unity of molluscs from different areas implies continuous exchange of genes between molluscan populations (Gubanov & Felitsyn, 1999). The narrow seaway model is also in accordance with geological and palaeontological evidence supporting the close relationship between Laurentia and Siberia, and between Siberia and northwestern Africa at the same time (Pelechaty, 1996; Liberman, 1997), evidence difficult to explain within the wide ocean model. Keto & Jacobsen (1988) estimated the size of the Panthalassa Ocean to be 90% of the total Cambrian ocean area with all other oceans accounting for the remaining 10%. The idea of narrow seaways between early Cambrian continental fragments is mostly supported by palaeontological data (Moczydłowska, 1995; Vidal & Moczydłowska, 1996; Gubanov, 1998; Debrenne, Maidanskaya & Zhuravlev, 1999).

Because enhanced flux of radiogenic Nd is considered to mark the juvenile crust of magmatic arcs (Bertram & Elderfield, 1993; Keto & Jacobsen, 1988), the spatial distribution of the original Nd isotope signature (Fig. 4) reflects the position of convergent margins during early Cambrian times: the most radiogenic $\varepsilon_{Nd}(t)$ corresponds to basins bordered by magmatic arcs and/or cordillera. The Cadomian belt and immense subduction-accretion complexes along the Tuva-Mongol/Comb Altay and the giant magmatic arc of the Turkestan Ocean (Sengör, Natal'in & Burtman, 1993) added juvenile material to the continental crust since the early Cambrian, and the most radiogenic Nd has been recorded in biogenic apatite from relevant units. Erosion of young elevated volcanogenic rocks could supply an increased flux of nutrients into epeiric basins. Thus, a pronounced impact on benthic and pelagic communities should be expected. While the Mongolian fauna is one of the most diverse and abundant, it is difficult to separate the contribution of climate, and the problem of the relationship between continental nutrient flux, trophic chains and the diversification of early Cambrian biota is still unclear.

5. Conclusions

Traditional substrate (conodont elements, organophosphatic brachiopod shells, bones and teeth of marine vertebrates) is not available in the reconstruction of the Nd isotope composition of the early Cambrian seawater. The phosphatized remnants of the early Cambrian Small Shelly Fossils may represent suitable material for such studies because they could (a) retain Nd isotope signatures of the overlying seawater layer and (b) provide the basis for a detailed scheme of geological correlation.

Variations of the $\varepsilon_{Nd}(t)$ values in Greenland, as well as gradual spatial changes of these values between different terranes, imply a compact arrangement of the early Cambrian continents that is in accordance with the geographic distribution of helcionelloid molluscs suggested earlier (Gubanov, 1998, 2000).

Distribution of Nd isotope signatures shows a strong asymmetry and reveals three continental clusters with different provenance: Laurentia and eastern Gondwana with the lowest $\epsilon_{\rm Nd}(t)$ values, Mongolia, Transbaikal and Siberia with highest $\epsilon_{\rm Nd}(t)$ values, and Baltica, small terranes of the Cadomian–Avalonian belt and Iran with intermediate values.

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