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Sedimentary Geology 159 (2003) 241–256

Sedimentary Geology

www.elsevier.com/locate/sedgeo

Lower Palaeozoic iron oolites and volcanism from a Baltoscandian perspective

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Received 29 November 2001; accepted 11 September 2002

Abstract

The Ordovician iron oolites in Baltoscandia are generally geographically extensive but lean, [$<30\%$ ooids sensu (Bhattacharyya, D.P., 1989. Concentrated and lean oolites: examples from Nubia Formation at Aswan, Egypt, and significance of the oolite types in ironstone genesis. In Young, T.P., Taylor, W.E.G. (eds.) Phaneorozoic Ironstones. Geological Society Special Publication 46, 93–103)] and have undergone minimal reworking and diagenetic alteration. The ooids were formed in a normal shallow-marine environment around a nucleus of a calcite skeletal grain.

The oolites were formed during the period of the highest global iron oolite production ever. Most of the major oolites from this period have been altered in various ways, which has obscured their origin. The presence of volcanic matter in the Baltoscandian and some other European oolites points to a volcanic origin, a conclusion further supported by the REE distributions in iron ooids, which are close to those in associated volcanic tuffs.

The global $^{87}Sr/^{86}Sr$ curve for Phanerozoic seawater in general, and for the Palaeozoic in particular, shows that negative excursions in the Sr isotope ratio often coincide with periods of high global iron oolite productivity. This temporal coincidence points to a possible causal link.

Iron ooids, volcanic ashes and bentonite beds occur in the Ordovician of Baltoscandia during a negative excursion in the $^{87}Sr/^{86}Sr$ curve. The variation in the $^{87}Sr/^{86}Sr$ ratio in seawater mirrors the balance between the two major sources of Sr, mid-ocean ridge volcanism and continental weathering, and indicate that volcanism could be the general cause of most Palaeozoic iron oolites. Two Cambrian iron oolites occur in Baltoscandia, and at least one of them is suggested to be of volcanic origin.

Keywords: Iron ooids; Cambrian; Ordovician; Baltoscandia; Volcanism; Strontium isotopes

1. Introduction

Cambrian iron oolites are relatively uncommon and occur mainly as uneconomic deposits in North America and Morocco (Petranek and Van Houten, 1997). In the Baltoscandian area, two Cambrian iron oolites are known. In central Sweden (Fig. 1, locality 1), iron-bearing beds have been known at least since about 1850 when the iron was mined for local use. The ore contains only about 25–35% Fe_2O_3 and has received little scientific attention. The maximum thickness of the beds is 2 m, and the age of the ore is estimated to be late Vendian–Early Cambrian (Tegengren, 1962). The clastic material consists of

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doi:10.1016/S0037-0738(02)00330-5

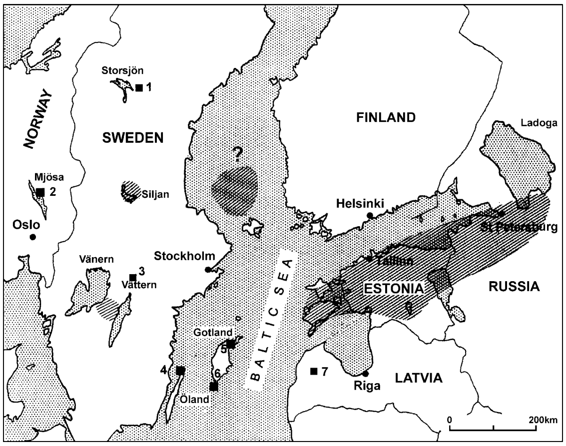


Fig. 1. Map of the Ordovician iron ooid distribution in Baltoscandia. The stippled areas include the two levels of ooids in Fig. 3. Filled squares denote local occurrences and drill cores (see text).

abundant unweathered feldspar and quartz (Fig. 2), and the source of the iron is thought to be sub-aquatic volcanic exhalations (Tegengren, 1962).

Pirrus (1986) described an Early Cambrian iron oolite with extensive lateral distribution from N Poland to NW Estonia. The oolite is of marine origin, and thicker beds (2–5 m) in the central part of the basin occur in association with clay deposits. The iron content is about 60–70% ($Fe_2O_3 + FeO$). The ooids consist mostly of goethite, but also siderite and chamosite occur, and quartz grains are commonly the nucleus (Fig. 2).

A third Middle Cambrian oolite in Närke, south–central Sweden (Fig. 2, locality 3) could be a remnant of an iron oolite. The ooids consist of francolite and chamosite hosted in sandstone cemented by calcite and phosphate. The iron content is low and the origin could be nonmarine (Sturesson, 1988c).

Oolitic ironstones of Ordovician age occur in many places in Europe, North Africa and North America (see review by Young, 1992). Some of the oolites have a wide lateral persistence, such as the early Llanvirn ironstones in Europe which might have been formed within an area of about 200,000 km^2 during a rather short time (Young, 1992). These oolites are often of great commercial value. Thin oolite layers are also very common and can be important as stratigraphic marker beds. The genesis of oolitic ironstones has for a long time remained a mystery and has generated a large number of articles with various interpretations (see Young and Taylor, 1989; Petranek and Van Houten, 1997). One model, which envisions volcanism as a source of iron, aluminium and silica for iron ooid formation in a marine environment (Hessland, 1949; Sturesson, 1992a), has recently gained a strong support (Heikoop et al., 1996; Sturesson et al., 2000). The discovery of modern iron ooids in a shallow-marine volcanic setting in Indonesia (Heikoop et al., 1996) does not only reveal the close relationship between volcanism and iron oolites, but also provide clues to the original ooid mineralogy. The Indonesian ooids consist of amorphous iron oxides with silica and aluminium. In interaction with seawater or pore water, the ooids can be transformed to various iron oxyhydroxides and iron silicates (Sturesson et al., 2000). Iron ooid formation seems to be a fairly rapid process, probably in the range of 100–1000 years. Geographically extensive iron oolites can thus be regarded as synchronous and constitute valuable reference horizons for stratigraphic correlation. The Ordovician iron ooids in Baltoscandia (Norway, Sweden, Estonia and W Russia) show similarities to the Indonesian ooids, and could have been formed in a similar way (Sturesson et al., 2000).

Younger Palaeozoic iron oolites (Silurian to Permian) do not occur in Baltoscandia.

The aim of this study is to shed new light on the origin of the Cambrian to Ordovician iron oolites in Baltoscandia in particular, and on Palaeozoic iron oolites in general, in view of the above-published results in conjunction with recent studies about paleogeography, temporal Sr isotope variations, clay mineralogy and volcanic ash composition.

1.1. Geological setting

Ordovician iron oolites occur at two stratigraphic levels in Baltoscandia (Fig. 3): (1) The Middle Ordovician Llanvirn (Aseri to Lasnamägi Stages) oolite, best developed in northern Estonia and continuing eastwards to the St. Petersburg area (Orviku, 1940; Sturesson and Bauert, 1994; Sturesson, 1995), also occurs in south–central Sweden (Sturesson, 1989, 1992a,b); (2) The Lower Ordovician Arenig–Llanvirn (Kunda Stage) oolite that is the most extensive and can be traced from Norway to the east of Lake Ladoga (Fig. 2) (Sturesson, 1986, 1988a,b; Sturesson and Bauert, 1994; Sturesson et al., 1999). The ooids are hosted mostly in red or grey limestones and are usually thin and lean (Bhattacharyya, 1989), but can locally be enriched.

1.2. Regional developments

1.2.1. Norway

The oolite in Norway (Fig. 1, locality 2) is the westernmost extension of the Kunda oolite in Baltoscandia and contains diagenetically altered ooids. The ooids occur in the Svartodden member of the Huk formation, contained within the upper part of *Eoplacognatus* conodont zone (Owen et al., 1990), and commonly trapped in pits in a corroded hardground. Most of the berthierine has been lost and the voids are filled with carbonates such as calcite, ferroan calcite and ankerite, but the original oolitic texture is partly preserved (Sturesson, 1994). Low δ^{18}O values of the carbonates ($\delta^{18}O_{PDB} = -12.4$ to -10.5) indicate elevated temperatures and/or interaction with unstable volcanic material (Morad and de Ros, 1994). There is no visible volcanic matter in the beds, however, but there is ample evidence of contemporary volcanism in the area (Roberts et al., 1984; Pedersen et al., 1992). The Aseri oolite is not known in Norway.

1.2.2. Sweden

In central Sweden (Siljan area in Fig. 2), the Lower Ordovician (Kunda) oolite occurs at several places (Sturesson, 1988b). In one location, the evolution of limonitic ooids from superficial grains at the base to fully developed ooids at the top can be observed. Lenses of ooidal clay can also be seen here. In another section, chamosite and limonite (mainly goethite) ooids occur together. The ooids are associated with a change from red to grey limestones perhaps reflecting the development of more normal marine conditions. In a third locality, Hessland (1949) reports a bentonite bed, and possibly also altered glass particles from basic ashes, and lumps of chalcedony in the oolites. The maximum thickness of the oolites in the Siljan area is ca. 2.5 m. The Aseri oolite is not discovered here.

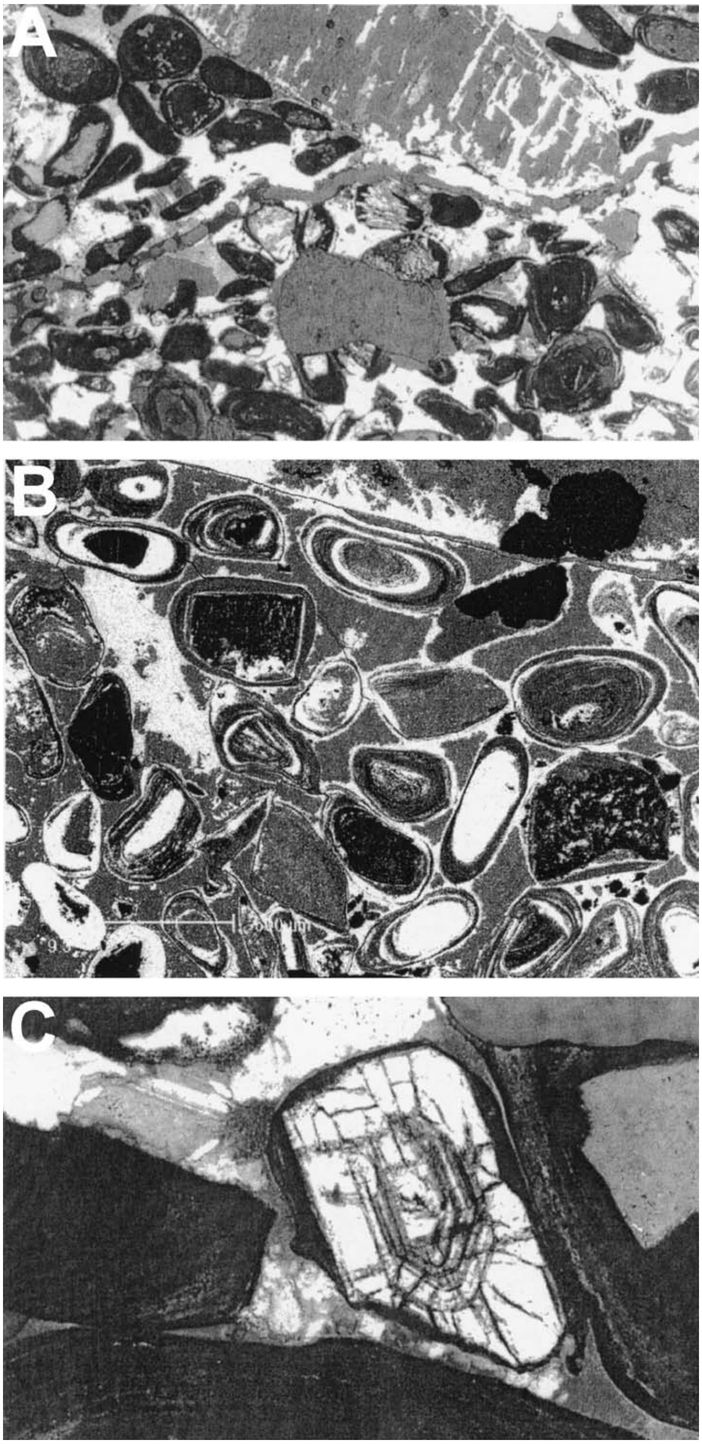
In south central Sweden, the Kunda oolite is not present, but the Aseri oolite occurs in two quarries (Fig. 1, between Vänern and Vättern). The Aserian oolitic limestone occur within the *Didymograptus murchisoni* graptolite zone (Jaanusson, 1964). The oolitic beds rest on a conspicuous hardground that marks a major break in the sedimentation, probably encompassing most of Aseri and Lasnamägi (Holmer, 1983). In one quarry, this hardground is a black, thin phosphorite with a bleached zone below, whereas in the other, the hardground is mainly impregnated by iron oxide. The ooids are composed of chamosite, but also phosphatic and hematitic ooids occur (Sturesson, 1989, 1992b). At both localities, traces of volcanic ash occur. In one quarry, several lenses of calcitized ash with well-preserved shard textures occur together with beds of iron ooids in the red limestone (Sturesson, 1992a). In the other quarry glass shards, phenocrysts such as bipyramidal quartz and angular zircons occur in the phosphorite (Sturesson, 1992b).

On the islands in the Baltic Sea (Fig. 2, localities 2, localities 4, 5 and 6), several beds in the lower parts of the Kunda stage contains various types of ooids (Sturesson, 1986). Iron ooids of chamosite, goethite and hematite commonly occur together, whereas at some localities, only phosphatic ooids are observed. Based on chemical composition and inner structures, Sturesson (1988a) suggested that the goethite and hematite ooids are the result of a diagenetic alteration (oxidation) of chamosite ooids, which in turn might have had an unknown precursor. These oolites are biostratigraphically correlated with two bentonite beds in southernmost Sweden, deposited in deeper water black shale (Bagnoli and Stouge, 1999). The Aseri iron oolite is absent in this area.

The Kunda oolite on southern Gotland in the Baltic Sea is ca. 0.6 m thick and contains chamosite ooids mixed with hematite ooids. The oolite rests on a glauconitic limestone terminated by a discontinuity surface and glauconite forms the nucleus in many ooids (Sturesson, 1995). On northern Gotland, two beds of iron ooids of Aseri–Lasnamägi age similar to those in Estonia occur (Torslund and Westergård, 1938).

1.2.3. Estonia and Russia

In Estonia, well-developed ooids occur in the Kunda as well as in the Aseri–Lasnamägi stages, being coeval to the *D. murchisoni* graptolite zone (Männil, 1990). Regular Aseri iron ooids occur only in the northern part of the indicated area (Fig. 2) from the Estonian islands in the west to the east of Tallinn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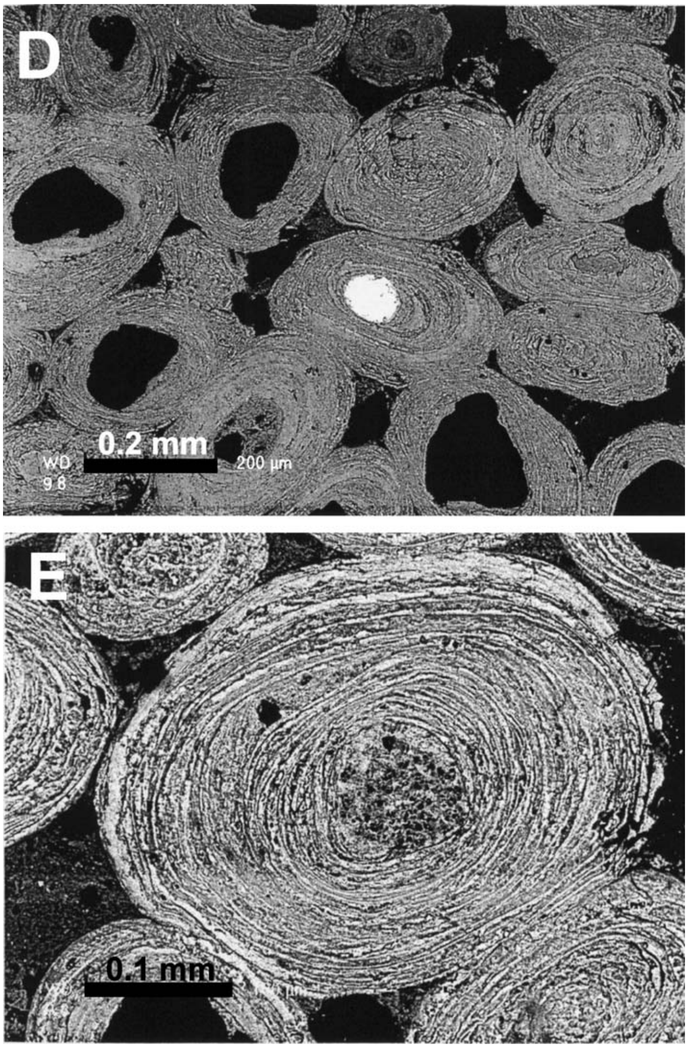

Fig. 2. Precambrian–Cambrian iron oolites from Sweden and Latvia. (A) is an overview with ooids, large feldspar grains (top) and a rock fragment of unknown origin. Transmission microscopy, polarized light. Scale as in (B). (B) is a backscatter electron (BSE) image from the same sample showing the variety in nuclei character and the distribution of lighter (dark) and heavier (light) material. The cement is calcite (BSE-EDS). (C) shows a zoned zircon grain with a thin coating of iron oxide. The length of the grain is 0.27 mm. (D) is a BSE image of closely packed iron ooids from Latvia. Quartz grains (black) and clay particles (grey) commonly form the nuclei, but also rounded zircon grains occur (white). (E) is a BSE image of a Latvian iron ooid with well-preserved lamination with at least three generations of ooid formation.

(Sturesson and Bauert, 1994). Männil (1966) indicates the presence of Aseri iron ooids farther east to St. Petersburg area as well as in Byelorussia. The Aseri ooids in Estonia are entirely confined to grey limestones in contrast to red limestones for the coeval Swedish ooids. There is also a difference in mineralogy. The Swedish iron ooids are composed of chamosite and hematite, whereas the Estonian ooids are limonitic (goethitic). There is no field evidence of volcanic material in these beds as at the corresponding levels in Sweden (Sturesson and Bauert, 1994).

The Kunda oolite in Estonia and western Russia consists of oolitic limestone intercalated with ooidal clay beds. This oolite is usually thin, seldom more

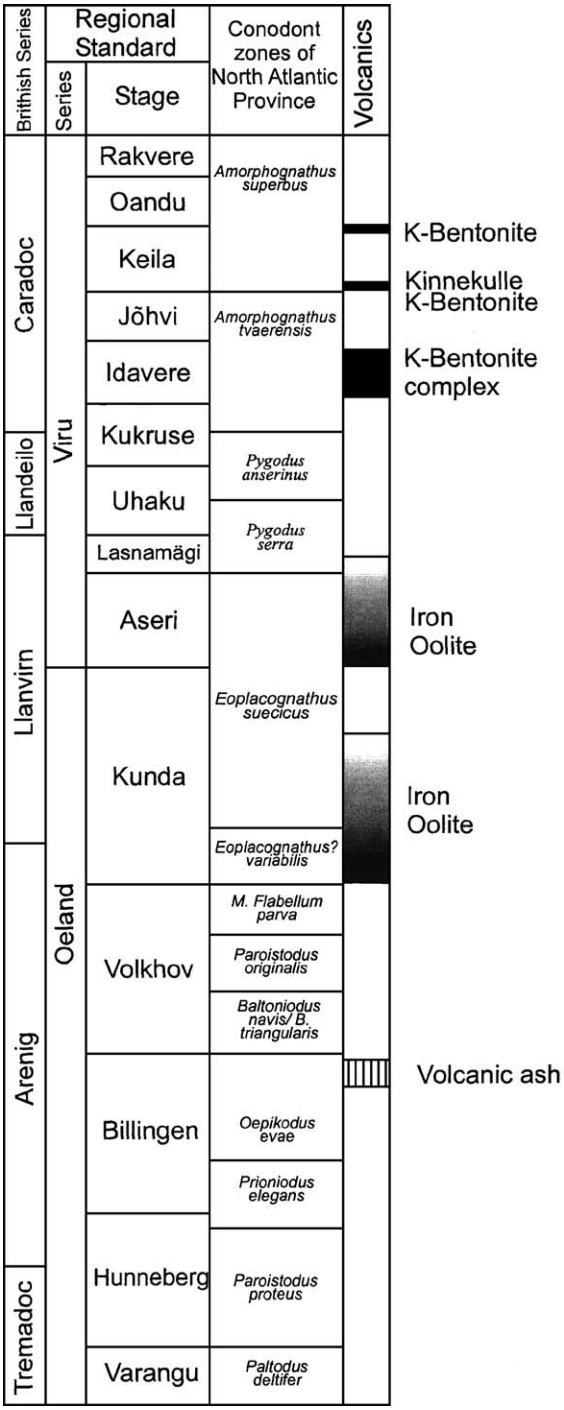

Fig. 3. A stratigraphic column showing the position of the Ordovician volcanic deposits and iron oolites. The K-bentonite complex is a set of several closely spaced K-bentonite beds. The oolite beds are referred to in the text as the Aseri and Kunda oolites.

than 0.5 m, but the most extensive one in Baltoscandia. It can be followed in outcrops and drill cores from the islands in the west to the east of Lake Ladoga (Sturesson et al., 1999). The ooids are large and well developed and consist of limonite without any traces of chamosite. Several lines of evidence points to a volcanic origin of the clays and the ooids (Sturesson et al., 1999).

1.2.4. Adjacent areas

Polish iron ooids of Ordovician age occur in the Holy Cross Mountains, and in northern Poland in highly condensed sections covering the *Didymograptus bifidus (artus)* and *Glyptograptus teretiusculus* zones (Tomczykowa and Tomczyk, 1970). In the southern parts of the Holy Cross Mountains, sandy and calcareous deposits with some intercalation of tuffs prevail; in the western part, a 4-cm-thick bentonite bed is formed, and in the east, up-to-5-m-thick sediments with pyroclastics occur (Chlebowski, 1971; Łącka, 1990). All traces of volcanic activity in this area seem related to acid volcanism (Chlebowski, 1978). Coated grains in these sediments have a mixed composition of goethite, kaolinite, apatite, calcite, quartz and illite/smectite (Łącka, 1990). The close association of iron ooids (coated grains) and pyroclastics led Chlebowski (1978) to the conclusion that airborne volcanic ash and sub-aqueous exhalations resulted in the origin of different iron ooids in the basin depending on bathymetry and changes in pH and Eh in the environment.

In the Prague Basin, the Ejpovice oolitic iron ore has a maximum thickness in the Šárka Formation, which represents the whole Llanvirn (Havlícek and Vanék, 1966). The ore consists of red hematite and grey chamosite ooids in a matrix of similar composition. The ore is underlain by tuffs of Arenig age, and glass shards, bipyramidal quartz grains and pumice fragments occur frequently within the oolite (Sturesson et al., 2000).

In addition, in North Wales, there is a close connection between the oolitic iron ore formation and volcanism (Beckley, 1987). Arc volcanism occurred from the end of Tremadoc to late Caradoc times in marginal basins. The iron oolites are developed close to the Arenig/Llanvirn boundary on top of a siltstone or sandstone together with volcanoclastic material (Bassett et al., 1992). There are two phases of iron oolite deposition in the North Wales Basin: a minor Upper Arenig phase and an upper Llanvirn to basal Caradoc phase. Most of the latter were formed during the *G. teretiusculus* to *gracilis* Biozones above a stratigraphic hiatus (Trythall, 1989).

2. Material and methods

Sturesson (1988a,b, 1989, 1992a,b, 1995), Sturesson and Bauert (1994) and Sturesson et al. (1999, 2000) described the chemical and isotopic compositions of Baltoscandian iron ooids and host rocks. For this study, additional analyses of trace elements and Nd isotopes in iron ooids and volcanoclastics from Sweden, Latvia and the Czech Republic were made according to methods described by Sturesson (1995) and Felitsyn et al. (1998).

3. Results

3.1. Chemical composition of ooids

The two oldest Cambrian oolites in Baltoscandia, the Precambrian–Cambrian from Lit and the Early Cambrian one from Latvia show similar REE distributions, with a slight enrichment of the LREE and with no or small Ce and Eu anomalies. The Middle Cambrian phosphatic ooids from Sweden have a similar REE distribution but with a minor Eu anomaly (Fig. 4).

The major and minor element composition is more varied. The Lit oolite has generally a higher amount of most elements, particularly Ca, Mg, P, Ti, Ba, Cr, V and W, but the iron content is lower (Table 1). Bulk samples were used in both cases and the presence of pyroclasts in the Lit sample could be the reason for the difference.

The major element chemical composition of the Baltoscandian Ordovician ooids shows only minor local variations, and the variation in the iron content

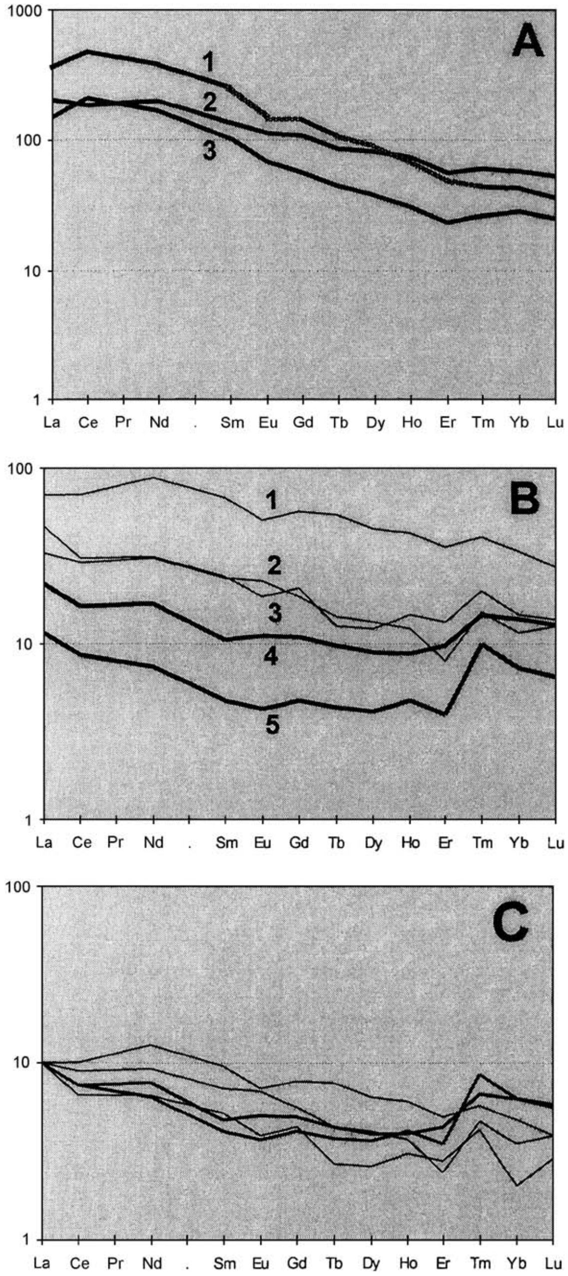

Fig. 4. Rare-earth element distributions in ooids and volcanic matter. Normalized to chondrite standard (Boynton, 1984). (A) 1 = Middle Cambrian clay ooids from south–central Sweden. 2 = Precambrian–Early Cambrian iron oolite from Lit, Sweden (see map). 3 = Early Cambrian iron oolite from Latvia (Aispute bore hole 1297.8 m). Sample 1 consists of selected ooids and Samples 2 and 3 are bulk rock samples. (B) Iron ooids and associated tuffs from the Prague Basin. 1 = pyroclast from Ejpovice within the oolite bed from which Samples 4 and 5 was taken. 2 = Tuff from Komárov, ca. Middle Arenig. 3 = Tuff from Ejpovice, Klabava Formation, Upper Arenig. 4 = Chamosite ooids from Ejpovice. 5 = Hematite ooids from Ejpovice. (C) Same as in (B) but normalised to La. The minor differences are mainly due to different phosphate contents.

Table 1
Chemical composition of iron ooids and volcanic tuffs from the Prague Basin, and of two Cambrian iron oolites from Baltoscandia

Element	1	2	3	4	5	6	7	8
A								
Al_2O_3 (%)	13.1	10.9	13.1	22.1	4.86	3.15	9.39	2.54
CaO (%)	3.46	7.29	7.61	0.407	0.233	0.301	4.23	46.9
Fe_2O_3 (%)	19.0	11.1	14.8	36.0	82.2	61.7	34.6	4.48
K_2O (%)	0.535	1.01	3.56	0.751	0.086	0.19	0.438	0.333
MgO (%)	2.57	1.24	4.04	3.79	0.445	0.479	1.47	0.218
MnO_2 (%)	0.089	0.3	0.317	0.027	0.009	0.125	0.206	0.59
P_2O_5 (%)	2.8	0.348	0.386	0.309	0.173	0.636	2.68	12.5
SiO_2 (%)	52.7	57.5	38.6	27.8	7.67	19.9	35.0	6.31
TiO_2 (%)	0.317	1.35	1.89	0.413	0.008	0.093	1.57	0.05
LOI (%)	6.8	9.8	16.4	9.3	3.0	10.8	10.1	25.6
B								
Ba (ppm)	275	147	413	51.5	123	17.7	17.4	112
Co (ppm)	23.7	31.3	30	21	< 5	30.8	88.9	11.8
Cr (ppm)	75.4	104	89.6	169	< 10	41.2	145	125
Cu (ppm)	17.2	36.8	5.72	25.8	9.03	16.2	12.6	48.3
Ga (ppm)	14.1	14.7	21.8	24.5	5.92	6.96	2.67	12.6
Hf (ppm)	3.24	3.15	3.9	1.86	0.587	6.63	2.13	4.35
Nb (ppm)	5.97	12	13.5	7.5	0.849	2.62	2.88	28.4
Ni (ppm)	43.9	58.7	55.8	59.9	< 10	< 10	57.5	44.2
Rb (ppm)	18.2	26.5	71.3	26.8	7.17	5.12	10.7	13.2
Sc (ppm)	12.8	17.4	18.7	15.3	1.44	16.8	8.28	8.75
Sr (ppm)	75	21.1	234	15.6	10.3	39.7	173	74.7
Ta (ppm)	0.534	0.848	1.38	0.574	0.08	0.173	0.15	3.32
Th (ppm)	7.8	1.18	2.22	6.72	3.62	21.2	17.2	25.9
V (ppm)	170	139	175	403	4.19	158	403	1540
W (ppm)	2.06	1.32	1.53	1.7	3.93	8.44	0.466	59.4
Y (ppm)	73.2	27.4	25.4	15.9	4.67	49.4	151	149
Zn (ppm)	154	109	132	264	128	90.9	126	43.5
Zr (ppm)	132	150	179	64.7	13.7	338	62.6	231
C								
La (ppm)	21.9	10.2	14.6	6.81	3.58	46.9	63.9	112
Ce (ppm)	57.3	23.7	25	13.2	6.98	168	151	387
Nd (ppm)	53.2	18.4	18.8	10.2	4.43	100	120	232
Sm (ppm)	13.2	4.6	4.75	2.05	0.934	20.3	26.9	49.5
Eu (ppm)	3.72	1.67	1.37	0.822	0.317	5.04	8.4	10.8
Gd (ppm)	14.5	4.88	5.39	2.84	1.24	14.8	28	37.9
Tb (ppm)	2.59	0.687	0.597	0.462	0.208	2.14	4.11	5.1
Dy (ppm)	14.5	4.3	3.93	2.86	1.33	12.2	26.8	29.4
Ho (ppm)	3.1	0.874	1.05	0.626	0.341	2.19	5.35	4.96
Er (ppm)	7.47	1.67	2.81	2.05	0.841	4.91	11.9	10.4
Tm (ppm)	1.32	0.498	0.648	0.475	0.323	0.852	1.96	1.45
Yb (ppm)	7.08	2.44	3.06	2.91	1.53	5.96	12.2	9.25
Lu (ppm)	0.882	0.409	0.445	0.417	0.212	0.821	1.71	1.17

1 = Ejpovice pyroclast, 2 = Tuff from Kómarov, 3 = Tuff from Ejpovice, Klabava Formation, 4 = Ejpovice black ooids, 5 = Ejpovice red ooids, 6 = Latvia ooids, 7 = Lit ooids, 8 = Närke ooids.

is due to differences in mineralogy (Table 2A and B). Limonite ooids generally have more iron than chamosite ooids and the latter a higher amount of phosphate. Values for all ooids normalised to Al_2O_3 show small variations and fairly stable element ratios, and SiO_2 is present in all types of ooids. Some trace

Table 2
Major element chemical composition of iron ooids from Baltoscandia normalised to Al_2O_3

	SiO_2/ Al_2O_3	Fe_2O_3/Al_2O_3		MgO/ Al_2O_3	TiO_2/ Al_2O_3
		Estonia + Russia	Sweden		
A					
Mean	1.51	12.2	6.38	0.22	0.139
Standard deviation	0.176	1.06	4.15	0.02	0.073
N	27	16	11	27	27
B					
Mean	2.6	14.5	2.6	0.21	0.13
Standard deviation	0.7	2.8	0.6	0.05	0.11
N	15	4	3	5	2

(A) The Kunda iron oolite. Analyses made by ICP. (B) The Aseri oolite. Analyses made by INAA and EDS (SiO_2). The composition shows only minor regional variation except for iron. Estonian and Russian ooids consist of limonite, whereas the Swedish oolites also contain chamosite ooids with lower iron content. Data compiled from Sturesson (1995), Sturesson and Bauert (1994) and Sturesson et al. (1999, 2000).

elements like the REE are highly enriched in the phosphate phase, and phosphate-rich ooids therefore show correspondingly larger variations in their composition.

The REE distribution patterns for Ordovician iron ooids are similar all over Baltoscandia. Chondrite-normalised values show a typical negative Eu anomaly, a minor Ce anomaly and enrichment of LREE (Sturesson, 1995; Sturesson et al., 1999). The patterns are influenced, however, by the amount of incorporated phosphate. A high content of phosphate leads to an increase of the total amount of REE and particularly the MREE. The oolitic clays in the area have REE patterns similar to phosphate-poor iron ooids (Sturesson, 1995).

Iron ooids and associated tuffs from the Prague basin show similar REE distributions for LREE and MREE (Fig. 4B and C). The ΣREE and MREE enrichment are directly related to the amount of phosphate. Ooids as well as tuffs show a minor negative Ce anomaly and a characteristic, positive Tm anomaly, which could indicate a genetic link. The tuffs contain in sufficient amounts all the elements needed for iron ooid formation (Table 1).

3.2. Neodymium isotopes

Isotope values for Nd, expressed as $\varepsilon_{Nd}(t)$, in the iron ooids and in biogenic apatite from oolitic beds do not differ significantly from apatite from non-oolitic beds, with values between -4.5 and -8.6 (Table 3), whereas carbonate-free volcanic ash from south–central Sweden has $\varepsilon_{Nd}(t) = -2.82$ (Sturesson et al., 1999).

3.3. Clay mineralogy

The epicontinental Baltoscandian Sea received clastic sediments both from the continental shield in the east and from island arcs along the continental margin in the west. Recent investigations of ooid-rich, unconsolidated clays from Estonia revealed a mixture of illite together with 10–20% smectite R1 ordered I–S (Kirsimää, 2000, personal communication). Based on the presence of euhedral non-clay minerals, this result supports a previous conclusion that the clay is a mixture of detrital clay with a low $\varepsilon_{Nd}(t)$ and clay

Table 3
(A) ε_{Nd} values from Kunda iron ooids, clays and biogenic apatite from Sweden, Estonia and Russia; (B) the data compiled for a comparison of the ε_{Nd} values in ooids, clay and biogenic apatite.

A

	Sweden	Estonia	Russia	Material
Mean	-8.34	-7.43	-6.01	Kunda
Standard deviation	1.88	0.77	2.05	iron
N	5	3	2	ooids
Mean	-7.71	-7.14	-7.26	Kunda
Standard deviation	1.27	1.15	1.12	clays
N	2	3	4	
Mean	-8.07	-5.99	-5.67	Kunda
Standard deviation	0.67	1.75	x	biogenic
N	2	5	1	apatite

B

	Iron ooids	Clays	Biogenic apatite
Mean	-7.60	-7.32	-6.47
Standard deviation	1.66	1.03	1.68
N	11	13	8

formed from devitrified ash with a higher $\varepsilon_{Nd}(t)$ (Sturesson et al., 1999).

4. Discussion

Although the Ordovician Period is characterized by widespread volcanic activity around the Iapetus Ocean with large amounts of ashes and other volcanoclastic matter deposited in the basins, volcanism is seldom regarded as a possible source for the Ordovician iron oolites. At early Arenig time, it seems that the continents were at their furthest distance from each other, but various terranes had split off from Gondwana and begun to move northwards. Avalonia and Baltic came closer, both moving towards the paleoequator and with a dwindling Iapetus Ocean (Cocks, 2000, Fig. 9). These plate movements created numerous subduction zone-related island arc volcanoes during most of the Ordovician. Such volcanism starts commonly abruptly at a volcanic front roughly parallel to the oceanic trenches (Condie, 1984). Harper et al. (1996) have shown a string of such islands located along the margin of Laurentia facing Baltica. This kind of volcanism is largely of intermediate composition, producing explosive eruptions with pyroclastic ejecta (Stillman, 1984). The volcanic material produced is mainly preserved in Baltoscandia as K-bentonites, but under certain circumstances, iron ooids could be formed upon interaction of this material with seawater (Sturesson, 1992a). Visible volcanic matter appears for the first time in the Middle Arenig (Fig. 3) as a bed of calcitized tephra (Lindström, 1979). Lindström (1974) also showed in a geochemical study of the non-calcareous material in Lower–Middle Ordovician limestones in south–central Sweden that the covariance between Al, Fe, Mg and Ti points to volcanic ashes as a common source for these elements, and the ratios indicate a predominantly basaltic composition. Si or Al substitution in ferrihydrite formed from these ashes suppresses goethite formation and instead favours hematite formation (Cornell and Schwertmann, 1996). This authigenic hematite may explain the red colour of the Ordovician limestones (Kiipli et al., 2000).

In the Upper Ordovician and Silurian strata, the ash is only preserved as numerous K-bentonite beds of various thicknesses, which are stained red due to the presence of hematite. This difference in preservation of the volcanic evidence is so far not fully understood, but could be due to differences in the depositional environment or differences in the chemical composition of the ashes. The results show, however, that volcanic contributions to the sediment could have been more frequent and extensive than believed. It should also be remembered that Ordovician and Silurian iron oolite formation occurred on the other side of the closing Iapetus along the North American Appalachian Mountains from Newfoundland to Alabama (Petranek and Van Houten, 1997). Numerous beds of K-bentonite from collision zone volcanism within and associated with these oolites point to a possible genetic link also here (Chowns and McKinney, 1980; Hunter, 1970; Kolata et al., 1996; Ludvigson et al., 1996; Nelson, 1922).

4.1. Geochemistry

Mineralogy and the content of phosphate influence the geochemical composition of the Baltoscandian ooids. Chamositic ooids generally have higher amounts of phosphate than the limonitic ones and thereby a higher content of incorporated trace elements like the REE, which are highly enriched in the apatite (Sturesson, 1995). Variations in the phosphate content lead to a scatter in the data, and when comparing ooids from different parts of Baltoscandia, this must be considered.

4.2. Nd isotopes

The modern iron ooids from Indonesia have $\varepsilon_{Nd}(t)$ values of -1.46, typical for material from a young crust and representing the composition of fluids from which the ooids were formed. These ooids are mainly amorphous, but upon prolonged contact with seawater, they are altered to limonite or berthierine, and finally to chamosite ooids (Sturesson et al., 2000). The Indonesian ooids all have an incipient thin crust of iron oxyhydroxide (goethite), indicating that the transformation from an amorphous state to limonite probably takes much longer time than the ooid formation. Even if the Ordovician ooids initially had a higher $\varepsilon_{Nd}(t)$ value inherited from the volcanic ash, when they later altered, the transformation occurred on a seafloor with a mixture of detrital and volcanic matter and the $\varepsilon_{\mathrm{Nd}}(t)$ values became more negative and similar to the biogenic apatite from the same level. Modern ooids and most Baltoscandian ooids have about 1% of apatite, and that is probably the site of REE and other trace elements.

4.3. Towards a general model for Palaeozoic iron oolite formation

Although it seems likely that some Ordovician iron oolites in Baltoscandia and adjacent areas have a volcanic origin, other modes of formation must also be considered for a general model. One major problem is the source of iron. Van Houten (1985) suggested that the high levels of carbon dioxide in the atmosphere during the Ordovician–Silurian and the Jurassic caused a higher rate of weathering than at present and resulted in the release of Fe. The iron is supposed to be transported by rivers to the sea as a coating on clay particles (Young, 1989a,b, 1992), but Maynard (1983) demonstrated that it would require excessive amounts of clays. As all iron oolites are formed during periods with low sedimentation rates, this model has little or no support in the geological record or in present settings. Veizer et al. (2000) also conclude that the role of CO_2 as the driving force of global climate changes is questionable, or that the reconstructed past CO_2 levels might be incorrect.

A high pCO_2 in the atmosphere can also be regarded as an indication of input of CO_2 from volcanism at higher rates than what can be removed by silicate weathering. If so, not only gases but also considerable amounts of volcanic ash and other volcanoclastic material must have been introduced into the atmosphere and into the seawater during periods of high pCO_2.

4.4. Strontium isotopes in the Ordovician seawater

The long residence time and short mixing time for Sr in seawater leads to the same isotopic composition for all oceans, with a present ratio of 0.70906 ± 0.00003 (Faure, 1986), close to the values for Early Ordovician. The seawater composition of $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ is controlled mainly by river input of Sr from weathered $^{87}\mathrm{Sr}$-enriched continental crust and from seawater interaction with $^{87}\mathrm{Sr}$-depleted basalts at mid-ocean ridges. There is a significant negative excursion in the oceanic isotope ratio from the Cambrian/Ordovician boundary to Early Silurian (Fig. 5), which can be due to an increase of the seafloor activity or a decrease in the weathering of the continental crust.

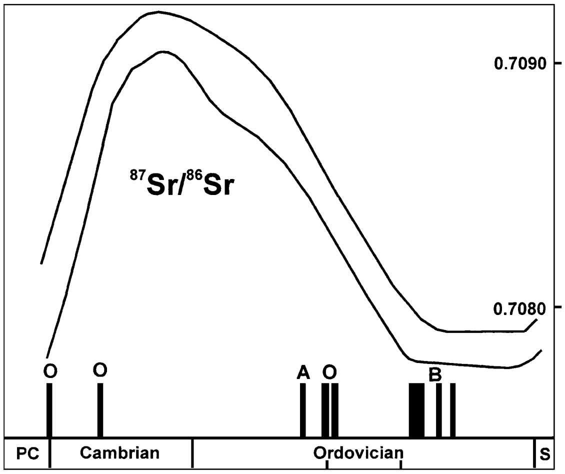

Fig. 5. The global $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ variations for Cambrian and Ordovician (Denison et al., 1998), and the occurrence of volcanic matter in the Baltoscandian basin. (A) is a calcitized ash bed, (O) are the iron oolites and (B) indicates some of the major K-bentonite beds (Bergström et al., 1995). The first bentonite band consists of several closely spaced thin K-bentonite beds.

The first major stage in the closure of the Iapetus Ocean occurred near the Cambrian–Ordovician boundary and culminated with arc volcanites onto a westward extension of the Baltoscandian margin during Early Arenig to earliest Llanvirn (Sturt and Roberts, 1991). The first visible evidence of volcanic input into the Baltoscandian basin is close to this Sr isotope excursion like the occurrence of the iron oolites, followed by several beds of K-bentonite (Fig. 5).

4.5. Global Sr isotope and iron ooid distribution

The general trend of $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ in Palaeozoic seawater, preserved in calcite and phosphatic shells, shows a general decreasing trend from Cambrian to the beginning of Cretaceous and a rapid increase in the Cenozoic (Veizer et al., 1999). A number of negative and positive excursions superimposed on the general trend show when weathering of older rocks dominated, and when hydrothermal systems and volcanism were the major sources for Sr. The stratigraphic record of ironstones in the Palaeozoic can be constrained in terms of these variations. There are two major periods of global ironstone formation, Ordovician–Silurian and Devonian, (Petranek and Van Houten, 1997), both reaching a maximum during negative excursions in the global Sr isotope curve (Fig. 6). This temporal coincidence indicates that the Palaeozoic iron oolites were formed during periods with low input to the oceans of radiogenic Sr from weathering. The assembly of Pangea during Permian caused a decrease of the riverine flux due to continental aridity and led to a decrease in the $^{87}Sr/^{86}Sr$ ratio (Martin and Macdougall, 1995). Welding of the continents also led to a reduction of the coastlines and the conditions for iron oolite formation were not favourable and few economic deposits occur from this period.

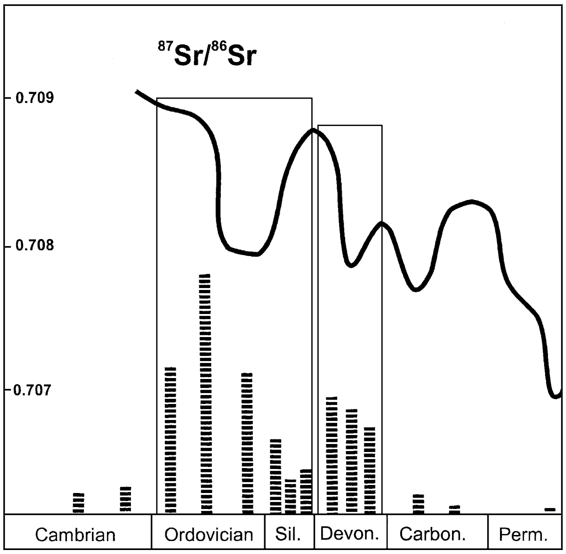

Fig. 6. (A) The global $^{87}Sr/^{86}Sr$ variations for the Paleozoic (Veizer et al., 1999) and the stratigraphic distribution of Phanerozoic ooidal ironstones (Petranek and Van Houten, 1997). Diagenesis generally raises the carbonate $^{87}Sr/^{86}Sr$ ratio due to release of radiogenic Sr from continental siliciclastic matter. The $^{87}Sr/^{86}Sr$ curve represents the lowest values in the data set as a best estimate (Jones and Jenkyns, 2001). The ooid distribution is based on the amount of known ooidal ironstones around the world. The data from Petranek and Van Houten (1997) have been recalculated. The oolites have been classified into four groups based on their estimated total amount of iron, and each period is divided in three equal parts. The ooid distribution is not perfect. The stratigraphic age of larger ore bodies can be difficult to estimate as they often lack fossils for dating and their age can span over several tens of million years. The general distribution is reasonably accurate for this purpose, although some minor iron oolites probably remain unknown.

4.6. Volcanic sources

Volcanic ash as the source for oolitic iron ore is not a common theme in the geological literature. The ashes are supposed to contain too little iron to be a realistic source for larger ore bodies (Oftedahl, 1958). The iron content of the ash depends on the nature of the volcanism but is usually within 1–5% (Fe^{3+} + Fe^{2+}), which means that for each ton of iron ooids (Fe = 50%) about 10–50 t of ash will be needed. However, volcanic ash also contains a considerable amount of water-soluble metal salts adsorbed to the surface of the ash particles. The ash from the 2000 Mount Hekla eruption contained about 8.5% of Fe_2O_3, including the soluble fraction. These salts dissolve in contact with seawater in a few hours, which is much faster than the dissolution of the volcanic glass (Frogner et al., 2001). The eruption of Mount St. Helens in 1980, a medium-scale example of arc volcanism, produced 500 Mt of ash with about 3–4% Fe (Sarna-Wojcicki et al., 1981; Lipman et al., 1981), corresponding to 30–40 Mt of iron ooids. However, the Baltoscandian oolites were not formed by only one eruption. In south–central Sweden, three to four coeval ash beds are preserved, and several more might have disappeared, as their chance for preservation is very small (Sturesson, 1992a,b). Arc volcanism is most effective in producing large volumes of volcaniclastic material (Einsele, 1992), so the string of subduction-related island arc volcanoes in the west could have produced enough iron to explain the rather thin and lean oolites in the area, even if only a fraction was transformed to ooids. To this category of possible sources, pumice is also included. Prevailing westerly winds and currents (Björlykke, 1974) could have carried floating pumice into the basin to be deposited along the shores.

The larger commercial ore bodies were formed over a long time span. More than half of the worlds iron oolites are restricted to ten major sedimentary basins were they developed repeatedly over many tens of million years (Van Houten and Hong-fei, 1990).

Devonian iron oolites were also formed worldwide during a negative Sr isotope excursion (Fig. 6). Oolites from this period do not occur in Baltoscandia, however, but Dreesen (1989) describes extensive but thin Upper Devonian iron oolites south of the London–Brabant Massif, Belgium. The presence of volcanic glass, idiomorphic zircon crystals in the host sediment led to the conclusion that the iron ooids could have originated from volcanic ashes.

The Precambrian and Cambrian iron oolites in Baltoscandia have probably also been formed close to a negative excursion in the $^{87}Sr/^{86}Sr$ ratio. This part of the strontium curve is based on few samples, however, and not as accurate as the rest. Tegengren's (1962) suggestion of a volcanic origin is supported by the presence of relicts of pumice clasts in the matrix and in the ooid nuclei (Fig. 2).

The study of modern iron ooids in Indonesia clearly showed that the ooids are formed by chemical precipitation (Heikoop et al., 1996; Sturesson et al., 2000) from exhalative fluids in an area of active volcanism. The details of the reactions involved need further studies, but silica seems to play an important role in forming intermediate colloids. A prerequisite for the formation is that all the elements involved must be present simultaneously and in solution. Rapidly dissolving iron salts on the glass shards and devitrifying volcanic ash and pumice on the seafloor meet these requirements. All the elements are present in the ash and are released to the seawater as the adsorbed salts and glass dissolve, and the composition is essentially the same all over the deposited area. The excess of Si and Al precipitated as smectite or kaolinite clays.

4.7. Gas exhalation

The close genetic relationship between gas exhalations and volcanic explosions was pointed out by Oftedahl (1958), who proposed the idea of exhalative gases as the source for the ooids in Baltoscandia. The gases are rich in iron, copper, zinc, lead, etc., as chlorides and fluorides, and when expelled from the seafloor into the seawater, they readily go into solution as metal-rich ore-forming fluids (James and Elderfield, 1996). The model is tempting as exhalation can produce large amounts of iron in a short time, and is believed to be responsible for deposits of iron and copper sulfides in Norway. To explain extended iron oolites like those in Baltoscandia, however, requires some modification of Oftedahl's model. The amount of Fe and Al in ocean water is very low due to a short residence time as insoluble oxides rapidly form and precipitate close to the source (Martin et al., 1994). From an assumed volcanic source in the west, the iron oxide-rich water must be transported across the basin all the way to the Ladoga area and beyond. The epicontinental sea was shallow and the exchange of water restricted, and the transport time was probably much longer than the residence time for the iron. Most of the iron and other elements should then have been precipitated along the route, and also been subsequently diluted. In Oftedahl's model, the ash is thus only an indication of an ongoing volcanic activity and the metal-rich fluids are the true source of iron. Oftedahl's model does not seem to work for geographically extensive iron oolites like those in Baltoscandia, but can explain oolite deposits close to the source volcano as the modern ones in Indonesia (Heikoop et al., 1996; Sturesson et al., 2000). In older deposits, the volcanic origin can be difficult to identify, as such fluids leave few visible traces.

4.8. Iron ooids and tectonic setting of volcanoes

In the geological record, there are cases with no visible traces of volcanism related to the iron ooid formation. This can be due to the volcanic setting. The Baltoscandian iron oolites discussed here were formed at convergent margin volcanic settings, which characteristically produce large volumes of pyroclastic ejecta at Plinian-type (explosive) volcanic eruptions. This explains the wide lateral synchronous distribution of the oolites and their similar chemical composition. Of active subaerial volcanoes associated with plate boundaries, about 80% are of this kind. Divergent margins constitute about 15% and the remaining 5% are intraplate (hot spot) volcanoes (Fisher and Schmincke, 1984). These latter settings generate dominantly basaltic magma in mostly nonexplosive eruptions. Diagenetic and hydrothermal alteration of such material can locally produce large amounts of iron and other elements for iron ooid formation. The importance of these types of volcanism in a general model for iron oolite formation needs further investigations and is not within the aims of this study.

5. Conclusions

Plate movements and related seafloor spreading when Baltica and other continents moved northward is the probable major cause for a pronounced drop in the seawater $^{87}Sr/^{86}Sr$ ratio during the Ordovician. This drop coincides with the most prominent iron oolite formation period in the earth's history. In addition, the Devonian–early Carboniferous iron oolites were formed during a similar negative excursion in the strontium isotope ratio. Repeated eruptions from subduction zone volcanism produced easily soluble volcaniclastic material containing all the elements needed for iron ooid formation, and the ooids were produced in shallow environments along the plate margins.

Volcanism as a source for iron ooids is often rejected because of the absence of visible evidence for volcanic matter in the oolite. The volcanic model refers to autochthonous oolites, but during sea level changes, oolites are commonly reworked and mixed with other clastic material. In such cases, the volcanic origin can be difficult to reveal. It should be emphasized that elements from other kinds of volcanic emanations, such as metal-rich hydrothermal fluids, etc., are also potential constituents of the iron ooids. The aim for the future is therefore to establish methods to differentiate between ooids from different volcanic sources.

Acknowledgements

This study was financially supported by a grant from the Swedish Natural Science Research Board (NFR), grant no. G-AA/GU 9708-329, and is a contribution to the IGCP Project 410 "The Great Ordovician Biodiversification Event". Michal Mergl kindly supplied samples of the volcanic material from the Prague Basin, and E. Pirrus supplied drill core samples of the Cambrian oolite in Latvia. I am grateful to S. Morad and W. Huff for constructive criticism of the manuscript and to S. Felitsyn for the determination of Nd isotopes. SGAB Analytica, Sweden made the chemical analyses.

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