Vivianite formation and distribution in Lake Baikal sediments

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Abstract

In an effort to better understand vivianite formation processes, four Lake Baikal sediment cores spanning two to four interglacial stages in the northern, central and southern basins and under various biogeochemical environments are scrutinized. The vivianite-rich layers were detected by anomalous P-enrichments in bulk geochemistry and visually by observations on X-radiographs. The millimetric concretions of vivianite were isolated by sieving and analysed by X-ray diffraction, scanning electron microscope (SEM), microprobe, infrared spectroscopy, inductively coupled plasma atomic emission spectrometry and mass spectrometry (ICP-AES, ICP-MS). All the vivianites display similar morphological, mineralogical and geochemical signature, suggesting a common diagenetic origin. Their geochemical signature is sensitive to secondary alteration where vivianite concretions are gradually transformed from the rim to the center into an amorphous santabarbaraite phase with a decreasing Mn content. We analysed the spatial and temporal distribution of the concretions in order to determine the primary parameters controlling the vivianite formation, e.g., lithology, sedimentation rates, and porewater chemistry. We conclude that vivianite formation in Lake Baikal is mainly controlled by porewater chemistry and sedimentation rates, and it is not a proxy for lacustrine paleoproductivity. Vivianite accumulation is not restricted to areas of slow sedimentation rates (e.g., Academician and Continent ridges). At the site of relatively fast sedimentation rate, i.e., the Posolsky Bank near the Selenga Delta, vivianite production may be more or less related to the Selenga River inputs. It could be also indirectly related to the past intensive methane escapes from the sediments. While reflecting an early diagenetic signal, the source of P and Fe porewater for vivianites genesis is still unclear.

Keywords: Lake Baikal ; Late Quaternary ; sediment ; vivianite ; geochemistry

1. Introduction

Phosphate minerals, such as vivianite or hydroxyl apatite, have been identified in lacustrine sediments worldwide, e.g., in North America (Nriagu and Dell, 1974; Dean, 1993; Brooks and Edgington, 1994), in Europe (Norway: Rosenquist, 1970; Denmark: Kjensmo, 1968; Great Britain: Mackareth, 1966; Northern Ireland: Anderson and Rippey, 1988; in central Greece: Stamatakis and Koukouzas, 2001), in Eastern Africa (Müller and Forstner, 1973; Staffers and Hecky, 1978) and in Asia in Lake Baikal (Knyazeva, 1954; Romashkin et al., 1993; Deike et al., 1997; Grachev et al., 1997; Zhmodik et al., 2001, 2002).

Vivianite is probably the most stable Fe^{2+} orthophosphate in sedimentary environments (Nriagu, 1972). Its solubility mainly controls the geochemical migration or immobilisation of phosphorus within aquatic systems (Einsele, 1938; Mortimer, 1941). Vivianite is a widespread mineral in lacustrine sediments, yet its origin and conditions of formation are not well understood. The aim of this work is to analyse the distribution and chemistry of vivianites throughout sedimentary columns from different locations in Lake Baikal. We focus on identifying the sedimentological environments (i.e., lithology, sedimentation rate, content of sedimentary organic carbon, etc.) that favour the vivianite genesis and preservation in order to determine whether vivianite can be used as a proxy for environmental conditions, in particular paleoproductivity.

2. Previous studies

2.1. Thermodynamic stability fields of vivianite and lacustrine occurrences

Vivianite, $Fe_3^{2+}(PO_4)_2.8H_2O$, is formed under reducing redox environments and alkaline conditions (Rosenquist, 1970). High ferrous ions and phosphate activities, as well as low sulphide activity, are required to stabilise vivianite in most chemical systems (Nriagu, 1972). In naturally reducing environments, the most stable phosphate mineral is a solid solution of vivianite and reddingite, $Mn_3^{2+}(PO_4)_2.3H_2O$, rather than a pure phase (Nriagu and Dell, 1974). In marine systems, Fe is highly correlated with sulphur, produced by bacterial sulphate reduction to form ferrous sulphides (Berner, 1984; Glasauer et al., 2003), and marine Fe-Mn phosphates only occur if Fe and Mn are in excess relative to sulphur. In freshwater lake sediments, while the content of porewater

sulphate and sulphide is low, ferrous Fe substantially exceeds sulphur and may be combined with phosphates (Dean, 1993). As a result, vivianite is a major authigenic iron mineral that may precipitate directly from porewater (Nriagu and Dell, 1974). Vivianite is a stable constituent in lacustrine-reduced sediments (Nriagu, 1972), but Fe-Mn phosphate concretions are not ubiquitous.

Lake Baikal is an oligotrophic lake and the phosphate content in the water column is low, ranging from 0.004 mg P l^{-1} in the surface waters to 0.018 mg P l^{-1} near the bottom (Weiss et al., 1991). In Lake Baikal sediments, the measured porewater phosphorus concentrations are higher, i.e., from 0.01 to 0.65 mg P l^{-1} (Callender and Granina, 1997a; Granina and Callender, 2001). In fact, some pelagic sites display porewater phosphorus content up to 1-3 mg P l^{-1} and considerable inclusions of vivianite are found in these sediments (Granina and Callender, 2001). In Lake Baikal-reduced pelagic sediments, the ranges of redox potential and pH values [εh: 50 to -300 mV, pH: 6.9 to 7.4, respectively (Mizandrontsev, 1975)] combined with the absence of carbonates (Knyazeva, 1954) favour the formation of diagenetic vivianite.

2.2. Relationship between Fe-Mn crusts and vivianites in Lake Baikal

In Lake Baikal surface sediments, it was suggested that the formation of vivianite could be related to accumulations of Fe and Mn hydroxides within the oxidized sediments (Knyazeva, 1954; Deike et al., 1997). Due to constant oxygen enrichment throughout the water column, most of the sediments are oxidized at the sediment/water interface. Two types of Fe and Mn diagenesis have been recently characterised, according to the sedimentation rates (Granina et al., 2004). In high sedimentation areas (South and Central Baikal, area near the Selenga River Delta), relatively small amounts of Fe and Mn hydroxides accumulate on the sediment-water interface. In low sedimentation areas (Academician Ridge and North Baikal), high contents of Fe and Mn hydroxides are concentrated at the redox fronts, i.e., 10 to 20 cm deep down the core. The oxidized Fe sedimentary layers are enriched with phosphorus (Knyazeva, 1954; Patrikeeva, 1963) reaching enrichment factors of 1.6 to 14 (Deike et al., 1997; Müller et al., 2002). Sorption of P on preexisting amorphous ferric hydroxides could be responsible for high P content in Lake Baikal Fe/ Mn layers (Deike et al., 1997). This has been confirmed by laboratory experiments, which showed high coefficients of phosphorus adsorption on the natural Fe (and Mn) hydroxides from Lake Baikal sediments (Granina, 1987).

Vivianite from Quaternary sediments is associated either with (1) compact indurate dark-green to green-olive Fe/Mn crusts (called "green layers") composed of irregularly laminated red-brown submillimetric granular masses or, (2) up to 5-mm-thick zones defined by an accumulation of those grains (Deike et al., 1997). Since these accumulations have Fe, Mn and P contents similar to those of crusts from recent oxidized zones, they could be relicts of existing Fe and Mn layers buried in response to global paleoclimate changes (Granina et al., 1993). For instance, on Academician Ridge, the enrichment in both vivianites and Fe/Mn crusts was observed in >100 µm fraction within the sediment interval 400-600 cm below the sediment surface (Grachev et al., 1997). Deike et al. (1997) suggested that buried Fe/Mn crusts form at the transition between glacial and interglacial periods, after high glacial melt-water discharge but before high biological productivity in the lake. In the region of Academician Ridge, Mats et al. (2000) proposed that ancient Fe/Mn crusts of continental origin might be submerged by tectonic events. Such material might serve as an initial source for further Fe and Mn diagenetic redistribution under conditions of slow sedimentation and a deficit of sedimentary organic carbon typical of an oxidation front in a nonsteady-state diagenetic system (Granina et al., 2003). Thus, Fe/Mn crusts found deep below surface sediments may not be markers of past climatic events, as was suggested previously (Deike et al., 1997), but may be a result of downwards deepening of the oxidation front downwards the sediments (Granina et al., 2003).

3. Materials and methods

3.1. Sampling sites and material

We investigate four cores from South Baikal (Pos-olsky Bank: CON01-604, 52.0795°N 105.8575°E, at a water depth of 133 m), Academician Ridge (VER98-1-3: 53.7489°N 108.3172°E at a water depth of 373 m; VER98-1-14: 53.5230°N 107.9694°E at a water depth of 412 m) and North Baikal ("Continent Ridge": CON01-603, 59.9633°N 108.9130°E, at a water depth of 386 m) (Fig. 1, Table 1). The cores, sampled on the underwater uplifts, are unaffected by turbidite-like deposits. The hemipelagic sediments are composed of terrigenic clayey silt and/or silty clay mud, interlayered with biogenic diatom-rich mud (Fig. 2). The detailed lithological descriptions are presented elsewhere (see Fagel et al., 2003 for Academician Ridge VER98-1-3 and VER98-1-14 cores; Charlet et al., 2005-this issue for the Posolsky and Continent cores). On both Academician and Continent Ridges, the sedimentological features contain zones of sediment reworking (e.g., by slumping and/or creeping) related to the complex tectonic history of those heights (Ceramicola et al., 2001; Charlet et al., 2005-this issue). Continent Ridge is a more or less isolated high, partly connected to the Academician Ridge. Posolsky Bank is located in the vicinity of the Selenga Delta, on a complex boundary system between the Southern and the Central Baikal sub-basins. The core was recovered on the crest of the tilted fault block, in an area characterised by

undisturbed sedimentation relative to the margins.

Fig. 1. *Location of investigated cores (stations are shown by open circles) in Lake Baikal, Siberia. In addition, the shaded region highlights the area where the accumulations of vivianite were found at the stations shown by numbers (Romashkin et al., 1993; Granina and Callender, 2001; Granin and Granina, 2002; A. Gvozdkov, personal communication). This area located opposite the Selenga Delta is noted "vivianite area" in the text.*
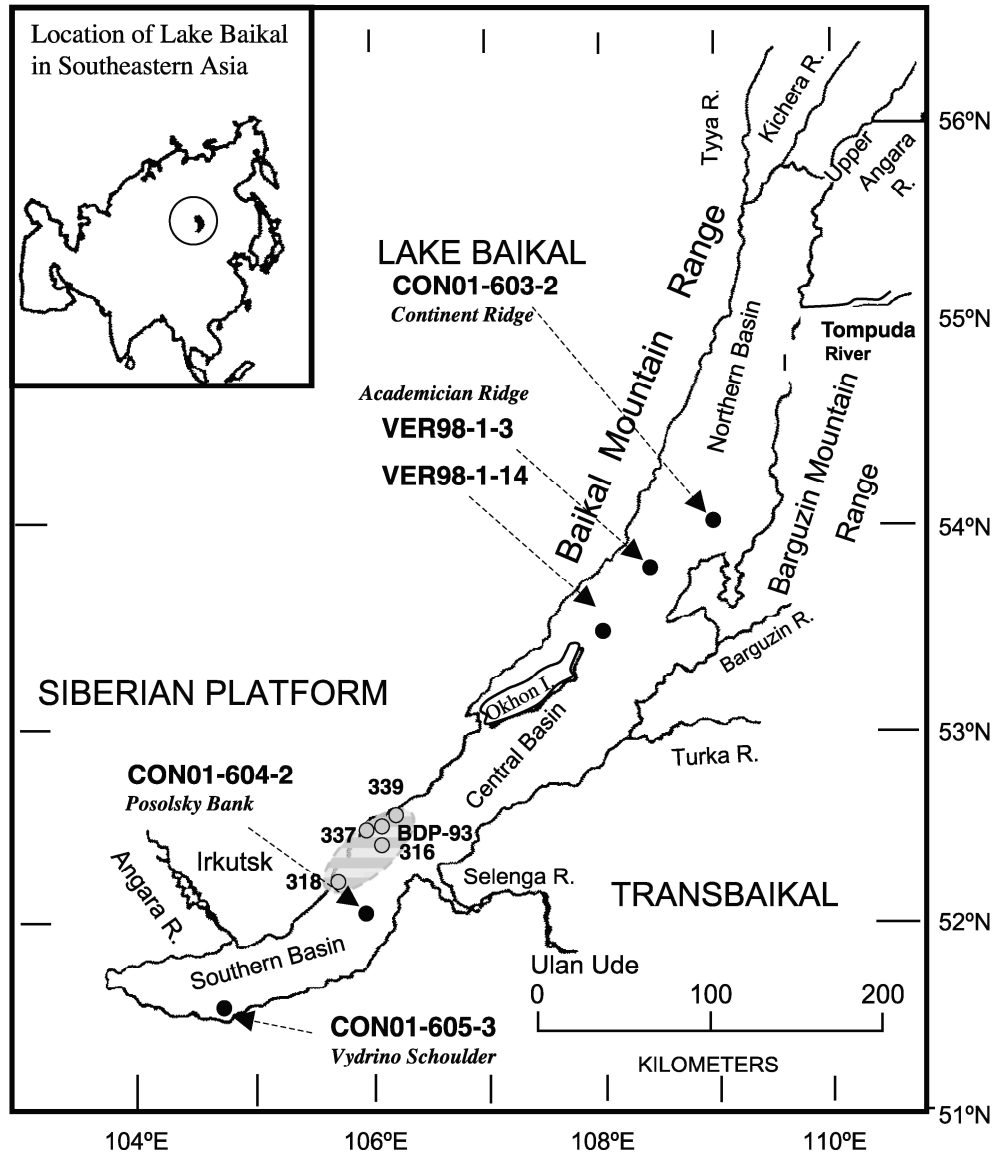
In Lake Baikal sediments, stratigraphy and core correlation are derived from diatom assemblages (Bradbury et al., 1994; Likhoshway, 1998) and a few ^{14}C AMS dates (Colman et al., 1995). The diatom-rich sedimentary layers correspond to warm, interglacial intervals, and the clay-rich layers to the cold, glacial intervals. The age model for the two Academician Ridge cores has already been detailed by Fagel et al. (2003). The proposed correlations between Posolsky and Continent cores reported in Fig. 2 are based on sediment texture, abundance of diatom frustules (Hauregard, unpublished data) and magnetic susceptibility (Demory et al., 2005-this issue). All the sediment cores cover the last two to four interglacial stages (>250 ky). Taking into account the thickness of clay-rich intervals in the different cores, we estimate that sedimentation rates are at least twice as high in core CON01-604-2 (Posolsky Bank) than in the three other cores. This is partly due to the close location of the Posolsky Bank to the Selenga River, which brings about 75% of the total suspended sediments into the lake (Agafonov, 1990). The mean sedimentation rates are estimated to be ca. 11.7 cm/ky for Posolsky Bank, and ca. 6.3 cm/ky for Continent Ridge (Demory et al., 2005-this issue).

In the text, we refer to an additional core taken from the Vydrino Shoulder in the Southern basin (core CON01-605-3, Fig. 1). The lithology of this site contrasts with the four previous cores; the sediment is mainly terrigenous in nature, consisting of sandy (turbidites) or silty sediments with a few diatom frustules in its upper part (Charlet et al., 2005-this issue). The site is characterised by high sedimentation rates, ca. >12 cm/ky (Demory et al., 2005-this issue).

Table 1 *Location of piston cores, Lake Baikal*

Location	Site name	Core name	Latitude, °N	Longitude, °E	Water depth, m	Core length, m	Studied interval, m
South Basin	Posolsky Bank	CONO 1-604-2	52.08	105.86	133	10.03	0-6.24
Sill between Central and North basins	Academician Ridge	VER98-1-14	53.52	107.97	412	9.80	0-7.73
Sills between Central and North basins	Academician Ridge	VER98-1-3	53.75	108.52	373	10.92	0-8.35
North Basins	Continent Ridge	CONO 1-603-2	53.96	108.91	386	11.30	0-11.30

3.2. Methods

3.2.1. Major and trace geochemistry of bulk sediments and concretions

The sediment cores were sampled with a resolution of 10 cm, resulting in a total of 290 samples (Table 2). Around 250 mg of dried sediments was mechanically crushed through 100-200-µm mesh then processed by an alkaline digestion (Lithium meta-borate) in a Pt crucible at 1000 °C for 1 h. The residue was dissolved over night in a nitric acid matrix and then major and minor elements (Al, Ba, Ca, Fe, K, Mg, Mn, Na, P, S, Si, Sr, Ti) were analysed by Atomic Emission Spectrometry ICP-AES (Thermo Optek Iris Advantage, Royal Museum for Central Africa, Tervuren, Belgium). Y and Au internal standards were used to correct for instrumental drift. For both trace and major elements analyses, external calibrations were performed using artificial standard solutions and dissolved mineralised natural rock standard (e.g., BHVO-1, DWA, CCH-1 SGR-1, JGB-1).

In order to get a complete geochemical signature, 14 P-rich concretions, chosen among the different cores, were acid digested (Tables 3a, 3b). In a clean laboratory, 1.7 to 36 mg of concretions were digested overnight in a concentrated mixture of Suprapur acid (3 ml HC1/2 ml HNO_3/1 ml HF) at 90 °C in sealed Teflon beakers. After evaporation to dryness, the residue was dissolved in 2.5 ml of 2% HNO_3 Suprapur and diluted to 12 ml with Milli-Q water. During the same procedure, we have also dissolved and analysed, for comparison, a pure vivianite from Anlua, Cameroon (tubular crystals, MRAC collection).

Major elements were analysed, like the sediment samples, by Atomic Emission Spectrometry ICP-AES, and trace elements by Inductively Coupled Plasma Mass Spectrometry ICP-MS (VG *Elemental Plasmaquad PQ2+).* The following trace elements were measured in triplicates (Sc, Co, Cu, Zn, Ga, Ge, Rb, Sr, Y, Zr, Nb, Mo, Cs, Ba, La, Ce, Pr, Nd, Eu Sm, Gd, Dy, Ho, Er, Yb, Lu, Hf, Ta, W, Pb, Th, U). Oxides were minimised by checking that ThO^+ is less than 2% of the total Th in an artificial standard solution. Matrix and instrumental drift effects were continuously monitored and corrected by measuring the fluctuations of four internal standards (^{99}Ru, ^{115}In, ^{185}Re, ^{209}Bi) added to the samples. Accuracy determined on international mineralised rock standards was typically within 10% of literature values for most elements. Experimental blanks (acid digestion blanks) were processed under the same conditions as the samples and the blank signals were subtracted.

3.2.2. Mineralogy of the concretions

Using the bulk geochemistry data, we have systematically selected the samples (i.e., *n*=24) that contain enrichments in Fe and P. Samples were sieved under water at 63 µm in order to concentrate the concretions. Those layers are usually well identified on the X-radiographies of the sediments, characterised by the occurrence of millimeter-sized rounded grains, isolated or concentrated within a continuous or discontinuous lamination (Fig. 2). In addition, we have also sampled and sieved the continuous concretion-bearing layers evidenced on the X-radiographs, although not sampled for bulk geochemistry. The concretions were isolated by handpicking under binocular lens.

The morphology of the concretions and their semiquantitative chemical analyses were obtained with a JEOL Scanning Electron Microscope with Energy Dispersive Spectrometry (SEM-EDX, ULg, Belgium). Identifications of the minerals were performed with a Philips PW-3710 diffractometer using 1.9373 Å FeK_α radiation. The unit-cell parameters (Table 4) were calculated with the least-squares refinement program LCLSQ 8.4 (Burnham, 1991), from the *d*-spacings corrected with an internal standard of Pb(NO$_3$)$_2$. Electron-microprobe analyses (Table 5) were completed on a selection of grains from 11 samples, with a CAMECA SX-50 instrument

(University of Louvain-la-Neuve, Belgium), under an accelerating voltage of 15 kV and a probe current of 20 nA. The standards used were the Kabira graftonite (Fe, Mn, P; Fransolet, 1975), corundum (Al), olivine (Mg), wollastonite (Si), and willemite (Zn). Infrared spectra were recorded on a NICOLET Nexus spectrometer, from 50 scans with a 2-cm^{-1} resolution, in the range 400-4000 cm^{-1}. The samples were prepared by mixing 2 mg of mineral powder with KBr, in order to obtain a 150-mg homogeneous pellet. To prevent water contamination, the measurements were made under a dry air purge.

Fig. 2. *Simplified lithological columns of investigated sediment cores (plotted from South to North). Modified from Hauregard, unpublished data. The tentative correlation between the cores is based on lithology and magnetic susceptibility (Hauregard, unpublished data; Demory et al., 2003). The depths of concretion-rich layers are reported with regard to the lithological columns. Plain line: direct observation of X-radiographs; dotted line: observations after >63 µm sieving.*
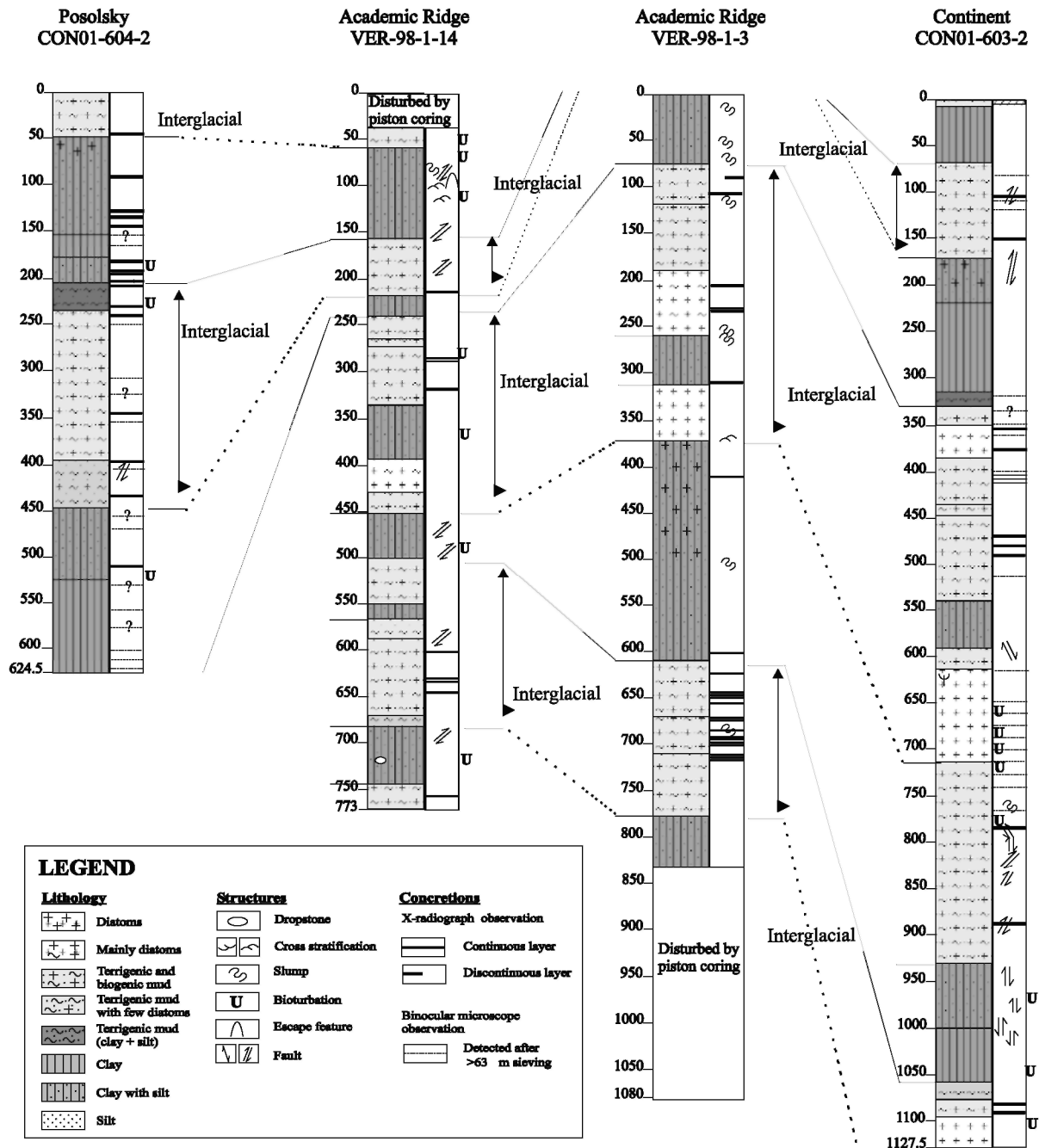
Table 2 *Composition of major oxide in bulk sediments from lake Baikal: ICP-AES data from P-rich samples*

Location	Core	Depth cm	Lithology	Al_2O_3, %	SiO_2, %	$Fe_2O_{3\,tot}$, %	TiO_2, %	MgO, %	MnO, %	CaO, %	Na_2O, %	K_2O, %	P_2O_5, %	PF, %	S %	Total, %	$SiO_{2\,xs}$, %
American Ridge	VER98-1-3	87.9	Diatom+Clay, Silt	14.3	55.3	12.0	0.63	2.04	0.79	1.68	1.80	2.35	3.13	6.61	0.06	100.6	14.4
		208.5	Diatom+Silt	11.3	68.1	6.00	0.51	1.61	0.21	1.41	1.65	1.96	0.91	6.64	0.07	100.3	45.1
		316.7	Diatom	11.0	68.2	6.33	0.55	1.67	0.23	1.64	1.62	1.87	0.90	6.02	0.11	100.2	46.4
		416.2	Clay+(Silt, Diatom)	16.2	57.2	9.45	0.81	2.43	0.21	1.99	2.05	2.98	0.60	5.80	0.42	100.2	5.8
		549.9	Clay, Silt	17.1	55.3	10.2	0.80	2.72	0.33	1.83	2.00	3.16	1.43	5.29	0.11	100.3	0.0
		638.3	Diatom+Clay, Silt	10.7	65.0	5.05	0.50	1.58	0.17	1.41	1.57	1.74	0.66	n.d.	0.04	88.5	45.3
		705.0	Clay, Silt+(Diatom)	15.9	59.8	7.95	0.74	2.62	0.26	1.92	2.16	2.79	0.92	5.47	0.11	100.7	11.8
American Ridge	VER98-1-14	280.7	Diatom+Clay, Silt	13.7	63.9	7.73	0.57	1.94	0.24	1.50	1.62	2.27	0.85	5.65	0.14	100.1	28.4
		599.2	Diatom+Clay, Silt	11.4	70.3	5.98	0.46	1.58	0.14	1.42	1.61	1.88	0.39	5.32	0.13	100.7	45.7
		630.2	Diatom+Clay, Silt	14.7	61.7	7.69	0.60	2.09	0.42	1.44	1.67	2.48	1.21	6.25	0.16	100.4	20.5
		640.8	Diatom+Clay, Silt	14.0	64.0	7.07	0.59	2.15	0.30	1.60	1.78	2.42	0.74	6.13	0.09	100.9	26.8
Continent Ridge	CON01-603	190.0	Clay, Silt+(Diatom)	17.0	57.8	9.09	0.86	2.75	0.48	1.88	2.09	3.13	1.37	5.91	-	102.3	2.1
		380.0	Diatom+Silt	13.8	62.7	8.23	0.63	2.00	0.28	1.62	1.86	2.36	1.68	6.24	-	101.4	26.8
		500.0	Diatom+Clay, Silt	14.1	64.2	7.87	0.66	2.16	0.36	1.68	1.83	2.43	1.23	5.83	-	102.4	27.0
Posolsky Bank	CON01-604	90.0	Clay+Silt	18.2	53.2	8.73	0.97	2.89	0.23	1.89	2.13	3.18	0.56	5.01	-	97.0	0.0
		170.0	Clay	17.4	56.4	8.06	0.96	2.69	0.19	1.79	1.98	2.92	0.41	6.55	-	99.3	0.0
		180.0	Clay+(Silt)	17.4	58.4	7.68	0.95	2.60	0.18	1.88	2.14	2.93	0.50	6.02	-	100.6	1.0
		220.0	Clay+Silt	16.2	54.2	7.91	0.89	2.44	0.25	2.04	2.35	2.83	0.65	5.73	-	95.5	0.4
		240.0	Diatom+Clay, Silt	16.6	56.2	7.81	0.90	2.50	0.20	1.93	2.20	2.86	0.48	6.26	-	98.0	1.9
		320.0	Diatom+Clay, Silt	17.2	57.5	8.21	0.89	2.51	0.18	1.77	2.04	2.90	0.52	6.38	-	100.1	0.6
		420.0	Clay, Silt +(Diatom)	17.1	58.9	8.67	0.90	2.55	0.41	1.84	2.14	2.95	1.06	6.41	-	102.9	3.3
		450.0	Clay+(Silt)	16.7	53.5	8.20	0.91	2.62	0.22	1.82	2.04	2.86	0.60	6.65	-	96.0	0.0
		510.0	Clay+(Silt)	16.5	56.8	8.06	0.93	2.57	0.28	1.98	2.17	2.85	0.75	6.11	-	99.0	3.3

Table 3a *Major composition (wt.%) of concretions, ICP-AES measurements*

Location	Core name	Depth, cm	Type	Al, %	Si, %	Ti, %	Ca, %	Mg, %	Na, %	K, %	Fe, %	Mn, %	P, %	s, %	Fe/Mn wt/wt	P/Mn wt/wt	Fe	Mn	P
																	normalised wt.%		
Academician Ridge																			
	VER98/1/3	208	1	1.4	0.00	0.05	0.48	0.19	0.16	0.35	22	1.7	11	0.10	13	6.5	64	4.8	31
	VER98/1/3	316	1	1.0	0.00	0.05	0.24	0.20	0.09	0.25	21	2.5	10	0.29	8.4	4.0	63	7.4	30
	VER98/1/3	416	2	1.2	0.00	0.07	0.41	0.33	0.15	0.39	24	1.4	15	0.37	17	11	59	3.4	37
	VER98/1/3	638	2	0.79	0.00	0.04	0.32	0.20	0.06	0.17	24	3.4	12	0.02	7.1	3.4	62	8.7	29
	VER98/1/3	705	1	1.1	0.00	0.07	0.41	0.30	0.30	0.40	20	5.4	14	0.10	3.7	2.7	50	14	36
	VER98/1/3	723	1	0.82	0.00	0.05	0.33	0.24	0.12	0.27	21	6.7	12	0.36	3.2	1,8	53	17	31
	VER98/1/3	728	1	0.80	0.33	0.04	0.35	0.24	0.15	0.24	25	5.5	11	0.17	4.5	2.0	60	13	27
	VER98/1/14	600	1	0.33	0.00	0.02	0.29	0.14	0.03	0.11	26	3.2	14	0.05	7.9	4.4	59	7.5	33
	VER98/1/14	630	1	0.63	0.00	0.04	0.28	0.20	0.00	0.24	23	7.6	12	0.14	3.0	1.6	54	18	28
	VER98/1/14	640	1	0.83	0.14	0.04	0.31	0.24	0.11	0.23	22	7.1	11	0.17	3.1	1.5	55	18	27
North Basin																			
	CON01-603-2	381	3	0.75	0.26	0.03	0.31	0.22	0.08	0.17	28	3.1	11	0.00	9.0	3.8	66	7.2	27
	CON01-603-2	500	2	1.1	0.47	0.05	0.34	0.30	0.29	0.30	23	5.0	11	0.18	4.7	2.2	60	13	28
South Basin																			
	CON0 1-604-2	180	3	1.3	0.00	0.07	0.39	0.33	0.15	0.41	18	3.6	7	0.25	5.0	2.0	62	12	25
	CON0 1-604-2	510	3	2.0	0.00	0.13	0.58	0.46	0.06	0.34	24	6.5	11	0.08	3.7	1.6	58	16	26
Min baikal				0.33	0.00	0.02	0.24	0.14	0.00	0.11	18	1.4	7.3	0.00	3.0	1.5	50	3.4	25
Max baikal				2.0	0.47	0.13	0.58	0.46	0.30	0.41	28	7.6	15	0.37	17	11	66	18	37
Cameroon			pure	0.18	0.16	0.03	0.02	0.14	0.00	0.01	35	0.07	14	0.00	494.19	206.7	70.4	0.142	29.5
EF baikal/ Cameroon				11	2.9	4.0	26	3.3		31	0.8	108	1.1	190					

Table 3b *Trace element composition of concretions, ICP MS measurements*

Location	Core name	Depth cm	Type	Co, ppm	Cu, ppm	Zn, ppm	Rb, ppm	Sr, ppm	Y, ppm	Zr, ppm	Nb, ppm	Ba, ppm	La, ppm	Ce, ppm	Pr, ppm	Nd, ppm	Eu, ppm	Sm, ppm	Gd, ppm	Dy, ppm	Ho, ppm	Er, ppm	Yb, ppm	Lu, ppm	Hf, ppm	Ta, ppm	Pb, ppm	Th, ppm	U, ppm
Academician Ridge																													
	VER98/1/3	208	1	11	167	56	17	257	120	9.4	2.3	643	119	220	23	78	3.41	16	19	18	3.5	10	8.3	1.3	0.40	0.18	13	2.8	55
	VER98/1/3	316	1	29	84	44	13	94	45	6.5	1.9	179	48	118	12	37	1.80	8.7	8.8	8.4	1.5	4.6	4.4	0.65	0.29	0.17	40	2.1	260
	VER98/1/3	416	2	14	54	34	20	118	37	13	2.4	210	40	96	8.6	30	1.34	5.8	6.8	5.4	1.2	3.5	2.9	0.45	0.38	0.18	6.6	2.9	2.8
	VER98/1/3	638	2	16	120	77	11	100	53	7.8	2.2	234	45	76	8.7	29	1.41	6.4	7.8	8.1	1.6	5.0	4.1	0.71	0.33	0.17	7.1	2.0	14
	VER98/1/3	705	1	40	48	46	21	106	9.2	11	2.6	330	13	23	2.8	10	0.42	1.9	1.9	1.4	0.29	0.85	0.76	0.12	0.32	0.17	6.1	3.5	10
	VER98/1/3	723	1	133	55	55	14	82	7.9	10	2.0	221	8.4	15	1.9	7.1	0.37	1.5	1.5	1.1	0.24	0.73	0.60	0.11	0.34	0.15	6.5	2.6	5.3
	VER98/1/3	728	1	34	48	35	12	67	7.4	7.8	1.5	174	7.3	13	1.7	6.3	0.27	1.3	1.3	0.97	0.21	0.65	0.52	0.09	0.23	0.11	4.5	2.1	5.2
	VER98/1/4	600	1	29	44	29	5.4	64	6.1	5.6	0.86	237	3.6	6.6	0.96	3.8	0.23	0.97	1.1	0.93	0.19	0.56	0.41	0.09	0.19	0.09	2.8	1.0	8.1
	VER98/1/14	630	1	33	44	53	11	57	10	8.5	1.6	162	11	17	2.1	8.1	0.42	1.9	2.2	1.5	0.34	1.0	0.85	0.15	0.31	0.17	5.3	2.1	2.0
	VER98/1/14	640	1	84	41	31	15	64	8.4	11	1.8	212	8.1	16	1.9	6.8	0.29	1.4	1.4	1.1	0.24	0.68	0.60	0.10	0.31	0.12	4.4	2.6	8.7
North Basin																													
	CON01-603-2	381	3	20	56	26	13	62	8.6	12	1.7	281	9.1	17	2.2	8.2	0.36	1.7	1.6	1.3	0.26	0.76	0.68	0.11	0.33	0.19	5.3	2.6	6.1
	CON01-603-2	500	2	55	73	37	17	79	11	16	2.4	379	11	18	2.5	9.6	0.39	1.9	1.9	1.4	0.29	0.86	0.76	0.12	0.44	0.26	6.8	3.1	7.9
South Basin																													
	CON01-604-2	180	3	65	19	56	22	78	8.8	20	3.5	281	9.4	20	2.6	10	0.57	2.3	2.3	1.6	0.32	0.95	0.87	0.14	0.67	0.36	6.8	3.1	0.82
	CON01-604-2	510	3	24	39	195	29	102	8.3	17	3.8	477	10	20	2.7	10	0.63	2.5	1.9	1.5	0.30	1.02	0.99	0.20	0.66	0.47	9.5	3.6	1.4
Min baikal				11	19	26	5.4	0	6.1	5.6	0.86	162	3.6	6.6	1.0	3.8	0.23	1.0	1.1	0.93	0.19	0.56	0.41	0.09	0.19	0.09	2.8	1.0	0.82
Max baikal				133	167	195	29	257	120	20	3.8	643	119	220	23	78	3.4	16	19	18	3.5	10	8.3	1.3	0.67	0.47	40	3.6	260
Cameroon			pure	1	14	7.1	0.42	7	0.72	8.5	2.1	20	1.6	3.0	0.38	1.4	0.09	0.30	0.25	0.18	0.03	0.08	0.06	0.01	0.20	0.13	0.80	0.26	0.08
EF baikal/ Cameroon				197	116	28	69	39	167	2	2	32	75	73	60	56	38	55	74	100	109	132	142	155	3	4	51	14	3092

Table 4 *Unit-cell parameters and Mn(Fe+Mn) ratios of vivianites from Lake Baikal*

Position core	Sample depth (cm)	*a* (Å)	*b* (Å)	*c* (Å)	_(°)	Vol. (Å³)	Mn/(Fe+Mn)
VER98-1-14	630	10.097(9)	13.505(7)	4.727(3)	104.66(6)	623.7(5)	0.26
VER98-1-14	640	10.116(9)	13.489(7)	4.724(3)	104.77(6)	623.2(6)	0.32
VER98-1-3	208	10.082(9)	13.461(7)	4.712(3)	104.61(7)	618.9(5)	0.16
VER98-1-3	638	10.117(7)	13.43(1)	4.714(4)	104.79(8)	619.2(6)	0.16
VER98-1-3	728	10.114(6)	13.453(7)	4.709(4)	104.77(6)	619.5(5)	0.28
CON01-603-2	500	10.109(7)	13.441(7)	4.713(3)	104.86(5)	618.9(4)	0.27
CON01-603-2	180	10.10(1)	13.46(1)	4.715(3)	104.66(8)	620.4(7)	0.20
	Catavi, Bolivia[a]	10.030	13.434	4.714	102.73	619.6	0.00

[a] Rodgers et al. (1993).

Table 5 *Selected electron-microprobe analyses of vivianite and santabarbaraite from Lake Baikal*

Piston core	VER 98-1-14	VER 98-1-14	VER 98-1-3	VER 98-1-3	VER 98-1-3	VER 98-1-3	CON01-603-2	CON01-604-2
Sample depth (cm)	630	640	208	208	638	728	500	180
Number of analyses	6	4	9	5[a]	3	2	5	2
SiO_2	0.12	0.13	0.04	0.23	0.72	0.16	0.04	0.96
Al_2O_3	0.03	0.03	0.03	1.91	0.29	0.04	0.01	0.41
P_2O_5	29.12	28.91	29.14	26.99	30.18	29.49	28.71	28.28
MgO	0.18	0.21	0.1	0	0.24	0.15	0.25	0.24
ZnO	0.71	0.62	0.64	0.66	0.64	0.79	0.71	0.58
FeO	30.79	28.07	34.93	34.29	30.72	31.63	31.63	31.97
MnO	10.89	12.79	6.46	0.27	6.96	11.55	8.91	8.11
H_2O[b]	29.54	29.32	29.56	-	29.1	29.92	29.13	28.69
Total	101.38	100.08	100.9	64.35	103.9	102.82	99.39	99.24
Cation numbers								
Si	0.01	0.1	tr.	0.02	0.07	0.01	tr.	0.08
Al	tr.	tr.	tr.	0.2	0.02	tr.	tr.	0.04
P	2	2	2	2	2	2	2	2
Mg	0.02	0.03	0.01	0	0.03	0.02	0.03	0.03
Zn	0.04	0.04	0.04	0.04	0.04	0.05	0.04	0.04
Mn	0.75	0.89	0.44	0.02	0.46	0.78	0.62	0.57

Analyst: J. Wautier. The cation numbers were calculated on the basis of 2 P per formula unit.
[a] Santabarbaraite sample.
[b] Calculated values assuming 8 H_2O in the structural formula of vivianite.

4. Results

4.1. Distribution of vivianite concretions in sediments

All of the studied cores feature numerous occurrences of tiny vivianite concretions. They were observed at different scales, from X-radiography to SEM (Fig. 3). On X-radiographs, the concretions occur as dispersed grains up to 5 mm in size, scattered millimeter-sized streaks or concentrated and aligned forming millimetric to centimetric layers (Fig. 3A).

The concretions appear along the whole length of each sedimentary record with no clear general relationship with lithology (Fig. 2). In diatom-rich intervals, the concretions are observed either in homogeneous sediment or in diffuse to faintly laminated sediments, whereas in clay-rich intervals, the concretions often underlie coarsely laminated sediments. There is no obvious relationship between the occurrence of the concretion-rich layers and sedimentary features related to bioturbation or tectonics. However, 42 of the 47 concretion-rich samples observed on X-radiographs for the Academician Ridge and Continent Ridge sites occur in diatom-rich intervals (and only the remaining 5 in clay-rich intervals). By contrast, in Posolsky Bank, most of the concretions are observed in clay-rich intervals (9 out of 16). If we take into account the timespans covered by the Continent and Posolsky piston cores, the number of concretions observed during the same time period is similar at both sites (on average 1 concretion each per 3-4 ky).

Within the framework of the EU-CONTINENT proposal (EVK2-CT-2000-0057), the sediments of Continent and Posolsky sites have been systematically sieved with a 10-cm sampling resolution. We observe at least 11 supplementary levels characterised by vivianite occurrence in the Posolsky core and at least 18 in the Continent core (Fig. 2). This observation confirms the peculiar distribution of the concretions at Posolsky site (60% in clay-rich samples) compared to the Academician Ridge and Continent Ridge sites (90% in diatomrich samples). In the Continent core, numerous concretions have been only detected by binocular observation at the base of a diatom-rich and highly bioturbated interval (CON01-603-2 at 619-709 cm, Fig. 2). By contrast, at the Vydrino Shoulder from the South basin (core CON01-605-3, Fig. 1), no concretions (at least in the >63-µm fraction) were detected.

Fig. 3. *Vivianite morphology at different scales. (A) X-radiograph photography—Distribution of concretions in sediment core: the concretions are concentrated at specific depths along the core, defining repeated laminations every few millimetres. Sample: Diatom-rich level from VER98-1-3, Academician Ridge. (B) Thin section image—Concretion showing a colour zonation from a blue central part to a yellow border. Sample: Short core from Posolsky site, CON01-427-8 (X. Boes, unpublished data). (C) SEM microphotography-Fine lamellar structure of a blue, fresh concretion. Sample: Diatom ooze from VER98-1-3, Academician Ridge, 705 cm. (D) Microprobe photography—Colour and structural zonation of one concretion: its center part displays a lighter and lamellar structure, its border is darker with no visible internal structure. Sample: Diatom ooze with clays from VER98-1-3, Academician Ridge, 208.5 cm.*
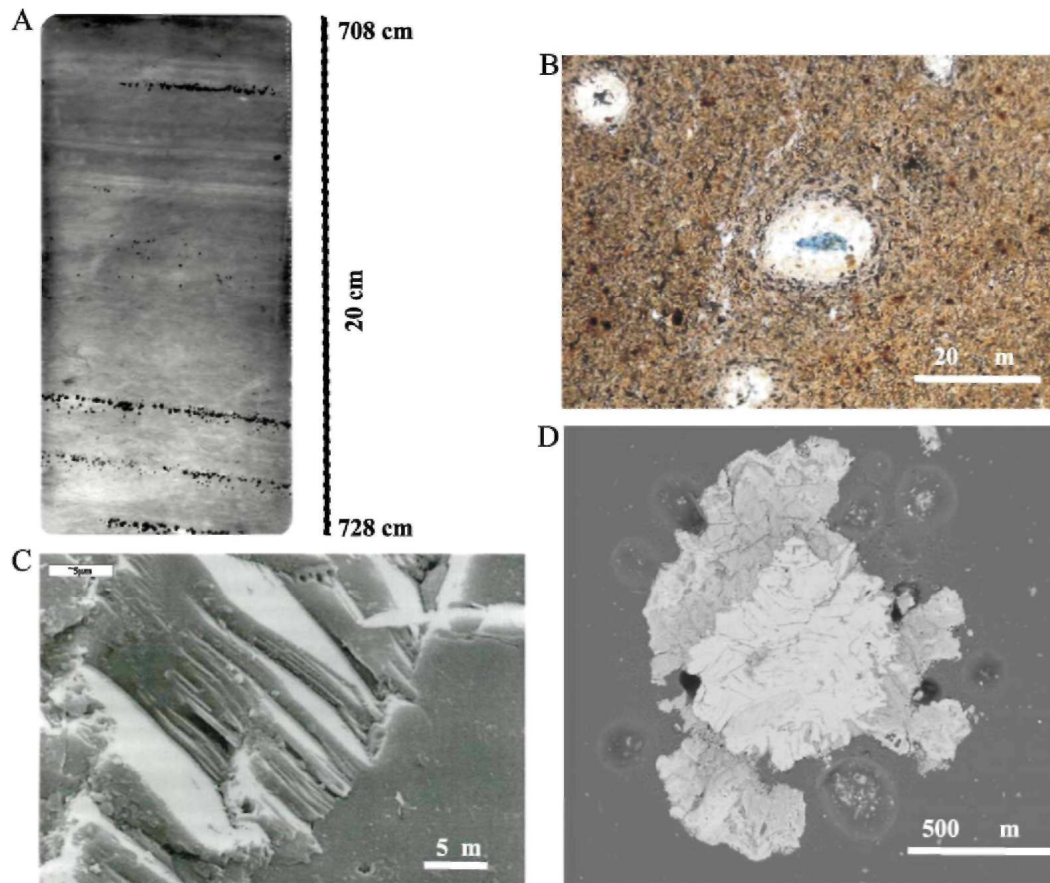
4.2. Geochemistry of bulk sediments

The geochemistry data of all the studied sediments samples are available upon request to the first author. Results are expressed as weight of % oxides. The major oxides Al_2O_3, TiO_2, MgO, CaO, Na_2O, K_2O evolve in parallel and in an opposite way to total SiO_2. This mainly reflects the dilution of detrital clayey intervals by biogenic SiO_2 derived principally from diatom frustules (other constituents include sponge spicules and chrsyphyte scales and cysts). The calculation of the excess SiO_2 gives a good estimation of the biogenic silica, in accordance with the diatom abundance curves (data for Academician Ridge from Fagel et al., 2003; data for Continent and Posolsky cores from Morley and Rioual et al., unpublished data).

For each core, the chemical composition of major oxides within the P-enriched layers is reported in Table 2. P_2O_5

and MnO exhibit peculiar distribution curves with coincident peaks in both profiles. Nine peaks are identified in core CON01-604, seven in VER98-1-3, four in core VER98-1-14, and three in core CON01-603-2 (Table 2). In addition, Fe_2O_3 displays systematically high content at the same level but with a less pronounced enrichment relative to the background signal. Maxima of P_2O_5 and MnO reach 3.13% and 0.79%, respectively, and in those layers, phosphorus is characterised by enrichment factors of up to 11 times with respect to the mean "background" sediment composition (Fig. 4A). Note that Patrikeeva (1963) reported P_2O_5 enrichments up to 100 times in Lake Baikal vivianites compared to the surrounding bulk sediments. The manganese is enriched up to six times (Fig. 4A). The Fe content (max. 12% of Fe_2O_3, not shown on figure) reaches up to 1.6 times the mean sediment content. For comparison, previous bulk geochemical analyses of Lake Baikal sediments from three sub-basins recorded similar maxima values of 3% for P_2O_5, 1.3% for MnO, and 12% for Fe_2O_3 (e.g., Romashkin et al., 1993). There is no obvious relationship between the abundance of biogenic silica (estimated by excess SiO_2) and the enrichment in phosphorus (Fig. 4B).

Fig. 4. *Bulk geochemical signature of sediments from cores CON01-604 (Posolsky Bank), CON01-603 (Continent Ridge), VER98-1-3 and VER98-1-14 (Academician Ridge). Data from ICP-AES (MRAC, Belgium). (A) MnO vs. P_2O_5 (wt.%) diagram; P-rich samples compared with the background samples. (B) $SiO_{2\ xs}$ vs. P_2O_5 (wt.%) diagram. The excess of silica is an estimation of biogenic silica and consequently reflects the diatom abundance in the sediments. It is defined as followed: $SiO_{2\ xs}=SiO_{2\ total}-SiO_{2\ detrital}$; SiO_2 detrital is estimated from measured Al_2O_3 and reference Si/Al crustal ratio (Taylor and McLennan, 1985). The diagram emphasizes the range of biogenic silica content of the P-rich samples. The P-rich samples do not coincide with the richest diatom-samples in any of the core sediment samples.*
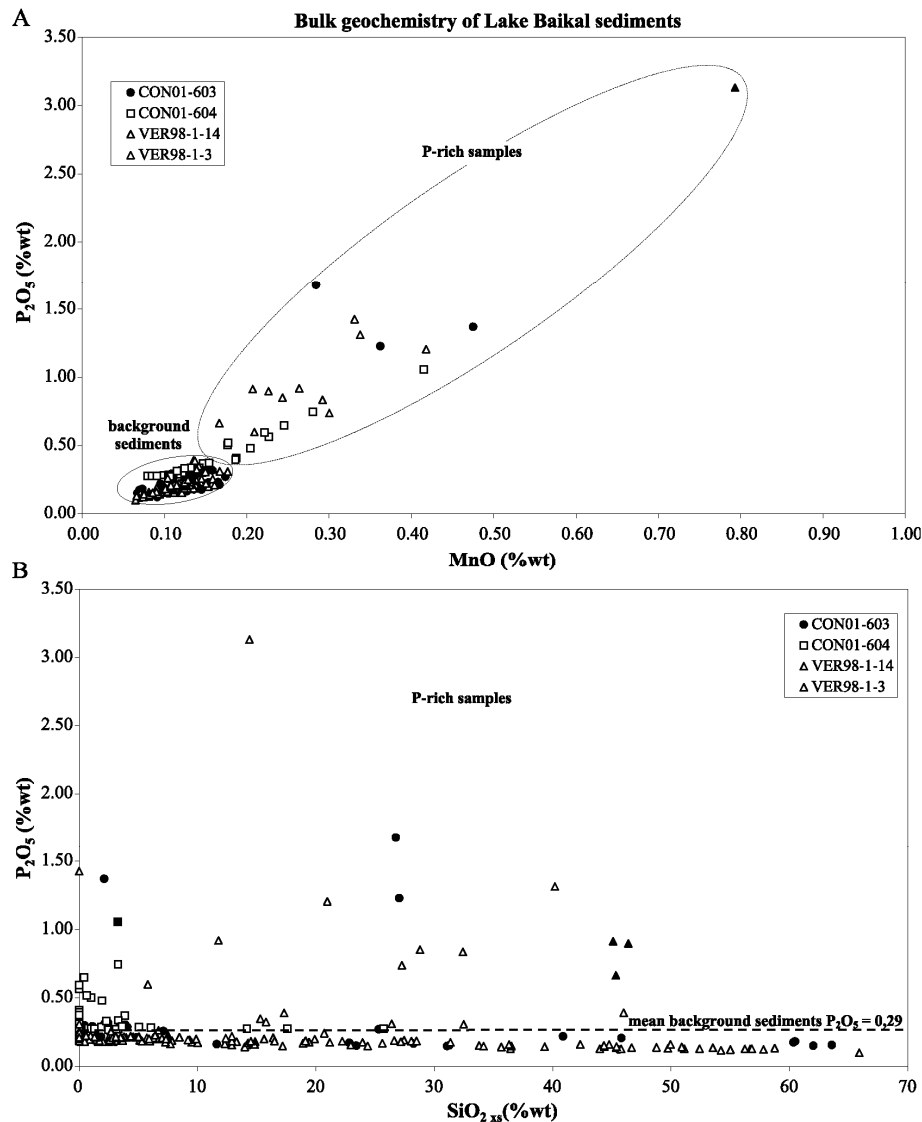
4.3. Mineralogy and geochemistry of vivianite concretions

4.3.1. Mineralogy of the concretions

Examination of the concretions in thin sections indicates the occurrence of two different phases. The first one exhibits a blue colour, and is characterised by a perfect cleavage, visible on the SEM photographs (Fig. 3C). X-ray powder diffraction indicates that this phase corresponds to vivianite, $Fe_3^{2+}(PO_4)_2.8H_2O$. The unit-cell parameters of selected vivianite samples are shown in Table 4, whereas their microprobe analyses are shown in Table 5.

Some concretions display a yellow to brownish rim, surrounding the blue center of vivianite. This mineral zonation is noticeably visible on the back-scattered electron microscope photographs, as shown in Fig. 3D. The yellowish mineral, which does not show any cleavage, is amorphous (X-ray powder diffraction). This indicates that it probably corresponds to santabarbaraite, $Fe_3^{3+}(PO_4)_2(OH)_3.5H_2O$, a recently described mineral species which is an amorphous alteration product of vivianite (Pratesi et al., 2003). The electron-microprobe analyses (Table 5) confirm this identification, as well as the infrared spectrum shown in Fig. 5. Compared to the spectrum of vivianite, the infrared spectrum of santabarbaraite shows broad absorption bands (Fig. 5), thus confirming its amorphous nature. This broadness is clearly evidenced in the 1100-400-cm^{-1} regions, which corresponds to the PO_4 stretching and bending vibration modes (Farmer, 1974).

Fig. 5. *Infrared spectra of vivianite (VER 98-1-3, 728 cm) and santabarbaraite (VER 98-1-3, 208.5 cm) from Lake Baikal.*
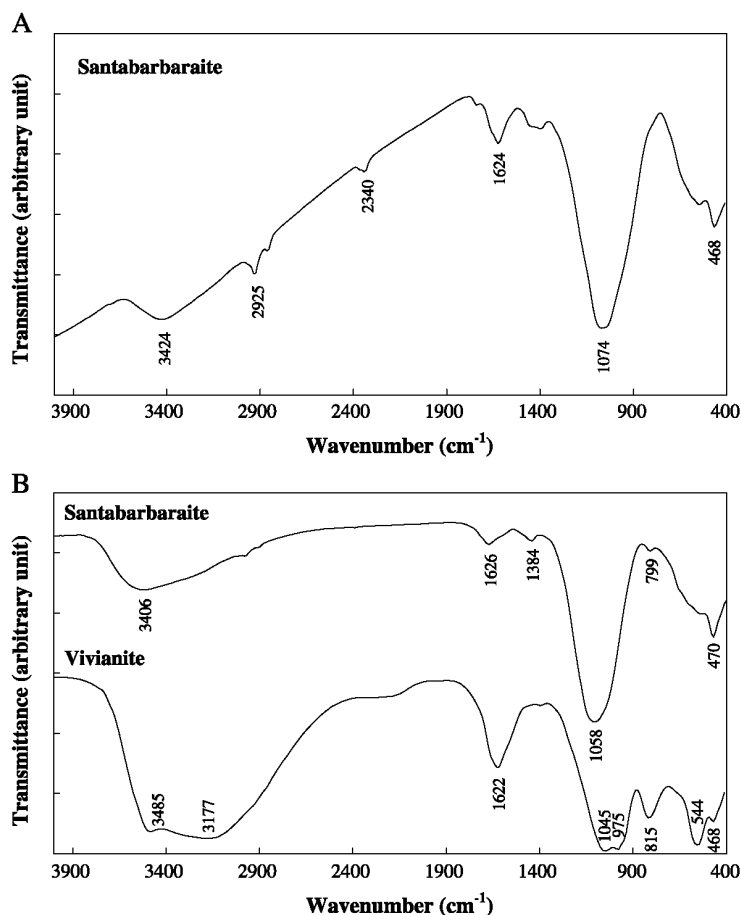
4.3.2. Geochemistry of the concretions

The ICP-AES analyses confirm the wide range of variations in the Mn content of the Lake Baikal concretions (Table 3a): elemental Mn varies between 1.4% and 7.6%. By contrast, the P content varies only by a factor of 2 (from 7.3% to 15%). Consequently, the P/Mn (wt/wt) ratio fluctuates between 1 and 10. There is no significant correlation between Mn and any other trace elements analysed (Table 3b).

However, the geochemistries of concretions from Lake Baikal sediments are significantly different than the signature of a pure vivianite from Cameroon (Tables 3a, 3b). The shale-normalised REE pattern of Lake Baikal

concretions is flat, and the REE (and especially the HREE) are 50 to 150 times more concentrated than in Cameroon vivianite (Fig. 6). This REE-enrichment reflects a contamination by a detrital component of the Lake Baikal concretions. Samples from core VER98-1-3 are the most scattered: the sample collected at 208 cm is the most enriched in REE, with values up to five times higher than the shale reference (Taylor and McLennan, 1985). Samples from core VER98-1-14 are usually depleted relative to shale, and the sample taken from 600 cm in this core is the closest to the Cameroon vivianite reference. The samples from Posolsky and Continent sites display intermediate values between the shale and the vivianite reference. Among the other trace elements, Co, Cu, and especially U are strongly enriched in the Lake Baikal concretions with respect to the Cameroon vivianite (enrichment factor=197, 116, and 3092 times, respectively—Table 5). We noticed that the samples richest in U also contain the highest REE content (VER98-1-3 208 and 316 cm). They correspond to secondarily altered Mn-poor samples, characterised by a yellowish border; these samples systematically display the highest REE values (Fig. 6).

Fig. 6. Shales-normalised geochemical signature of isolated vivianite concretions from Lake Baikal sediment cores. Analyses by ICP-AES (Mn content, data from Table 3a) or ICP-MS (trace elements, data from Table 3b). The composition of the vivianite from Anlua, Cameroon (MRAC collection) is plotted for comparison. The Lake Baikal concretions are usually enriched with respect to the Cameroun vivianite. See text for discussion.
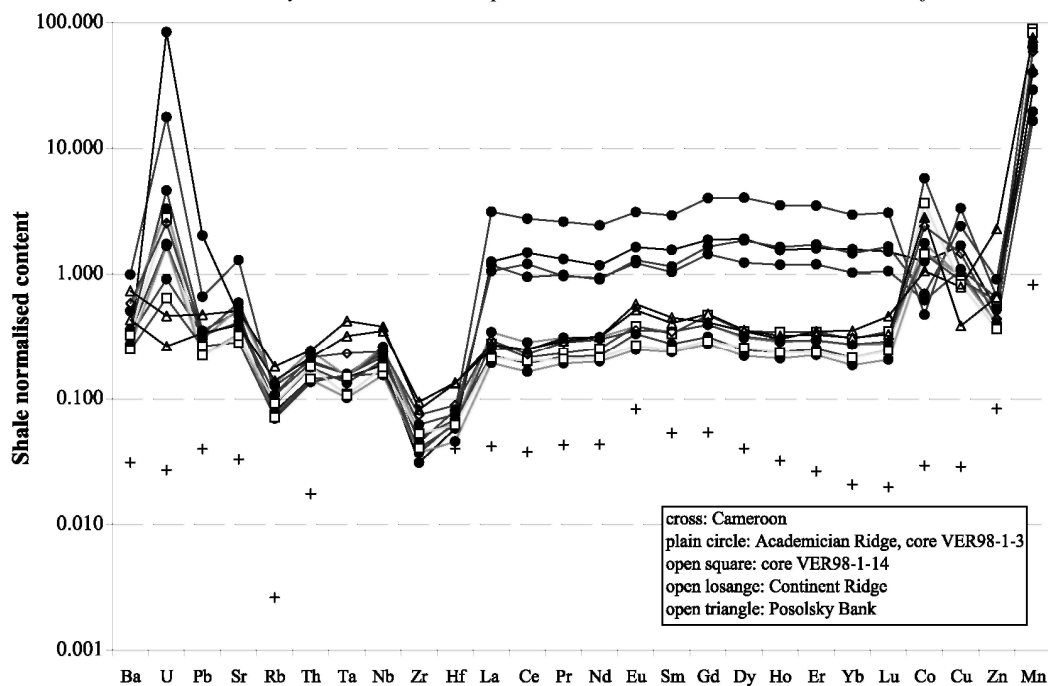
5. Discussion

5.1. Origin of vivianite in Lake Baikal sediments

In lakes, the formation of iron phosphates, and vivianite in particular, could be either authigenic or diagenetic. In the first case, vivianite is a primary mineral formed by authigenesis in the water column (see, for example, Dean, 2002). The diagenetic model has been proposed by Einsele (1938) and Mortimer (1941). When the hypolimion is well aerated by water overturn, most of the iron is oxidized to the ferric form. The ferric hydroxides precipitated from the overlying water are stabilised in the sediments by their subsequent interaction with P from porewaters. The ferrosoferric hydroxyphosphates are stable at the water/sediment interface. Beneath this level, the more reducing conditions cause the complexes to dissolve and form vivianite by direct precipitation from porewaters (Nriagu and Dell, 1974).

In Lake Baikal, the entire water column is constantly enriched with oxygen due to low biological productivity and regular deep water renewal of oxygen-rich surface waters. As a result, the reduced iron does not exist in the water and vivianite cannot precipitate directly from the water column. The diagenetic model of vivianite formation is a better candidate for the lake. The oxic stage of diagenesis is widely represented in Lake Baikal sediments, especially in the areas of low sedimentation rates, where thick oxidized layers are formed at the sediment/water interface. These layers may be related to the vivianite formation.

5.2. Temporal and spatial distribution of vivianite in Lake Baikal sediments

The temporal and spatial distribution of vivianite in Lake Baikal sediments is unusual, and below we make an attempt to analyse which factors (i.e., biological productivity, sedimentation rate, porewater chemistry and lithology) could favour the vivianite formation and preservation.

5.2.1. Influence of biological productivity

There is no correlation between excess silica and P content in vivianite concretions (Fig. 4B), thus no relationship of concretions genesis with diatom paleoproductivity of the lake. Moreover, the south basin of Lake Baikal is characterised nowadays, by higher bioproductivity compared to north and central basin of the lake. The content of sedimentary organic carbon (Corg.) is also (on average) the highest in the southern basin, i.e., 2.2% $C_{org.}$, whereas values for $C_{org.}$ in the surface sediments of the north basin and Academician Ridge are only 1.8% and 1.3% respectively (Granina et al., 2000). The estimates of biogeochemical mass balance show that very little, if any, biogenic P is needed to support P burial in Lake Baikal sediments; the content of P in surface sediments is almost the same in all basins (Callender and Granina, 1997a). This suggests that bioproductivity does not affect significantly the vivianite formation, and the same might have been the case in the past.

5.2.2. Influence of sedimentation rates

The sedimentation rates for both the Academician (1.5 cm/ky reported in Vologina et al., 2003; 2.6 cm/ ky in Colman et al., 1993; around 4 cm/ky in Fagel et al., 2003) and Continent Ridges (around 6 cm/ky, Demory et al., 2005-this issue) are the lowest of the lake. Occurrence of vivianites in these sites is in agreement with the statement that formation of vivianite is related to substantial accumulations of Fe and Mn hydroxides within oxidized sedimentary layers and crusts (Knyazeva, 1954; Deike et al., 1997). In the north basin and on the Academician Ridge formation of sedimentary layers, highly enriched in Fe and Mn hydroxides are favoured by low, constant sedimentation rates, low content of sedimentary $C_{org.}$, high oxygen concentrations in the near-bottom water, and deep oxygen penetration into the sediments (Granina et al., 2000; Müller et al., 2002). Slow dissolution and re-precipitation of these layers takes 2 to 8 ky and thus allows vertical movement of the layers to keep a constant position with respect to the sediment surface and prevents their burial as long as the sedimentation regime is constant (Granina et al., 2004). Changes in the sedimentation regime could produce buried Fe/Mn layers, which might serve as proxy indicators. Deike et al. (1997) analysed such older layers with ages up to 65 ky, and found evidence for their gradual conversion into vivianite and siliceous mineral phases. These transformations are supported by high Fe, Mn and P concentrations of porewater, which are maximal in the vicinity of both recent and buried Fe/Mn layers (Granina, 1991; Müller et al., 2002).

The absence of any vivianite concretions in the Vydrino Shoulder core (a site characterised by faster sedimentation rates) agrees with the idea that vivianites in the Academician Ridge and the Continent Ridge sediments are related to large accumulations of sedimentary Fe and Mn hydroxides, typical of areas with slow sedimentation. However, vivianite displaying similar morphology and chemistry parameters was also found in the Posolsky core, i.e., a site characterised by the a sedimentation rate of 11.7 cm/ky (Demory et al., same issue), which is at least twice as fast than in the other vivianite-rich sites investigated in this study. Therefore, the occurrence of vivianite in the Posolsky core weakens the hypothesis of a control of the vivianite formation only by sedimentation rate. Moreover, vivianites are widely spread in the southern basin (see Fig. 1) which in general are characterised by higher sedimentation rates (about 6.5 cm/ky on average reported by Edgington et al., 1991) compared to the central and the northern basins. Such discrepancies could underline the influence of porewater chemistry in the different sub-basins of Lake Baikal.

5.2.3. Influence of porewater chemistry

Calculations show that vivianite production is most likely to be formed within the sedimentary interval just below the thick oxidized layers. This is confirmed by the co-existence of vivianite concretions and Fe/Mn crusts in the Academician Ridge sediments (Deike et al., 1997; Grachev et al., 1997). Reductive dissolution of the lower part of thick Fe/Mn layers supplies up to 10^{-6} mol 1^{-1} of porewater Fe and P, to 7×10^{-5} mol 1^{-1} of porewater Mn (Granina, 1991; Müller et al., 2002), which are sufficient to provide diagenetic formation of vivianites just below the oxidized layers.

The saturation index of porewater with respect to vivianite is much lower for the Academician Ridge area compared to Southern Lake Baikal. Extremely high porewater PO_4^{3-} and Fe concentrations [up to 9.4 and 5.4 mg 1^{-1}, respectively (Granina and Callender, 2001)] were found at sites located opposite to the Selenga Delta, close to the western shore near the Buguldeika River mouth (see "vivianite area" in Fig. 1). In these sediments, the highest supersaturation of the porewater with respect to vivianite was recorded from 2-5 to 20-30 cm below the sediment/ water interface (Granina and Callender, 2001). Within this sedimentary interval, the porewater is most enriched in Fe and D due to intensive microbiological processes and reductive dissolution of the lower part of the oxidized zone. Moreover, the highest microbial activity was recorded in the sediments directly affected by the Selenga

inputs (Mladova, 1971). The question arises as to what the reason may be for vivianite formation in this region of relatively high sedimentation rates that in turn prevent the development of a thick oxidized layer and large accumulations of Fe and Mn. The simplest idea might be the influence of the Selenga waters. The Selenga River is the main contributor of P (about 82% of riverine suspended particulate P inputs to Lake Baikal; (Callender and Granina, 1997a)] and Fe (Callender and Granina, 1997b). These inputs could explain the highest contents of porewater P recorded in the sediments opposite the Selenga Delta (Granina and Callender, 2001) and in the area of Posolsky Bank (Patrikeeva, 1963).

The source of P and Fe porewater for abundant vivianite genesis in South Baikal ("vivianite area" on Fig. 1) is still not assured. One of the possible scenarios (Granin and Granina, 2002) could be related to the methane gas hydrates recently discovered in South Baikal sediments (e.g., Vanneste et al., 2001; Van Rensberg et al., 2002), and in particular in the region of the Posolsky Bank (Klerkx et al., 2003). We know from historical literature that the abundant death of fishes used to happen occasionally in the lake. According to Granin and Granina (2002), it may be related to intensive methane escapes caused by decomposition of gas hydrates in the past. Abundant "burial" of dead fish could in turn lead to diagenetic formation of vivianites due to the phosphorus release from these decaying fishes accumulated in the sediments (Granin and Granina, 2002). Zhmodik et al. (2002) share the same idea about the possible phosphorus sources for phosphorite's formation in Academician Ridge sediments. If this is confirmed, localized vivianite accumulations could serve as indirect evidence of ancient methane seepages in Lake Baikal. All these speculations need more studies to be confirmed or rejected.

5.2.4. Influence of lithology

In the Posolsky core, vivianite mainly occurs in the clay-rich intervals (60%) and the concretions often underlie coarsely laminated sediments. This would suggest that vivianite formation is related to the input of suspended sediments transported by the Selenga waters. However, as shown in Fig. 2, the sediments in South Baikal are different from those in North Baikal and the Academician Ridge, due mainly to the presence of numerous turbidites, the admixture of coarser sediments, and substantially less diatom-rich material (e.g., Vologina et al., 2003; Charlet et al., 2005-this issue). Thus, the accumulation of vivianites in clay-rich intervals in Posolsky core, in contrast to diatom-rich intervals in sediments from Academician and Continent Ridges, may just result from a specific composition of sedimentary material at that site. Assemblages of organic matter (Knyazeva, 1954) and/or frustules of diatoms within vivianites or phosphorites described by Deike et al. (1997) and Zhmodik et al. (2001, 2002) may initiate concentration of vivianites. Thus, the predominance of one or another within sediments could influence formation of vivianite concretions mainly in clay-rich intervals (Posolsky site) or in diatom-reach intervals (Academician Ridge and Continent Ridge sites).

5.3. Chemical composition of vivianite

Vivianites from Lake Baikal are characterised by a peculiar chemical signature. Our vivianites are enriched in MnO (up to 0.80% of MnO in bulk sediment—Table 2) with respect to previous measurements on Lake Baikal vivianites (mean MnO=0.16% in Knyazeva, 1954). However, it is not easy to compare our analyses with literature data since previously reported chemical compositions were usually not obtained from a pure vivianite but a mixture of vivianite and alteration products (e.g., vivianite and ludlamite in Great American Lakes—Nriagu and Dell, 1974). We suspect the low Mn content reported by Knyazeva (1954) may be due to Mn loss during vivianite alteration.

When exposed to the air, vivianite rapidly transforms to santabarbaraite, a more oxidized phosphate mineral (Pratesi et al., 2003). This transformation explains the occurrence of an oxidized santabarbaraite rim, which surrounds a center of vivianite in some samples. Microprobe analyses (Table 4) indicate also that santabarbaraite is significantly depleted in Mn, compared to vivianite. The relationship between Mn content and level of the vivianite alteration is in agreement with Zhmodik et al. (2001, 2002) who analysed phosphorites crusts from an Academician Ridge core (53°E, 108°N, 277 m of water depth). These crusts are similar in composition to vivianites but are made of an amorphous phase: MnO content is quite low, ranging between 0.12 and 0.7 (Zhmodik et al., 2001), i.e., within a similar range as our altered vivianite concretions. Their amorphous structure and composition are similar to those of the buried Fe-crusts depleted in Mn found in the same area by Deike et al. (1997).

Lake Baikal vivianites display a pronounced enrichment in MnO (Fig. 7) in comparison to pure vivianite that, according to Rodgers et al. (1993), does not contain significant amounts of Mn. We estimate the maximum enrichment of Baikal vivianites, i.e., EFBaikal, by the ratio between the maximum measured Mn content in our samples and Mn data from the literature. For example, geochemical analyses on Bolivian vivianites gave 0.01% to 0.04% MnO: EFBaikal ranges between 245 and 981. In Greece, Stamatakis and Koukouzas (2001) have emphasised the genetic relationship of FeO and MnO in phosphate phases found in lacustrine clayey diatomites. They noted that the vivianite is the richest phosphate in MnO, with up to 2.5% (wt.) within the nodule. Vivianite from Greece appears as anhedral masses, including diatom frustules, clays and detrital feldspars and quartz. In

Lake Baikal, Mn/P ratios of vivianites are clustered within the same core but differ from one site to another (Deike et al., 1997). This is related to porewater Mn content varying significantly from site to site due to different intensities of diagenetic remobilization of sedimentary manganese (Granina, 1991). A relationship between Mn and (Fe+Mg+Zn) per formula unit (p.f.u.) for selected vivianite samples from Cameroon and Greece (Stamatakis and Koukouzas, 2001), Bolivia (Rodgers et al., 1993) and Lake Baikal is shown in Fig. 8. This good correlation, with a slope close to -1.00, confirms a substitution mechanism $Mn^{2+} \rightarrow (Fe^{2+}, Mg^{2+}, Zn^{2+})$, responsible for the insertion of Mn into the vivianite structure. It is also important to note the very low Mn content of santabarbaraite, compared to that of vivianite (Fig. 8). Because vivianite samples from Lake Baikal show variable Mn contents, we attempted to correlate the unit-cell parameters of vivianite with the Mn/(Fe+Mn) ratio calculated from the electron-microprobe analyses (Table 5). However, no satisfactory correlations were observed. This may be explained by the heterogeneity of vivianite grains, which prevents comparison of unit-cell parameters from single-point electronmicroprobe analyses with parameters from analyses of a mixture of several whole vivianite grains.

Vivianite also displays a marked enrichment in REE, U, Co and Cu. U enrichment (up to 90 ppm) has been reported in phosphate crusts (called "phosphorites", with 21.8 wt.% P_2O_5; <0.7% MnO) evidenced in diatom-rich sediments from the Academician Ridge (Zhmodik et al., 2001). These crusts are compositionally similar to vivianite, but are amorphous by X-ray diffraction and exhibit different Ca-, P-, and Fe-contents. One possible mechanism of P concentration could be a post-sedimentary diage-netic redistribution (Zhmodrk et al., 2001). The enrichment of both REE and U could reflect an adsorption process of large ions of lithophile trace elements (and trace metals) onto P-rich phases during diagenetic processes.

Fig. 7. *Evolution of Mn content (normalised wt.%) measured on isolated concretions from Lake Baikal cores, i.e., from South to North: CON01-604 (Posolsky Bank), VER98-1-14 (Academician Ridge), VER98-1-3 (Academician Ridge) and CON01-603 (Continent Ridge). Analyses by microprobe (UCL, Belgium) or ICP-AES (MRAC, Belgium). Data from Table 3a. The Mn content is calculated taking into account only the measured % of FeO, MnO and, P_2O_5 (the sum being at 100%). For Lake Baikal data, each core is identified by the same symbol. Within the same core, the label indicates the depth of the sample. Data from literature are also reported: for Academician Ridge and North Baikal, from (Deike et al., 1997); Bolivia from (Rodgers et al., 1993); Greece from (Stamatakis and Koukouzas, 2001). The composition of vivianite from Cameroon (MRAC collection) has been determined during the same analytical run as the Lake Baikal vivianite samples. In Lake Baikal, the Mn content is highly variable throughout a core and from one site to another. The concretions from the Academician Ridge display the highest measured Mn content (up to 19% Mn). The Lake Baikal samples (except one reported by Deike et al., 1997) are enriched in Mn with respect to worldwide vivianites. See text for explanation.*
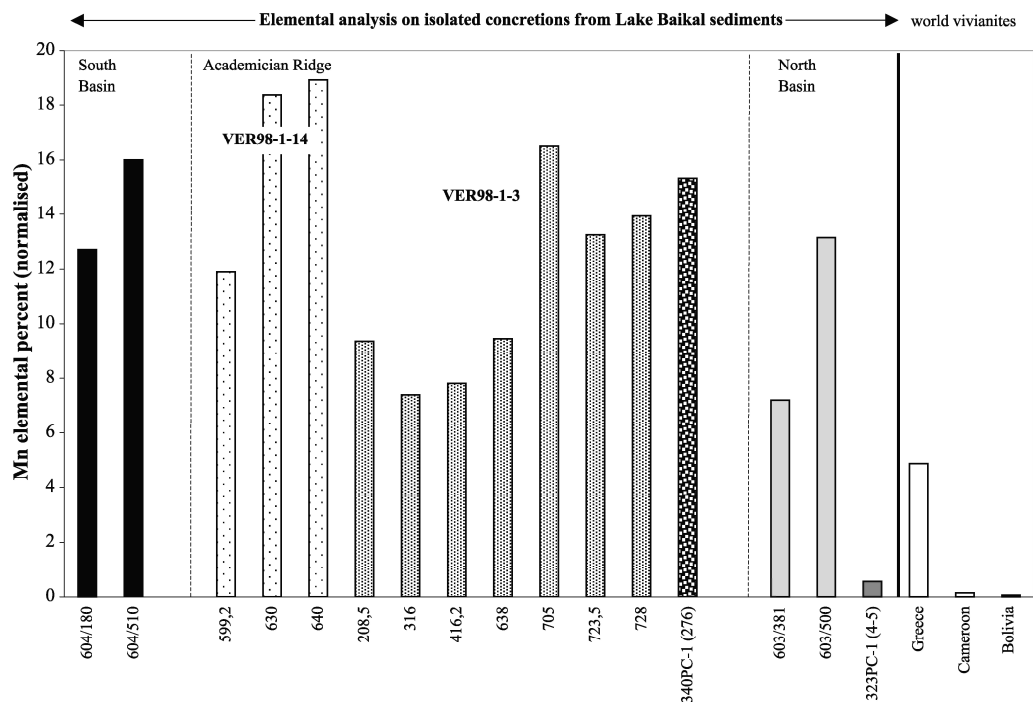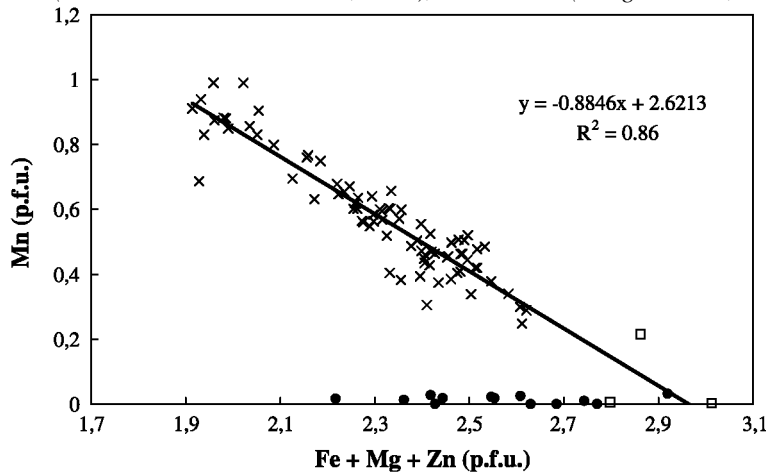
Fig. 8. *Relation between Mn and (Fe^{2+}+Mg+Zn) per formula unit, for selected vivianite and santabarbaraite samples. × : vivianite from Lake Baikal, ●: santabarbaraite from Lake Baikal, □: vivianites from Cameroon, Greece (Stamatakis and Koukouzas, 2001), and Bolivia (Rodgers et al., 1993).*

6. Conclusion

(1) In Lake Baikal, vivianites are diagenetic in origin. They could not be applied as a proxy for paleoproductivity The distribution of vivianites within sediments is not controlled by the lithology and there is no systematic vivianite accumulation in the interglacial diatom-rich intervals. We thus conclude that vivianites are diagenetic in origin. Sedimentation rates and porewater chemistry are major factors controlling the formation of vivianites in Lake Baikal as long as P and Fe are supplied in sufficient amount.

(2) Lake Baikal vivianites are Mn-rich compared to worldwide vivianites. Mn enrichment probably reflects diagenetic redistribution from precursor Fe and Mn hydroxides.

(3) In North Baikal and the Academician Ridge areas, internal sedimentary cycling during periods of slow sedimentation provides a constant source of abundant porewater P and Fe by the slow dissolution of large amounts of autochthonous Fe and Mn hydroxides accumulated in recent and/or buried Fe/Mn layers. Changes in sedimentation regime could gradually transform buried oxidized Fe/Mn layers into vivianites. The numerous layers bearing tiny vivianite concretions in North Baikal and Academician Ridge sediments may represent traces of former oxidized Fe/Mn layers and thus serve as paleomarkers of low and changing sedimentation regime.

(4) By contrast, in the Posolsky core sampled close to the Selenga Delta, a site of relatively fast sedimentation, vivianites may be related to the composition of the Selenga River inputs. They reflect an early diagenetic signal, although the source of porewater P and Fe for vivianites formation is not clear yet. In South Baikal, and in particular at the Posolsky site, vivianite accumulation could reflect past intensive methane escape from the sediments but this is yet to be confirmed by further studies.

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