

Carbon and Oxygen Isotopic Compositions of Carbonates from Precambrian Apatite-Bearing Carbonate Rocks of the Aldan Shield

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Abstract—Geostructural setting, as well as mineral and isotopic compositions, of separate apatite deposits and occurrences in the Aldan Shield composed of Precambrian metasedimentary apatite-carbonate rocks are considered. In terms of carbon and oxygen isotopic compositions, they differ from other carbonate rocks of the Aldan Shield, including carbonatites and Ca-Mg metasomatites, and resemble Phanerozoic and Precambrian metasedimentary carbonates. They formed in oxidizing conditions. The contribution of evaporite processes at different stages of their formation is supported by the carbonate enrichment in ¹³C and the presence of sulfates. It was established that apatite-carbonate rocks represent the product of complex alternation of sedimentary processes at different values of salinity in the basins occasionally characterized by the decomposition of older sediments under subaerial conditions.

INTRODUCTION

Metasedimentary carbonate rocks are typical of the Precambrian metamorphic complexes, although their share in the Precambrian sequence is insignificant (no more than a few percents, according to different sources). They are commonly used as markers of important geohistorical boundaries related to changes in the dynamic equilibrium of paleocean with sediments and atmosphere, variations of oxygen and carbon dioxide concentrations, proportions of Ca and Mg, and so on. The economic-grade mineralization is spatially (and sometimes genetically) associated with carbonate rocks. In particular, stratiform lead-zinc deposits in the Canadian Shield are confined to the protoevaporite carbonate sequence of the Grenville Group (Whelan *et al.*, 1990); magnesite deposits of the Sino-Korean Shield associate with dolomites (So Bar Son *et al.*, 1989); lazurite, spinel, and ruby deposits of the Pamirs are localized among magnesites and dolomites of the Goran Formation (Kiselev, 1977); and several nonmetallic deposits in the Baikal region are related to the carbonate sedimentation (Vishnyakov *et al.*, 1981).

Apatite mineralization associated with carbonate rocks is known in nearly all Precambrian shields, e.g., Obrub and Slyudyanka deposits in the Slyudyanka Group of the Baikal region (Yudin and Arsen'ev, 1970), Sino-Korean Shield (Marakushev, 1968), deposits of the Sa Song group in the North Chinese platform (Sang and You, 1988), deposits in the Grenville Group of the Canadian Shield (Currie, 1951), Karaiba Complex of Brasilia (Signinofi *et al.*, 1980), Oasis marble of Australia (McNaughton and Wilson, 1983), and others. The

Seligdar apatite deposit and several similar occurrences (Mustolaakh, Niryandzha, Birikeen and others), which were discovered and explored in the Aldan Shield, are confined to carbonate and calc-silicate rocks of the Fedorov Formation or its coeval counterparts (Vinogradov *et al.*, 1975; Bulakh *et al.*, 1990; Guliy, 1995). Based on the development of apatite mineralization in carbonate rocks, some geologists suggest genetic relationship between carbonate and phosphate sedimentation (Yudin, 1981). However, detailed study of the geological setting and composition of all carbonate rock types in the Aldan Shield revealed their inhomogeneous nature, and only some of them have the economic-grade phosphorus content. The P-rich carbonate rocks of the Aldan Shield differ from other carbonates in high Fe³⁺/Fe⁺ ratio, presence of specific mineral assemblages, including sulfates, which are scarce or alien for carbonate rocks of other types. This indicates specific conditions of their formation (Guliy, 1994).

Previous isotopic investigations of carbonates of all genetic types from the Aldan Shield (Guliy, 1994, 1995) showed that apatite-carbonate rocks differ from other carbonate rocks, particularly carbonatites and Ca-Mg metasomatites, in carbon and oxygen isotopic compositions (Kuleshov, 1986). Apatite-carbonate rocks are also heterogeneous and composed of several types. Their mineral composition and abundance are variable in different sectors. This paper presents results of the systematic study of carbon and oxygen isotopic compositions in carbonates from various types of apatite-carbonate rocks and ores in the majority of apatite

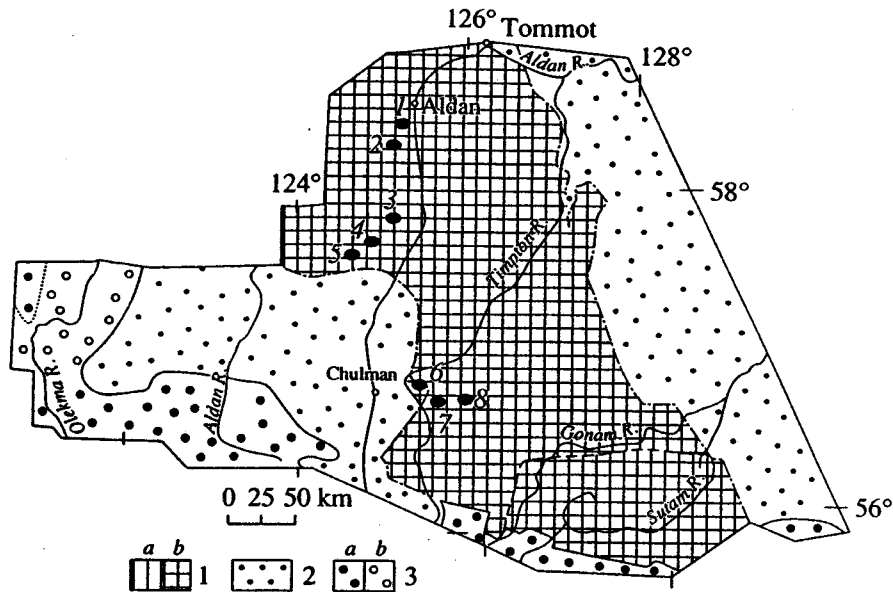


Fig. 1. Location scheme of apatite deposits of the Aldan shield. (1) Seligdar, (2) Niryandzha, (3) Dorozhnyi; (4) Mustolaakh; (5) Tagnarar; (6) Levyi Burnyi, (7) Birikeen, (8) Chukurdun. (1) high-grade metamorphism: (a) intermediate between garnet-cordierite-biotite and garnet-cordierite-hypersthene facies, (b) hypersthene-sillimanite facies; (2) transitional metamorphic facies; (3) relatively low-grade metamorphism: (a) granulite facies, (b) amphibolite facies (Kitsul *et al.*, 1979).

deposits and occurrences of the Aldan Shield and draws conclusions on possible conditions of their formation.

GEOSTRUCTURAL SETTING AND CHEMICAL COMPOSITION OF APATITE-CARBONATE ROCKS IN THE ALDAN SHIELD

Geostructural Position of Apatite-Carbonate Rocks

Apatite-carbonate rocks of the Aldan Shield occur in the Seligdar-type apatite deposits and often associate with apatite-bearing diopside and chlorite rocks that are typical ores of the Khani-type deposits (Guliy, 1989). We studied apatite-carbonate rocks in the Seligdar, Niryandzha, Mustolaakh, Tagnarar, Trubka, Dorozhnyi, Ust-Chul'man, Birikeen, Chukurdan, Levyi Burnyi, and Khayumkan areas (Fig. 1).

The apatite mineralization is largest in the Seligdar deposit. The overturned synclinal fold recognized in this area (Bulakh, Zolotarev, 1983) is composed of a conformable intercalation of gneisses and crystalline schists with calciphyres, marbles, diopsides, and apatite-carbonate rocks of the Fedorov Formation. Individual interbeds range from a few centimeters to several tens of meters in thickness. The number and thickness of beds of the apatite-carbonate rocks significantly increase in the economic zone of the deposit. The primary thickness of the alternating rock sequence is estimated at approximately 600 m (Bulakh *et al.*, 1990). The identified P_2O_5 reserve is 85.6 Mt, while the inferred reserve explored down to a depth of 1600 m is estimated at 200 Mt (Éntin *et al.*, 1987).

South of the Seligdar deposit, apatite-bearing rocks of the Fedorov Formation incorporates the Niryandzha

and Nimgerkan deposits with P_2O_5 reserves reaching a few million tons (Fig. 1) and several sectors with low-grade apatite mineralization (Éntin *et al.*, 1987). They are dominated by silicate rocks (gneisses and crystalline schists) conformably intercalating with meter-scale apatite-carbonate rock lenses. In the Niryandzha deposit, the apatite-bearing rocks include several zones with apatite-poor quartz-carbonate varieties, while carbonate rocks often contain clastic apatite (Guliy *et al.*, 1999).

Further south of the Seligdar deposit in the Bol'shoi Nimnyr and Khardogas (Fig. 1) river basin, the number of orebodies and thickness of apatite-bearing carbonate, diopside, and hematite-chlorite rocks increase in noneroded areas. In the Mustolaakh and Dorozhnyi deposits, these rocks dominate over gneisses and crystalline schists of the Fedorov Formation. The quantitative proportion of the apatite-bearing rock types is variable in these deposits. For example, diopside varieties are absent in the Dorozhnyi sector, account for up to 20% in the Mustolaakh deposit, and predominate in the Tagnarar deposit. Ores in the Mustolaakh deposit compose sheeted or lenslike bodies up to 200 m thick. The orebodies are no more than 50 m thick in the Tagnarar deposit. In terms of the total P_2O_5 reserve, the Mustolaakh and Dorozhnyi deposits are classified as small objects. The Tagnarar deposit has an insignificant P_2O_5 reserve.

The Birikeen, Chukurdan, and Levyi Burnyi deposits located in the Timpton River basin also have small P_2O_5 reserves (Fig. 1). They are confined to the Gorbylyakh Formation consisting of gneisses and crystalline schists conformably intercalated with apatite-bearing

Table 1. Mineral composition of natural apatite ore types in the Seligdar deposit (vol %)

Minerals	Apatite-bearing carbonate rocks and ores				
	Dolomite	Calcite	Martite-quartz-carbonate	Sulfate-carbonate	Silicate-carbonate
Apatite	5.1	10.6	21.2	4.7	24.9
Carbonates	87.9	73.2	49.0	73.4	20.3
Layered Mg-hydrosilicates	–	2.1	6.2	2.0	36.6
Phlogopite and other micas	1.2	1.0	1.0	0.4	–
Iron oxides	1.9	3.3	8.8	1.8	12.4
Quartz	1.3	7.2	8.4	–	3.1
Sulfates	–	1.5	2.5	17.0	0.5
Feldspar	2.6	1.1	2.9	0.7	2.2
Total	100	100	100	100	100

Note: (–) Not detected.

silicate and carbonate rocks (Reutov, 1981). With depth and along the strike, the thickness of individual rocks types can vary from a few meters to a few hundreds of meters in different deposits (Guliy, 1995). Apatite-bearing units are represented by carbonate, diopside, and hematite–chlorite rocks in the Chukurdan deposit and apatite–carbonate rocks with interbeds from several tens to few hundreds of meters thick in the western Birikeen deposit. Further in the west, the Levyi Buran deposit contains meter-scale apatite-bearing diopside and carbonate rocks, which often associate with areas enriched in clastic apatite (Guliy and Reed, 1999). Marginal sectors of the area located in the Ust-Chul'man River mouth of and south of the Levyi Burnyi deposit (e.g., the Khayumkan sector) are composed of carbonate rock bodies up to 2 m thick.

The conformable intercalation of apatite–carbonate ores and metamorphic silicate rocks within and around the Levyi Burnyi deposit indicates that apatite-bearing carbonate rocks are coeval to the host gneisses and crystalline schists. Datings based on apatite (apatite–dolomite ores) and phlogopite (crystalline schists) of the Seligdar deposit yielded approximately similar values within 1.8–2.0 Ga (Bulakh *et al.*, 1990). They are consistent with previous datings of apatite mineralization within the Aldan Shield reported in (Tugarinov *et al.*, 1977). The Pb–Pb isochron datings of apatite from apatite–carbonate and apatite–silicate rocks of different deposits in the Aldan Shield yielded the same age (Pushkarev *et al.*, 1989).

Mineral Composition of Apatite–Carbonate Rocks

We studied several groups of apatite–carbonate rocks. Group 1 includes apatite–carbonate rocks (ores) developed within orebody of the Seligdar deposit and other similar separate apatite occurrences in the Aldan Shield. Group 2 includes apatite–carbonate and apatite–sulfate–carbonate rocks underlying the Seligdar orebody. Group 3 includes apatite–silicate–carbonate

rocks that are transitional from apatite–carbonate to apatite–silicate types. For comparison, we also used original isotope data on the later carbonate veins and pockets, which accompany sheeted orebodies, and dolomites of the Yudoma Group overlying apatite deposits.

The apatite–carbonate rocks are distinguished from other rocks by characteristic yellowish pink and dark brown to brownish color related to their pigmentation by finely dispersed hematite. They are commonly inequigranular rocks. Depending on the content and distribution of apatite and accessory minerals, they are characterized by massive, spotted, or banded structures. Massive apatite–carbonate varieties, which are most abundant, consist of the major apatite and carbonates (dolomite and/or calcite) and the subordinate silicates, martite, quartz, and sulfates (Tables 1, 2). Based on the abundance of subordinate minerals, one can distinguish the silicate–carbonate, quartz–dolomite, martite–dolomite, and sulfate–carbonate varieties, (Bulakh and Zolotarev, 1983; Bulakh *et al.*, 1990); Guliy, 1995). They are shown in order of the relative formation sequence and decreasing apatite content. The Seligdar deposit contains all aforesaid varieties (Table 1), whereas other areas mainly contain apatite–carbonate and quartz–silicate varieties (Table 2). In addition to the Seligdar deposit, only the Birikeen area locally contains martite-rich rocks (Guliy, 1995). Sulfates were sporadically found at a depth of more than 100 m in borehole cores from the Mustolaakh and Chukurdan deposits.

Apatite–dolomite and apatite–sulfate–carbonate rocks of Group 2 have grayish green color and massive or spotted structure. They were recovered by boreholes 407–410 beyond the Seligdar orebody. Like ores, these rocks are composed of apatite, carbonates, and sulfates, but they are characterized by the presence of spinel, chondrodite, phlogopite, and other minerals (Table 3) and the absence of finely dispersed hematite.

Table 2. Mineral composition of Precambrian apatite-bearing carbonate rocks of the Aldan shield (vol %)

Area	Rocks	Sample no.	Minerals					
			Apatite	Carbonates	Chlorite	Martite	Quartz	Diopside
Niryandzha	Quartz-carbonate	3/2488	1.2	37.0	–	–	62.0	–
		3/3045	8.7	61.0	–	–	30.3	–
Dorozhnyi	Carbonate	3/2419	6.7	88.0	4.0	–	1.3	–
		3/2775	23.3	70.0	6.7	–	–	–
		K-1	8.7	84.0	7.3	–	–	–
		K-2	22.5	58.0	14.0	1.5	4.0	–
Mustolaakh		44348	36.0	64.0	–	–	–	–
		44343	1.6	98.4	–	–	–	–
		8	1.7	88.3	10.0	–	–	–
Tagnarar	Silicate-carbonate	10	72.2	6.4	13.4	–	8.0	–
		9	3.4	56.6	40.0	–	–	–
		Kh-9A	8.5	10.0	81.5	–	–	–
Birikeen		500/18	18.3	54.5	–	–	–	27.2
Chukurdun		T103-3	11.0	68.5	20.4	0.1	–	–
		ChuK-20	5.1	31.6	–	–	–	63.3
	Carbonate	ChuK-10	19.2	77.7	3.1	–	–	–

Note: (–) Not detected.

Table 3. Mineral composition of apatite-bearing carbonate rocks of the Verkhni Seligdar area (vol %)

Minerals	Sample no.				
	407/53515	407/53518	408/52861	410/1293	410/1959
Apatite	47.5	20.0	46.5	1.4	3.7
Dolomite	15.0	58.6	45.0	–	1.4
Calcite	26.0	1.4	–	4.0	86.4
Tremolite	–	–	–	66.3	–
Chlorite	10.0	1.0	5.0	15.0	1.2
Talc	–	–	–	2.0	–
Magnetite	–	5.4	3.5	11.3	–
Pyrite	1.5	–	–	–	4.1
Spinel	–	7.1	–	–	–
Clinohumite	–	5.2	–	–	–
Anhydrite	–	–	–	–	3.2
Serpentine	–	0.9	–	–	–
Epidote	–	0.4	–	–	–
Total	100.0	100.0	100.0	100.0	100.0

Note: (–) Not detected.

Apatite-silicate-carbonate rocks were recovered in boreholes 23, CIG-2, and others of the Seligdar deposit. They universally occur in the Tagnarar and Chukurdan deposits. Unlike apatite-carbonate rocks, they contain magnetite, which is responsible for the low Fe^{3+}/Fe^{2+} ratio and indicates more reducing conditions of their formation.

ISOTOPIC INVESTIGATIONS AND INTERPRETATION OF RESULTS

Experimental

The oxygen and carbon isotopic compositions in the whole-rock carbonates were analyzed in the Laboratory of Stable Isotopes (Institute of the Lithosphere of Marginal Seas, Moscow). Carbon dioxide was released from carbonates using the $PbCl_2$ method (Borshchevskii *et al.*, 1974). The relative difference in oxygen and carbon isotope ratios in CO_2 (gas) was measured on a Varian MAT-250 mass spectrometer. The laboratory CO_2 was used as standard during isotopic measurements. The accuracy of $\delta^{13}C$ and $\delta^{18}O$ measurement in the whole-rock samples was $\pm 0.1\%$ and $\pm 0.2\%$, respectively. The Craig correction was taken into consideration for the determination of $\delta^{13}C_{\text{samp}}$ (PDB) and $\delta^{18}O_{\text{samp}}$ (SMOW). The oxygen correction was taken into account for $\delta^{13}C_{\text{samp}}$ (PDB).

The carbon and oxygen isotopic compositions in individual carbonate grains were determined in Shizuoka University using a special method for microsamples (Wada, 1988). Measurements were performed on a Finnigan MAT-250 mass spectrometer equipped with an additional system for the supply of trace amounts of sample and a cooling section (*n*-pentane-liquid nitrogen) for freezing out the water vapor. The reference standard was calibrated relative to the NSB-20 calcite standard. The reproducibility of $\delta^{13}C$ and $\delta^{18}O$ determination was 0.03‰ and 0.05‰, respectively.

Carbon dioxide was extracted from the relatively phosphoric acid-resistant dolomite, ankerite, and other carbonates using the reaction with concentrated phosphoric acid in a 9-mm pyrex vacuum tube embedded in oil bath at 100°C (Nagai and Wada, 1993). The boundary volume of the powdered samples used for such technique was preliminarily determined by the analysis of two calcite and dolomite standards. According to (Nagai, Wada, 1993), accuracy of the analysis of more than 10 μl of CO_2 (gas) is similar to that of a sample of normal volume. The error increases if the CO_2 (gas) volume is lower.

Results and Discussion

Results of the isotopic investigation of whole-rock carbonate samples are given in δ values relative to the PDB standard for carbon and the SMOW standard for oxygen (Tables 4, 5). In the $\delta^{13}C$ - $\delta^{18}O$ diagram based

Table 4. Carbon and oxygen isotopic compositions of carbonates from different types of apatite-carbonate rocks of the Seligdar apatite deposit

Rocks	Morphological type	Sample no.	Isotopic composition	
			$\delta^{13}C$, ‰ PDB	$\delta^{18}O$, ‰ SMOW
Apatite-quartz-carbonate	Sheeted bodies	IK 19	+1.6	+20.4
		IK 20	+1.1	+20.0
Apatite-silicate-carbonate	"	IK 21	+2.9	+13.6
		IC 70	+1.8	+19.3
		IK 31	+3.1	+19.1
Apatite-carbonate	"	IK 22	+1.7	+20.8
		IK 24	+0.7	+18.1
		IK 26	+2.3	+19.4
		IK 28	+2.4	+16.2
Calciphyres	"	IK 34	+1.5	+12.5
		IK 15	+1.0	+14.8
Marbles	"	IK 32	+1.7	+9.6
		IC 40	-0.3	+20.1
		IC 38	+0.6	+21.1
		IK 16	-1.4	+17.6
		IK 18	+0.1	+19.9
Late carbonates	Veinlets	IK 17	+0.5	+18.8
		IK 30	-1.5	+17.0
	Pocket	IK 29	+1.9	+18.1
		IK 27	-2.6	+11.5
		IK 25	-0.5	+22.5
"	IK 23	-1.1	+16.4	
"	IC 15	-1.2	+19.2	

on whole-rock and microsample data (Fig. 2), the isotopic compositions of carbonates from apatite-carbonate rocks of all apatite deposits yield a scatter of $\delta^{13}C$ value from -0.5 to +5.5‰ and $\delta^{18}O$ value from +13.6 to +22.2‰. These values distinctly differ from data points of carbonates from apatite-free basement rocks (marbles and calciphyres) and limestones of the Yudoma Formation. The significant scatter of $\delta^{13}C$ and $\delta^{18}O$ values in carbonates from apatite-carbonate rocks is related to significant variations in the mineral and chemical composition of their individual varieties in separate deposits.

The studied carbonates are characterized by positive $\delta^{13}C$ values in sheeted carbonate bodies of the Seligdar deposit and its surrounding and negative values in spatially associated veinlets and pockets.

Unlike marbles and calciphyres developed beyond the apatite deposits, carbonates from the apatite-bearing calciphyres and marbles, which underlie the Seligdar orebody (Verkhni Seligdar area), are typically

Table 5. Carbon and oxygen isotopic compositions of carbonates from different types of apatite-bearing carbonate rocks of the Aldan Shield

Deposits	Rocks	Morphological type	Sample no.	Isotopic composition	
				$\delta^{13}\text{C}$, ‰ PDB	$\delta^{18}\text{O}$, ‰ SMOW
Mustolaakh	Apatite-carbonate	Sheeted body	IK 7	+0.6	+20.2
		"	IK 10	-0.5	+18.6
		"	IK 11	+0.5	+20.8
		"	IK 12	+1.7	+20.1
		"	IK 13	+0.7	+19.9
		"	IC 61	+1.4	+20.0
		"	IC 66	+0.8	+20.8
	Late carbonates	Pocket	IK 8	-0.7	+20.1
		"	IK 9	-2.6	+11.8
		Veinlet	IK 14	0.0	+18.2
"		IC 24	+5.3	+11.8	
Niryandzha	Apatite-carbonate	Sheeted body	IK 1	+1.9	+22.2
		"	IK 2	+1.8	+21.5
		"	IK 3	+2.1	+21.6
	Late carbonates	Veinlet	IK 4	-4.4	+17.9
		"	IK 5	-2.9	+17.6
		"	IK 6	-1.5	+17.6
Birikeen	Apatite-carbonate	Pocket	IK 52	+0.2	+17.3
		Sheeted body	IK 42	+1.9	+16.5
	Late carbonates	"	IC 26	+4.0	+16.3
		"	IC 58	+3.0	+19.0
		"	IK 43	+1.1	+16.7
		"	IK 53	+2.6	+16.4
		"	CO 29	+4.4	+18.0
Chukurdan	Late carbonates	Veinlet	CO 28	-5.1	+19.9
Ust Chul'man	"	"	IC 60	-4.8	+17.6
Khayumkan	"	"	CO 30	-5.2	+20.0
Tagnarar	Apatite-silicate-carbonate	Sheeted body	IC 69	+2.3	+14.9
Levyi Burnyi	Dolomites of the Yudoma Formation	"	IK 49	-8.0	+21.7
		"	IK 55	-5.3	+22.6
Seligdar	"	"	IK 56	-4.4	+24.5

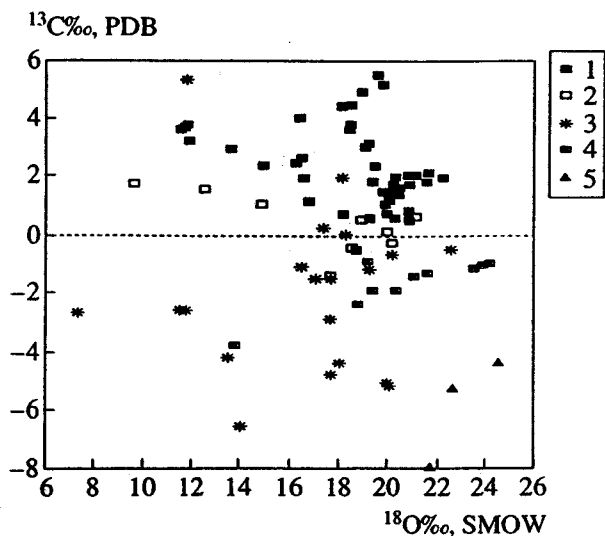


Fig. 2. The $\delta^{13}\text{C}$ - $\delta^{18}\text{O}$ diagram for carbonates from different types of the apatite-carbonate ores and carbonate rocks of the Aldan shield. (1) Ores from sheeted bodies, (2) ores from the Verkhni Seligdar area, (3) carbonate veins and pockets, (4) marbles and calciphyres, (5) limestones of the Yudoma Formation.

characterized by positive $\delta^{13}\text{C}$ values. Carbonates from calciphyres of the Seligdar deposit are significantly more depleted in heavy oxygen ($\delta^{18}\text{O} = 9.6\text{--}14.8\text{‰}$ SMOW) relative to the ore-hosted carbonates.

Carbonates from different apatite-carbonate rocks of the Seligdar deposit have generally similar carbon and oxygen isotopic compositions (Table 4). The apatite-silicate-carbonate varieties include an anomalous carbonate. It is enriched in ^{13}C ($\delta^{13}\text{C}_{\text{aver}} = +2.3\text{‰}$, PDB),

but depleted in ^{18}O (e.g., $\delta^{18}\text{O} = 13.6\text{‰}$, SMOW in Sample IK-21 with). Carbonates in calciphyres therein have the same oxygen isotopic composition. The micro-scale isotopic investigation of ankerite from one of the earliest carbonates of the apatite-silicate-carbonate rocks yielded an even higher $\delta^{13}\text{C}$ value (up to $+3.78\text{‰}$, PDB), whereas the $\delta^{18}\text{O}$ value is typical of other apatite-bearing rocks (Fig. 3a).

The micro-scale isotopic investigation showed that ankerite from apatite-sulfate-carbonate rocks is characterized by 1-2‰ lower $\delta^{13}\text{C}$ value (Fig. 3b) and 1-2‰ higher $\delta^{18}\text{O}$ value relative to ankerite from silicate-carbonate rocks. Dolomite and calcite from sulfate-bearing mineral assemblages in marbles have 1-2‰ lower $\delta^{13}\text{C}$ values than ankerite from sulfate-carbonate ores of the Seligdar deposit (Table 4).

In the $\delta^{13}\text{C}$ - $\delta^{18}\text{O}$ diagram (Fig. 4), data points of carbonates from sheeted apatite-carbonate bodies from different deposits make up partially or completely overlapping fields. The highest $\delta^{13}\text{C}$ values ($+4.4\text{‰}$, PDB) are found in whole-rock samples of carbonates from the Chukurdan deposit, while the lowest values (-0.5‰ , PDB) are observed in dolomites from the Mustolaakh deposit (Table 5). Carbonates from the Birikeen deposit are also enriched in heavy ^{13}C isotopes ($\delta^{13}\text{C}$ up to $+4.0\text{‰}$, PDB). Data points of carbonates from the Seligdar and Mustolaakh deposits are partially overlapped, but carbonates from the Mustolaakh deposit are depleted in ^{13}C ($\delta^{13}\text{C}_{\text{aver}} = +0.8\text{‰}$, PDB).

Micro-scale isotopic investigations revealed high $\delta^{13}\text{C}$ values (up to $+5.45\text{‰}$, PDB) in carbonates from the Chukurdan deposit (Fig. 5). Calcite from apatite-silicate-carbonate rocks of this deposit is similar to that from the Seligdar deposit and enriched in ^{13}C (up to

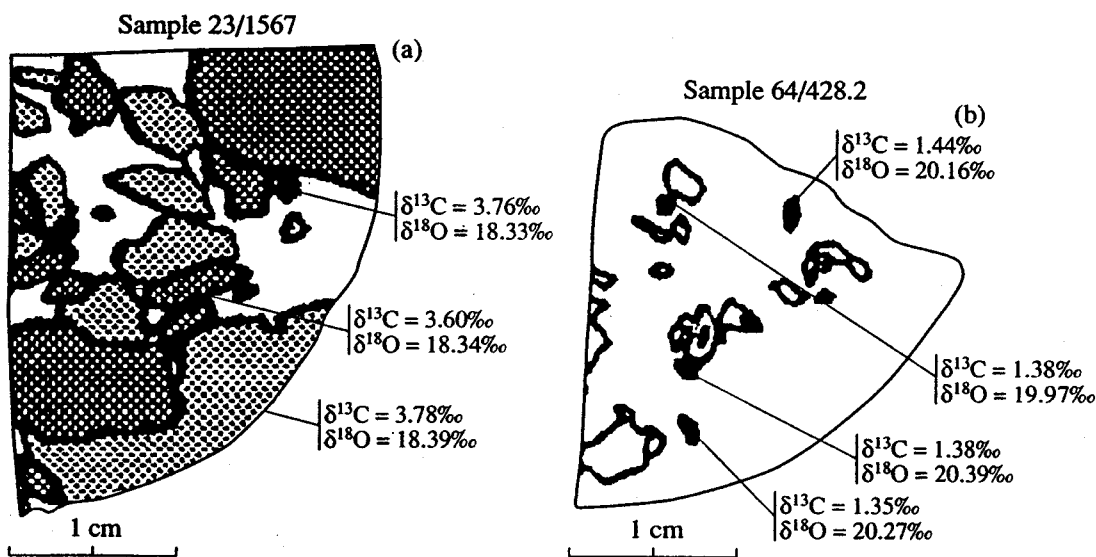


Fig. 3. Isotopic composition of individual carbonate grains from (a) apatite-silicate-carbonate and (b) apatite-sulfate-carbonate ores of the Seligdar deposit (sketch).

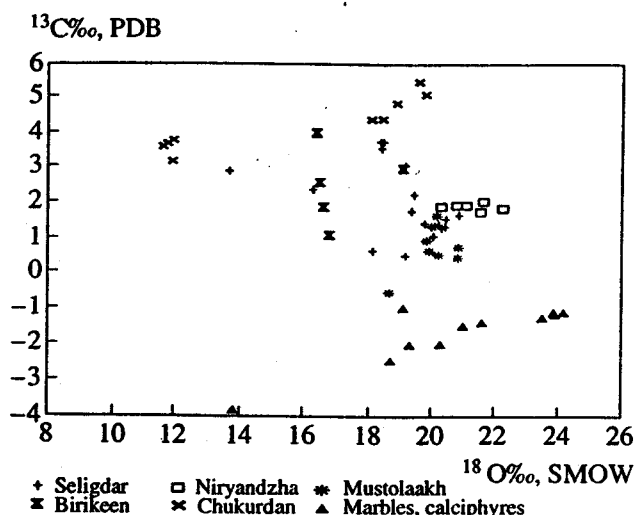


Fig. 4. The $\delta^{13}\text{C}$ - $\delta^{18}\text{O}$ diagram for carbonates from different apatite deposits of the Aldan shield.

+4.42‰, PDB). However, unlike silicate-free varieties, it is marked by low and strongly variable $\delta^{18}\text{O}$ values (Table 6). In carbonate veins within the apatite-diopside-carbonate rock, the highest $\delta^{13}\text{C}$ (+4.42‰, PDB) and $\delta^{18}\text{O}$ (18.39‰, SMOW) values are recorded in carbonates adjacent to diopside. Carbonates developed away from the contact have significantly lower $\delta^{18}\text{O}$ values (up to 11.54‰, SMOW).

Carbonates from the Tagnarar deposit have analogous carbon and oxygen isotopic compositions ($\delta^{13}\text{C}$ = +2.3‰, PDB, $\delta^{18}\text{O}$ = +14.9‰, SMOW). These values are similar those in carbonates from calciphyres and apatite-silicate-carbonate rocks of the Seligdar deposit.

The highest $\delta^{18}\text{O}$ values are typical of carbonates from the Niryandzha deposit (up to 22.2‰, SMOW), whereas low $\delta^{18}\text{O}$ values are recorded in carbonates from the Chukurdan deposit (Table 6). Data points of carbonates from the Niryandzha deposit make up a more compact cluster in the diagram (Fig. 2). In this deposit, carbonate interbeds with different contents of

Table 6. Carbon and oxygen isotopic compositions of carbonates from apatite-diopside-carbonate rocks of the Chukurdan deposit based on micro-scale investigations (Sample 2850/10)

Sample no.	Gas sample volume, μl	Isotopic composition	
		$\delta^{13}\text{C}$, ‰ PDB	$\delta^{18}\text{O}$, ‰ SMOW
1	2.67	3.66	11.70
2	6.84	3.58	11.54
3	10.98	3.76	11.87
4	4.16	3.17	11.88
5	6.57	4.42	18.39

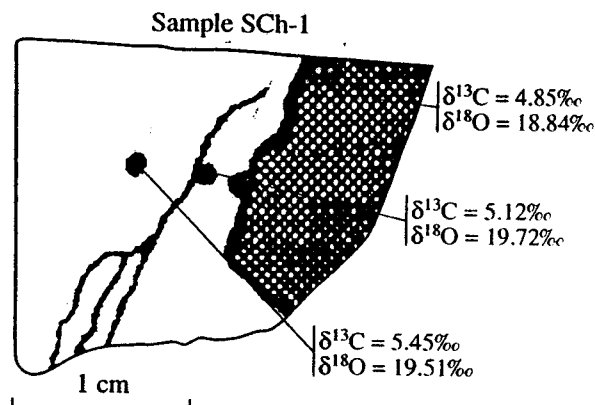


Fig. 5 Isotopic composition of individual carbonate grains from apatite-carbonate rocks of the Chukurdan deposit. The sketch shows carbonate (light field) and apatite (dark field).

clastic apatite show no significant difference in carbon and oxygen isotopic compositions (Fig. 6).

Carbonates from the Ust-Chul'man and Khayumkan areas are significantly enriched in light carbon isotope. Such carbon isotopic composition was found in carbonates from veinlets and pockets that postdated apatite-carbonate rocks.

The compositional similarity of apatite-carbonate rocks within different areas suggests their formation in a single paleobasin, which is now represented by non-eroded relicts of a single succession, or in several isolated small paleobasins with different salinity regimes.

Study of carbonates from different types of sedimentary basin showed that carbon and oxygen isotopic exchange occurred under closed or open systems (Feitser, 1987; Hudson, 1977; Kuleshov, 2001; Talbot, 1990). The correlation coefficient between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in carbonates is higher than 0.8 in carbonate deposits confined to hydrologically closed basins (lakes) (Talbot, 1990) and significantly lower in the open or partially closed (lagoon) marine basins (Feitser, 1987; Hudson, 1977). Carbonates from all apatite-carbonate rocks of the Aldan Shield lack any correlation between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ (regression coefficient $R = 0.07$; $n = 55$). The correlation should be observed if they are crystallized in a hydrologically closed basin. Such pattern is typical of carbon and oxygen isotopic compositions in the carbonates from apatite-carbonate rocks of all deposits ($R = 0.10$; $n = 22$) and the Seligdar deposit, in particular ($R = 0.07$; $n = 6$). Carbonates from apatite-carbonate rocks of the Birikeen deposit show a strong scatter of isotopic values ($R < 0.01$; $n = 6$).

MAIN FEATURES OF THE ORIGIN OF APATITE-CARBONATE ROCKS IN THE ALDAN SHIELD

Carbonate rocks are similar to Phanerozoic and Precambrian sedimentary carbonates (Feitser, 1987; Schidlowski *et al.*, 1975; Hudson, 1977). However,

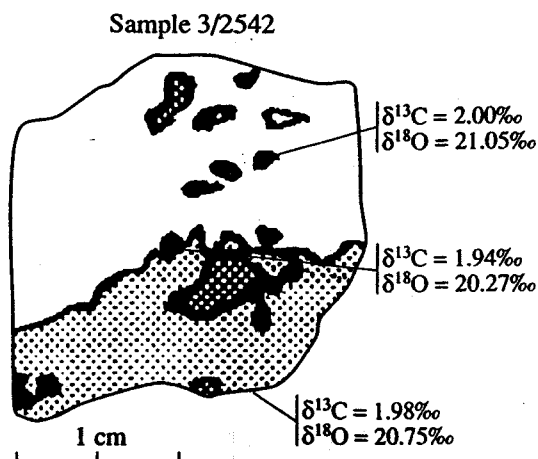


Fig. 6. Isotopic composition of carbonates from apatite-carbonate rocks of the Niryandzha deposit enriched (shaded) and depleted (white) in clastic apatite (sketch).

they are distinguished from other carbonate rocks of the Aldan Shield by higher $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values. As was mentioned above (Guliy, 1994), they formed under more oxidizing conditions owing to the presence of free oxygen, as compared to marbles and calciphyres. The possible contribution of evaporation at different stages of carbonate formation is directly supported by the frequent presence of sulfates in the apatite-carbonate rocks of other Precambrian regions (Schidlowski *et al.*, 1975; McNaughton and Wilson, 1983).

Periodic uplifts of individual areas facilitated the formation of paleokarsts and intraformational apatite-bearing conglomerates (Guliy, 1995; Guliy and Reed, 1999). Thus, apatite-carbonate rocks are products of the complex alternation of sedimentary processes at different regimes of basin salinity occasionally marked by the decomposition of older sediments under sub-aerial conditions.

All apatite deposits and occurrences of the Aldan Shield occur in a similar geostructural setting, but they sharply differ in orebody thickness and total P_2O_5 reserve. They include different proportions of similar apatite-bearing rocks and low-P silicate rocks owing to different facies settings of primary sedimentary rocks at each deposit. The morphological similarity of sheeted or lenslike apatite-carbonate bodies in primary bedding indicates that the paleobasins had a flat bottom and shallow profile, but their phosphorus potential depended on the intensity of tectonic movements and size of separate areas.

The studied rocks are characterized by a heterogeneous layered distribution of phosphorus and absence of compositional homogenization during regional metamorphism (Guliy, 1989). Hence, phosphate accumulated only in certain facies of paleobasins. This is consistent with the concept of lithological control of apatite (Vinogradov *et al.*, 1975) and magnetite (Pavlov *et al.*, 1987) mineralizations in Precambrian sequences

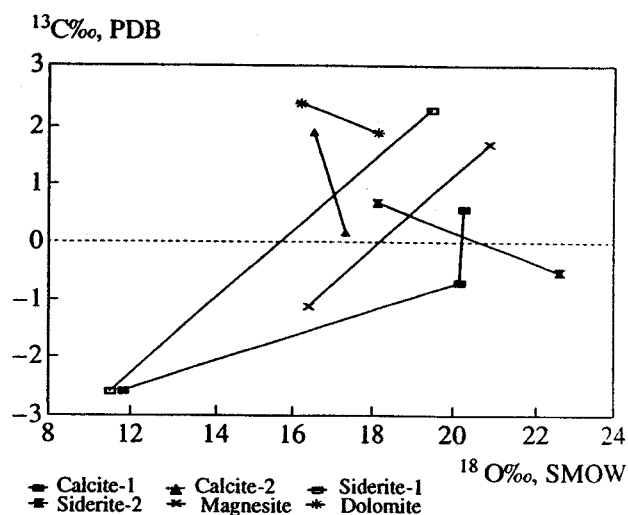


Fig. 7. The $\delta^{13}\text{C}$ - $\delta^{18}\text{O}$ diagram for primary and late carbonates from the apatite-carbonate rocks and ores.

of the Aldan Shield. The facts mentioned above make it possible to predict the possible scale of mineralization depending on the type of geological succession of the area.

When passing from the earlier (high-P apatite-silicate-carbonate) rocks to the late (low-P apatite-sulfate-carbonate) rocks, which complete the formation of apatite ores (Bulakh *et al.*, 1990), carbonates are gradually depleted in heavy ^{13}C and ^{18}O isotopes. Their concentrations are minimal in late pockets and veins, indicating limited volumes of high-P solutions and their gradual depletion at the end of carbonate protolith crystallization. Carbonate rocks enriched in light carbon and oxygen isotopes are significantly depleted in apatite. At the same time, carbonate and phosphate formations in such basins are independent and occasionally coeval processes. This fact has an applied significance. Their temporal coincidence is caused by similar physicochemical conditions, which are relatively favorable for the formation of stable crystalline phases of both carbonates and phosphates, but the amount of phosphates was governed by the total P content in paleobasins.

The relatively close carbon and oxygen isotopic compositions of carbonates from different apatite-bearing rocks can be explained by the relative stability of CO_2 partial pressure, marking a single nature of carbonate source. This is especially true for samples from massive and spotted rocks, which do not contain carbonate veins and pockets with strongly different isotopic signature.

After the precipitation of apatite and coexisting carbonates, the crystallization of subsequent phases was related to the mineral-forming environment characterized by a different cation content and depletion in ^{13}C and ^{18}O . The early dolomite is universally enriched in ^{13}C (Fig. 7) with insignificant variations in different

sectors. The enrichment of late carbonates in the light carbon and oxygen isotopes indicates the possible involvement of a fresh-water CO₂-H₂O system (Kuleshov, 2001). This is supported by the change of carbon and oxygen isotopic compositions in dolomite, late dolomite, and calcite (Guliy, 1994), reflecting the general crystallization scheme of apatite, hematite, and carbonates in a single sample. Judging from small volume of late carbonate segregations, relative to predominant early carbonates, the final transformations under the influence of solutions enriched in light carbon and oxygen were insignificant.

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