Macro- and Microvariations in the Carbon and Oxygen Isotopic Composition of Precambrian Carbonates from the Aldan Shield

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Abstract—The isotopic composition of carbon and oxygen was determined by two techniques in whole-rock samples and single grains of carbonates from rocks of various morphogenetic types from the Aldan Shield. The isotopic values obtained by different methods in carbonates of the same types are generally similar. The values of $\delta^{13}C$ and $\delta^{18}O$ for the marbles, calciphyres, and apatite–carbonate rocks reflect their primary values and are close to those in sedimentary Precambrian carbonate rocks elsewhere. Among the rocks examined, high $\delta^{13}C$ values (up to 5.45‰, PDB) were shown by apatite–carbonate rocks, whose protolith was produced chemogenically in shallow evaporitic basins with significantly oxidizing conditions and a limited influx of terrigenous material. The subsequent transformations of the primary rocks by meteoric waters and metasomatic fluids can be identified using low $\delta^{18}O$ and negative $\delta^{13}C$ values.

INTRODUCTION

Carbonate rocks are widespread in Precambrian metamorphic complexes of the Aldan Shield [1–3]. The rocks comprise a number of genetic types, including primary sedimentary [3] and various later rocks, whose geneses are related to metamorphic and metasomatic processes [4, 5]. The discovery of unusual apatite–carbonate rocks and the Seligdar apatite deposit by TUGRE geologists in the 1970s has demonstrated that the carbonate rocks of the shield are even more diverse and stimulated vivid discussions of their genesis. Following the first concepts of the folded tectonics of the deposit, which were later confirmed by detailed data on the core of several prospecting boreholes, and the sedimentary accumulation of the phosphorus [6], it was proposed that the deposit is of a carbonatitic nature [7, 8] and was produced by the processes of Ca–Mg metasomatism [9].

There are now extensive materials on the isotopic compositions of carbonates from metamorphic and metasomatic rocks both in Russia and elsewhere [4, 5, 10–12]. It was established that an increase in the grades of metamorphic and metasomatic alterations is associated with the enrichment of carbonates in light carbon and oxygen isotopes and the most significant shifts in $\delta^{13}C$ and $\delta^{18}O$ from those of the initial sedimentary rocks result in values similar to those typical of skarns and carbonatites. It was also demonstrated [11] that these shifts are caused by the involvement of carbon dioxide that had passed through a magmatic melt in the processes of magmatic-stage Mg-skarn formation. The manifestations of these shifts in postmagmatic-stage Ca-skarns are of universal character. This opens up possibilities for using isotopic data to assay the extent of transformations of the primary rocks even when their evaluation cannot be accomplished by other techniques [11, 13].

The carbon and oxygen isotopic composition of carbonate samples composed of a mixture of individual grains or their aggregates (which can be regarded as whole-rock samples) reflect the isotopic composition of the carbonate rock as a whole. At the same time, the microscale isotopic study of individual carbonate grains [14–17] indicates that the distribution of carbon and oxygen isotopes in them can be zoned and result from both systematic variations in the physicochemical conditions of carbonate deposition [16] and more complicated and unsystematic variations in response to diagenetic processes on different scales [16, 17] or fluid filtration during the latest metamorphic episode of polymetamorphism and subsequent metasomatism [14, 15]. If fluids actively participate in metamorphic or metasomatic transformations, there should be oxygen and carbon isotopic exchange between the carbonates and pore water, and this process can be identified by $\delta^{18}O$ and $\delta^{13}C$ changes. If these transformations are insignificant, their traces can be left unnoticed in the isotopic analysis of the whole-rock carbonate sample but may be discerned when individual grains are analyzed. In the light of these considerations, we attempted to reproduce the crystallization history of Precambrian carbonate rocks in the Aldan Shield based on the micro- and macrovariations in the carbon and oxygen isotopic composition of their carbonates.

Table 1. Chemical composition (wt %) of the main types of Precambrian carbonate rocks from deposits at the Aldan Shield

Compo-nent	Deposit		
	Seligdar	Mariika	Medvedevka
	Rock		
	apatite–car-bonate rock	marble	calciphyre
	Sel-1	M-1	M-2	45000
SiO_2	9.93	8.81	7.74	18.00
TiO_2	0.14	0.06	0.09	0.02
Al_2O_3	1.97	2.10	2.77	4.41
Fe_2O_3	5.37	0.52	0.41	0.35
FeO	–	0.71	0.64	–
MnO	0.17	0.02	0.02	0.02
MgO	14.17	8.16	10.49	2.47
CaO	29.60	42.98	41.08	41.74
Na_2O	0.23	0.49	0.31	0.64
K_2O	0.35	0.25	0.31	0.48
H_2O	0.37	–	–	–
P_2O_5	6.06	0.04	0.03	0.08
SO_3	2.12	–	–	0.03
LOI	29.71	36.78	37.79	32.26
SrO	0.03	0.41	03.5	0.14
Total	99.85	99.52	99.46	100.63

GEOLOGY AND COMPOSITION OF THE CARBONATE ROCKS IN THE ALDAN SHIELD

We analyzed carbonate rocks of two morphogenetic types: (1) stratiform and lenticular bodies and (2) younger carbonate pockets and veins, which most often developed after the rocks of type I, and metasomatic rocks related to magnesian skarns.

The stratiform and lenticular carbonate rocks are restricted to the Fedorovskaya Formation of the Aldan Shield or its analogues [1, 2]. They conformably intercalate with diopside rocks and related gneisses and crystalline schists and have similar structural styles. The thicknesses of individual carbonate bodies vary from a few centimeters to 100 m or more. The rocks of the formation are metamorphosed to the granulite and amphibolite facies [1, 18], and their U–Pb age is 1.8–2.0 Ga [19]. The Pb–Pb isochron age of apatite from the apatite–carbonate rocks is 1854 ± 7 Ma [20].

The stratiform and lenticular carbonate rocks can be classified into the following groups according to their mineral assemblages and textural–structural features [21]: (a) marbles with >95% carbonates, (b) calciphyres with 10 to 75% silicates, and (c) apatite–carbonate rocks, which usually possess apatite and are thus regarded as phosphate ores [6].

We examined the isotopic composition of carbonates from the marbles and calciphyres, which were sampled in open-pit mines, exposures, and the core of prospecting boreholes at the Medvedevka, Sivagli, and Mariika deposits. The apatite–carbonate rocks for the analyses were taken from the borehole core of the Seligdar, Niryandzha, Levyi Buryi, Birikeen, and Chukurdan deposits (Fig. 1).

In hand-specimens, the marbles and calciphyres are white, pink, or greenish, and have massive or unclearly patchy structures and equally grained, granoblastic from medium-grained (3–4 mm) to coarse-grained (4–8 mm) textures.

The marbles and calciphyres consist mostly of calcite and dolomite with subordinate amounts of diopside, fluorite, scapolite, forsterite, graphite, and other minerals. Table 1 lists full chemical analyses of typical marbles and calciphyres from the Aldan Shield.

The apatite–carbonate rocks are usually unequally grained, massive, patchy, banded, or brecciated. Their color varies from yellowish red and brownish in massive varieties to greenish brown and dark brown in patchy and banded rocks. The banding is caused by different grain sizes, crystal shapes, color, and content of apatite, carbonates, hematite, and magnesium phyllosilicates. Dark rock portions are usually richer in apatite and fine-grained hematite.

The microtextures of the apatite–carbonate rocks are granoblastic, caused by roughly equal apatite and carbonate crystals, or clastic, with angular and rounded fragments 1–5 mm across. The fragments are parts of crystals or grains of apatite, hematite (martite), and carbonates, which are often surrounded by hematite rims. The cement usually consists of carbonates and fine-grained hematite.

The principal minerals of the apatite–carbonate rocks are carbonates (20–95%) and apatite (up to 25%); the minor minerals are phlogopite, chlorite, talc, hematite (martite), quartz, and sulfates (gypsum and anhydrite). When contained in amounts greater than 5%, minor minerals define apatite–silicate, apatite–martite–quartz, and apatite–sulfate varieties of the apatite–carbonate rocks [6].

The carbonates are dominated by calcite and dolomite, with ankerite, siderite, and magnesite composing occasional small segregations. The dolomite is usually small (from 0.1 to a few millimeters), equally grained, and brownish or pinkish in the groundmass of the rocks because of small inclusions of syngenetic hematite. The calcite is commonly white, and its grains are larger than those of dolomite. When occurring in aggregates with dolomite, calcite is usually younger than this mineral.

The typical apatite–carbonate rocks differ from the marbles and calciphyres by high P_2O_5 and SO_3 concentrations and high Fe^{3+}/Fe^{2+} ratios (Table 1).
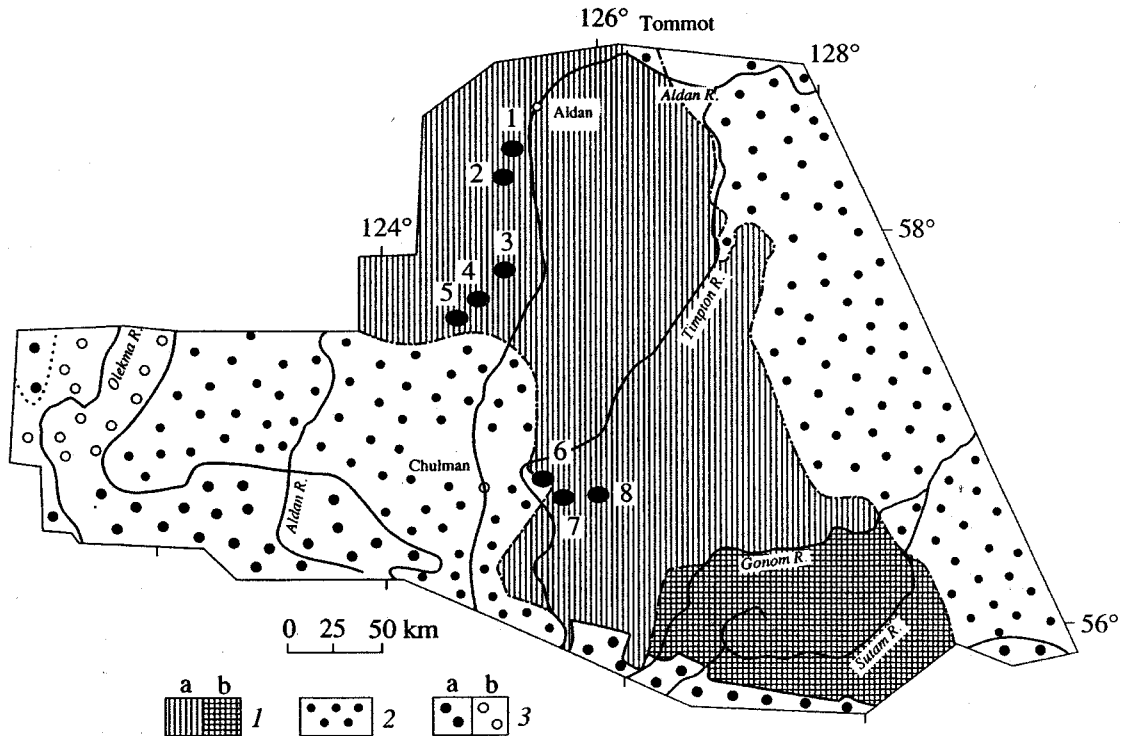
Fig. 1. Schematic map showing the setting of the deposits in the Aldan Shield. (1) Seligdar; (2) Niryandzha; (3) Medvedevka; (4) Sivagli; (5) Mariika; (6) Levyi Burnyi; (7) Birikeen; (8) Chukurdan. Legend: (*1*) high-grade metamorphic rocks: (a) facies intermediate between the garnet–cordierite–biotite and garnet–cordierite hypersthene facies, (b) hypersthene–sillimanite facies; (2) transitional metamorphic facies; (*3*) lower grade metamorphic rocks: (a) granulite facies, (b) amphibolite facies, after [20].

Late carbonates are ubiquitously present in the apatite–carbonate ores in the form of veinlets and pockets from a few millimeters to a few dozen centimeters across. They are also common at skarn deposits, where their thickness varies from a few centimeters to a few dozen meters. The veins and pockets consist mostly of coarse-crystalline calcite and occasionally present dolomite, magnesite, and ankerite. If other carbonates are present, carbonate aggregates can be zonal [21]. The mineralogic composition of the skarn veins is much more diverse owing to the occurrence of silicates. Our research is based on materials sampled at the Emel'dzhak, Kanku, and El'konka phlogopite deposits and the Seligdar, Niryandzha, Mustolaakh, Khayumkan, Chukurdan, Tagnarar, and Ust'-Chul'man apatite deposits.

ANALYTICAL TECHNIQUES

Oxygen and carbon isotopes were analyzed in whole-rock carbonate samples at the Laboratory of Stable Isotopes of the Institute of the Lithosphere, Russian Academy of Sciences (Moscow). To liberate CO_2 from carbonates, we used the $PbCl_2$ technique [22]. The $\delta^{13}C$ and $\delta^{18}O$ values were measured on a Varian MAT-250 mass spectrometer accurate to ±0.1‰ for $\delta^{13}C$ and ±0.2‰ for $\delta^{18}O$.

The microscale analyses were conducted on the material from rocks whose whole-rock isotopic analyses had shown the most contrasting $\delta^{13}C$ and $\delta^{18}O$ values. This allowed us to identify possible newly formed material in the relict, the least altered patches of the protolith. The carbon and oxygen isotopic composition of such single carbonate grains was analyzed at Shizuoka University with the use of a specialized technique for microsamples [14] on a Finnigan MAT-250 mass spectrometer. The precision was 0.03‰ for $\delta^{13}C$ and 0.05‰ for $\delta^{18}O$.

Carbon dioxide was released from dolomite, ankerite, and other carbonates by reacting the samples with concentrated phosphoric acid in an evacuated 9-mm Pyrex tube placed in an oil bath at a temperature of 100°C [23].

RESULTS AND INTERPRETATIONS

Our data on the isotopic composition of whole-rock carbonate samples are generalized for each type of the carbonate rocks and listed in Table 2.

In the diagram of Fig. 2, $\delta^{13}C$ and $\delta^{18}O$ values group within discrete fields, corresponding to the types of carbonate rocks distinguished. The fields of carbonates from different varieties of stratiform and lenticular bodies overlap (Fig. 2). The fields of carbonates from marbles and calciphyres are shifted by approximately 2–

Table 2. Carbon and oxygen isotopic composition of Precambrian carbonates in the main types of Precambrian carbonate rocks from the Aldan Shield

Rock (number of samples)	$\delta^{13}C$, ‰ PDB	$\delta^{18}O$, ‰ SMOW
Marble (11)*	$\dfrac{-1.9}{-4.0-0.0}$	$\dfrac{+19.7}{+13.0\ldots+25.0}$
Apatite–carbonate rock (42)	$\dfrac{+1.6}{-0.5\ldots+4.4}$	$\dfrac{+19.4}{+16.5\ldots+22.5}$
Calciphyre (12)*	$\dfrac{-4.0}{-7\ldots-0.5}$	$\dfrac{+14.8}{+11.0-23.0}$
Vein rock (11)	$\dfrac{-2.9}{-5.2-0.0}$	$\dfrac{+16.3}{+7.3\ldots+20.1}$
Skarn (14)*	$\dfrac{-5.8}{-9.5\ldots-4.5}$	$\dfrac{+13.8}{+13.8\ldots+20.0}$

* In the calculations, we also used data on marbles, calciphyres, and skarns from [5].

4‰ toward lower $\delta^{13}C$ values relative to the field of the apatite–carbonate rocks. There also are significant overlaps of the fields of carbonates from the calciphyres and skarns and the fields of carbonates from younger veinlets and pockets with all other types of the carbonate rocks (Fig. 2).

The highest (usually positive) $\delta^{13}C$ values are characteristic of apatite–carbonate rocks, and the $\delta^{18}O$ values vary from 16.5 to 22.5‰. The points plotting outside this range represent some carbonates from the Seligdar deposit (samples ID 221/97.6 and AG205/273) and the Tagnarar prospect (sample 500/18), where lower $\delta^{18}O$ values were detected (13.6, 9.6, and 14.9,

respectively). These data are not plotted in the diagram (Fig. 2), because they pertain to carbonates from varieties of apatite–carbonate rocks high in silicates, which are transitional to apatite–diopside rocks.

Carbonates from the younger veins and pockets usually exhibit negative $\delta^{13}C$ values and the lowest (up to 7.3‰) and strongly variable $\delta^{18}O$ values. The $\delta^{13}C$ and $\delta^{18}O$ values of late carbonates are most often lower and attain 5–10‰. A rare exception is calcite veinlets in granite at the Mustolaakh prospect (sample 1/93.7), where high positive values of $\delta^{13}C$ (5.3‰) were detected at relatively low $\delta^{18}O$ (11.8‰).

Within heterogeneous rock volumes, in which carbonates of many morphogenetic types can occur simultaneously and the temporal succession of their formation was determined [21], the $\delta^{13}C$ and $\delta^{18}O$ values of the early dolomite are always higher than the analogous values of the late dolomite (Table 3). Siderite, calcite, and magnesite, which are deposited in an evolving mineralizing environment later than dolomite, are characterized by low $\delta^{13}C$ values (Table 3). The differences in the carbon and oxygen isotopic composition between earlier and later carbonates are always from 1 to 4‰.

Among carbonates of all morphogenetic types, the lowest $\delta^{13}C$ values (–9.5‰) are characteristic of carbonates from the skarns, which makes them similar to carbonatites [10, 11], but this feature and the relatively low $\delta^{18}O$ values of these rocks are remarkably different from the analogous values of the apatite–carbonate rocks.

The results of our microscale analysis of the distribution of carbon and oxygen isotopes in individual carbonate grains (Table 4) lie within the corresponding fields in the $\delta^{13}C$ vs. $\delta^{18}O$ diagram (Fig. 2) for whole-rock carbonate samples. When the micro- and macroscale (whole-rock) analyses of the carbonates (Table 4) are generally consistent, it was determined that the $\delta^{13}C$ values of microscale analyses are often 0.2–1.0‰ higher. The $\delta^{18}O$ values determined in individual carbonate grains and whole-rock samples (Table 4) are also different, but their differences are smaller than those between the corresponding $\delta^{13}C$ values and are unsystematic.

The exceptions to the overall consistency between the results obtained by the two techniques are the data on marble samples from the Medvedevka and Sivagli deposits (Table 4). The values of $\delta^{13}C$ in some calcite grains in marble from the Medvedevka deposit are higher than the whole-rock values, but their $\delta^{18}O$ value is lower by approximately 4.5‰. Conversely, carbonates from the Sivagli marble show higher microanalytical $\delta^{18}O$ values (Fig. 3) than those for the whole-rock samples. It is worth noting the highly heterogeneous C and O isotopic composition of some carbonate grains (Fig. 3).

The lowest $\delta^{13}C$ values (–0.45‰) were yielded by dolomite from the apatite–carbonate rock underlying the main orebody of the Seligdar deposit, but the oxy-
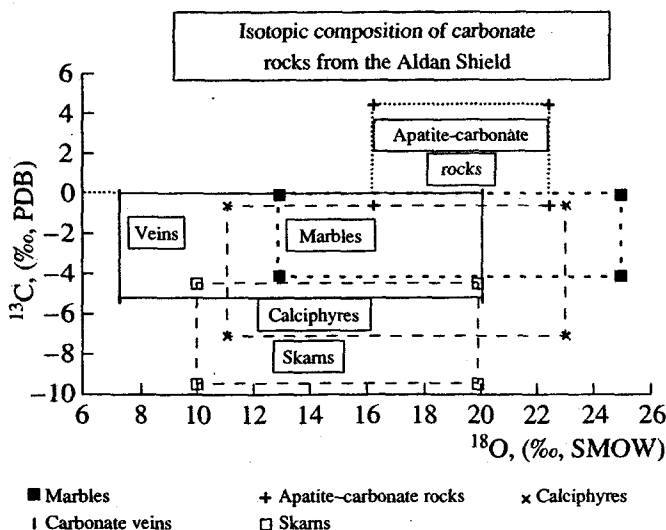
Fig. 2. Isotopic composition of carbonates in different types of carbonate rocks from the Aldan Shield.

Table 3. Carbon and oxygen isotopic composition of coexisting carbonates of different generations in apatite–carbonate rocks

Sample	Mineral	Deposit	Isotopic composition	
			$\delta^{13}C$, ‰ PDB	$\delta^{18}O$, ‰ SMOW
148B1	Dolomite I	Mustolaakh	+0.6	20.2
148B2	Dolomite II	"	–0.7	20.1
148B3	Calcite	"	–2.6	11.8
143/853	Dolomite	Seligdar	+1.7	20.8
143/853	Magnesite	"	–1.1	16.4
48/942.3	Dolomite	Seligdar	+2.3	19.4
48/942.3	Siderite	"	–2.6	11.5

gen isotopic composition of the dolomite does not differ from that of the orebody carbonates.

The $\delta^{13}C$ values measured in ankerite grains from the apatite–silicate–carbonate rocks (Fig. 4a) are higher than the analogous values in the whole-rock sample (Table 4) by 0.5–0.7‰ and by more than 2‰ than the values for ankerite from the apatite–sulfate–carbonate rocks (Fig. 4b). Calcite from the carbonate rocks of the Birikeen and Chukurdan deposits is strongly enriched in the ^{13}C isotope ($\delta^{13}C$ = 3.0 and 4.0‰). The carbonate–apatite rocks at these deposits show the highest $\delta^{13}C$ values (5.45‰) among analogous rocks in the Aldan Shield. It should be mentioned that these values are highly homogeneous, coincide with the values for the whole-rock samples, and, hence, are characteristic of the rock as a whole.

The variations in the $\delta^{18}O$ of the analyzed carbonate grains are insignificant, except a patch in the heterogeneous apatite–diopside–carbonate rocks at the Chukurdan deposit (Fig. 5). Here, the central part of a carbonate vein rock, associated with a diopside rock, was determined to contain calcite grains (Fig. 5, analytical points 1–4) with very low $\delta^{18}O$ values (11.54–11.88),

which increase toward the contact with the diopside rock to 18.39‰ (Fig. 5, point 5) and, hence, correspond to values typical of carbonates from apatite–carbonate rocks. The decrease in the $\delta^{18}O$ values is coupled with an increase in the grain size of the calcite toward the center of the carbonate interval and a moderate decrease in the $\delta^{13}C$ values. Since the number of phases with a heterogeneous isotopic composition is not large, and they are dissembled by numerous "normal" grains, "abnormal" values were not identified during the analysis of the whole-rock sample (sample 2831/44), in which only high values were determined for both $\delta^{13}C$ (4.4‰) and $\delta^{18}O$ (18.0‰).

The carbon and oxygen isotopic composition of carbonate grains from portions of the carbonate–apatite rocks that are rich and poor in apatite grain fragments differs insignificantly. At the same time, dolomite from a rock patch (from the Seligdar deposit) enriched in fragments of apatite grains shows $\delta^{13}C$ and $\delta^{18}O$ values higher than those of dolomite from a rock with rare apatite fragments, which rules out regarding the carbonate cement as newly formed material.

It follows that the isotopic analysis of carbonates in a whole-rock sample makes it possible to discern a general tendency in the formation of the carbonate rock and the character of its possible later transformations, while the microanlysis of individual grains enables one to determine their heterogeneity degree and to evaluate the scale of these transformations.

DISCUSSION

The data-point fields of different types of carbonate rocks from the Aldan Shield (Fig. 2) define a trend from the highest positive $\delta^{13}C$ and $\delta^{18}O$ values of the apatite–carbonate rocks to the lowest $\delta^{18}O$ and negative $\delta^{13}C$ values for the skarns. The intermediate fields of marbles and calciphyres partly overlap. Taking into consideration the analogous character of the $\delta^{13}C$ and $\delta^{18}O$ variations depending on the degree of metasomatic

Table 4. Isotopic composition of individual carbonate grains in different types of carbonate rocks from the Aldan Shield

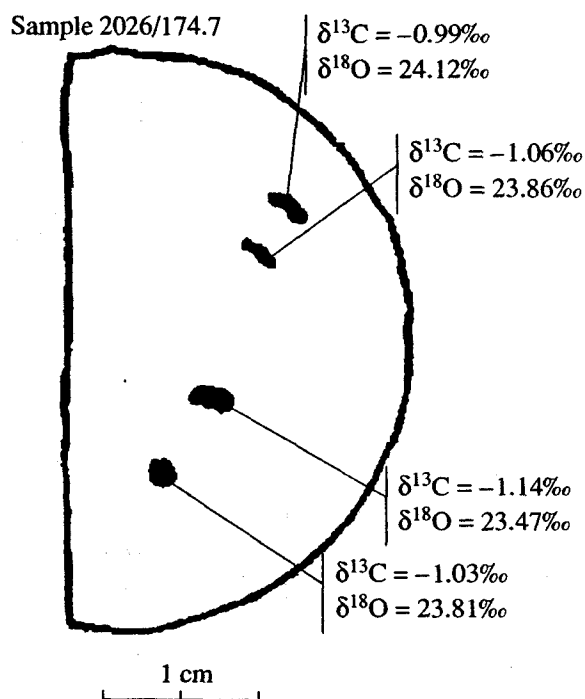| Sample	Prospect	Rock, composition (%)	Isotopic composition	
			$\delta^{13}C$, ‰ PDB	$\delta^{18}O$, ‰ SMOW
1-M	Medvedevka	Marble (calcite = 99, graphite = 1)	–1.7…+1.6	+14.0…+15.0
2026/174.7	Sivagli	Marble (calcite = 95, serpentine, chlorite = 5)	–1.1…+1.0	+23.5…+24.1
410/1062	Seligdar	Apatite–carbonate rock (dolomite = 91, apatite = 9)	–0.5	+18.4
23/1567	Seligdar	Apatite–silicate–carbonate rock (ankerite = 31, apatite = 14, chlorite = 55)	+3.6…+3.8	+18.3…+18.4
64/428.2	Seligdar	Apatite–sulfate–carbonate rock (ankerite = 87, apatite = 9, gypsum = 4)	+1.4…+1.4	+20.0…+20.4
2831/44	Chukurdan	Apatite–carbonate rock (dolomite = 55, apatite = 45)	+4.9…+5.5	+18.8…+19.7
3/A2542	Niryandzha	Apatite–carbonate rock rich in apatite fragments (apatite = 25)	+1.9…+2.0	+20.3…+20.8
3/B2542	Niryandzha	Apatite–carbonate rock poor in apatite fragments (apatite = 10)	+2.0	+21.1

Sample 2026/174.7

$\delta^{13}C = -0.99‰$
$\delta^{18}O = 24.12‰$

$\delta^{13}C = -1.06‰$
$\delta^{18}O = 23.86‰$

$\delta^{13}C = -1.14‰$
$\delta^{18}O = 23.47‰$

$\delta^{13}C = -1.03‰$
$\delta^{18}O = 23.81‰$

1 cm

Fig. 3. Isotopic composition of individual carbonate grains in marble from the Sivagli deposit.

(a)

Sample 23/1567

$\delta^{13}C = 3.76‰$
$\delta^{18}O = 18.33‰$

$\delta^{13}C = 3.60‰$
$\delta^{18}O = 18.34‰$

$\delta^{13}C = 3.78‰$
$\delta^{18}O = 18.39‰$

1 cm

(b)

Sample 64/428.2

$\delta^{13}C = 1.44‰$
$\delta^{18}O = 20.16‰$

$\delta^{13}C = 1.38‰$
$\delta^{18}O = 19.97‰$

$\delta^{13}C = 1.38‰$
$\delta^{18}O = 20.39‰$

$\delta^{13}C = 1.35‰$
$\delta^{18}O = 20.27‰$

1 cm

Fig. 4. Isotopic composition of individual carbonate grains in (a) apatite–silicate–carbonate rock and (b) apatite–sulfate–carbonate rock from the Seligdar deposit.

transformations of the pristine carbonate and calc–silicate rocks during skarn development, as was determined previously at several skarn occurrences [5, 10, 12], the least altered of our rocks should be those composing stratiform and lenticular bodies. Their high $\delta^{13}C$ and $\delta^{18}O$ values were inherited from their sedimentary protoliths and remained unchanged during the regional metamorphism on the scale of a mineral, hand specimen, and rock outcrop. They could be modified and decreased only locally in the course of diagenesis, during interaction with surface waters, or owing to metasomatic alterations under the effect of deep CO_2 enriched in the ^{12}C isotope, in compliance with the classic scheme for the development of magnesian skarn [10, 11].

Judging from their geologic and tectonic setting, mineralogical and petrographic characteristics, and carbon and oxygen isotopic composition, the stratiform and lenticular bodies of carbonate rocks in the shield are of sedimentary genesis and differ only slightly from other similar Precambrian and Phanerozoic carbonate rocks [24–32]. The apatite–carbonate rocks differ from the others in that they have high $\delta^{13}C$ and $\delta^{18}O$ values, which are typical of normal sedimentary marine carbonates [24, 30, 31] or lacustrine rocks [32].

The anomalously high concentrations of ^{13}C in some varieties of the apatite–carbonate rocks are comparable with those of Precambrian carbonate rocks of the Lomagundi Group in Zimbabwe [24], Caraiba Complex in Brazil [25], Jatulian rocks of the Kola Peninsula [26] and Karelia [27, 28], and the Oasis marbles in Queensland [29], whose genesis is reportedly related
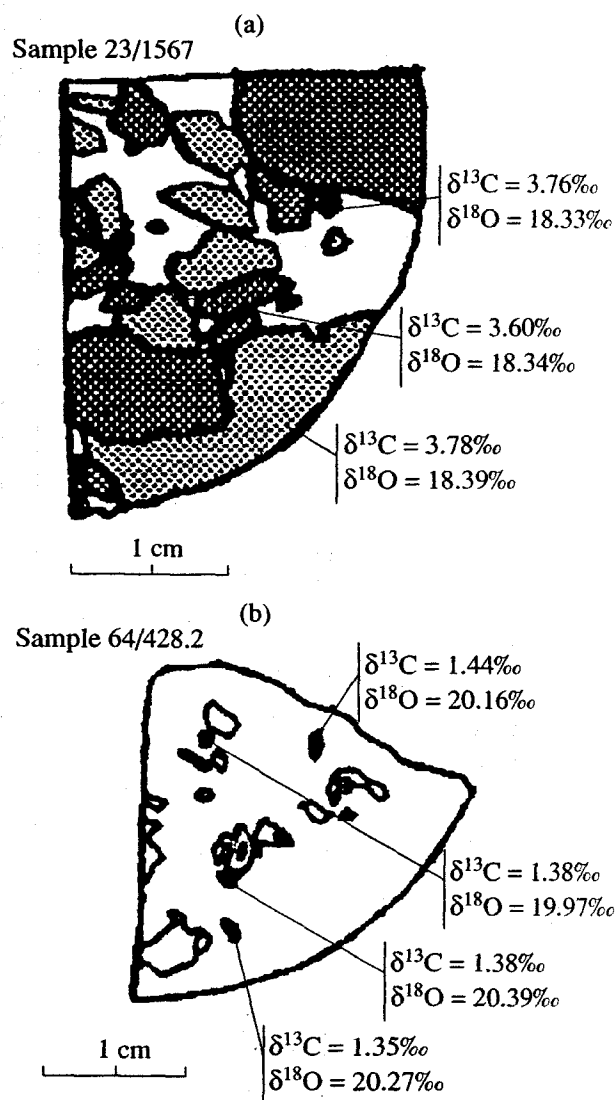
to sedimentation in hypersaline ancient basins, a process associated with an enrichment in the heavy ^{13}C isotope.

The evaporitic character of the protolith of the Aldan apatite–carbonate rocks is confirmed by numerous finds of gypsum and anhydrite in these rocks. Considering the lenticular and stratiform morphology of their bodies, which often branch and generally have insignificant and variable thicknesses and extensions, it is realistic to propose that the protolithic rocks were most probably formed in isolated basins resembling lagoons or salt lakes [24, 31, 32], which existed as closed physicochemical systems with a limited inflow of water and salts. The sedimentation environment was oxidizing, as follows from the high Fe^{3+}/Fe^{2+} ratio of the rocks and the ubiquitous occurrence of hematite in the absolute absence of sulfides and graphite [21].

When the protolith of the apatite–carbonate rocks was produced, the stability fields of the carbonates and their precipitation order were determined by the pH and the bulk CO_2 concentration [21, 33]. In the case of equal activities of cations in the mineralizing environment in a closed physicochemical system, carbonates should have crystallized in the succession siderite $\longrightarrow$ dolomite $\longrightarrow$ magnesite $\longrightarrow$ calcite, although the development of the real protolithic mineral assemblages in an oxidizing environment starts with the crystallization of dolomite (but not siderite, which crystallizes under reduced conditions). This mineral binds the bulk of the Mg and part of the Ca in the system. Other minerals among the first to crystallize are hematite and, if the system contains P and the F activity is high enough, also apatite. Thus, magnesite can appear in this system only if Mg is in excess, siderite crystallizes if Fe is in excess, and calcite is precipitated if enough Ca remains after dolomite and apatite crystallization.

The systematic enrichment of the ^{12}C and ^{16}O isotopes in the carbonates during their crystallization in the protolith of the apatite–carbonate rocks was identified in the succession from the early dolomite in association with apatite to the late dolomite, calcite, siderite, and magnesite (Table 3).

The similar distribution character of the $\delta^{13}C$ and $\delta^{18}O$ values within texturally and structurally analogous rock volumes, as was determined by our microscale study, testifies to a highly conservative carbon dioxide regime during the crystallization of the carbonates.

At the same time, the locally observed $\delta^{13}C$ and $\delta^{18}O$ variations (Fig. 5) may characterize carbonates that crystallized in systems with a locally varying CO_2 regime. The differences between the mineral compositions of the apatite–carbonate rocks *per se* and their varieties that are high in silicates at the Chukurdan prospect (Fig. 5) were caused by the differences in their paleofacies, with the heterogeneous distribution of the isotopes most probably reflecting the boundary between the facies.

The inflow of freshwater and salt portions into the paleobasin disturbed equilibrium in the physicochemical system and brought about the development of calcite and dolomite pockets and veinlets with $\delta^{13}C$ and $\delta^{18}O$ values lower than those of the early carbonates. A similar carbon and oxygen isotopic composition was determined in carbonates both related to postsedimentation alterations [31, 34, 35] and developing in the course of erosion and redeposition in continental environments under the effect of surface waters [36, 37], which makes it difficult to distinguish between the two types. Inasmuch as it is hard to imagine the development of a carbonate rock without diagenetic or catagenetic transformations, we believe that the late carbonates, which are mostly restricted to bodies of apatite–carbonate rocks, were produced by postsedimentation processes, while carbonate veins cutting them and
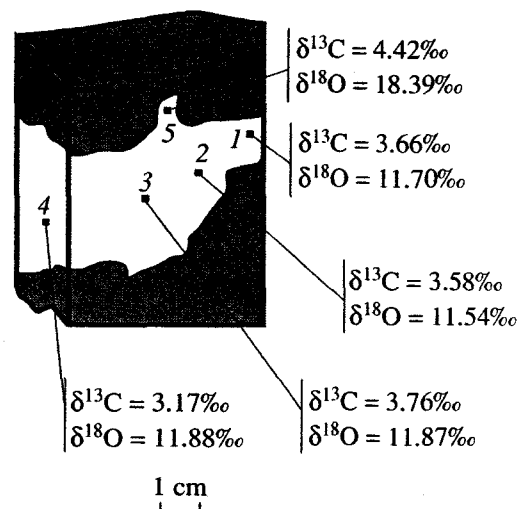

Fig. 5. Isotopic composition of individual carbonate grains in an apatite–carbonate rock from the Chukurdan deposit.

obviously spatially separated from the primary rocks were produced by surface waters. Judging by the limited development of newly formed carbonates, both processes were not very extensive, and the masses of the newly formed phases are incommensurably smaller than the masses of the unaltered material.

The close spatial association of apatite deposits with carbonate rocks suggests that the factors controlling the origin of these rocks were also favorable for phosphorus accumulation. The occurrence of apatite grain fragments in the apatite–carbonate rocks indicates that they were produced by the terrigenous–chemogenic accumulation of phosphorus [21, 33]. The similar carbon and oxygen isotopic composition of dolomite from rock volumes that are rich and poor in clastic apatite suggests that the chemogenic and terrigenous–chemogenic rocks were deposited under similar physicochemical conditions. Hence, the differences between the apatite contents in the rocks were controlled by the amounts of phosphorus in the primary sedimentation basins.

Most of the marbles and calciphyres also show a homogeneous distribution of $\delta^{13}C$ and $\delta^{18}O$ values. Taking into account this fact and the high resistibility of marbles to metamorphic transformations [38], it is reasonable to suggest that both the marbles and the apatite–carbonate rocks largely preserved the signatures of the paleofacies conditions of their protolith. Along with $\delta^{13}C$ and $\delta^{18}O$ values typical of marine carbonates, they sometimes exhibit anomalously high $\delta^{13}C$ and $\delta^{18}O$, which were earlier documented in the Sutam block [39], in high-grade regionally metamorphosed carbonate rocks. The relative enrichment of the marbles and calciphyres in the light ^{12}C isotope, the graphite admixture with low $\delta^{13}C$ usually contained in them, and the common occurrence of sulfides at a low Fe^{3+}/Fe^{2+} ratio [21] indicate that their protolith was produced in a

reduced environment, a feature that makes these rocks different from the apatite–carbonate rocks.

The genesis of skarn bodies is related to large-scale deep-seated transformations of the country rocks [10]. Usually, they geologically clearly demonstrate spatial and genetic relations to magmatic rocks, and the fairly low $\delta^{13}C$ values of their carbonates definitely point to the determining role of CO_2 from a deep-seated source in their genesis [10, 11].

CONCLUSIONS

(1) The practically identical $\delta^{13}C$ and $\delta^{18}O$ values of carbonates in whole-rock samples and individual grains point to the same tendencies in the origin of each genetic type of carbonate rocks from the Aldan Shield. The apatite–carbonate rocks, marbles, and calciphyres preserve their premetamorphic isotopic signatures, which reflect the genesis of the sedimentary protolith.

(2) Later carbonates developed in close spatial and, often, genetic relations with the primary carbonate rocks. They were produced by postsedimentation alterations under the effect of surface waters and metasomatic processes, whose scale and direction can be inferred from isotopic, geological, and petrographic evidence.

(3) The highest $\delta^{13}C$ and $\delta^{18}O$ values were found in the apatite–carbonate rocks, whose protolith was produced chemogenically in shallow, most probably evaporitic basins, in a significantly reducing environment, at a limited inflow of terrigenous material. The amount of apatite in the protolith was determined by the phosphorus concentration in solutions of the primary sedimentation basins and the fractions of clastic apatite, which was produced by intraformation erosion and weathering of nearby apatite-bearing rocks.

The results of our microscale isotopic examination of carbonates are consistent with data on the whole-rock samples. Our microanalytical research indicates that the carbon and oxygen isotopic composition of the rocks shows local variations, which mark the pathways of fluids (regardless of their nature). These pathways were usually contact zones between carbonates and minerals coexisting with them. Since these zones are the most permeable, further systematic microscale isotopic studies should be focused on them.

ACKNOWLEDGMENTS

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