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**ISOTOPE COMPOSITION OF GREISEN CARBON DEPOSITS (KALGUTINSK DEPOSIT)**

A.A. Potseluev, D.I. Babkin, A.G. Talibova\*

Tomsk Polytechnical University

\*Institute of Geology and Mineralogy Siberian Branch of the Russian Academy of Science, Novosibirsk city

E-mail: poan@ign.tpu.ru

*Isotope composition of graphite carbon in the main industrial vein and near-vein greisens of the Kalgutinsk rare-metal deposit (Mountainous Altai) has been studied. Formation of graphite is connected with allocation of carbon during partial oxidation of primarily restored ore-forming metal-bearing fluid. The content of  $C_{org}$  in a vein – 0,036 %, in greisens – 0,022 %. Carbon is characterized by «light» isotope composition,  $\delta^{13}C_{org}$  in a vein – 23,9 ‰, in greisens – 25,3 ‰. The «weighting» of the element upwards on revolt of the vein, which is explained by fluid evolution, is revealed. Regular fractionation of isotopes in the system vein – near-vein greisen is established. Isotope fractionation varies in vein's sections, differs by capacity and content of ore components. The conclusion is drawn on homogeneity and the deep nature of carbon.*

**Introduction**

Last years the convincing geological data has been obtained, showing significant, and in some cases prevailing influence of nuclear-mantle processes on evolution, magma and ore formation within the limits of large continental blocks at certain stages of their development [1–4]. One of the objects, where these processes had showed contrastly enough, is the Kalgutinsk rare-metal deposit (Mountainous Altai). During its formation the influence of a deep fluid accrues and reaches its maximum during formation of mineral associations of the mineral-forming main stage [5].

The major agents of the deep fluid are various compounds of carbon, including organometallic. Thus, the question on the source of carbon is sharply debatable. In formation of ores of many endogenous deposits, localized in sedimentary and especially black-slates strata, carbon of bearing strata actively participates alongside with «deep». To estimate the role of various sources of carbon during ore-formation appears extremely difficult, also because of isotopes mixture.

Ore veins of the Kalgutinsk deposit are localized within the limits of rare-metal granites massifs, breaking through effusives' strata of the middle-Devonian age, united into the same volcano-plutonic depression. The executed researches allow considering geological formations of the deposit as development products of unified evolable fluid-magmatic system [6, 7]. The proof of it is the proximity of absolute age, the geochemical characteristic of geological formations and the analysis of correlational relations of geochemical spectra. Thus, it is possible to exclude sedimentary strata substance influence within the limits of accessible depths on formation processes of the Kalgutinsk greisen deposit.

In composition of deposit rear-metal veins, various forms of virgin carbon from amorphous (fullerene-like) up to crystal (graphite) [8] have been revealed. In grains of graphite high content of sidero- and chalcophile metals is fixed, including Au, Ag, Te, Bi, Hg, etc. At the same time, the distribution of precious-metal mineralizations (Au, Pt, Pd) in ore veins is co-ordinated to  $C_{org}$  distribution [9]. By detailed mineral-geochemical researches it is established that occurrence of virgin forms

of carbon and precious metals is caused by peculiarities of composition evolution of primarily restored metal-bearing fluid in conditions of partial oxidation in the field of ore deposition [10, 11].

The main purpose of work is the studying of graphite nature according to research data of carbon isotopes and their fractionation in veins and deposit near-vein greisens.

**Researches technique**

Researches has been done within the limits of the basic industrial vein 87 on three accessible to studying adit horizons 18 (the bottom horizon), 19, 20 (the top horizon). The distance between horizons makes approximately 60 m. The test has been executed by the furrow method, the vein and near-vein greisens have been separately tested.

The content of carbon has been defined by coulometric titrations method in the laboratory of LIMA SSRIGandMM (lab. manager T.E. Chujkova). The absolute error of definition of the element content has made 0,01 %.

During realization of isotope researches the additional sample-preparation has been done. In connection with the low content of organic carbon ( $C_{org}$ ) additional measures on elimination of carbonate impurity, which in small amounts meets in composition of late mineral associations, have been taken. Samples (part of the initial sample with the mass of 0,1...1,0 g) have been heated up in 6 % HCl solution at temperature 50...80 °C. Then samples have been washed by tridistilled water and dried up.

Isotope composition  $C_{org}$  has been defined in the laboratory of isotopes geochemistry of the Institute of geology and mineralogy of the Siberian Branch of the Russian Academy of Science (lab. manager V.A. Ponomarchuk) on weights-spectrometers MAT 253 made by Thermo company, at pressure  $1,5 \cdot 10^{-4}$  Pa with use of sample-preparation line on-line – ConFloIII + Flash EA in a constant stream of helium 90...95 ml/min. The temperature of the oxidizing reactor (reactant – CuO) made 900...950 °C, and regenerative (reactant metal copper) – reached 680 °C. The supply of oxygen has been carried out during 3 sec. at a stream of 110 ml/min.

The control of measurements accuracy has been carried out with application of the international standards, values of which during analytical work process were the following: for NBS 222 (oil)  $\delta^{13}C_{VPDB} = -29,7 \text{ ‰}$ , an error (at number of samples  $N=14$ )  $0,08 \text{ ‰}$ , and for USGS 24 (graphite)  $\delta^{13}C_{VPDB} = -16 \text{ ‰}$ , an error (at  $N=10$ )  $0,5 \text{ ‰}$ .

**Main results**

The obtained estimations of  $C_{org}$  content in the vein, near-vein greisens and its isotope characteristics are shown in tab. 1. Average  $C_{org}$  content in the vein makes  $0,036 \pm 0,006 \text{ ‰}$ , at the same time, significant variations of concentrations from 0,02 up to 0,12 % are noticed. It is necessary to note that in separate concentrates of ore minerals the content of the element reaches 0,34 %.

Natural changes of the element content in the vein plane (fig. 1) are marked. From the central part of the bottom horizon where its maximal concentration (0,12 %) is marked, the content of the element stably decreases upwards and to flanks of the vein. Such character of distribution testifies to natural participation of carbon in the process of ore-formation, which also has been confirmed by studying of fluid inclusions [10]. Generalized characteristics on horizons show that with depth the concentration  $C_{org}$  stably increases from 0,024 up to 0,048 % (table 1, fig. 2).

In near-vein greisens  $C_{org}$  content is considerably lower than in the vein and amounts to  $0,022 \pm 0,002$ . Practically in all samples element's content corresponds to the bottom limit of detection (0,02 %) and only in one of the samples it makes 0,04 % (fig. 1). Accordingly it is possible to make the conclusion that the essential change with depth content  $C_{org}$  in near-vein greisens has not been established.

**Table 1.**  $C_{org}$  content and its isotope characteristic in the vein 87 and near-vein greisens

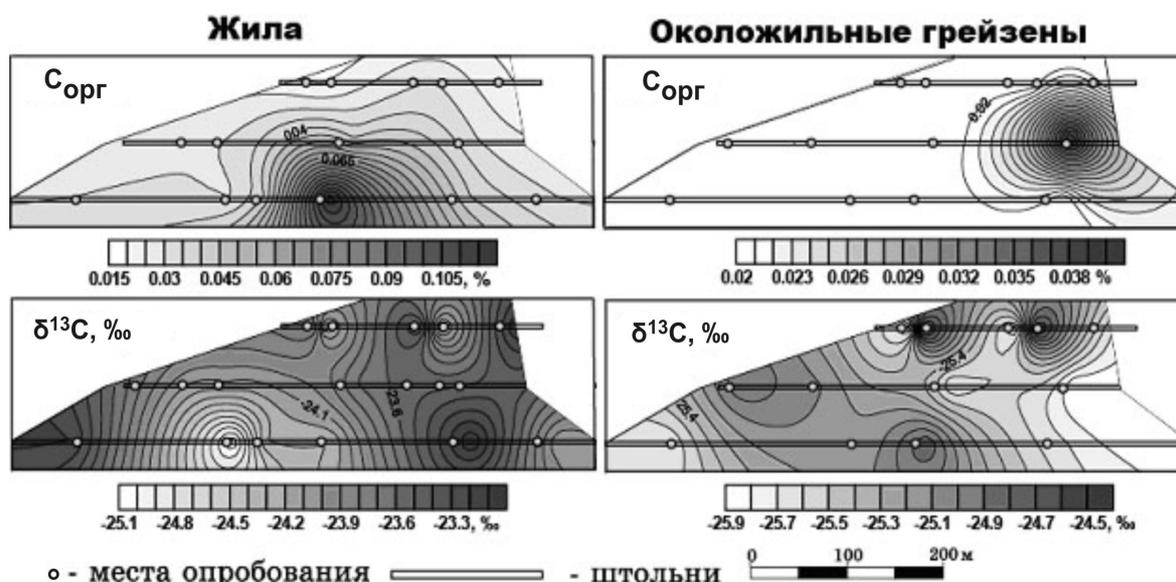
Horizon	Vein 87			Near-vein greisens		
	Quantity of samples	$C_{org}, \%$	$\delta^{13}C_{org}, \text{‰}$	Quantity of samples	$C_{org}, \%$	$\delta^{13}C_{org}, \text{‰}$
20	5	$\frac{0,024}{0,02..0,03}$	$\frac{-23,7}{-24,3..-23,1}$	5	$\frac{0,020}{0,02..0,02}$	$\frac{-25,2}{-25,8..-24,4}$
19	4	$\frac{0,033}{0,03..0,04}$	$\frac{-23,9}{-24,1..-23,5}$	4	$\frac{0,025}{0,02..0,04}$	$\frac{-25,4}{-25,9..-24,9}$
18	6	$\frac{0,048}{0,03..0,12}$	$\frac{-24,0}{-25,1..-23,0}$	4	$\frac{0,020}{0,02..0,02}$	$\frac{-25,4}{-25,7..-24,8}$
Average	15	$\frac{0,036}{0,02..0,12}$	$\frac{-23,9}{-25,1..-23,0}$	13	$\frac{0,022}{0,02..0,04}$	$\frac{-25,3}{-25,9..-24,4}$

Note. The numerator – average, the denominator – minimal and maximal content

$C_{org}$  in the vein and near-vein greisens of the Kalgutinsk deposit is characterized by «light» isotope structure.

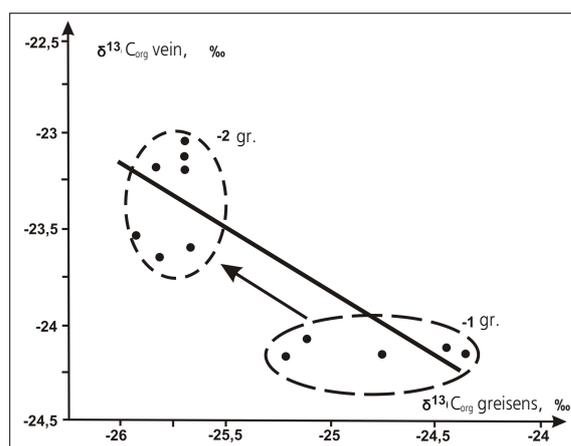
Volume  $\delta^{13}C_{org}$  in the vein changes in rather narrow range from  $-25,1$  up to  $-23,0$  and in average makes  $-23,9 \text{ ‰}$ . The analysis of  $\delta^{13}C_{org}$  change in the vein plane, shows that it has mosaic (nested) character and contrastly differs from  $C_{org}$  natural distribution. The steady tendency of «weighting» of  $\delta^{13}C_{org}$  average value on horizons upwards on revolt of the vein from  $-24,0$  up to  $-23,7 \text{ ‰}$  is planned (table 1).

In deposit near-vein greisens carbon is characterized by even more «light» composition than veins. The average size of  $\delta^{13}C_{org}$  makes  $-25,3 \text{ ‰}$  at insignificant fluctuations of extreme values from  $-25,9$  up to  $-24,4 \text{ ‰}$ . With depth the carbon isotopy in greisens varies slightly, but it is necessary to note weak «weighting» to the top horizon, similar to one that is observed in the vein.



**Fig. 1.** Change of  $C_{org}$  content and its isotope composition in the vein and near-vein greisens (projection to a vertical plane). Left column – vein; Right column – near-vein greisens. o – test areas; — – adits

The analysis of fig.1 shows that in greisens in a projection to a vertical plane, sections (linear zones) of changes  $\delta^{13}C_{org}$  are noticed, at the same time the character of change  $\delta^{13}C_{org}$  on a projection in greisens in certain degree is inverse in relation to distribution of isotopes in the vein. Dependence in the ratio of carbon isotopes in vein samples and interfaced to them samples of greisens is evidently expressed in fig. 2, which emphasizes the relation of carbon distribution character and its isotopes in the vein and near-vein metasomatites.



**Fig. 2.** The schedule of dependence between isotope characteristics  $C_{org}$  in samples of the vein and the interfaced samples of near-vein greisens. The arrow designates a direction of isotopes differentiation, other explanations are in the text

Two groups of samples are clearly singling out in the schedule. The first group is characterized by close values of average sizes  $\delta^{13}C_{org}$ , which make in the vein  $-24,3\text{‰}$ , and in greisens  $-24,8\text{‰}$  (table 2). The difference is minimal and makes  $0,5\text{‰}$ . In the second group of samples the average value  $\delta^{13}C_{org}$  in the vein is  $-23,4$ , and in greisens it is  $-25,8\text{‰}$ . The difference has increased up to  $2,4\text{‰}$ . At the same time, analyzing change dynamics of isotope characteristics between groups, it is necessary to emphasize that «weighting» of carbon in samples of veins on  $0,9\text{‰}$  is accompanied by «facilitation» of the element in greisens on a very close size  $-1,0\text{‰}$ .

**Table 2.** Mutual relation of various parameters of the vein and near-vein greisens in two sample groups, allocated by isotope characteristics

Parameters (average)	First sample group (5 pairs of samples)		Second sample group (7 pairs of samples)	
	Vein	Greisen	Vein	Greisen
Capacity, m	0,64	0,50	0,45	0,50
$C_{org}$ , %	0,048	0,020	0,030	0,020
$\delta^{13}C_{org}$ , ‰	-24,3	-24,8	-23,4	-25,8
W, %	1,66	1,35	0,91	0,12
Mo, %	0,162	0,146	0,042	0,051
Bi, g/t	1600	180	997	44
Be, g/t	405	65	10	9
Au, g/t	0,021	0,028	0,014	0,016
Ag, g/t	21,6	2,3	3,5	1,8

Parameters of the vein and greisens are essentially different in allocated groups of samples (table 2). The

first sample group characterizes sections of the vein with greater capacity. Here, both in the vein and in greisens, the content of the basic industrial components and precious metals is considerably higher.

#### Discussion and main conclusions

The content of carbon in veins and greisens of the Kalgutinsk deposit, on the one hand, corresponds to a clark of the element, but, on the other hand, is rather high in comparison to sour magmatic rocks and formations of deep (mantle) origins. So, in generalizing work [12] on the big actual material it has been shown that in overwhelming number of the studied samples of mantle ksenolites the total content of carbon makes  $<0,01\text{‰}$ . Thus, deposit veins and greisens are characterized by rather high content of carbon, which testifies to its active participation during ore formation.

Organic forms of carbon have been revealed in many magmatic formations and in products of high-temperature metasomatose, down to pegmatite formations [13]. With graphitization processes in particular, a number of researchers link it to accumulation of most metals, especially precious, which quite often reaches industrial scales [3, 4, 8, 9, 13–15].

Close to the data on the Kalgutinsk deposit carbon isotope parameters are noticed in many geological formations, in crust nature and connected with mantle processes. They are typical as a whole for the restored forms of carbon [16].

The analysis of great volume of representative data on mantle ksenolites [12] shows that in distribution of  $\delta^{13}C$  two intervals with strongly pronounced modal values  $-5$  and  $-25\text{‰}$  are allocated. At this, lower sizes ( $-25\text{‰}$ ) are typical for samples where carbon is present or extracted in the form of graphite. Lead by Deines P. research of graphites isotopes, allocated from minerals of rocks of «hot (hotspot)» (Hawaii) and «not hot (non-hotspot)» (Stromboli) points, has shown their «light» composition which in the first case makes  $-(29,4...25,0)\text{‰}$ , and in the second  $-(24,6...20,2)\text{‰}$ . At the same time, the author comparing graphites from clinopyroxenes and olivines, does a conclusion that the mineral structure of rocks essentially influences carbon isotopes. Similar isotope characteristics  $-(21,96...26,46)\text{‰}$  have been received by E.M. Galimov with colleagues [17] at studying the graphite disseminated in mantle silicate mass of rocks.

Noted tendency in change of carbon isotope on revolt of the vein is explained by conditions of graphite formation. As it has been shown earlier [10], graphite formation is caused by matriculation in primarily restored fluid of the limited oxygen quantity; therefore, the oxidation of hydrocarbons and increase in water concentration in the system has begun. Liberated carbon partially mixed up in carbonic acid and remained in the fluid, and has been partially allocated in the mineral phase (graphite), which has been accompanied by decrease in general concentration of carbon in the fluid. It can be presented in the form of development of non-equilibrium system – transition of the gaseous restored

forms of carbon (hydrocarbons) in gaseous oxide and solid graphite under the scheme:



In these conditions, according to known patterns, [18] fractionation of carbon isotopes occurs and lighter isotope collects in compounds where the element located in more restored condition, and heavier isotope collects in the oxidized forms. It is obvious, that isotope of the hydrocarbons, which have remained in a fluid, also changes and their subsequent oxidation leads to allocation of somewhere «heavier» graphite.

Fractionation of carbon isotopes has been noticed by researchers in various processes especially it is great in cases of carbon presence in the system in several forms (oxide, restored, solid, gaseous). In such way, in the work [17] on the example of mantle metasomatically changed rocks it has been shown that enrichment of graphite by light isotope relatively to equilibrium with it carbonate can make up to 17...23 ‰. Significant variations of carbon isotope have been marked in golden-ore quartz-vein zones of the Soviet deposit [20]. Here in various gold-bearing veins the change of  $\delta^{13}C$  fluid carbonic acid reaches 3,2...15,4 ‰, and between methane and carbonic acid of fluids the difference makes 38,2 ‰.

Relative enrichment of the Kalgutinsk deposit greisens by isotope  $^{12}C$  in relation to  $^{13}C$  is explained by its smaller mass (size), agreeably by greater mobility and better ability to penetration into lateral rocks in fluid structure on pores or due to diffusion.

The established differences in carbon isotope characteristics in vein sections with various capacity, find following explanations. Obviously, in vein sections with greater capacity there has been more active transport of metal-bearing fluids and accordingly more intensive allocation of ore mineralization. In vein sections with smaller capacity, as it has been underlined earlier [11], in quieter atmosphere the conditions of fluid «preservation» has been created, which promoted more expressed fractionation of carbon isotopes in the system vein – greisen. The second sample group represents vein sections where for the period of ore-formation there have

been more favorable conditions (probably longer time) for an output of «light carbon» in lateral rocks. It emphasizes the genetic unity of carbon isotope characteristics in veins and greisens.

Probably, in a similar way the fractionation of carbon isotopes in carbon-dioxide fluid took place, at formation of the Soviet golden-ore deposit [19]. Here, carbon (carbonic acid) «weighting» in the veins has also been noted, characterized by higher gold-bearing.

Thus, the results of the research of content and characteristics of carbon isotope specify the general source of the element and the unified nature of graphite in veins and near-vein greisens of the Kalgutinsk deposit. These data in aggregate with the received mineral-geochemical information [5, 8–11] confirm earlier drawn conclusion about the deep source of ore-forming metal-bearing fluids.

### Conclusions

During the executed researches:

- It has been established that carbon is characterized by «light» isotope structure,  $\delta^{13}C_{org}$  makes in the vein –23,9, in greisens –25,3 ‰;
- The tendency of carbon composition «weighting» upwards on revolt of the vein has been revealed;
- Natural isotope fractionation in the system vein – near-vein greisen has been noted, expressed in selective accumulation  $C^{12}$  in greisens at corresponding reduction of its content in the vein. Isotope fractionation varies on the vein sections, differing on capacity and content of ore components;
- It has been shown that data on geochemistry and carbon isotope in veins and greisens of the Kalgutinsk rare-metal deposit testify to its united source and confirm earlier drawn conclusion about its deep nature.

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## LITHOLOGIC-PETROGRAPHIC FEATURES AND CONDITIONS OF REGIONAL CYCLITIS $J_{15}$ ROCK FORMATION, REVEALED BY PARAMETRICAL WELL 1<sup>st</sup> OF WESTERN-TOMSK AREA

E.N. Osipova, A.V. Ezshova, N.M. Nedolivko, T.G. Perevertailo, E.D. Polumogina

Tomsk Polytechnical University  
E-mail: ezsovaav@ngf.tomsk.ru

*The implemented lithologic-petrographic researches have shown that formation of regional cyclitis  $U_{15}$  rocks, revealed by the parametrical well 1 of the Western-Tymusk area (Tomsk region), occurred during two alternating transgressive cycles, features of which are reflected in lithological structure of lower and upper zonal cyclitis. Inclusions of glauconite and chlorite, organic fossils, faunae, various stratification, washout and redeposition traces of underlying sediments indicates the formation of the studied strata in shallow marine basin with an active hydrodynamic mode.*

The detailed lithologic-focal analysis of the core selected in the parametrical well 1 of the Western-Tymusk area, has been conducted with the purpose of an establishment of construction peculiarities and formation conditions of the Jurassic and Cretaceous deposits, not enough studied in the northwest part of the Tomsk region.

Regional cyclitis  $J_{15}$  (the Aalenskiy stage) has been revealed in the interval of depths of 3141...3072 m. In its basis lie conglomerates (fig. 1) and the gravel-sandstones containing polycomponental pebble and gravel, consisting of quartz, effusives, siliceous rocks, clay slates, etc. The psephitic material is well rounded, and focused in layers. Cementation of pebble and gravel has been carried out by the sandy matrix which is implementing a role of basal cement. Such conglomerates called basal (extraformational), they begin a new cycle of precipitation accumulation.

In primary cyclitis volume homogeneous medium-grained sandstones prevail. Thin faltering and threadlike lamination is periodically marked: horizontal, flatly-waived, poorly inclined, sometimes wedge-shaped caused by an alluvium of carbon detritus and micas on

planes of stratification. Sometimes low-power (few sm) prolayers of clay-siltstone structure appear. Layered character of deposits is emphasized by identical level-by-level orientation of flat informational pebble siderite and clay rocks (fig. 2).

Unlike basal of pebble conglomerates lying in the cyclitis basis, the pebble of intraformational conglomerates has been presented poorly by rounded fragments of the dim sedimentary strata. Such conglomerates occur in the cyclitis basis, both regional and finer character – zonal and local. As a rule, slanting types of stratification are connected with the same streaks.

Sandstones have large charred vegetative rests, fragments of wood, inclusion of coal material, prints of stalks and large leaves of plants. More often they are dated to interbed with intraformational washout.

In the cyclitis upper part the infringement of stratification has been noted: microdumps, sliding, laminae contortion, dim lenses of aleurolites. In fig. 3, microshifts in the sample of the core presented by grey aleurolite with clay light-grey layers are clearly visible.