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S.A. Sadykov

Institute of Mineralogy UB RAS, Miass, Russia; sadykov1965@gmail.com

MAGNETIC FIELD EFFECT ON FRACTIONATION OF CARBON ISOTOPES IN THE REACTION OF Ca(OH)₂ WITH AIR CARBON DIOXIDE

Проведена серия экспериментов по изучению влияния магнитного поля на изотопный состав углерода в карбонате кальция, образующемся при взаимодействии $Ca(OH)_2$ с углекислотой воздуха. Изучение изотопного состава углерода образцов $CaCO_3$, синтезированных в магнитном поле и вне поля, показало, что под воздействием магнитного поля происходит обогащение карбоната кальция изотопом ^{13}C. Различия в величинах $\delta^{13}C$ достигает 14 ‰, PDB. Область максимального обогащения тяжелым изотопом углерода располагается там, где магнитное поле имеет максимальную напряженность. Вне зависимости от величины напряженности магнитного поля все изученные образцы имеют существенно облегченный изотопный состав по сравнению с изотопным составом углерода в углекислом газе атмосферы.

The nuclear spin (magnetic) isotope effect was discovered by A.L. Buchachenko and coworkers in 1976 [Buchachenko et al, 1976]. In the present work, we revealed for the first time the magnetic field effect on the carbon isotope composition in the course of formation of an inorganic compound, calcite $CaCO_3$. The experiments on studying the magnetic field effect on the carbon isotope fractionation during formation of calcite were carried out by the following scheme.

$$CaCO_3 \rightarrow CaO + CO_2 \uparrow \rightarrow CaO + H_2O \rightarrow Ca(OH)_2 + CO_2(air) \rightarrow CaCO_3.$$
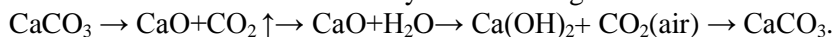
In all experiments, two plates with calcium hydroxide were used simultaneously. One of them was placed in the magnetic field, another, control one, was out of the field. The plates were disposed perpendicular to Earth's magnetic field.

In the first run, the plate with $Ca(OH)_2$ was placed in the field of a permanent magnet, which was located on the edge of the plate. The isotopic compositions at different distances from the magnet were determined in 500 h. The $\delta^{13}C$ values at distances equal to 0.5, 1, and 2 cm from the magnet were –22, –26, and –27‰, respectively. The isotopic composition of $Ca(OH)_2$ on the control plate was $\delta^{13}C = -26.65‰$, PDB. A similar result was obtained when $Ca(OH)_2$ was applied to a steel plate not exposed to the magnetic field.
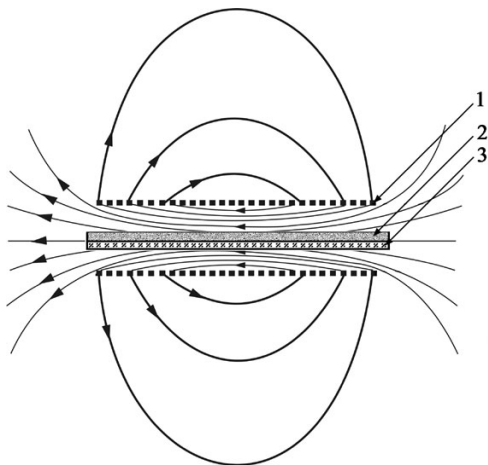
Fig. 1. The scheme of the experiment in the coil. Directions of the magnetic field strength are shown by arrows. Designations: (1) coil rings, (2) Ca(OH)$_2$ layer; (3) glassplate.

In the second run, a glass plate with dimensions of 90 ? 15 mm uniformly covered with Ca(OH)$_2$ obtained from the limestone was placed inside a DC coil 70 mm in length and 15 mm in inner diameter (Fig. 1). The plate with a sample was arranged along the coil axis and parallel to the solenoid magnetic field. The magnetic field strength inside the coil was 8700 A/m (110 Oe). The sample was kept in the solenoid field for 500 h. The isotopic composition of carbon on this plate was determined in 5 mm increments in the direction parallel to the coil magnetic field. The average values $\delta^{13}C$, PDB, obtained at the plate edge (coil south pole) and at a distance of 50–60 mm from the plate edge were – 29.18 and –21.33 ‰, PDB, respectively; and the isotopic compositions at the points to the right and to the left from the latter point changed in favor of ^{12}C (Fig.2, curve 1). At the opposite edge (North Pole), $\delta^{13}C$ = –26.24‰, PDB. In the control experiment, at the plate without the magnetic field, $\delta^{13}C$ = –26.55‰, PDB.

To exclude the influence of admixtures, which can be present in limestone, all further experiments were carried out with calcium carbonate of reagent grade.

A sample of calcium hydroxide prepared from CaCO$_3$ of reagent grade was kept in the coil (the magnetic field strength of 8700A/m) for 500 h. The value of $\delta^{13}C$ for the control plate was –35.22 ‰, PDB. The isotopic compositions ($\delta^{13}C$) determined at the plate placed in the magnetic field were as follows: –28.47 and –28.73‰, PDB, at the edges of the plate, and –17.62 ‰, PDB, at a distance of 40 mm from the south pole of the coil. In the opposite directions from this point, an increase in the ^{12}C concentration was observed. The maximum difference between the ratios $^{13}C/^{12}C$ at the plate edge and at the points distant from the edges amounts to 11‰ at a distance of 50 mm. The carbon isotopic compositions along the profile of sampling are shown in Fig. 2, curve 1. The $\delta^{13}C$ value in the control experiment was –35.64 ‰, PDB.

In the third run, the sample was kept in the magnetic field with the magnetic field strength of 4350 A/m for 770 h. After this exposure, 18 probes 5 ? 15 mm in size were sampled. The plate was arranged parallel to the solenoid axis. The carbon isotopic compositions along the profile of sampling are shown in Fig. 2, curve 2. The $\delta^{13}C$ value in the middle of the plate was –20.69 ‰, PDB. In the control run, in the absence of a magnetic field, the value was equal to – 35.61 ‰, PDB. The different $\delta^{13}C$ values in the second and third runs were due to different degrees of conversion of calcium hydroxide into CaCO$_3$ over the experiment time. The conversion was no more than 30% for experiment durations within 500–700 h.

The formation of calcite in all experiments is accompanied by an increase in the ^{12}C content compared with the isotopic composition of air carbon dioxide. However, the enrichment of CaCO$_3$ with ^{13}C isotope in the magnetic field is larger by 14% than in the runs without magnetic field.

In the fourth run, the sample was kept in the magnetic field with the magnetic field strength of 1750 A/m for 672 h. The carbon isotopic compositions along the profile of sampling are shown in Fig. 2. The $\delta^{13}C$ value have 2 minimum (– 29.60 and – 29.77 ‰; PDB). A distance is between minimums 45 mm (Fig. 2, curve 3). A deployment don't have well-marked from sampling points. The difference is between the values equal to 2.7 ‰; PDB. This is a heavy isotope ^{13}C enrichment is not located in the middle of the coil with a current. In this case, the magnetic field has a limit, at which there are noticeable changes in the isotopic composition of carbon. On further reduction of the strength of the current in the coil already practically there will be no nuclear isotope effect. But, and this value of the magnetic field there is still enrichment isotope ^{13}C of the newly formed CaCO$_3$. The $\delta^{13}C$ value in the control experiment was – 36.00 ‰, PDB.

In 5-th experiment study the formation of calcite occurred in the coil without input (0 A). The experiment was run for 1008 h. In the control experiment value is $\delta^{13}C$ = – 35.54 ‰; PDB. Control plate was located in another room. Profile isotopic composition is presented in Fig. 3, curve 4. This experiment was conducted to determine the additional factors that could change the isotopic composi-
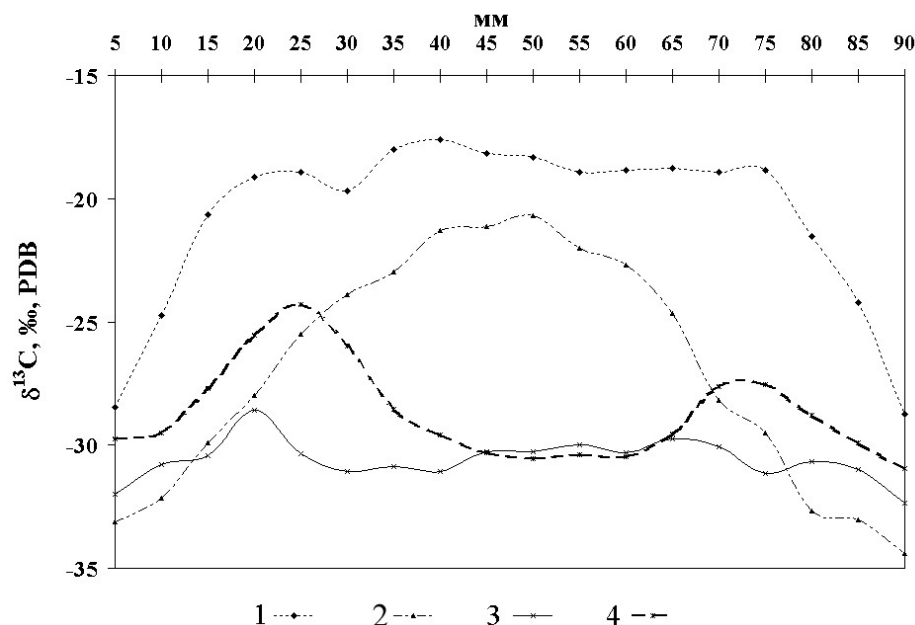
Fig. 2. Profiles of the isotopic composition of carbon in $CaCO_3$ formed in the solenoid magnetic field: 1 – the value of $\delta^{13}C$ in 2 experiment; 2 – value $\delta^{13}C$ in 3 experiment; 3 – the value $\delta^{13}C$ in 4 experiment; 4 – the value $\delta^{13}C$ in 5 experiment.

tion of carbon. There are two areas which were enriched with the heavy isotope ^{13}C, on the profile of the isotopic composition of carbon, as in previous experience. The distance between these points is equal to 50 mm, This distance is approximately equal to the length between the entries in the coil. Between are the terminals of the coil, the distance is 52 mm. They are made of steel, which is in the process of the electric current passing is magnetized. Accordingly, there is residual magnetic field, which affects the carbon isotope composition in 4 and 5 experiments. Where residual magnetic field has almost no effect, carbon isotopic compositions do not differ by more than 1 ‰; PDB.

The main difference is in the reaction of $CaCO_3$ at the interaction of $Ca(OH)_2$ with carbon dioxide air that no radical groups that are present in the photochemical reaction collapse of the dibenzylketone and subsequent recombination [Buchachenko, 2007; Galimov,1979]. It is known that two stable carbon isotope ^{12}C and ^{13}C have respectively zero and is half-integer spin. The oxygen isotopes ^{16}O and ^{18}O have zero spin, and isotope ^{17}O has spin equal to the 5/2 [Galimov,1979]. If to consider options for CO_2 molecule with different isotopes of carbon, the molecules $^{16}O^{13}C^{16}O$, $^{18}O^{13}C^{16}O$ and $^{18}O^{13}C^{18}O$ have is half-integer spin. In these molecules electrons are paired, and the electron spins are compensated, i.e. the total electronic spin is zero.

In the magnetic field of a molecule with half-integer spin behave as paramagnetic with the passage of the reaction, i.e. they have an additional component of the velocity in the thermal motion, which makes them move along the field lines. The direction of movement of molecules with half-integer spin along the lines of the magnetic field affects the probability of reaction of $CaCO_3$ with isotope ^{13}C. Maximum enrichment isotope ^{13}C is located in the middle of the coil with a current density of the magnetic field lines greatest experiments approximately.

Enrichment of the heavy isotope ^{13}C at the formation of $CaCO_3$ in a magnetic field is another factor that affects the isotopic composition of natural carbonates. In particular, in natural systems have magnetic minerals. Pyrrhotite and magnetite have its own magnetic field. Weakly magnetic minerals, acquire magnetic properties under the action of electric field. These minerals can change the isotopic composition of carbon in carbonates in sequential education. These changes will be localized around the magnetic minerals.

Another aspect of the manifestations of nuclear-magnetic effect may be holding paleomagnetic studies. You can imagine the Earth's magnetic field present in the form of a coil with electric shock. Proceeding from the above experiments, it is possible to change attitudes of stable isotopes of carbon $^{13}C/^{12}C$, spend paleomagnetic reconstructions. To conduct reconstruction requires a large amount of data on isotopic composition and careful selection of samples that should be strictly oriented.

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N.P. Safina[1, 2], **I.Yu. Melekestseva**[1], **N.N. Ankusheva**[1, 2], **A.M. Yuminov**[1, 2], **P. Nimis**[3], **V.A. Kotlyarov**[1]

[1] *Institute of Mineralogy UB RAS, Miass, Russia, safina@ilmeny.ac.ru*
[2] *National Research South Ural State University, Chelyabinsk, Russia*
[3] *Padova University, Padova, Italy*

BARITE FROM THE ANCIENT VMS-DEPOSIT AND MODERN HYDROTHERMAL SULFIDE FIELDS: A COMPARISON OF FORMATION CONDITIONS

В работе изложены результаты изучения минеральных ассоциаций, химического и изотопного составов, термобарогеохимических характеристик флюида, образовавшего барит из серноколчеданных колломорфных и обломочных руд палеозойского Сафьяновского месторождения (Средний Урал) и кайнозойских гидротермальных полей Семенов-1 и Семенов-3 (САХ).

В результате проведенных исследований установлены черты сходства и отличия процессов образования баритсодержащих минеральных ассоциаций в различных текстурных типах руд из разновозрастных колчеданных построек. В брекчиях, в отличие от колломорфных и тонкозернистых руд, отмечается сходство минеральных ассоциаций баритов. Отличия выявлены в содержании микропримесей, изотопном составе и параметрах флюида, образовавшего барит.

Barite is one of the widespread gangue minerals both in on-land volcanogenic-hosted massive sulfide deposits and submarine hydrothermal sulfide vent systems. The different formation conditions of barite are recorded in its morphology, chemical and isotopic composition, and fluid inclusions [Paytan et al., 2002], thus it may serve as an indicator of formation conditions of accompanying massive sulfides. This work presents the comparative study of barite from low-metamorphoused Devonian Saf'yanovka VMS-deposit in the Central Urals and Cenozoic Semenov-1 and Semenov-3 hydrothermal sulfide fields in the Mid-Atlantic Ridge. The mineral assemblage, chemical and isotopic composition, and fluid inclusions were analyzed in barite from colloform, fine-crystalline and clastic sulfides.

The barite-bearing ore samples from the Saf'yanovka deposit were collected from the main orebody in the operating open pit. The deposit hosted by rhyolitic–dacitic–andesitic–basaltic volcanic complex [Yazeva et al., 1991]. Based on the detail ore-facial mapping, the major subvertical triangle-shaped ore lens was reconstructed as a destroyed sulfide mound [Maslennikov, 2006]. The colloform pyrite ores with barite and quartz in the top of the sulfide body represent the fragments of seafloor hydrothermal slabs. The sulfide breccias and sandstones with clasts of massive and colloform ores and black smoker chimneys cemented by barite, quartz and, locally, by C-bearing silty sandstones are located in the southern flank of the main orebody.

Massive sulfides from the Semenov-1 and -3 hydrothermal fields were collected in the 30th cruise of the R/V *Professor Logachev* in 2007. The hydrothermal fields are the part of the large Semenov massive sulfide cluster [Beltenev et al., 2007]. The Semenov-1 field (13°30.87?N, 44°59.24? W) is situated near the seamount foot at a depth of 2570–2620 m. It represents a single mound or, more probably, a series of coalescent sulfide mounds and their destruction products [Ivanov et al., 2008]. The dredged samples included serpentinized ultramafic rocks, altered basalts, and massive sulfides, containing up to 20 vol % of barite. The Semenov-3 field (13°30.70?N, 44°55.00?W) is located on the northeastern slope of the seamount at a depth of 2400–2600 m and is associated with altered basalts [Beltenev et al., 2007]. Sulfide breccias with marcasite–pyrite clasts enclosed in the fine-grained sulfide–quartz cement were recovered from the seafloor.