ISSN 1028-334X, Doklady Earth Sciences, 2007, Vol. 413, No. 2, pp. 210–212. © Pleiades Publishing, Ltd., 2007.
Original Russian Text © D.P. Krylov, V.A. Glebovitsky, 2007, published in Doklady Akademii Nauk, 2007, Vol. 412, No. 5, pp. 679–681.

GEOCHEMISTRY

Oxygen Isotopic Composition and Nature of Fluid during the Formation of High-Al Corundum-Bearing Rocks of Mt. Dyadina, Northern Karelia

D. P. Krylov and Corresponding Member of the RAS V. A. Glebovitsky

Received October 2, 2006

DOI: 10.1134/S1028334X0702016X

The Al-oversaturated corundum-bearing rocks of high-grade complexes are characterized by unusual chemical composition (high contents of Al and Mg at relatively low Si contents), unique mineral assemblages (sapphirine, hogbömite, spinel, gedrite, and others), but their origin remains unclear at present. The main hypothesis is that they were formed through metasomatism of the host rocks under the influence of fluid filtration. The origin of the protolith and the role of fluids in the transportation of matter and transformation of mineral assemblages are the most important problems in the genesis of corundum-bearing rocks.

In this paper, the high-Al mineral assemblages were studied using oxygen isotopy. The target objects are corundum-bearing assemblages of Mt. Dyadina (northern Karelia), the host rocks of the Chupa nappe, and magmatic rocks at the contact with high-Al sequences.

The studied rocks are located in the Mt. Dyadina area (northern Karelia) within the Chupa nappe [1] of the Chupa metamorphic complex, of the southwestern Lapland–Belomorian belt [2]. The Chupa Complex is believed to be related to subduction and was formed under moderate-pressure granulite-facies conditions (2855 ± 5 Ma, U–Pb zircon dating [3]; T_{max} = 700–730°C up to 800°C, P_{max} 6–7 to 8 kbar [4, 5]). The second metamorphic stage was caused by collision at 2.73–2.71 Ma [1, 5]. The *PT*-path of this stage is traced from 800°C and 6 kbar with a further pressure increase up to 12–13 kbar (at T = 650–750°C) followed by decompression. The subsequent Svecofennian collision (1875 ± 5 Ma [6]) was accompanied by metamorphism that peaked at T = 590–600°C and P = 5.8–5.9 kbar [7]. The latter process is considered to be responsible for the formation of the high-Al mineral assemblages in the lenslike rocks at the contact of the Chupa Formation with amphibolized gabbroanorthosites [8].

The following samples were taken for study: (1) kyanite–garnet–biotite plagiogneisses of the Chupa Formation, which are the predominant rocks of the metamorphic complex of Mt. Dyadina; (2) unaltered and amphibolized two-pyroxene–plagioclase gabbroanorthosites.

The studied high-Al rocks are represented by the following assemblages: (3) garnet–tschermakite–plagioclase–corundum–biotite–staurolite–rutile–gedrite assemblage; (4) garnet–tschermakite–plagioclase–corundum–biotite–chlorite–rutile assemblage; and (5) garnet–chlorite–amphibole assemblage. They were taken from an area of approximately 50 × 20 m from the so-called axial zone [8], i.e., from the area with the maximum manifestation of fluid activity (table) during the formation of later parageneses.

The oxygen isotope ratios were determined with the conventional technique including decomposition of powdered samples (10–12 mg) by reaction with BrF_5 [9] and subsequent oxygen conversion in CO_2 on a hot coal in the presence of a Pt catalyst. The oxygen release relative to the calculated one was no less than 97–98% in each experiment. The isotope ratios were measured on a modernized MI-1305 mass spectrometer with an error no worse than 0.05‰. Each sample was analyzed at least twice (including sample decomposition), and the average error of values listed in the table was ±0.08‰ (1σ). All oxygen isotope ratios are shown in δ (‰) relative to VSMOW standard

$$\delta^{18}O_i \equiv \left[\frac{(^{18}O/^{16}O)_i}{(^{18}O/^{16}O)_{VSMOW}} - 1\right] \cdot 1000.$$

The systematic error was estimated with GIN-1 and NBS-28 standards. The latter standard was kindly given by S. Hoernes. In addition, we analyzed two samples with minimum values of $\delta^{18}O$ in the laboratory of Bonn University for control (samples were decomposed by purified F [10]). Since no significant deviations were

Institute of Precambrian Geology and Geochronology, Russian Academy of Sciences, nab. Makarova 2, St. Petersburg, 199034 Russia;
e-mail: dkrylov@dk1988.spb.edu

Oxygen isotope ratios in the rocks of Mt. Dyadina

Mineral	1	2	3	4	5	6	*A*	*B*
Wr	9.1 ± 0.7(5)	6.4 ± 0.4(4)	6.7 ± 0.2(2)	2.2 ± 0.7(3)	1.6 ± 0.3(2)	1.2		
Qtz	11.1 ± 0.9(5)						–3.7	4.1
Pl	8.4 ± 0.6(4)	6.8 ± 0.4(4)		4.2 ± 0.3(2)	3.3 ± 0.2(2)		–3.7	3.13–1.04*n*
Amp				2.4 ± 0.1(2)	1.9 ± 0.4(2)		–3.4	0.95
Bt	5.3 ± 0.5(4)			2.1 ± 0.5(3)	1.2 ± 0.6(2)		–3.1	0.41
Rt				–0.4	–1.6		–3.7	–0.68
Grt				1.8	1.1 ± 0.8(2)		–3.7	1.22
Opx		6.4 ± 0.4(3)						
Cpx		6.3 ± 0.5(3)					–3.7	1.35
Chl					–0.4	–0.5	–2.07	–1.34

Note: (1) Ky–Grt–Bt gneisses of the Chupa Formation; (2) gabbronorites; (3) amphibolized gabbronorites; (4–6) assemblages in high-Al rocks: (4) Grt–Ts–Pl_{32}–Crn–Bt–St–Rt–Ged; (5) Grt–Ts–Pl_{30}–Crn–Bt–Chl–Rt; (6) Grt–Chl–Amph. (*A, B*) Constants of isotope fractionation between a mineral and H_2O (Eq. (1), see text) [11]; (*n*) the anorthite content in Pl. Number of analyzed samples is shown in parentheses. Mineral abbreviations: (Amp) amphibole, (Bt) biotite, (Chl) chlorite, (Cpx) clinopyroxene, (Crn) corundum, (Ged) gedrite, (Grt) garnet, (Ky) kyanite, (Opx) orthopyroxene, (Pl) plagioclase, (Qtz) quartz, (Rt) rutile, (St) staurolite, (Ts) tschermakite, (Wr) whole-rock.

found, the table demonstrates the average values for all experiments.

The fractionation of oxygen isotopes between phases *i* and *j*, $\Delta_{ij} \equiv \delta^{18}O_i - \delta^{18}O_j$ is approximated by Eq. [11]

$$\Delta_{ij} = A_{ij}x + B_{ij}x^2, \quad (1)$$

where $x = 10^3/T$ (K) and A_{ij} and B_{ij} are constant for these two phases. In accordance with this ratio, it is convenient to show the results in the B_{ir} vs. $\Delta_{ij} - A_{ij}$ diagram, where *r* is the reference phase. The diagram has the following properties: (a) if several phases are in isotope equilibrium, the corresponding data points in the diagram (within the accuracy of the estimate of parameters *A* and *B* and experimental errors) are plotted in a straight curve, the slope of which is $10^6/T^2$; (b) if H_2O is taken as the *r* phase, the intersection of vertical axis at $B = 0$ corresponds to the oxygen isotopic composition of H_2O in fluid located in equilibrium with the minerals.

The table shows the results of oxygen isotope measurements in rocks and minerals. The isotope ratios in host gneisses vary from 8.7 to 10.1‰, which is within "normal" values for high-grade (metasedimentary) rocks [12]. Magmatic rocks (gabbronorites, amphibolized gabbronorites) also show uniform $\delta^{18}O$ values, which attest to deep-seated (mantle) sources insignificantly contaminated by crustal material. The amphibolized gabbronorites are close to unaltered varieties in oxygen isotopic composition, with an insignificant shift to an increase in $^{18}O/^{16}O$. At the same time, the high-Al rocks of Mt. Dyadina are characterized by unusually low $\delta^{18}O$ values (1.2‰).

Temperature variations obtained from oxygen isotope distribution between minerals (Fig. 1) of the corundum-bearing rocks (580–610°C) are within the errors of determination and coincide with temperature estimates for late stages of the formation of high-Al assemblages based on cation distribution between phases [8].

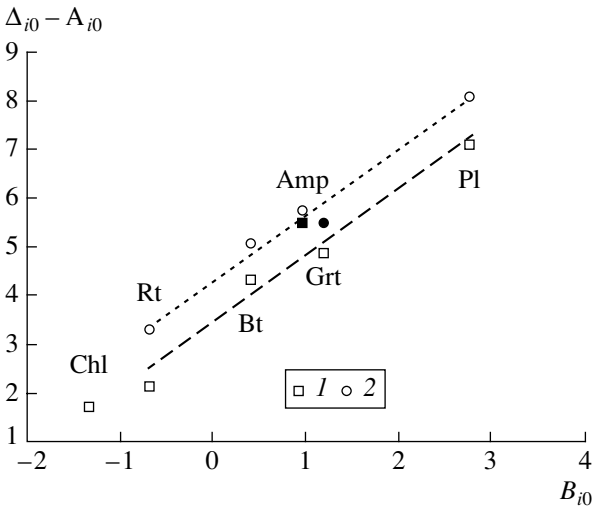

Fig. 1. B_{i0} vs. $\Delta_{i0} - A_{i0}$ diagram for the corundum-bearing rocks. Index o denotes fluid; *i* corresponds to the different minerals from assemblages (1) Cpx–Ts–Pl_{30}–Crn–Bt–Chl–Rt and (2) Grt–Ts–Pl_{32}–Crn–Bt–St–Rt–Ged (values of constants *A, B* and designations of phases are shown in the table). Filled symbols denote isotopically disequilibrium phases. Temperatures were calculated from the slope of regression lines. The method of temperature calculations using diagrams is given in text. (*1*) $y = 1.345_{\pm 0.08} + 4.27_{\pm 0.20}$, $T = 589\ _{\pm 50}$°C, (*2*) $y = 1.389_{\pm 0.06} + 3.19_{\pm 0.09}$, $T = 575_{\pm 40}$°C.

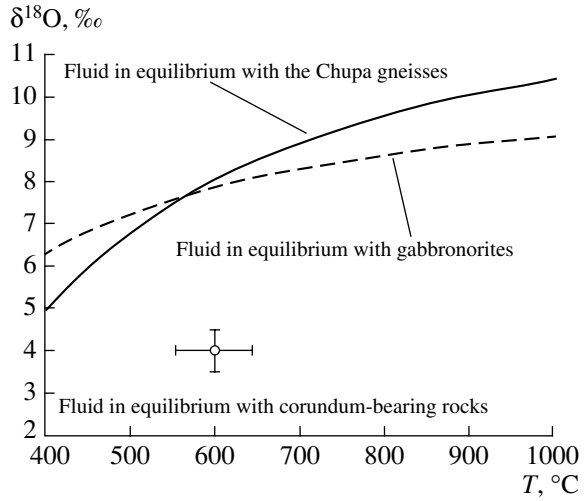

Fig. 2. Estimates of oxygen isotopic composition of fluid depending on temperature.

Discussion. The oxygen isotopic composition of the fluid in equilibrium with the Chupa gneisses and gabbronorites (at temperature variations from 600 to 900°C) is within approximately 7–10 and 7–8‰, respectively (Fig. 2). The $\delta^{18}O$ values in fluid calculated from the distribution between phases of the corundum-bearing assemblages (3–4‰) are *n*‰ lower than those in deep-seated (lower crustal or mantle) fluids and significantly lower as compared to fluids that could be released from the host Chupa gneisses. Hence, neither host metamorphic rocks nor adjacent gabbronorite bodies can be considered as the main fluid sources during the formation of high-Al rocks of Mt. Dyadina. Similar $\delta^{18}O$ values are recorded very rarely in the rocks of high-grade complexes (for example, Mt. Dabi in China [13]) owing to significant influence of *meteoric* waters.

Contrasting values of isotope ratios in the high-Al corundum-bearing and host rocks, the absence of signs of isotope exchange between them, and extremely low $\delta^{18}O$ values in the corundum-bearing rocks indicate the possible preservation of the oxygen isotope ratio of protoliths, primary lithological heterogeneity of the rock sequence, and premetamorphic exchange with meteoric waters.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (project no. 06-05-65160) and the Federal Program for the Support of Leading Scientific Schools (project no. 4732.2006.05).

REFERENCES

1. Yu. V. Miller, V. A. Glebovitsky, T. A. Myskova, et al., Dokl. Earth Sci. **366**, 486 (1999) [Dokl Akad. Nauk **366**, 379 (1999)].
2. V. A. Glebovitsky, Yu. V. Miller, G. M. Drugova, et al., Geotectonics **30**, 53 (1996) [Geotektonika, No. 1, 63 (1996)].
3. E. V. Bibikova, T. Skiöld, S. V. Bogdanova, et al., Geokhimiya, No. 10, 1393 (1993).
4. V. I. Volodichev, *The Belomorian Complex of Karelia: Geology and Petrology* (Nauka, Leningrad, 1990) [in Russian].
5. E. V. Bibikova, E. Yu. Borisova, G. M. Drugova, et al., Geochem. Int. **35**, 775 (1997) [Geokhimiya, No. 9, 883 (1997)].
6. E. V. Bibikova, S. Claesson, V. A. Glebovitsky, et al., Geochem. Int. **39**, 1023 (1997) [Geokhimiya, No. 10, 1116 (2001)].
7. I. S. Sedova, V. A. Glebovitsky, and V. S. Semenov, Petrology **4**, 137 (1996) [Petrologiya **4**, 150 (1996)].
8. N. S. Serebryakov, Candidate's Dissertation in Geology and Mineralogy (Moscow, 2004).
9. R. N. Clayton and T. K. Mayeda, Geochim. Cosmochim. Acta **27**, 43 (1963).
10. L. B. Asprey, J. Fluorine Chem. **7**, 359 (1976).
11. Y. Bottinga and M. Javoy, Revs. Geophys. Space Phys. **3**, 401 (1975).
12. J. Hoefs, *Stable Isotope Geochemistry* (Springer, New York, 1980; Mir, Moscow, 1983).
13. J. Baker, A. Matthews, et al., Geochim. Cosmochim. Acta **61**, 1685 (1997).