## **GEOCHEMISTRY** =

## Isotope Characteristics of Carbonates from Rocks of Greenstone Belts as an Indicator of a Possible Source of Fluids in Precambrian Granulite Complexes: An Example from the Giyani Greenstone Belt and the Limpopo Granulite Complex, South Africa

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Abstract—Data on the carbon and oxygen isotopic composition of carbonates from the rocks of the Givani greenstone belt, Kaapvaal craton, South Africa are presented. This belt is immediately adjacent to the Hout River Shear Zone, along which the Southern Marginal Zone (SMZ) of the Limpopo granulite complex is overthrusted onto the Kaapvaal craton. The  $\delta^{13}C$  values are -2.1 and -2.2% for carbonates from two metapelite samples, -5.1% for a meta ultrabasite sample, and -7.1 and -7.7% for two metabasite samples, respectively. The  $\delta^{18}$ O values are 17.1 and 17.5% for carbonates from the metapelites, 14.3% for carbonates from the metaultrabasite, and 12.9 and 13.0% for carbonates from the metabasites. The comparison of the data obtained to the published data on the isotopic composition of carbonates from the rocks of the different greenstone belts indicates both hydrothermal (in the metabasites and the metaultrabasite) and sedimentary (in the metapelites) origins of the carbonate material in the rocks studied. Based on the comparison of these data to  $\delta^{13}$ C of magnesite that formed in ultrabasic granulites during the interaction of the Limpopo complex with the craton, the graphite and fluid inclusions in leucocratic garnet-bearing granitoids that transported fluids, and the carbon isotopic composition of graphite from metapelites of the SMZ, it is concluded that the carbon source was located outside the SMZ and represented a heterogeneous carbonate-bearing lithologies. It could be carbonate-bearing volcanogenic-sedimentary sequences of the greenstone belts of the Kaapvaal craton, which underwent prograde metamorphism during the interaction with the SMZ granulites.

**Keywords:** carbon isotopy, fluids, greenstone belts, Limpopo complex, carbonates, Archaean **DOI:** 10.1134/S1028334X20050153

The  $CO_2$ -rich fluids played a defining role in the processes of formation of the Precambrian granulite complexes located along the periphery of the ancient continental blocks (cratons) [1]. Carbonates and graphite that were contained in the rocks before meta-morphism could serve as an internal source of  $CO_2$  in granulites. However, the production of  $CO_2$  as a result

of carbonate decomposition or graphite oxidation is the most efficient at the progressive stage of metamorphism, while the active influence of carbonate fluids at the regressive stage of evolution of granulite complexes was primarily associated with the various external sources. The  $CO_2$ -bearing basic magmas that accumulated at the base of the continental crust during melting in the upper mantle and also served a source of heat for metamorphism are considered as such a main source [2]. At the regressive stage of metamorphism related to the uplift to the surface, the granulite complexes interacted actively with the ancient continental blocks. The rocks of these blocks could also serve as a source of fluids, including  $CO_2$ -rich ones that have an impact on granulites.

The active interaction of hot granulites with the craton is well characterized for the Southern Marginal Zone (SMZ) of the Neoarchean–Paleoproterozoic (2.72–2.01 Ga) Limpopo granulite complex, South Africa [3]. This zone is a classic example of overthrusting of highly metamorphosed rocks onto the ancient

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Kaapvaal craton [3]. The progressive metamorphism of the craton rocks during the overthrusting of the SMZ granulites in the interval 2.69-2.66 Ga was accompanied by the release of aqueous-carbonic fluids that interacted with granulites along the tectonic zones or through the granitoid intrusions. The  $\delta^{13}$ C values of magnesite (-5.5...-6.0%) that appeared in ultrabasic granulites during this interaction [4], of graphite (-6.5...-8.6%) and fluid inclusions  $(-4.1 \pm$ 1.2%) in leucocratic garnet-bearing granitoids [5] transporting fluids differ considerably from the carbon isotopic composition of graphite from the SMZ metapelites (-12.5...-15.2%) [6]. This fact confirms the presence of a certain carbon source that was located beyond the SMZ and was likely to represent a heterogenous carbonate-bearing substrate. It could have been carbonate-bearing volcanogenic-sedimentary sequences of the greenstone belts of the Kaapvaal craton that underwent prograde metamorphism during the interaction with the SMZ granulites. This conclusion was made in [5] based on the comparison of the above isotope data to the generalized data on the isotopic composition of carbonates of rocks from the greenstone belts of different cratons, including the belts of the Kaapvaal craton that are distant from the Limpopo complex (e.g., the Barberton belt [7]). No data for the rocks from the greenstone belts that were immediately adjacent to the Limpopo complex were available.

This work presents the results of determining the isotopic composition of carbon and oxygen in the carbonates of rocks from the Giyani greenstone belt adjacent to the Hout River regional Shear Zone, along which the SMZ granulites are thrusted over the Kaapvaal craton. The Giyani belt is composed primarily of weakly metamorphosed ultrabasic, basic, and sometimes silicic schists, as well as of banded iron formations, metapelites, and dolomites [8]. In the northern part of the belt, there are blocks of rocks that underwent metamorphism at pressures up to 6.5 kbar and temperatures of 550-600°C under the influence of granulites [9]. These blocks are confined within rocks of lower grade metamorphism, among which the carbonate-bearing varieties are very common. The prograde metamorphism of such rocks could lead to the release of aqueous-carbonic fluids that penetrated granulites through the Hout River Zone.

Five samples of carbonate-bearing rocks from the northern part of the Giyani belt were studied [8, 9]. Metaultrabasite (sample 17-6) consists of zonal crystals of amphibole and accessory ilmenite and magnetite plunged into a chlorite–carbonate matrix. Carbonate comprising about 8 vol % of the rock is represented by dolomite–ankerite with the magnesium content  $X_{Mg} = Mg/(Mg + Fe) = 0.40-0.45$  (the compositions of the minerals were analyzed using a Tescan Vega IIXMU scanning electron microscope with an INCA Energy 450 energy-dispersive spectrometer at

the Korzhinskii Institute of Experimental Mineralogy, Russian Academy of Sciences). Two samples of metabasites, 17-8 and 17-5, contain amphibole zonal crystals with varying concentrations of CaO, biotite with  $X_{\rm Mg} = 0.42 - 0.46$  and 1.6-2.3 wt % of TiO<sub>2</sub>, quartz, plagioclase ( $X_{An} = 0.25$ ), accessory ilmenite, apatite, and iron sulfides. The content of carbonate minerals in the samples is  $\sim 10$  vol %. In addition to the dominant calcite, sample 17-8 contains two dolomiteankerite carbonates with magnesium contents of 0.6 and 0.4, respectively. In 17-5 metabasite, the carbonate is represented only by calcite. The greater content of biotite is expressed in a higher bulk content of  $K_2O$ (2.28 wt % in contrast to 0.36 wt % in sample 17-8). Samples of carbonate-bearing metapelites, MAS-13 and MAS-18, differ in the modal ratios of quartz, plagioclase ( $X_{An} = 0.23$ ), biotite ( $X_{Mg} = 0.48$ , TiO<sub>2</sub> = 2.5-3 wt %), accessory ilmenite, apatite, and REE phosphates. The rocks contain both calcite ( $\sim 9 \text{ vol } \%$ ) and dolomite–ankerite carbonate (<1%).

The analysis of the carbon and oxygen isotopic compositions from the samples indicated was performed at the Center for Collective Use of Scientific Equipment for Multielement and Isotope Studies, Siberian Branch, Russian Academy of Sciences (SB RAS), on the premises of the Sobolev Institute of Geology and Mineralogy, SB RAS (Novosibirsk). The carbonate material was selected from the samples with an abrasive drill. Then the carbonate powder was broken down in orthophosphoric acid at a temperature of 60°C in a GasBenchII. For Fe-bearing carbonates, the reaction duration was extended to 160 h. The carbon isotopic composition in the pure CO<sub>2</sub> released was analyzed using a Finnigan MAT-253 mass spectrometer in the regime of constant helium flow. The accuracy of measuring  $\delta^{13}$ C in carbonate material was controlled by the NBS-19 international standard ( $\delta^{13}C =$ +1.9%,  $\delta^{18}O = -2.2\%$ ) and equaled 0.1% for  $\delta^{13}C$ and 0.3% for  $\delta^{18}O$ .

The measured values of  $\delta^{13}C$  and  $\delta^{18}O$  are presented in Table 1. The values of  $\delta^{13}$ C are found within the interval  $\delta^{13}C_{PDB} = -0.5$  to -9%, which are typical of carbonates in the rocks of Archean greenstone belts (see review table in [7]). The  $\delta^{13}$ C values for carbonates from the samples of metaultrabasite and metabasites coincide with the values that are typical of deep carbon sources,  $-6 \pm 2\%$  PDB [10] (Fig. 1), which is justified for the products of metamorphism of ultrabasic and basic volcanic rocks. However, the  $\delta^{\rm 18}O$  values of these carbonates are noticeably higher than those ones that characterize the deep-seated sources [10] (Fig. 1). The values of  $\delta^{13}$ C and  $\delta^{18}$ O obtained for carbonates from metaultrabasite and metabasites (Table 1) are close to the intervals -4...-6% and 8-14%, respectively, identified by D. Groves et al. [11] for carbonates in the zones of regional fluid penetration of ultrabasic and basic rocks from the Archean green-



Fig. 1. The  $\delta^{13}C_{PDB} - \delta^{18}O_{SMOW}$  correlations for carbonates from the MAS-13 and MAS-18 metapelites studied (gray triangles), 17-5 and 17-8 metabasites (gray circles), and 17-6 meta ultramafite (gray square) compared to the published data: (1)–(3) carbonates from the rocks of the different Archean greenstone belts [7], (4) the field identified by D. Groves et al. [11] for carbonates in the zones of regional fluid penetration of ultrabasic and basic rocks into the Archean greenstone belts of western Australia, (5) the field identified by the same authors [11] for carbonates, which are the products of influence of seawater on the seafloor rocks. The fields are designated for the deep carbon source [10], for metamorphosed sedimentary carbonates [13].

stone belts of western Australia (Fig. 1). The "heavier" values of  $\delta^{13}$ C for carbonates of the MAS-13 and MAS-18 metapelites (Table 1) fall into the interval -1 to -2.5%, which was identified by the same authors [11] for carbonates, being the products of the effect of seawater on the seafloor rocks (Fig. 1). However, the  $\delta^{18}$ O values for such carbonates (8-12%; [11]) are much lower than those obtained for carbonates from the MAS-13 and MAS-18 metapelites (17.1 and 17.5%); Table 1, Fig. 1). The  $\delta^{18}$ O values for carbonates from the MAS-13 and MAS-18 metapelites are displaced towards values that are typical of carbonates in equilibrium with seawater at low temperatures (>20%; e.g., in [12]) and are close to values that are typical of the Precambrian marine carbonates [13] (Fig. 1). The recalculation of the bulk compositions of these rocks using the A.A. Predovskii's method with respect to ~6 vol % of CaCO<sub>3</sub> in their composition showed that the geochemical characteristics of the MAS-13 and MAS-18 metapelites correspond to greywackes. Thus, they are likely to represent the products of metamorphism of clastic material with an admixture of carbonates of both hydrothermal and chemogenic sedimentary origin.

In Fig. 2, the  $\delta^{13}$ C values obtained for carbonates from the Giyani greenstone belt were compared to the data on the carbon isotopic composition in the different rocks of the SMZ in the Limpopo granulite complex that adjoins this greenstone belt. The  $\delta^{13}$ C values for dolo-



Fig. 2. The carbon isotopic composition of carbonates from the rocks of the Giyani greenstone belt: MAS-13 and MAS-18 pelites (large white circles), 17-6 metaultrabasite (large light-gray circle), 17-5 and 17-8 metabasites (large dark-gray circles). For comparison, published data on the  $\delta^{13}C_{PDB}$  of graphite from metapelites of the Banderlierkop formation [6] (asterisks), of graphite from the garnet-bearing trondhjemite vein [6] (small gray circle), and of carbonates from metaultrabasic granulites of the Banderlierkop formation [4] (gray squares) are presented. The dark-gray rectangle shows the interval of  $\delta^{13}C_{PDB}$  for hydrothermal carbonates from the greenstone belts [7]. The light-gray rectangle depicts the interval of  $\delta^{13}C_{PDB}$  for fluid inclusions in quartz and carbonates of hydrothermal veins in the greenstone belts [7]. The white polygons denote  $\delta^{13}C_{PDB}$  for fluid inclusions, and the small black circles denote  $\delta^{13}C_{PDB}$  for graphite from the leucocratic garnet-bearing granitoids in the SMZ of the Limpopo complex [5].

mite–ankerite from 17-6 metaultrabasite (Table 1) are close to the values of  $\delta^{13}C = -5.5...-6.0\%$  for magnesite from ultrabasic granulites in the SMZ [4] (Fig. 2). However, this coincidence hardly means inheritance of carbonates in granulites from the ultrabasic rocks of the greenstone belts. Magnesite in granulites is not a mineral of the peak of metamorphism; it appeared only at the retrograde stage at temperatures of about  $670^{\circ}C$  and pressures of 6 kbar due to the influence of the aqueous-carbonic fluids [4]. In our opinion, the

Table 1. The  $\delta^{13}C$  and  $\delta^{18}O$  values for carbonates from the rocks of the Giyani greenstone belt, South Africa

Sample	Rock	$\delta^{13}C$	$\delta^{18}O$
17-6	Metaultrabasite	-5.1	14.3
17-8	Metabasite	-7.7	12.9
17-5	Metabasite	-7.1	13.0
MAS-13	Metapelite	-2.1	17.1
MAS-18	Metapelite	-2.2	17.5

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coincidence of the  $\delta^{13}$ C values indicates that the rocks from the greenstone belts immersed beneath the SMZ granulites might be the source of these fluids.

O.G. Safonov et al. [5] determined the variations in  $\delta^{13}C = -5.6... - 2.5\%$  for carbon of fluid inclusions in the minerals of garnet-bearing leucocratic granitoids intruded into the SMZ metapelites at the retrograde stage of metamorphism (Fig. 2). The upper value of this interval is close to  $\delta^{13}$ C for carbonates from the MAS-13 and MAS-18 metapelites (Table 1, Fig. 2). The rock-forming assemblage of silicate minerals in these metapelites *biotite+plagioclase+quartz* is a potential substrate for the formation of garnet-bearing granitoid magmas during anatexis [14], while the carbonates in these rocks may serve as a CO<sub>2</sub> source that further accompanied these magmas [5]. The lower value of  $\delta^{13}$ C, which is higher than the interval of  $\delta^{13}$ C presented, is similar to the carbon isotopic composition of carbonates from 17-6 metaultrabasite (Table 1, Fig. 2). This indicates that the fluids released during the metamorphism of ultrabasic rocks of the greenstone belts might also participate in the formation of granitoid magmas at the base of the granulite complex during its interaction with the craton. Thus, the isotope date obtained confirm the conclusion we made earlier based on study of the unique magnesite-bearing inclusions in garnets of the SMZ leucocratic granitoids [15].

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