The case of the carbonatite-like dyke of the Madenska River complex at the Kriva Lakavica section in the Republic of Macedonia: oxygen and carbon isotopic constraints

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Abstract: The oxygen and carbon isotope compositions of carbonate samples from the carbonatite-like dyke of the Madenska River complex at the Kriva Lakavica section, samples of calcite skarns from the Damjan Fe-ore deposit and the Sasa Pb-Zn ore deposit, and samples of marbles from the Pohorje Mountains were analyzed to provide critical evidence in favor of the magmatic or sedimentary origin of this carbonatite-like dyke.

We suggest that the carbonatite-like dyke is not a "normal" carbonatite, but instead represents melted carbonates, which can be associated with an unexposed, deep-seated, causative magmatic body. This dyke has a fluidal texture and carries xenoliths of ultramafic rocks that can be up to 35 cm in size. Its isotopic composition plots between primary unaltered carbonatites and marine carbonates, and ranges between 13.79‰ and 18.89‰ for $\delta^{18}O_{VSMOW}$ and between –1.22‰ and 1.31‰ for $\delta^{13}C_{VPDB}$. These values are significantly lower than those observed in carbonatites analyzed during this study and range between 6.53‰ and 8.10‰ for $\delta^{18}O_{VSMOW}$ and between –5.82‰ and –4.32‰ for $\delta^{13}C_{VPDB}$, which is the primary isotope signature of most magmatic carbonatites. Similarly high $\delta^{18}O$ and $\delta^{13}C$ values were found in skarns of the Damjan Fe deposit close to the Madanska River complex and in the Sasa Pb-Zn deposit, as well as in high-grade regional metamorphic calcitic marbles of the Pohorje massive.

The emplacement levels of the carbonatite-like dyke, due to several tectonic processes, are uncertain. The type of country rocks (sedimentary carbonates, ultramafic, mafic, and granitic rocks), hydrothermal alternation, and metasomatic and regional metamorphic processes seem to be the most important parameters that affect the O and C isotopic patterns found in the Kriva Lakavica carbonatite-like dyke and in the investigated samples.

Key words: Carbonatite-like dyke, carbonatite, skarn, marble, stable O and C isotopes, Republic of Macedonia

1. Introduction

Carbonatites are mantle-derived igneous, intrusive (as well as extrusive) rocks mainly found in stable, intraplate continental settings (Heinrich and von Eckermann, 1966; Bell, 1989) that are composed of more than 50 modal percent primary magmatic carbonate minerals containing less than 20 wt.% SiO_2 (Le Maitre, 2002) and are markedly different from most other igneous rocks (Huang et al., 1995). There are now more than 500 known occurrences of carbonatites. They have been found on all continents except for Antarctica, but have only been identified at two oceanic localities (the Cape Verde and Canary Islands) (Bell, 1998; Ray et al., 2000; Hoernle et al., 2002).

Carbonatites range in age from Archean to recent, and are closely associated with alkaline intrusions and intracontinental rifting (Woolley, 1989; Woolley and Kempe, 1989). They are formed by the crystallization of carbonate-rich magmas. In contrast to the intracontinental occurrences, the same carbonatites were also found at two intraoceanic localities (the Cape Verde and Canary Islands) (Bell, 1998).

The origin of carbonatites is still the subject of debate. There are a variety of petrogenetic models that can be generated in the formation of this rock type. Several studies provide evidence that carbonatites can be produced from the mantle by the partial melting of a carbonate-bearing mantle source (Dalton and Wood, 1993; Sweeney, 1994; Harmer and Gittins, 1998; Srivastava et al., 2005b). The generation of a carbonatitic melt evolved through magmatic differentiation or fractional crystallization, including the immiscible separation of carbonatite-rich and silicate magmas from the parent carbonatite silicate

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magma, also suggests the formation of carbonatitic rock compositions. Such evidence is provided in the experimental studies of Van Groos (1975), Twyman and Gittins (1987), Wallace and Green (1988), Gittins (1989), and Kjarsgaard et al. (1995). Geochemical investigations further indicate that carbonatites can also be generated by low-temperature residual melts, not generated by immiscibility from the crystallization of a carbonate-rich silicate melt (Pearce and Leng, 1996; Harmer and Gittins, 1998; Harmer et al., 1998).

Previous theories of the genesis of carbonatites demonstrated that carbonatites are related to sedimentary limestones (Bell et al., 1982; Bell and Blenkinsop, 1987). The melting of this rock type is, in principle, possible, as shown by a number of experimental studies (Wyllie and Tuttle, 1960; Fanelli et al., 1986; Lentz, 1998; Lentz, 1999). For the same carbonate-rich rocks, however, it is not yet known whether they primarily formed as igneous or sedimentary rock (Krishnamurthy et al., 2000; Le Bas et al., 2002). Sedimentary carbonates characteristically display geochemically lower Sr, Ba, and total REE than carbonatites (Xu et al., 2010). Therefore, the Sr, Ba, and REE content in carbonate minerals is an alternative geochemical parameter that can be used to judge the carbonatite's origin. However, several problems still remain unsolved. These include the melting of the carbonate wall-rock around the magmatic bodies at magmatic temperatures (Wenzel et al., 2002 and references therein), some aspects of the magma-carbonate interaction (Frezzotti et al., 2007; Iacono Marziano et al., 2007; Iacono Marziano et al., 2008; Freda et al., 2008; Iacono Marziano et al., 2009; Peccerillo et al., 2010), and carbonate assimilation occurring due to a reaction between the silicate magma and the solid wall-rocks (Iacono Marziano et al., 2007). These generated silica-poor and CaO-rich melts are compositionally similar to some melt inclusions found in skarns (Iacono Marziano et al., 2007). Skarns are generally associated with intermediates to felsic intermediate rocks, which commonly contain higher concentrations of fluids that can be the source of ore metals. Dry basic and ultramafic magma is not suitable for producing skarn mineralization because of its low content of fluid phases (Karimzadeh Somarin and Moayyed, 2002).

The magmatic and metamorphic complex of the Madenska River, which includes metamorphic carbonate rocks, different dykes and veins of granitic rocks, and metamorphosed ultrabasic and basic magmatic rocks at the Kriva Lakavica, close to the town of Štip, has been the subject of a long-standing debate. Some petrologists considered the metamorphosed carbonate-silicate rocks to be genetically related to carbonatite magmatism (Ivanov, 1987, 1988 and references therein). On the other hand, the results of preliminary petrological studies and a rare

geochemical study (Pendžerkovski et al., 1973, 1978; Stojanov and Svešnikova, 1985) suggest that the unusual metamorphic and metasomatic carbonate-silicate rocks are skarns, while a study by Sijakova-Ivanova et al. (2012) identified them as metamorphosed carbonate and calc-silicate, which suffered amphibolite facies of Abukyma regional metamorphism.

In this study oxygen and carbon isotopic analyses of carbonates of the unusual carbonatite-like dyke of the Kriva Lakavica section, appearing as dyke containing ultramafic xenoliths, were performed. The main purpose of this study was to shed some light on their possible relations with the suggested carbonatitic magmatism of the Madenska River complex and to distinguish the metamorphic carbonates and related carbonatites. Furthermore, the results of this study are compared with those from whole-rock samples affected by the contact metamorphism associated with the Fe and Pb-Zn skarn deposits in Damjan and Sasa, respectively (Republic of Macedonia), as well as in the high-grade regional metamorphic calcitic marbles of the Pohorje massive (Slovenia).

2. Materials and methods
### 2.1. Geological background and earlier studies
The magmatic and metamorphic complex of the Madenska River includes different regional and contact-metamorphic rocks penetrated with dykes and veins of granitic rock (biotite granite, granosyenite) as well as metamorphosed ultramafic and mafic magmatic rocks (pyroxenite, amphibolite, serpentine). In the investigated section of Kriva Lakovica metamorphic, ultramafic, mafic, and contact metamorphosed carbonate sedimentary rocks penetrated with dykes of biotite granites and small veins of aplite and leucocratic granosyenites were reported (Stojanov and Svešnikova, 1985). According to some petrologists (Bončev, 1920; Stojanov and Svešnikova, 1985) the precrystalized carbonate rocks, which contain contact metamorphic and metasomatic minerals, are calcareous skarns. Contact metamorphic minerals in the skarns of the Madenska River complex, and in amphibolized ultramafic and mafic rocks, correspond to the typical contact metasomatic metamorphism of pyroxene-amphibole cornite facies with changes related to acid magma (granitic–syenitic composition) and postmagmatic solutions originating from larger granitic and/or granosyenitic bodies (Stojanov and Svešnikova, 1985).

Further studies (Ivanov, 1987, 1988) from the complex of the Madenska River suggest that the carbonatic rocks might be carbonatites. A geophysical investigation (gravimetry and magnetometry) that was carried out in the period 1987–1988 indicates that this complex has a circular structure, characteristic of the carbonatitic

complex (Bilibajkić, 1965; Ivanov, 1987, 1988). Additional facts that favor the magmatic origin of the carbonatic rocks of the Madenska River complex are also the many xenoliths of ultramafic and mafic rocks that are found in the carbonatitic rocks (Figure 1). The presence of xenoliths can most easily be explained with the enclosure of carbonatitic magma by the surrounding silicate host rocks (Ivanov, 1987, 1988). Based on the mineralogical results obtained from the xenoliths present in the calcite-silicate

rocks and in the calcite-silicate rocks from Novo Selo, Kriva Lakovica, a report by Sijakova-Ivanova (2012) claims that those carbonate rocks are regional metamorphic calc-silicate, but not carbonatites or skarns.

In this study we present an interpretation of the Madenska River carbonate-silicate rocks based in the well-exposed carbonatite-like dyke at the Kriva Lakavica section in terms of oxygen and carbon isotopes.
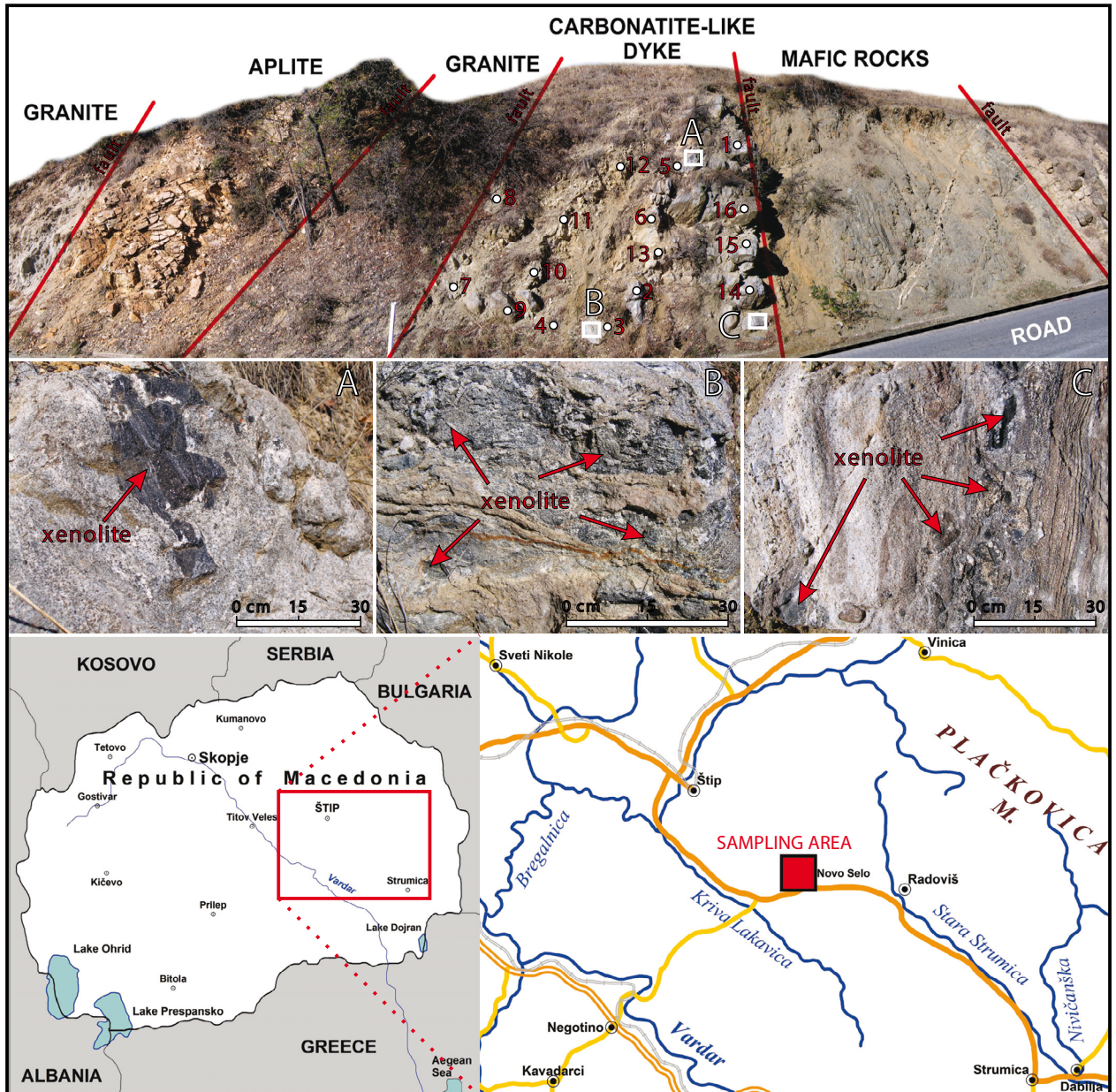
Figure 1. Locality and geological setting of the study location and position of the samples of the Kriva Lakavica carbonatite-like dyke. A) A photograph showing clinopyroxene-rich xenolith up to 35 cm in size in the carbonatite-like dyke; B) and C) the fluidal structure of carbonatite-like dyke showing different sizes of clinopyroxene-rich xenoliths in the carbonate matrix.

2.2. Sample description and analytical methods

The samples investigated in this study consist of a group of calcitic samples collected from a carbonatite-like dyke, including ultramafic xenoliths that hosted the carbonatite-like dyke in a fault contact with granitic, ultramafic, and mafic rocks at the Kriva Lakavica section (Figure 1). We collected a total of 16 samples of carbonatite-like dyke. For comparison, we also collected a total of 12 samples of carbonatite, 10 samples of skarns, and an additional 10 samples of regional metamorphic marble.

The carbonatite samples were collected from the Panda Hill carbonatitic complex (5 samples) in Tanzania, which has an age of 116 My (Cahen et al., 1984), and the Matonga carbonatitic complex in Burundi (4 samples), which has an estimated age of 729 My (Tack et al., 1994). Both carbonatitic complexes are situated in the western branch of the East African Rift, which hosts numerous carbonatite and alkaline complexes. The carbonatitic samples were provided by M Dolenec (Geological Survey, Ljubljana, Slovenia). Further samples (3) represent carbonatite tuffs of the Kaiserstuhl in Germany. Kaiserstuhl is a volcanic complex in the Upper Rhine Graben of Miocene age (Sutherland, 1967). The specimens are from the collection of the University of Ljubljana, Faculty of Natural Sciences and Engineering, Department of Geology, Slovenia.

The samples of skarns were collected during field trips in October 2011. The samples were focused on the contact aureole of the Damjan skarn magnetite-hematite deposit (5 samples) about 20 km SE of the Madenska River complex. The skarns are located at the contact of the andesite/dacite with a Cretaceous flysh sediment containing limestone. Five samples come from Pb-Zn calcite skarns from the Sasa deposit in the Osogovo Mountains in eastern Macedonia. These skarns and mineralization are genetically closely related to a quartz latite intrusion of the Tertiary age (24.5 My) (Serafimovski et al., 2006).

We also collected 10 samples of regional metamorphic marble from the Pohorje Mountains in Slovenia. The regional metamorphic sequence, which includes marbles, was metamorphosed in almandine amphibole facies conditions ranging in age from Silurian to Devonian (Hinterlechner-Ravnik, 1973; 1974). The samples were selected by us from metamorphic rocks during a research program (Geochemical Investigation of Magmatic and Metamorphic Rocks in Slovenia) accepted in 1991 by the Ministry of Science and Technology.

The whole-rock samples for bulk rock oxygen and carbon isotopic composition were carefully crushed and ground in an agate mill to a grain size of about 125 μm. The samples selected for the isotope analyses represent the carbonatite-like dyke, close to the contact with metamorphosed ultramafic rocks, and a range of contact and regional metamorphose of granitic and sedimentary rocks (skarns and marbles) was used for comparison.

Petrographic thin and polished sections were prepared for each rock sample. The mineralogy of the samples was determined by X-ray diffractometry and by examinations of the thin and polished section by standard optical methods. A Philips PW3710 X-ray diffractometer was used with Cu-Kα 1.5418 Å radiation generated at 40 kV and 30 mV. The samples were scanned at a rate of 2°/min, over the range of 2°–70° (2θ). The results were quantitatively evaluated using data from the PAN-ICSD database, version 2.3, by the Rietveld method. The Xray patterns showed the carbonatite species of the investigated sample set to be calcite. In the doubtful cases, the mineralogy of the samples was confirmed using a JEOL JS M 5800 scanning electron microscope equipped with an energy-dispersive system (ISIS 300 EDS) (unpublished data). The petrographic studies revealed that, apart from the calcite, the carbonatite-like dyke also contained other minerals, including pyroxenes, amphiboles, biotite, plagioclase, orthoclase, garnet (grossular-andradite), and a substantial amount of sulfides and crystals of titanite and apatite.

The oxygen and carbon isotope compositions of the whole-rock carbonate data were determined using anhydrous phosphoric acid of a specific gravity of >1.80 in a vacuum for 24 h at 25 °C, following the method of McCrea (1950). The liberated CO_2 captured off-line in the sample tubes was cryogenically cleaned and analyzed for oxygen and carbon on a Varian MAT mass spectrometer at the Jožef Stefan Institute in Ljubljana. The calcite-phosphoric acid fractionation factor used in the extraction procedures was 1.01025 at 25 °C (Friedman and O'Neil, 1977), corrected from Sharma and Clayton (1965). The O and C isotope ratios are reported in the common δ-notation in per mil (‰):

$$\delta^{18}O_{VSMOW} = \frac{{}^{18}O/{}^{16}O_{sample}}{{}^{18}O/{}^{16}O_{standard}} - 1;$$

$$\delta^{18}O_{VPDB} = \frac{{}^{13}C/{}^{12}C_{sample}}{{}^{13}C/{}^{12}C_{standard}} - 1$$

where ${}^{18}O/{}^{16}O_{sample}$ or ${}^{13}C/{}^{12}C_{sample}$ is the isotopic ratio in the sample, and ${}^{18}O/{}^{16}O_{standard}$ or ${}^{13}C/{}^{12}C_{standard}$ is the corresponding ratio of that standard (VSMOW for O and VPDB for C).

The measured $\delta^{18}O$ and $\delta^{13}C$ values were calibrated by assuming $\delta^{18}O$ and $\delta^{13}C$ values of –23.01 ± 0.1‰ and –5.014 ±0.035 ‰ for the NBS-18 standard on the PDB scale. All the samples were analyzed in duplicate. The internal laboratory carbonate standard was pure calcitic powder from Pohorje marble, which yielded values of $\delta^{18}O$ = –9.20 ± 0.05‰ and $\delta^{13}C$ = –0.15 ± 0.02‰ (1σ, n = 10) during the measurement procedures. The VPDB-

VSMOW conversion for $\delta^{18}O$ was made by applying the formula given by Friedman and O'Neil (1977). The overall analytical reproducibility of the isotopic data was ±0.15‰ for the oxygen and ±0.10‰ for the carbonate carbon.

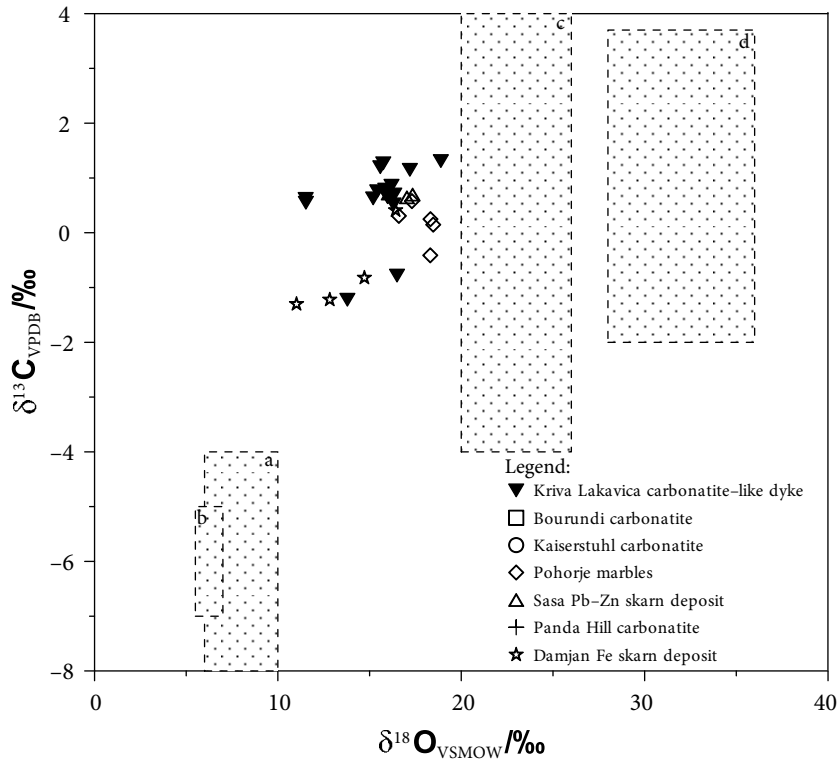## 3. Results

The results of the $\delta^{18}O$ and $\delta^{13}C$ values for the carbonatite-like dyke from the Madenska River complex, the different carbonatite samples, the skarns associated with magnetite-hematite, the Pb-Zn mineralization, and the regional metamorphic marbles are shown in the Table and Figure 2. The calcite of the carbonatite-like dyke of the Kriva Lakavica section had $\delta^{18}O_{VSMOW}$ values ranging between

11.52‰ and 18.89‰ (with an average of 15.51‰) whereas the $\delta^{13}C_{VPDB}$ values cover a much smaller range from −1.22‰ to 1.31‰, (with an average of 0.60‰). There were no sample plots in the primary igneous carbonatite field (Figure 2), as defined by Taylor et al. (1967). Moreover, the oxygen and carbon isotopic compositions of the calcites fall within a narrow range between the primary carbonatite and the marine carbonates in the diagram of $\delta^{18}O_{VSMOW}$ vs. $\delta^{13}C_{VPDB}$. The calcite from the Kriva Lakavica section also shows a conspicuous enrichment in $\delta^{13}C$ relative to the investigated skarns, marble, and carbonatites, but a similar isotopic composition of oxygen, comparable to that of the skarns of the Damjan ore deposit.

Table. The carbon and oxygen isotopic composition of the analyzed samples.

Sample	$\delta^{18}O_{VSMOW}$/‰	$\delta^{13}C_{VPDB}$/‰	Location	Sample	$\delta^{18}O_{VSMOW}$/‰	$\delta^{13}C_{VPDB}$/‰	Location
1 MAD	15.86	0.79		25 BOU	6.63	-5.58	
2 MAD	15.42	0.76		26 KAI	7.62	-4.32	*Kaiserstuhl volcanic complex in Upper Rhine Graben (Germany)*
3 MAD	15.97	0.66		27 KAI	8.07	-4.35	
4 MAD	16.00	0.65		28 KAI	7.71	-4.75	
5 MAD	11.52	0.62		29 DAM	11.02	-1.30	*Fe skarn deposit Damjan (Republic Macedonia)*
6 MAD	11.53	0.55		30 DAM	20.34	0.15	
7 MAD	15.75	1.27		31 DAM	16.42	0.41	
8 MAD	15.59	1.20	*Carbonatite-like dyke of Madenska River Complex at Kriva Lakavica section (Republic Macedonia)*	32 DAM	14.72	-0.82	
9 MAD	18.89	1.31		33 DAM	12.83	-1.22	
10 MAD	16.20	0.86		34 SAS	22.45	0.85	*Pb-Zn skarn deposit Sasa (Republic Macedonia)*
11 MAD	16.35	0.70		35 SAS	16.05	0.72	
12 MAD	17.20	1.15		36 SAS	17.04	0.65	
13 MAD	13.79	-1.22		37 SAS	17.35	0.70	
14 MAD	16.50	-0.78		38 SAS	21.13	0.80	
15 MAD	15.20	0.63		39 POH	18.47	0.15	
16 MAD	16.31	0.52		40 POH	17.31	0.58	
17 PAH	7.20	-5.10	*Panda Hill carbonatite complex East African Rift (Bourundi)*	41 POH	16.60	0.31	
18 PAH	7.41	-4.62		42 POH	22.06	0.03	
19 PAH	7.53	-4.81		43 POH	21.65	0.45	
20 PAH	7.80	-4.95		44 POH	18.31	-0.41	*High-grade regional metamorphic marbles of Pohorje Mountains (Slovenia)*
21 PAH	7.60	-4.89		45 POH	18.32	0.25	
22 BOU	6.53	-5.61	*Matonga carbonatite complex East African Rift (Bourundi)*	46 POH	23.31	-0.12	
23 BOU	6.81	-5.82		47 POH	22.13	0.30	
24 BOU	6.75	-5.78		48 POH	21.58	0.26	

Figure 2. Stable oxygen and carbon isotopic compositions of carbonate samples in this study (relative to VSMOW and VPDB, respectively) plotted in a conventional $\delta^{18}O$–$\delta^{13}C$ diagram. The rectangular boxes represent the field for unaltered primary carbonatites in the studies of: a) Taylor et al. (1967); and b) Keller and Hoefs, (1995). The samples from the carbonatite-like dyke of Kriva Lakavica (q) plot as a close cluster within the field of primary carbonatites and typical marine carbonates of the Paleozoic age (c) (Keith and Weber, (1964)); and (d) marine carbonates (Ohmoto and Rye, 1979). Similar $\delta^{18}O$ and $\delta^{13}C$ values are shown by the sampled ore scarns and Pohorje marble.

The carbonatite samples (from Panda Hill, Burundi, and Kaiserstuhl, Germany) that are plotted inside the primary igneous carbonatitic field represent the primary isotope composition from the source of typical carbonatites with a restricted isotopic composition ranging between 6.0‰ and 10.0‰ for $\delta^{18}O_{VSMOW}$ and between –4.0‰ and –8‰ for $\delta^{13}C_{VPDB}$ (Taylor et al., 1967). All the measured isotopic values for the carbonatitic calcites listed in Table are typically of those carbonatite complexes (Deines, 1989). Their $\delta^{18}O_{VSMOW}$ and $\delta^{13}C_{VPDB}$ values are 6.63‰ to 8.07‰ and –4.32‰ to –5.82‰ respectively, and do not show any effects of late hydrothermal alteration, which tends to elevate the oxygen and carbon isotopic composition (Deines, 1989).

The calcite from the Fe-skarn deposit shows $\delta^{18}O_{VSMOW}$ values in the range from 11.02‰ to 20.34‰ and $\delta^{13}C_{VPDB}$ values from 1.30‰ to 0.41‰, and exhibits a remarkable overlap with those reported from the carbonatite-like dyke of the Madenska River. The isotopic values decrease towards the contact and show a close spatial relationship to the ore body. The intrusion of the andesite/dacite caused the isotopic depletion of the $\delta^{18}O$ and $\delta^{13}C$ in the carbonate rocks. The $\delta^{18}O$ and $\delta^{13}C$ values may reflect the temperature and, more or less, the variable presence of deep-seated carbon in the hydrothermal fluids.

Carbonates from the Pb-Zn skarn-type mineralization exhibit a wide range of $\delta^{18}O_{VSMOW}$ (from 16.05‰ to 22.45‰ VSMOW), while the carbon values suggest a more limited enrichment of $\delta^{13}C_{VPDB}$ (from 0.65‰ to 0.85‰). Thus, the skarns possibly indicate the interaction of carbonates with hydrothermal fluids at low temperatures, originating from granodiorite magma. The $\delta^{18}O$ and $\delta^{13}C$ values of these skarn samples are positively correlated (Figure 2). It must be kept in mind, however, that five skarn samples from the magnetite-hematite and five from the Pb-Zn ore deposit seem to be insufficient to elucidate the magmatic-metasomatic and secondary (hydrothermal alteration) processes as well as the interaction of carbonate rocks with hydrothermal fluids at low temperatures and/or meteoric water in these ore deposits.

The calcitic marble from the Pohorje Mountains shows a depletion of both $\delta^{18}O_{VSMOW}$ and $\delta^{13}C_{VPDB}$ values relative to the marine carbonate ranging from 16.60‰ to 23.31‰ (with an average of 19.97‰) for oxygen, and from –0.41‰ to 0.58‰ (with an average of 0.18 ‰) for carbon. Data from the marine carbonates are also added (Figure 2). The $\delta^{18}O$ values of typical marine carbonates of the Paleozoic age vary from 20‰ to 26‰, while the $\delta^{13}C$ values range from –4‰ to + 4‰ (Keith and Weber, 1964). The marbles show a narrow range of $\delta^{13}C$ values, which do not exceed 1‰, but the variation of the $\delta^{18}O$ values is comparable with that of the skarns from the Sasa ore deposit.

4. Discussion

The carbonatites are normally closely associated with alkaline volcanic rocks and intracontinental rifting, and are also formed in oceanic fracture zones such as the Canary and Cape Verde Islands (Woolley and Platt, 1986; Woolley, 1989). According to Taylor et al. (1967), $\delta^{18}O$ values in primary igneous carbonatites (PICs) range between 6‰ and 10‰, and $\delta^{13}C$ values range between –4‰ and –8‰, representing values for magmatic carbonatites that have been affected by mainly high-temperature magmatic processes and can be related to the plutonic emplacement level. Based on data from fresh and unaltered natrocarbonatites from Oldono Lengai, Keller and Hoefs (1995) proposed a much narrower range of O and C isotopic compositions (from –7‰ to –5‰ and from 5.5‰ to 7‰, respectively), which can be considered to represent an undergassed and uncontaminated mantle composition (Pandit et al., 2002).

However, many carbonatites have an isotope composition deviating from the values typical for the PIC box in the $\delta^{18}O$–$\delta^{13}C$ diagram defined by Taylor et al. (1967). The isotopic variation of $\delta^{18}O$ and $\delta^{13}C$ in these carbonatites indicates the involvement of different magmatic or hydrothermal processes, modification by low-temperature hydrothermal fluids and/or meteoric water, and contamination by country rocks such as limestones from the crust (Pineau et al., 1973; Deines, 1989; Eriksson, 1989; Pandit and Golani, 2001). The Panda Hill carbonatite intrusion has been mostly altered and fenitized, while the samples of the Burundi carbonatite were affected by high-temperature magmatic processes.

Carbonatites are mainly thought to be emplaced in shallow levels and frequently contain higher O and C isotopic compositions (Deines, 1989; Santos and Clayton, 1995; Horstmann and Verwoerd, 1997). Such an extrusive carbonatite is from the ancient Kaiserstuhl volcano, formed along the continental rift called the Upper Rhine Graben, and shows high $\delta^{18}O$ and $\delta^{13}C$ values. However, the intrusive Kaiserstuhl carbonatite shows average $\delta^{18}O$ and

$\delta^{13}C$ values of 6.6‰ and –5.8‰, respectively, while those of low-temperature calcite cement in carbonatite tuffs have average $\delta^{18}O$ and $\delta^{13}C$ values of 21.8‰ and –14.9‰, respectively (Hay and O'Neil, 1983). The ^{18}O-rich and ^{13}C-rich isotopes, therefore, appear to be late magmatic/metasomatic processes involving low-temperature hydrothermal alteration and isotope exchange between the carbonatites and the meteoric water. Considering the range of $\delta^{18}O$ for the normal mantle reservoir (5.0‰ to 8.0‰ (Kyser, 1990)), the $\delta^{18}O$ of the carbonatite parent magma is believed to be slightly ^{18}O-rich as compared with the mantle reservoirs, while the $\delta^{13}C$ values fall in the range of –7.0‰ to –5.0‰ (Ray et al., 1999). The oxygen and carbon isotope compositions for the carbonatite calcite from the analyzed samples in this study (Table) are typical of those carbonatite complexes in other parts of the world (Deines, 1989) and do not show any of the effects of late hydrothermal alteration, which tend to exhibit elevated carbon and oxygen isotope composition. According to Deines (1970), these carbonatites retain their primary isotope signature.

The $\delta^{18}O$ values of the carbonatites of the Burundi parent magma are believed to have similar isotopic composition to the mantle reservoirs, while the carbonatite magma of the Panda Hill and Kaiserstuhl complexes may have deviated slightly from values typical of the mantle's origin and contain a higher ^{18}O-rich isotope composition. The observed $\delta^{13}C$ values of the carbonatite of Burundi are in the range proposed by Ray et al. (1999), indicating crystallization from magma derived from "normal" mantle; they are not the result of any primary or secondary magmatic fractional processes.

The carbonatites of Panda Hill and Kaiserstuhl were slightly enriched in ^{13}C, implying that either the source was already enriched in ^{13}C prior to the magma generation or the ^{13}C enrichment of carbonatites took place during their evolution (Ray et al., 1999). The subvolcanic carbonatites have a $\delta^{13}C$ of around 1‰, which is uncommonly heavy for carbonatites in general, and is accompanied by slightly higher values of $\delta^{18}O$ (11.7‰ to 13.7‰) relative to the fresh plutonic carbonatite (Andrade et al., 1999). From an examination of the $\delta^{18}O$ and $\delta^{13}C$ values, it is evident that these sampled carbonatites retain their primary isotope signature and exhibit an isotopic composition inside the PIC box (Taylor et al., 1967), which suggests a primary process unique to carbonatite petrogenesis.

In Figure 2, the oxygen and carbon isotopic compositions of the carbonatite-like dyke of the Kriva Lakavica section fall within a range between primary carbonatite and marine carbonatites, and/or skarns of Damjan and Sasa ore deposits and of the regional marbles of the Pohorje Mountains. The proposed melts that form the carbonatite-like dyke are thought to be compatible

with melting sedimentary limestone (Tuttle and Gittins, 1966), contain pyroxene xenoliths, and show $\delta^{18}O$ in the range of 11.50‰ to 18.89‰ and $\delta^{13}C$ values close to 1.0‰. The presence of older limestones in the Madenska River complex indicates a high possibility that the high $\delta^{13}C$ values of the calcitic parent magma are due to assimilation. According to Wyllie and Tuttle (1960), limestones in the presence of H_2O and at a pressure of 1 kbar begin to melt at 740 °C, while the eutectic temperature of the CO_2 - H_2O - CO_2 system was as low as about 600 °C when MgO was added (Fanelli et al., 1986). The isotopic characteristic of the carbonatite-like dyke of the Kriva Lakavica section could therefore be explained by sedimentary contamination and magmatic fluids, which may be related to granitic magma. According to Stojanov and Svešnikova (1985), the granitic rocks of the Madenska River are of Cretaceous age. In other words, the carbonatite-like dyke could be interpreted as being of "magmatic origin" when the sedimentary contaminated magma from a deep-seated magma chamber was injected during tectonically derived processes in the surrounding rocks before the final consolidation. The magmatic processes are followed by metasomatic processes related to an unexposed, deep-seated, causative magmatic body followed by metasomatic processes and, finally, regional metamorphic processes in amphibolite facies, with medium to high temperatures and low pressures (Ivanov, 1987, 1988; Majer and Lugović, 1991; Sijakova-Ivanova et al., 2012). From an examination of the $\delta^{18}O$ and $\delta^{13}C$ values for the carbonatite-like dyke, it is evident that carbonates do not retain their primary carbonatite isotope signature, which is unique to several carbonatite formations, but are similar to those of carbonate magmas produced at crustal levels by melting sedimentary carbonates. The observed $\delta^{18}O$ and $\delta^{13}C$ values are clearly much higher than the range of the suggested values reported by Taylor et al. (1967), implying that the carbonatite-like dyke is not a normal "carbonatite" related to any carbonatitic magmatism. Preliminary geochemical data on the carbonatite-like dyke of the Madenska River revealed Ba, U, Th, Na, Pb, and REE content and slightly higher values of Sr in the range from 1470 to 3588 pm, which are not typical for normal carbonatites (Pirc et al., 2007) and are much lower than the normal abundance levels for carbonatites (Bell, 1981; Xu et al., 2010).

Similar $\delta^{18}O$ and $\delta^{13}C$ values ranging from 8‰ to 24.4‰ and 0.80‰ to 3.55‰, respectively, described by Liu et al. (2006) in carbonatite-like dykes from the eastern Himalayan syntaxes, were formed as melts from sedimentary carbonates at the crustal levels. They carry xenoliths and show chilled margin and alteration haloes. These dyke rocks are poor in REE, Ba, Sr, U, Th, Nb, FG, and P, which characterizes marbles of sedimentary origin (Liu et al., 2006).

The complexes at Borra, Eastern Ghats, India, which are interpreted as formerly of carbonatite origin, show that Borra rocks are metasedimentary (Le Bas et al., 2002). These rocks are strongly metamorphosed and recrystallized, and consist of folded carbonate sediments and foliated pyroxenites, which could be interpreted as either of igneous or high-grade metamorphic origin (Le Bas et al., 2002). Using oxygen and carbon isotope data (17‰ to 21‰ and 0‰ to 5‰, respectively), Bhowmik et al. (1995) deduced that Borra carbonate sediments are marbles, and that this ruled out any carbonatitic affinity for these rocks. The low Sr and REE content, the europium anomaly, and the aluminous minerals suggest a sedimentary origin (Le Bas et al., 2002).

Similar O and C isotopic data that suggest a significant sedimentary component for the ankeritic carbonatites (with $\delta^{18}O$ values between 7.5‰ and 28.4‰, and $\delta^{13}C$ values between –5.2‰ and –0.2‰) of the Neumania "carbonatites" also plotted away from the "mantle carbonatite box" (Grunau et al., 1975).

Marbles with a carbonatite-like geochemical signature have been found at several localities of the Bohemian Massif (Czech Republic) (Houzar and Novak, 2002). These marbles are very similar to the other marbles of sedimentary origin and are formed by strong metamorphism in the amphibolite facies and do not exhibit any apparent differences in terms of the major element.

Many authors fail to distinguish carbonatites from limestones when they are metamorphosed in amphibolite/ granulite facies, hornblende/pyroxene-hornfels facies, and even in sanidinite facies (Le Bas et al., 2002, 2004; Srivastava et al., 2005a; Casillas et al., 2011) due to the difficulties of distinguishing metamorphosed carbonatite (metacarbonatite) from marble or skarns produced by metamorphisms of limestone. Marbles of sedimentary origin can be mineralogically identical to carbonatites: the assemblage phlogopite-magnetite-apatite-calcite belongs to both, and pyroxenite can be of either origin (Le Bas et al., 2002). It is difficult to distinguish carbonatite from calcitic marbles of amphibolite and higher grades of metamorphism as well as from skarns. Information about the origin of these rocks (Casillas et al., 2011 and references therein) may be obtained by following features such as structural and spatial–temporal relations with ultraalkaline rocks, textural evidence, mineralogy, chemistry of the main minerals, and whole-rock geochemistry, including REE content and the C, O, H, Sr, Nd, and Pb ratios.

Oxygen and carbon stable isotope compositions of carbonates from the skarn deposits of Damjan and Sasa, and those of marbles from the Pohorje Mountains confirmed that the oxygen and carbon isotope compositions deviated from typical igneous carbonatites and sedimentary marine carbonates (Figure 2). This observation could

be explained by the magmatic-metasomatic and hydrothermal processes at high and low temperatures, including the possible contamination meteoric water. The low $\delta^{18}O$ values possibly indicate the involvement of high-temperature hydrothermal phases during the genesis of the Damjan and Sasa skarn ore deposits and an isotopic variation in the regional metamorphic marbles of the Pohorje Mountains, which trace the variations due to diagenesis to prograde metamorphism of amphibolitic grade. Low $\delta^{18}O$ values mostly suggest changes due to late-stage hydrothermal processes, alteration, or a reaction with country carbonatic rocks and hydrothermal and/or meteoric water and temperatures in which minerals are formed. A positive $\delta^{18}O$ shift in the carbonate can be found due to the increasing carbonate-water oxygen isotope fractionation at decreasing temperatures (O'Neil et al., 1969).

Marbles have an oxygen isotopic composition that is almost certainly lower than the precursor limestone and dolostone of marine origin (Veizer and Hoefs, 1976) as a result of postdepositional, metamorphic, and postmetamorphic processes that operated at the Pohorje Mountains and lower the $\delta^{18}O$ values of these rocks. The absence of extremely low $\delta^{18}O$ values provides firm evidence that meteoric water migration during the regional metamorphism was absent or minimal.

The oxygen isotopic compositions of the skarns are controlled by the fractionation of oxygen between the minerals and the hydrothermal and/or metamorphic fluids, and by the metamorphic devolatilization reactions (Valley, 1986). However, the variations of $\delta^{13}C$ values of the skarns of Damjan and Sasa and the marbles of the Pohorje Mountains can be modified by hydrothermal fluids and/or metamorphic fluids intruding into the sedimentary carbonate sequences, which may contain organic carbon. The carbon isotopic composition of all the studied samples of skarns and marbles fall in the range of normal marine sedimentary carbonates of –2‰ to 2‰ (Keith and Weber, 1964).

Most of the variations in $\delta^{18}O$ and $\delta^{13}C$ values from the investigated skarns and marbles have been explained by interactions involving hydrothermal ore-bearing fluids and metasomatic processes that involve Fe and Pb-Zn ore mineralization of Damjan and Sasa, respectively, and the metamorphism of the Pohorje Mountains, which shows the absence of any discernible covariance between the O and C isotopic compositions. The near constancy of the $\delta^{13}C$ values for the Pohorje marbles may indicate that the metamorphic fluids were rich in oxygen and poor in carbon and had the capacity to moderately change $\delta^{18}O$ values and only slightly affect $\delta^{13}C$ values (Brady et al., 1998). However, the isotopic variations in the skarns seem to be related both to a possible influx of meteoric water in the hydrothermal system and temperature.

5. Conclusion

The oxygen and carbon isotope compositions from the analyzed samples from the primary carbonatites of Burundi, Panda Hill, and the Kaiserstuhl complex do not show any significant effects of secondary processes of late hydrothermal alteration, which tend to provide elevated oxygen and carbon isotope compositions and retain their primary isotope signature inside the PIC box (Taylor et al., 1967).

The isotopic composition of the carbonatite-like dyke of the Madenska River complex at the Kriva Lakovica section falls within the range between the primary carbonatite of Taylor et al. (1967) and the marine carbonates (Keith and Weber, 1964). Similar values were found at the calcitic skarns of Damjan and Sasa as well as the regional marbles of the Pohorje Mountains.

The observed $\delta^{18}O$ and $\delta^{13}C$ values of the carbonatite-like dyke are evidently much higher than the range of the suggested values of carbonatites of Taylor et al. (1967). That is to say, the carbonatite-like dyke is not a normal carbonatite related to any carbonatite magmatism, but could be interpreted by the interaction of magma produced at the crustal level by melting sedimentary carbonates. Carbonate melting has been demonstrated to be likely at magmatic temperatures (Wenzel et al., 2002 and references therein). The magmatic processes of the Madenska River complex were followed by metasomatic processes related to an unexposed, deep-seated causative magmatic body, and finally by regional metamorphic processes. However, the $\delta^{18}O$ and $\delta^{13}C$ values of the Madenska River carbonatite-like dyke are very similar to those reported by Liu et al. (2006) for the great Himalayan crystallines, which formed as melts from the crustal levels.

One of the important arguments in favor of the magmatic formation of the Kriva Lakavica carbonatite-like dyke also comes from field and microscopic observations. This dyke has a fluidal structure and carries xenoliths of mafic rocks (pyroxenes) that can be up to 35 cm in size (Figure 3). The reaction rim was developed at the margins of the xenoliths.

The calcitic skarns of the Damjan Fe ore deposit are genetically related to andesite/dacite volcanism, while the calcitic skarns of the Sasa Pb-Zn ore deposit are related to quartz latite intrusion, confirming that the O and C isotope composition could be explained by thermal metamorphism, which was accompanied by magmatic–metasomatic and hydrothermal processes at high and low temperatures, including the possibility of contamination with meteoric water. Their $\delta^{13}C$ values do not suffer the intense contribution of ^{13}C-depleted carbon from deep-seated sources or organic matter in sedimentary wall rocks.

The marbles of the Pohorje Mountains have undergone polyphase regional metamorphism at least under
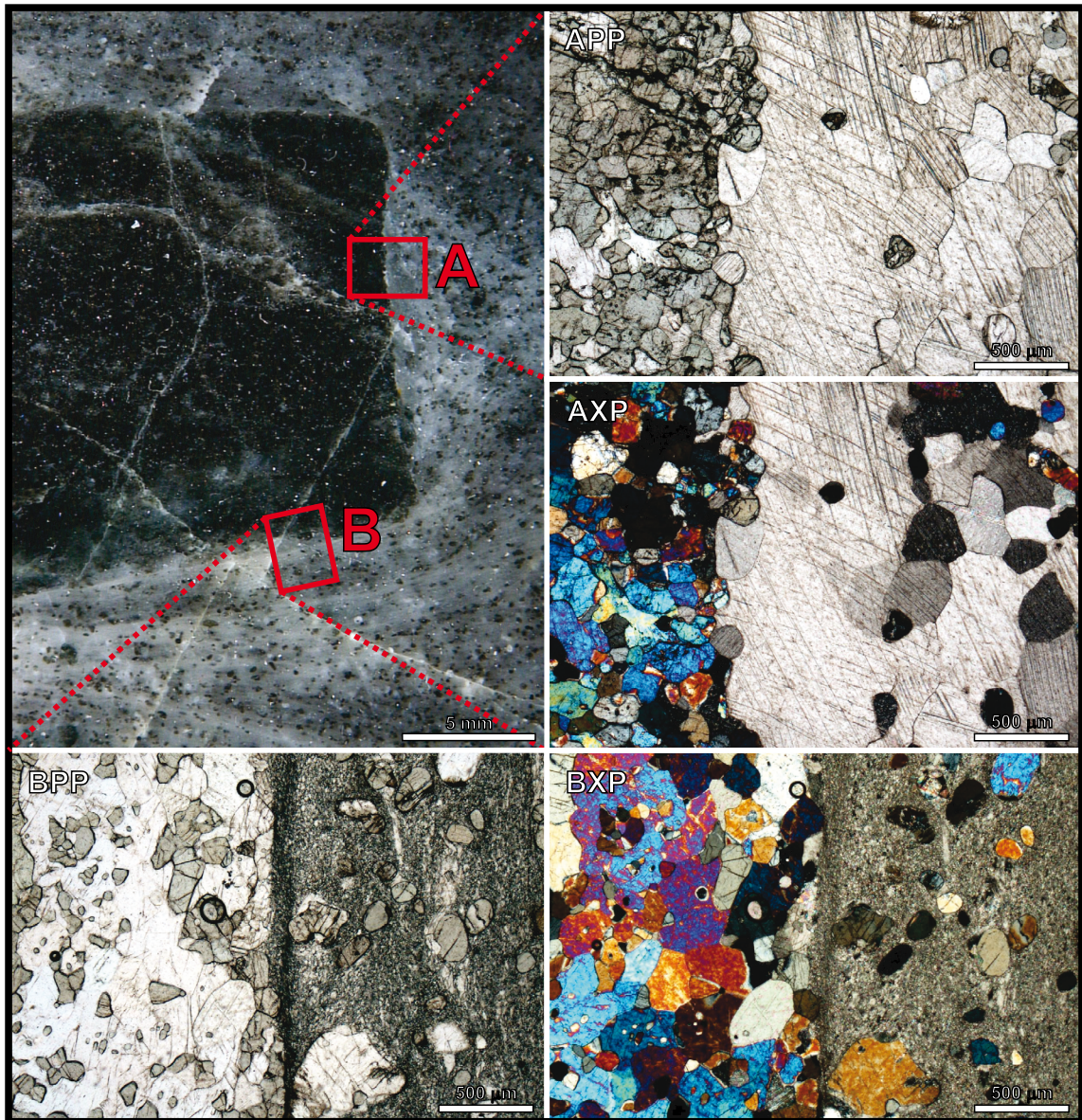
Figure 3. Photographs of Kriva Lakavica carbonatite-like dyke showing a clinopyroxene-rich xenolith in a carbonatite matrix. APP: a plane-polarized view of a clinopyroxene-rich xenolith, showing the boundary between clinopyroxene grains (light green) and the calcite matrix (white with a 120° cleavage) containing diopside grains; AXP: a cross-polarized view; BPP: a plane-polarized view of the same clinopyroxene-rich xenolith showing diopside-hedenbergite grains (light green to light brown) and fluidal structure composed of very small calcitic grains containing rounded diopside grains; BXP: a cross-polarized view.

amphibolite facies. This metamorphism was accompanied and favored by the infiltration of metamorphic fluids that were rich in oxygen and poor in carbon, and moderately changed the $\delta^{18}O$ values, but had little effect on the $\delta^{13}C$ values.

Acknowledgments

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