Influence of Host Marble Rocks on the Formation of Intrusive Alkaline Rocks and Carbonatites of Sangilen (E. Siberia, Russia)

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Abstract: The study of the O and C isotope composition of calcite from nepheline syenites, ijolites and carbonatites of the Chik intrusion and the intrusions of the Erzin–Tarbagatay group of Sangilen (Eastern Siberia, Russia) showed derivation from alkaline melts enriched with a carbonate component from the host marbleized sedimentary rocks. The calculations showed that about 40% of the initial mass of carbonates involved in the interaction with silicate melts have remained after decarbonation. During the assimilation of the carbonate, an oxygen isotope exchange took place between the residual carbonate material and the silicate phase. Crystallization products of such hybrid magmas are carbonatite veins, calcite-rich nepheline rocks and their pegmatites with a calcite core.

Keywords: alkaline magmatism; carbonatites; petrogenesis; isotope geochemistry; oxygen isotopes; carbon isotopes; assimilation; decarbonation; Sangilen; Central Asian Orogenic Belt

1. Introduction

It is assumed that typical carbonatites, for example, in the Paleozoic complexes of Fennoscandia, occurred due to the multistage evolution of a single silicate–carbonate magma generated from a mantle source at low degrees of partial melting [1–4]. Among the 530 currently known carbonatites [5,6], there are some whose genesis has more questions than answers.

First of all, the source of carbonates in magmas is debatable, especially when the host rocks are carbonate sedimentary or metasedimentary rocks.

The identification of the source of carbonates is generally simple, as, for example, in the intrusions of the Maimecha-Kotuiskaya province (Eastern Siberia, Russia) [7]. However, when carbonatites are sharply subordinate to alkaline rocks, identification is difficult. The clearest example is the Vitim, Sangilen or Kuznetsk Alatau alkaline provinces (Eastern Siberia, Russia), where, among a large number of alkaline intrusions, there are some complexes with carbonatites: Petropavlovsky in Kuznetsk Alatau, Chik and Kharly on Sangilen and Saizhensky on Vitim [8].

Available data indicate an important role of crustal contribution in the evolution of alkaline magmas. For example, A.A. Konev [9] established the important role of crustal lithology in the diversity of alkaline associations of the Vitim plateau and the Olkhon region. Predominantly alkaline gabbroids, including ijolites and urtites, are associated with carbonate host rocks, while nepheline syenites and alkaline granites are associated with silicic host rocks. Similar patterns were noted by V.I. Kovalenko [10] in the magmatism of the Eastern Sayan and R.M. Yashina [11] and V.A. Kononova [12] for Sangilen and Khubsugul’ magmatism. The influence of carbonate rocks on alkaline volcanics of the
Roman province of Italy, which has a multi-kilometer (7–8 km) sedimentary carbonate strata at its basement, is especially actively discussed [13,14]. Recent studies of the Vitim, Sangilen, and Kuznetsk Alatau alkaline provinces also indicate an active interaction of magmas with the surrounding carbonate rocks [15–19]. However, the scale of these phenomena, the role of carbonatites in these processes, and, most importantly, the proportion of involved sedimentary carbonate component are still not estimated.

In this paper, using the example of the Chik and Kharly intrusions of the Sangilen, we show that the original silicate melts were significantly enriched by a carbonate component from the host sedimentary rocks, resulting in the formation of carbonatite veins and calcite-rich (>25%) nepheline-bearing rocks.

2. Geological Framework

The Sangilen Highlands covers the western continental margin of the Tuva-Mongolian microcontinent, also known as the Tuva-Mongolian terrane (Figure 1A). This is one of the largest fragments of the Late Precambrian continental crust of the Central Asian Foldbelt, which stretches across the Siberian craton, the North China craton and the Tarim craton.

The geological structure and evolution stages of the northern and southern parts of the Tuva-Mongolian terrane are radically different. The area under consideration belongs to the Sangilen block. The latter includes lithotectonic units of different age and formation conditions, which were amalgamated during the Early Paleozoic geodynamic evolution [20]. Presently, it is a complex thrust-fold structure of sub-latitudinal strike with a folded basement and less dislocated carbonate and carbonate-terrigenous cover. This structure contains numerous intrusions of gabbro-diorite-granodiorite, syenite–diorite and granitoid associations, including spodumene and rare-metal granites. About a dozen intrusions of alkaline nepheline-bearing rocks are known—melteigites, ijolites and nepheline syenites (Figure 1).

Basement rocks are exposed at the western closure of the Sangilen and represent several lithotectonic units (metavolcanic and metaterrigenous). Further, after accretion, they underwent low-pressure amphibolite metamorphism in the Early Paleozoic ca. 500–490 Ma [20–24]. The rocks of the shelf-basin cover, which date from the Neoproterozoic (Ediacaran) and the Lower Cambrian, overlap the basement rocks with erosion and basal conglomerates. They are fragmented into numerous blocks and thrust over each other, rarely metamorphosed. The degree of metamorphism of sedimentary deposits is not uniform and does not depend on the position of rocks in the strata. Limestones are clarified and changed into marble, and the organogenic material into graphite. In terrigenous rocks, the garnet-biotite-muscovite-plagioclase-rutile association sometimes appears. Available geological mapping data at a scale of 1:200,000 clearly show the Balaktygkhem, Chart, Naryn, and Chakhyrtoy suites.

Sangilen’s alkaline nepheline syenite rocks are currently attributed to two different age groups of rocks of the Early Paleozoic and Late Paleozoic [11,25–27]. The studied intrusions belong to the Early Paleozoic group, which unites the Kharly and Ulan-Erge nepheline syenite intrusions, the Dakhunur and Chik ijolite-melteigite intrusions. There are no reliable geochronological data for other intrusions.
3. Chik Intrusion

The intrusion is an elongated body of 0.25 km × 1 km with a minor satellite of 0.05 km × 0.1 km, which lies among graphite-bearing calcite marbles (Figure 2).

The intrusion is composed of a subvertically oriented schlieren-banded bodies of ijolites-melteigites, their calcite varieties (calcite up to 50% vol.) and pegmatites with calcite cores, as well as predominantly carbonate rocks (calcite > 50 vol.%). Carbonate rocks, called carbonatites [8], are developed in the central and southern parts of the intrusion, and are represented by rocks of various granularity and mineral composition: calcite–nepheline–pyroxene, calcite–nepheline and calcite–nepheline–pyroxene–garnet–melilitite rocks. These carbonate rocks are quite distinct from the recrystallized large xenoliths of host marbles that are sometimes found among them. Figure 3 shows the section (profile) of a site in the southern part of the intrusion, composed of predominantly carbonate rocks and recrystallized xenoliths of marble. It also shows the position and the quantitative mineral composition of the studied samples within its limits.
Marbles are massive rocks with a characteristic coarse-grained granoblastic, often heterogranoblastic structure, almost entirely composed of calcite, which contains graphite flakes relatively evenly. Interlayers enriched with diopside and/or apatite grains are rare. The recrystallization of marbles in xenoliths and in some sites of ijolite intrusion contacts is expressed primarily in the purification of carbonates from graphite impurities. Sites of coarse-grained and giant calcite and sites of fine-grained calcite–graphite aggregates appear (Figure 4). The proportion of graphite in such fine-grained sites can reach 95%.

Ijolites and melteigites are coarse-grained rocks composed of nepheline and pyroxene in different proportions, containing apatite (0.5–5%), titanite (0.5–3%), sometimes calcite (up to 10%) and garnet of the andradite–morimotoite–schorlomite range (up to 10%). Graphite is rare, and calcite–nepheline and calcite–pyroxene symplectites appear in the pegmatoid sites (Figure 5).

4. Kharly, Tarbagatay and Skalny Intrusions

In the upper reaches of the Erzin and Tarbagatay rivers, there is a distribution area 5x10 km wide. Small vein bodies and a series of larger (0.5–1 km) subisometric bodies are mapped here, described in detail in previous studies by Yu. L. Kapustin [29,30] and R.M. Yashina [31–33], as Kharly, Oruktyg, Sailyg, Skalny and Tarbagatay intrusions (Figure 1). Hereafter, they will be considered as the intrusions of the Erzin–Tarbagatay group (ETG). In contrast to the Chik intrusion, the intrusions of this group are predominantly enriched in feldspar-bearing varieties: nepheline syenites.

**Figure 2.** A simplified geological map of the Chik intrusion.

**Figure 3.** Geological scheme along section V-1 in Figure 2 with modal compositions of respective sampling points.
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The host rocks are the low part of the sedimentary lithology of the Tuva-Mongolian microcontinent. The basement of the sedimentary strata (about 200 m) is composed of limestones saturated with organic matter, which are partially metamorphosed, up to the appearance of marbles, and above the thick (up to 2000 m) terrigenous carbonate and sandy schist strata with limestone lenses [30].

The intrusions are well exposed in the rocky sides of the valleys to a depth of over 900 m. In the lower parts, they are monolithic (homogeneous and cogenetic), and on the watersheds, they pass into a branching system of vein bodies with areas of fenites. The deep parts of the intrusions are dominated by light gray massive or hedenbergite-bearing nepheline syenites, which consist of nepheline (10–25%), hedenbergite (15–20%), orthoclase-perthite (about 55–60%). The trachytoid texture is due to the orientation of tabular feldspar crystals.

At the upper parts of the intrusion, the quantitative and mineral composition of the rocks varies considerably and areas appear enriched in nepheline (up to 60%), pyroxene (up to 60%), calcite (up to 25%), apatite (up to 15%), andradite–schorlomite (up to 15%), wollastonite (up to 10%) and titanite (up to 5%). Graphite is often present. Hastingsite, biotite, ilmenite, magnetite and zircon are noted. The secondary minerals include albite, sericite, sodalite and cancrinite. In addition to silicate rocks, there are also carbonates containing apatite–nepheline–calcite association (more than 50% calcite), which were called calciphyles by previous researchers. These rocks are found in the external contact zone of intrusions and, as a rule, lie in accordance with the layering of the host marbles. Rarely, they form crosscutting veins in the upper parts of the intrusions.

5. Methods

Oxygen and carbon isotope composition of carbonates was analyzed by decomposition with phosphoric acid technique at 70 °C using CF-IRMS DeltaV+ (Thermo, Finnigan) at the GasBenchII configuration and PAL autosampler (Laboratory of Isotope Geochemistry and Geochronology of the IGEM RAS). Pure carbonate samples (0.2 mg) or carbonate-bearing
rocks (1–10 mg) were finely ground before the analysis. Calibration of $\delta^{18}O$ and $\delta^{13}C$ values in VSMOW and VPDB scales were done by measuring of the NBS 19 and NBS 18 international standards in the same analytical series. The accuracy of $\delta^{18}O$ and $\delta^{13}C$ values estimated from the repeatedly measured standards and replicate samples were ±0.1% and ±0.05% (1σ), respectively. Measured $\delta^{18}O$ and $\delta^{13}C$ values are expressed in Appendix A at the VSMOW and VPDB scales, respectively.

Oxygen isotope composition of pyroxene was carried out using the laser fluorination technique [34] at the Laboratory of Isotope Geochemistry and Geochronology (IGEM RAS). The results were calibrated relatively to VSMOW by the measurements of NBS 28 quartz and UWG 2 garnet [35]. The accuracy of $\delta^{18}O$ determination was ±0.1‰ or better [36].

6. Results
6.1. Isotope Study of Alkaline Rocks and Host Marbles of the Chik Intrusion

Samples for isotope studies of the Chik intrusion were collected from host rocks, blocks of recrystallized marbles, ijolites and their pegmatites with calcite cores, silicate–carbonate rocks, differing in composition and crystal structure. The mineral composition of the studied samples and the isotope composition of oxygen and carbon of carbonates are shown in Appendix A. Samples of host marbles collected to the north and south of the intrusion have a similar oxygen and carbon isotope composition $\delta^{18}O$ 15 ± 1‰ and $\delta^{13}C$ 3 ± 1‰, showing the homogeneous isotope composition of metamorphosed sedimentary strata. The $\delta^{18}O$ and $\delta^{13}C$ values of the carbonate part in more than 30 samples of ijolites, pegmatites and silicate–carbonate rocks also range in relatively narrow intervals: from 15‰ to 19‰ and from −0.3‰ to + 1.7‰, respectively (Figure 6). No regular changes in the O and C isotope composition of the rocks depending on both the position and mineral composition have been noticed. In the samples of micropegmatites, represented by calcite–pyroxene graphic intergrowths, oxygen isotope composition was determined in both the carbonate and silicate parts of the rock. The $\delta^{18}O$ value of pyroxene determined by laser fluorination is +12.4‰, while calcite from these intergrowths is characterized by $\delta^{18}O = 15.5‰$. For this pair, the temperature of isotope equilibration was calculated, taking into account that the composition of pyroxene is complex and corresponds to the isomorphic changes from Ti-Al ferrosalite to aegirine-hedenbergite. Based on the existing equations of oxygen isotope fractionation in the calcite–pyroxene system, the range of the closing temperature of the oxygen isotope system turned out to be narrow. According to the equation of oxygen isotope fractionation in the calcite–diopside system [37], T (Cc-Px) is equal to 600 °C. The minimum estimate is given by the equation of oxygen isotope fractionation in the calcite–hedenbergite system (550 °C, [38]). Thus, the temperature of formation of calcite–pyroxene symplectites could be in the range of 550–600 °C. The O and C isotope composition of calcite from two xenoliths of the host marble, which has clear traces of recrystallization, is intermediate between the carbonate component of ijolites and unaltered marbles. However, the $\delta^{18}O$ and $\delta^{13}C$ values determined for the carbonates of xenoliths are closer to the carbonate component of the ijolites than to the original marbles. No relation between the isotope characteristics and the granularity of carbonates or the content of graphite occurs in them.
Figure 6. Isotope composition of the carbonate component of rocks of alkaline intrusions and host carbonate strata: (I) Chik intrusion, and (II) intrusions of the Erzin–Tarbagatay group.

6.2. Alkaline Rocks and Host Marbles of the Erzin–Tarbagatay Group (ETG)

The collection of samples from the Erzin–Tarbagatay group of intrusions is not as numerous as for the Chik intrusion. In this study, our data are considered with previously published results for the Kharly intrusion [27,39]. The carbon isotope composition of the ETG host calcite marbles differs significantly from the composition of the Chik host marbles ($\delta^{13}$C = $-0.5 \ldots 2.9$‰ and $+3.2 \ldots +3.7$‰, respectively). Apparently, this is the result of multi-temporal sedimentation, hosting the Chik and ETG intrusions. The same difference in the isotope composition of carbon is observed in the carbonate part of silicate and silicate–carbonate rocks in the internal and external contact zones of the studied intrusions. In general, the $\delta^{13}$C value of carbonates of alkaline rocks of the Chik intrusion is $0.2 \pm 0.5$‰, and in the host marbles, it is $3.5 \pm 0.6$‰. At the same time, the $\delta^{13}$C value of carbonate component of the ETG alkaline rocks is significantly lower and in the host marbles, it is also low ($-3.5 \pm 1.5$‰).

These relations show that the isotope characteristics of alkaline rocks in both studied sites were inherited from the host lithology. Accordingly, this could lead to depletion of carbonates from alkaline rocks of the Erzin–Tarbagatay group in the $^{13}$C isotope by more than 2‰, compared to similar rocks of the Chik intrusion (Figure 6).

7. Discussion

The points of view on the genesis of carbonate–silicate rocks are highly controversial. According to some researchers [11,12], the main process is the interaction of silicate melts with host marbles. This point of view considered the studied rocks as a product of contact-reaction or metasomatism. All authors note gradual transitions between host rocks through fenites into internal contact zones of intrusions and also discuss the complex diagnostics
of certain rocks in the series. Thus, to classify these alkaline rocks as intrusive formations, including carbonatites, their magmatic nature should be established.

The dissected relief allows one to observe both the lower and upper parts of the Erzin–Tarbagatay intrusions \[29,30\]. In the lower parts, the intrusions are homogeneous and have a structure typical of magmatic bodies—uniform quantitative and mineral composition, signs of melt flow (trachytoid texture) and hot active contact zones. However, in the upper parts of the intrusions, the rocks are separated by blocks of marble and change into a series of vein-like bodies. These rocks are extremely heterogeneous in composition, their thickness is small, and usually dramatic changes in mineral associations occur.

The ijolites of the Chik intrusion apparently also belong to the upper parts of the section. These rocks show numerous signs of an active fluid–magmatic exchange on the host carbonate rocks: dramatic changes in mineral composition, enrichment of rocks with a carbonate component and the presence of graphite in silicate–carbonate rocks. Despite this, high-temperature melt inclusions \(T_{\text{hom}} = 920–1100^\circ \text{C}\) were diagnosed in nepheline of ijolite-urtites and pyroxene of pyroxene–calcite micropegmatites of the Chik intrusion \[40\].

Isotope composition of oxygen and carbon indicates an active interaction of silicate melts and with the surrounding carbonate rocks. First, within the Chik intrusion, the carbonate component of rocks with different compositions (calcite–pyroxene, calcite–nepheline, calcite–nepheline–garnet, etc.), located far from each other (10–100s of meters), has a relatively homogeneous isotope composition of carbon and oxygen.

The values of \(\delta^{18} \text{O}\) and \(\delta^{13} \text{C}\), established for these rocks, range in narrow intervals, and indicate depletion in heavy isotopes of oxygen and carbon relative to the host marbles (Figure 6).

Second, the isotope composition of carbon in the carbonate component of alkaline rocks reflects the inheritance of isotope characteristics of the host marbles. It is obvious that the controlling role of host marbles in the formation of carbon isotope characteristics of the carbonate component of alkaline rocks is manifested in both the Chik intrusion and the ETG intrusions.

In both cases, the \(\delta^{13} \text{C}\) and \(\delta^{18} \text{O}\) values of the carbonate component of alkaline rocks are depleted in heavy \(^{13}\text{C}\) and \(^{18}\text{O}\) isotopes in comparison with the host marbles by approximately the same value (\(\approx 8\%\)). The minimum \(\delta^{18} \text{O}\) values in the carbonate component of alkaline rocks reach 16 ± 2\% and the nominal \(\delta^{13} \text{C}\) values are low (−6\%). Positive correlation between the \(\delta^{13} \text{C}\) and \(\delta^{18} \text{O}\) values in carbonates can occur when isotopes of both elements fractionate, for example, during decarbonation (removal of \(\text{CO}_2\) as a result of metamorphism \[41\]).

In the \(\delta^{13} \text{C}-\delta^{18} \text{O}\) space, the rest of the decarbonized carbonate-bearing rocks (in our case, this is the carbonate component of alkaline rocks and xenoliths in the contact zone) should follow a trend that starts from the point of the host carbonate composition and is directed towards a decrease in both \(\delta^{13} \text{C}\) and \(\delta^{18} \text{O}\) values. The slope and shape of the trend are determined by the temperature and type of degassing process (Batch or Rayleigh decarbonation, \[41\]). In Figure 7, we compare the obtained data with the published decarbonation trends of sedimentary rocks during contact metamorphism of various localities and scale—from a few centimeters to hundreds of meters. Trends mimic one another, starting from the area close to normal marine limestone \((\delta^{18} \text{O} = 20 \ldots 26\%\), \(\delta^{13} \text{C} = -2 \ldots + 4\%)\) and decreasing towards low (both \(\delta^{18} \text{O}\) and \(\delta^{13} \text{C}\)) values.

Indeed, Figure 7 shows that the carbonate component of alkaline rocks and xenoliths can be inherited from partially decarbonized host carbonate rocks, during carbon dioxide outgassing due to thermal effect of the intruding magmas. For more accurate conclusions, it is necessary to calculate decarbonation trends using the real compositions of the host carbonate rocks and the minimum temperature of contact metamorphism. We used the averaged values of \(\delta^{13} \text{C}\) and \(\delta^{18} \text{O}\) determined in host marbles sampled at a distance 3–700 m from the contact zones of the Chik intrusion \((3.7 ± 0.3\%\) and \(24.7 ± 1.2\%\), respectively). These values are taken as the initial carbonate composition for the calculation.
The decarbonation trends of the Chik host marbles were calculated using the fractionation factors “calcite-CO$_2$” for 500 and 600 °C [43,44]. Position of datapoints obtained for the Chik rocks in the Figure 8 show that at 500–600 °C the decarbonation of the Chik intrusion host marbles was significant: only \( \approx 40\% \) of the initial mass of carbonates involved in the interaction with silicate melts have remained after decarbonation. After the decarbonation, a gradual equilibration of the remaining carbonate phase with cooling silicate minerals should occur to explain the decrease in $\delta^{18}$O values in carbonates with close to constant $\delta^{13}$C values (Figure 8).

The proposed scenario for the interaction of silicate melts with surrounding carbonates is consistent with the fact that the closing temperature of oxygen isotope system in carbonates is lower than that in silicate minerals [45]. The described scheme implies the chemical interaction of the silicate melt with the host carbonate rocks during decarbonation. For example, the interaction could proceed according to a reaction that was observed experimentally during the gradual dissolution of carbonates in a silicate melt [46]:

\[
\text{CaCO}_3 \text{ solid + SiO}_2 \text{ melt + MgO melt + FeO melt + Al}_2\text{O}_3 \text{ melt } \rightarrow \text{(Di-Hd-CaTs) solid + CO}_2 \text{ fluid}
\]

The proposed scenario explains a partial change in the isotope characteristics of carbonates along the decarbonation trend and a further change in only the $\delta^{18}$O values. No other processes, for example, interaction with an aqueous fluid or mixing with the carbonate component of mantle genesis, are required to explain the measured data. Moreover, this mechanism implies that the associations of carbonate-bearing rocks are mainly attributed to the upper contact zones of the studied intrusions.

Similar processes of chemical interaction of silicate magmas with carbonate host rocks, leading to a change in the geochemical features of the magmas, have been repeatedly noted in studies since the publications of the last century [9,47]. For example, the occurrence of alkaline rocks at Mt. Vesuvius is associated with the assimilation of carbonates [14].
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Figure 8. Scheme of decarbonation and carbonate–silicate equilibration processes, which took place during Chick intrusion formation. The decarbonation lines (red solid lines) were calculated using the fractionation factors “calcite-CO$_2$” for 500 and 600 $^\circ$C [43,44]. The arrow shows the direction of partial isotope exchange of carbonate with igneous silicate melt or hot silicate rock. PIC is the primary igneous carbonatites box according to [42]. The symbols are the same as in Figure 6.

Similar explanations were used, for example, to explain the isotope and geochemical features of Late Miocene high Sr-Ba granitoids in the Caucasian Mineral Waters region [48]. The change in the isotope parameters of the alkaline rocks originated in the Vitim province was also referred to the contamination of magmas with sedimentary carbonates [16].

The chemical interaction of alkaline melts with the host carbonates was confirmed by experimental studies, which showed a change in the composition of primitive K-basalts and the formation of alkaline magmas (along with solid phases of clinopyroxene and a fluid phase of CO$_2$) due to the assimilation of carbonate material [46]. Apparently, for the alkaline nepheline-bearing rocks of the Sangilen, the assimilation of the carbonate component of the host rocks plays a decisive role. However, the estimate of chemical composition of the initial silicate melts is highly desirable. The reaction of the melt with carbonates should lead to the formation of new reaction phases (for example, Ca-Cx), enrichment of melt with alkalis, and depletion of SiO$_2$. Preliminary estimates show that the initial parental magmas that formed the ijolites and nepheline syenites of the Sangilen Highlands could have a composition close to syenite–diorite, with a SiO$_2$ content of more than 53 wt%.

The studied rocks of the upper zones of the Erzin–Tarbagatay intrusions and the part of the Chik intrusion available for study show reactionary assimilation at the contact with the host marbles. However, the question of the origin of the melts that form the nepheline syenites of the “lower” parts of the intrusions remains open. It is possible that they are the products of processing of the host strata that occupied this volume, but this assumption requires additional research.
8. Conclusions

The proposed scenario of the reaction interaction with the carbonates of the host rocks describes well the isotope characteristics of the Chik and Erzin–Tarbagatay intrusions. Despite the mineral diversity, rather narrow ranges of the $\delta^{18}O$ and $\delta^{13}C$ values of the carbonate component are observed here, which implies the inheritance of the isotope characteristics of the host marbles. In general terms, we can suggest the following scenario of contact interaction:

1. assimilation of host carbonate rocks by silicate magma;
2. reaction of carbonates with magmatic melt, resulting in the removal of carbon dioxide from the system and the formation of specific mineral associations. For the Chik area, we estimate that about 40% of the initial mass of carbonates involved in the interaction with silicate melts should remain after decarbonation;
3. isotope exchange of oxygen between residual carbonate material and silicate phases during crystallization of melts and further cooling of intrusions.

As a result, homogeneous isotope $\delta^{18}O$ and $\delta^{13}C$ characteristics are observed in the carbonate composition of the Sangilen Highlands rocks, which have retained a relation with the primary isotope parameters of the host marbles.

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Table A1. Stable carbon and oxygen isotope compositions of calcite in rocks of nepheline syenite intrusions and host marbles of Sangilen Highlands.

| Sample №  | Rock Type                              | Mineral Composition | δ¹³C ‰ (VPDB) | δ¹⁸O ‰ (VSMOW) |
|-----------|----------------------------------------|---------------------|---------------|----------------|
|           |                                        | Kfs Nph Cpx Gar Mic Cal Gf Ap Ttn |               |                |
| 270/2     | Garnet ijolite                         | 60 26 13            | <1            | <1             | 0.66 | 16.78 |
| V-1-0     | Urtite                                 | 71 23 5             | <1            | <1             | 0.10 | 16.45 |
|           | Chik intrusion rock types               |                     |               |                |
| V-1-21    | Pyroxene carbonatite                   | 49 1 50             | 0.55          | 15.49          |
| V-1-28    | Pyroxene carbonatite                   | 5 40 54             | 0.00          | 16.03          |
| V-2-1     | Pyroxene carbonatite                   | 5 50 50             | 0.12          | 16.31          |
| V-2-4     | Nepheline–pyroxene–garnet carbonatite  | 20 13 15 50 2       | 0.07          | 16.22          |
| V-2-17    | Nepheline carbonatite                  | 20 8 71 <1          | −0.15         | 15.34          |
| 272/3     | Nepheline–pyroxene carbonatite         | 10 36 53            | 0.06          | 15.69          |
|           | Chik intrusion, silicate–carbonate rocks, south contact zone, >50 % Cal | | | |
| V-1-20    | Calcite–graphite melteigite            | 50 34 10 6          | 0.27          | 16.86          |
| V-1-23    | Calcite ijolite                        | 39 36 25            | 0.13          | 16.41          |
| V-1-27    | Urtite                                 | 87 1 9 1            | 0.16          | 16.00          |
| V-1-29    | Ijolite                                | 50 41 8             | 0.05          | 16.94          |
| V-1-30    | Calcite–graphite ijolite               | 30 30 30 10         | 0.11          | 16.17          |
| V-1-34    | Urtite                                 | 91 5 3 <1           | 0.29          | 16.07          |
| V-1-35    | Carbonatite                            | 55 55 44 <1         | 0.12          | 15.74          |
| V-1-37    | Ijolite                                | 61 30 9             | 0.27          | 14.01          |
| V-2-8     | Calcite–garnet urtite                  | 60 10 15 14 <1      | 0.41          | 17.19          |
| V-2-10    | Calcite–garnet ijolite                 | 38 7 35 19 <1       | 0.56          | 16.89          |
| V-2-15    | Urtite                                 | 70 18 8             | 0.77          | 17.35          |
| V-3-1     | Ijolite                                | 37 57 5 <1          | 0.42          | 17.06          |
| V-3-5     | Calcite ijolite                        | 37 25 37 <1         | −0.05         | 16.03          |
| 272/2     | Calcite ijolite                        | 30 50 9 11          | 0.07          | 16.25          |
|           | Chik intrusion, silicate–carbonate rocks, south contact zone, <50 % Cal | | | |
| V-1-1     | Calcite–graphite rock                  | 40 60               | 0.36          | 17.34          |
| V-1-2     | Calcite–graphite rock                  | 60 40               | 1.66          | 20.53          |
| V-1-3     | Calcite–graphite rock                  | 15 85               | −0.01         | 15.37          |
Table A1. Cont.

| Sample № | Rock Type                        | Mineral Composition | $\delta^{13}$C ‰ (VPDB) | $\delta^{18}$O ‰ (VSMOW) |
|-----------|----------------------------------|---------------------|--------------------------|---------------------------|
| V-1-4     | Calcite–graphite rock            |                     | 60                       | 0.80                      | 16.26                    |
| V-1-5     | Graphite rock                    |                     | 5                        | 95                        | 4.94                     | 18.17                    |
| V-1-6     | Calcite coarse-grained           |                     | 100                      |                           | 0.74                     | 17.43                    |
| V-1-7     | Calcite–graphite rock            |                     | 45                       | 55                        | 0.79                     | 17.59                    |
| V-1-10    | Calcite coarse-grained           |                     | 98                       | 2                         | 0.59                     | 17.07                    |
| V-1-18    | Pyroxene–graphite carbonate      |                     | 35                       | 50                        | 14                       | 1                        | 0.77                     | 17.16                    |
| V-2-6     | Calcite coarse-grained           |                     | 45                       | 55                        |                           |                          | −0.18                    | 14.86                    |
| V-2-7     | Calcite marble                   |                     | 95                       | 5                         |                           |                          | 3.13                     | 22.06                    |
|           | Chik intrusion, host marbles     |                     |                          |                           |                          |                          |                          |                          |
| Chk-6     | Calcite marble, 5 m from contact |                     | 99                       | <1                        |                           |                          | 0.98                     | 26.17                    |
| 20-43g    | Calcite marble, 3 m from contact |                     | 99                       | <1                        |                           |                          | 4.11                     | 23.77                    |
| Chk-18    | Calcite marble, 700 m from contact|                     | 99                       |                           |                          |                          | 3.80                     | 26.55                    |
|           | Skalny intrusion of Erzin–Tarbagatay group |                     |                           |                          |                          |                          |                          |                          |
| Chk-17/1  | Calcite marble, >10 m to the north from contact | 99 | <1 | 3.70 | 23.82 |
| Chk-7/1   | Calcite marble, >10 m to the north from contact | 99 | <1 | 3.69 | 24.07 |
| Chk-7/2   | Calcite marble, >10 m to the north from contact | 99 | <1 | 3.17 | 25.31 |
| 273/1     | Calcite marble, 150 m to the north from contact | 99 | <1 | 3.11 | 23.80 |
| V-7-3     | Calcite coarse-grained from nepheline syenites | 100 |                           | −1.52 | 16.47 |
| V-7-4     | Calcite–pyroxene rock            |                     | 20                       | 80                        |                           | −1.41                    | 17.54                    |
| V-7-5     | Calcite rock different-grained   |                     | 99                       |                           | −1.29                    | 20.30                    |
| V-7-6     | Calcite rock fine-grained        |                     | <1                       | 98                        | 1                        | −0.89                    | 21.72                    |
| V-7-7     | Calcite coarse-grained           |                     | 99                       |                           | −2.71                    | 14.67                    |
|           | Tarbagatay intrusion of Erzin–Tarbagatay group |                     |                           |                          |                          |                          |                          |                          |
| V-064-2   | Calcite rock coarse-grained with apatite | <1 | 95 | 5 | −2.73 | 17.86 |
Table A1. Cont.

| Sample № | Rock Type                                      | Mineral Composition | $\delta^{13}C$ ‰ (VPDB) | $\delta^{18}O$ ‰ (VSMOW) |
|----------|-----------------------------------------------|---------------------|--------------------------|---------------------------|
|          |                                               | Kfs | Nph | Cpx | Gar | Mic | Cal | Gf | Ap | Ttn |
| Kharly intrusion of Erzin–Tarbagatay group |
| V-8-2    | Nepheline syenite                            | 30  | 35  | 30  | 5   | 5   | 5   | 5  | 5  | 5   |
| V-8-4    | Calcite–pyroxene–nepheline rock              | 50  | 30  | 20  | 20  | 20  | 20  | 20 | 20 | 20  |
| V-8-5    | Feldspar urtite                              | 20  | 78  | <1  | 1   | 1   | 1   | 1  | 1  | 1   |
| V-8-6    | Calcite–pyroxene–nepheline rock              | 20  | 39  | <1  | 40  | 40  | 40  | 40 | 40 | 40  |
| V-8-7    | Calcite–pyroxene–nepheline rock with apatite | 10  | 10  | <1  | 75  | 75  | 75  | 75 | 75 | 75  |
|          |                                               |      |     |     |     |     |     |     |     |     |
| Host marbles of the Skalny, Tarbagatay and Kharly intrusions of Erzin–Tarbagatay group |
| V-91     | Marble medium-grained from the Kharly river mouth (>1 km from contact) | 99  | <1  | <1  | 99  | <1  | <1  | 99 | <1 | 99  |
| 268/26   | Calcite marble                               | 99  | <1  | <1  | 268/26 | <1  | <1  | 268/26 | <1  | <1  |
|          |                                               |      |     |     |     |     |     |     |     |     |
| Marble, Kharly intrusion (Kuleshov, 1986) [39] |
| 497      | Calcite marble, south-east contact            |      |     |     |     | 497 |     |     | 497 |     |
| 961      | Banded dolomite-bearing marble from external contact zone | 961 |     |     |     | 961 |     |     | 961 |     |
| 961 a    | Altered marble with apatite and pyroxene from external contact zone | 961 a |     |     |     | 961 a |     |     | 961 a |     |
| 850      | Marble xenolith within ijolite                | 850 |     |     |     | 850 |     |     | 850 |     |
| 1008     | Banded marble                                | 1008 |     |     |     | 1008 |     |     | 1008 |     |
| 1060     | Marble xenolith within ijolite                | 1060 |     |     |     | 1060 |     |     | 1060 |     |
| 1135     | Marble xenolith within granites               | 1135 |     |     |     | 1135 |     |     | 1135 |     |
| 1399     | Banded marble                                | 1399 |     |     |     | 1399 |     |     | 1399 |     |
|          |                                               |      |     |     |     |     |     |     |     |     |
| Calciphyres, Kharly intrusion (Kuleshov, 1986) [39] |
| 488      | Altered marble with feldspathoids            | 488 |     |     |     | 488 |     |     | 488 |     |
| 957      | Apatite–pyroxene–calcite rock                | 957 |     |     |     | 957 |     |     | 957 |     |
| 521      | Apatite–pyroxene–calcite rock                | 521 |     |     |     | 521 |     |     | 521 |     |
| 1022 a   | Nepheline–calcite rock                       | 1022 a |     |     |     | 1022 a |     |     | 1022 a |     |
| 1025     | Nepheline–calcite rock                       | 1025 |     |     |     | 1025 |     |     | 1025 |     |
| 1026     | Nepheline–calcite rock                       | 1026 |     |     |     | 1026 |     |     | 1026 |     |
| 1032 a   | Flogopite–calcite rock                       | 1032 a |     |     |     | 1032 a |     |     | 1032 a |     |
| 1032 δ   | Calciphyre                                   | 1032 δ |     |     |     | 1032 δ |     |     | 1032 δ |     |
| 1098 a   | Ijolite                                      | 1098 a |     |     |     | 1098 a |     |     | 1098 a |     |
| Sample № | Rock Type                                              | Mineral Composition | $\delta^{13}$C ‰ (VPDB) | $\delta^{18}$O ‰ (VSMOW) |
|----------|--------------------------------------------------------|---------------------|--------------------------|---------------------------|
| 1084     | Pegmatite with calcite from nepheline syenites         |                     | −5                       | 13                        |
| 499      | Calcite vein with apatite, magnetite and mica from nepheline syenite |                     | −3.8                     | 18.6                      |
| 498      | Calcite vein with apatite, magnetite and mica from nepheline syenite |                     | −0.7                     | 16.4                      |
| 908      | Calcite vein with apatite, magnetite and mica from nepheline syenite |                     | −3.4                     | 16.6                      |
| 798      | Central part of the calcite vein from nepheline syenite |                     | −3.3                     | 17.6                      |
| 929      | Calcite vein from nepheline syenites                    |                     | −3.1                     | 17.5                      |
| 971      | Calcite vein from ijolites                              |                     | −2.5                     | 16                        |
| 1179     | Silicate–carbonate rock from ijolite and marble contact zone |                     | −4                       | 16                        |
| 1186     | Calcite vein with apatite and mica from ijolite         |                     | −3.9                     | 17.1                      |
| 1190     | Calcite vein with feldspar from ijolite                 |                     | −3.8                     | 14                        |
| 1198     | Dyke of calcite–pyroxene–apatite–mica rock, cutting ijolites |                     | −3.4                     | 17.1                      |
| 1197     | Calcite vein with pyroxene from ijolite                 |                     | −3.6                     | 17.3                      |
| 1203     | Calcite vein with pyroxene                              |                     | −0.7                     | 16.4                      |
| 1220     | Calcite vein from nepheline syenite                      |                     | −3.4                     | 16.6                      |
| 1308     | Silicate–carbonate rock                                 |                     | −2.9                     | 15.9                      |
| 950      | Ijolite                                                |                     | −2.2                     | 16.9                      |
| 2540     | Carbonatite-like rock                                   |                     | −2.7                     | 15.2                      |
| 498/2    | Carbonatite-like rock with apatite                        |                     | −2.3                     | 16.4                      |
| 268/10   | Carbonatite-like rock c microcline                             |                     | −2.6                     | 15                        |
| 268/11   | Carbonatite-like rock                                    |                     | −2.3                     | 19.5                      |
| 2843/35  | Calcite vein                                           |                     | −0.5                     | 17.3                      |
| 2843/31  | Calcite vein                                           |                     | −0.6                     | 17.5                      |

Annotation. For the literature data, the quantitative mineral composition is not given. Kfs—K-feldspar, Nph—nepheline, Cpx—clinopyroxene, Gar—garnet, Mic—biotite, phlogopite, Cal—calcite, Gf—graphite, Ap—apatite, Ttn—titanite.
