

Application of Proxy Minerals for Evaluation of the Oxygen Isotope Composition of Felsic Melts

E. O. Dubinina^a, * and L. Ya. Aranovich^a

^a *Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry, Russian Academy of Sciences, Moscow, Russia*

**e-mail: elenadelta@inbox.ru*

Received October 25, 2022; revised December 23, 2022; accepted February 18, 2023

Abstract—The problems associated with the use of quartz and zircon as proxy minerals for the reconstruction of $\delta^{18}\text{O}$ values in acidic melts are considered. It is shown that the correction values $\Delta(Qz-R)$ and $\Delta(R-Zrn)$ used for the reconstructions are not strictly constant and depend on the mineral composition of the rock and the closure temperature of the oxygen isotopic system of the proxy mineral (T_q , T_z —closure temperature of quartz and zircon, respectively). The applicability of quartz was estimated using an equation for $\Delta(Qz-R)$ calculation, which takes into account T_q and the mineral composition of rocks. Using the leucogranites of the Raamid massif (South Pamirs) as an example, it was shown that this correction can be approximated by constant value only under definite conditions. The value of $\Delta(R-Zrn)$ was estimated using approach based on calculating the weighted average fractionation coefficient and independent estimates T_z using a zirconium thermometer. It was shown for leucogranite porphyries of the Omsukchan trough that this correction for identical rocks varies from 1.3 to 1.9 ‰, unlike $\Delta(R-Zrn) = 2.1$ determined by the dependence on the SiO_2 content (Lackey et al., 2008). The advantages and limitations on the application of quartz and zircon as proxy minerals have been analyzed.

Keywords: proxy minerals, oxygen isotope composition, $\delta^{18}\text{O}$, quartz, zircon, retrograde isotope exchange, granites, phenocrysts, lavas, rhyolites, diffusion, leucogranites

DOI: 10.1134/S0869591123060073

INTRODUCTION

The reconstruction of $\delta^{18}\text{O}$ values of melts based on the oxygen isotope composition of proxy mineral (this term refers to the mineral—indicator of nature of parental melts) is required in solving many petrological problems (see overviews, e.g., Bindeman, 2008; Valley, 2003; Valley et al., 2005). The proxy mineral for mafic and ultramafic melts is olivine phenocrysts (e.g., Eiler et al., 2011, 1996; Gurenko and Chaussidon, 2002), which record the earliest isotope composition of parental melt due to the low diffusion rate of oxygen in it. Further processes related to the emplacement of magmatic body could lead to a change of $\delta^{18}\text{O}$ in the melt, but olivine records the early stages of the evolution of magmatic system.

During crystallization of felsic melts, for instance, rhyolite or granite porphyry, rock-forming minerals with low diffusion rate are not formed. Zircon having the minimum diffusion rates for many components, including oxygen, can be regarded as the suitable proxy mineral for estimating the nature of protolith or parental melt (Watson and Cherniak, 1997; Farver, 2010). However, this mineral occurs in accessory amounts and frequently has a more complex nature

than the host rock. In addition, it is difficult to analyze a large amount of matter and estimate reliably isotope homogeneity of zircon, as well as to determine the affiliation of all analyzed grains to the studied magmatic process. Nevertheless, zircon has been increasingly applied as mineral reflecting the evolution of sources of felsic rocks (e.g., Colón et al., 2018; Pietranik et al., 2013; Kitajima et al., 2012). Quartz can be conditionally regarded as the second proxy-mineral for oxygen isotope composition of felsic melts, although it is characterized by the high oxygen diffusion rates (Farver, 2010; Dennis, 1984a, 1984b). At the same time, it has the lowest diffusion rates among minerals of granite association and can be conditionally considered as stable mineral compared to other minerals of felsic rocks. It should be taken into account that the oxygen diffusion rates in quartz are significant and the $\delta^{18}\text{O}(Qz)$ value can be modified, for instance, by interaction with external fluid or by contamination (e.g., Dubinina et al., 2010). However, the main process responsible for a change of $\delta^{18}\text{O}(Qz)$ value in felsic rocks is a retrograde isotope exchange (Giletti, 1986; Harris et al., 1997; Jenkin et al., 1994; Kohn and Valley, 1998), which proceeds from the onset of mineral crystallization to the closure tem-

perature of its oxygen isotope system (T_q). This process is the least expressed in phenocrysts of rapidly cooling felsic lavas and is very common in minerals of the holocrystalline rocks. The retrograde exchange could be ignored only in the first case, unless the $\delta^{18}\text{O}(Qz)$ value was not modified during later process. For instance, the direct evidence for the late fluid impact is the lowered $\delta^{18}\text{O}$ value in other less “stable” minerals of the rock: *Pl* or *Kfs*. Evidence for reactive contamination could be disequilibrium relations between phenocryst minerals and groundmass (Dubinina et al., 2010). However, these observations require the measurement of not only quartz, but also other minerals, while reconstruction performed using $\delta^{18}\text{O}(Qz)$ value alone, even with correction, could be erroneous.

In order to reconstruct $\delta^{18}\text{O}$ value of felsic melts using quartz and (or) zircon as proxy minerals, the values of $\Delta(Qz-R)$ and $\Delta(R-Zrn)$ representing the equilibrium oxygen isotope shift between minerals and rock are required. In this paper, we attempted to estimate these parameters.

There are two variants of $\Delta(Qz-R)$ correction. In the first variant, the correction is constant (1‰ for quartz porphyry and 2‰ for coarse-grained granites) and proposed in (Harris et al., 1997). This correction takes into account only “cooling effect” of granitoid rocks. It is applied to calculate the oxygen isotope composition of initial felsic rock at the moment of its crystallization using known $\delta^{18}\text{O}(Qz)$ value, assuming that the oxygen isotope system of quartz was not disturbed after closure. This correction is empirical and does not involve the mineral composition of rock and the closure temperature of minerals, which depends not only on grain size but also on the cooling environment.

The second variant of correction $\Delta(Qz-R)$ was proposed for rapidly cooling felsic lavas (Bindeman et al., 2004; Bindeman, 2008). It represents an oxygen isotope shift between quartz and melt (rock) at crystallization temperature of phenocrysts, which is estimated based on the SiO_2 and alkali contents in the rock. The rock is approximated by a set of normative minerals, for which the weighted average fractionation coefficient relative to quartz is calculated. This correction $\Delta(Qz-R)$ does not imply the subsolidus isotope exchange at cooling. In addition, this correction is insignificant at high temperatures of formation of quartz phenocrysts. For instance, it was constant (0.45‰, Akinin and Bindeman, 2021) for rhyolites of the Okhotsk–Chukotka volcanic belt. Of great importance in this approach is the problem of oxygen isotope equilibrium between quartz and groundmass (Bindeman et al., 2008; Dubinina et al., 2020).

Only one variant of reconstruction was proposed for zircon based on the dependence of $\Delta(R-Zrn)$ correction on the SiO_2 content in the rock (Lackey et al., 2008). This dependence was established empirically,

although it is obvious that the isotope fractionation in the system *Zrn*–melt (rock) is controlled not only by SiO_2 content in the melt or rock.

We carried out the theoretical evaluation of $\Delta(Qz-R)$ and $\Delta(R-Zrn)$ and considered factors that determined these values. The efficiency of these corrections compared to those available in the literature was tested using definite examples in order to understand the strategy of application of quartz and zircon as proxy minerals for the reconstruction of $\delta^{18}\text{O}$ value of felsic melts.

EVALUATION OF OXYGEN ISOTOPE FRACTIONATION BETWEEN QUARTZ AND OTHER MINERALS OF GRANITIC ROCKS

The oxygen system of quartz is the first to close (at T_q) among rock-forming minerals of a cooling rock. Up to this moment, the $\delta^{18}\text{O}(Qz)$ value is controlled by the oxygen isotope composition of all other minerals of the rock (Giletti, 1986; Kohn and Valley, 1998; Farquhar et al., 1993), and the lower the T_q the stronger is this influence. Assume that T_q is known, while the oxygen isotope system of rock was not disturbed by later events. In this case, we can apply approach based on the thermometric equations and mass-balance conditions for definite domain of the rock (e.g., Jenkin et al., 1994; Farquhar et al., 1993). A simplified order of closure of the oxygen isotope system of the granitic rock is assumed: $Qz \rightarrow Bt \rightarrow (P)$, where P is the K-feldspar and plagioclase, which are considered as a single mineral phase. Combining *Kfs* and *Pl* into a single phase for most felsic rocks is quite justified, as at the plagioclase composition close to albite (An_{10-20}), the isotope fractionation between *Kfs* and *Pl* is negligible and comparable with analytical error (within 400–800°C, it is $\approx 0.3\%$ for $Pl(An_{20})$ and $\approx 0.2\%$ for $Pl(An_{10})$, Chacko et al., 2001; Vho et al., 2020). In addition, *Kfs* and *Pl* are characterized by the similar oxygen diffusion rates, i.e., their closure temperature also should be close at similar crystal sizes. A simplified temperature dependence of fractionation coefficient ($\Delta \approx 10^3 \text{Ln}\alpha(a-b) = A_{a-b} \times 10^6 T^{-2}$) is taken, which is usually used for the description of magmatic processes (Valley, 2001; Chacko et al., 2001). It was also suggested that the transitional zone in the closure temperature region of the oxygen isotope system of minerals is minimum or absent (Valley, 2001), i.e., the values of T_q , T_b , and T_p (closure temperature of quartz, biotite, and feldspar, respectively) are the minimum boundary temperatures at which mineral is in isotope equilibrium with other isotopically open minerals. Up to approaching temperature T_q , all minerals of the rock are in isotope equilibrium with each other. Therefore, isotope shifts between feldspars and biotite,

as well as between quartz and feldspar at T_q can be written as follows:

$$\Delta_{p-b}^q = A_{p-b} \times 10^6 T_q^{-2}$$

and

$$\Delta_{q-p}^q = A_{q-p} \times 10^6 T_q^{-2}, \quad (2)$$

where indices q, b, and p designate quartz, biotite, and feldspars, while A_{p-b} and A_{q-p} values are coefficients in the corresponding thermometric equations ($10^3 \text{Ln}\alpha(a-b) = A_{a-b} \times 10^6 T^{-2}$). Equilibria (2) can be combined, omitting T_q :

$$X_q = k(q) X(q) / [k(q) X(q) + k(b) X(b) + k(p) X(p)].$$

δ_q in equation (4) corresponds to the measured $\delta^{18}\text{O}(Qz)$ value. The oxygen isotope composition of other minerals at T_q is:

$$\begin{aligned} \delta_b &= \delta_p - (\Delta_{p-b}^q)_{T_q} = \delta_q - (\Delta_{q-p}^q)_{T_q} - (\Delta_{p-b}^q)_{T_q} \\ \text{and } \delta_p &= \delta_q - (\Delta_{q-p}^q)_{T_q}. \end{aligned} \quad (5)$$

Substituting (2), (4), and (5) in equation (3) yields the following equation for whole-rock oxygen isotope composition:

$$\delta_R = \delta_q - (\Delta_{q-p}^q)_{T_q} \left(X_p + X_b \left(1 + \frac{A_{p-b}}{A_{q-p}} \right) \right), \quad (6)$$

From this equation, we obtain $\Delta(Qz-R)$:

$$\begin{aligned} \Delta(Qz-R) &= \delta_q - \delta_R \\ &= (\Delta_{q-p}^q)_{T_q} \left(X_p + X_b \left(1 + \frac{A_{p-b}}{A_{q-p}} \right) \right). \end{aligned} \quad (7)$$

Equation (7) shows that $\Delta(Qz-R)$ is not a constant value, but depends on two factors: closure temperature of the oxygen isotope system of quartz, T_q , and proportions of other rock-forming minerals, biotite and feldspars. The role of the last factor is illustrated by the calculation presented in Figs. 1a–1d. The calculation was carried out at varying fraction of quartz in the rock (X_q from 0.05 to 0.5) for two variants of feldspars and biotite proportions: fixed X_b at variable X_p (Figs. 1a, 1b) and fixed X_p : X_b ratio (Figs. 1c, 1d). Two temperatures were given for calculations: 900°C and 600°C, which corresponded, respectively, to conditions close to quenching of igneous felsic melt (at 900°C, Figs. 1a, 1c) and conditions of retrograde cooling of granitic intrusion up to $T_q = 600^\circ\text{C}$ (Figs. 1b, 1d). It should be noted that T_q in many cases can decrease up to 400°C and lower depending on the quartz grain size and cooling rate of the rock (Dodson, 1973). Values of cor-

$$\frac{\Delta_{p-b}^q}{A_{p-b}} = \frac{\Delta_{q-p}^q}{A_{q-p}} \quad \text{and} \quad \Delta_{p-b}^q = \Delta_{q-p}^q \frac{A_{p-b}}{A_{q-p}}. \quad (3)$$

Oxygen mass balance for rock consisting of three minerals (q – Qz , b – Bt and p – ($Kfs + Pl$)) has the following form:

$$\delta_R = X_q \delta_q + X_b \delta_b + X_p \delta_p, \quad (4)$$

where X_q , X_b , and X_p are the oxygen fractions of rock in the corresponding mineral ($X_q + X_b + X_p = 1$). The stoichiometric coefficient $k(i)$ (mass fraction of oxygen in mineral formula) should be taken into account in calculation. For instance, the oxygen content in quartz ($k(q) = 0.53$) with mass fraction of $x(q)$ can be written as follows:

rections for quartz porphyry ($\Delta(Qz-R) \approx 1\%$, Harris et al., 1997) and felsic lavas ($\Delta(Qz-R) \approx 0.45\%$, Bindeman et al., 2004; Akinin and Bindeman, 2021) are plotted in Fig. 1 for comparison.

The calculated value $\Delta(Qz-R)$ for $T_q = 900^\circ\text{C}$ (i.e., at quenching of felsic melt) could be close both to the correction for quartz porphyry and for felsic lavas, depending on the quartz content in the rock. An increase of biotite content in the rock also leads to the increase of $\Delta(Qz-R)$. At lower temperature, the value always exceeds the correction for felsic lavas and varies between the cooling rate corrections for coarse-grained granites and quartz porphyries (1–2%, Harris et al., 1997). Thus, the mineral composition of rocks should be taken into account at evaluating $\Delta(Qz-R)$. For instance, rock with high biotite and low quartz contents requires the higher correction than typical leucogranites and rocks with high quartz content.

Indeed, the value of $\Delta(Qz-R)$ is also controlled by the closure temperature of the oxygen isotope system of quartz. To illustrate the T_q influence, the coefficient was calculated for several fixed compositions of felsic rock (at $X_q = 0.3$, $X_b = 0.05$, 0.1, and 0.2) at T_q varied from 1000 to 400°C T_q (Fig. 2). This calculation demonstrates that $\Delta(Qz-R)$ at high T_q values ($\approx 900^\circ\text{C}$ and higher) is close to the correction for felsic lavas (Bindeman et al., 2004), while within the range of $T_q \approx 500$ – 600°C it is close to values for quartz porphyries (Harris et al., 1997) and approaches that for coarse-grained granites (2%) at even lower closure temperature of the oxygen isotope system of quartz. In general, $\Delta(Qz-R)$ increases with decreasing T_q , which means that T_q is required to reconstruct the compositions of slowly cooling granitic melts.

It is obvious that the application of constant correction $\Delta(Qz-R)$ based on the rock petrography (e.g., rhyolite or porphyritic granite) is not correct, even if

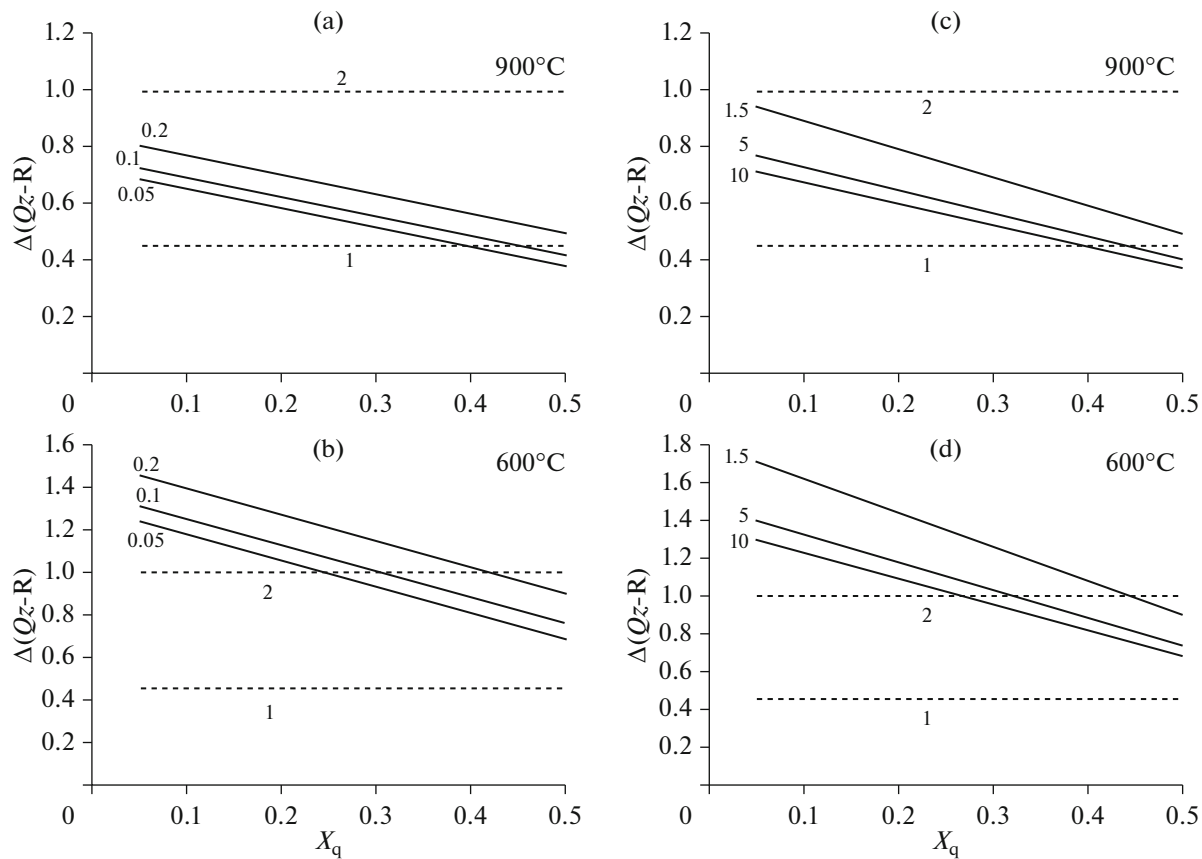


Fig. 1. Values of isotope shift between quartz and granitoid rock $\Delta(Qz-R)$ at $T_q = 900^\circ\text{C}$ (a, c) and retrograde cooling up to $T_q = 600^\circ\text{C}$ (b, d). Dashes 1 and 2 are values of constant corrections for felsic lavas (Bindeman et al., 2004) and quartz porphyry (Harris et al., 1997), respectively. Proportions of biotite and feldspars taken in calculations: (a, b) biotite content was taken to be constant ($X_b = 0.05, 0.1$ and 0.2 —numbers near curves), the value of X_p decreases with the growth of X_q ; (c, d) the proportions of feldspars and biotite were taken to be constant ($X_p : X_b = 1.5, 5, 10$ —numbers near curves).

isotope system of the rock was not disturbed. Nevertheless, $\Delta(Qz-R)$ in real rocks can weakly vary, and can be taken to be constant within conditional accuracy of its estimates. This is related to two factors: (1) proportions of rock-forming minerals in similar felsic rocks show limited variations and (2) oxygen isotope fractionation coefficients between quartz and feldspar, which determine $\Delta(Qz-R)$, weakly depend on temperature. Thus, the effects of both these factors could be not critical, and empirical approach can be justified. However, any corrections (constant or no) are valid only if the oxygen isotope system of quartz was not disturbed after closure. The absence of such disturbances is illustrated by the example of the Eocene leucogranite porphyry of the Raumid massif.

Example 1: Leucogranite Porphyry of the Raumid Massif

These rocks form a multiphase (eight intrusive phases) massif of Eocene age (35.5 ± 0.9 Ma, Kostitsyn et al., 2007a; Volkov et al., 2016) located in the South Pamirs. The geological description of the massif is reported in (Volkov and Negrei, 1974; Kostitsyn et al.,

2007b; Volkov et al., 2016). We studied petrological, geochemical, and oxygen isotope characteristics of the rocks of the Raumid massif (Dubinina et al., 2023a). Based on our data and works by other authors, the rocks of the Raumid massif did not experience any external influence, besides sufficiently complex cooling scheme caused by the multiphase emplacement of the massif. The $\delta^{18}\text{O}$ values of quartz and rock simultaneously changes from one phase to another (Fig. 3a), with $\Delta(Qz-R)$ variations from 0.73 to 1.17‰ (Fig. 3b). These variations mainly reflect different closure temperatures of quartz, since the mineral composition of rocks of all phases is almost identical. On average, the estimated $\Delta(Qz-R)$ value is $0.98 \pm 0.2\text{‰}$, which is very close to the correction for cooling effect of leucogranites (1‰, Harris et al., 1997). Therefore, the $\delta^{18}\text{O}(R)$ value reconstructed using a constant correction of 1‰ is very close to the measured $\delta^{18}\text{O}$ of leucogranite porphyries of the Raumid massif (dashed line in Fig. 4). Unambiguously, such coincidence is caused by the absence of later external impact on the rocks of the Raumid massif and proximity of their mineral composition to typical leucogranites, correction for

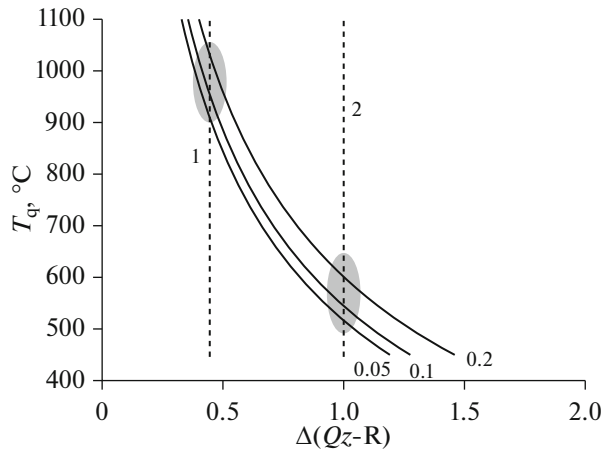


Fig. 2. Values of isotope shift between quartz and granitoid rock at change of the closure temperature of quartz (T_q). Dashes 1 and 2 are values of constant corrections for felsic lavas (Bindeman et al., 2004) and for quartz porphyries (Harris et al., 1997), respectively. In all calculations, quartz content was taken to be constant ($X_q = 0.3$), whereas other minerals varied at $X_b = 0.05, 0.1$, and 0.2 ; $X_p = 0.65, 0.6$, and 0.5 , respectively. Numerals near calculated curves mean the fraction of biotite in rock (X_b).

which was introduced in (Harris et al., 1997). In this case, quartz well operates as a proxy mineral.

The second example illustrates the erroneous reconstruction of composition of initial rocks (or melts) using quartz due to the rock alteration by the isotopically light fluid.

Example 2: Leucogranites of the Omsukchan Trough

The Late Cretaceous leucogranite porphyries (nevadites) are developed within the Omsukchan trough (Northeast Russia), being confined to numerous ore deposits and occurrences. In particular, they surround the structure of the Dukat ore field (Konstantinov et al., 1998; Struzhkov and Konstantinov, 2005; Bannikova, 1990; Dubinina et al., 2019; Filimonova et al., 2014). Data obtained in (Dubinina et al., 2023b) confirmed intense influence of isotopically light fluid on these rocks (Fig. 4): the $\delta^{18}\text{O}$ value for whole-rock samples of leucogranites decreases to the strong negative values ($< -7\text{‰}$). The isotope lightening mainly spanned feldspar, but fluid also affected the isotope systems of quartz and even zircon (Dubinina et al., 2023b). The values of $\delta^{18}\text{O}(Qz)$ decrease from 10–10.5 to 4‰ with depletion of rocks in heavy oxygen isotope, while $\delta^{18}\text{O}(Zrn)$ weakly varies within 5.2–3.9‰, systematically decreasing with isotope lightening of the rock. The initial oxygen isotope composition of the rocks reconstructed using $\delta^{18}\text{O}(Qz)$ and any constant (and variable) corrections yields the wide range of $\delta^{18}\text{O}(R)$ from 3 to 10‰, which indicates the contribution of different sources of felsic melts: ^{18}O -depleted and ^{18}O -enriched ones. However, this

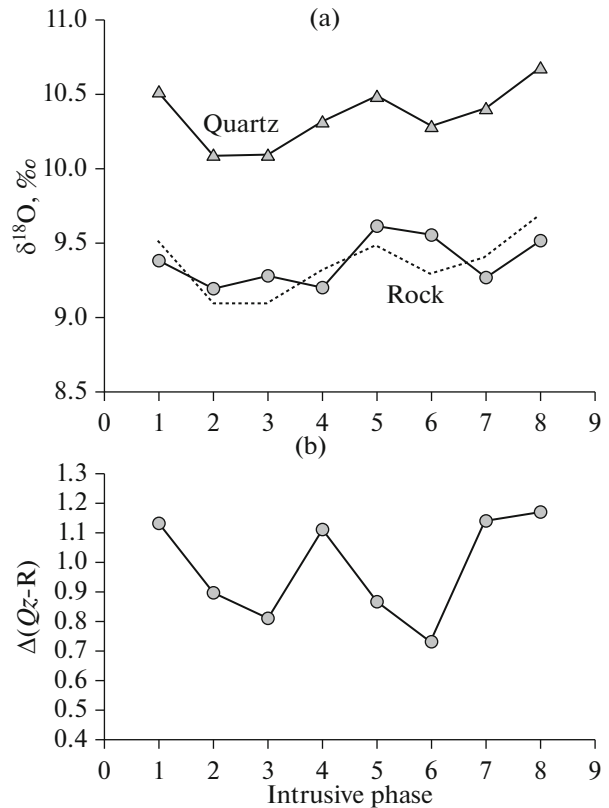


Fig. 3. Oxygen isotope composition of quartz and whole-rock samples of leucogranite porphyry of the Raucid massif (a) and observed value of $\Delta(Qz-R)$ (b). Dashes in fig. (a) is the calculation of $\delta^{18}\text{O}(R)$ using constant correction for quartz porphyry ($\Delta(Qz-R) = 1\text{‰}$, Harris et al., 1997).

conclusion is likely premature, because it is based only on $\delta^{18}\text{O}$ values of quartz, the isotope system of which is clearly disturbed.

We attempted to reconstruct $\delta^{18}\text{O}(R)$ using other proxy mineral, zircon, which is more resistant to the diffusion isotope exchange than quartz (Watson and Cherniak, 1997; Farver, 2010) and does not require correction for cooling rate. However, only euhedral zircon with no traces of hydrothermal alteration can be used as proxy mineral. In the leucogranites of the Omsukchan trough, zircon experienced insignificant hydrothermal alteration (maximum decrease of $\delta^{18}\text{O}(Zrn)$ is no more than 1.3‰). This alteration was likely caused by fluid-assisted partial recrystallization of *Zrn* (Dubinina et al., 2023b). For this reason, our reconstruction with zircon is only approximate. However, the measured $\delta^{18}\text{O}(Zrn)$ value even in partially altered zircon indicates a normal magma source, which was homogenous for all studied rocks (Valley, 2003; Fu et al., 2014). Below we consider the approach to reconstruction of $\delta^{18}\text{O}(R)$ using zircon as proxy mineral. For this purpose, the isotope exchange $\Delta(R-Zrn)$ between zircon and granitic rock (or melt) was estimated.

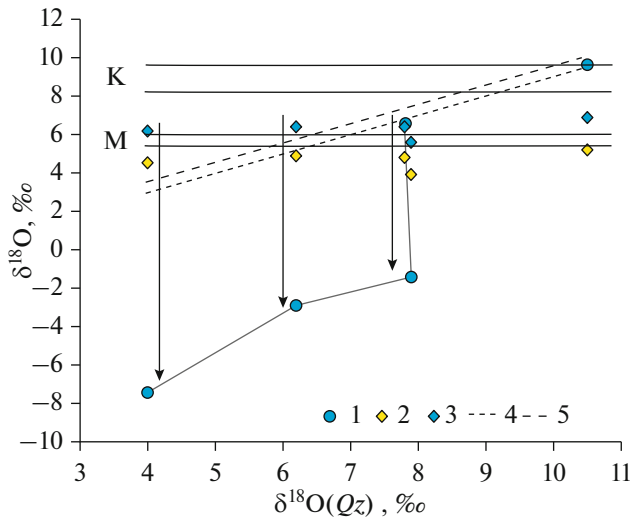


Fig. 4. Oxygen isotope composition of zircon and whole-rock samples of Late Cretaceous leucogranite porphyry of the Omsukchan trough relative to the oxygen isotope composition of quartz. (1) whole-rock samples; (2) zircon; (3) initial composition of felsic melts reconstructed using $\delta^{18}\text{O}(\text{Zrn})$ and corrections calculated from Zr content in the rock (see text). Dashed curves 4, 5 are reconstructions of initial composition of felsic melts using $\delta^{18}\text{O}(\text{Qz})$ and constant corrections for felsic lavas (Bindeman et al., 2004) and quartz porphyry (Harris et al., 1997), respectively. Horizontal fields: (M) mantle melts, (K) average composition of continental crust (Simon and Lécuyer, 2005). Arrows show the direction of isotope shift in the whole-rock isotope composition due to the influence of isotopically light fluid.

ESTIMATION OF OXYGEN ISOTOPE FRACTIONATION BETWEEN ZIRCON AND OTHER MINERALS OF GRANITIC ROCK

Zircon is not a rock-forming mineral and its oxygen isotope system usually closes earlier than that of relatively stable quartz. Thus, both quartz and all other rock-forming minerals will affect the $\Delta(\text{R}-\text{Zrn})$ ($=\delta^{18}\text{O}(\text{R}) - \delta^{18}\text{O}(\text{Zrn})$). Unlike quartz, the fractionation coefficient between zircon and major minerals of

felsic rocks is higher and shows more significant temperature dependence (Vho et al., 2019; Valley, 2003). Hence, variations in the content of rock-forming minerals should more significantly affect $\Delta(\text{R}-\text{Zrn})$ than $\Delta(\text{Qz}-\text{R})$. This calls into question the use of constant $\Delta(\text{R}-\text{Zrn})$, unlike $\Delta(\text{Qz}-\text{R})$, and highlights the need in the individual estimate of this parameter for each rock or rock group. For this purpose, the simplified empirical equation is proposed, in which correction between zircon and melt is determined by the SiO_2 content in rock (Lackey et al., 2008).

It is proposed to calculate the value of $\Delta(\text{R}-\text{Zrn})$ as weighted average fractionation coefficient between zircon and rock-forming minerals of granitic rock: *Qz*, *Bt*, *Kfs*, and *Pl* (Fig. 5). As an example, we calculated the temperature dependence of $\Delta(\text{R}-\text{Zrn})$ for three variants of rocks with variable proportions of the indicated minerals (see captions to Fig. 5). The coefficients of thermometric equations for the quartz–mineral system, which were applied in calculations and summarized in Table 1, were taken from the internally consistent data base (Vho et al., 2019). In addition to the coefficients, the closure temperature of zircon is required to estimate $\Delta(\text{R}-\text{Zrn})$. Available variant of $\Delta(\text{R}-\text{Zrn})$ estimation according to (Lackey et al., 2008) indirectly implies temperature factor, because it is based on the degree of silica saturation of rock ($\Delta(\text{R}-\text{Zrn}) = 0.0612\text{SiO}_2 - 2.50$). Using this equation yields $\Delta(\text{R}-\text{Zrn}) = 2.1\text{‰}$ for leucogranite porphyry of the Omsukchan trough ($\text{SiO}_2 \approx 75$ wt %). In order to compare this value with calculated weighted average fractionation coefficients, it is sufficient to calculate the SiO_2 content in the rock from normative mineral composition (in Fig. 5, they are indicated for each variant of calculation). The mineral composition of leucogranite porphyry of the Omsukchan trough corresponds to the calculated curve 3 in Fig. 5, and correction of 2.1‰ in this line corresponds to the closure temperature of zircon $T_z \approx 650^\circ\text{C}$. It is unclear whether this temperature is valid, but it is seen in Fig. 5 that T_z values calculated for other variants of rocks ($\text{SiO}_2 \approx 63$ and 70 wt %) are also close to 650°C . It is hardly likely that the closure temperature remains the same in rocks that significantly differ in SiO_2 and mineral composition.

Table 1. Coefficients in thermometric equation $10^3 \text{Ln}\alpha(\text{Qz}-\text{mineral}) = A \times 10^6 T^{-2} + B \times 10^3 T^{-1}$, used for calculation*

Mineral pair	A	B
<i>Qz</i> – <i>Zrn</i>	1.56	1.23
<i>Qz</i> – <i>Kfs</i>	0.19	1.08
<i>Qz</i> – <i>Bt</i>	0.90	2.67
<i>Qz</i> – <i>Ab</i> **	0.33	0.53
<i>Qz</i> – <i>An</i> **	0.71	1.13

* Coefficients taken from internally consistent data base (Vho et al., 2019); ** $A(\text{Qz}-\text{Pl})$ and $B(\text{Qz}-\text{Pl})$ were calculated using anorthite fraction (X_{An}) in plagioclase: $A(\text{Qz}-\text{Pl}) = X_{\text{An}} \times A(\text{Qz}-\text{An}) + (1 - X_{\text{An}}) \times A(\text{Qz}-\text{Ab})$; $B(\text{Qz}-\text{Pl}) = X_{\text{An}} \times B(\text{Qz}-\text{An}) + (1 - X_{\text{An}}) \times B(\text{Qz}-\text{Ab})$.

Thus, independent evaluation of the T_z is required, which is possible for zircon, unlike quartz. For instance, we can apply *Zrn* thermometer, which determines the melt saturation temperature in *Zrn* (Watson and Harrison, 1983; Boehnke et al., 2013; Borisov and Aranovich, 2019) and records the beginning of zircon crystallization from melt. At extremely low oxygen diffusion rate in zircon, the temperature estimated using zircon thermometer should be close to T_z . This approach was applied by us to estimate T_z for leucogranite porphyries of the Omsukchan trough. According to the Zr (120–300 ppm) and major oxides content in these rocks (Filimonova et al., 2014), the

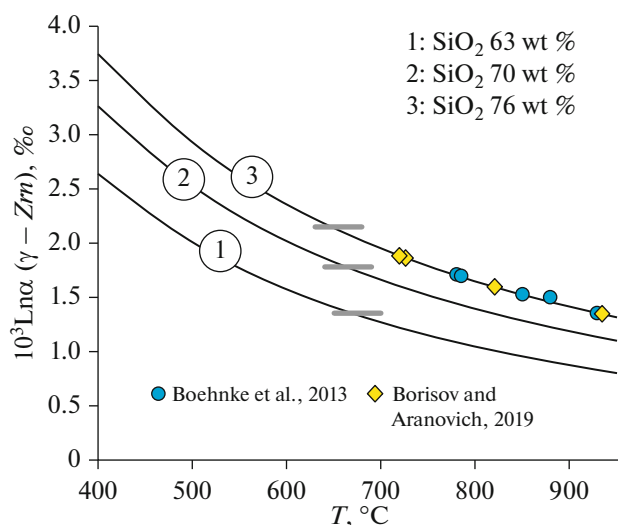


Fig. 5. Weighted average oxygen fractionation coefficient between granitic rock and zircon depending on temperature. Curves 1–3 were calculated for the following rock compositions: (1) $X_q = 0.1$, $X_{pl} = 0.3$, $X_{Kfs} = 0.4$, $X_b = 0.2$, $SiO_2 \approx 63$ wt %; (2) $X_q = 0.35$, $X_{pl} = 0.2$, $X_{Kfs} = 0.4$, $X_b = 0.05$, $SiO_2 \approx 70$ wt %; (3) $X_q = 0.2$, $X_{pl} = 0.15$, $X_{Kfs} = 0.35$, $X_b = 0.1$, $SiO_2 \approx 76$ wt %. Horizontal lines show zircon–rock isotope shift calculated from SiO_2 content (Lackey et al., 2008). Temperatures estimated using zirconium thermometer are shown in curve 3 (calculated using equations Boehnke et al., 2013; Borisov and Aranovich, 2019) for the same leucogranite porphyry samples from the Omsukchan trough (see text).

values of T_z vary from 780 to 930°C according to equation (Boehnke et al., 2013) or from 726 to 934°C according to equation (Borisov and Aranovich, 2019). Depending on the chosen thermometer, $\Delta(R-Zrn)$ calculated from curve 3 varies in the same samples from 1.36 to 1.71‰ or from 1.35 to 1.88‰, respectively. These estimates significantly differ from the constant correction calculated from SiO_2 content in these rocks (≈ 2.1 ‰, Lackey et al., 2008), and this difference reaches 0.8‰ with the growth of temperature (Fig. 5).

Initial $\delta^{18}O(R)$ estimates for the melt reconstructed using the above mentioned $\Delta(R-Zrn)$ values vary within a narrow range from 5.6 to 6.9‰ (Fig. 5), which is typical of normal melts and occupies position between $\delta^{18}O$ of mantle (5.7 ± 0.3 , Taylor and Shepard, 1986) and average continental crust (8.9 ± 0.7 ‰, Simon and Lecuyer, 2005). It should be noted that the obtained $\delta^{18}O(R)$ estimates for the leucogranite porphyry of the Omsukchan trough could be slightly underestimated (by no more than 1.3‰), because estimates of $\delta^{18}O(Zrn)$ in these leucogranites could be hydrothermally modified during strong impact of meteoric fluid (Dubinina et al., 2023b). Nevertheless, the estimated $\delta^{18}O(R)$ values indicate that the initial melts of leucogranite of the Omsukchan massif were derived through a simple interaction of

mantle melts with continental crust, and do not require the contribution of some exotic high- or low- $\delta^{18}O$ melt sources.

An example of leucogranites of the Omsukchan massif shows that an approach based on the study of a single “ubiquitous” mineral (for instance, quartz, Akinin and Bindeman, 2021) would lead us to erroneous conclusions concerning the nature of melt source. The application of zircon as proxy mineral could yield more reliable results, especially with allowance for the independent estimate of T_z . In addition to zircon thermometer, other approaches can be used. For instance, the T_z can be estimated from Ti content in zircon (Trail et al., 2007) or from zirconium–hafnium geothermometer (Aranovich and Bortnikov, 2018). Indeed, some errors can be caused by the choice of equation for T_z calculation. There are some other complicating factors for zircons. For instance, it is difficult to extract the sufficient amount of zircon for oxygen isotope analysis by laser heating fluorination (≈ 1 mg). In most cases, the value of $\delta^{18}O(Zrn)$ is determined by local methods (for instance, by SIMS), which, however, require to exclude xenomorphic and inherited zircons (Bindeman, 2008). Unlike quartz, the application of constant corrections $\Delta(R-Zrn)$ is hardly possible, especially at significant variations of the mineral composition of rock. In addition, the value of $\delta^{18}O(Zrn)$ can be disturbed, although with lower probability than $\delta^{18}O$ of quartz during fluid-assisted hydrothermal recrystallization (e.g., Chen and Zhou, 2017). The zircon isotope system also could be disturbed by metamict breakdown. In spite of all these difficulties, zircon has a high promise for the reconstruction of oxygen isotope composition of felsic silicate melts (Lackey et al., 2008).

CONCLUSIONS

Calculations and presented examples show that the application of quartz as proxy mineral has several strong limitations. It can be used only if the isotope system of mineral was not disturbed by later events. For common granitoids and rocks cooling with a finite (not instant) rate, the accurate reconstruction requires the involvement of the mineral composition of rocks and closure temperature of the quartz isotope system. In this case, the value of isotope shift $\Delta(Qz-R)$ between quartz and a given rock can be calculated using equation (7). At weakly varying mineral composition of rocks with similar textures and cooling rates, the constant correction for cooling effect can be applied for porphyritic and coarse-grained granites (Harris et al., 1997). The value of this correction could be corrected for rocks whose mineral composition strongly differs from standard granite. Correction proposed for felsic lavas (Bindeman et al., 2004) can be applied only to phenocrysts that did not experience retrograde isotope exchange and show no disturbance

of oxygen isotope system. This requirement is true for any minerals with significant diffusion rates (quartz, feldspars, micas).

Evidences for the disturbance of quartz isotope system in rock are not only the absence of equilibrium relations between $\delta^{18}\text{O}$ values of its minerals (which could be caused by cooling), but also the correlation of $\delta^{18}\text{O}$ values between altered minerals. Additional petrological, geochemical, and isotope studies should be carried out to reveal the possible disturbances. For instance, an indicator of fluid impact for granites is altered $\delta^{18}\text{O}$ value for feldspars, because this group of minerals differs in the higher diffusion rates of oxygen (Farver, 2010) and ability to interact with fluid even at moderate temperatures (O'Neil and Taylor, 1967; Fiebig and Hoefs, 2002). Thus, quartz can be used as a proxy mineral for reconstruction of oxygen isotope composition of initial rocks or melts only under a number of conditions, for instance, the measurements of oxygen isotope composition not only in quartz (approach of "ubiquitous" mineral) but also in the whole rock, as well as in other rock-forming minerals, in order to estimate the preservation of oxygen isotope system of the whole rock and quartz.

An approach of "ubiquitous" mineral is also frequently applied to zircon, especially in studies performed by local methods (SIMS, SHRIMP), when $\delta^{18}\text{O}(\text{Zrn})$ value is analyzed, without determination of oxygen isotope composition in rock. In this case, it is required to estimate the possible disturbances of oxygen isotope system of mineral, as well as to ensure in primary magmatic origin of the zircon. In all other respects, zircon has a high promise as proxy mineral not only due to the extremely low oxygen diffusion rate, but also owing to the possibility of independent estimates of crystallization temperature of magmatic zircon (Zr thermometer, Ti-in-Zrn thermometer). It is reasonable to improve approaches to estimating the $\Delta(\text{R}-\text{Zrn})$ values for rocks of different composition and different geodynamic settings.

ACKNOWLEDGMENTS

We are grateful to B.G. Pokrovsky and A.V. Samsonov, whose comments significantly improved the manuscript.

FUNDING

This work was supported by the Russian Science Foundation (project no. 22-17-00052).

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

OPEN ACCESS

This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this license, visit <http://creativecommons.org/licenses/by/4.0/>.

REFERENCES

- Akinin, V.V. and Bindeman, I.N., Variations of oxygen isotopic composition in magmas of Okhotsk–Chukotka volcanic belt, *Dokl. Earth Sci.*, 2021, vol. 499, no. 1, pp. 550–555 (2021).
- Aranovich, L.Y. and Bortnikov, N.S., New Zr–Hf geothermometer for magmatic zircons, *Petrology*, 2018, vol. 26, pp. 115–120.
- Bannikova, L.A., *Organicheskoe veshchestvo v gidrotermal'nom rudoobrazovanii* (Organic Matter in the Hydrothermal Ore Formation), Moscow: Nauka, 1990.
- Bindeman, I.N., Oxygen isotopes in mantle and crustal magmas as revealed by single crystal analysis, *Rev. Mineral. Geochem.*, 2008, vol. 69, pp. 445–478.
- Bindeman, I.N., Ponomareva, V.V., Bailey, J.C., and Valley, J.W., Volcanic arc of Kamchatka: a province with high- $\delta^{18}\text{O}$ magma sources and large-scale $^{18}\text{O}/^{16}\text{O}$ depletion of the upper crust, *Geochem. Cosmoch. Acta*, 2004, vol. 68, pp. 841–865.
- Bindeman, I.N., Gurenko, A.A., Sigmarsson, O., and Chaussidon, M., Oxygen isotope heterogeneity and disequilibria of olivine phenocrysts in large volume basalts from Iceland: evidence for magmatic digestion and erosion of Pleistocene hyaloclastites, *Geochim. Cosmochim. Acta*, 2008, vol. 72, pp. 4397–4420.
- Boehnke, P., Watson, E.B., Trail, D., et al., Zircon saturation re-revisited, *Chem. Geol.*, 2013, vol. 351, pp. 324–334.
- Borisov, A. and Aranovich, L., Zircon solubility in silicate melts: new experiments and probability of zircon crystallization in deeply evolved basic melts, *Chem. Geol.*, 2019, vol. 510, pp. 103–112.
- Chacko, T., Cole, D.R., and Horita, J., *Equilibrium oxygen, hydrogen and carbon isotope fractionation factors applicable to geological systems, Stable Isotope Geochemistry. Rev. Mineral. Geochem.*, 2001, vol. 43, pp. 1–81.
- Chen, W.T. and Zhou, M.-F., Hydrothermal alteration of magmatic zircon related to NaCl-rich brines: diffusion-reaction and dissolution–precipitation processes, *Am. J. Sci.*, 2017, vol. 317, pp. 177–215.

- Colon, D.P., Bindeman, I.N., Wotzlaw, J.-F., et al., Origins and evolution of rhyolitic magmas in the Central Snake River Plain: insights from coupled high-precision geochronology, oxygen isotope, and hafnium isotope analyses of zircon, *Contrib. Mineral. Petrol.*, 2018, vol. 173, 11. <https://doi.org/10.1007/s00410-017-1437-y>
- Dennis, P.F., Oxygen self-diffusion in quartz under hydrothermal conditions, *J. Geophys. Res.*, 1984a, vol. 89, pp. 4047–4057.
- Dennis, P.F., Oxygen self-diffusion in quartz, *Prog. Exp. Petrol. NERC Publ. D.*, 1984b, vol. 25, pp. 260–265.
- Dodson, M.I., Closure temperature in cooling geochronological and petrological systems, *Contrib. Mineral. Petrol.*, 1973, vol. 40, pp. 259–274.
- Dubinina, E.O., Filimonova, L.G., Kossova, S.A., Isotope ($\delta^{34}\text{S}$, $\delta^{13}\text{C}$, $\delta^{18}\text{O}$) compositions of disseminated sulfide mineralization in igneous rocks of the Dukat Ore Deposit (Northeastern Russia), *Geol. Ore Deposits*, 2019, vol. 61, no. 1, pp. 38–49.
- Dubinina, E.O., Andreeva, O.A., Avdeenko, A.S., et al., Oxygen isotope fractionation between phenocrysts and melt: equilibrium estimation for the alkaline lavas of Changbaishan Volcano (Northeast China), *Petrology*, 2020, vol. 28, no. 3, pp. 287–300.
- Dubinina, E.O., Avdeenko, A.S., Volkov, V.N., et al., Highly fractionated granites of the Raumid Massif (S. Pamir): oxygen isotope and geochemical study, *Petrology*, 2023a, vol. 31, no. 2, pp. 179–203.
- Dubinina, E.O., Filimonova, L.G., Avdeenko, A.S., et al., Oxygen isotope system of leucogranites of the Omsukchan trough (NW Russia): conditions and mechanisms of fluid–rock interaction, *Dokl. Earth Sci.*, 2023b (in press).
- Dubinina, E.O., Nosova, A.A., Avdeenko, A.S., Aranovich, L.Ya., Isotopic (Sr, Nd, O) systematics of the high Sr–Ba Late Miocene granitoid intrusions from the Caucasian Mineral Waters region, *Petrology*, 2010, vol. 18, no. 3, Pp. 211–238.
- Eiler, J.M., Valley, J.W., and Stolper, E.M., Oxygen isotope ratios in olivine from the Hawaii scientific drilling project, *J. Geophys. Res.*, 1996, vol. 101, pp. 11807–11813.
- Eiler, J., M., Stolper, E.M., McCanta, M.C., Intra- and intercrystalline oxygen isotope variations in minerals from basalts and peridotites, *J. Petrol.*, 2011, vol. 52, nos. 7–8, pp. 1393–1413.
- Farquhar, J., Chacko, T., and Frost, B.R., Strategies for high-temperature oxygen isotope thermometry: a worked example from the Laramie anorthosite complex, Wyoming, USA, *Geotektonika*, 1993, vol. 117, pp. 407–422.
- Farver, J.R., Oxygen and hydrogen diffusion in minerals, *Rev. Mineral. Geochem.*, 2010, vol. 72, pp. 447–507.
- Fiebig, J. and Hoefs, J., Hydrothermal alteration of biotite and plagioclase as inferred from intragranular oxygen isotope- and cation-distribution patterns, *Eur. J. Mineral.*, 2002, vol. 14, pp. 49–60.
- Filimonova, L.G., Trubkin, N.V., and Chugaev, A.V., Mineral types of hydrothermal alteration zones in the Dukat ore field and their relationships to leucogranite and epithermal gold–silver ore, Northeastern Russia, *Geol. Ore Deposits*, 2014, vol. 56, no. 3, pp. 169–199.
- Fu, B., Cliff, J., and Zartman, R.E., Zircon oxygen isotopic constraints from plutonic rocks on the magmatic and crustal evolution of the northern Appalachians in southern New England, USA, *Can. J. Earth Sci.*, 2014, vol. 51. <https://doi.org/10.1139/cjes-2013-0189>
- Giletti, B.J., Diffusion effects on oxygen isotope temperatures of slowly cooled igneous and metamorphic rocks, *Earth Planet. Sci. Lett.*, 1986, vol. 77, pp. 218–228.
- Gurenko, A.A. and Chaussidon, M., Oxygen isotope variations in primitive tholeiites of Iceland: evidence from a sims study of glass inclusions, olivine phenocrysts and pillow rim glasses, *Earth Planet. Sci. Lett.*, 2002, vol. 205, pp. 63–79.
- Harris, C., Faure, K., Diamond, R.E., and Scheepers, R., Oxygen and hydrogen isotope geochemistry of S- and I-type granitoids: the Cape Granite suite, South Africa, *Chem. Geol.*, 1997, vol. 143, pp. 95–114.
- Jenkin, G.R.T., Farrow, C.M., Fallic, A.E., and Higgins, D., Oxygen isotope exchange and closure temperatures in cooling rocks, *J. Metamorph. Petrol.*, 1994, vol. 12, pp. 221–215.
- Kitajima, K., Ushikubo, T., Kita, N.T., et al., Relative retention of trace element and oxygen isotope ratios in zircon from Archean rhyolite, Panorama Formation, North Pole Dome, Pilbara Craton, Western Australia, *Chem. Geol.*, 2012, vol. 332–333, pp. 102–115.
- Kohn, M.J. and Valley, J.W., Obtaining equilibrium oxygen isotope fractionations from rocks: theory and examples, *Contrib. Mineral. Petrol.*, 1998, vol. 132, pp. 209–224.
- Konstantinov, M.M., Natalenko, V.E., Kalinin, A.I., Struzhkov, S.F., *Zolotoserebryanoe mestorozhdenie Dukat* (The Dukat Gold–Silver Deposit), Moscow: Nedra, 1998.
- Kostitsyn, Yu.A., Belousova, E.A., Volkov, V.N., and Shatagin, K.N., Comparative isotope and element composition of zircons and host granites of the Raumid massif, *Materialy XVIII simpoziuma po geokhimi izotopov im. A.P. Vinogradova, Moskva, 2007* (Proc. 18th Vinogradov Symp. Isotope Geochem.), Moscow: GEOKhI RAN, 2007a, pp. 51–52.
- Kostitsyn, Yu.A., Volkov, V.N., and Zhuravlev, D.Z., Trace Elements and evolution of granite melt as exemplified by the Raumid Pluton, Southern Pamirs, *Geochem. Int.*, 2007b, vol. 45, no. 10, pp. 971–982.
- Lackey, J.S., Valley, J.W., Chen, J.H., and Stockli, D.F., Dynamic magma systems, crustal recycling, and alteration in the central Sierra Nevada Batholith: the oxygen isotope record, *J. Petrol.*, 2008, vol. 49, no. 7, pp. 1397–1426.
- O’Neil, J.R. and Taylor, H.P.J., The oxygen isotope and cation exchange, *Am. Mineral.*, 1967, vol. 52, pp. 1414–1437.
- Pietranik, A., Slodczyk, E.S., Hawkesworth, C.J., et al., Heterogeneous zircon cargo in voluminous late paleozoic rhyolites: Hf, O isotope and Zr/Hf records of plutonic to volcanic magma evolution, *J. Petrol.*, 2013, vol. 54, no. 8, pp. 1483–1501.
- Simon, L. and Lecuyer, C., Continental recycling: the oxygen isotope point of view, *Geochem. Geophys. Geosyst.*, 2005, vol. 6, no. 8, pp. 1–10.
- Struzhkov S.F., Konstantinov M.M. Metallogeniya zolota i serebra Okhotsko-Chukotskogo vulkanogenogo poyasa (Gold and Silver Metallogeny of the Okhotsk–Chukotka Volcanogenic Belt), Mpscow: Nauchnyi mir, 2005.

- Taylor, H.P. and Sheppard, S.M.F., Igneous rocks: I. Processes of isotopic fractionation and isotope systematics, *Temperature Geological Processes. Rev. Mineral.*, Valley, J.W., Eds. 1986, vol. 16, pp. 227–271.
- Trail, D., Mojzsis, S.J., Harrison, T.M., et al., Constraints on hadean zircon protoliths from oxygen isotopes, Ti-thermometry, and rare earth elements, *Geochem. Geophys. Geosyst.*, 2007, vol. 8, no. 6, p. Q06014.
<https://doi.org/10.1029/2006GC001449>
- Valley, J.W., *Stable isotope thermometry at high temperatures, Stable Isotope Geochemistry. Rev. Mineral. Geochem.*, 2001, vol. 43, pp. 365–414.
- Valley, J.W., *Oxygen isotopes in zircon, Zircon. Rev. Mineral. Geochem.*, Hanchar, J.M. and Hoskin, P.W.O., Eds., 2003, vol. 53, pp. 343–385.
- Valley, J.W., Lackey, J.S., Cavosie, A.J., et al., 4.4 billion years of crustal maturation: oxygen isotope ratios of magmatic zircon, *Contrib. Mineral. Petrol.*, 2005, vol. 150, pp. 561–580.
- Vho, A., Lanari, P., and Rubatto, D., An internally-consistent database for oxygen isotope fractionation between minerals, *J. Petrol.*, 2020, vol. 60.
- Volkov, V.N. and Negrei, E.V., Structure of the Raamid pluton and problem of the emplacement of granite intrusions, *Sov. Geologiya*, 1974, no. 3, pp. 46–59.
- Volkov, V.N., Shatagin, K.N., and Kramchaninov, A.Yu., On the role of contamination and hybridism in formation of the composite Raamid Pluton granites (Pamir Mnts.): results of Sm–Nd isotope study, *Dokl. Earth Sci.*, 2016, vol. 470, no. 1, pp. 981–984.
- Watson, E.B. and Harrison, M., Zircon saturation revisited: temperature and composition effects in a variety of crustal magma types, *Earth Planet. Sci. Lett.*, 1983, vol. 64, pp. 295–304.
- Watson, E.B. and Cherniak, D.J., Oxygen diffusion in zircon, *Earth Planet. Sci. Lett.*, 1997, vol. 148, pp. 527–544.

Translated by M. Bogina