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Electron probe determination of trace elements in olivine: thermometry of depleted peridotites

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Abstract

A method for calculation of the maximum permissible (for thermometry) error of analyte determination by trace elements is presented based on the example of the De Hoog–Gall Al-in-olivine thermometer. Analytical conditions ensuring an acceptable analytical error have been established, and the possibility to reach them has been estimated. A technique of JEOL JXA-8100 analysis of olivines for trace elements has been elaborated: Accelerating voltage is 20 kV, probe current is 400 nA, and counting time per line and background measurement is 10 s. The number of measurements per analysis is 25. Metrological characteristics of determination of Na_2O, Al_2O_3, CaO, Cr_2O_3, and MnO have been calculated. Their detection limit (with confidence probability of 0.842) does not exceed 9 ppm. For an error of 10 rel.%, the quantitation limit of these oxides is within 45–100 ppm. Compositional peculiarities of olivines from depleted megacrystalline peridotites of the Udachnaya pipe have been revealed. The content of Mn significantly decreases with Mg# increase. The contents of Na, Al, Ca, and Cr show a strong mutual positive correlation. It is shown that electron probe microanalysis can provide an error sufficient for evaluating temperature by trace elements. The results of temperature determination by the Al-in-olivine thermometer agree with the thermometry data by H. O'Neil and B. Wood and differ considerably from the lower values estimated by D. Canil and C. Ryan with Ni thermometers.

Keywords: electron probe microanalysis; olivines; trace elements; peridotites; geothermometry

Introduction

Evaluation of the temperature and pressure of formation of depleted megacrystalline peridotites is a crucial problem of mantle petrology. These peridotites are composed mainly of olivine and contain occasional garnet or chromite grains. Such almost single-mineral rocks cannot always be analyzed by common mineral thermobarometry based on the dependence of the composition of coexisting phases on the formation conditions of rocks. The only possible mineralogical method in this case is estimation of the *PT* conditions from the contents of indicator trace components in an individual phase. The fact that trace elements in minerals of deep-seated rocks bear genetic information was first noticed by N.V. Sobolev and A.J. Erlank (Bishop et al., 1978). In olivines, Na_2O, Al_2O_3, CaO, Cr_2O_3, and MnO represent these informative components (Sobolev et al., 2008, 2009). In particular, the content of MnO in olivine shows correlation with its Mg#. The contents of the other four oxides depend mostly on the temperature of rock formation; moreover, these parameters are in positive correlation (De Hoog et al., 2010).

The structure of olivine permits limited substitution of divalent and tetravalent cations by univalent and trivalent ions. In mantle olivines Na, Al, and Cr cations are predominant. An ion exchange between olivine and coexisting phases follows the mechanism of pair heterovalent substitution, which proceeds in the positions M and T of olivine crystal in two ways (De Hoog et al., 2010; Gudfinnsson and Wood, 1998; Kurosawa et al., 1997; Taura et al., 1998). Let us express the chemical formula of this mineral via Na, Mg, Al, Si, Cr, and Fe for both cases.

(1) The sites of divalent and tetravalent cations in the positions M and T, respectively, of the crystal lattice are partly occupied by two trivalent ions: $Me^{2+} + Me^{4+} \leftrightarrow 2Me^{3+}$. In this case, the sites of $m\ (Fe_xMg_{1-x})$ + Si atomic pairs in the growing crystal with $Fe:Mg = x:(1-x)$ are occupied by the same number of Al and Cr atoms in the proportion $Al:Cr = y:(1-y)$, i.e., substitution $m\,[(Fe_xMg_{1-x})\,Si] \leftrightarrow 2m\,(Al_yCr_{1-y})$ takes place. Thus, the mineral has chemical formula

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$(Fe_xMg_{1-x})_{2-m}(Al_yCr_{1-y})_{2m}Si_{1-m}O_4$.

Analysis of the crystal structure of olivine shows that Cr cannot substitute Si in the position T (Ozawa, 1991). That is, this substitution is impossible at the deficit of Al in the mineral-forming medium. In wadsleite (high-pressure β-modification of olivine), however, the exchange $(Fe_xMg_{1-x}) + Si \leftrightarrow 2Cr$ can take place (Gudfinnsson and Wood, 1998).

(2) Univalent and trivalent atoms substitute divalent cations in the M-positions by the scheme $2Me^{2+} \leftrightarrow Me^{1+} + Me^{3+}$. It is not ruled out that Al and Cr participate in this substitution in proportions different from those in the first variant: $2n(Fe_xMg_{1-x}) \leftrightarrow n[Na(Al_zCr_{1-z})]$. In this case, olivine has chemical formula

$(Fe_xMg_{1-x})_{2-2n}[Na(Al_zCr_{1-z})]_nSiO_4$.

The considered processes of heterovalent isomorphism can run simultaneously but with different probabilities. Therefore, the general mineral formula is

$(Fe_xMg_{1-x})_{2-0.5m-n}Na_{0.5n}(Al_{y+z}Cr_{2-y-z})_{m+0.5n}Si_{1-0.5m}O_4$.

Taura et al. (1998) studied the pressure dependence of the distribution coefficients of trace elements. The experiments in the system olivine–melt at 30–140 kbar showed a predominance of the substitution $Si + Mg \leftrightarrow Al + Cr$ at low pressures. They also think that Cr occupies only the M-positions. At high pressures, the exchange processes $Si + Mg \leftrightarrow 2Al$ and $2Mg \leftrightarrow Na + Al$ prevail. Thus, the incorporation of trace elements into the crystal structure and their contents depend also on the *PT* conditions of mineral crystallization. The researchers attempted to make a quantitative expression of these dependences. Below we will consider one of them as an equation relating the content of Al in olivine to the temperature of its formation.

Changes in *PT* conditions influence the solubility of trace elements in olivine. This influence can be expressed differently. Under rapid quenching, elements are preserved in the mineral structure. Slower cooling leads to olivine exsolution and formation of regularly oriented inclusions in the crystals. Their mineral composition depends on the type of atomic substitution. The first scheme of atomic exchange leads to a deficit of Si in olivine and the formation of oxides. In the second scheme, silicon is excessive relative to divalent cations and thus forms a silicate phase in the regular crystal lattice of the mineral. When both substitution mechanisms work, the exsolution structures are silicates and oxides. Recent experimental studies of the substitution mechanisms (De Hoog et al., 2010; Gudfinnsson and Wood, 1998; Kurosawa et al., 1997; Taura et al., 1998) have confirmed the conclusions drawn more than 40 years ago (Agafonov et al., 1974; Smirnova, 1971): Regularly oriented inclusions of silicate and oxide phases are olivine exsolution products.

Trace elements used in thermobarogeochemical calculations amount to tens or hundreds of ppm in minerals. An acceptable analytical error at low contents of elements is ensured by using high-sensitivity and precision LA–ICP-MS, SIMS, and IMP methods (De Hoog et al., 2010; Griffin et al., 1989; Köhler and Brey, 1990; Watson et al., 2006). These methods are not always accessible or provide the unsatisfactory locality of analysis. In these cases, the researchers apply electron probe microanalysis (EPMA) ensuring the locality of analysis nearly an order of magnitude higher as compared with other methods. They must estimate an acceptable analytical error of element determination and the capability of the method to ensure this error. Solution of these problems can be demonstrated by the example of a geothermometer designed for evaluating the temperature of formation of garnet peridotite (De Hoog and Gall, 2005):

$$T(^\circ C) = 11390/(12.52 - \ln c) - 273. \quad (1)$$

The temperature is calculated based upon the content of Al_2O_3 (c, ppm) in olivine. The thermometer is calibrated for the interval 800–1500 °C, which corresponds to variations in Al_2O_3 contents from 7 to 444 ppm. Equation (1) is approximate; therefore, to reduce the error of temperature determination, it is necessary to stipulate that it must not exceed ±25 °C because of the indefinite value of c.

There are particular technical prerequisites for reaching the required metrological characteristics of EPMA. Modern electron microprobes ensure long-term stable operation at high current. They are equipped with spectrometers with high illumination due to the reduced radius of the Rowland circle or the enlarged operation area of the analyzing crystals and due to switching to the spectrometer focus by the Johansson method. The perfected microprobes make it possible to obtain a higher intensity. Along with synchronous recording of element radiation in several channels, this ensures a significant decrease in the detection limit of the analyte. Thus, EPMA is close in metrological characteristics to high-sensitivity analytical methods.

Theoretical part

Estimation of a permissible analytical error. Let us calculate the error of determination of Al_2O_3 content at which the standard temperature deviation s_T does not exceed ±25 °C, i.e., $\Delta T = s_T \le |25\ ^\circ C|$. According to the law of error accumulation, the dispersion of T value due to the uncertainty of c value is expressed as $s_T = (\partial T/\partial c)^2 s_c^2$. Using Eq. (1), we make differentiation $\partial T/\partial c$ and obtain

$$s_T^2 = \left\{11390/[c(12.52 - \ln c)^2]\right\}^2 s_c^2.$$

Then we pass to the dependence of the relative dispersion of Al_2O_3 content, V^2, upon the absolute dispersion of temperature, s_T^2:

$$V^2 = s_c^2/c^2 = [(12.52 - \ln c)^2/11390]^2 s_T^2. \quad (2)$$

As follows from Eq. (2), the maximum permissible relative error V is a variable value. Figure 1 shows the dependence of V (rel.%) upon the Al_2O_3 content. As the latter increases from 7 to 444 ppm, the maximum permissible relative error of its