Analytical Note

Determination of divalent iron content in igneous rocks of ultrabasic, basic and intermediate compositions by a wavelength-dispersive X-ray fluorescence spectrometric method

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This paper proposes the quantitative wavelength-dispersive X-ray fluorescence (XRF) technique of divalent iron content determination in igneous rocks and reports specifics of this technique in terms of classifying rocks into ultrabasic, basic, intermediate and acid ones. Unlike the widely used technique of titration, the proposed XRF technique does not require a labor-consuming procedure for sample preparation. In the fields of $FeK\beta_5$ line, and $FeK\beta'$ and $FeK\beta''$ satellites relative intensities of XRF emission spectrum lines are dependent on the valence state of iron in minerals. The ratio $FeK\beta_5/FeK\beta_{1,3}$ is preferred as the analytical parameter. The XRF method allows divalent iron content (expressed as FeO oxide) over 1.5% to be measured in igneous rocks of ultrabasic and basic compositions by the common calibration equation with the error below 10 rel. %, that is comparable with the error of titrimetric analysis. The samples of igneous rocks of intermediate composition and granodiorites should be analyzed using calibration equations obtained with certified reference materials corresponding in composition to the study samples. For the samples of alkaline rocks the errors of FeO content determination might be in excess of 50 rel. %.

1. Introduction

The valence state of iron in rocks and minerals is commonly determined in geological, geochemical and petrologic studies, e.g. to identify oxygen activity in magma and equilibrium between minerals and silicate melts [1,2]. The principal routine method to determine the valence state of iron in rocks is titration based on sample decomposition with an acid mix in the inert atmosphere [3,4,5,6]. The X-ray fluorescence (XRF) method is commonly used for a quantitative determination of petrogenic element contents in rocks [7,8,9,10]. The position of peak, shape and intensity of XRF spectrum lines preconditioned by transitions from the valence shells to the internal ones are affected by the valence state of iron. Some papers report the change of intensity of $K\beta_5$ line and intensive satellites $K\beta'$ and $K\beta''$ for iron and other transitional element compounds in a different valence state [11,12,13,14,15,16,17]. We formerly demonstrated a good linear correlation between the ratios of intensities of L- and K-series X-ray emission lines measured by a conventional wavelength dispersive XRF spectrometer and valence state of iron for a set of oxide, hydroxide and silicate minerals involved in rock composition and received single calibration equation for semiquantitative determination of the iron valence state in igneous rocks [18,19]. This paper considers the possibility of using K-series satellites as the analytical lines, proposes the quantitative XRF technique of divalent iron determination in igneous rocks and reports specifics of this technique in terms of classifying rocks into ultrabasic, basic, intermediate and acid ones.

2. Experimental

2.1. Instrumentation

The research was performed using equipment of Baikal analytical joint use center of SB RAS. The measurements of X-ray emission spectra are performed by a wavelength-dispersive XRF spectrometer S4 Pioneer (Bruker AXS, Germany). The spectrometer is supplied with a Soller optical system; the X-ray tube equipped with a Rh anode is used to excite the radiation; voltage was 50 kV and current was 60 mA. The LiF (220) crystal with collimator 0.23° was employed as a monochromator. The X-ray radiation is registered by a scintillation counter. Samples were prepared by pressing powder on the boric acid substrate. The values of characteristic line energy were taken from the NIST database (http://www.nist.gov/pml/data/index.cfm).

2.2. Measurements of iron X-ray fluorescence K-series spectra

Fig. 1a provides the X-ray emission spectra in the field of $FeK\beta_{1,3}$ line (E = 7.058 keV) stipulated by transition $K–M_2,M_3$ and $FeK\beta_5$ line

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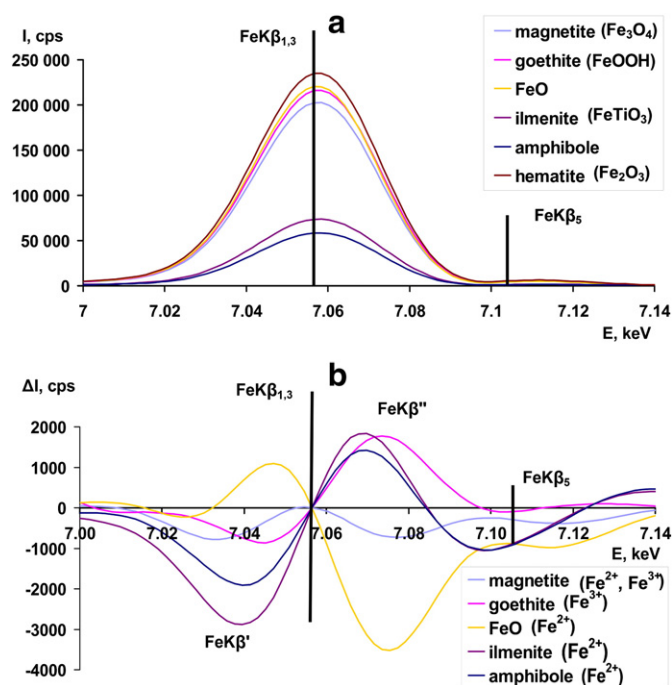*E-mail address:* master-17@rambler.ru (V.M. Chubarov).

Fig. 1. X-ray (panel a) and difference (panel b) spectra of iron mineral samples in the field of $FeK\beta_{1,3}$ and $FeK\beta_5$ lines. Difference spectra were received by normalizing spectra of the samples studied per maximum intensity of $FeK\beta_{1,3}$ lines for hematite sample and a consequent subtraction of intensities of hematite sample spectrum from the intensities of normalized spectra of each sample.

(E = 7.108 keV) stipulated by transition $K–M_4,M_5$ for the samples of iron minerals. Since the mineral of divalent iron oxide (wustite) is infrequently found in nature, we analyzed the FeO reagent. The ratio of line intensities $FeK\beta_5/FeK\beta_{1,3}$ varies from 0.034 (in goethite and hematite samples containing trivalent iron Fe^{3+}) to 0.026 (in samples of FeO reagent, ilmenite and amphibole primarily containing divalent iron Fe^{2+}). Fig. 1b displays the difference spectra received by normalizing spectra of the samples studied per maximum intensity of $FeK\beta_{1,3}$ lines for hematite sample and a consequent subtraction of intensities of hematite spectrum from the intensities of normalized spectra of each sample. The satellites available in the iron spectrum are not resolved in Fig. 1a; they however occur on the difference spectrum (Fig. 1b). The extremes in the field of 7.03–7.05 keV energy probably correspond to satellite $FeK\beta'$, while those of 7.06–7.08 keV energy probably correspond to satellite $FeK\beta''$. The change of their position on the difference spectra for various minerals is the evidence of chemical shifts of satellites and $FeK\beta_{1,3}$ within the spectrum. Figures in Appendix A offer dependences of intensity differences (ΔI) in the position corresponding to satellites $FeK\beta'$ (Fig. S1) and $FeK\beta''$ (Fig. S2) and $FeK\beta_5$ (Fig. S3) line represented in Fig. 1b on the valence state of iron for the examined minerals. In the field of $FeK\beta'$ satellite the dependence of relative intensities of emission spectrum lines on the valence state of iron is observed in all samples except the FeO reagent. In the field of $FeK\beta''$ satellite the dependence appears only in oxide compounds of iron (FeO reagent, magnetite Fe_3O_4 and hematite Fe_2O_3). In the field of $FeK\beta_5$ line the relative intensities of emission spectrum lines are linearly dependent on the iron valence state in all analyzed samples. Igneous rocks contain both oxide and silicate minerals of iron, therefore only $FeK\beta_5$ line and $FeK\beta'$ satellite, but not $FeK\beta''$ satellite can be used as analytical lines.

2.3. Repeatability of X-ray fluorescence analysis

To evaluate the repeatability of measuring the ratios of $FeK\beta_5/FeK\beta_{1,3}$ and $FeK\beta'/FeK\beta_{1,3}$ line intensities three samples of each one of certified reference materials (CRM) of igneous rocks (dunite SDU-1,

trap ST-1a, quartz diorite SKD-1 and granite SG-3) were prepared. The intensity of $FeK\beta'$ satellite was measured in position E = 7.038 keV. The expositions of measuring $FeK\beta_{1,3}$ (10 s), $FeK\beta'$ (200 s) and $FeK\beta_5$ (300 s) lines provide the error of intensity measurement stipulated by the statistics of counting detector impulses at the level less than 1%. The background was measured in position E = 7.216 keV, where the intensive lines of the other elements are not available. The total relative standard deviation (RSD), including the repeatability of sample preparation and measurement, was not in excess of 0.30% for $FeK\beta_5/FeK\beta_{1,3}$ and 0.15% for $FeK\beta'/FeK\beta_{1,3}$ ratio of line intensities.

3. Result and discussion

3.1. Certified reference materials of igneous rocks

In this research we employed CRM of igneous rocks of ultrabasic, basic, intermediate and acid compositions, wherein the total and divalent iron contents have been certified or defined by titration analysis. Composition and origin of CRM were taken from the GeoReM database (http://georem.mpch-mainz.gwdg.de). We collected CRM of Geological Surveys of Mongolia, Japan and United States, Russian Academy of Sciences, Irkutsk State University (Russia), Analytical working group (France), Zentrales Geologisches Institut (Germany) and Bulgaria, as well as the samples which composition was defined through the GeoPT program (http://www.geoanalyst.org). The accuracy of the titration analysis technique of divalent iron content (expressed as FeO oxide) determination was evaluated by analyzing CRM of ultrabasic (SDU-1, C(FeO) = 5.54%), basic (ST-1a, C(FeO) = 10.26%), intermediate (SKD-1, C(FeO) = 3.79%) and acid (SG-3, C(FeO) = 1.61%) compositions; each sample was doubly analyzed. The absolute error of titrimetric FeO content determination in CRM was not over 0.30%. In all studied CRM the RSD value was measured as 4.3%.

3.2. X-ray fluorescence determination of divalent iron content in igneous rocks of ultrabasic and basic compositions

In igneous rocks iron is basically presented in oxide and silicate minerals. To build the calibration curve we selected 19 CRM of igneous rocks of basic composition (basalts JB-1, JB-2, JB-3 and MBL-1, gabbros JGB-1, MGR-N, MGR-T and SGD-2, diabase W-2, trap ST-2, dolerites DNC-1 and OU-5, anorthosite AN-G), ultrabasic composition (dunites SDU-1 and DTS-1, peridotite JP-1, meymechite DVM-1) and also two CRM of metamorphic rocks of ultrabasic composition (serpentinites SW and GAS). The total iron content expressed ad $Fe_2O_3^{tot}$ oxide in the calibration selection varies from 3.36 to 15.16%; the divalent iron content expressed as FeO oxide varies within 0.28–10.33%. The valence state was characterized by the value of ratio between the divalent iron content (expressed as FeO oxide) and total iron content (expressed as Fe_2O_3 oxide) $R^C = C(FeO)/C(Fe_2O_3^{tot})$.

Figs. 2 and 3 demonstrate dependence of the ratio (R^I) of line intensities $FeK\beta_5/FeK\beta_{1,3}$ (Fig. 2) and $FeK\beta'/FeK\beta_{1,3}$ (Fig. 3) on the ratio R^C for calibration selection. Vertical bars show the repeatability of measuring the ratios R^I (2·RSD = 0.6 rel. % for $FeK\beta_5/FeK\beta_{1,3}$ and 0.3 rel. % for $FeK\beta'/FeK\beta_{1,3}$) that correspond to the repeatability of FeO content determination less than 1 rel. %.

The dependence of R^C on R^I was approximated by the equation:

$$R^C = a_0 + a_1 \cdot R^I + a_2 \cdot \left(R^I\right)^2, \qquad (1)$$

where a_0, a_1 and a_2 are the regression coefficients. The obtained Eq. (1) is characterized by the correlation coefficient $r_{xy} = -0.98$ for the $FeK\beta_5/FeK\beta_{1,3}$ ratio (the standard deviation (SD) value was 0.03) and by $r_{xy} = -0.81$ for the $FeK\beta'/FeK\beta_{1,3}$ ratio with SD = 0.09. Thus, it is reasonable to use the ratio of line intensities $FeK\beta_5/FeK\beta_{1,3}$ as the