Geological Interpretation of the Results of Factor Analysis of XRF- and XRD-Data on Carbonatites and Aluminosilicate Rocks of the Kontozero Alkaline Complex (Kola Peninsula, NW Russia)

Evgeniy Kozlov 1, Ekaterina Fomina 1
1 Geological Institute of Kola Science Centre of Russian Academy of Sciences (GI KSC RAS), 14 Fersmana Street, Apatity, 184209 Russia
e.kozlov@ksc.ru

Abstract. We applied factor analysis (FA) for statistical comparison of XRF and XRD data on 198 carbonatite and aluminosilicate rock samples of the Kontozero Devonian paleovolcano. This method helps to identify main, secondary, and some accessory minerals, as well as to estimate the approximate contents of these minerals and to assess their contribution on the distribution of major and trace elements (Fomina et al., 2019). With the view of control purposes, qualitative and semiquantitative analysis of diffraction data were performed. Several dozen factors quickly yielded to mineralogical interpretation. For the studied samples, a functional relationship was established between the calculated mineral content and the score of the factor (FS) corresponding to the mineral. Thus, the FS can serve as a handy tool for assessing the contents of minerals. Thereby we visualise the distribution of minerals in the space of the studied complex. We also found out which mineral phases are ubiquitous, and which present only in certain parts of the section or occur sporadically. These data allowed us to make a mineralogical interpretation of the results of FA, performed solely for the geochemical variables. The main trends in the mineralogical and geochemical evolution of carbonatite and aluminosilicate rocks of the Kontozero Devonian paleovolcano were thus determined and statistically substantiated. All these results were obtained in a short time at the earliest stages of the research. A “blind” statistical method guarantees the independence of the results on a priori hypothesis of the researcher. The time-consuming classical techniques (e.g., petrography, mineralogical studies, and quantitative analysis of diffraction data) verified the geological model described by statistics.

1. Introduction
Three methods typically determined the mineralogical phase composition: (1) point-counting techniques using optical microscopy (optical modal analysis), supplemented by image digitalisation and analysis and the application of electron microscopy techniques; (2) normative calculation from bulk chemical data; and (3) modal X-ray powder diffraction. These methods are described and compared in [1]. When processing extensive collections of samples, for example, when exploring deposits, the assessment of mineral contents becomes a very time-consuming task. Faced with this problem, researchers prefer normative calculation from bulk chemical data using methods of statistical data processing as the least labour-intensive technique [2], [3]. Optical modal analysis and modal X-ray powder diffraction are usually used to verify the results.
However, the normative calculation requires *a priori* information on the mineral composition, which is absent in the case of poorly studied geological objects. Also, an unusual or complex mineral composition may hamper the calculations. We encountered these problems when studying the alkaline-carbonatite volcanic-plutonic Kontozero complex. First, this complex has been little studied. Second, its rocks often contain high amounts of such minerals as albite, analcime, and/or natrolite, the chemistry of which differs only in the content of SiO$_2$ ($\pm$H$_2$O). There is also an association of monticellite and diopside, which differ chemically only in silica content. An additional complicating factor for distinguishing these minerals is the frequent occurrence of dolomite in the rocks. At the same time, quartz is often present in rock-forming quantities. Such a complex mineral composition of Kontozero rocks does not allow the use of a single algorithm for normative calculation for the entire sample set, consisting of almost two hundred samples. In this regard, we applied an original technique based on statistical processing of XRD data using factor analysis [4]. This method is “blind”, i.e. does not require information on the mineral composition. On the contrary, this information is the result of applying the technique. This paper shows how to use factor scores as a tool for semiquantitative analysis of mineral composition. We also provide an example of how the use of FS as additional variables in the statistical study of XRF data allows for a mineralogical interpretation of the identified geochemical trends.

2. Materials and methods

2.1. Samples description

The investigated rock collection comprises 198 core samples from the Kontozero volcano-plutonic alkaline-carbonatite paleovolcanic complex. Kontozero is one of the complexes of the Devonian Kola Alkaline Province [5], [6], dating from the age of about 360-380 Ma [7]. It forms a caldera filled with layers of volcanic rocks, mainly lavas and tuffs of carbonatite, carbonatite-picroite, alkaline-picroite, augitite, limburgite, melanephelinite, nephelinite, phonolite, and tephrite composition [8], [9]. Samples from two parts of its section were studied. We examined the upper layers of the section (an interval from 4.5 to 293.0 m) using the core from well # 7 and its lower part (an interval from 496.0 to 925.0 m) using the core from well # 6. The core sampling step averaged about 4 m. The chemical analysis has shown that the sample collection includes: 1) carbonatites *sensu stricto* (calcic, magnesian, and ferroan) containing < 20 wt% SiO$_2$, 2) silicocarbonatites (essentially carbonate rocks of endogenous origin containing > 20 wt% SiO$_2$), and 3) a variety of aluminosilicate rocks (from normal to alkaline; with both Na and K alkalinity type).

2.2. Analytical techniques

The primary source of information on the mineral composition was X-ray powder diffraction (XRD) from bulk rock samples. The chemical compositions of each sample were determined by X-ray fluorescence analysis (XRF).

2.2.1. XRD. The X-ray powder diffraction data (XRD) of the bulk rock samples were collected at room temperature by the Shimadzu XRD-6000 diffractometer (Shimadzu Corp., Kyoto, Japan), using a Cu target X-ray generator with graphite monochromator. The scan range of the Bragg angle ($2\theta$) was from 4.00° to 70.00° in the continuous regime with a scan speed of 2.00 °/min; sampling pitch was 0.02°. The work was performed on the analytical equipment of IM UB RAS, Miass, Russia (http://www.mineralogy.ru).

2.2.2. XRF. The X-ray fluorescence (XRF) data of the bulk rock samples were collected by the wavelength dispersive X-ray fluorescence spectrometer S4 Pioneer (Bruker AXS, Germany). Instrumental operation conditions for the main rock-forming (Na, Mg, Al, Si, P, K, Ca, Ti, Mn, Fe) and some minor elements (Ba, Sr, Zr) were the following: 30 kV at 80 mA for NaKα, MgKα, AlKα, SiKα, PKα, KKα, and CaKα analytical lines and 50 kV at 40 mA for TiKα, MnKα, FeKα, SrKα, BaKα, ZrKα, and RhKα lines (RhKα Compton line was used as background standard for Sr and Zr.
determination). For minimisation mineral and particle size effects, the samples were homogenised using the fusion sample preparation technique. Samples were preliminarily dried and calcined to determine loss of ignition (L.O.I.) values. Then 0.5 g of calcined sample was mixed with 7.5 g of flux (a mixture of lithium metaborate and lithium tetraborate) and fused in electric furnace TheOX (Claisse, Canada) to obtain glasses appropriate for the further analysis. Certified reference materials of igneous and sedimentary rocks, as well asapatite concentrates, were applied to build calibration curves. The expositions of analytical lines measuring provide the relative count statistic error at the level of less than 0.3% for Al, Si, Fe and less than 1% for other elements. Total exposition of one sample measuring was about 20 min. The lower detection limits were 0.05 wt % for all measured elements. Analytical procedure accounting of spectral overlaps and matrix effects correction using the fundamental parameters method, as well as the calculation of Sr and Zr contents utilising the intensity of the incoherent (Compton) anode emission (Rh) scatter peak. The used XRF analysis technique, including estimates of measurement errors, is detailed in [10]. The research was performed using equipment of the Joint use Center «Isotope-geochemical Research» (IG SB RAS, Irkutsk, http://www.igc.irk.ru).

2.3. Data processing
This work is based on the results of the factor analysis of XRD and XRF data for Kontozero rocks, carried out according to the method described in [4]. XRD data were also the basis for semiquantitative phase analysis, performed using the QualX v. 2.24 program (Institute of Crystallography (IC)-CNR, Bari, Italy; http://www.ba.ic.cnr.it/softwareic/qualx/) [11], and quantitative phase analysis conducted using MAUD v. 2.94 program (University of Trento, Trento, Italy; http://maud.radiographema.eu/) [12]. In both cases, the XRD-database POW_COD [13] was used. The classical FA for geochemical variables (from XRF-data) in the modification of the Principal Component Analysis (PCA) was performed in Statistica v. 12.0 software (StatSoft, Tulsa, USA).

3. Results and discussions
The XRD and XRF data of the investigated Kontozero rock sample collection were statistically processed using factor analysis according to the method described in [4]. The FA identified many factors, more than 20 of which are interpretable. They correspond to the following minerals: Ca-Mg-Fe carbonates (calcite, ferruginous dolomite, and siderite), strotianite, burbankite, feldspars (orthoclase, albite), garnet (andradite), monticellite, diopside, biotite, chlorite, serpentinite, zeolites (natrolite, analcime), quartz, magnetite, ilmenite, fluorite, fluorapatite, pyrite, anatase. Petrographic and mineralogical studies have confirmed that all these minerals present in the tested rocks. In the database of XRD data COD [13], CIF files of the listed minerals were selected. To do this, using the QualX program [11], we chose the standards closest to the minerals of the Kontozero rocks both in terms of peak positions and intensity. A working database compiled from these CIF files served as the basis for semiquantitative analysis of the mineral composition of all samples in the QualX program. In this program, a semiquantitative analysis bases on the Reference Intensity Ratio (RIR;[14] and references therein) and an idea of the mineral contents. However, high errors are characteristic of such content calculations. Factors that have received a mineralogical interpretation showed a functional relationship between FS and estimates of the content of minerals corresponding to the factors (figure 1A-F).
Figure 1. The examples of the functional relationship between FS and semiquantitative estimates of the mineral contents.

This relationship validates the mineralogical interpretation of the factors. Moreover, this relationship makes the FS a reliable tool for assessing the content of a mineral corresponding to a factor. The relationship between the FS and the content of the corresponding mineral is evident in the example of alkaline amphibole. The diffraction patterns of the studied samples exhibit a pronounced peak of amphibole in the 2θ region from 10.4° to 10.6° (figure 2A, inset), not overlapped by the neighbouring lines of other minerals. We collated all diffraction patterns on a single scale of intensity values and compared the maximum peak with the intensities of other peaks in this region. This analysis divided the diffraction patterns and the corresponding samples into four groups:

1) GROUP I with peak intensity in the considered region above half the maximum peak for the studied sample set (in figure 2, fragments of the diffraction patterns and the figurative points of the samples included in this group are red-coloured);

2) GROUP II with peak intensities from a quarter to half of the maximum peak height (in figure 2, the elements related to this group are orange-coloured);

3) GROUP III with a peak intensity of less than a quarter of the maximum peak height (in figure 2, the elements related to this group are green-coloured);

4) GROUP IV with no peaks in the considered area (in figure 2, the details associated with this group are blue-coloured).
Given this separation, the graph of the ranked series of FS was analysed (figure 2A). In a narrow segment of the left side of the graph (in the case of the amphibole factor, in the first 22 samples), the FS values drop sharply, up to the inflexion point. Samples whose diffraction patterns contain only high peaks in the considered region (red points) are located to the left of this inflexion. After the inflexion point, the graph flattens and gradually turns into a straight line. A narrow segment of the diagram (n = 16) immediately after the inflexion shows a mixture of representatives of all rock groups. The linear portion of the graph (n = 160) is composed of figurative points of the sample, most diffractograms of which do not have the amphibole peak in question (blue dots).

Thus, we documented two boundary values of FS: 0.8 (all samples of rocks with a higher FS are rich in amphibole) and 0.2 (most samples with a lower FS do not contain amphibole). With this in mind, we sorted the samples by FS in sections of the studied cores. It was found that the core from well # 7 (an interval from 4.5 m to 293.0 m) contains several layers of about 30 m in thickness composed of amphibole-rich rocks, while the core from well # 6 (an interval from 496.0 m to 925.0 m) does not contain these rocks. Petrographic and mineralogical studies fully confirmed the results of the
analysis of the FS distribution. Let us show the distribution of FS for several other mineral phases (figure 3).

**Figure 3.** The ranked series of FS for (A) andradite, (B) analcime, and (C) monticellite (the contents of the corresponding minerals in some samples are indicated); The distribution of FS for (D) andradite, (E) analcime, and (F) monticellite in the cores.

The graphs of the FS ranked series for andradite, analcime, and monticellite (as well as all other factors) have the same “scree plot” morphology as the above graph for the amphibole factor. For control purposes, we selectively calculated the mineral content in some samples from both before and after inflexion points (see figures 3A-C). Quantitative phase analysis was performed in the MAUD program [12] using the Rietveld full-pattern fitting method ([15] and references therein). In this analysis, the same CIF files were used as those in the semiquantitative calculations. Similar to amphibole, to the left of the inflexion are the sample points rich in the considered minerals. On the right side of the inflexion, the content of these minerals is by the detection limit. In this way, an individual FS threshold was traced for each phase. All samples above this threshold are rich in the mineral in question relative to other samples in the collection. The content of the listed minerals in “rich” samples is 10–40 wt % and the number of such samples ranges from units (e.g., for monticellite) to tens (e.g., for andradite). For other minerals, this is different. The analysis of burbankite factor showed about 10 samples rich in this mineral phase, but quantitative analysis counted no more than 2–3 wt % burbankite in these samples. According to the analysis of FS, the number of samples rich in some most common minerals (for example, calcite) exceeds a hundred (more than half of our sample collection).
Analysis of the distribution of FS in the cores showed that rocks enriched with various minerals occupy different positions in the structure of the Kontozero complex. Thus, the rocks abundant in the most common minerals, such as calcite, dolomite, and andradite (figure 3D), found to be ubiquitous. Some minerals abound only in the upper part of the section, outcropped by well # 7 (e.g., amphibole, see figure 2B). The intervals rich in other minerals (e.g., orthoclase and/or albite), on the contrary, occur only in the lower part of the section, outcropped by well # 6. This layer-by-layer mineralisation of rocks by various mineral phases is natural for a differentiated volcanic-plutonic complex. The third group of minerals (e.g., fluorite or analcime discussed above, figure 3E) reaches high concentrations in local intervals, composing cement of brecciated rock sections. Some minerals, such as monticellite, are abundant in sparse samples (figure 3F). Monticellite is also rare in the carbonatite volcanic-plutonic complex Kaiserstuhl, Germany [16]. Despite the singularity of samples with monticellite, the very fact of its presence allowed researchers to draw valuable petrological conclusions [17].

The discovered relationship between the mineral content and the score of the corresponding factor allowed us to make a mineralogical interpretation of the results of the classical FA, which bases on geochemical variables (figure 4).

![Figure 4](image)

**Figure 4.** (A) Projection of the cases on the factor-plane (Factor I vs Factor II), the fields outline the sample groups (explanations are in the text); (B) Projection of the variables on the factor-plane (Factor I vs Factor II), red points – active variables (component contents), blue points – supplementary variables (factor scores).

Classic FA traditionally has two objectives: (a) the classification of observations (in our case, rock samples) and (b) the search for correlation between geochemical variables (in our case, element contents in the rocks). As applied to the chemical compositions of Kontozero rocks, the classical FA has shown effectiveness in achieving both goals. For instance, when projecting Factors I and II according to the explained dispersion (48% and 17%, respectively) on the factor-plane, all points divided into three groups connected by mutual transitions (figure 4A).

The positive pole of Factor I explains the group 1 cluster of points (the green field on figure 4A). Three geochemical variables, namely L.O.I., Ca, and Sr, are associated with this pole (figure 4B). These variables show high factor loadings (the factor loading is the correlation coefficient between the factor and the original variable, which varies from -1 to 1): $F_{I}L_{Ca} = 0.98$, $F_{I}L_{L.O.I.} = 0.94$, and $F_{I}L_{Sr} = \ldots$
Groups 2 and 3 (blue and red fields in figure 4A, respectively) are the results of the negative pole of Factor I and are separated due to the poles of Factor II. Silica and titanium are associated exclusively with the negative pole of Factor I (F₁L\text{Si}=-0.97 at F₁L\text{Si}=0.05; F₁L\text{Ti}=-0.85 at F₁L\text{Ti}=0.00). Sodium, potassium, aluminium, and zirconium are associated both with the negative pole of Factor I (F₁L\text{Na}=-0.67, F₁L\text{K}=-0.70, F₁L\text{Al}=-0.77, and F₁L\text{Zr}=-0.54) and with the positive pole of Factor II (F₂L\text{Na}=0.40, F₂L\text{K}=0.47, F₂L\text{Al}=0.58, and F₂L\text{Zr}=0.63). Magnesium, manganese, and iron are related both to the negative pole of Factor I (F₁L\text{Mg}=-0.59, F₁L\text{Mn}=-0.41, and F₁L\text{Fe}=-0.86) and with the negative pole of Factor II (F₂L\text{Mg}=0.75, F₂L\text{Mn}=0.55, and F₂L\text{Fe}=0.40). The barium, strontium, and sulfur contents contribute to the shift of the observation points toward the positive pole of Factor II (F₃L\text{Ba}=0.37, F₃L\text{Sr}=0.31, and F₃L\text{S}=0.30). However, unlike strontium, barium and sulfur are not related to Factor I (F₁L\text{Ba}=0.01 and F₁L\text{S}=0.05). Phosphorus has no relationship with either of the two factors considered (F₁L\text{P}=0.10 and F₁L\text{P}=0.04). Instead, phosphorus and sulfur jointly form their separate geochemical factor (F₃L\text{P}=0.87 and F₃L\text{S}=0.70), as does barium (F₃L\text{Ba}=0.86).

In total, combinations of the considered geochemical variables yielded three geochemical vectors (shown by coloured arrows in figure 4B). Since displaced along these vectors, the points divided into three groups, outlined by fields in figure 4A (the colours of the fields correspond to the colours of the vectors):

1) The influence of vector 1, related to the high content of L.O.I., Ca, and Sr in the rock, leads to a shift of the figurative points into group 1;

2) High contents of both Si (+ Ti) and Na-K-Al (+ Zr), with an essential contribution of Ba-Sr-S, cause a shift of points along vector 2 (towards group 2);

3) High contents of Si (+ Ti) and Mg-Fe (+ Mn) result in the shift of points along vector 3 (towards group 3).

To interpret the above geochemical vectors and groups, we projected the scores of mineralogically explained factors on the factor plane of Factors I and II (see figure 4B, blue points). These FS were supplementary variables, i.e. did not participate in the identification of factors. Their position relative to the “active” geochemical variables (see figure 4B, red points) allows us to draw the following conclusions:

1) Vector 1 (and the corresponding group) is associated with calcite content in the rock. Consequently, group 1 predominantly represents calcicarbonateites (apparently enriched in strontium);

2) Vector 2 is due to the presence of albite, orthoclase, and/or analcime (± natrolite) in the rock. Thus, group 2 includes samples rich in alkaline salic minerals;

3) Vector 3 is a response to the presence of diopside, magnetite, andradite, monticellite, amphibole, serpentine (secondary phase), and/or biotite. Thus, group 3 includes rocks rich in femic minerals;

4) The titanium phases (anatase and ilmenite) gravitate toward group 2, rich in alkaline sialic minerals. However, titanium did not participate in the discrimination of groups 2 and 3. It suggests that the rocks of group 3 are equally rich in titanium and its host phases are not oxides but silicates, e.g., biotite and/or garnet (confirmed by EPMA);
5) None of the considered factors tracks the presence of quartz (supposedly, its content is approximately equal in all types of rocks). Several mineral phases, e.g., apatite, baryte, strontianite, burbankite, and fluorite, show a barely noticeable relation to this separation. Nevertheless, FS of these phases correlates with scores of other factors identified by classical FA. For example, the scores of apatite and pyrite factors are close to the positive pole of the previously mentioned “phosphate” Factor III ($F_{III\text{Ap}}=0.77$ and $F_{III\text{Py}}=0.37$). The scores of the burbankite, baryte, strontianite, fluorite, and quartz factors form the shift vector towards the positive pole of the “baryte” Factor IV. In the studied rocks, these minerals form a specific mineral paragenesis superimposed on earlier associations.

Thus, the main trends in the mineralogical and geochemical evolution of carbonatites and aluminosilicate rocks of the Kontozero Devonian carbonatite paleovolcano were determined and statistically substantiated through the original method of statistical comparison of XRD and XRF data.

4. Conclusions
Statistical analysis of the collection of XRF and XRD data allowed us to obtain the factor scores, providing a mineralogical interpretation. It is shown that the scores of such factors functionally related to the content of minerals corresponding to the factor. This fact allows the use of factor scores as a tool for semiquantitative analysis of mineral composition. Analysis of the distribution of factor scores yielded a model of the distribution of each rock variety, rich in a particular mineral, in the structure of the studied complex. Notably, this model was built at the earliest stage of the study. The discovered relationship between the mineral content and the score of the corresponding factor allowed us to make a mineralogical interpretation of the results of the classical factor analysis, which bases on geochemical variables. The projection of the factor score onto the factor plane constructed from geochemical variables makes it possible to trace the main trends in the mineralogical and geochemical evolution of the studied rocks.

Acknowledgments
This research was funded by the Russian Science Foundation, grant number № 19-77-10039. Core sampling was carried out in TFGI NWFD (Apatity, Russia) under the GI KSC RAS research topic № 0226-2019-0053. The authors express their deepest gratitude to the TFGI NWFD employees for their assistance and Sidorov M.Yu (GI KSC RAS, Apatity, Russia) for his help with sample preparation. The authors thank Chuparina E.V. (IGC SB RAS, Irkutsk, Russia) for XRF analysis, Khvorov P.V. (IM UB RAS, Miass, Russia) for XRD analysis, and Bazai A.V. (GI KSC RAS, Apatity, Russia) for electron microprobe analysis and BSE images.

References
[1] M. M. Nistor, N. Har, S. M. Dori, S. Bigi, and A. F. Gualtieri, “Progress in mineralogical quantitative analysis of rock samples: application to quartzites from Denali National Park, Alaska Range (USA),” Powder Diffr., vol. 31, no. 1, pp. 31–39, 2016, doi: 10.1017/S0885715615000871.

[2] C. Jiang, Z. Chen, D. Lavoie, J. B. Percival, and P. Kabanov, “Mineral carbon MinC(%) from Rock-Eval analysis as a reliable and cost-effective measurement of carbonate contents in shale source and reservoir rocks,” Mar. Pet. Geol., vol. 83, pp. 184–194, 2017, doi: 10.1016/j.marpetgeo.2017.03.017.

[3] X. Wang, H. Sanei, S. Dai, O. H. Ardalaki, N. Isinguzo, D. Kondla, and Y. Tang, “A novel method to estimate mineral compositions of mudrocks: A case study for the Canadian unconventional petroleum systems,” Mar. Pet. Geol., vol. 73, pp. 322–332, 2016, doi: 10.1016/j.marpetgeo.2016.03.013.

[4] E. Fomina, E. Kozlov, and S. Ivashevkaja, “Study of diffraction data sets using factor analysis: a new technique for comparing mineralogical and geochemical data and rapid diagnostics of the mineral composition of large collections of rock samples,” Powder Diffr., vol. 34, no. S1,
pp. S59–S70, 2019, doi: 10.1017/S0885715619000435.

[5] H. Downes, E. Balaganskaya, A. Beard, R. Lifervich, and D. Demaiffé, “Petrogenetic processes in the ultramafic, alkaline and carbonatitic magmatism in the Kola Alkaline Province: A review,” Lithos, vol. 85, no. 1–4, pp. 48–75, 2005, doi: 10.1016/j.lithos.2005.03.020.

[6] A. G. Bulakh, V. V. Ivanikov, and M. P. Orlova, “Overview of carbonatite-phoscorite complexes of the Kola Alkaline Province in the context of a Scandinavian North Atlantic Alkaline Province,” in Phoscorites and carbonatites from mantle to mine, F. Wall and A. N. Zaitsev, Eds. London: Mineralogical Society of Great Britain and Ireland, 2004, pp. 1–43.

[7] U. Kramm, L. N. Kogarko, V. A. Kononova, and H. Vartiainen, “The Kola Alkaline Province of the CIS and Finland: Precise Rb-Sr ages define 380–360 Ma age range for all magmatism,” Lithos, vol. 30, no. 1, pp. 33–44, 1993, doi: 10.1016/0024-4937(93)90004-V.

[8] M. N. Petrovsky, E. A. Savchenko, and V. Y. Kalachev, “Formation of eudialyte-bearing phonolite from Kontozo carbonatite paleovolcano, Kola Peninsula,” Geol. Ore Depos., vol. 54, no. 7, pp. 540–556, 2012, doi: 10.1134/S1075701512070057.

[9] A. Arzamastsev and M. N. Petrovsky, “Alkaline volcanism in the Kola Peninsula, Russia: Paleozoic Khibiny, Lovozero and Kontozo calderas,” Proc. MSTU, vol. 15, no. 2, pp. 277–299, 2012.

[10] A. A. Arzamastsev and M. N. Petrovsky, “Alkaline volcanism in the Kola Peninsula, Russia: Paleozoic Khibiny, Lovozero and Kontozo calderas,” Proc. MSTU, vol. 15, no. 2, pp. 277–299, 2012.

[11] A. Altomare, N. Corriero, C. Cuocci, A. Falcicchio, A. Moliterni, and R. Rizzi, “QUALX2.0: a qualitative phase analysis software using the freely available database POW_COD,” J. Appl. Crystallogr., vol. 48, no. 2, pp. 598–603, 2015, doi: 10.1107/S1600576715002319.

[12] L. Lutterotti, S. Matthies, and H.-R. Wenk, “MAUD: a friendly Java program for materials analysis using diffraction,” Int. Union Crystallogr. Comm. Powder Diffr. Newsl., vol. 21, pp. 14–15, 1999.

[13] S. Gražulis, A. Daškevič, A. Merkys, D. Chatieigner, L. Lutterotti, M. Quirós, N. R. Serebryanaya, P. Moeck, R. T. Downs, A. Le Bail, “Crystallography Open Database (COD): an open-access collection of crystal structures and platform for world-wide collaboration,” Nucleic Acids Res., vol. 40, no. D1, pp. D420–D427, 2012, doi: 10.1093/nar/gkr900.

[14] B. L. Davis, R. Kath, and M. Spilde, “The Reference Intensity Ratio: Its Measurement and Significance,” Powder Diffr., vol. 5, no. 2, pp. 76–78, 1990, doi: 10.1017/S0885715600015372.

[15] D. L. Bish and J. E. Post, “Quantitative mineralogical analysis using the Rietveld full-pattern fitting method,” Am. Mineral., vol. 78, no. 9–10, pp. 932–940, 1993.

[16] R. J. Giebel, A. Parsapoorn, B. F. Walter, S. Braunger, M. A. W. Marks, T. Wenzel, and G. Markl, “Evidence for Magma–Wall Rock Interaction in Carbonatites from the Kaiserstuhl Volcanic Complex (Southwest Germany),” J. Petrol., vol. 60, no. 6, pp. 1163–1194, 2019, doi: 10.1093/petrology/egz028.

[17] D. S. Barker, “Calculated silica activities in carbonatite liquids,” Contrib. to Mineral. Petrol., vol. 141, no. 6, pp. 704–709, 2001, doi: 10.1007/s004100100281.