

As an example of the nature of the correlations between the calculated and experimental content of the minerals, we give a graph for the main mineral - enstatite (Fig. 1).

The purpose of development of liquidus thermobarometers is not in prediction of compositions of solid phases in the form of molar fractions of minerals, but in prediction of their compositions in the form of weight percent of oxides, because when modeling the fractionation of minerals it is in the form of oxides will be carried out extraction (or addition) of components from (in) the melt. The composition of experimental pigeonites is presented in weight percent, so verification of the calculated compositions must be performed in the same parameters. In addition, when calculating the pigeonites for minerals, a number of postulates have been adopted, whose fairness also needs to be verified.

Thus, the contents of the calculated minerals were recalculated by weight percent of oxide contents. The result is shown in Figures 2-3.

According to histograms in Figures 2-3, the distribution of residues is close to normal. This is also confirmed by the criterion of consent. Despite the relative friability of point clouds in some charts, thanks to the large sample size, the width of trust corridors is small, and lines of equal values lie within these narrow corridors (Figures 2-3).

Another important quality characteristic of thermobarometers is the average value of differences between the experimental and calculated concentrations of components in minerals. The proximity of this characteristic to zero means that there is no offset of the estimated value. The average values for the oxides in our sample are less than 0.08% for main components and 0.03% for small components.

In the temperature range from 960°C to 1400°C with a 95% probability the calculated value of the pigeonite liquidus temperature differs from the unknown true one by a value not exceeding 4.9°C.

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- Seliutina N.E.^{1,2}, Safonov O.G.^{2,1}, Varlamov D.A.² Petrological and experimental study of syenitization of tonalite gneisses exemplified by the Madiapala massif, Limpopo complex, South Africa. UDC 552.11**
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- Abstract.** The paper describes the process of syenitization of tonalite-trondhjemite-granodiorite (TTG) gneisses exemplified by the rocks of the Madiapala syenite massif, Limpopo Complex, South Africa. Petrological and geochemical study of the Madiapala syenites and syenitized gneisses indicated that the rocks of this massif were formed as a result of interaction of the Alldays TTG gneisses with complex CO₂-H₂O-salt fluids at temperatures of 800-850°C and pressures of 6-9 kbar. An experimental study confirms the possibility of the formation of the assemblage clinopyroxene + titanite ± K-feldspar coexisting with the syenite melt due to reactions of Ti-bearing biotite with quartz and plagioclase at 850°C and 6 kbar.
- Keywords:** syenites; TTG gneisses; fluids; Limpopo complex
- The Madiapala syenite massif is located in the western part of the Central Zone (CZ) of the Limpopo Complex (South Africa) within the host Alldays tonalite-trondhjemite-granodiorite (TTG) gneisses of an age of 2610-2650 Ma. According to the geochronological data obtained by the SHRIMP method (Rigby et al., 2011), the age of the syenites is 2010.3 ± 4.5 Ma. This age corresponds to the latest Paleoproterozoic event (D3/M3) in the Central Zone, which was characterized by active fluid penetration along regional and local shear-zones. Using the pseudosection method (THERMOCALC software), Rigby et al. (2008) established the maximum PT parameters of 6 kbar and 770°C for syenites. These data were interpreted as conditions of metamorphism of pre-existing syenites during the D3/M3 stage. A alternative model of the formation of syenites in the TTG gneisses (Safonov, Aranovich, 2014; Safonov et

Interaction in the systems of fluid–melt–crystal

al., 2014) is based on experiments on the interaction of biotite-amphibole tonalite gneiss with fluids $\text{H}_2\text{O}-\text{CO}_2-(\text{K}, \text{Na})\text{Cl}$ at 750 and 800°C and 5.5 kbar (Safonov et al., 2012, 2014). These experiments demonstrated that the leading factor for formation of the syenite assemblages from tonalite gneiss is an increase of alkali activity in a fluid. Thus, the syenite rocks could have been a product of syenitization of tonalite gneisses due to the effect of salt-rich aqueous-carbonic fluids.

Geochemical data (ICP-MS, ICP-AES) for the syenite rocks, syenitized gneisses and host TTG gneisses of the Madiapala complex distinguished two types of the syenite rocks (syenites and syenodiorites), confirmed the crustal nature of the syenite rocks and their close genetic relationship to the country tonalite gneisses. The REE spectra for the syenites indicate an extensive crystallization differentiation within the massif.

The earliest assemblage of the syenite rocks is potassium feldspar + clinopyroxene + titanite $\pm$ apatite and the later assemblage is amphibole + albite. In order to estimate the conditions for formation of the primary assemblage, the P-T pseudosections and isopleths of Mg# and Na content in clinopyroxene in association with alkali feldspar and titanite were constructed using the PERPLE_X software (version 6.7.7 for Windows) (Connolly, 2005) for the bulk compositions of the syenites. They

revealed that the primary magmatic syenite assemblage corresponded to a temperature range of 800-850°C and pressures of 6-9 kbar. Estimates on the potassium activity effect on the Alldays gneisses by calculating the $\lg(a\text{H}_2\text{O}) - \lg(a\text{K}_2\text{O})$ pseudosections showed that transformation of the gneiss into syenite is possible at constant P and T due to an increase of K_2O activity.

In order to reproduce the syenite assemblage, experiments on the interaction of a biotite tonalite gneiss (Alldays gneiss) with a $\text{H}_2\text{O}-\text{CO}_2-(\text{K}, \text{Na})\text{Cl}$ fluid were performed at 850°C and 6 kbar using gas pressure vessel with internal heating. The experiments were set for 10 days. The initial starting materials were solid cylindrical fragments of the Alldays gneiss and fluid mixture of oxalic acid with KCl and NaCl. The experiments reproduced the assemblage clinopyroxene + titanite $\pm$ K-feldspar (Fig. 1) via reactions of Ti-bearing biotite with quartz and plagioclase, initiated by the alkali-rich fluid. Under the run temperature, the assemblage clinopyroxene + titanite coexists with the melt of syenite composition enriched in volatiles (F, Cl and H_2O) (Table 1), which was confirmed using Raman spectroscopy. This is consistent with the proposed model for the syenite formation. Amphibole-bearing assemblages were produced in the experiments with high contents of NaCl in the fluid.

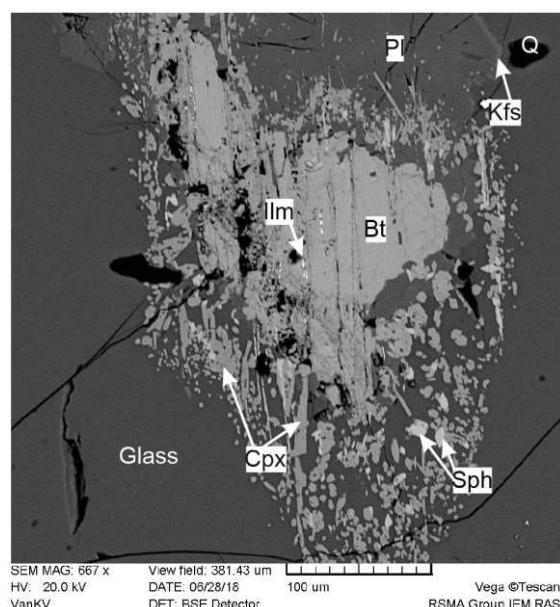


Fig. 1. Formation of the clinopyroxene (Cpx) + titanite (Sph) $\pm$ K-feldspar (Kfs) associated with the melt due to reactions of biotite, quartz and plagioclase.

Thus, the rocks of the Madiapala massif are a product of the syenitization of tonalite gneisses, which is in essence similar to granitization. Syenites of the Madiapala massif were formed at 6-9 kbar and

800-850°C via the active interaction of the Alldays TTG gneisses with an aqueous-carbonic-salt potassic fluids. The determining factor for the formation of the syenite assemblage was the increased potassium

Table 1. Average compositions of glasses in the run products.

Sample	SiO_2	Al_2O_3	CaO	Na_2O	K_2O	H_2O	Cl	F
1	70.55	12.07	0.90	2.67	6.26	1.57	0.04	0.11
3	64.96	15.87	1.56	3.79	4.85	4.27	0.04	0.25
4	61.08	20.69	2.63	5.79	5.47	2.94	0.03	0.03
5	68.15	12.23	0.92	4.59	3.35	1.87	0.34	0.26
6	62.20	15.50	1.25	3.95	4.81	2.36	0.04	bdl
7	66.93	15.46	0.70	2.86	7.11	3.95	0.04	0.26
8	67.10	12.78	0.65	2.67	5.37	2.82	bdl	bdl

activity in the fluid. Later amphibole-bearing assemblages were formed in the course of the syenite magma cooling. This stage corresponded to a change in the regime of alkaline components in fluid, so that the increase in Na₂O activity led to the replacement of the clinopyroxene + K-feldspar assemblage with the amphibole + albite assemblage.

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Particularities of scandium distribution between silicate and salt melts and crystal phases in the Si-Al-Na-K-Li-F-O-H system AT 800°-500°C and 1 kbar. UDC 552.11, 550.42

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Abstract. The distribution of Sc in the Si-Al-Na-KFOH model granite system between aluminosilicate and LiKNa-aluminofluoride (salt) melts is studied at temperatures

800°-600°C and pressure 1 kbar. It is shown that in the range of 800° - 700°C scandium accumulates along with rare-earth elements in salt melt with high distribution ratios >> 1. With a further decrease in temperature to 500 °C, along with silicate (supercooled) and salt melts, crystalline phases are formed in the system - quartz, K-Na - aluminofluorides of the cryolite-elpasolite series and Li-containing polyolithionite. It was found that scandium is included not only in the composition of silicate and salt melts, but also in aluminofluorides and mica. The Sc partition coefficient between aluminofluoride and silicate melt is about 5-15, between Na-aluminofluorides and the melt about 0.5; Na-K aluminofluorides - close to 5; between REE fluorides and silicate melt - 1-2, between mica and melt - 20. The highest partition coefficients of about 40 are observed between potassium and scandium rich fluoride and silicate melt. In all the mentioned crystalline phases of scandium, aluminum is apparently isomorphically replaced. This feature of scandium sharply distinguishes it from rare-earth elements and yttrium, which practically do not form part of cryolite-like phases and mica, and in the system under study only form their own fluoride phases of the LnF₃ type, sometimes containing alkaline elements.

Keywords: *distribution, partition, rare-earth elements, scandium, lithium, silicate and aluminofluoride salt melts*

In previous works (Gramenitsky et al., 2005; Shchekina et al., 2013), it was shown that in a granite system with limiting fluorine contents at temperatures of 700-800 °C, two immiscible melts are formed - silicate and salt (alkaline aluminum fluoride). The aim of the work was to establish the conditions and order of crystallization of these melts and the distribution of rare-earth elements, yttrium and scandium between the phases formed when the temperature of the system decreases from liquidus to solidus (from 800 to 500 °C) at a pressure of 1 kbar. Previously, it was also found that in the range of 800 °C - 700 °C, scandium, along with rare-earth elements, accumulates in a salt melt with high separation coefficients >> 1. At lower temperatures, the distribution of these elements has not been studied. Compared to REE and Y, the behavior of Sc is characterized by a number of features (Shchekina and Gramenitsky, 2008; Shchekina et al., 2003), which are considered in this paper.

Technique and experimental technique.
Analytical methods. Source materials. A silicate-salt mixture of reagents corresponding to composition A-40/11 was used as the initial charge. It was a composition of the aluminosilicate melt in the granite eutectic region, saturated with water and containing 1% F. The aluminofluoride component was added to this silicate composition (stoichiometric corresponding to the compound (Na, K, Li) 3AlF₆ in an amount sufficient to saturate the aluminosilicate melt and appearance of the isolate aluminofluoride phase (Table. 1).

For the article, those experiments were selected in which the water content in the system was about 10 wt.%. The following reagents and compounds