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GEOTHERMOMETERS FOR ALKALI ROCKS

(Figs. 11, Tab. 1)

Abstract: Series of geothermometers has been experimentally developed by applying a phase correspondence method for leucocratic minerals from alkali rocks. Among feldspar-bearing alkali rocks a nepheline-feldspar thermometer is mostly wide-spread in versions to consider a feldspar structural state and the influence of excess silica in the nepheline solid solution. The mineral equilibria temperature of nepheline and feldspar from plutonic and volcanic rocks varies over the range 1050—400 °C (by the Ne-Fsp thermometer). In the feldspar-free assemblages of alkali rocks the temperature has been taken by way of leucite-nepheline, sodalite-nepheline, cancrinite-nepheline and sodalite-cancrinite geothermometers. The nepheline-leucite equilibria temperature from alkali lavas (790—820 °C) and nepheline-sodalite one from a sodalite phonolite (900 °C) has been estimated by leucite-nepheline and nepheline-sodalite thermometers. The nepheline-sodalite equilibria temperature from the changed alkali rocks has been determined by a nepheline-sodalite thermometer over the range 460—600 °C. The lower temperature was determined by nepheline-cancrinite and sodalite-cancrinite thermometers. The upper limit of postmagmatic cancrinitization, therewith, was established to be about 400 °C. The temperature measurements by experimentally constructed geothermometers well agree with the data on homogenization of inclusions and with direct experiments on melting and crystallization of alkali rocks.

Резюме: На основании экспериментального изучения равновесий твердых растворов лейкократовых минералов щелочных пород создана серия геотермометров, базирующихся на принципе фазового соответствия. Для полевошпатсодержащих щелочных пород наибольшее распространение получил нефелин-полевошпатовый термометр, представленный вариантами, учитывающими сруктурное состояние полевого шпата и влияние избыточного кремнезема в твердом растворе нефелина. Температура, найденная с помощью этого термометра в равновесиях минералов из вулканических щелочных пород, колеблется в пределах 1050—400 °C. В парагенезисах бесполевошпатовых щелочных пород температура измерялась с помощью лейцит-нефелинового, содалит-нефелинового, канкринит-нефелинового и содалит-канкринитового геотермометров. По лейцит-нефелиновому и нефелин-содалитовому термометрам оценивалась температура равновесий нефелина и лейцита из щелочных лав (790—820 °C) и нефелина и содалита из содалитового фонолита (900 °C). Температура равновесий нефелина и содалита из измененных щелочных пород была определена по нефелин-содалитовому термометру в пределах 450—600 °C. Более низкая температура фиксировалась по нефелин-канкринитовому и содалит-канкринитовому термометрам, позволившим установить верхний предел постмагматической канкринитизации около 400 °C. Результаты измерения температуры с помощью, созданных экспериментально, геотермометров обнаружили хорошее совпадение с данными гомогенизации включений и с прямыми экспериментами по плавлению и кристаллизации щелочных пород.

Alkali rocks are known to be formed by petrogenetic processes that are more complex than those for rocks of normal series. Hence, there exists an abun-

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dance of various, often conflicting hypotheses on their formation. The persisting interest in these rocks is explained by the fact that they give rise to many, often unique, mineral deposits. The estimation of the temperature conditions of the rock formation is one of the key-problems and the purpose of the present study. A major difficulty in all these investigations is to estimate the temperatures at which alkali melts were generated. Commonly employed methods of homogenization of melt and gas-liquid mineral inclusions are rather laborious, they require special facilities and expertise. In addition, it is rather difficult to identify primary and secondary inclusions, especially in the rocks changed by metasomatic processes. Numerous temperature measurements on alkali massif mapping and detailed study of ore deposits are restricted by some difficulties involving detection and classification, mainly in altered rocks.

A reliable method for measuring temperatures in alkaline rocks involves geothermometers based on the partitioning of isomorphous elements between coexisting minerals. Such thermometers, or phase correspondence diagrams, have been derived from our experimental and thermodynamic data on the potassium and sodium partitioning between solid solutions of alkali feldspars, nepheline, sodalite, cancrinite and leucite at 400—1100 °C and 1—5000 bar. These parameters cover virtually occurring mineral parageneses of alkali rocks. The method for constructing a phase correspondence diagram is exemplified by the system nepheline-alkali feldspar. The effect of temperature on the exchange equilibrium:

$$NaAlSi_3O_8 + KAlSiO_4 = KAlSi_3O_8 + NaAlSiO_4 \qquad (1)$$

was, therewith, studied. Mineral-fluid and mineral-anhydrous chloride melt interactions were studied between 400—700 °C at 1 kbar and 800—1100 °C at 6 bar, respectively. The K/Na ratio in a fluid or melt was so given that the composition of a mineral may be changed at the expense of the following exchange reactions:

$$KAlSi_3O_8 + NaCl = NaAlSi_3O_8 + KCl \qquad (2)$$

and

$$KAlSiO_4 + NaCl = NaAlSiO_4 + KCl \qquad (3)$$

Substracting eq. (3) from eq. (2) gives eq. (1) whose thermodynamic parameters are dependent on the structural state of crystalline phases, all other things being equal. Consequently, the diagrams of phase correspondence for nepheline and alkali feldspar or any other minerals in equilibrium may be derived from those of mineral-fluid and mineral-melt types. Consider an $X_K^{fl} - X_K^{min}$ diagram in Fig. 1A. The diagram shows equilibrium curves of nepheline and alkali feldspar solid solutions after Zyryanov—Perchuk—Podlessky (1978). Using this diagram we can construct an equilibrium curve for nepheline and alkali feldspar. For that, the compositions of nepheline and alkali feldspar obtained from equilibrium curves Fsp + (K, Na) Cl and Ne + (K, Na) Cl with the same fluid composition are plotted on a similar diagram of X_K^{Ne} versus

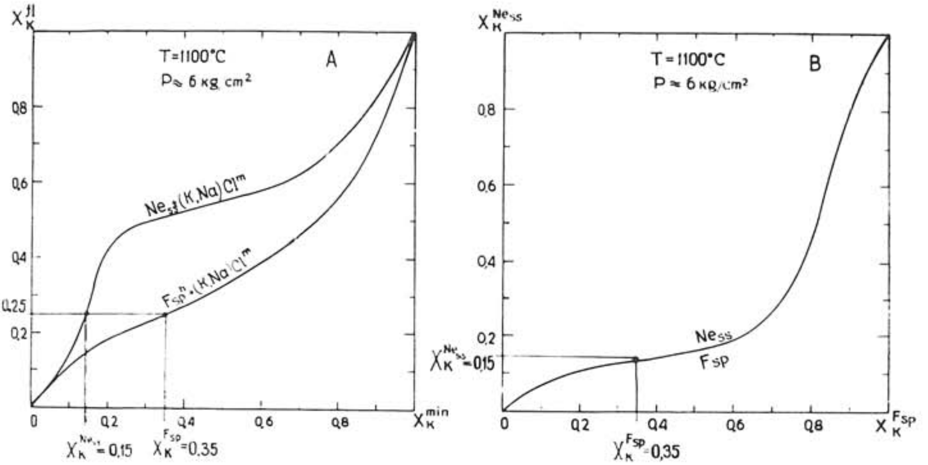

Fig. 1. The distribution of K and Na between "fluid" (K,Na)Cl^m, nepheline (Ne_{ss}) and alkali feldspar (Fsp), (A). The diagram of nepheline and alkali feldspar solid solutions phase correspondence derived from equilibria Ne_{ss}—(K,Na)Cl^m and Fsp^h—(K,Na)Cl^m (B).

X_K^{Fsp} (Fig. 1B). The use of mineral-fluid equilibria is believed to be thermodynamically valid, for it is insignificant, whether the chemical equilibrium on distribution of cations between minerals is realized directly or through an intermediate phase. The system nepheline-alkali feldspar of petrological importance was studied in more detail. Thus quantitative criteria for distinguishing structural series of alkali feldspar solid solutions through the values $\triangle bc$ and $\triangle 2\Theta_{204-060}$ were proposed. The mechanism and causes of anomalous alkali feldspar formation were studied and a method for estimating their structural state and composition was introduced by Zyryanov (1981). There was experimentally determined phase transition temperature between series of alkali feldspars (Zyryanov, 1977; 1978). A miscibility gap for the regions of temperature stabilities of alkali feldspar was constructed. Conditions of formation, ordering and breakdown of solid solution of perthites and their structural evolution in nature according to temperature were also determined by Zyryanov (1983).

The effect of excess silica in a nepheline solid solution on the nature of distribution of sodium and potasium between a nepheline and coexisting fluid was estimated. Being in equilibrium with the fluid constant composition nepheline with excess silica is more sodium-enriched than stoichiometric one. Experimentally determined effect of excess silica in the nepheline solid solution on its equilibrium in the alkali feldspar allows to explain a higher sodium content of nephelines from the nepheline-alkali feldspar paragenesis of volcanic rocks (Zyryanov—Perchuk—Podlessky, 1977). Thermodynamic analysis of experimental results indicates that with increasing temperature potassium moves from the alkali feldspar into the nepheline, while sodium goes in the oposite direction. Diagrams (mineralogical thermometers) which were derived for this system made it possible to estimate the mineral equilibrium temperature for intrusive, metasomatic, subvolcanic and effusive rocks. In the system cancrinite-sodalite-leucite-nepheline, which covers paragenesis of feldspar-free alkaline rocks, increase in temperature caused potassium to move from leucite, nepheline and cancrinite to sodalite, from leucite to nepheline and from nepheline to cancrinite, the sodium redistribution taking place in the opposite direction (Zyryanov, 1980; $1981_{2,3}$).

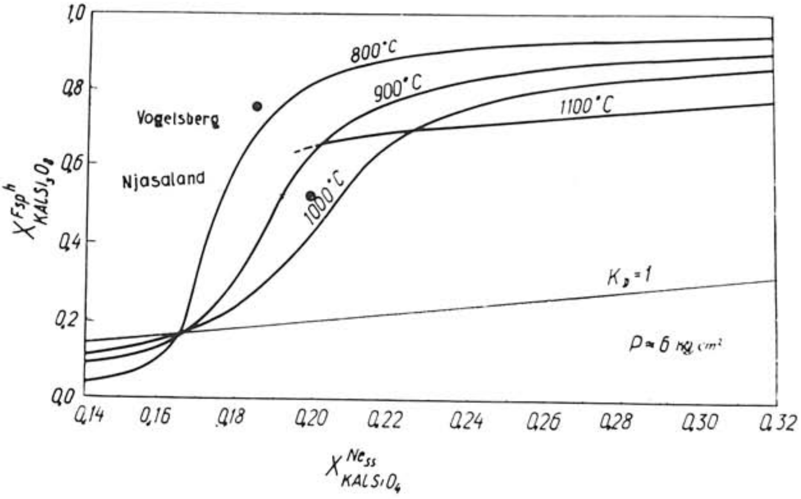

Fig. 2. The diagram of nepheline ($X_K^{Ne_{ss}} < 0.32$) and alkali feldspar (sanidine-high albite series) phase correspondence at 800—1100 °C and 6 kg/cm².

Experimental geological thermometers are capable of recording the lowest equilibrium temperature for paragenesis of coexisting minerals. Equilibrium is believed to have been reached once the fluid disappeared from the rock. The component exchange among the minerals through the fluid takes place under subsolidus conditions, during development of intrusive and subvolcanic massifs and also when rocks undergo metamorphic changes (nepheline gneiss). Exchange processes in effusive rocks are initiated below liquidus among different mineral phenocrysts and a melt and will continue in the presence of a high-temperature fluid. In spite of considerably higher rates of volcanic rocks as compared with that of intrusive rocks, the equilibria between minerals may be attained through higher temperatures and saturation of rocks with volatiles.

Our experiments with nepheline, leucite, sodalite and alkali feldspar under dry conditions at 800—1100 °C showed that duration of cooling of volcanic rocks was quite sufficient for components to attain equilibrium distribution (Zyryanov—Perchuk—Podlessky, 1978).

Using phase correspondence diagram one should take into account wide compositional ranges of nepheline ($X_K^{Ne} = 0.07—0.37$) which coexists with high temperature feldspars, and more narrow ranges of its composition ($X_K^{Ne} =$

0.14—0.23) in paragenesises of plutonic rocks. To choose an appropriate diagram of phase correspondence one should take into consideration both: excess SiO_2 in nepheline solid solution for paragenesises of volcanic rocks and estimation of structural states of alkali feldspar in paragenesises of plutonic rocks.

By way of illustration, the proposed geothermometers were used to estimate mineral equilibrium temperatures for alkaline rocks from different magmatic

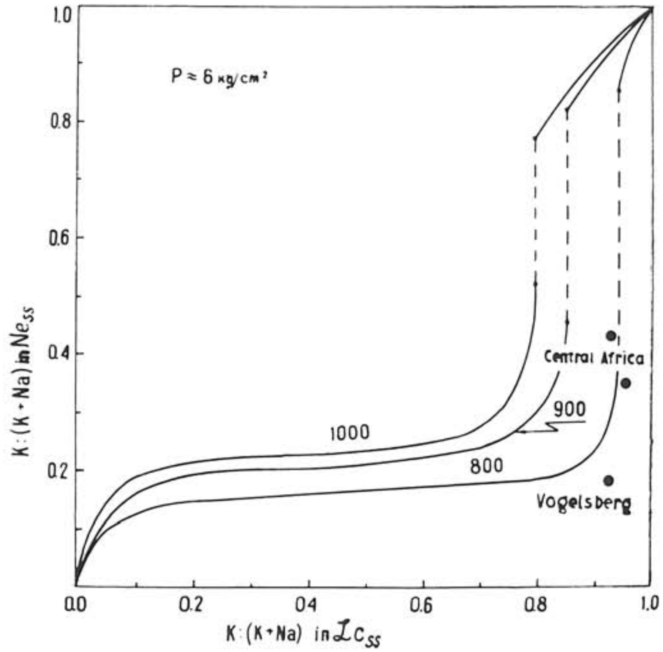

Fig. 3. The diagram of leucite and nepheline solid solutions phase correspondence at 800—1000 °C and 6 kg/cm².

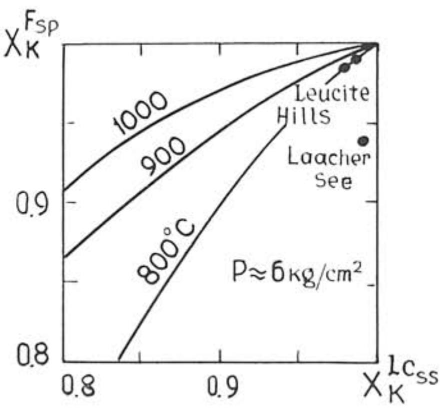

Fig. 4. The diagram of leucite and sanidine solid solutions phase correspondence at 800—1000 °C and 6 kg/cm².

formations. The available data on the homogenization of mineral primary inclusions were combined with the estimated mineral equilibrium temperatures for the same samples and enabled to determine the temperature range of the massifs. Temperature estimates done by mineralogical thermometers and a method of homogenization of secondary inclusions commonly coincide, thus allowing the data obtained by the two independent methods to be checked. The highest temperature was recorded for paragenesis from Nyasaland intrusive rocks (Tilley, 1961) using the phase correspondence diagram for solid solutions of nepheline and alkali feldspar of the series sanidine-high albite (Fig. 2). The estimated value (950 °C) is very close to the directly measured temperature for the nephelinite lava (980 °C) from the Nyiragongo lake region (Lee — Clark, 1966). The equilibrium temperature of 780 °C was recorded in a leucite-nepheline dolerite representative sample from Vogelsherg (Tilley, 1958). The same value (780 °C) was obtained for this sample with the leucite-nepheline thermometer (Fig. 3). The equilibria in the range 790—820 °C were also recorded by these thermometers in two nepheline-leucite assembages in the lavas from Central Africa (Sahama, 1952). Close temperature values were obtained with leucite-feldspar thermometer (Fig. 4) for the anorthoclase-leucite equilibrium (800 °C) from the groundmass of Quaternary basanite, Laaher See (Duda — Schminke, 1978) and for leucite-sandine equilibria (900 °C) from the Leucite Hills, U.S.A. (Carmichael, 1967) In experimental study on the Leucite-Hills rocks, Carmichael located the solidus temperature at 960—1100° C and 1000 bar.

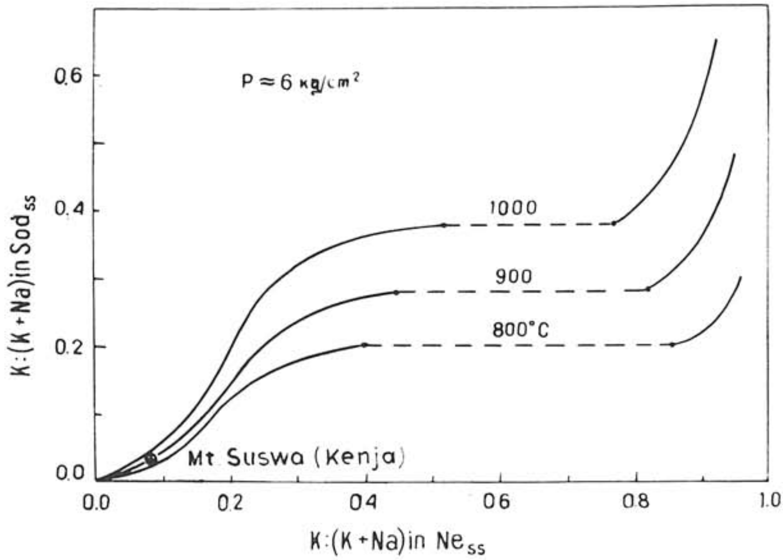

Fig. 5. The diagram of nepheline and sodalite solid solution phase correspondence at 800—1000 °C and 6 kg/cm^2.

The equilibrium of high-temperature paragenesis nepheline-sodalite formed at about 900 °C, was recorded by the nepheline-sodalite thermometer (Fig. 5) in a sodalite phonolite from the Quaternary volcano Suswa in the Rift valley of Kenya (Nash — Carmichael — Johnson, 1969). Measurements based on the ulvospinel content in titanomagnetite using the Lindsley thermometer gave a similar value.

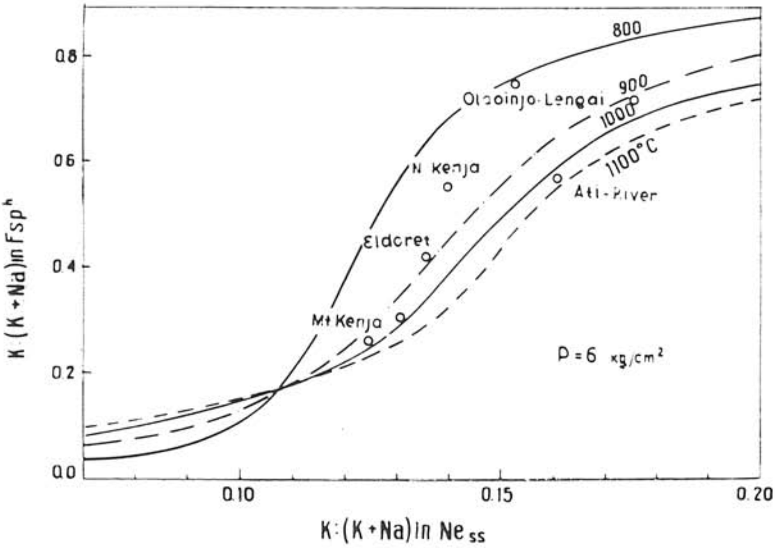

Fig. 6. The diagram of sodium-rich of region of the system nepheline-alkali feldspar at 800—1000 °C provided nepheline solid solution is saturated with normative silica.

Equilibrium temperatures in nepheline-feldspar paragenesises from effusive rocks were determined with the phase-correspondence diagram derived for sanidine and nepheline solid solution with excess silica (Fig. 6).

A rich sodium content in the nephelines from effusive rock paragenesises was first explained by the effect of excess SiO_2 in the nepheline-feldspar equilibrium (Zyryanov — Perchuk — Podlesskii, 1977). This effect was allowed for the nepheline-feldspar thermometer (Fig. 6) which was used to measure the equilibrium temperatures in nepheline-feldspar paragenesises from volcanic rocks from the East African Rift region (Zyryanov, 1981). The values thus determined for different samples over the 800—1050 °C range were compared with the homogenization temperatures for the primary inclusions and the calculated liquidi for the same samples. The mineral equilibrium temperatures were 100—200 °C lower than the rock liquidi. Direct melting experiments on the Leucite Hills alkali rocks at atmospheric presure and $P_{fl} = 1000$ bar revealed the same temperature difference between the solidus and liquidus for these rocks (Carmichael, 1967).

If no coexisting minerals can be obtained for the analyses or no data are available on the primary inclusions homogenization, the rock liquidus can be calculated from their chemical compositions using the method suggested by Perchuk (1984) for mafic and ultramafic rocks. The temperature for a rock dry liquidus is calculated by the polynomian:

$$
\begin{gathered}
t_{\text{liq}}\,(^\circ\text{C}) = 1039.62 = 43.738\, X^{01}_{\text{Mg}} + 35.86y + \\
+ 0.001182\,.\,(100\, X^{01}_{\text{Mg}}) + 0.125186y\,(100\, X^{01}_{\text{Mg}})^2 - \\
- 0.000031y\,.\,(100\, X^{01}_{\text{Mg}})^3, \text{ where} \\
y = (\text{Mg} + \text{Fe} + \text{Mn}) : 0.5\, \text{O}_2 \\
X^{01}_{\text{Mg}} = 3.15\, X^{\text{rock}}_{\text{Mg}} : (1 + 2.15\, X^{\text{rock}}_{\text{Mg}})
\end{gathered}
$$

This method was also applied to the liquidi calculations for the leucitites and ugandites from the West Rift region of Eastern Africa. The estimated temperatures are in the range 1100—1450 °C. The homogenization temperatures of inclusions in the nephelines and leucites from these rocks range from 1140 to 1400 °C. A 50 °C fitting the inclusions homogenization temperatures with liquidus temperatures calculated by polynomian makes this method suitable for studies of alkali rocks. Using the calculated liquidi for rocks of the Khibin massif,

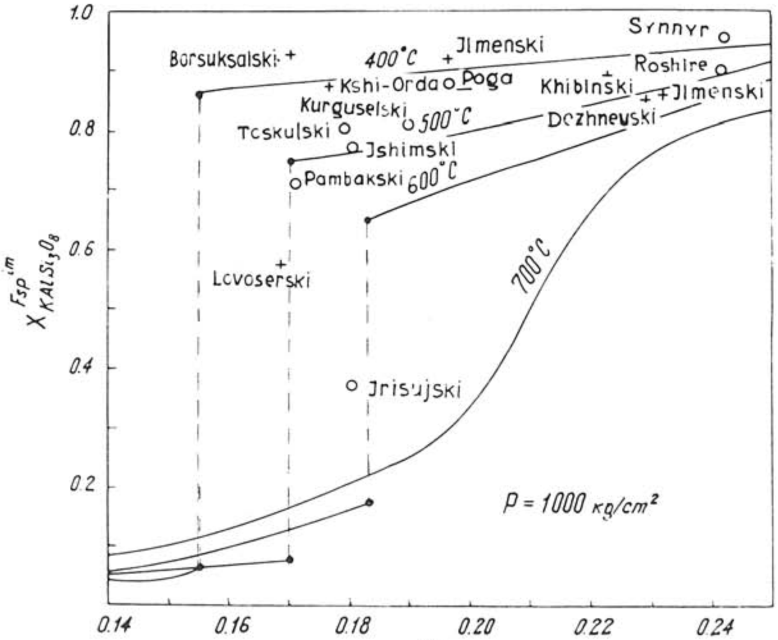

Fig. 7. The diagram of nepheline ($X^{\text{Ne}_{ss}}_{\text{K}} < 0.3$) and alkali feldspar (orthoclase-intermediate albite series) phase correspondence at 400—700 °C and 1000 kg/cm².

it was possible to determine that leucocratic khibinites, lavochorrites, foyaites and rischorrites had crystallized at 1080—1090 °C, and the crystallization temperature of melanocratic yolites, uvites, urtites and malinyites was 1105—1200 °C (Zyryanov — Kozyreva, 1981). The obtained data indicate that all the rock types of the massif were developed under the similar thermodynamic conditions.

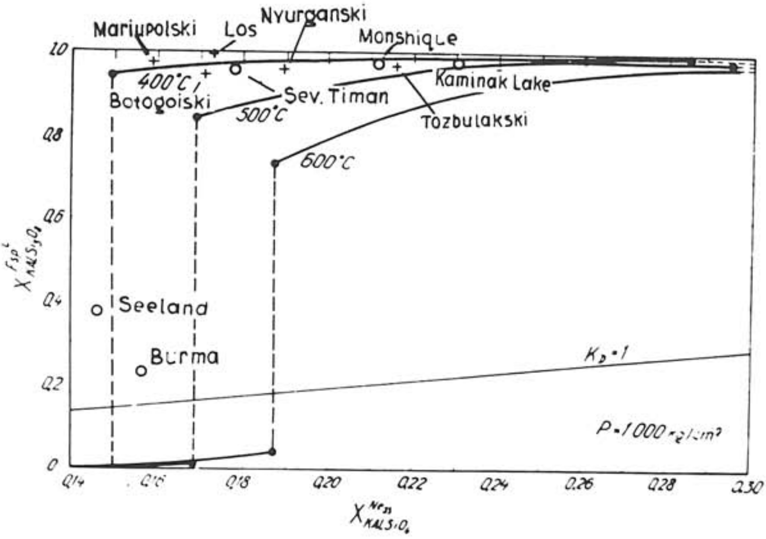

Fig. 8. The diagram of nepheline ($X_K^{Ne_{ss}} < 0.3$) and alkali feldspar (microcline-low albite series) phase correspondence at 400—800 °C and 1000 kg/cm².

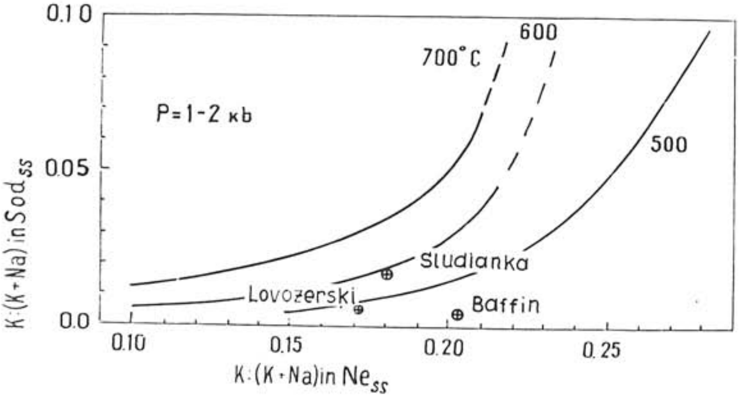

Fig. 9. The diagram of nepheline and sodalite solid solutions phase correspondence at 500—700 °C and 1000—2000 kg/cm².

The mineral equilibria temperature in intrusive massifs being always considerably lower than the homogenization temperatures of primary mineral inclusions and usually is in good agreement with the temperature at which secondary inclusions are homogenized. The maximum temperature determined with the phase correspondence diagrams in intrusive massifs of the alkali-gabbro formation are 675—770 °C (Zyryanov, 1981).

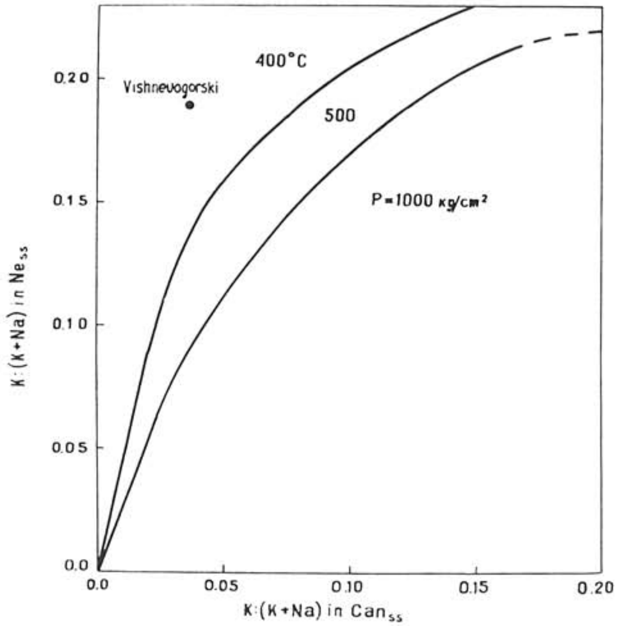

Fig. 10. The diagram of cancrinite and nepheline solid solutions phase correspondence at 400, 500 °C and 1000 kg/cm^2.

These values are close to the experimentally obtained melting temperature (775 °C) of nepheline syenite at 1000 bar water pressure (Milhollen, 1971). It should be noted that most mineral equilibria temperatures for intrusive massifs are lower than these maximum values.

Alkaline rock massifs contain abundant manifestations of postmagmatic proceses in the range 400—500 °C. The temperature of the nepheline-alkali feldspar equilibrium at the postmagmatic stage was determined with two geothermometers: one for the nepheline-intermediate (Fig. 7) and other for nepheline-low alkali feldspar (Fig. 8) equilibrium. The choice of the thermometer was based on the alkali feldspar structural state showing the existence of the phase transitions, which were found in our experiments to be at 375 ± 25 °C for microcline-orthoclase series and 680 ± 15 °C for orthoclase-sanidine series (Zÿryanov, 1977; 1978).

The nepheline-sodalite thermometer was used to measure the temperature in weakly altered feldspar-free alkali rocks (Fig. 9). The diagram gives the mineral equilibria temperature for the Sludyanka skarns, sodalite syenites from the Lovosersky massif and meta-evaporites from Baffin Island. The obtained values are in good agreement with the data available on gas-liquid inclusions and also with the results of other thermometers (Zyryanov, 1981). The lowest-temperature postmagmatic processes in alkali massifs took place during cancrinitization. The temperature of these proceses has been determined with the nepheline-cancrinite (Fig. 10) and sodalite-cancrinite (Fig. 11) thermometers. These data well coincide with the homogenization results of the secondary gas-liquid inclusions and determine the cancrinitization temperature at not higher than 400 °C.

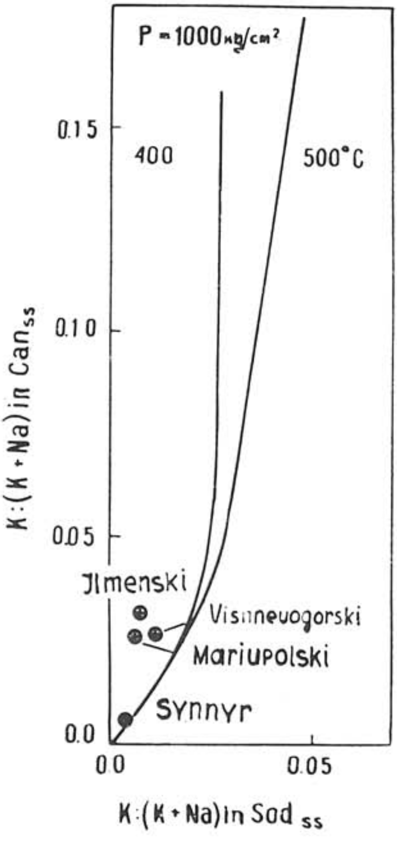

Fig. 11. The diagram of sodalite and cancrinite solid solutions phase correspondence at 400, 500 °C and 1000 kg/cm^2.

Differences in the temperatures determined with geothermometers or by inclusion homogenization has been a matter for argument between the supporters and opponents of the particular method. In fact, however it is not so much the contradicting results as different stages in the mineral formation of alkali rock massifs. Tab. 1 presents the temperatures for the same samples as given by these two methods.

Table 1

Comparison of the temperature determined with geothermometers and by the inclusion homogenization method

Rock, locality	Structural state of Fsp	Temperature °C		
		Geothermometers: Ne—Fsp; Ne—Can; Sod—Can	Homogenization of inclusions	
			primary	secondary
Platophonolite, Kenya	San	990	1100	
Pyroxene nepheline syenite Kuznetsk, Alatau	Or	480	950	
Synnyrite N. Pribaikalye	Or	425	840	
Ditroite N. Pribaikalye	Or	395	990	
Nepheline syenite, S-E Tuva	Mic	415	715	
Nepheline-natrolite syenite-pegmatite, S-E Tuva	Mic	410	715	400
Mariupolite, Ukraine	Mic	410	715	400
Miaskite, Urals	Mic	395		390

The mineral equilibrium values are seen to be in excellent agreement with the results given by the homogenization of secondary mineral inclusions. The higher homogenization temperatures for the primary inclusions reflect the beginning of the crystallization in the melt, while the mineral equilibrium temperatures record the disappearance of the fluid, normally at the postmagmatic stage in the development of the massif. The similar values produced by the two methods are typical of high-temperature assemblages in volcanic rocks. On the basis of the given data one could determine the temperature range of the alkali rock formation (1450—400 °C) and recommend to use the phase correspondence diagrams as of the liquidus temperature calculations for petrological study of the alkali rock massifs and related deposits.

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