

**Fluid evolution in the nepheline syenites of the Ditrău Alkaline Massif,  
Transylvania, Romania**

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## Abstract

The Ditrău Alkaline Massif (Romania) is located in the Eastern Carpathians, as an intrusion in the Bukovina nappe system of the Mesozoic crystalline zone. Nepheline syenites are the most abundant rocks occurring in the central and eastern part of the Massif, and represent the youngest intrusion of the complex. Petrographic observations and fluid inclusion studies were performed on nepheline syenites in order to examine the evolution and the effect of the magmatic fluids on the alteration of nepheline to secondary minerals as sodalite, cancrinite and analcime. Fluid inclusion studies in nepheline, aegirine, albite and cancrinite provide evidence for the role of highly saline fluids in incongruent transformation reactions by which sodalite, cancrinite and analcime crystallize mostly on the expense of nepheline. The fluids, in most cases, can be modeled by the H<sub>2</sub>O-NaCl system with various NaCl contents; however inclusions with more complex fluid (containing also K, Ca, CO<sub>3</sub>, etc. besides H<sub>2</sub>O and NaCl) composition are abundant. Raman spectroscopic studies of daughter minerals in inclusions demonstrate the presence of alkali-carbonatic fluids in some of the earliest inclusions of nepheline, aegirine and albite. The alteration process is supported by the presence of H<sub>2</sub>O-NaCl fluid inclusions in cancrinite, showing lower salinity compared to those in nepheline. During the crystallization period of the nepheline syenites the rock was in equilibrium with a high salinity, carbonate rich solution that evolved to decreased salinity with time. The following observations support this:

- paragenesis of mineral phases and their fluid inclusions: the early phases have high salinity inclusions and the late phases have low-salinity inclusions
- the partitioning of chlorine depends on the pressure of the system: at about 2.0 kbars, the fluids coexisting with the melt have a high initial salinity and the salinity decreases with time; inclusions in nepheline show the lowest trapping pressure at ~2.5 kbars, hence the system has a high initial salinity and decreases with time
- $a_{\text{H}_2\text{O}}$  increases with time, resulting in the formation of H<sub>2</sub>O-bearing phases in a late stage of the crystallization of nepheline syenites.

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## 1. Introduction

The predominantly nepheline syenitic intrusion of the Ditrău Alkaline Massif in Romania occurs within a rift related continental province. The complex also contains felsic silica-saturated and oversaturated syenites and granites and ultramafic/mafic rocks. The intrusion has a quasi-circular structure and a relatively small size and chemically is characterized by high alkali and low silica contents, and high volatiles and rare element contents. Their mineral assemblage is dominated by alkali ferromagnesian silicates, alkali feldspars, nepheline, cancrinite, sodalite and analcime. These features are all characteristics of classic alkaline massifs (Sørensen, 1974).

As silicate magmas crystallize they may become saturated in volatiles and exsolve a wide range of volatile phases that include aqueous-carbonic or hydrosaline chloride rich liquids, among others (Webster, 2004). The important role that these volatiles play during the generation, emplacement and crystallization of alkaline rocks has been emphasized by many authors (Kogarko, 1974; Sobolev et al., 1974; Morogan and Lindblom, 1995, Böhn and Rankin, 1999). The composition of the initial volatile that exsolves from the melt depends on the chemical composition of the silicate melt. The evolution in volatile composition during crystallization additionally depends on the pressure of the system. Evidence that fluids were present during the formation of a mineral or rock is provided by fluid inclusions in minerals. Primary fluid inclusions from minerals representing different stages in the paragenesis document the evolving composition of the exsolved fluid. This chemical evolution of the exsolved magmatic fluid in the Ditrău massif was investigated using petrographic and fluid inclusion studies, in order to determine the role of the fluids in the crystallization of late primary and secondary phases in the nepheline syenites of the Ditrău Alkaline Massif (DAM), Romania.

## 2. Geological setting

The DAM in Transylvania, Romania (Fig. 1) is a Mesozoic alkaline igneous complex formed during an extensional phase of the Alpine evolution associated with a rifted continental margin. The massif cuts the Pre-Alpine metamorphic rocks of the Bucovina nappe system near the Neogene-Quaternary volcanic arc of the Calimani-Gurghiu-Harghita Mountain chain (Ianovici, 1938, Kräutner and Bindea, 1998). The nappe system is the upper unit of the Central Eastern Carpathian nappes which formed during the Middle Cretaceous (Săndulescu, 1975). Plio-Pleistocene sedimentary lacustrine deposits and calc-alkaline andesitic pyroclastics and basalt-andesite lava flows overlay parts of the DAM. The intrusion developed a marked hornfels contact aureole against the countryrocks in which cordierite, sillimanite, corundum, spinel and alkali amphibole occur (Streckeisen and Hunziker, 1974, Jakab, 1998; Hîrtopanu et al., 2000).

The DAM is an intermediate size massif (about 800 km<sup>2</sup>) and presents a quasi-circular shape with imperfect ring structure and irregular indentations. The DAM is characterized by a systematic lithology and complex internal structure. The lithology includes a series of ultramafic rocks in the northwest, silica-oversaturated alkaline rock mostly at the northern end and undersaturated alkaline rocks dominating the central and eastern margin of the massif. According to Morogan et al. (2000), the complete complex comprises the following rocks: alkali gabbros, alkali diorites, monzodiorites, monzosyenites, syenites, nepheline syenites, with gradation from syenites through quartz syenites to alkali granites. Numerous dikes, including lamprophyre varieties, tinguaite, microsyenites and nepheline syenite, cut the whole complex.

Since its discovery by Herbich (1859) the massif has been the subject of many investigations. However, because of its structural complexity and wide petrographic variety the

petrogenesis is still not completely understood, and different studies led to different petrologic interpretations. The most important investigations are those of Streckeisen, who initially explained the genesis of the massif according to Daly's limestone assimilation theory and later by an origin through magmatic differentiation of an alkali syenite parent magma (Streckeisen, 1938, 1960). Anastasiu and Constantinescu (1982) considered a magmatic derivation with two principal rock suites generated from a mantle-derived basic magma and a felsic alkaline magma formed through partial melting of silica-poor crustal rocks. More recently, Kräutner and Bindea (1995, 1998) concluded that the complex formed by three main stages in the Triassic and Jurassic: a) emplacement of a mantle derived gabbro-dioritic magma; b) rising of the gabbro-dioritic mass into the crust in a subsolidus stage, with magma mingling and mixing produced a variety of hybrid rocks; c) mantle derived nepheline syenite magma, formed by partial melting, intruded into the Triassic massif, followed by local hydrothermal alteration and mineralization. Pál Molnár (2000) suggested a two-stage emplacement with the mid-Triassic formation of ultramafic rocks followed by formation of nepheline syenite by fractionation, and granites by fractionation and assimilation. A second stage (mid-Jurassic/lower Cretaceous), involved the emplacement of syenites and diorites. Morogan et al. (2000) suggested a basanitic OIB-like character for the parent magma and that the multistage intrusions were caused by a mantle plume with a long existence; in the process of formation of the massif they attribute an important role to assimilation and fractionation.

The ultramafic rocks have been dated at about 230 Ma, the gabbros, diorites, monzodiorites, monzonites, syenites and granites are about 215 Ma, and the nepheline syenites have ages of about 165-160 Ma, all determined using K/Ar and  $^{40}\text{Ar}/^{39}\text{Ar}$  chronology. The final stages of hydrothermal activity and cooling continued until about 115 Ma (Badgasarian, 1972;

Streckeisen and Hunziker, 1974; Pál Molnár and Árvai-Sós, 1995; Dallmeyer et al., 1997; Kräutner and Bindea, 1998). Slightly different data were obtained for the nepheline syenites by Pál Molnár and Árvai-Sós, who reported nepheline ages of about 210-230 Ma and biotite ages of about 180 Ma.

### **3. Petrography and mineralogy of nepheline syenites**

The nepheline syenites predominate in the central and eastern part of the massif and are the most abundant rocks of the DAM. However, they appear only as dikes in the northern part (Fig. 1). The variety of nepheline syenite with sodalite, calcite and cancrinite in the alkaline rocks nomenclature is known by the name of “ditroite”, name introduced by Zirkel (1866). Recently, Mitchell (1996) proposed the term hypersolvus sodalite nepheline syenite for rocks with the aforementioned mineral composition. On the basis of chemical composition the nepheline syenites of DAM can be characterized as miaskitic rocks since the aluminosity index of the rock  $(\text{Na}+\text{K}/\text{Al})$  varies between 0.8 and 1.0, and  $\text{Na}+\text{K} > 1/6 \text{ Si}$  (Streckeisen and Hunziker, 1974; Sørensen, 1974). The most common variety, the fresh white nepheline syenites are coarse- to medium-grained rocks, occur in massive or foliated varieties and consist of large (5-10 mm) euhedral grains of feldspar and nepheline. The mafic components are present in smaller amounts, and include biotite and clinopyroxene and rarely amphibole. Other important phases are calcite, cancrinite, sodalite and analcime. Apatite, titanite and zircon are present as accessory phases. The feldspars are mostly microcline-perthite and antiperthite (Fig. 2A), and plagioclase with anorthite content of  $\text{An}_4$  to  $\text{An}_{28}$  (Anastasiu and Constantinescu, 1975), corresponding to albite

(Fig. 2B) and oligoclase, that occurs as prismatic crystals without crystallographic faces, and occasionally as interstitial grains. The nephelines (Fig. 2D) frequently occur as idiomorphic crystals with hexagonal, short prismatic or square outline, and sometimes as subhedral or anhedral smaller crystals. The (10<sup>-10</sup>) cleavage of the crystals is distinct and the hexagonal symmetry is typical of the low temperature (< 775 °C) form of nephelines (Hamilton, 1961). The clinopyroxene content of the rocks varies from 3 to 4 % and chemically are mostly dark green subhedral and anhedral crystals of aegirine (Fig. 2C) and aegirine-augite. The nepheline is often altered to secondary phases including cancrinite, sodalite and analcime (Fig. 2D,E,F). These phases occur as reaction rims, marginal accumulations, crack fillings or pseudomorphs after nepheline. The presence of cancrinite at the boundary between nepheline and calcite indicates that calcite is used to produce cancrinite during alteration of nepheline (Fig. 2D). In the northeast fresh white nepheline syenites grade into reddish, hydrothermally altered nepheline syenites. The alteration products of nepheline are micaceous aggregates (liebenerite) and smaller amounts of cancrinite. The nepheline, albite, aegirine and cancrinite of the nepheline syenites contain primary fluid inclusions, which were used in the present study to monitor the evolution of the fluids in the nepheline syenites.

## 4. Fluid inclusions

### 4.1. Fluid inclusion petrography

Primary aqueous fluid inclusions were observed in nepheline, albite, aegirine and cancrinite. Pintea (1992) and Pintea and Diamond (1994) described immiscible, hypersaline CO<sub>2</sub>-H<sub>2</sub>O fluid inclusions from diorites and hornblendites of the northern part of DAM in hydrothermal veins associated with REE and MoS<sub>2</sub> mineralization. The authors also mentioned fluid inclusions in nepheline representing a heterogeneous low-T high salinity fluid. This latter fluid type, trapped as primary inclusions, is the subject of this study.

Nepheline contains a complex and varied assemblage of fluid inclusions. At room temperature the inclusions range from polyphase high salinity inclusions (L+V+solids), to 2-phase low salinity inclusions (L+V). The large polyphase inclusions (Type I) consist of L+V and 3 or more solid phases and occur randomly, isolated (Fig. 3A) or in small clusters. Rarely, intragranular pseudosecondary inclusion trails can be observed. The 3- (Type II) and 2-phase (Type III) inclusions occur mostly in clusters, oriented parallel to the cleavage direction (10<sup>-10</sup>) of the nepheline (Fig. 3B,C). The inclusion size ranges from less than 5 μm to 40 μm; in extreme cases the Type I inclusions reach 100 μm. The inclusions are either irregularly shaped, or more frequently, show negative crystal geometry after the host mineral nepheline. In most the cases all compositional varieties occur in the same crystal, however some of the crystals contain only Type II or Type III inclusions (Fig. 4). The polyphase inclusions are considered to be primary based on their shape and distribution. The Type II and III primary inclusions also occur in late stage nepheline. When all compositional varieties occur in the same crystal, the Type II and III

inclusions are considered secondary relative to Type I inclusions. The crystals are considered to have formed early and fluids representing Type II and III inclusions were trapped along the cleavage plans of the crystals.

In the aegirine (Fig. 3D) and albite (Fig. 3E) only Type I inclusions were observed (L+V+3 solids). They occur randomly, as individual inclusions, and have irregular shapes. However, some of the inclusions in albite show negative crystal geometry after the host mineral. The size of the inclusions are smaller than those in nepheline and vary between 5-20  $\mu\text{m}$ . The cancrinite trapped 2-phase (L+V) inclusions (Fig. 3F) and most of the inclusions have a specific elongated triangular shape. The “tip” of the inclusions faces opposite to the growth direction of the host mineral. The size of the inclusions varies between 5-25  $\mu\text{m}$ .

#### *4.2. Microthermometry*

Fluid inclusion petrography and microthermometry were performed on doubly polished thin sections (80-120  $\mu\text{m}$  thick) of nepheline syenite. The microthermometric analyses were conducted on a Linkam THMSG 600 heating-freezing stage and a Fluid Inc. USGS type gas-flow stage calibrated using synthetic fluid inclusion standards. The inclusions were chosen to be representative of fluid inclusions assemblages, within the host mineral (Goldstein and Reynolds, 1994). Because the host minerals have well-developed cleavage that could lead to leakage (Bodnar, 2003a) the inclusions first were cooled and then heated to homogenization. Type I inclusions were only heated, since the ice melting temperatures would not have given useful information regarding the chemical composition of the inclusions. However, heating of these

inclusions provided information on the dissolution properties of the different solid phases. This information was useful in the identification of phases after Raman spectroscopic analysis, as described below.

The chemical composition and salinity of Type II, III and cancrinite fluid inclusions were determined from ice melting temperatures. The initial ice melting temperatures occur between  $-23$  and  $-21^{\circ}\text{C}$ , therefore these inclusions were interpreted using the  $\text{H}_2\text{O}-\text{NaCl}$  system (Bodnar, 1993). For Type II inclusions the salinity was determined from halite dissolution temperatures (Bodnar, 2003b). Halite dissolved between  $264$  and  $325^{\circ}\text{C}$ . However, in some cases the inclusions decrepitated above  $315^{\circ}\text{C}$  and the homogenization temperatures for those inclusions was not determined. The bubble disappearance temperatures ranged from  $250$  to  $315^{\circ}\text{C}$ . The halite dissolution temperatures were used to calculate the salinity of these inclusions using the equation of Sterner et al. (1988), that gives a salinity ranging between  $35.6$  and  $40.2$  wt% NaCl eqv. For Type III inclusions and for inclusions in cancrinite the salinity was determined by the last ice melting temperature (or freezing point depression) using the equation of Bodnar (1993). Type III inclusions showed last ice melting temperatures between  $-17.3$  and  $-20.7^{\circ}\text{C}$ , giving salinity values between  $20.3$  and  $22.8$  wt% NaCl eqv., and total homogenization temperature range from  $243$  to  $305^{\circ}\text{C}$ . The inclusions in cancrinite show last ice melting temperatures between  $-6.3$  and  $-3.7^{\circ}\text{C}$  and corresponding salinity of  $6.0$  to  $9.6$  wt% NaCl eqv., and have bubble disappearance temperatures between  $180$  and  $230^{\circ}\text{C}$ .

The relationship between salinity and homogenization temperature for the different inclusion types is shown on Fig. 5.

### 4.3. Raman spectroscopy

Raman spectroscopic analyses were performed to identify the daughter minerals in the Type I inclusions and this information was used to estimate the chemical composition of fluids trapped in these inclusions. The instrument was a Jobin Yvon Horiba HR 800 LabRAM Raman microprobe equipped with a cooled charge-coupled device (CCD) detector, using a 514.57 nm Ar ion laser (green), operated in confocal mode with the hole set to 150  $\mu\text{m}$ . The laser was focused on the daughter minerals through an Olympus UPLAPO 60x objective (NA = 0.9, working distance = 0.2 mm above cover glass, Adar et al., 2004). The acquisition time varied from 30 to 60 second, but was increased to 10 min for some weaker signals. The polarized nature of the laser beam causes important differences in the spectra with the orientation of the crystal (Burke, 2001), therefore the samples were orientated in a position to provide the maximum intensity.

The Type I inclusions contain 3 or more solid phases. The phases are described in the order in which they dissolve during heating. The first solid is a tabular, elongated, anisotropic phase that dissolved at about 138-148°C. Raman spectrum displays two fundamental vibrations at 152 and 1062  $\text{cm}^{-1}$  (Fig. 6A). Raman spectra correlate most closely with the spectra of thermonatrite (156 and 1062  $\text{cm}^{-1}$ ,  $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ ), trona (164 and 1060  $\text{cm}^{-1}$ ,  $\text{Na}_3(\text{CO}_3)(\text{SO}_4)_2$ ), gaylussite (164 and 1071  $\text{cm}^{-1}$ ,  $\text{Na}_2\text{Ca}(\text{CO}_3)_2 \cdot 5\text{H}_2\text{O}$ ), or pirssonite ( $\text{Na}_2\text{Ca}(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}$ ). Pirssonite is similar in composition to gaylussite but with less  $\text{H}_2\text{O}$  and is more stable at higher temperatures (Lipin, 2001). The phase is probably a mixture of gaylussite and pirssonite and can thus be defined as a complex hydrated carbonate. The second solid is a tabular, anisotropic phase that dissolved around 173-187°C. The Raman spectrum displays fundamental vibrations at 145,

685, 1045, 1266 and 1434  $\text{cm}^{-1}$  (Fig. 6B). This phase was identified as the sodium bicarbonate, nahcolite ( $\text{NaHCO}_3$ ). All Type I inclusions contained a cubic, isotropic phase that showed a very weak Raman signal or no signal at all, and was identified as halite after the optical and dissolution properties (dissolved around 272-325°C). A few inclusions contained phases that showed Raman peaks at 157, 286, 715 and a very strong peak at 1089. This phase was identified as a complex “dry” carbonate that dissolved around 175-180°C. Muscovite was also identified during the Raman analyses. This phase is probably a previously formed crystal that was trapped by the inclusions. This is supported by the fact that this phase did not dissolve during heating.

The fluid inclusion studies indicate that the fluid, in equilibrium with the nepheline syenitic melt during crystallization of the rock, varied from a ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ), ( $\text{Cl}^-$ ) ( $\text{CO}_3^{2-}$ ) ( $\text{SO}_4^{2-}$ ) ( $\text{H}^+$ ,  $\text{OH}^-$ ) composition to a ( $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{H}^+$  and  $\text{OH}^-$ ) composition with decreasing NaCl content.

## 5. Discussion

The occurrence of primary fluid inclusions in the nepheline syenites of the DAM is direct evidence that a fluid was present during crystallization of the nepheline syenitic melt. The minerals trapped diverse fluid inclusion populations with varied compositions and salinities, documenting a decrease in salinity during formation of nepheline syenites. A range of observations described below, support this interpretation.

The paragenesis shows aegirine, nepheline and albite as early phases, followed by microcline-perthites, biotite and amphibole, followed by calcite and finally the secondary phases.

From petrographic observations it is obvious that the early phases trapped high salinity fluids and the late phases (part of the nepheline, and cancrinite) trapped lower salinity fluids. The fact that the early mineral phases contain fluid inclusions suggests that the nepheline syenitic melt was saturated in water early in the crystallization history. Kräutner and Bindea (1998) suggest that the intrusion of the nepheline syenites is the last phase in the formation of the massif and that the nepheline syenites are mantle derived, formed by partial melting. They do not discuss the composition of the parental magma or the origin of nepheline syenites. Pál Molnár (2000) clearly states that the nepheline syenites are a fractionation product of a primitive melt close to olivine-pyroxene hornblende composition. In his genetic model the nepheline syenites are formed by fractionation in the first major intrusion, followed by the intrusion of syenites, probably originating from a different source. However, according to all other authors, the nepheline syenites had penetrated and veined all previously formed rocks of the massif. Morogan et al. (2000) propose an origin of basanitic magma of OIB-like character, and the phonolitic magmas from which the nepheline syenites crystallized were produced as fractionation residues of the basanitic parent magma. Considering all these possibilities water-saturated nepheline syenite melts are most likely the result of fractionation of the parent magma.

The nepheline-kalsilite-silica diagram is a commonly used geothermometer (Hamilton and Mackenzie, 1960; Hamilton, 1961; Platt, 1996). In this system the limits of kalsilite and silica increase with temperature (Fig. 7). The nepheline compositions of the DAM (Constantinescu and Anastasiu, 1979; Morogan et al., 2000) are plotted on the Ne-Ks-Qz diagram indicating crystallization temperatures in the range 500-700°C. This temperature range is attributed to the slowly cooled plutonic nepheline syenites. The DAM nepheline compositions fall close to the low-temperature Morozewicz-Buerger convergence field (Tilley, 1954; Platt

1996). On the H<sub>2</sub>O-NaCl phase diagram are plotted the isochores representing the minimum and maximum homogenization temperatures of the Type III inclusions, and inclusions in cancrinite, for a salinity of 21 wt% NaCl, and 7 wt% NaCl, respectively (Fig. 8). These values are close to the average salinity of Type III, and inclusions in cancrinite, respectively. On the same phase diagram the calculated genetic T conditions of crystallization of nepheline are added. The intersection of the isochore field of Type III inclusions and genetic T conditions of nepheline result in the T trapping conditions of the inclusions in the nepheline. This intersection defines the lowest pressure limit of about 2.5 kbars for the system, pressure close to the value (2.0 kbars) used by Hamilton (1961) for his experiments on the temperature of formation of nepheline solid solutions. The highest pressure limit of 5.0 kbars is estimated by the position of DAM related to the units of the Bucovina nappe system penetrated by the massif according to which the cooling occurred at about 15 km depth. The deep crustal intrusion level is supported by a cooling period lasting about 20-25 Ma (Kräutner and Bindea, 1998), suggesting approximately isobaric cooling of the system. Hence, the P-T trapping conditions of the inclusions in cancrinite can also be estimated by the intersection of isochore field and pressure range (Fig. 8).

The partitioning of chlorine between the silicic melt and the exsolving aqueous fluid is strongly pressure dependent (Fig. 9, Cline and Bodnar, 1991). In low pressure systems (0.5 kbars) the initial salinity of that fluid is low and that salinity increases with progress of the crystallization. In intermediate pressure systems (1.3 kbars) the salinity does not change significantly with the progress of crystallization. In deep systems (2 kbars) the first fluid exsolved has high salinity and salinity decreases as the crystallization progresses. Phase equilibria confirm a minimum pressure of formation of the nepheline syenites of 2.5 kbars. As a

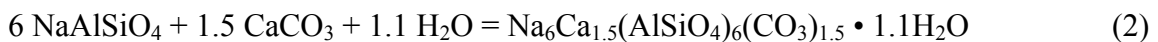
result the first exsolved fluids would have high salinity and salinity would decrease with time and progress of crystallization.

At this point is obvious that fluid inclusions trapped fluids with different chemical compositions and salinities during crystallization. The decreasing salinity is consistent with formation of late primary and secondary phases mostly at the expense of nepheline (and albite), in the following order: calcite crystallizes, as a late primary phase, removing most of the carbonate from the fluid; in the subsolidus region: cancrinite forms at the expense of nepheline removing from the fluid the rest of the carbonate, and eventually chlorine and sulfate. In situations where cancrinite is formed at the grain boundary between nepheline and calcite, the cancrinite uses the calcite; sodalite crystallizes at the expense of nepheline and to a lesser extent at the expense of albite. This reaction removes NaCl from the system and produces extra silica that reacts with nepheline to produce analcime. Knowing the composition of the fluids and the chemical formula of minerals of nepheline syenites, it is obvious that fluid composition played an important role in the crystallization of the late phases of the nepheline syenites, and simple incongruent chemical reactions can be written describing the transformation reactions: 1) the complex carbonates from the fluid react with nepheline to produce cancrinite:



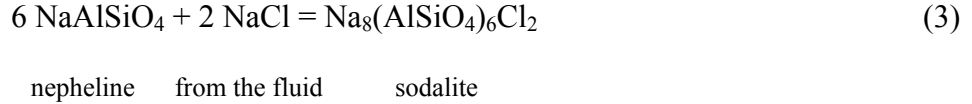
nepheline                  complex carbonate                  fluid                                  cancrinite

or

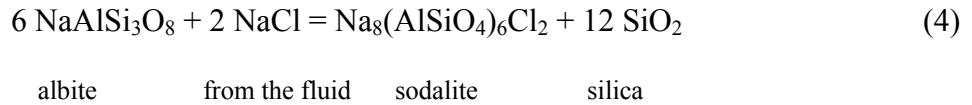


nepheline                  calcite                  fluid                                  cancrinite

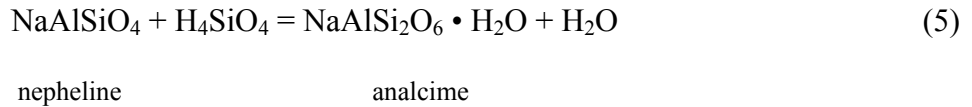
for the pure carbonate endmember of cancrinite, as suggested by experimental studies on the breakdown of cancrinite of Sîrbescu and Jenkins (1999). 2) the sodalite can form as a replacement of nepheline which reacts with NaCl from the fluid following the



reaction. In the reaction the potassic component in nepheline was ignored, which is presumably exchanged for sodium in the fluid during the reactions (Finch, 1991). 3) To a lesser extent, sodalite forms at the expense of albite. Albite also reacts with the NaCl from the fluid by the reaction



to produce sodalite and silica. 4) The nepheline syenites are silica undersaturated, and the produced silica is not in equilibrium with the existing mineral assemblage. Hence, it is consumed by the reaction that results analcime



These transformations must be accompanied by some dissolution or deformation of nepheline in order to accommodate the volume increase (Finch, 1991). However, to date, this process was not observed in the nepheline syenites of the DAM. An important consideration in the alteration process is the water content of nepheline, which in pristine unaltered crystals can be as high as 0.5 wt% (Beran and Rossman, 1989). Finch (1991) also suggested that hydrothermal alteration of nepheline occur not only by passage of fluids along grain boundaries, but also by fluid flow assisted by a permeable network of micropores within the nepheline themselves, observable using SEM. The origin of microporosoty is attributed to exsolution of water from nepheline. Nepheline also is inclined to low-temperature hydrothermal alteration caused by the instability of

nepheline in the temperature ranges of 400-500°C, as shown experimentally by Boettcher and Wyllie (1969).

## 6. Conclusions

The parent melt of the nepheline syenites of the Ditrău Alkaline Massif was saturated in an alkali-carbonate rich aqueous fluid near the beginning of crystallization of the nepheline syenites. This interpretation is consistent with the fractionation residua origin of the nepheline syenitic melt. Primary fluid inclusions in the different mineral phases of the nepheline syenites provide direct evidence for the presence of aqueous solutions. The fluid inclusion compositions range from a highly saline-carbonate rich end member, producing a varied assemblage of daughter minerals, to a low salinity end member. The diverse fluid inclusions document a decrease in the salinity of the aqueous fluid during crystallization of the different mineral phases. The decrease in salinity is consistent with formation of mineral phases that remove Cl, CO<sub>3</sub> and SO<sub>4</sub> from the aqueous solution during the formation of late primary phases, or secondary phases formed at the expense nepheline, or albite, in some cases of sodalite formation, in the following order: a) crystallization of calcite as the late primary phase that removes most of the carbonates from the solution; b) alteration of nepheline to produce cancrinite, what removes the remaining carbonates, eventually some Cl and SO<sub>4</sub>; formation of sodalite on the expense of nepheline or albite, what removes the NaCl from the aqueous fluid, and produces silica in the reaction with albite; c) finally the extra silica is reacting with nepheline and water to produce analcime. The alteration of the nepheline is assisted by the water content and permeable network of microspores of nephelines and instability of the nepheline under hydrothermal conditions. All these observations on the petrographic relations in the nepheline syenites suggest the existence of a powerful active hydrothermal system in the late stages of crystallization of the Ditrău Alkaline Massif.

## Figure captions

**Figure 1.** Geology of the Ditrău Alkaline Massif, with the sample locations (modified from Kräutner and Bindea, 1998).

**Figure 2.** Minerals and textural relations in the nepheline syenites of the DAM. A. Microcline-perthite; B. Aegirine; C. Albite; D. Cancrinite (Cn) at the boundary between calcite (Cc) and nepheline (Ne). Calcite is used by the cancrinite in the alteration of nepheline; E. Cancrinite and interstitial sodalite (So); F. Analcime (Acm) reaction rim around nepheline.

**Figure 3.** Photomicrographs of (A) Type I polyphase fluid inclusion (FI) in nepheline: **a** - complex hydrated carbonate daughter mineral; **b** - nahcolite daughter mineral; **H** - halite; **V** - vapor. (B) Type II, 3-phase FI in nepheline. (C) Type III, 2-phase fluid inclusion in nepheline. (D) Polyphase FI in aegirine. (E) Polyphase FI in albite. (F) 2-phase L-V FI in cancrinite oriented with the “tip” of the inclusions opposite to the growth direction of the crystals.

**Figure 4.** (A) Sketch of the different compositional varieties of fluid inclusions that occur in nepheline. (B) Photomicrograph of three dimensional fluid inclusion cluster, with inclusions oriented with the (10<sup>-10</sup>) cleavage direction of nepheline.

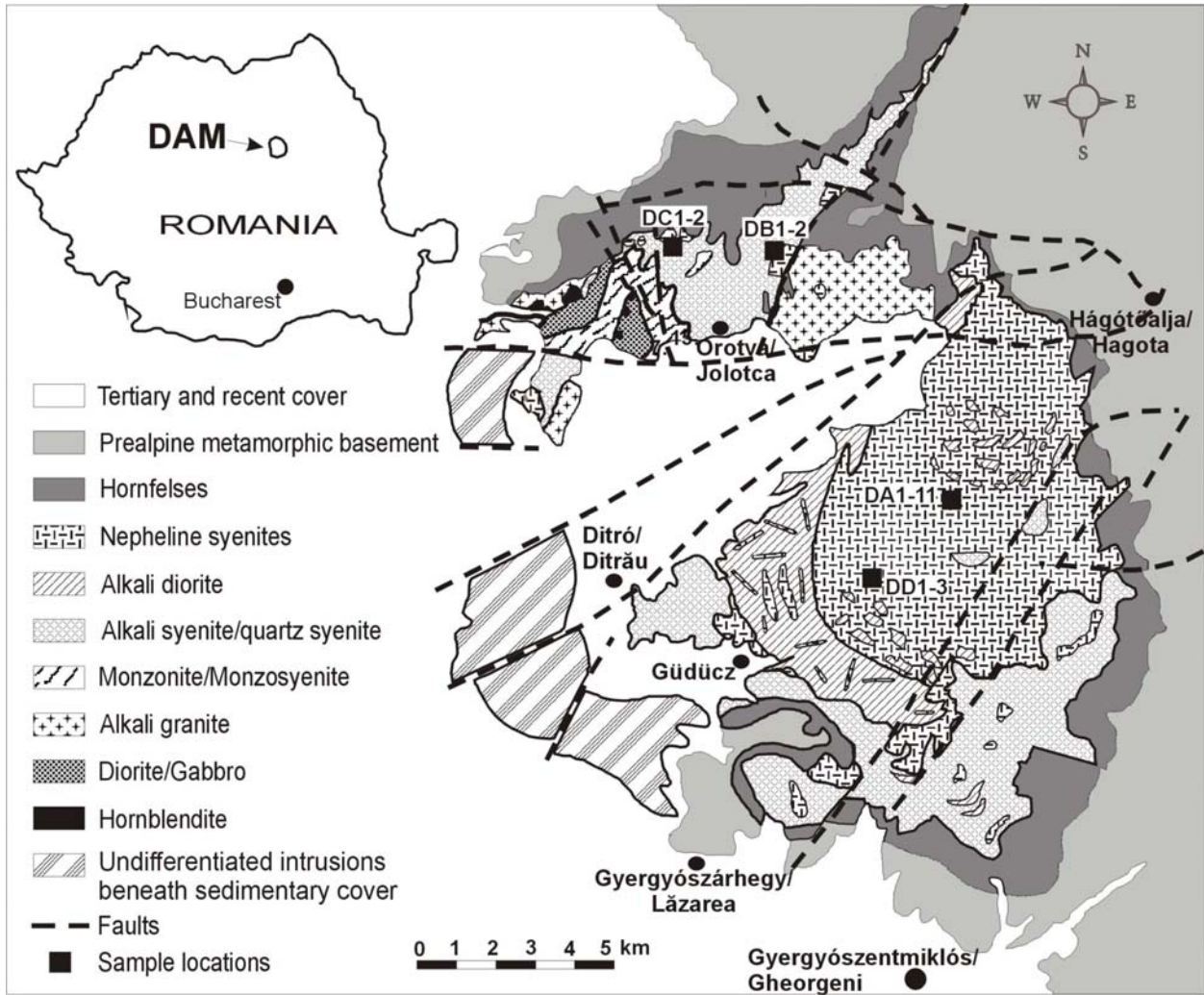
**Figure 5.** Relationship between salinity and homogenization temperatures for the various H<sub>2</sub>O-NaCl fluid inclusion types studied. Type II inclusions homogenize by halite dissolution after the bubble disappearance. Bubble disappearance temperatures for Type II inclusions are shown by the dashed-line field. The data show a decreasing salinity with decreasing homogenization temperature.

**Figure 6.** (A) Raman spectra of a complex hydrated carbonate and (B) nahcolite daughter minerals in the Type I fluid inclusions of nepheline, albite and aegirine.

**Figure 7.** Nepheline compositions of the DAM nepheline syenites (data from Constantinescu and Anastasiu, 1979; Morogan et al., 2000) plotted in the nepheline-kalsilite-silica diagram. Isotherms show the limits of nepheline solid solutions at various temperatures (modified from Hamilton, 1961). The nephelines from the DAM fall approximately between the 500 and 700°C isotherms. M and B are Morozewicz and Buerger ideal nepheline compositions reported by Tilley (1954) and Platt (1996).

**Figure 8.** P-T diagram showing the trapping conditions (dark field) of the Type III fluid inclusions with an average salinity of 21 wt% NaCl eqv. in nepheline and for inclusions in cancrinite (light filed) for an average salinity of 7 wt% NaCl eqv. The dashed line shows the estimated P-T conditions of the crystallization of nephelines.

**Figure 9.** Salinity of the aqueous fluids exsolved from a crystallizing silicic melt at different pressures. The fluid exsolved from the melt at 2.0 kbars has a high initial salinity and as the crystallization progresses the chlorine content of the fluids decreases (modified from Cline and Bodnar, 1991).



**Figure 1.**

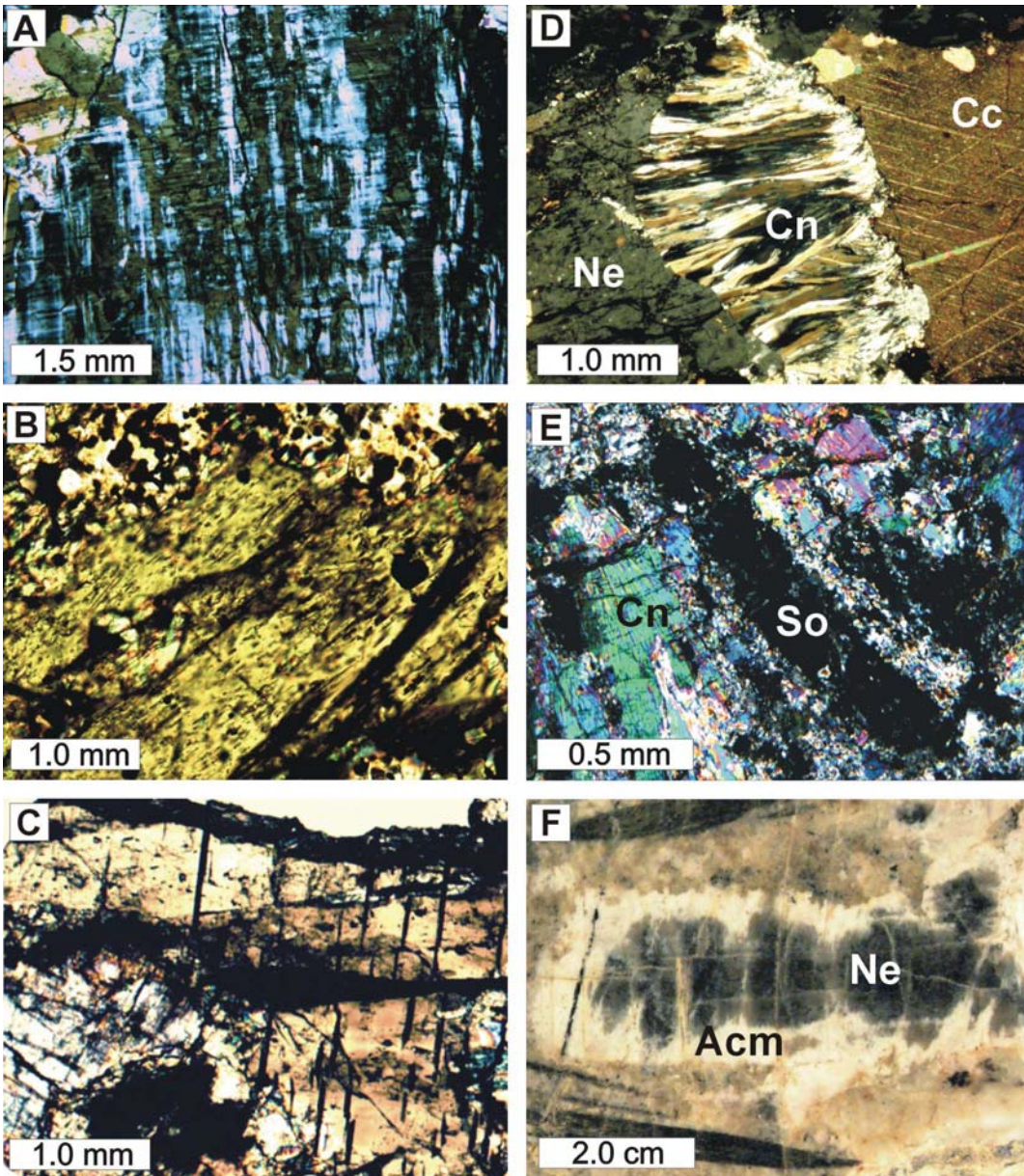
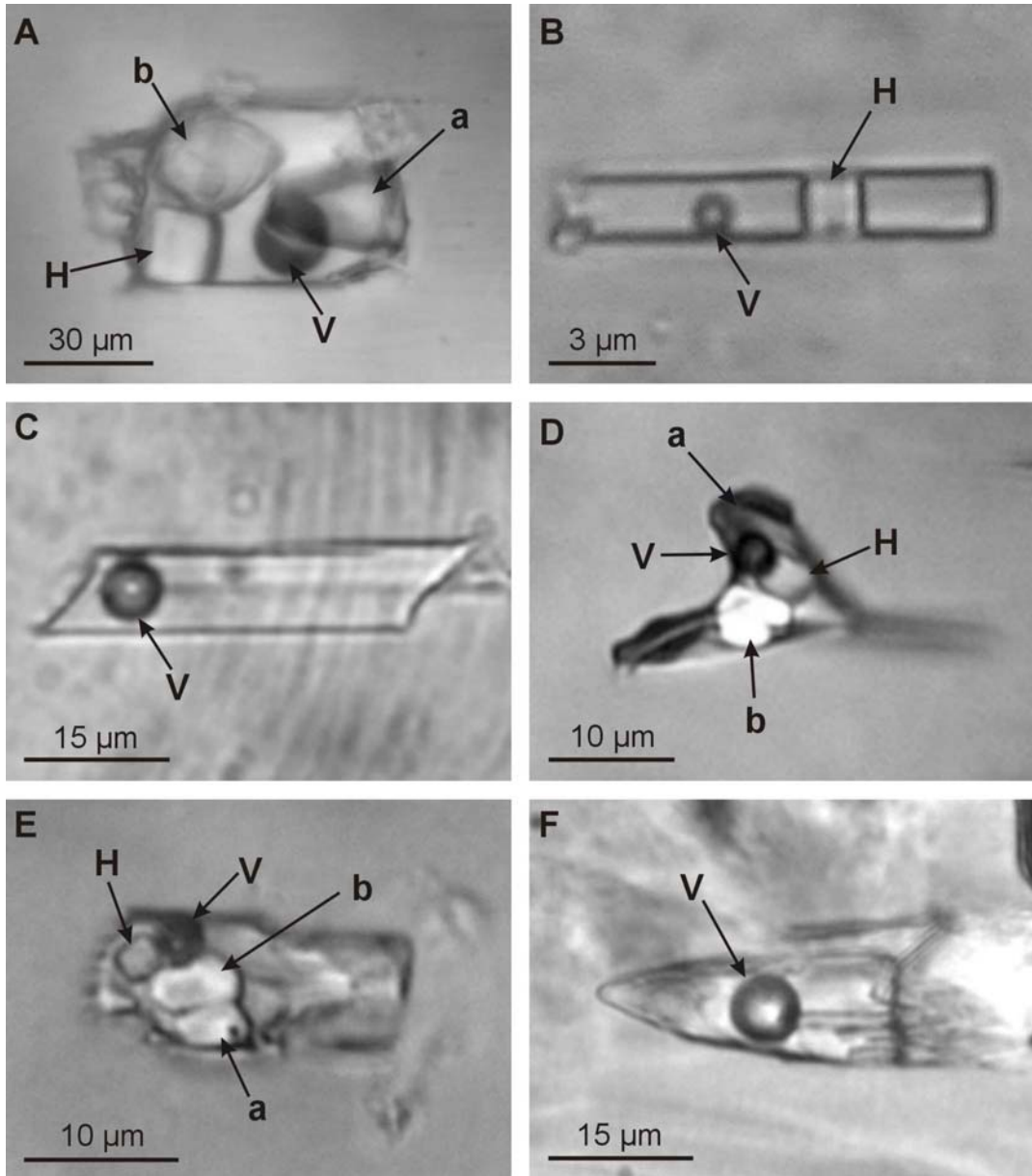
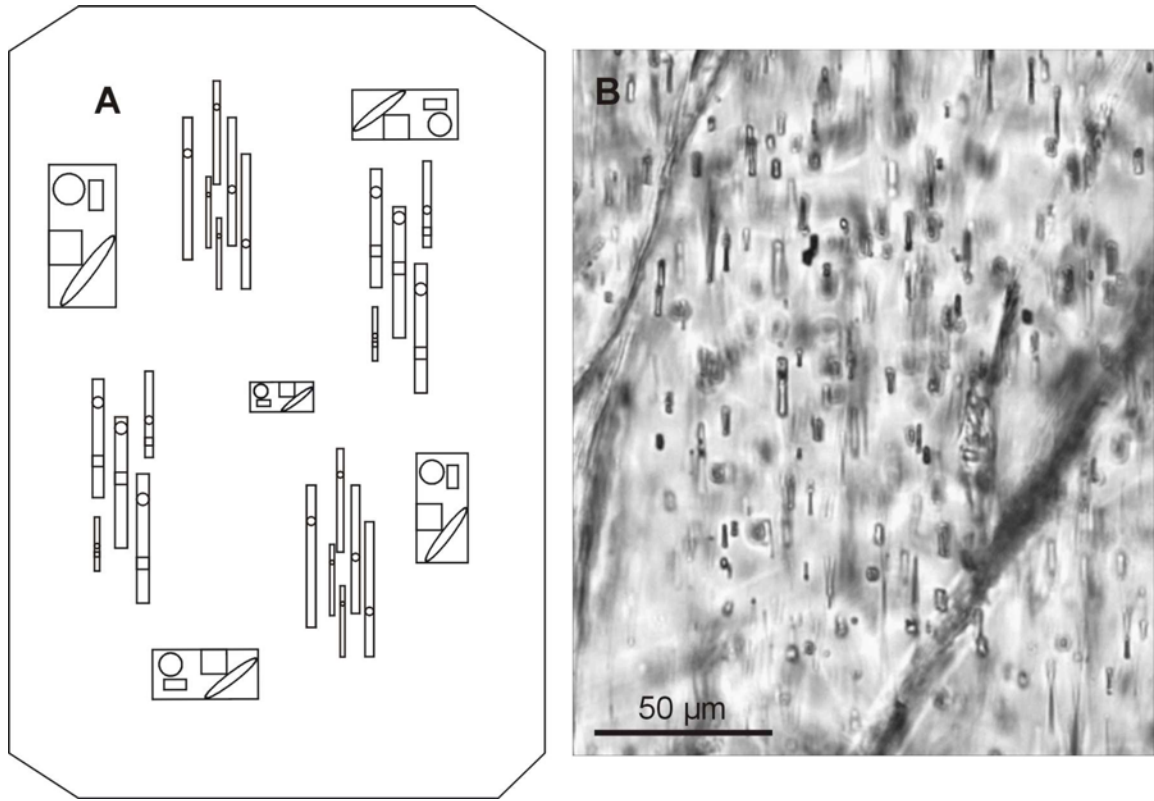


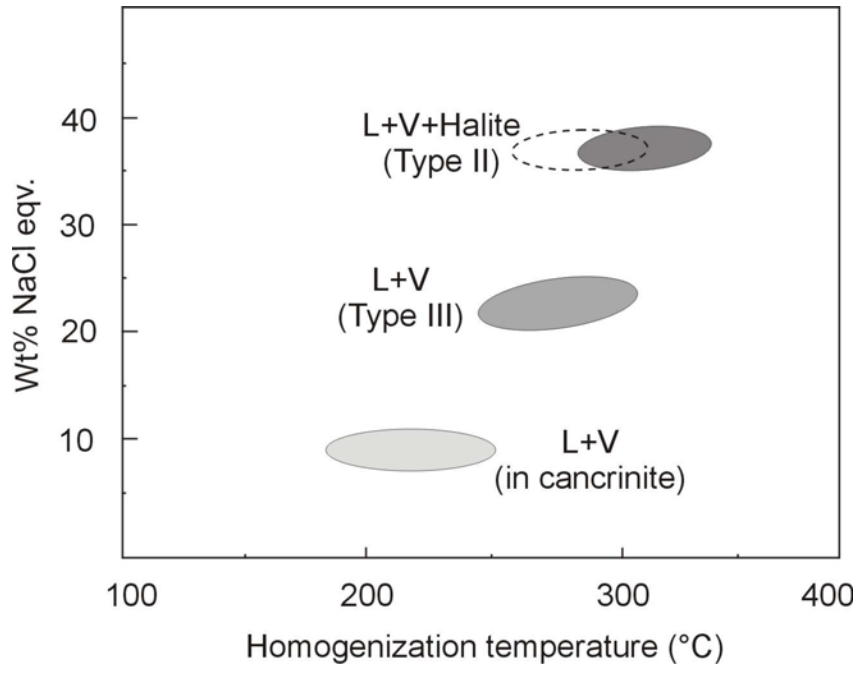
Figure 2.



**Figure 3.**



**Figure 4.**



**Figure 5.**

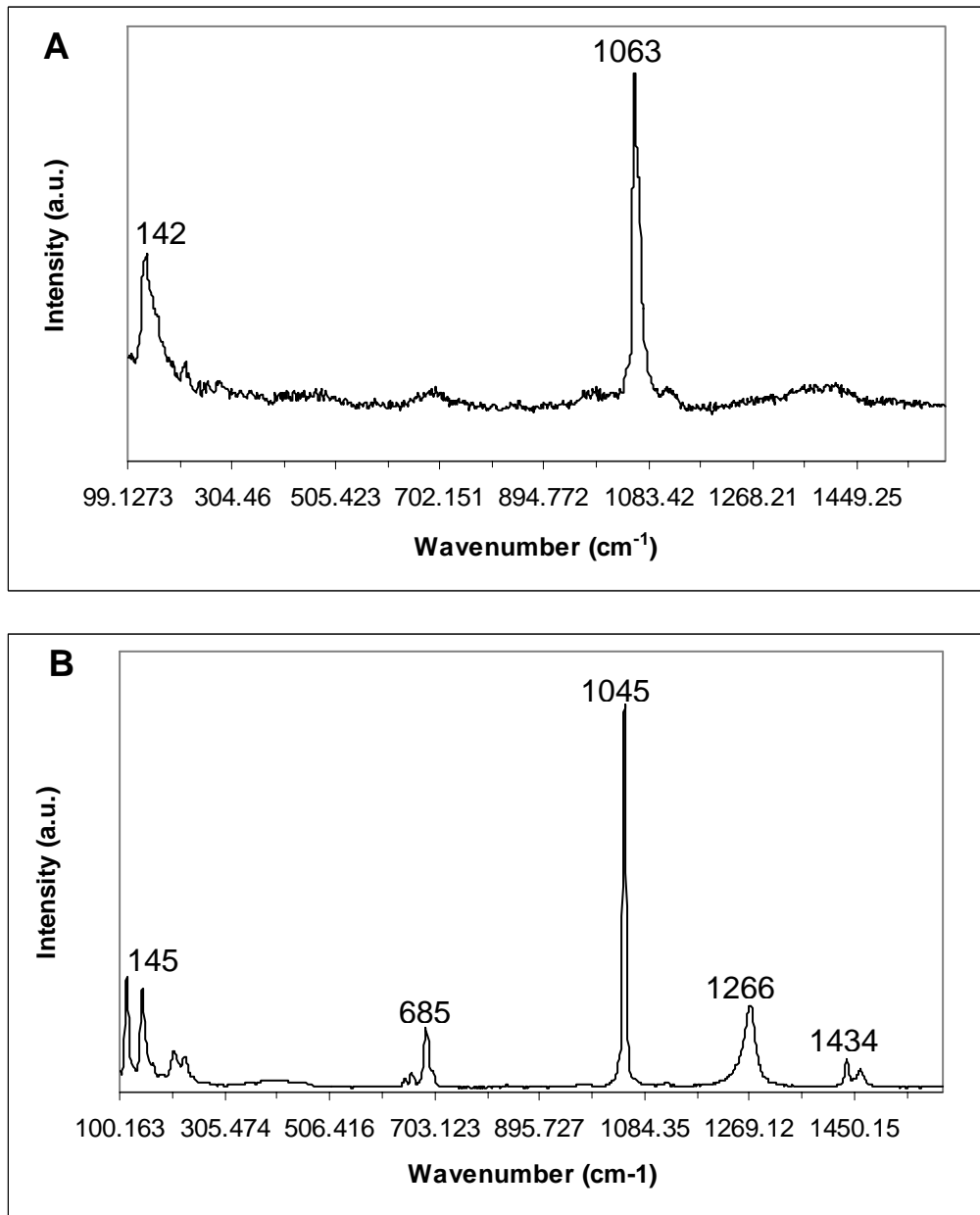
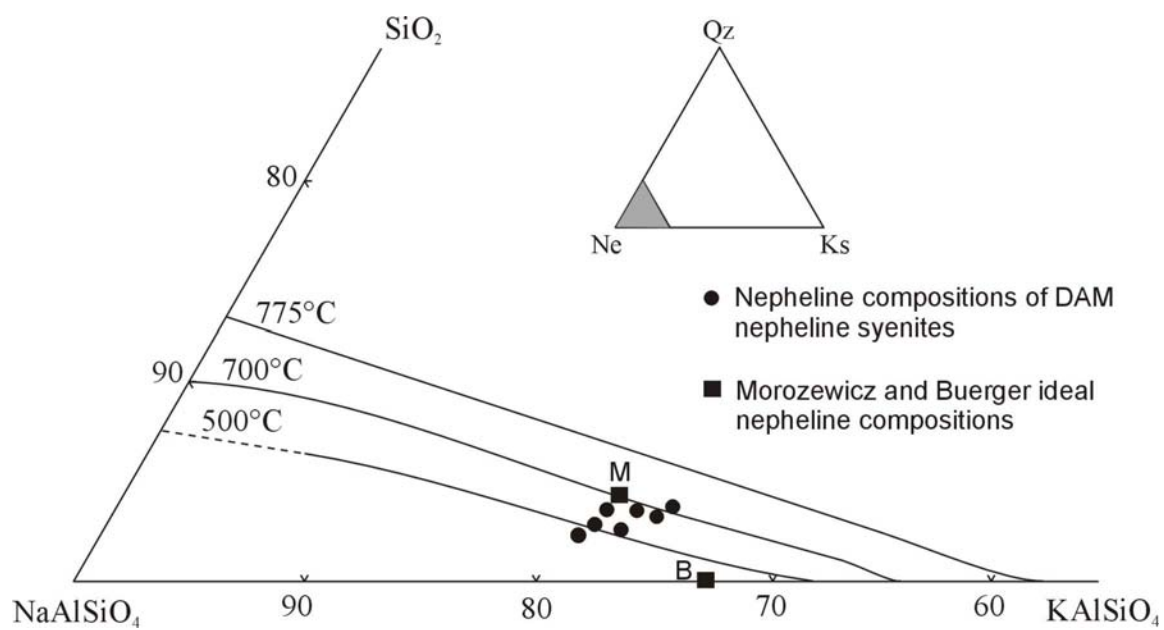
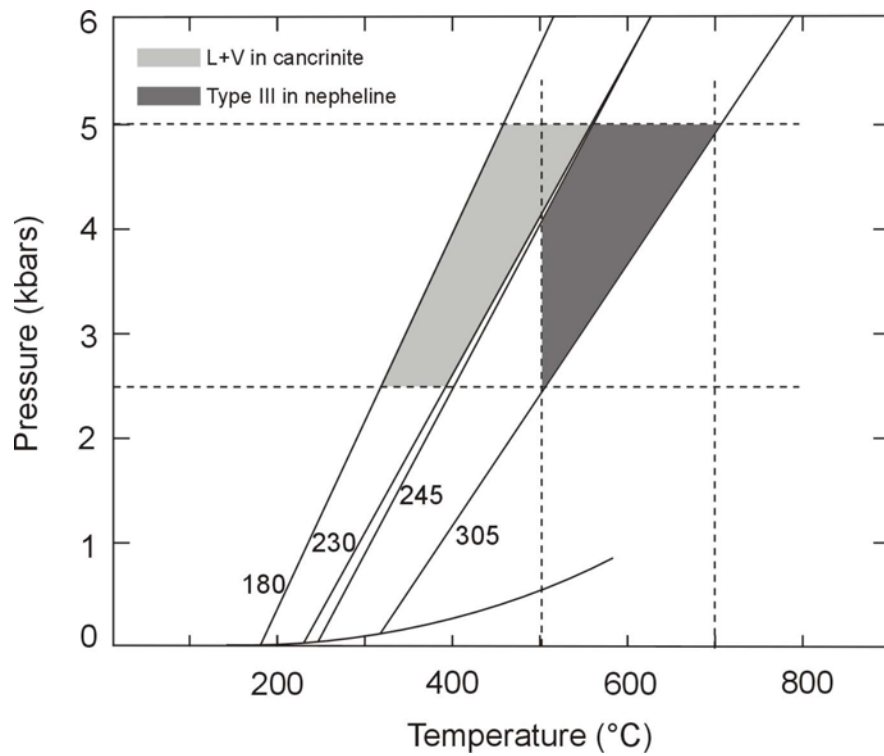


Figure 6.



**Figure 7.**



**Figure 8.**

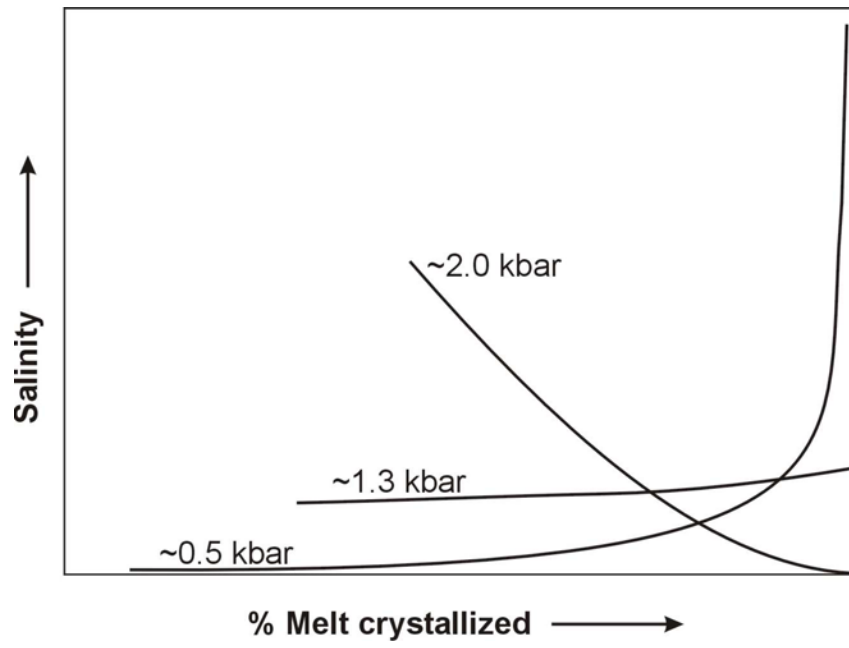


Figure 9.

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