Chemische Kristallographie fester Stoffe
Solid State Chemical Crystallography
Universität Bremen

CAU
Christian-Albrechts-Universität zu Kiel

# Symposiumsbeiträge

# Abstracts

„Variabilität und Komplexität
von Mineralen der Vulkaneifel und verwandter Provenienzen,
sowie ihrer synthetischen Analoga.“

“Variability and complexity of minerals
and their synthetic analogues
of the Vulkaneifel and related provinces”

## Symposium Contributions

# Low temperature (333 K) syntheses of nanocrystalline sodalites, cancrinites and intermediate structures between sodalite and cancrinite

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The systems “$Na_2O$-$SiO_2$-$Al_2O_3$-$H_2O$-salt” with template salts NaCl, $NaBH_4$, $NaNO_3$ or $Na_2CO_3$ were investigated within reaction periods of 1 - 96 h under strong alkaline low temperature conditions at 333 K. Syntheses under superalkaline conditions at unusual low temperature without addition of further template salts were first described by Fischer et al. (1991), Hadan and Fischer (1992) and Fischer et al. (1992). Formation of zeolites A or X and basic sodalite were observed by the authors. In contrast to these template salt free reactions the present study is an investigation of syntheses from mixtures of aluminosilicate gels with NaOH and the salts, mentioned above.

Nanoparticles of sodalites (SOD) or nanocrystalline intermediate phases (INT) between the structures of SOD and cancrinite (CAN) were successfully synthesized already after 3 h reaction time. Intermediate phases (INT) exhibit structural features between the structures of SOD and CAN as previously found in the carbonate system under common synthesis conditions from kaolinite by Hermeler et al. (1991). INT is characterized by one dimensional stacking disorder of aluminosilicate layers along hexagonal c-axis. In CAN framework these layers show hexagonal AB-stacking whereas SOD exhibits cubic ABC-sequence.

Triethanolamine (TEA) was added in further series of syntheses to study the influence on formation of SOD, CAN and INT, because deceleration of nucleation rate is well known in the zeolite A and X system due to the complexing effect of TEA on the reactive aluminium-species in the solution, as demonstrated by Charnell (1971) for these zeolites.

The products were characterized by X-ray powder diffraction, scanning electron microscopy, FTIR spectroscopy and thermal analysis in comparison with the microcrystalline samples of SOD and CAN, obtained from common hydrothermal synthesis at elevated temperatures and reaction times from 24 – 48 h.

Properties of the nanoparticles like crystal size, crystallinity of the whole batch, degree of filling with template or water, thermal stabilities and crystal morphology, obtained with and without TEA, were presented. A general review on phase formation under these special syntheses conditions will be given in the talk.

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# STRUCTURAL SPECIATION OF INTRACHANNEL ANIONS IN THE MINERALS OF ETTRINGITE-THAUMASITE FAMILY

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The minerals related to ettringite-thaumasite family play an important role in late-stage mineralogy of ancient volcanoes of Eifel area (Rheinland-Pfalz) and Zeilberg (Bavaria). Our recent studies carried out on a wide series of specimens from Eifel and Zeilberg resulted in description of two new natural representatives of this group: Hielscherite $Ca_3Si(SO_4)(SO_3)(OH)_6 \cdot 12H_2O$ (Chukanov et. al., IMA 2011-37) and Kottenheimite, $Ca_3Si(SO_4)_2(OH)_6 \cdot 12H_2O$ (Chukanov et al., IMA 2011-38). It is known that ettringite-thaumasite phases are not only of mineralogical interest but contribute significant part among cement and concrete compounds. However, study of cement mineralogy is always complicated due to fine-grained texture of cement matrix that, in general, precludes detailed structural investigation of cementitous compounds. In this respect, natural minerals – direct analogues of cement counterparts – give an excellent opportunity for in-depth understanding of crystal-chemical features of the latter, that is, in turn, helps in predicting chemical behavior of corresponding artificial compounds. Herein we will present a comparative review of structural features of the minerals related to ettringite-thaumasite family, with the emphasis on structural speciation of intrachannel anions ($SO_4^{2-}$, $CO_3^{2-}$, $SO_3^{2-}$) in a new, recently described minerals from Eifel and Zeilberg.

# High-temperature crystal chemistry of leucite family: crystal structure, thermal expansion and phase transitions.

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Leucite materials family is of special practical interest due to extreme tolerance towards ionic substitutions caused by the flexibility of tetrahedral framework. Aluminosilicates have first been studied widely as a result their frequent occurrence in nature and technological significance. Leucite materials show low thermal expansion, high cationic conductivity and other properties which enable them to be used for glass-ceramic production, immobilization of radioactive wastes and for other application.

In the leucite family the crystal structures of analcime and of pollucite were first solved by Taylor, Strunz and by Náray-Szabó in forties of the last century. The $RTSi_2O_6$ ANA-type structure exists over a wide range of $R$ cation size from $NH_4$ or K to Cs in leucites and pollucites or water molecules in analcime, where $T$ is Al, Fe, Ga or with an equimolar mixture of Si and a divalent cation like Zn, Mg, Cd, Cu and others. The highest possible symmetry of the ANA-type structure is cubic with space group $Ia\text{-}3d$. As the temperature decreases, seria of displacive polymorphic transitions occur with lower symmetry.

For last ten years our team has investigated high-temperature crystal chemistry of following seria of $K_{1-x}Rb_xBSi_2O_6$, $K_{1-x}Cs_xBSi_2O_6$ and $Rb_{1-x}Cs_xBSi_2O_6$ mixed boroleucites including its crystal structures, polymorphic transitions, thermal expansion and thermal decomposition and metastable melting. Here we summarize these results in comparison to those of natural and synthetic alumino- and ferrosilicates that led to revealing of common tendencies in thermal behavour for leucite-type structure. A few of them are unusual ones for example thermal expansion decreases clearly as the nontetrahadral cation $R$ size increases from K to Cs. In contrast to aluminosilicates melting borosilicate solid solutions decompose in the solid state during long heat treatment above 1000 °C. In the Cs-rich boropollucites a zeolite-like $CsBSi_5O_{12}$ borosilicate forms as a result of boropollucite decomposition while in K- or Rb-rich samples of the seria cristobalite or trydimite crystallize directly as a result of boroleucite decomposition.

# Crystal chemistry of phyllosilicates from the Aris phonolite and the Eifel volcanic complex

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The investigation of late (pneumatolitic and hydrothermal) parageneses of alkaline effusive complexes (Eifel in Germany and Aris in Namibia) demonstrates wide mineral diversity and already resulted in the discovery of new phyllosilicate minerals. Oxyphlogopite (Rothenberg, Eifel), $K(Mg_2Ti)(Si_3AlO_{10})O_2$, is an O-dominant, hydrogen-free analogue of phlogopite. Schüllerite (*Löhley, Eifel),* $Ba_2Na(Mn,Ca)(Fe^{3+},Mg,Fe^{2+})_2Ti_2(Si_2O_7)_2(O,F)_4$, is a triclinic $Fe^{3+}$-dominant mineral related to barytolamprophyllite with a different topology of the HOH layer. Lileyite (*Löhley, Eifel),* $Ba_2(Na,Fe,Ca)_3MgTi_2(Si_2O_7)_2O_2F_2$, is a Mg- and F-dominant of barytolamprophyllite-2M. A $Fe^{2+}$-analogue of lileyite was discovered at *Rother Kopf, Eifel, in the association with g*ünterblassite*.* Günterblassite (*Rother Kopf, Eifel),* $(K,Ca,Ba,Na,\square)_3Fe[(Si,Al)_{13}O_{25}(OH,O)_4]\cdot7H_2O$, is the first phyllosilicate with triple tetrahedral layer. It contains isolated polyhedra $[FeO_2(OH)_2(H_2O)_3]$ attached to tetrahedral layers. In its crystal structure, günterblassite is intermediate between common phyllosilicates and tectoaluminosilicates (zeolites). At *Löhley, Eifel*, we have found a*n* analogue of günterblassite with columns of Mg-centered octahedra instead of isolated polyhedra $[FeO_2(OH)_2(H_2O)_3]$. Windhoekite (Aris, Namibia), $Ca_2Fe^{3+}_{3-x}(Si_8O_{20})(OH)_4\cdot10H_2O$, is palygorskite-group mineral, a Ca-dominant analogue of tuperssuatsiaite, $Na_{2-x}(Fe^{3+},Mn)_3(Si_8O_{20})(OH)_2\cdot4H_2O$. As compared with tuperssuatsiaite, windhoekite bears additional octahedral site partially occupied by $Ca^{2+}$. A Ca-rich variety or analogue of palygorskite was found in the association with windhoekite*.*

# Modulated Structures in the Sodalite-Cancrinite Supergroup

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Both, sodalite (SOD) and cancrinite (CAN), belong to the so-called ABC-6 structure types of microporous framework structures. Thereby, 6-rings of **T**$O_4$-tetrahedra (**T** = Si, Al, Be,…) are stacked in a way similar to closest sphere packing, but linked to each other by common 4-rings. The cubic SOD-framework is characterized by a …ABC… packing, whereas in hexagonal CAN it is …AB… Rather symmetric $4^6 6^8$-cages are formed in SOD (sodalite cages), whereas in CAN smaller $4^6 6^5$-cages form narrow channels which in turn span wide channels. Cages and channels in both structure types host additional cations and anions (extra-framework ions). The presence of extra-framework anions distinguishes the SOD and CAN structures from most of the well-known zeolites, which only in a few cases show the same particularity. In addition to the simple …AB… and …ABC… stacking modes, more complicated long-periodic variants are possible and form the family of cancrinite-type structures. In a sense, these polytypes can be considered as topologically modulated. The highest periodicity found so far for these materials is 36 with a lattice parameter equal to about 95 Å along the stacking direction. A particular subgroup of the cancrinite-type structures can be described as a sequence of sodalite-type blocks of various thicknesses with regular insertion of "wrong" layers. Thereby, cancrinite-like $4^6 6^5$-cages or larger ones, like the $4^6 6^{11}$-losod or the $4^6 6^{17}$-liotite cages, are formed. Three of such structures have been found so far, viz. franzinite with a "wrong" layer after 9 regular ones, fantappiète with 10 and kircherite with 11 regular layers. The reasons why these different stacking modes occur are not fully understood so far, but are believed to depend more on the kind, amount and proportions of the extra-framework species than on temperature or pressure. Disordered CAN and SOD stacking variants are also known.

In both, SOD and CAN frameworks the extra-framework species can assume ordered distributions, thus forming substitutional modulations which may be commensurate or incommensurate with the underlying framework periodicitiy. Substitutional modulations are not in the focus of this contribution.

Both, the CAN as well as the SOD framework are highly flexible. The latter constitutes even an extreme case as it has been shown that the number of "rigid unit modes" is infinite, that is to say that virtually any kind of displacive modulation can be superimposed on the basic structure. Even more, by interference of different modes local distortions can, and do occur allowing the framework to adapt itself to any kind of defect or chemical impurity present. This means that natural minerals of the supergroup very often exhibit patterns of different, usually spatially limited modulations which can only be revealed by methods like TEM or NMR spectroscopy, but are averaged-out by x-ray diffraction. Thus, with the latter method the structures appear cubic (SOD) or hexagonal (CAN). Arguably, it is only possible with well-defined stoichiometric and, as far as possible, defect-free crystals to observe clear long-range modulation patterns. This seems to be the case for so-called aluminate sodalites of general composition $|\mathbf{M}_8(\mathbf{X}O_4)_2[Al_{12}O_{24})|$ (**M** = Ca, Sr,..; **X** = S, Cr, Mo, W,…). The assignment of the superspace group symmetries (if applicable) and the determination of the modulated structures are hampered by several facts. It is known that in (incommensurately) modulated structures the correlation length is in principle infinite. Defects of any kind coupling with the phase of the modulation wave have therefore a strong influence. Especially, when the density of the defects becomes sufficiently high, a defect-field will superimpose on the modulation. Thus, the crystals studied should be as pure as possible. In the case of aluminate sodalites another fact adds to the problem, as the appearance of modulations is inherently linked to phase transitions of ferroelastic or ferroelectric character. Thus, twinning and/or formation of out-of-phase domains are unavoidable and interact with the modulation. In addition, the intensity of the satellite reflections is often very weak and the strong pseudosymmetry also poses problems.

Several examples of modulated aluminate sodalites will be discussed and their static and, as far as possible, dynamic character described. Also, results of our studies on the effects of more or less well-defined deviations from ideal stoichiometries will be reported.

# Specific features of exhalations and exhalative minerals of basaltic volcanism (Tolbachik volcano, 1975-1976, Kamchatka, Russia)

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It is a third of century now from the beginning of fumaroles activity at new cinder cones and lavas of the basalt Great fracture Tolbachik eruption (GFTE, 1975-76), the largest eruption in the modern history of Kurilo-Kamchatka region. During this time 130 exhalative minerals were found in GFTE fumaroles including 30 new mineral species, whereas only 200 exhalative minerals are known in the world.

*Geochemistry*. The dominant elements in GFTE exhalative minerals are (in order of frequency): O, Cu, Cl, K, Na, F, Mg, S, Pb, Fe, Se, As, V. The O:Cl:S:F ratio of frequency of observations is 8:4:1:1 that shows that conditions at GFTE fumaroles are essentially oxidative.

*Mineralogy*. Mineralogy of fumaroles products is very diverse: sulfates and oxosulfates, chlorides, oxides and hydroxides, selenites, fluorides, arsenates, vanadetes, carbonates, silicates, native elements, etc. A clear tendency of mineralization development from initially high-temperature associations (mostly anhydrous chlorides, sulfates, arsenates and vanadates) to low-temperature associations (hydrous chlorides, sulfates, carbonates, etc.).

*Formation of Cu ores*. The maximum formation of ores was observed for Cu:Pb:Zn = 20:2:1. Nearly half of a hundred minerals contain Cu and two dozens of them are new mineral species. The key phases are tolbachite, melanothallite and ponomarevite (chlorides and oxochlorides), euchlorine, piypite, fedotovite, kamchatkite, klyuchevskite, alumoklyuchevskite (sulfates and oxosulfates).

*Formation of bauxites*. Lesukite and gibbsite were found in zones of metasomatic transformations of erupted materials that probably involve biological factors and lead to formation of Al mineralization with primarily hydroxy-hydrous chloride compositions.

*Crystal chemistry*. Determinations of crystal structures of GFTE exhalative minerals made it possible to find in them oxocentered $OA_4$ (mainly $OCu_4$) tetrahedra. On this basis, crystal chemistry of minerals and inorganic compounds with oxocentered tetrahedra has been developed and generalized.

*Transport of metals*. The existence of oxocentered tetrahedra in crystal structures allowed us to suggest that these complexes are present in gases and play an important role in transport of metals by volcanic gases.

# Temperature dependent behavior of sodalites

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Sodalites belong to the group of framework structures formed by tetrahedrally coordinated atoms [1]. Whereas the ligand of these tetrahedra is mainly oxygen the tetrahedra position (T) is most often occupied by $Si^{4+}$ or $Al^{3+}$, but also by $B^{3+}$, $Ga^{3+}$, $Ge^{4+}$ or $Be^{2+}$ [2]. The T atoms form a regular truncated cuboctahedron occupying the corners of this Archimedean solid. Because the framework tetrahedra forming the typical β-cage [3] are able to rotate around their local $\bar{4}$ axis the whole framework could collapse and fit its size of the cage filling templates and charge compensating cations. With respect to the size of the template the framework could show the phase transition from the partially collapsed state crystallizing in the case of the two different but ordered T atoms in space group $P\bar{4}3n$ to the fully expanded state described in the space group $Pm\bar{3}n$, e.g. $|Na_8(NO_3)_2|[AlSiO_4]_6$ [4]. Structurally interesting observations were described when the template anion itself forms a tetrahedra like in $|Ca_8(WO_4)_2|[AlO_4]_{12}$ [5]. Depmeier described for this compound type different types of symmetry reduced as well as commensurately modulated structures at room temperature. Similar observations are described for $|Na_8(B(OH)_4)_2|[AlSiO_4]_6$ [6], were the structurally unknown room temperature phase shows a phase transition to the cubic $P\bar{4}3n$ structure at temperatures between 313 K and 317 K with a = 904.6(2) pm (317 K). On the other hand $|Na_8(BH_4)_2|[AlSiO_4]_6$ [7], where the boron is also tetrahedrally coordinated, the room temperature phase could be described in space group $P\bar{4}3n$ with a = 891.61(2) pm [7]. The much smaller lattice parameter could be explained by approx. 138 pm shorter B-H distances in the $BH_4^-$ anion with respect to the corresponding $B(OH)_4^-$ anion because of the missing B-O bonds in the tetrahydroborate. In tetrahydroborate sodalites structural changes could be observed at lower temperatures. For the gallogermanate framework several superstructure refection could be observed first at ~ 250 K with increasing intensity while cooling the sample to 190 K. Further cooling decreases the intensity again till 130 K where no super structure reflex is observed anymore. We explain this behavior with a freezing of the free tetrahydroborate rotation in the β-cage. At 300 K a cubic lattice parameter of 912.94(1) pm is observed implicating the free template tetrahedra rotation. When lowering the temperature, the hydride anions are shortly “bonded” to the sodium atoms. This leads to a distortion of the $BH_4$ group resulting in a symmetry reduction or a force to the framework via the sodium – framework-oxygen-bonds which leads to a distortion of the framework resulting also in a symmetry reduction. While further lowering of the temperature more and more $BH_4$ tetrahedra a blocked in their movement. This statistical freezing finally shows the same force distribution within the cage as the dynamic movement, resulting again in a superstructure reflection free pattern with a cubic lattice parameter of 911.66(1) pm at 130 K. Heating the sample starting at 150 K, 5 different thermal expansions could be observed. First from 150 K to 300 K and second from 300 K to 380 K. This could probably relate to the low temperature super structure effect but could also be an artifact because of two different measurement environments. Above 380 K the thermal expansion decreases which might be correlated with minor traces of remaining water leaving the cage till 520 K where the oxidation of the $BH_4$ molecule to boron –oxides-hydroxides starts. This could be observed in a second order decrease of the thermal expansion. Above 670 K the sodalite itself slowly decomposes to the corresponding berillionite phase.

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# Sodalite layers as silicate fragments in hydrous layer silicates: Precursors to SOD-type frameworks.

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A number of hydrous layer silicates, HLS, are built from silicate layers which can be obtained from sections through the sodalite framework in different directions. A compilation of the different materials is given in the table below.

| | | | | |
|---|---|---|---|---|
| DLM-2 | Tetramethylammonium | sod | $(C_4H_{12}N)_8$ $[H_{16}Si_{32}O_{72}]$ • 20 $H_2O$ | Massueger et al., 2007 |
| RUB-15 | Tetramethylammonium | sod | $(C_4H_{12}N)_8$ $[H_8Si_{24}O_{56}]$ • 20 $H_2O$ | Oberhagemann et al., 1996 |
| RUB-51 | Benzyltrimethylammonium | sod | $(C_{10}H_{16}N)_4$ $[H_4Si_{12}O_{28}]$ | Li et al., 2008 |
| β-Helix-Layered-Silicate | Tetramethylammonium + $Na^+$ | ast* | $Na_8(C_4H_{12}N)_8$ $[H_{16}Si_{40}O_{96}]$ • 22 $H_2O$ | Ikeda et al. , 2001 |
| HUS-1 | Tetramethylammonium | ast* | $(C_4H_{12}N)_2$ $[H_6Si_{10}O_{24}]$ | Ikeda et al. , 2011 |

*sod and ast are codes for layer topologies. Ast is a section of the sodalite structure different from sod and also existing in AST-type materials

All materials have been obtained at rather low synthesis temperature (~100°C). At higher synthesis temperature microporous silicates have been obtained. This experimental results show that anionic precursor structures for framework silicates exist in solution which crystallize at low pT-conditions to HLS. In addition, it has been shown that topotactic condensation reactions of the layered precursor leads to a fully 3-dimensional framework silicate. In this presentation the different materials are reviewed and put into perspective with new results from structure analysis.

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# The anomalous annealing behaviour of Eifel sanidines
## Status quo and new approach with neutron diffraction

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Sanidines $(K,Na)[AlSi_3O_8]$ are alkali feldspars, part of the solid solution series Albite – Orthoclase and their typical composition is in a range between $Al_{35}Or_{65}$ and $Al_{15}Or_{85}$. The monoclinic tectosilicate occurs at two different modifications, low- and high-sanidine, mainly differing in their Al/Si distribution. Reordering is usually acquired by long-term-annealing (>1000h) at temperatures of 900°C and above, but with sanidine megacrystals from Eifel it's possible to reach much faster Al/Si disordering within short annealing time and starting temperatures around 700°C. Although numerous attempts and studies were carried out, the exact reasons for this anomalous behavior still remains unknown.

We want to outline the current status quo of research about this phenomenon as well as introduce our new approach, where we investigate the structure of Eifel sanidines with neutron diffraction experiments, in particular the Al/Si distribution. We will try to determine the cause and figure out possible catalysts or catalytic mechanics of this unusual annealing behavior.

# Experimental study of F- bearing sodalite

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Synthesis of fluorine- bearing sodalities was carried out at 400 - 800°C and P = 1-2 kbar under hydrothermal conditions. F- Sodalite was hydrothermally synthesized from nepheline (or gel of nepheline composition). The starting materials were gel of nepheline composition ($NaAlSiO_4$) and a nepheline + sodalite mixture, which was prepared from natural minerals (fraction 0.01) in the proportion (nepheline gel) : (nepheline + sodalite mixture) = 10 : 1. Some experiments were carried out with starting materials of natural nepheline from which K was expelled by ion exchange reactions with NaCl melt. The composition of the solution was specified by mixtures of dried salt (NaF) and distilled water. The experiments were carried out in high-pressure hydrothermal vessels with external heating and a cold seal (the temperature and pressure were maintained with an accuracy to ±5°C and ±50 bar, respectively). Some experiments were conducted in autoclaves, with temperature and pressure control accuracy ±5°C and ±100 bar, respectively. All experiments were accomplished in Pt capsules. The duration of experiments was 7–49 days. Run products were studied by microprobe and X-ray methods. Determination of structure of F- bearing sodalite have shown the space group *P*43*m* and fluorine incorporation into sodalite by the $[AlF6]^{3-}$ groups. Unit cell parameters of F-bearing sodalite are following: a = 9.046 (1) [A]; V = 740.2(2) $[A]^3$. Composition of F- bearing sodalite is corresponded to $|Na_{7.38}(AlF_6)_{0.70}(H_2O)_{4.88}|[(Si_{6.74}Al_{5.26})O_{24}]$.

# Synthesis of hydrocancrinite

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Hydrocancrinite was synthesized at 200°C and P = 500 bar under hydrothermal conditions. The starting materials consisted of natural kaolinite ($Al_4Si_4O_{10}[OH]_8$) which melted with certain amount of NaOH at 1200°C in 5-mm Pt- capsules. These capsules were sealed after melting immediately. IR spectroscopy method confirmed the absence of carbonate groups in these melts. Synthesis of hydrocancrinite was carried out using titanium autoclaves. The perforated 5-mm Pt- capsules with starting melts were loaded into large 8-mm Pt- capsules. The calculated amounts of distilled hot water were added and Pt- capsules were sealed by electric-arch weld. Then these capsules with certain amounts of water were loaded into Ti-autoclaves. The experiments were carried out with accuracy of temperature and pressure control ±5°C and ±50 bar, respectively. The duration of experiments was 14–15 days. The experimental products were investigated by the microprobe, IR spectroscopy and X-ray diffraction methods.

Composition of synthetic OH-cancrinite is compatible to theoretic formulae of sodium cancrinite. Carbonate group content is less than 0.5 wt.%. Unit cell parameters (for space group $P6_32$) are following: $a$ = 12.771(1) [A]; $c$ = 5.207(1) [A]; V = 735.5(2) $[A]^3$.

# Quantitative evaluation of structural complexity

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Which crystal structure is complex? Despite the obvious and widely accepted use of the adjective 'complex' in characterization of crystal structures, there is still no strict definition of crystal structure complexity that can be applied on the everyday basis in scientific research. Various approaches to structure complexity have been outlined (Baur et al., 1983; Burdett et al., 1994; Mackay, 2001; Estevez-Rams & González-Férez, 2009; Steurer, 2011) but none of them provided simple and unambiguous quantitative measures. At the same time, advances in complex network and chemical graph theories (Barabási, 2002; Dorogovtsev & Mendes, 2003) allowed to formulate a whole series of complexity measures for chemical, biological, technological and social networks (Dehmer, 2011). The most interesting parameters are based upon application of Shannon information concept.

Recently, we proposed to estimate topological complexity of a crystal structure using complexity measures of its quotient graph, which is defined as a projection of periodic network of atoms and bonds onto a finite graph [1]. The Shannon-information-based measures of complexity such as structural information content, $I_G$, and information content of the vertex-degree distribution of a quotient graph, $I_{vd}$, are shown to be efficient for the comparison of topological complexity of polymorphs and chemically related structures. The $I_G$ measure is sensitive to the symmetry of the structure, whereas the $I_{vd}$ measure better describes complexity of bonding network. Various possible applications of the proposed approach will be outlined.

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# High temperature crystal chemistry of borosilicate feldspars comparing to their aluminosilicate analogues

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Borosilicate based materials are widely used for many applications from cookware production up to nuclear waste immobilization. Since the preparation and exploitation of the materials are performing usually in a wide temperature range, data on phase diagrams, thermal transformations and thermal expansion coefficients are of unfailing interest.

Most of the currently known anhydrous alkali borosilicates are structurally similar to aluminosilicates. Up to now in the feldspar family only one borosilicate member, triclinic mineral redmergnerite, $NaBSi_3O_8$, was structurally described (Appleman, Clark 1965). Recently $KBSi_3O_8$ feldspar-type phase was obtained by us using hydrothermal synthesis ($500^oC$, 0.4 GPa, 4 weeks). Its structure is found to be isotypical with monoclinic *C*2/*m* feldspars. The boron and silicon distribution is not random; the expanded crystal-chemical formula could be written as $K(B_{0.4}Si_{0.6})_2(B_{0.1}Si_{0.9})_2O_8$. So the structure could be considered as being of low sanidine type (Krzhizhanovskaya, Bubnova, Depmeier et al. 2012).

Present study is devoted to the comparison of crystal structures and thermal behavior particularly expansion, transitions, melting/decomposition for structurally identical boro- and aluminosilicate feldspars. A new $KBSi_3O_8$ member of the family is compared with its natural and synthetic analogues. Similarity of structural deformation on heating and under substitution is discussed. It is shown that thermal behaviour of boro- and aluminosilicate feldspars is very similar, although the temperature points of melting or decomposition are considerably lower for borosilicates than that of aluminosilicates.

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# LOW-TEMPERATURE ALTERATION OF LOMONOSOVITE AND VUONNEMITE UNDER LABORATORY CONDITIONS: NEW DATA

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Several experiments have been conducted with alkaline heterophyllosilicates lomonosovite, $Na_{10}Ti_4(Si_2O_7)_2(PO_4)_2O_4$, and vuonnemite, $Na_{11}TiNb_2(Si_2O_7)_2(PO_4)_2O_3(F,OH)$, the typical minerals of the hyperagpaitic rocks. The processes of lomonosovite and vuonnemite alteration were studied in distilled water at 90ºC and at room temperature. The kinetics of processes was studied using conductometry. Samples after the experiments were examined by SEM, EMPA, XRD methods and IR and Raman sprctroscopy. The alteration processes are discrete and give several stable silicate phases unknown in nature.

# NMR studies on sodalites

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The magic angle spinning nuclear magnetic resonance (MAS NMR) was applied to investigate a number of sodalites using $^1$H, $^{11}$B, $^{23}$Na and $^{29}$Si nuclei. The alumosilicate and gallosilicate sodalites exhibit a single symmetric peak in the $^{29}$Si spectra. In the alumogallosilicate sodalite series, the replacement of aluminum by gallium leads to five signals due to $SiO_4(Al_4)$, $SiO_4(GaAl_3)$, $SiO_4(Ga_2Al_2)$, $SiO_4(Ga_3Al)$ and $SiO_4(Ga_4)$ environments around the $SiO_4$ tetrahedron. The corresponding signal of $^{29}$Si spectra shifted downfield due to Si-deshielding. On an average, each replacement of aluminum by gallium in the $SiO_4(Al)_4$ species showed a downfield shift of 1.3 ppm. The Al/Ga ratios calculated from the NMR spectra were found in good agreement with those obtained from the XRD results. In bromide, iodide and nitrite sodalites (Ga = 30-70%), the $SiO_4(Al_4)$ and $SiO_4(Ga_4)$ were found significantly higher than the other three species. Such behavior clearly demonstrates a non-statistical distribution of aluminum and gallium forming Al-enriched and Ga-enriched domains within the crystals. These domains could not be resolved quantitatively from the X-ray diffraction data as their sizes are assumed to be smaller than the coherence length of the used X-ray radiation, however, large enough to detect by MAS NMR technique. The chemical shift of $^1$H MAS NMR spectra clearly distinguish between the $OH^-$, $(OH\cdot H_2O)^-$ and $H_2O$ species in the SOD as well as possible adherence of proton on the crystallite surface as silanol ($Si(OH)_n$). Almost in all cases, the narrow $^1$H spectral lineshape and low intensity of the spinning side bands indicate that the $^1$H–$^1$H dipolar coupling of the water protons in the SOD are considerably reduced by fast dynamic site exchange which can average out the dipolar interaction on NMR timescale. Although $^{11}$B is a quadrupolar nucleus the $^{11}$B MAS NMR spectra exhibited a single sharp line for $BH_4^-$ enclathrated in the SOD. The discreetness, high symmetry of the $BH_4^-$ and the possible fast dynamic site exchange of the associated protons are explained for this lineshape. In many sodalites the $^{23}$Na MAS NMR signals show a narrow Gaussian lineshape due to a single type of sodium coordination, and a centrosymmetric charge distribution around the sodium atom. Nevertheless, this is not the common feature of $^{23}$Na MAS NMR spectra of many sodalites due to inherent complication of the second order quadrupolar interaction of the central transition. As a consequence, the resonances move from their isotropic chemical shift due to quadrupolar induced shift and show typical powder lineshape even under MAS conditions with high spin speed. To avoid this broadening complication multiple quantum (MQ) MAS NMR of $^{23}$Na was used, which helped showing the isotropic chemical shifts with an unambiguous assignment, in particular for sodalites with small domains within crystallites.

# Sulfite anion in thaumasite-group minerals: the thaumasite–hielscherite isomorphous series

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The continuous isomorphous series between thaumasite, $Ca_3Si(SO_4)(CO_3)(OH)_6{\bullet}12H_2O$, and its new sulfite-dominant analogue hielscherite, $Ca_3Si(SO_4)(SO_3)(OH)_6{\bullet}11\text{-}12H_2O$, was discovered. Their representatives are found in the late hydrothermal assemblages related to young alkaline volcanic rocks of Eifel and Franconia, both Germany. As crystal structure and IR spectroscopy data show, $SO_3^{2-}$ substitutes $CO_3^{2-}$ but not $SO_4^{2-}$ group. The $SO_3^{2-}$ anion first found in thaumasite-group members turned out typical constituent of these minerals from West Eifel.

# Synthesis, crystal structure and high temperature behavior of gallogermanate tetrahydroborate sodalite $Na_8[GaGeO_4]_6(BH_4)_2$

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Sodalites (SOD) are proposed for applications in future key technologies like hydrogen storage [1]. Especially the enclathration of hydride salts into SOD cages provides an interesting model system to study principles of hydrogen storage in zeolite A, X and Y cavities. The usage of zeolites as potential media for hydrogen storage was already suggested by Barrer [2] and Weitkamp et al [1].

An incorporation of hydrogen species in the form of hydride salt $NaBH_4$ was already obtained from mild hydrothermal syntheses for SOD with aluminosilicate, aluminogermanate and gallosilicate frameworks [3, 4]. With regard to the fine-tuning and controlled change of β-cage properties in zeolites the complete substitution of aluminosilicate framework atoms by Ga and Ge is of special interest.

Hydrothermal syntheses were carried out in Teflon coated steel autoclaves. Because of the different solubilities of $Ga_2O_3$ and $GeO_2$, the beryllonite analogous phase $NaGaGeO_4$ was used as a reactant to ensure an equal release of Ga- and Ge-ions into the hydrothermal solution. The synthesis route with layered reactants in the autoclaves was successfully used for the synthesis of aluminosilicate [3], gallosilicate [4] and aluminogermanate [4] tetrahydroborate SOD. However, it was not possible to synthesize gallogermanate tetrahydroborate SOD with these separated reactants. Thus, separate suspensions of $NaGaGeO_4$ [5] and $NaBH_4$ in sodium hydroxide solutions were prepared and combined before the hydrothermal treatment.

The products were characterized by XRD and FTIR spectroscopy. They all show a distinct amount of $NaGaGeO_4$, which seems to decrease with increasing time and temperature. The XRD pattern of the best product shows SOD as the main phase along with a small amount (<5 wt%) of $NaGaGeO_4$. The crystal structure was refined by the Rietveld method in space group P-43n. The presence of the $BH_4^-$-group is confirmed by the observation of its tetrahedral vibrational modes in the FTIR spectrum. Scanning electron microscopy combined with EDX-analysis provides rhombic dodecahedral crystallites and confirms the composition of the assumed framework, whereas boron could not be detected with the necessary accuracy.

The temperature dependent (TD) behavior was investigated by TG-DTA, XRD, FTIR- and Raman spectroscopy. A two-step decomposition reaction of the SOD to the beryllonite analogous phase $NaGaGeO_4$ was observed. The TD development of the sodalite structural parameters evaluated by Rietveld analysis of the XRD patterns indicate a beginning oxidation of the enclathrated $NaBH_4$ at about 528 K and a destruction of the sodalite framework starting at about 648 K, confirmed by the results obtained from TD Raman and FTIR data.

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# Thermal behavior of sodalites examined by autocorrelation analysis of temperature dependent FTIR spectra

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The analysis of FTIR spectra of solid state compounds by the autocorrelation (AC) method was proposed by Salje et al. [1] for the study of systematic changes in the FTIR spectra with external parameters like temperature or internal ones like the composition in solid solution systems.

The main advantage of the AC method is that no peak fitting is needed. Peak fitting procedures can be very problematic in FTIR spectra because the number of observable peaks must be known. Additionally the autocorrelation method is almost independent from user controllable experimental parameters. This is especially true if one sample pellet is measured under different environmental parameters (like temperature) in the same spectrometer [2]. The application of the AC function

$$Corr(\alpha,\omega') = \int_{-\infty}^{\infty} \alpha(\omega+\omega')\alpha(\omega)d\omega$$

on the FTIR data does not assumptions about peak numbers and positions; it gives information about the change of the broadness of the peaks with the external or internal parameter. The broadness of the peaks itself is directly related to the order parameter [1] and is thus able to provide information about the structural development.

Here we present the results of the application of the AC method on temperature dependent FTIR spectra of sodalites with different frameworks. The changes of the AC broadness parameter are correlated with structural data obtained by Rietveld analysis of temperature dependent X-ray diffraction.

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# Elastic and thermoelastic properties of sanidine megacrystals from the quaternary volcanic fields of the Eifel, Germany

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Sanidine megacrystals from the Eifel, Germany, are well-known for rapid irreversible changes of their optical properties at moderately high annealing temperatures, starting at about 1020 K [1]. This unique behaviour has not been observed on any alkali-feldspar from any other location so far. The composition, $K_{1-x}Na_xAlSi_3O_8$, of these megacrystals ranges from $x \approx 0.13$ to $x \approx 0.27$ with minor amounts of $Ba^{2+}$ and $Fe^{3+}$ and almost no $Ca^{2+}$. All megacrystals are high-sanidines as determined by X-ray diffraction methods. Polarised infrared spectra and NMR studies indicate a relatively high amount of water (~ 200 wt-ppm) in Eifel sanidines, compared to low-sanidine crystals from Madagascar (~ 1 wt-ppm) [2,3]. The megacrystals from the Eifel are further characterised by very low concentrations of dislocations indicating hydrothermal growth conditions [4].

As macroscopic elastic properties of single crystals exclusively arise from interactions between their constituents, elasticity provides an excellent probe for the investigation of structure-property relationships. In order to shed light onto the atomistic processes responsible for the optical anomalies we therefore studied the elastic behaviour of sanidines from various eruptive centres of the Eifel and from Madagascar, served as a reference, between room temperature and 1370 K using resonant ultrasound spectroscopy. Further, the structural state of the crystals was thoroughly characterized employing a combination of X-ray diffraction techniques with IR- and NMR-spectroscopy. All samples were of gem-quality without visible inclusions or cracks.

The individual elastic constants $c_{ij}$ depend clearly on the chemical composition of the sanidines, in particular on the K/Na ratio. Most sensitive, however, is the shear resistance $c_{44}$ which is closely related to the structural instability that drives the ferroelastic phase transition in alkali feldspars. With increasing albite component the transition temperature increases leading to a softening of $c_{44}$ at room temperature and an increase of $\partial c_{44}/\partial T$. At temperatures above about 1000 K distinct ultrasound dissipation effects occur in all sanidines. These effects are most pronounced in Eifel sanidines. Here the ultrasound dissipation increases exponentially above 1070 K, followed by rapid irreversible softening of all resonance frequencies by about 8 % above 1240 K. The latter phenomenon is most likely related to the development and propagation of micro-cracks in the samples. Both effects are probably caused by the increasing mobility and eventually the loss of water dissolved in the crystal structure of these nominally anhydrous minerals. The high mobility of the water molecules allows for a new, less ordered Al/Si equilibrium state to be reached on the time scale of the experiment. However, diffraction and spectroscopic experiments indicate, that changes of the Al/Si order cannot account for the observed optical anomalies.

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# Structural features of Pb and Tl oxysalt minerals originated from volcanic exhalations and subsurface water solutions.

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Understanding the structural factors that control the stereochemical activity of lone pairs in lead(II) and thallium(I) compounds is important for many reasons. The solubility of thallium compounds is relatively high so that monovalent thallium is readily transported through aqueous routes into the environment. The fascinating chemistry and high toxicity potential make thallium and its compounds of particular fundamental interest and environmental concern. Under natural conditions, thallium is concentrated mostly in sulfide minerals. However some amount of Tl oxysalt minerals is also known. But the variety of these minerals is very limited. Within the last three years 7 new Tl compounds were synthesized from the highly alkaline solutions. It is very likely that similar compounds may occur in natural environments also. The features of the crystal structures and some geochemical consequences will be discussed. Fascinating minerals of lead and thallium were also discovered within the last 3 decades from fumaroles of the Great fissure Tolbachik eruption in the Kamchatka Peninsula, Russia. Many of these minerals have the “host–guest” character which may be the result of their formation from volcanic gases. The metal oxide species tend to organize in such a structure that allows inclusion of metal chloride species into a basic oxide matrix. For instance, the structure of leningradite provides example of a fumarolic mineral based upon a threedimensional metal oxide framework. But the outstanding feature of many of these minerals is the formation of oxocentered units in its crystal structures. The crystal structures of some minerals and inorganic compounds with $OPb_4$ oxocentered tetrahedra will be reviewed. The high strength of the $OPb_4$ tetrahedral units involves interplay between high basicity of additional $O^{2-}$ anions and stereochemical activity of the 6s2 lone electron pairs on $Pb^{2+}$ cations.

# A new $NH_4$-bearing variety of rhodesite from Graulay, Eifel, Germany

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The new ammonium-enriched variety of rhodesite with the simplified formula $(K,NH_4)Ca_2[Si_8O_{18}(OH)]\cdot(6\text{-}x)H_2O$ was found in the low-temperature hydrothermal assemblage related to alkaline basalt at Graulay, Eifel, Germany. Its orthorhombic unit cell dimensions are: $a$ = 6.566, $b$ = 7.085, $c$ = 23.33 Å. The presence of significant impurity of ammonium in rhodesite is caused by the post-volcanic origin of the hydrothermalites.

# Celsian in xenoliths of high-calcium subvolcanic mafic rocks (Tastau volcanoplutonic structure, Eastern Kazakhstan)

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An unusual subvolcanic formation within Tastau volcanoplutonic complex, Eastern Kazakhstan including dykes and intrusions of high-calcium basite magma has been studied. These intrusions are clinopyroxene (salite) –plagioclase (anorthite) – quartz rocks with xenoliths of relatively high-temperature amphibole grains that contain break-up structures of celsian. Hypothetically, these barium minerals were a result of a melting composite mafic-felsic crust rocks in high-pressure condition at 12-14 kb and 800-850°C similarily post-eclogite decompression melting in Meso-Neoarchean Belomorian Eclogite Province (Northen Karelia, Gridina Area).

# Noble-metal mineralization in effusive ultrapotassic basic volcanites (the Polar Urals)

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The volcanic flow of ultrapotassic basic rocks is studied in the southern part of the Enganepe Uplift (the Polar Urals). Unusual non-sulfide noble metal mineralization presented by tiny segregations of Au and Pt in association with Cu, Hg, Ag, Tl, Sb impurities was discovered in these rocks.

The volcanic flow occurs conformable with general bedding of enclosed terrigenous rocks and is traced on nearby 60 m. The thickness of the flow changes from 3 to 0.6 m. Late Cambrian – Early Ordovician volcanites lie 6-7 m above the surface of sharp unconformity of the Uralides and Pre-Uralides. Usually rocks are amygdaloidal, less often – massive. Amygdules compose 5-20 vol. % of rock and they are fillев by of dolomite; calcite, sericite, quartz and chlorite, epidote, hematite, barite, and thread veinlets of anhydrite in calcite are also found in amygdules. The rocks contain phenocrysts of feldspar completely replaced by sericite and carbonate. Euhedral phenocrysts of mafic minerals are also present (possibly – clinopyroxenes which pseudomorphically replaced by chlorite, sericite, carbonate and quartz ). The rocks have relict intersertal and poikilophitic or trachytoid textures. Pseudomorphs of mafic minerals make up to 10 vol. % of the rocks. In matrix there are also recrystallized glass transformed into feldspar and quartz. Characteristic components of rocks are iron-titanium minerals. They are presented mainly by ilmenite, much less often ulvospinel and Zn-bearing chromespinel are found. Very unusual case-like crystals of Ti-bearing hematite are widespread in these rocks, bordering crystals of the former pyroxene. Accessory minerals are represented by idiomorphic grains of monazite-(Ce,Nd), fluorapatite, xenomorphic Sr-barite, and also small grains of zircon, baddeleyite and xenotime.

The presence of noble-metal mineralization is established in these volcanic rocks. Main components are Cu, Au, Hg and Pt, and minor – are Sb, Tl, Ag, Fe. The quantity of micrograins is sometimes great enough - up to 30-40 per 1 mm$^2$, up to hundreds per polish section, however, total content of gold does not exceed 3-4 ppb. The sizes of micro-segregations of minerals do not exceed several micrometers. Shapes of micrograins are various - roundish or isometric less often extended or jagged. Composition of micrograins is very unstable, however, multiphase structure of microphases is visible sometimes. Most often there are intermetallic phases of Cu-Au nonstoichiometric composition, segregations of Cu-Au-Hg composition, less often - Pt and almost pure Hg (globules) with Tl impurity. Also are found out rare individual segregations with composition: Au-Hg, Pt-Hg, Cu-Au-Pt, Au-Pt-Hg etc. Micrograins of high-tantalum phase (to 90 wt.% Ta) are found.

The compositions of the studied phases are very unusual (for example, Cu-Au phase coexist with Pt or Au-Hg-Pt alloys) and are unstable. We assume their genesis in obviously non-equilibrium conditions at the latest stages of formation of a volcanic flow or even later – in processes of latest transformations, may be due to possible sedimentation of metals from a gas phase in a mode of "blowing" already formed lava flow by thermal fluids at finishing stages of formation.

# The conditions of tacharanite formation.

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Tacharanite is an insufficiently investigated calcium hydrosilicate related to tobermorite. A model of the crystal structure of tacharanite (transitional from structures of inosilicates to that of tectosilicates) is suggested. Tacharanite structure can incorporate additional anions like $SO_4^{2-}$ and $Cl^-$ that makes it related to cancrinite- and sodalite-group minerals. A representative collection of tacharanite samples from hydrothermalites and metamorphosed xenoliths in alkaline basalts have been investigated using electron microprobe and SAED methods. Tacharanite occurs in close associations with zeolites, and is formed on the stage of the enhancement of Ca activity in alkaline fluids. Tacherenite is characterized by a wide variations of chemical composition (in particular, the ratio Ca:Mg and the contents of Al, $SO_4^{2-}$ and $Cl^-$), as well as unit-cell parameters. Most analyses correspond to cationic stoichiometry in the ranges: $Ca_{7-10}Mg_{0.1-2}(K,Na)_{0-1.5})_{7-10}(Si,Al_{2-3.5})_{\Sigma 20}$.

# Mineral chemistry and crystal structure of haüyne from the Oldoinyo Lengai volcano, northern Tanzania

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Haüyne, ideally $Na_6Ca_2(Al_6Si_6O_{24})(SO_4)_2$, is a member of the sodalite group minerals. It occurs in various volcanic, plutonic rocks and mantle xenoliths. Haüyne is also known from the active Oldoinyo Lengai carbonatitic volcano in Gregory rift, northern Tanzania. Recently, large crystals of gem-quality haüyne have been also described from Oldoinyo Lengai (Zaitsev *et al.,* 2009). Here, haüyne has a yellowish green/greenish yellow colour and occurs in a block of coarse-grained ijolite with diopside and nepheline as major minerals and minor perovskite, magnetite and apatite. Mineralogical, spectroscopic and crystal structure study of the gem-quality haüyne from Oldoinyo Lengai has revealed a very unusual chemical composition of the mineral (e.g. presence of carbon, hydrogen and possibly nitrogen).

# Mineralogy and geochemistry of the Sadiman volcano, Crater Highlands, northern Tanzania

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Sadiman volcano is located in the Crater Highlands area of northern Tanzania. It consists of interlayered phonolitic tuffs, agglomerates (with clasts of nephelinites) and nephelinitic lava flows. Phonolites and ijolites are rare rock types. No evidence for the presence of melilite-bearing and/or carbonatitic rocks was found during this study. On the basis of petrography, mineralogy and geochemistry the nephelinites are divided into cumulate nephelinite, wollastonite nephelinite and phonolitic nephelinite, the latter of which is the dominant variety at Sadiman. Nepheline + clinopyroxene + titanite ± perovskite ± andradite-schorlomite ± wollastonite ± sanidine ± sodalite are the principle pheno- and microphenocryst phases. The nephelinites are highly evolved (Mg# = 0.17-0.26) alkaline to peralkaline (AI = 0.88-1.21) rocks enriched in incompatible elements such as Rb, Ba, Th, U, Nb, Pb, Ta, Sr and light REE, and strongly depleted in P and Ti. This suggests derivation from enriched mantle source and fractionation of apatite and Ti-rich mineral(s). Primary melt inclusions in nepheline phenocrysts ($T_{homogenization}$ = 860-1100ºC) indicate enrichment of volatile components in the melts, particularly in fluorine (up to 1.8 wt.% in silicate glass) resulting in the formation of daughter fluorite in partly and complete crystallized inclusions. The Sadiman nephelinites crystallized at relatively oxidized conditions (above the FMQ buffer), which is different from the reduced conditions reported for trachytic and pantelleritic rocks from other parts of the Gregory rift. Similar rock types and relatively oxidized conditions are known from the Oldoinyo Lengai and other localities, which are always closely associated with carbonatites. By analogy, we thus conclude that andradite-schorlomite-rich nephelinites may indicate a pre-stage on the evolutionary path towards carbonatitic magmatism.

## Participants

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