SYENITE FORMATION AFTER TTG GNEISS: EVIDENCE FROM THE MADIAPALA MASSIF (LIMPOPO COMPLEX, SOUTH AFRICA) AND EXPERIMENT

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Limpopo complex

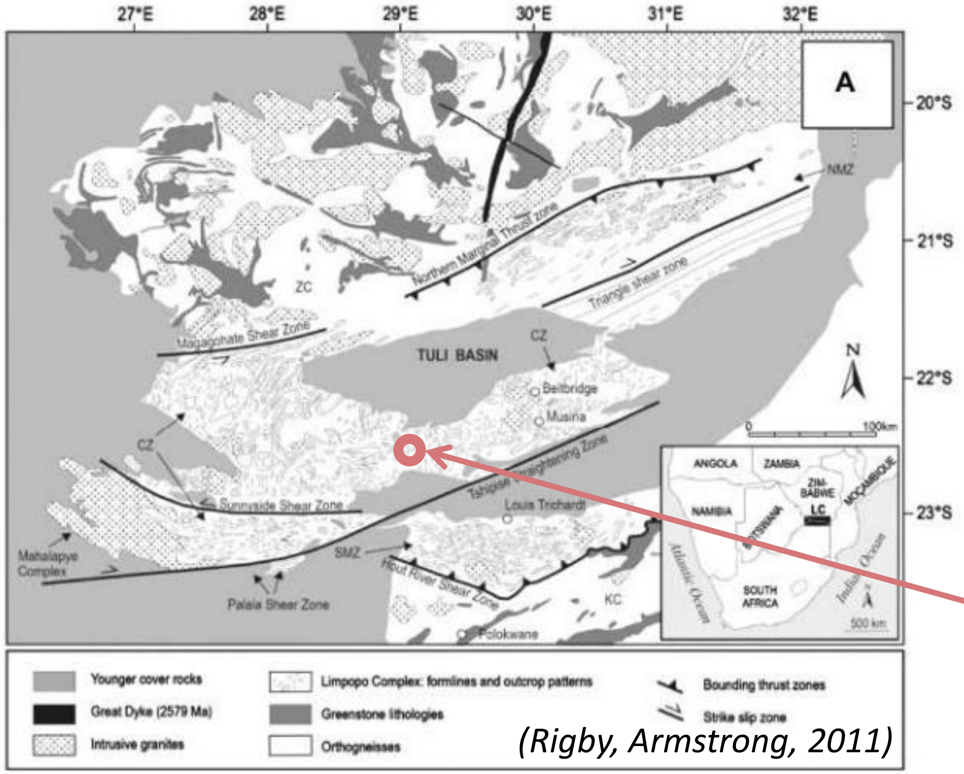
Age 2.5 - 2.7 Ga

Size 300x700 km

Located at the borders of South Africa, Zimbabwe and Botswana.

Formed at the borders of two cratons: Kaapvaal in the south and Zimbabwe in the north.

3 tectonic zones: Southern Marginal Zone (SMZ) , Central Zone (CZ) and Northern Marginal Zone (NMZ).



(Rigby, Armstrong, 2011)

Madiapala massif

Metamorphic evolution of CZ:

(1) 3.1-3.2 Ga - the Mesoarchaean event (D1/M1) - the intrusion of granitoids, which later became the gneisses of the Sand River, basic and ultrabasic magmas of the Messina layered complex.

(2) 2.66-2.61 Ga - the Neoarchean tectonic-metamorphic event (D2/M2) led to the formation of isoclinic folds in the north-south-east direction, numerous faults and shear-zones, the intrusion of granitoids, which served as a protolith for the Singelele gneisses; the collision of the Kaapvaal cratons and Zimbabwe is considered to be the reason of the D2/M2 event.

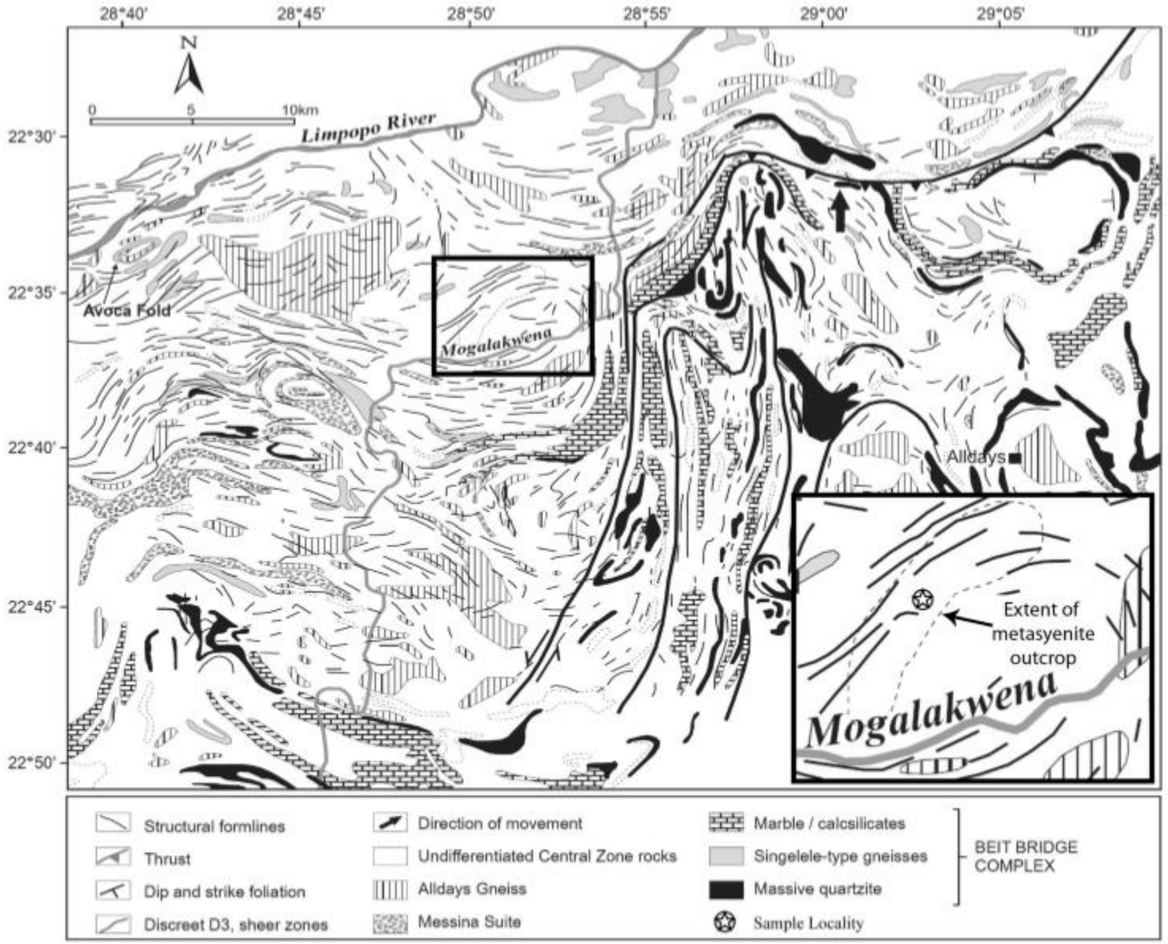
(3) 2.01-2.03 Ga - the Paleoproterozoic tectono-thermal activity (D3/M3), caused by the reactivation of the shear-zones of the D2/M2 event and is marked by granite magmatism and powerful fluid penetration along the numerous shear-zones.

Madiapala massif

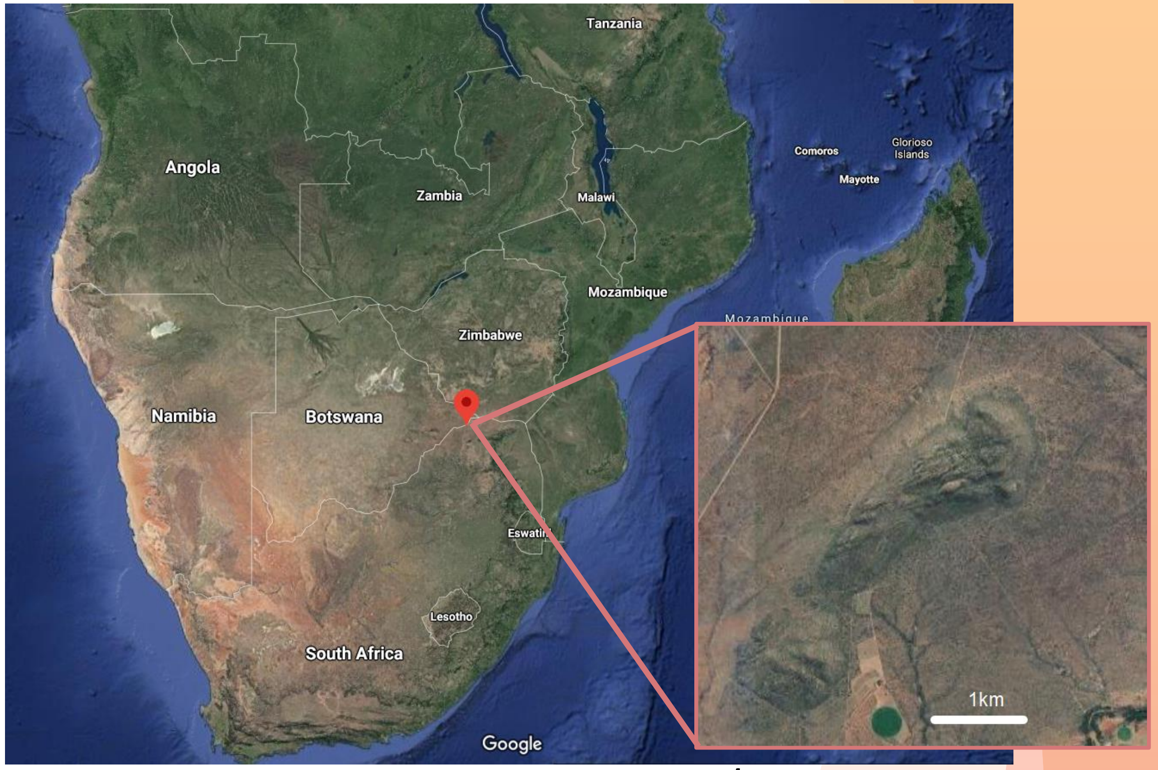
Located in the western part of the CZ of the Limpopo complex

Is included into the Alldays TTG

The age of the Madiapala syenites is 2010.3 ± 4.5 *Ma (Rigby, Armstrong, 2011)* corresponds to the D3 / M3 event



(Rigby et al, 2008)



Google Maps

Model for formation: the syenites could be a product of the syenitization of the tonalite gneisses, similar to granitization, but with the participation of alkalic aqueous-carbonic-salt fluids *(Safonov and Aranovich, 2014; Safonov et al., 2014).*

Aims

- Identification of the PT conditions and fluid regime of the formation of syenites of the Madiapala massif
- Thermodynamic substantiation of the process of their formation via syenitization of tonalite gneisses using the phase equilibria method (pseudosections)
- Reproduction of these associations in an experiment on an interaction of TTG gneiss with the H_2O-CO_2-(K,Na)Cl fluids

Methods

• Opton Optical Polarizing Microscope at the Department of Petrology, Moscow State University

• Jeol JSM-6480LV scanning electron microscope with the Link INCA Energy 350 energy dispersive microanalyzer and Oxford INCA Wave 500 wave microanalyzer

•Digital SEM Tescan VEGA-II XMU with energy-dispersive spectrometer (EDS) INCA Energy 450

•and wave-dispersive spectrometer (WDS) Oxford INCA Wave 700

• XRF with an Axios mAX sequential vacuum spectrometer (PANalytical)

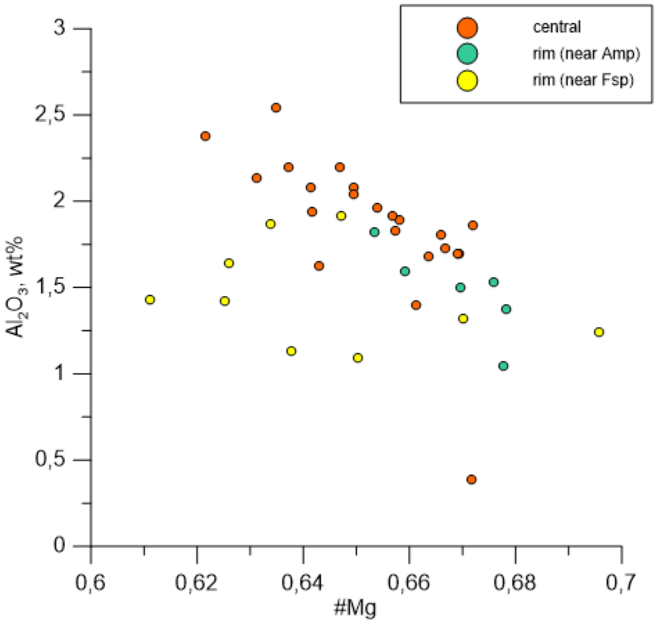
• XSeriesI quadrupole mass spectrometer and ICAP-61 atomic emission spectrometer

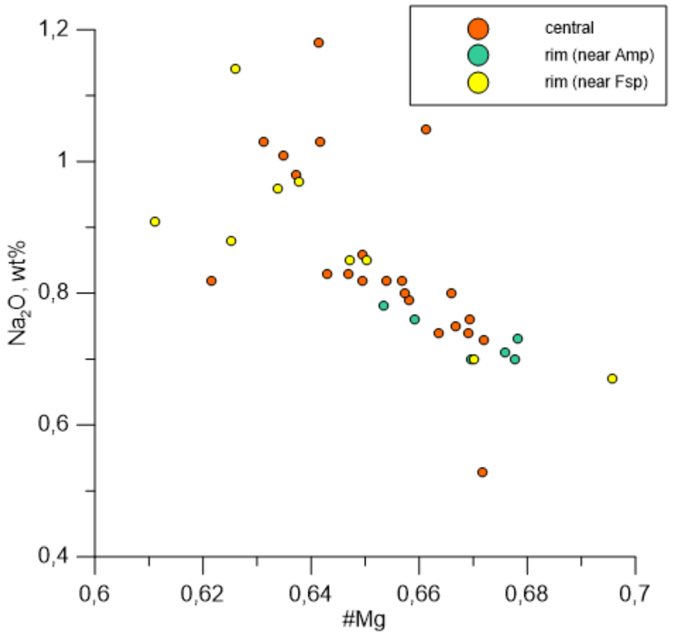
• XPloRA Raman spectrometer (Horba Scientific)

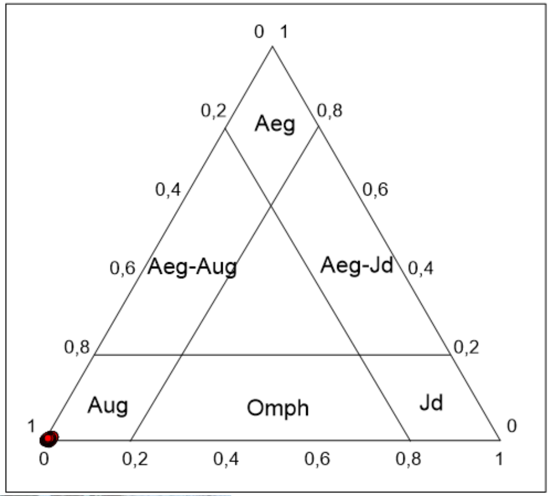
• Calculations were performed using the PERPLE_X software package *(Connolly, 2005)*, version 6.7.7 for Windows, using standard thermodynamic properties of the end-members and solid solutions from the database of Holland and Powell *(Holland and Powell, 2011; file hp11ver.dat)*

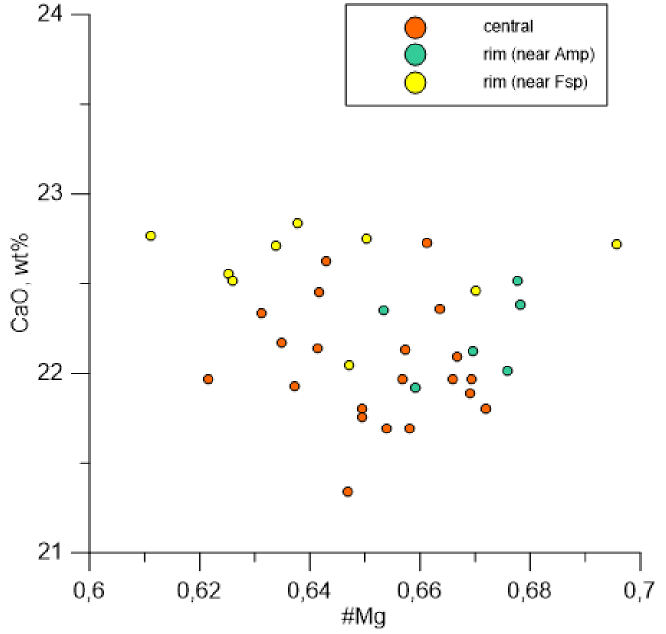
Primary assemblage of syenites Kfs+Cpx+Sph±Ap

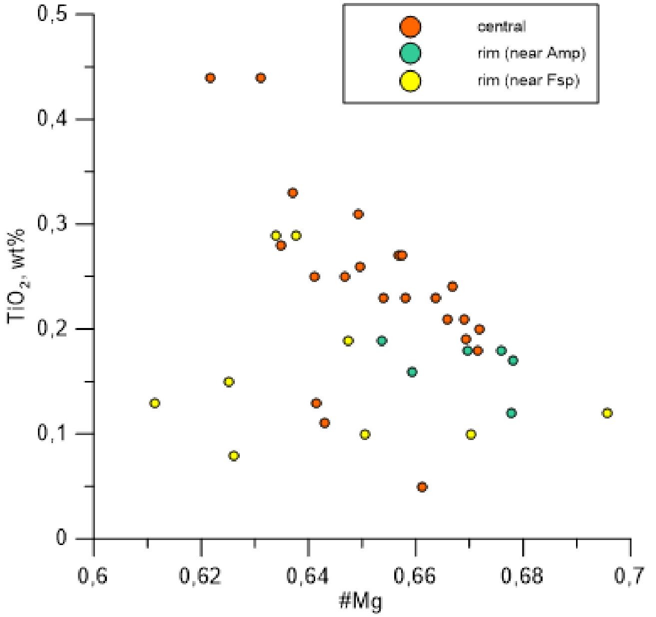
Clinopyroxene

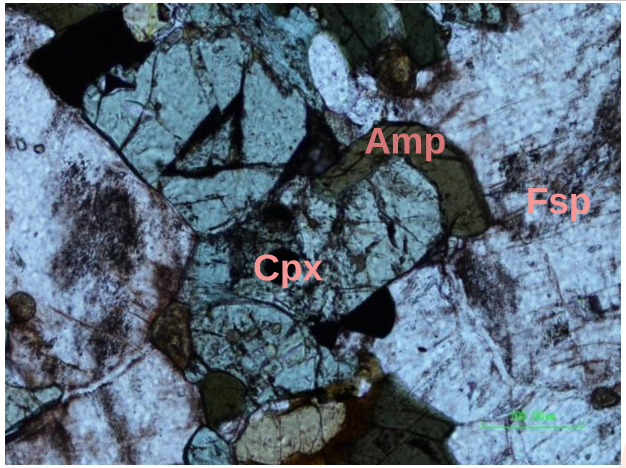


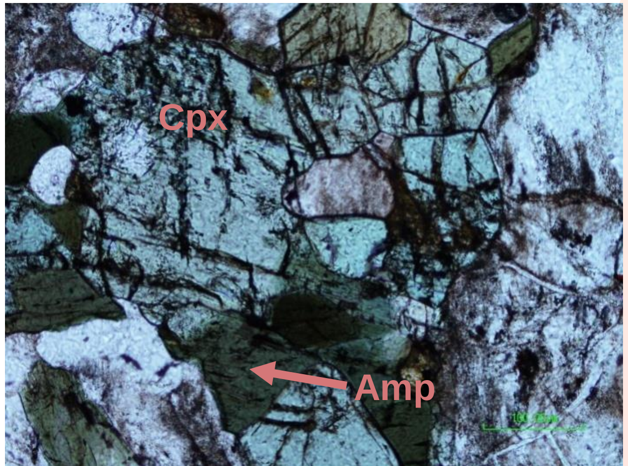






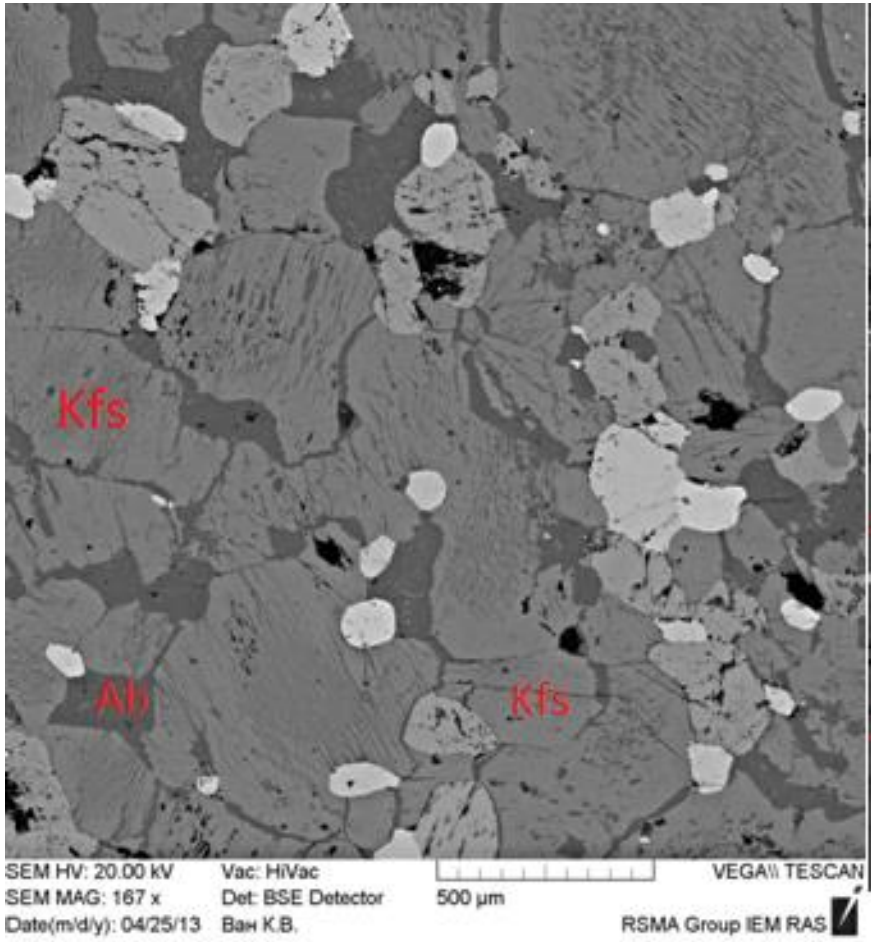


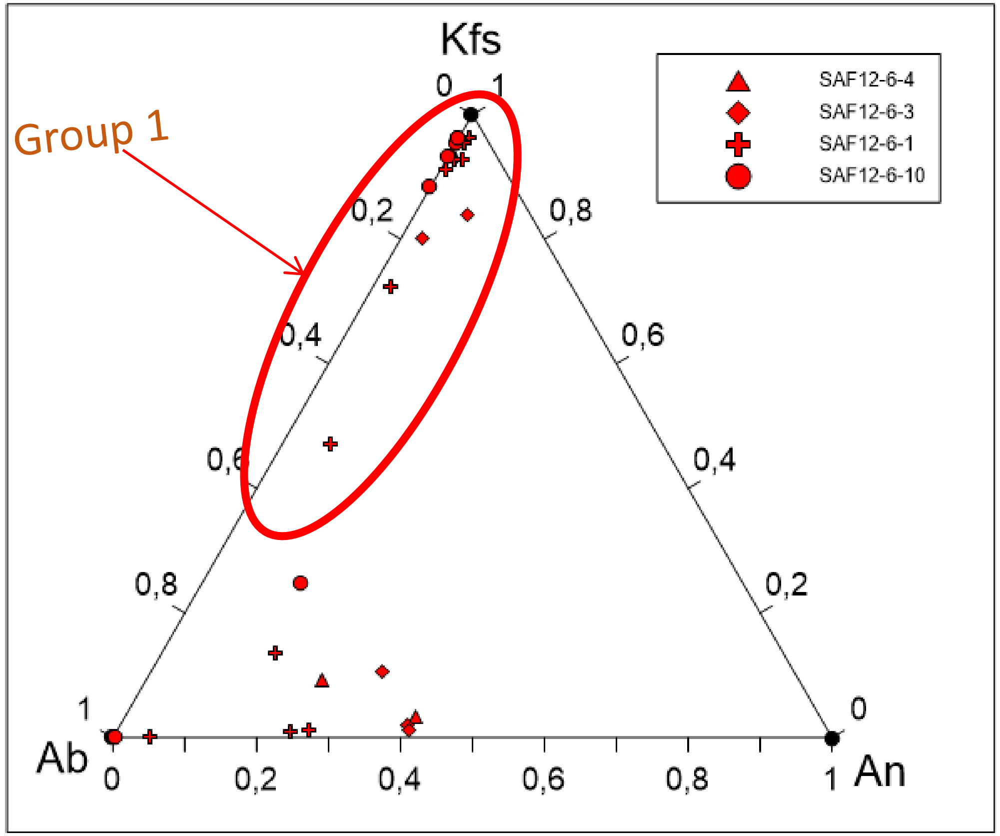




Primary asseemblage of syenites Kfs+Cpx+Sph±Ap	**Feldspar**

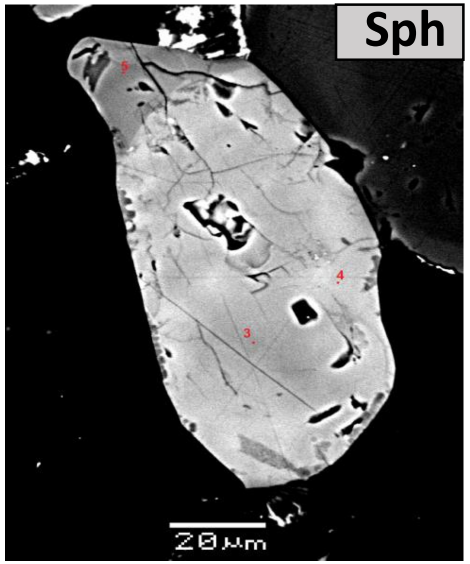
- K-feldspar contains perthite lamellae
- K_2O in analyzes of the area wt. % 13.87-15.51

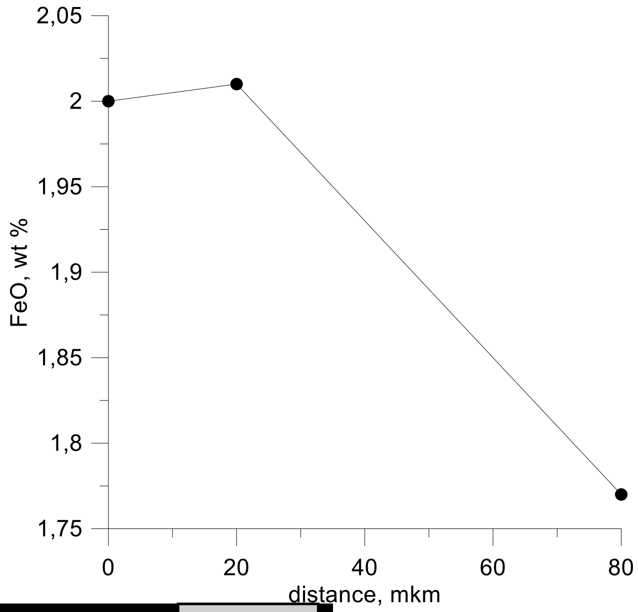


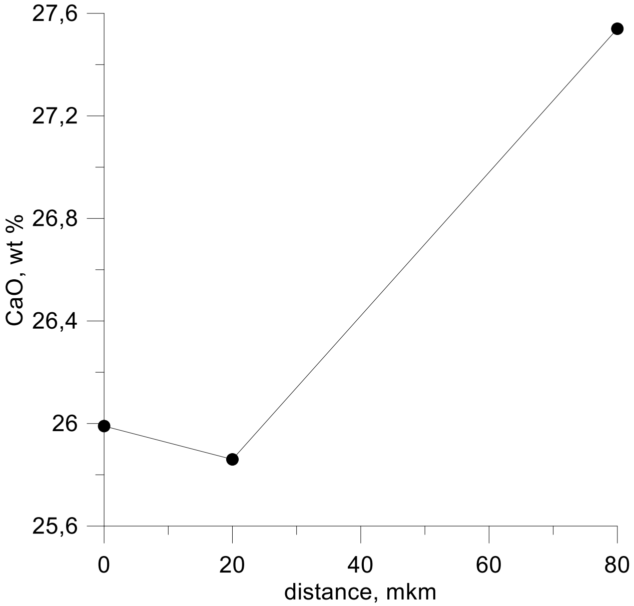


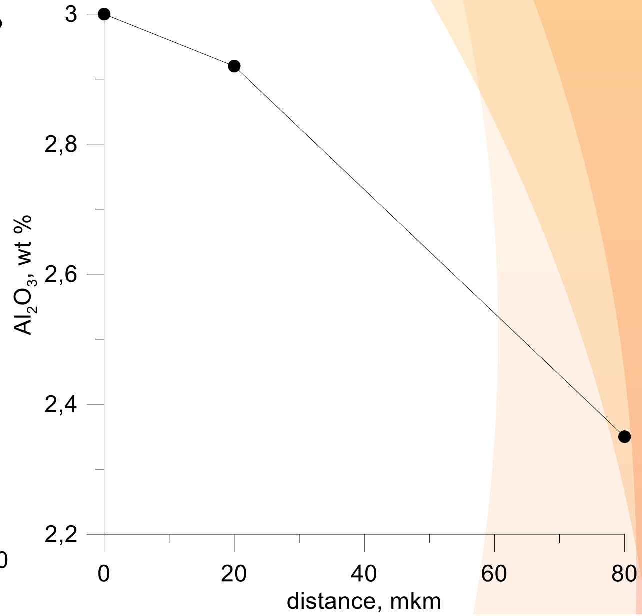
Primary assemblage of syenites Kfs+Cpx+Sph±Ap

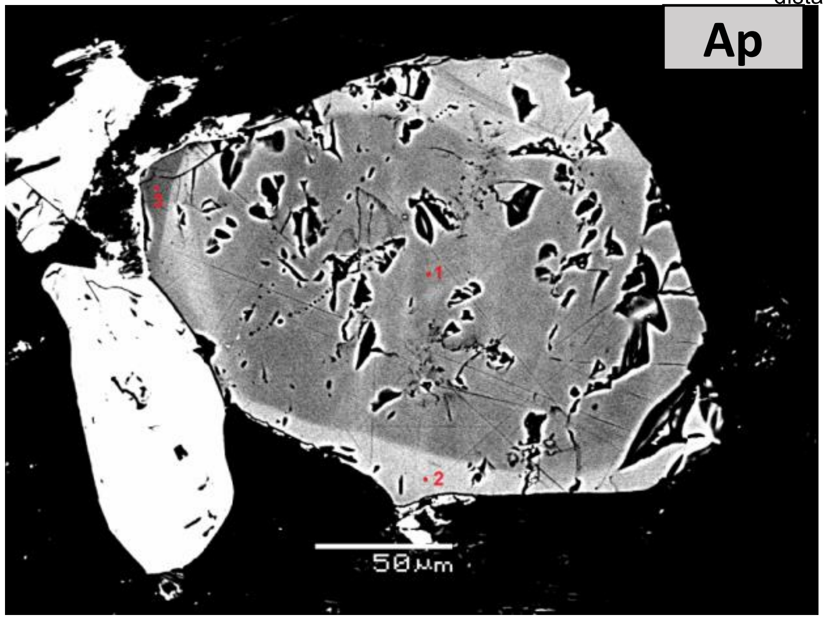
Sph+Ap





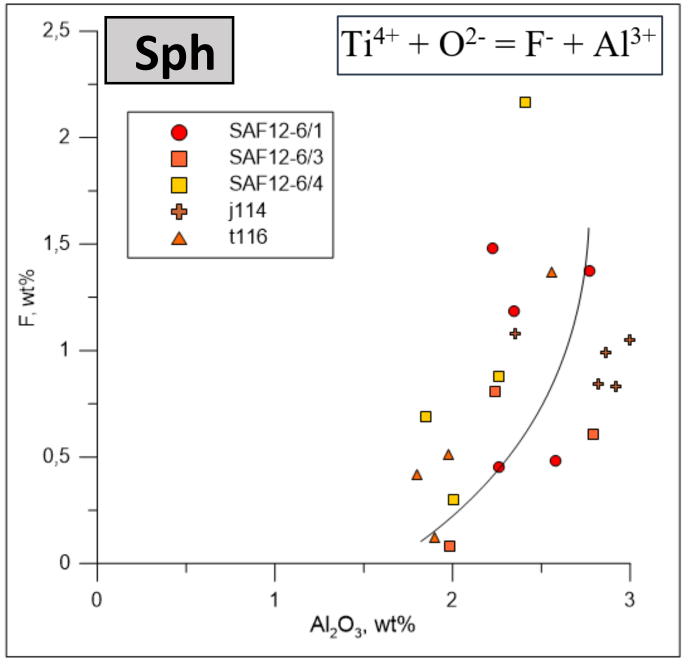






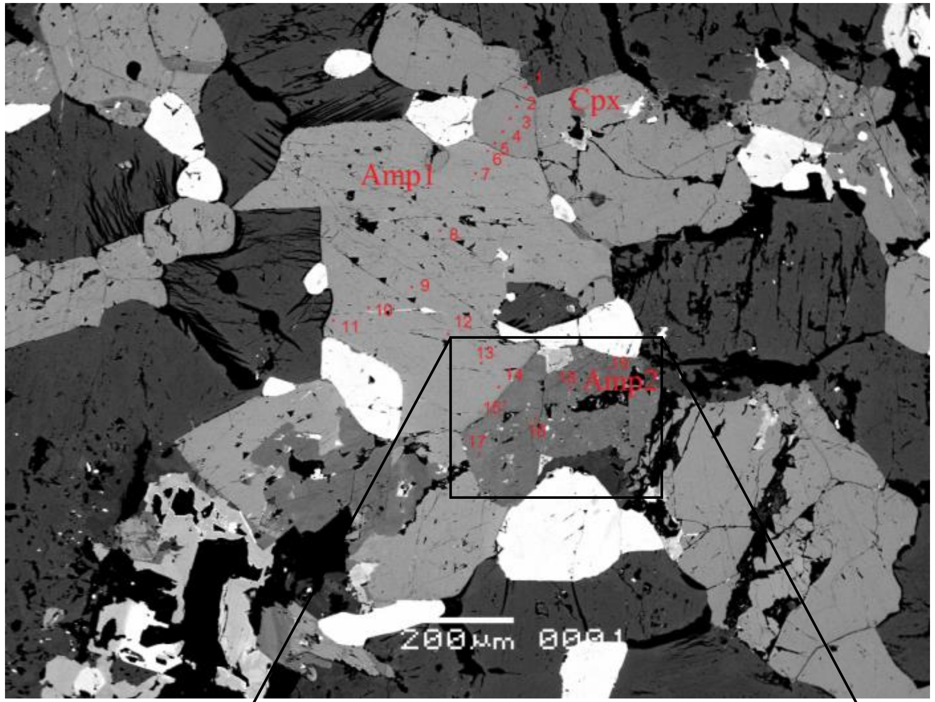
Sph	**F** content is 0.83-1.08 wt. % **Al_2O_3** content is up to 3 wt.%

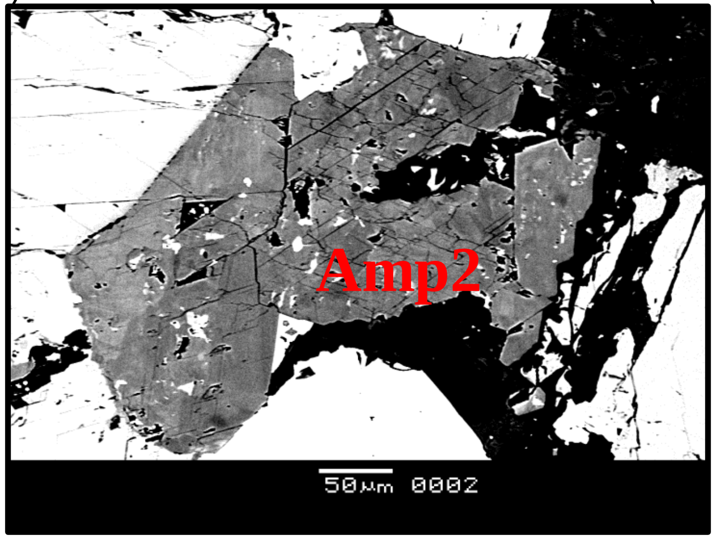
Ap	**F** content is 3.6-5.3 wt. % **Cl** content is up to 0.2 wt. %

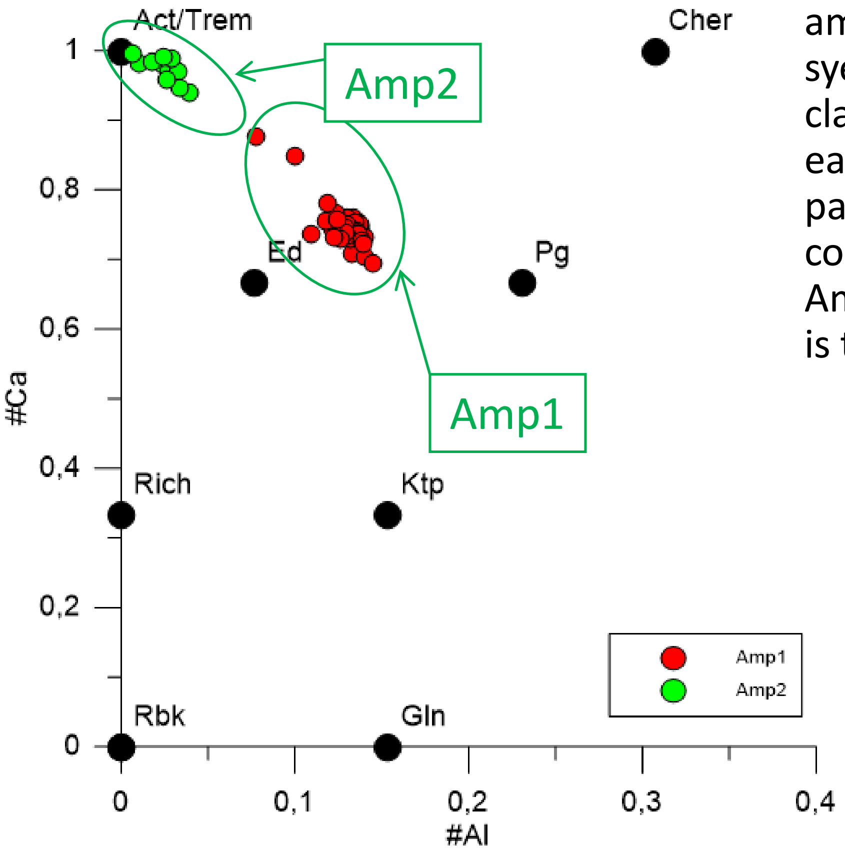


Late assemblage of syenites Amp+Ab

Amp



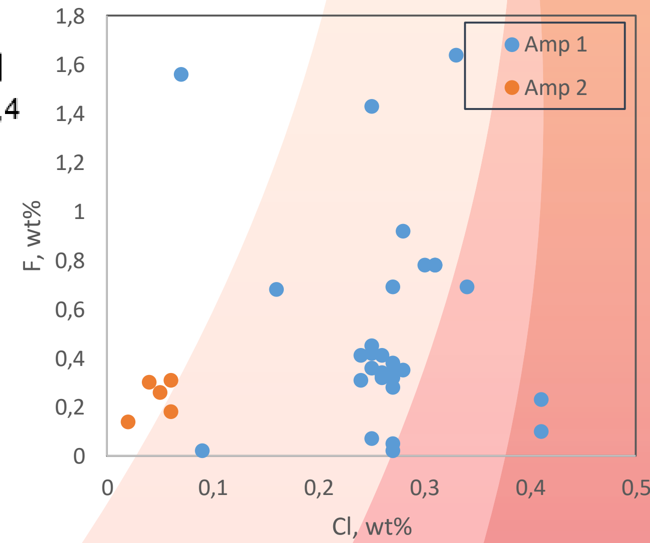




According to the petrographic and chemical features, two types of amphiboles are distinguished in the syenites. According to the classification *(Leake et al., 1997)*, early amphibole (Amp1) is edenite-pargasite solid solution with a low content of the tremolite component. Amphibole (Amp2), replacing Amp1, is tremolite-actinolite solid solution

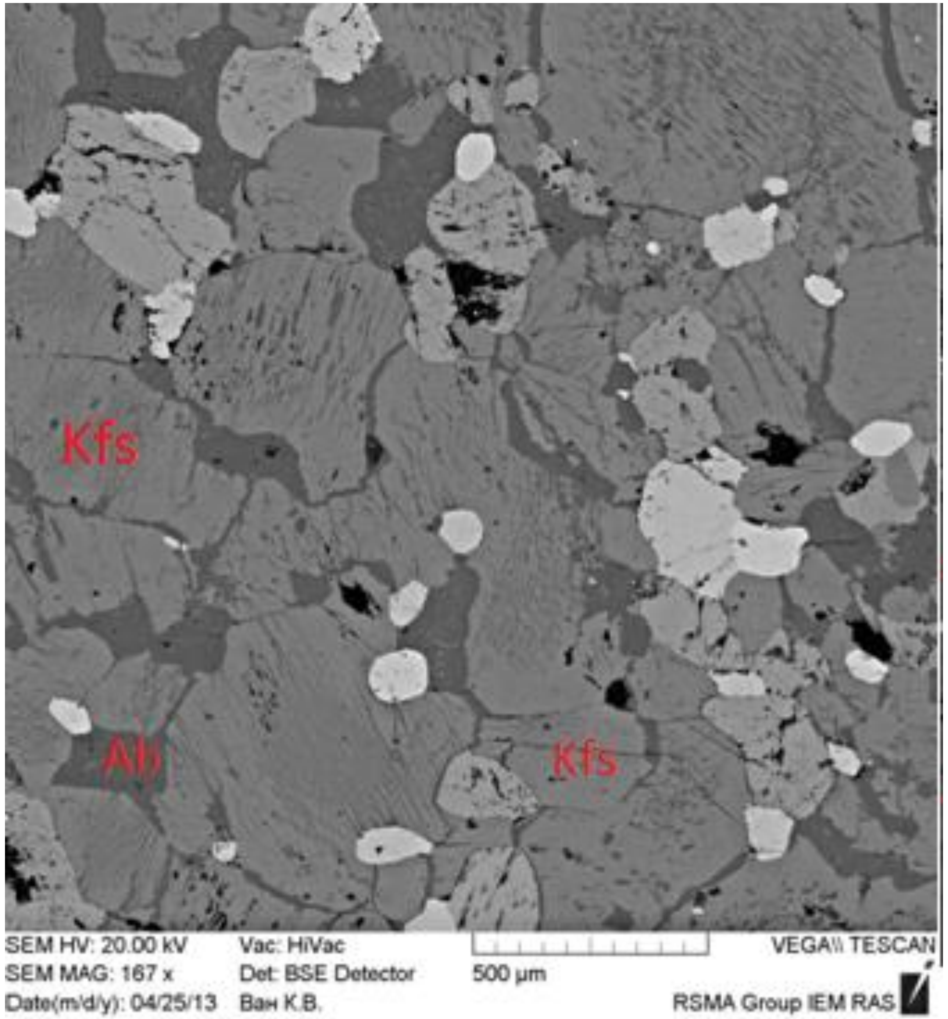
High concentrations of halogens in amphiboles are observed

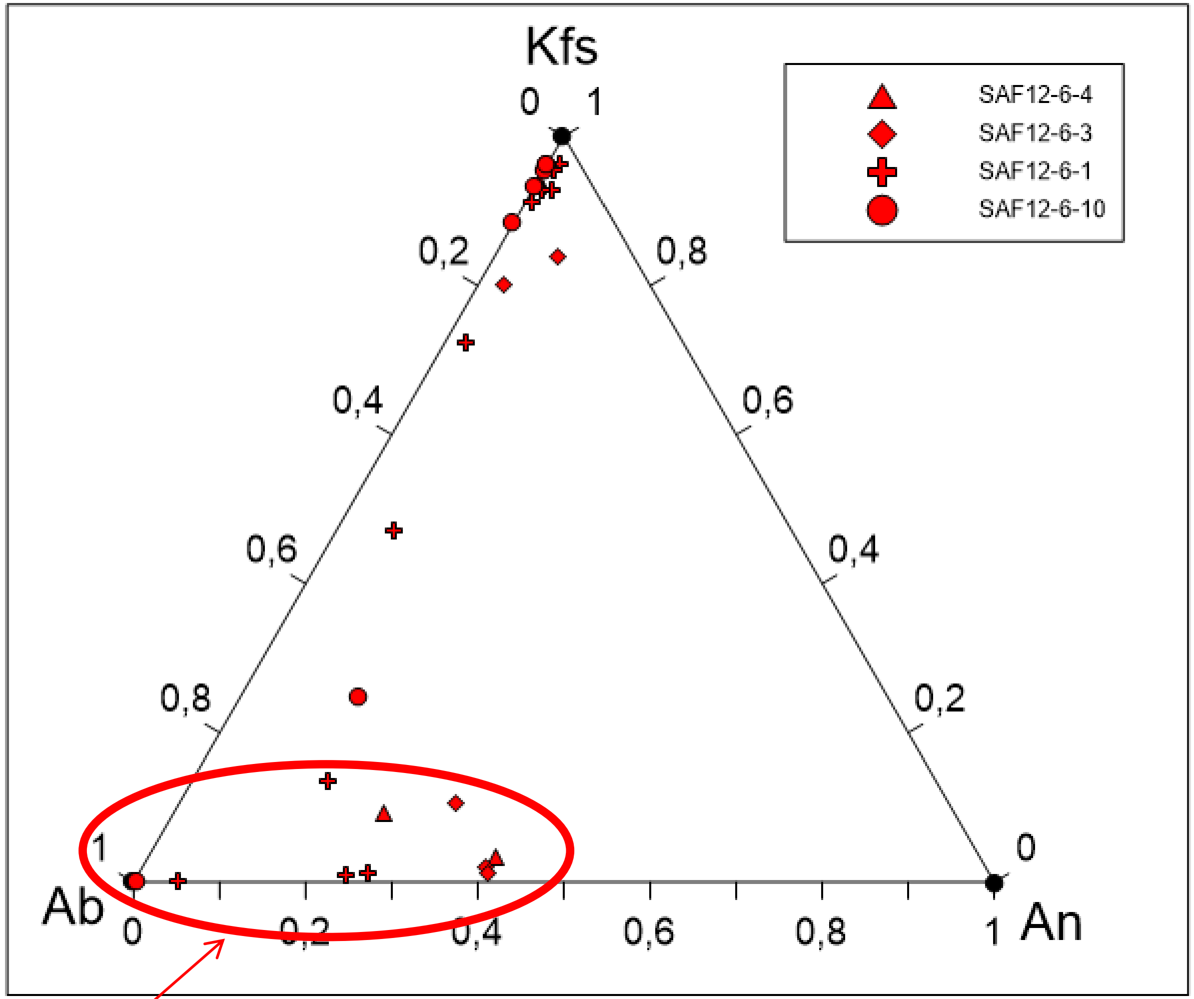
(up to 2 wt.% F and 0.5 wt.% Cl)



Late assemblage of syenites Amp+Ab

Ab

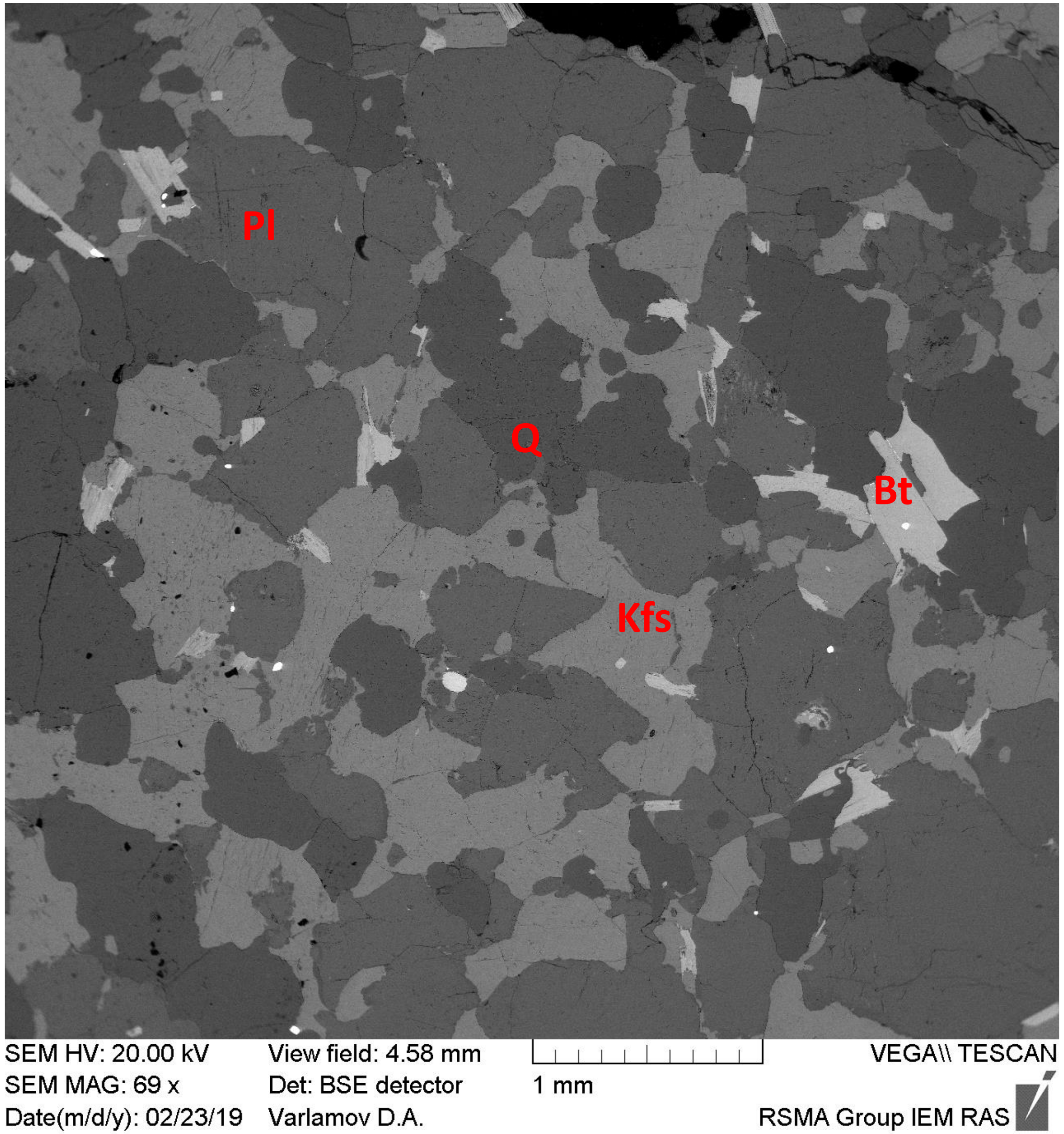


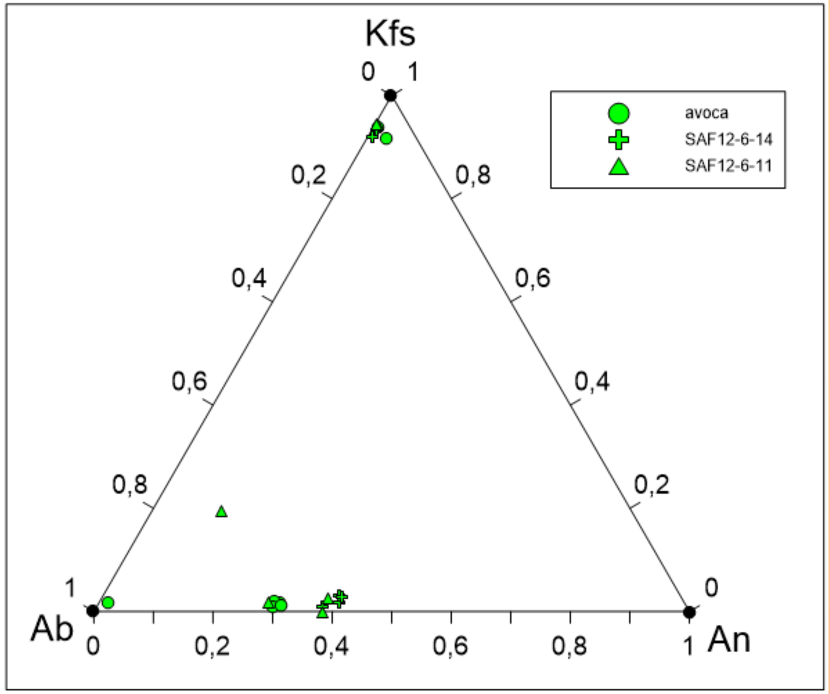


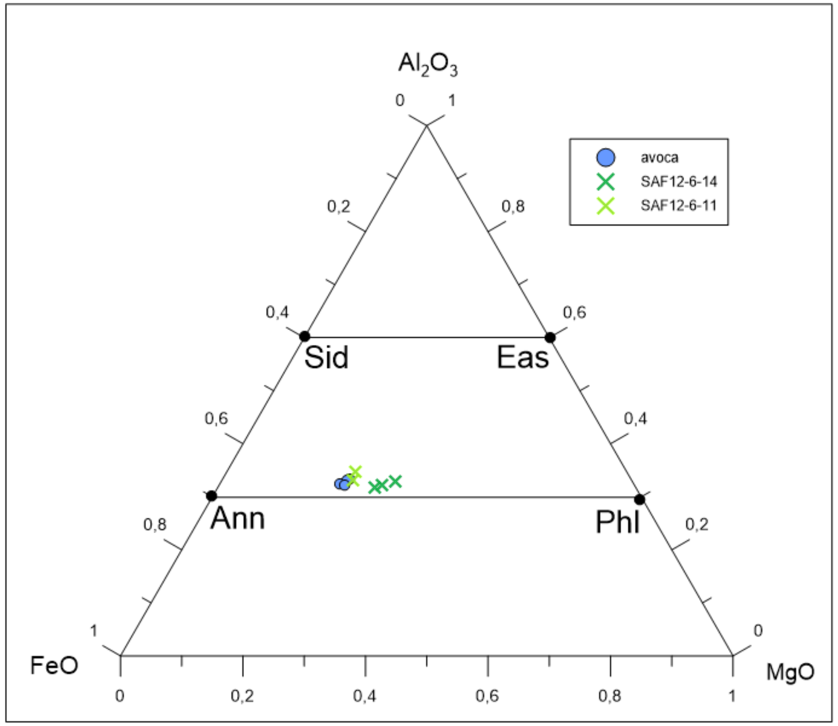
Group 2

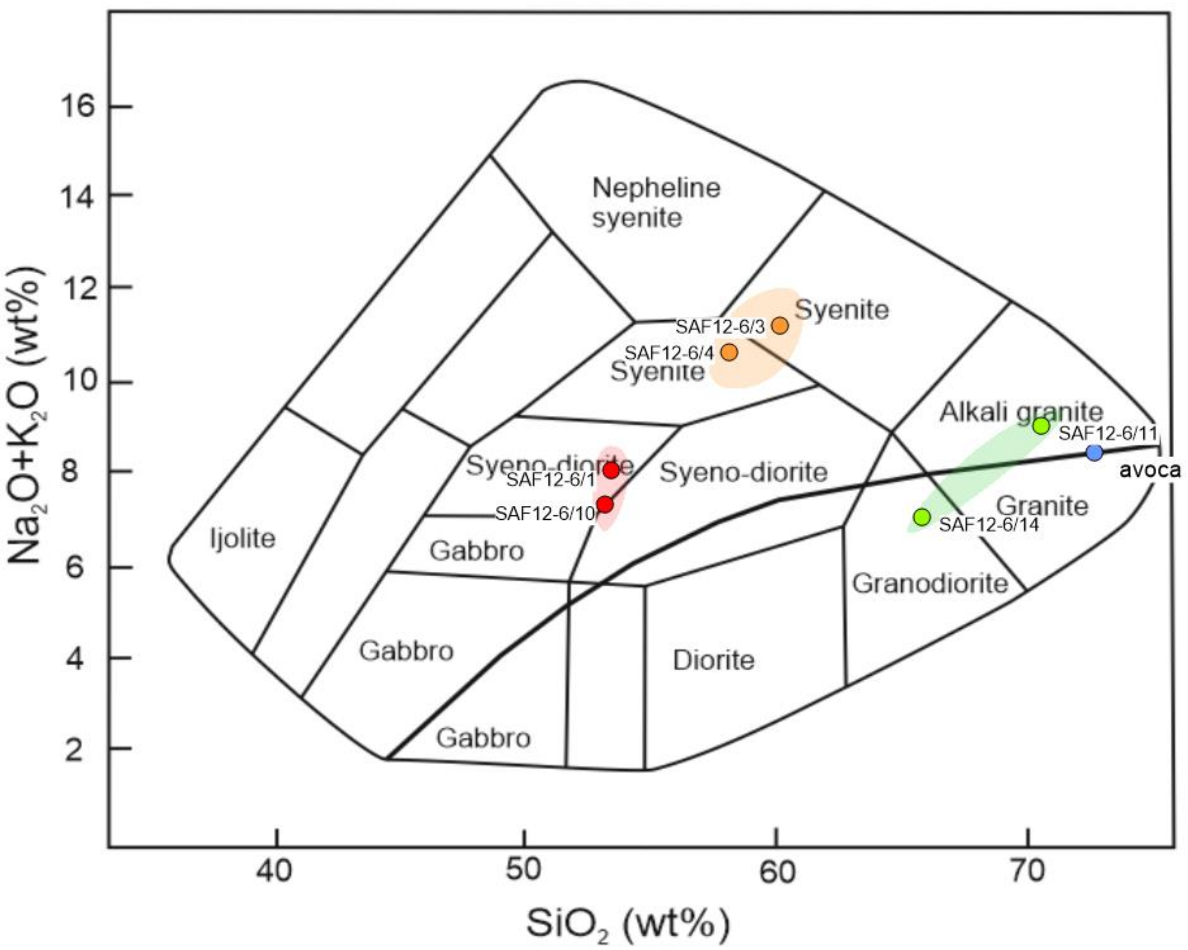
X_{An}= Ca/(Ca+Na+K) up to 0.4

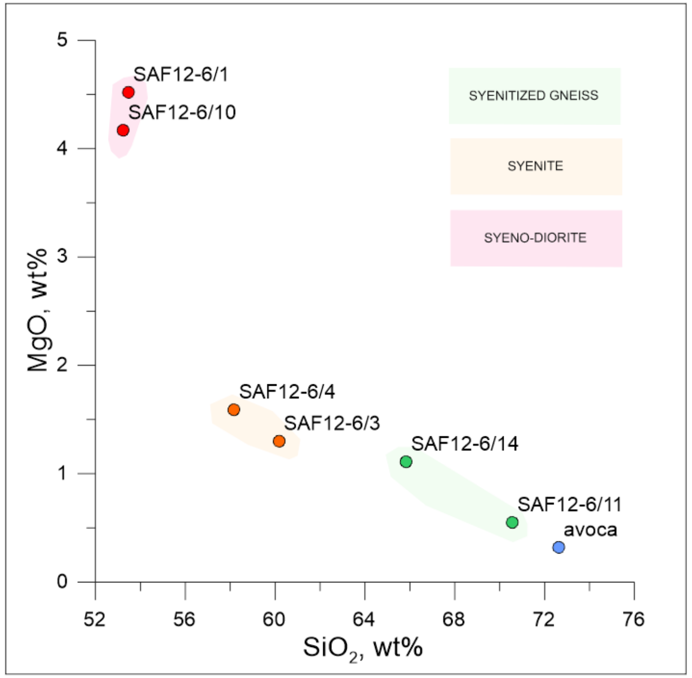
Alldays TTGs Bt+Kfs+Pl+Q	Fsp+Bt

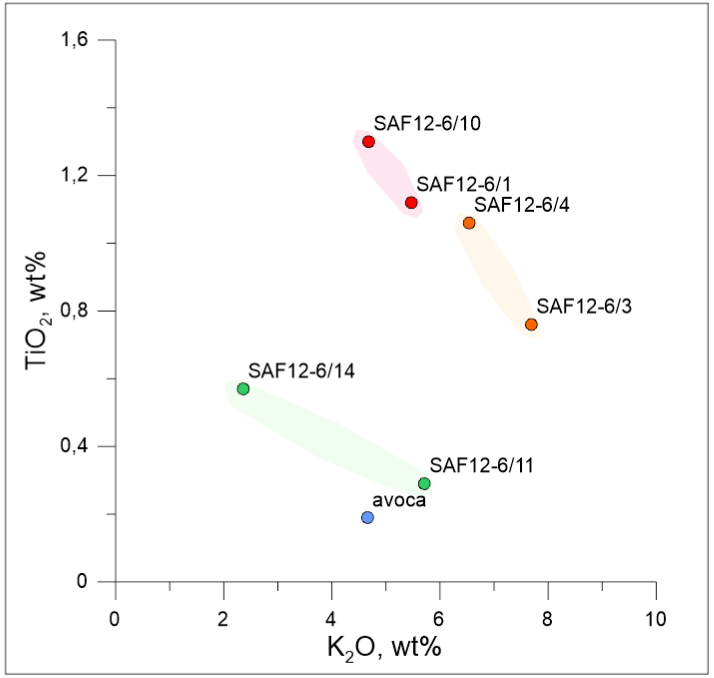










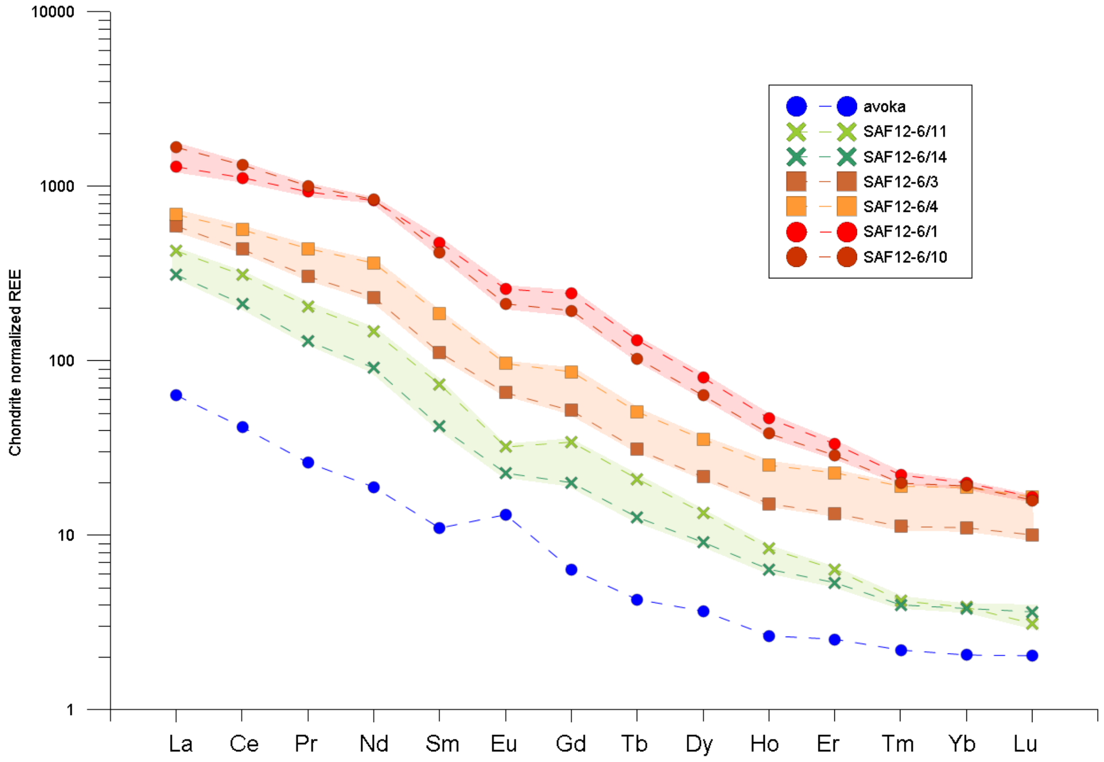


Geochemical data (XRF) revealed two types of the syenitic rocks in the massif:

syenites – samples SAF-12-6/3 and SAF-12-6/4

syenodiorites – samples SAF-12-6/1 and SAF-12-6/10

and confirmed a genetic relationship between the syenites and the host TTGs.

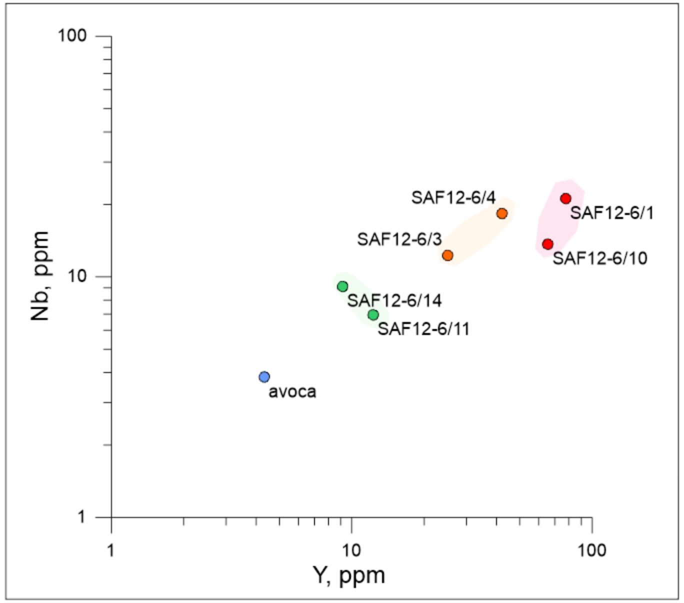


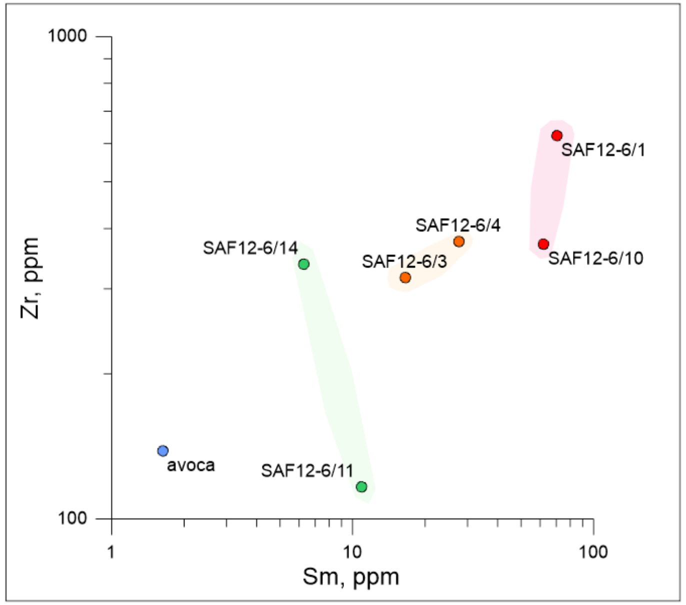
In all samples of syenites and syenitized gneisses, a negative Eu-anomaly is observed. A positive Eu anomaly is observed only in the host (Avoca) TTG, which is also characteristic for low-HREE TTGs according to Halla (2009).

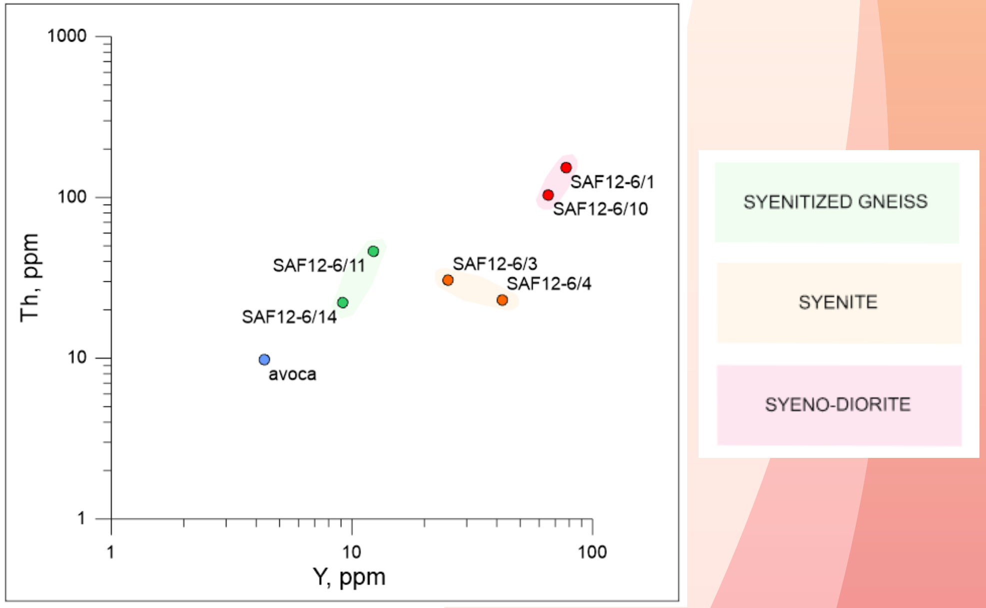
In syenitic rocks, two types of the REE patterns are observed. The first pattern is typical for syenites and syenitized gneiss SAF12-6/14. Flattening within HREE is characteristic, Eu anomalies are weak (values from 0.76 to 0.86). The second pattern is typical for the syenodiorites and syenitized gneiss SAF12-6/11. A less noticeable flattening within the HREE spectrum occurs and Eu anomalies are more noticeable (values from 0.64 to 0.76)

The proposed mechanism: as a result of gneiss melting and subsequent differentiation of a melt, a highly LREE-enriched melt was formed. Thus, it is assumed that gneisses were “divided” into more REE-enriched syenites and REE-depleted restite. Probably, this separation occurred as a result of differentiation of the melt produced by partial melting of gneisses.

	avoka	SAF12-6/11	SAF12-6/14	SAF12-6/1	SAF12-6/3	SAF12-6/4	SAF12-6/10
Eu anom	1.57	0.64	0.78	0.76	0.86	0.76	0.74

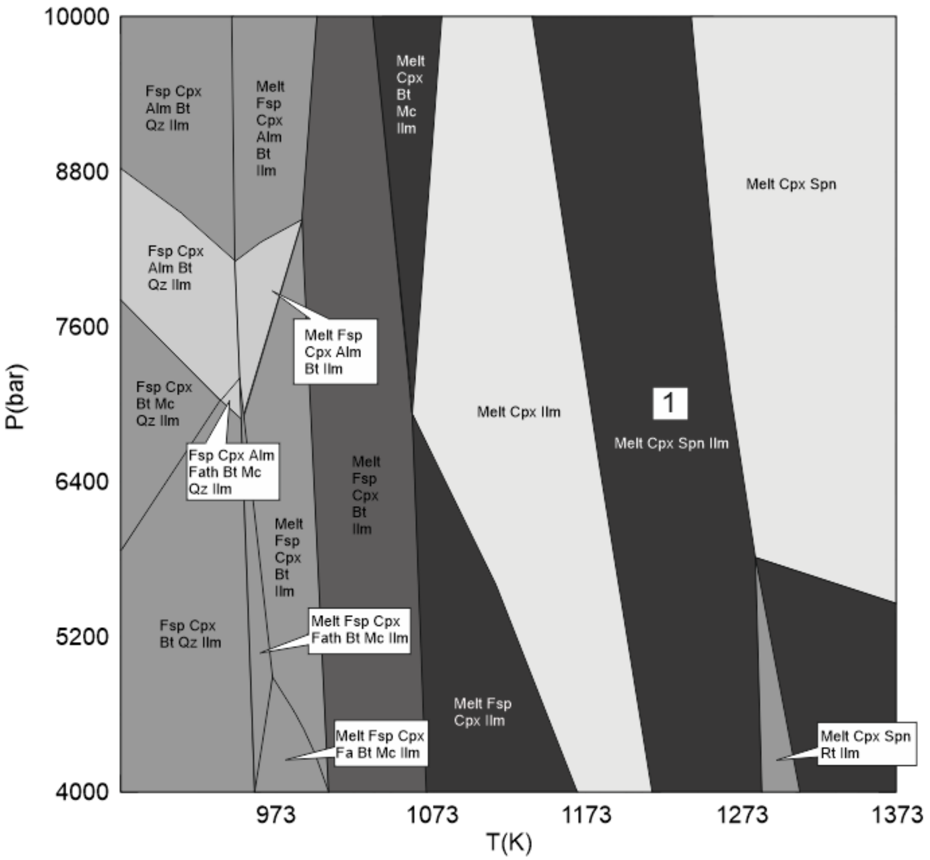




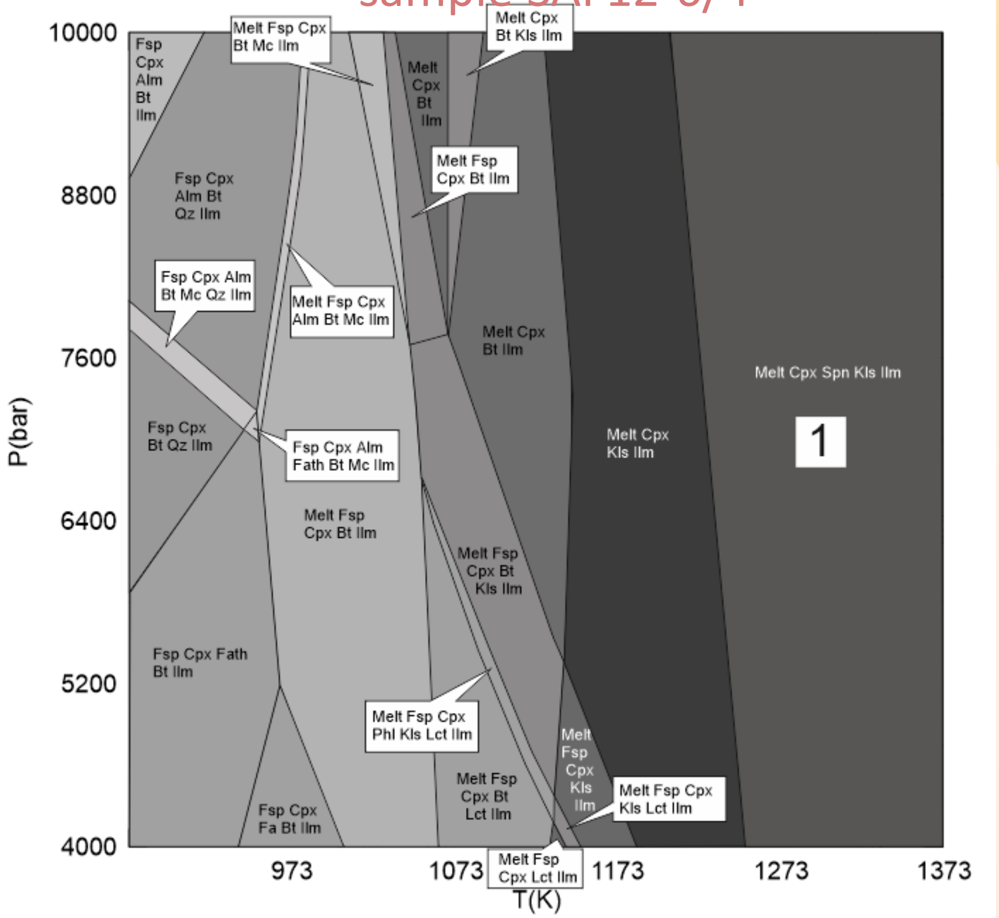


SYENITES

Sample SAF12-6/3



sample SAF12-6/4

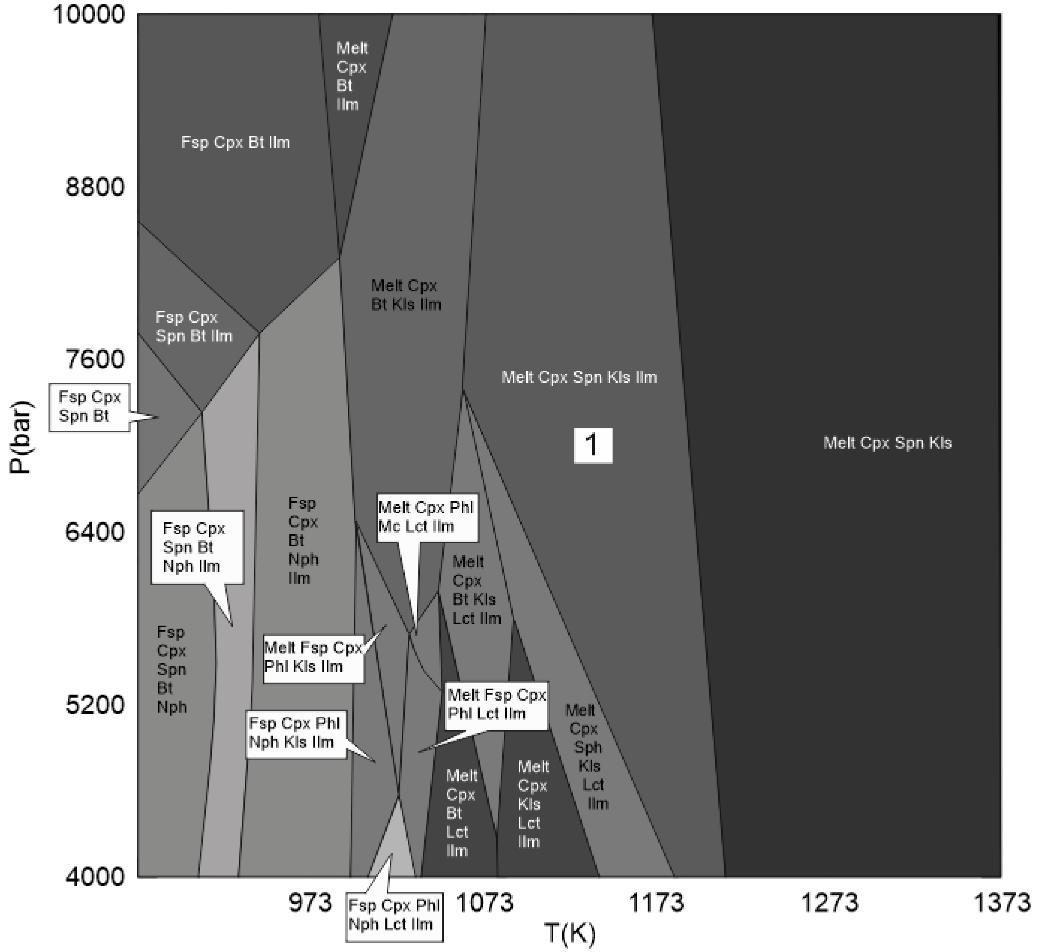


The formation temperature of the syenite association is about 900-1000°C.

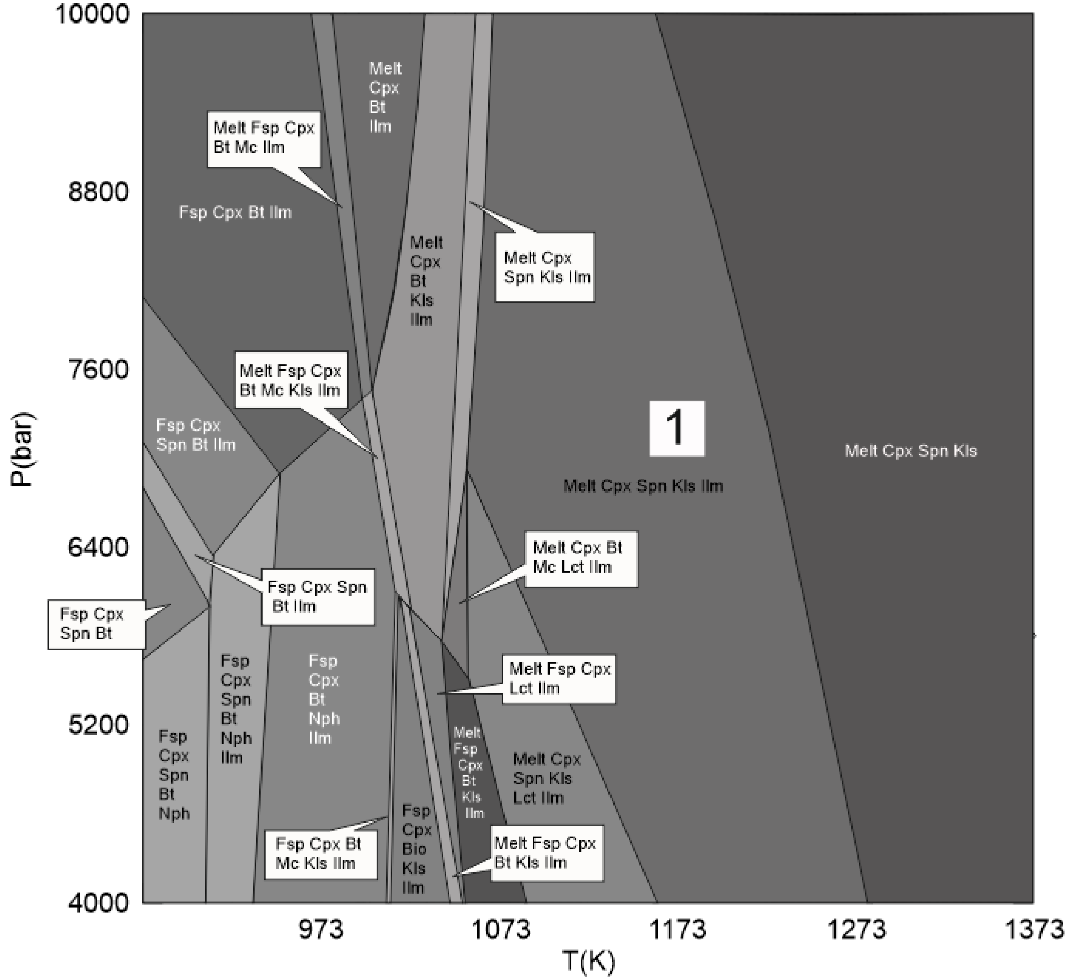
The appearance of kalsilite (Kls) and leucite (Lct) in the model association can be explained by reasons, which were not taken into account in the modeling procedure of PERPLE_X: “excess” Al, which causes the formation of Kls and Lct in the model association, can be distributed in titanites according to the scheme $Ti^{4+} + O^{2-} = F^{-} + Al^{3+}$. This is confirmed by high concentrations of Al_2O_3 (up to 3 wt.%) in titanites.

SYENODIORITES

Sample SAF12-6/1

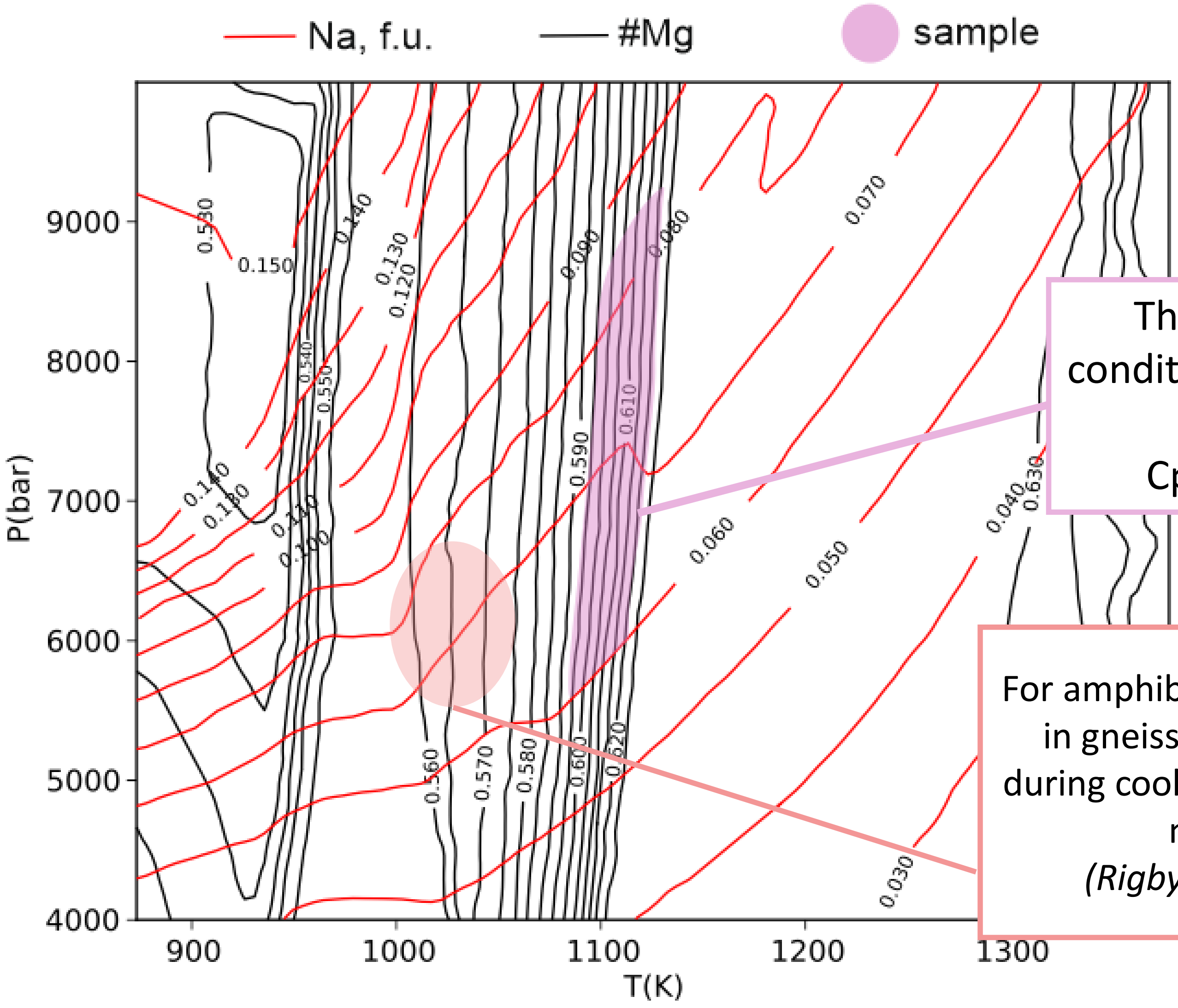


Sample SAF12-6/10



The formation temperature of the syenodiorite association is about 800-900°C.

Isoplets of #Mg and Na content (f.u.) for clinopyroxene



The crystallization conditions of the primary association Cpx+Kfs+Sph±Ap

For amphibole-bearing veins in gneisses that formed during cooling of the syenite magma *(Rigby et al, 2008)*

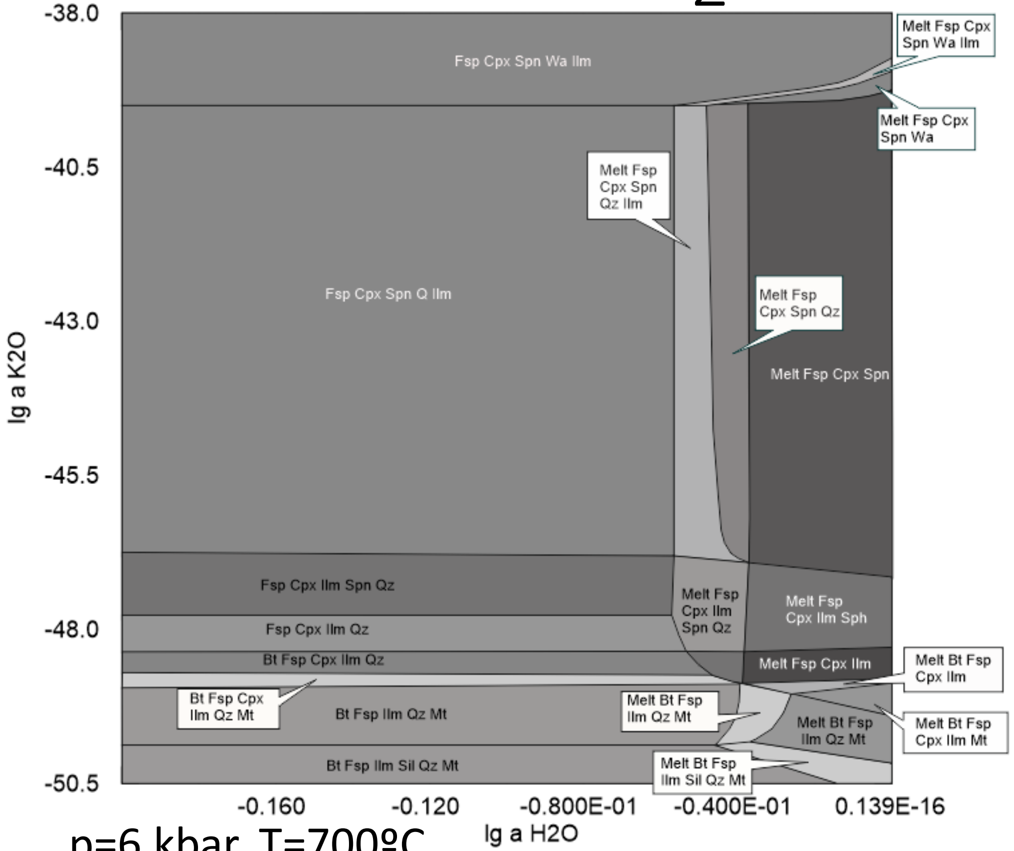
Cpx + Kfs + Sph is stable over a wide range of temperatures and pressures. In order to narrow the P-T range of formation of this association, isopleths of Mg# and Na content (f.u.) in clinopyroxene, the major Fe-Mg rock-forming mineral of syenites, were calculated.

Calculations for sample SAF12-6-1 showed that this association corresponds to a temperature range of 780-830^{o}C and pressures of 5-9 kbar.

The estimated temperatures and pressures are close to those estimated by *Rigby et al. (2008)* for amphibole-containing metasomatic veins in the syenite massif (6.4 ± 0.6 kbar, 770°C). However, the values obtained by us slightly higher than those obtained by *Rigby et al*. We suggest that higher temperatures correspond to crystallization conditions of the primary magmatic assemblage Cpx + Kfs + Spn ± Ap, whereas amphibole-bearing assemblages appeared during cooling of the syenite magma.

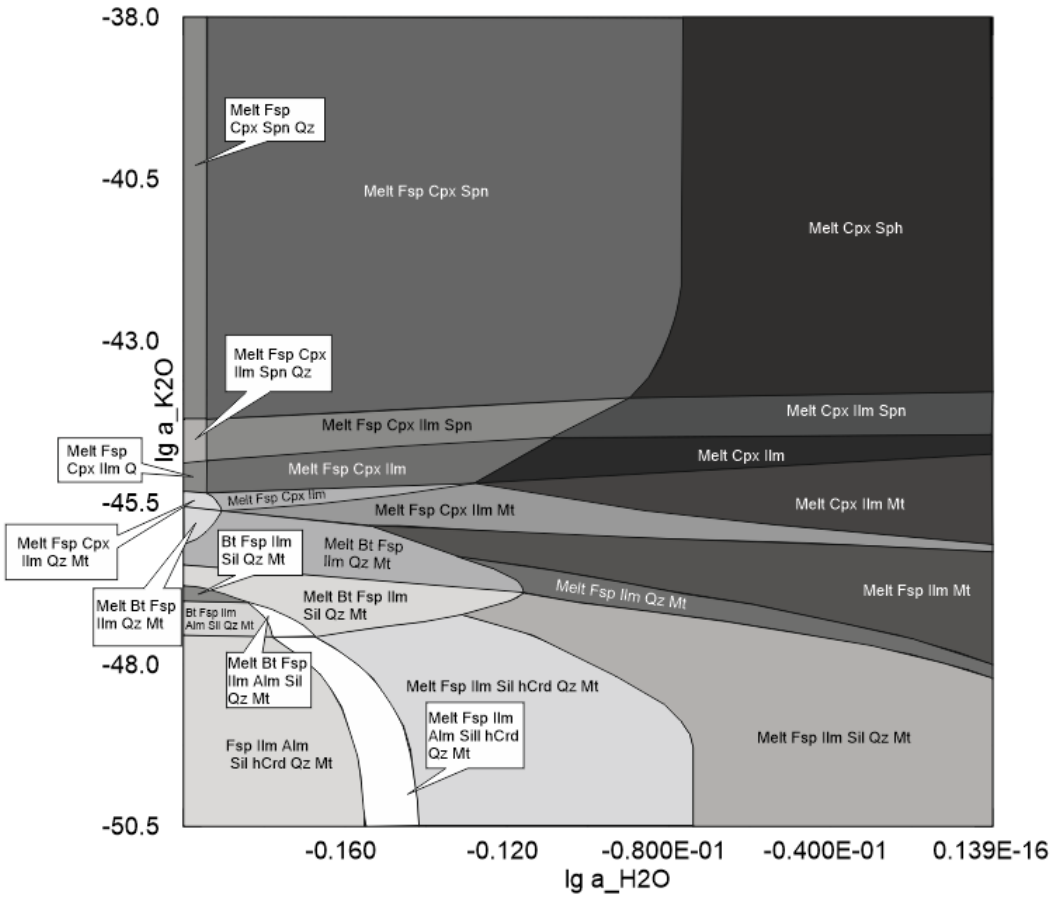
Effect of K_2O activity on gneiss

- The appearance of the syenite assemblages is triggered by an increase of the K activity.
- Reactions resulting in the transformation of the tonalite gneiss into the syenite are more dependent on the activity of alkalis than on the H_2O activity.



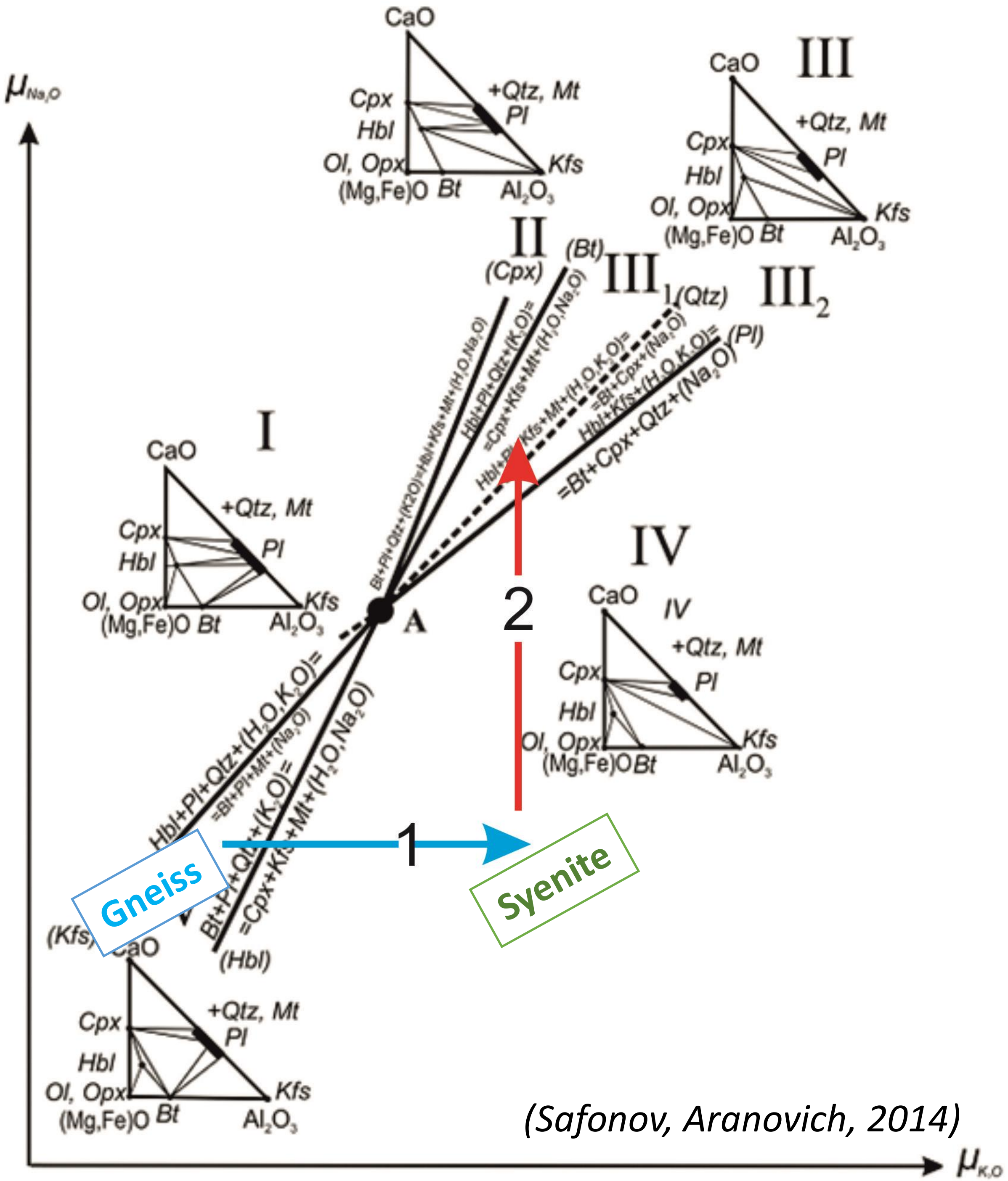
p=6 kbar, T=700ºC

The basis of this study is the results of experiments on interaction of tonalite gneiss with H_2O-CO_2-(K,Na)Cl fluids at 750 and 800ºC and 5.5 kbar (Safonov et al., 2012, 2014), which showed that the main factor in the formation of the syenite association from the initial tonalite gneiss was an increase in potassium activity of the fluid.



p=6 kbar, T=800ºC

Justification of the observed assemblages (Schreinemakers analysis)



(Safonov, Aranovich, 2014)

- Cpx+Kfs corresponds to the maximum μ_{K2O}
- μ_{K2O} plays a decisive role in the formation of this paragenesis
- an increase in μ_{Na2O} leads to stabilization of the amphibole-bearing assemblages

Experiment

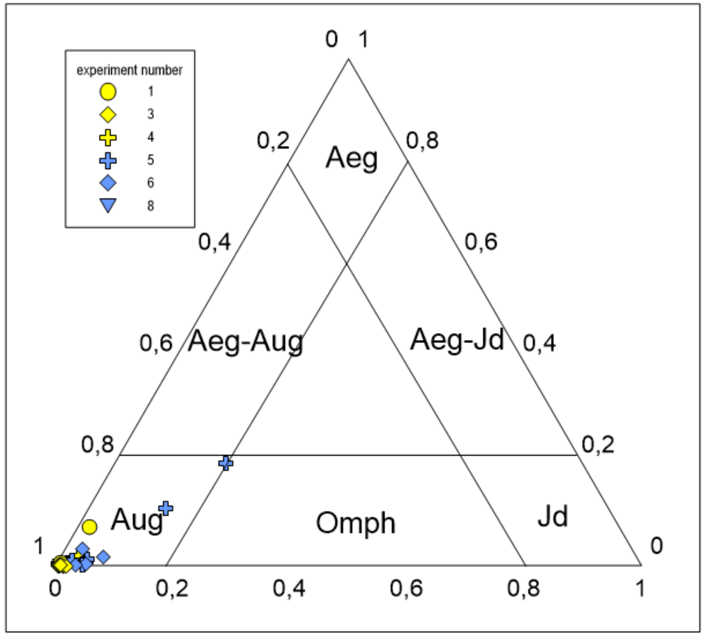
Run	Salt	Salt / oxalic acid ratio	X_{salt}	H_2O in glass, wt. %	Mineral assemblage
1	KCl	1:10	0,100	1,85	Pl+Bt+Q+glass+Cpx+Ttn+Ap+Zrn+Ilm
2	KCl	1:30	0,033	0,97	Pl+glass+Bt+Q+Ilm+Ttn
3	KCl	1:50	0,020	3,27	Pl+Bt+Q+glass+Cpx+Opx+Ilm
4	KCl	1:70	0,014	2,34	Pl+Bt+Q+glass+Cpx+Ilm
5	NaCl	1:10	0,100	1,87	Pl+glass+Q+Cpx+Amp+Bt+Ttn+Ilm
6	NaCl	1:30	0,033	2,36	Pl+glass+Cpx+Bt+Ttn+Ilm
7	NaCl	1:50	0,020	3,95	Pl+glass+Q+Bt+Cpx+Ilm
8	NaCl	1:70	0,014	2,82	Pl+glass+Q+Cpx+Ilm+Ap

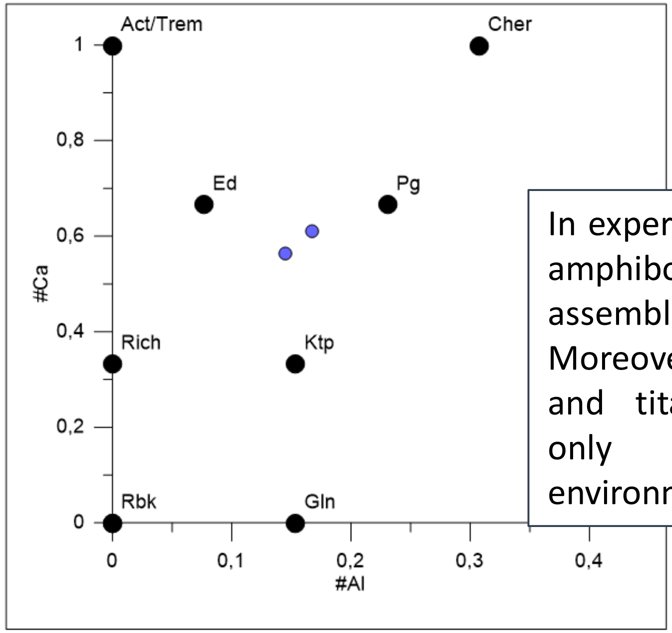
Bt + 3An (in Pl) + 18Q + 3 (K_2O) = 3Cpx + 7Kfs + (H_2O)
(Safonov et al, 2012)

The experiments reproduced the Cpx + Ttn assemblages formation from reactions of biotite, quartz, and plagioclase in presence of alkaline fluid. At the given temperature, the Cpx + Ttn assemblage coexists with a melt of the syenite composition, relatively enriched in F, Cl, H_2O. This is consistent with the proposed syenitization model.

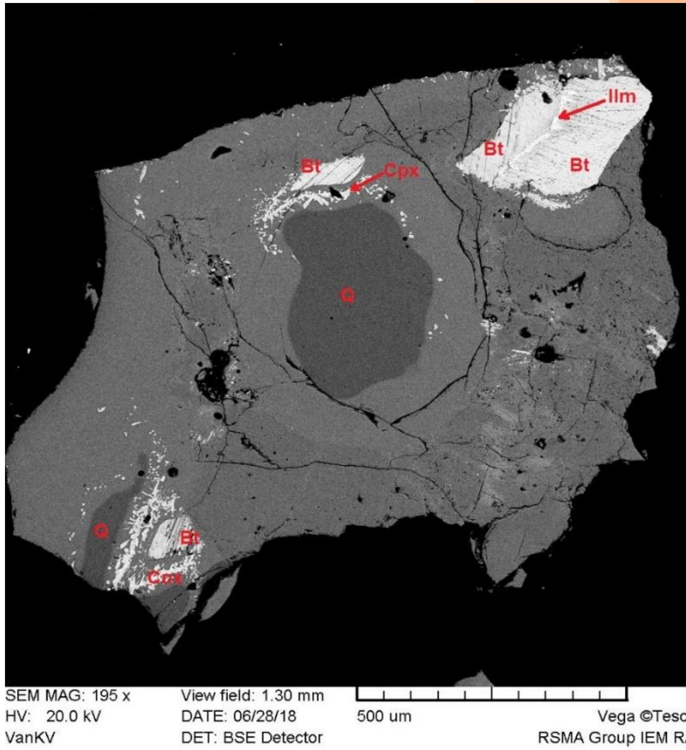
SiO2	TiO2	Al2O3	Cr2O3	MgO	FeO	MnO	CaO	K2O	Na2O	F	Cl
66,33	0,20	16,43	0,02	0,16	0,67	0,04	1,50	5,68	4,50	0,22	0,10

Average composition of glass (melt)





In experiments with NaCl, an amphibole-bearing assemblage was reproduced. Moreover, both amphibole and titanite are observed only in the salt-rich environments.

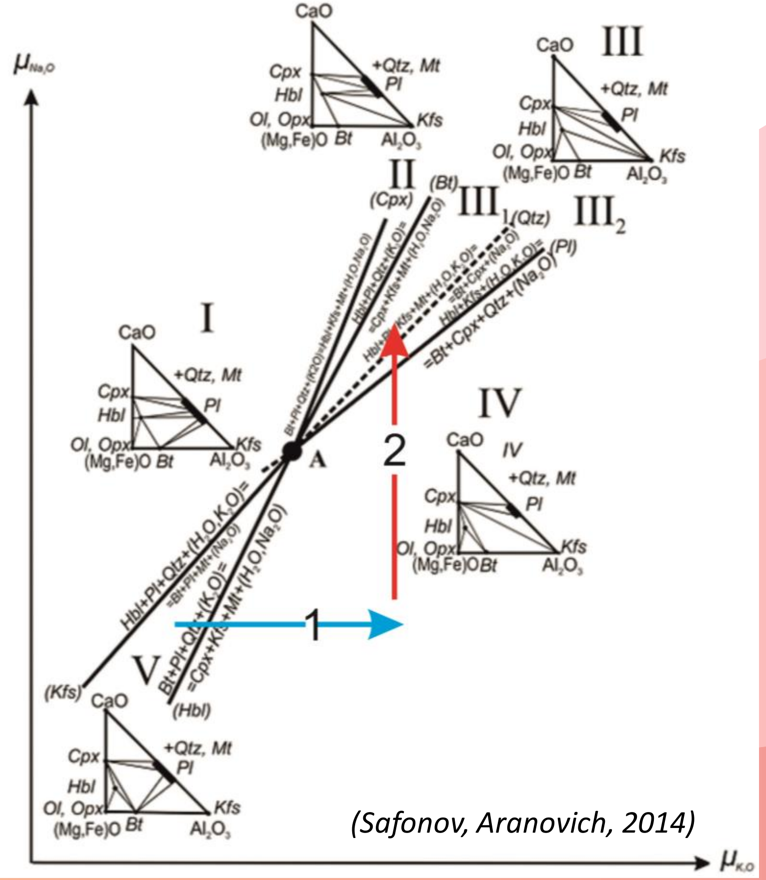


Products of the run 3

Conclusions

1. Madiapala syenites were formed during the Paleoproterozoic tectonic-metamorphic event D3/M3 (2.01 Ga) as products of the interaction of the Alldays TTG with H_2O-CO_2-salt fluids, which imposed high activity of alkaline (primarily, K) components.

2. Two stages of the evolution of the Madiapala massif are distinguished:
   - the early stage at 800-850ºC was characterized by an increase of the chemical potential of K in fluids interacting with the tonalite gneisses and caused the formation of the Cpx + Kfs + Sph ± Ap assemblages of the syenites.
   - the later stage was characterized by an increase of the chemical potential of Na, which led to the formation of the amphibole-bearing assemblages in the syenites during cooling of the magma down to temperatures below 700ºC.



(Safonov, Aranovich, 2014)

Thank you for your attention!