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Apatite and clinopyroxene as tracers for metasomatic processes in nepheline clinopyroxenites of Uralian-Alaskan-type complexes in the Ural Mountains, Russian Federation

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Abstract

Clinopyroxene and apatite are found to trace metasomatic processes in nepheline-bearing clinopyroxenites (tilaite) from the igneous, mafic–ultramafic Uralian-Alaskan-type complexes of Kytlym and Nizhny Tagil, Ural Mountains, Russian Federation. The clinopyroxenites consist predominantly of coarse-grained, partially to totally altered clinopyroxene phenocrysts in a matrix of fine-grained olivine, clinopyroxene, plagioclase, K-feldspar, and nepheline. Apatite occurs as idiomorphic inclusions (<25 µm) in the clinopyroxene and as xenomorphic grains in the matrix.

In the matrix, plagioclase is partially to totally replaced by a fine-grained symplectitic intergrowth of K-feldspar and nepheline most likely due to the influx of an K₂O-, Na₂O-, and Al₂O₃-bearing fluid. During conversion of the plagioclase, CaO and SiO₂ were partitioned into the fluid. Altered areas in the clinopyroxene phenocrysts are characterized by the redistribution of major and trace elements. This includes depletion in Mg, Rb, and Sr and enrichment in Al, Na, Ba, U, Th, REE except Eu, and HFSE compared to the original magmatic areas in the clinopyroxene. Apatite inclusions in the altered areas of the clinopyroxene and in the matrix are enriched in Cl relative to apatite inclusions in the unaltered areas of clinopyroxene.

It is proposed that these rocks experienced a two-stage metasomatic process. Stage 1 was the partial to total alteration of plagioclase to K-feldspar and nepheline due to interaction with an infiltrating (K,Na)Cl-rich brine (most likely late magmatic) with an Al component, which enriched the fluid in CaCl₂. Stage 2 consisted of the partial to total chemical alteration of the original magmatic clinopyroxene by this now CaCl₂-enriched fluid through the mechanism of coupled dissolution–reprecipitation. This process also chemically altered the apatite inclusions from fluor-chlorapatite to chlor-fluorapatite and redistributed as well as partially removed the titanomagnetite inclusions in the altered areas. This is supported experimentally by the fact that alteration of fluorapatite to Cl-rich apatite can only take place in the presence of CaCl₂-bearing fluids and by the fact that in general Fe and Ti, along with most metal cations, are relatively mobile in Cl-rich fluids.

If this scenario is correct, the implications from this study are that inclusions of one mineral in a host mineral can be chemically overprinted during metasomatic alteration of the host mineral. While at the same time the original crystal shape and orientation of both the host phase as well as that of the inclusions are preserved.

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1. INTRODUCTION

Fluid-aided, pseudomorphic replacement or chemical alteration of minerals is a common phenomenon in metamorphic and igneous rocks. Minerals for which this has been documented include feldspar (Putnis et al., 2007; Plümper and Putnis, 2009; Niedermeier et al., 2009; Hövelmann et al., 2010; Norberg et al., 2011), fluorapatite (Harlov and Förster, 2003; Harlov et al., 2005), chlorapatite (Harlov et al., 2002a), garnet (Röhr et al., 2007), zircon (Geisler et al., 2007), and monazite (Hetherington et al., 2010; Harlov and Hetherington, 2010; Harlov et al., 2011) to name some recent examples (see also Putnis, 2002, 2009).

One characteristic of this fluid-aided alteration is the growth of new mineral phases as inclusions in the metasomatically altered areas of the host mineral phase. For example, monazite and/or xenotime inclusions have been widely documented in metasomatised fluor- and chlorapatite in metamorphic rocks (Harlov and Förster, 2002, 2003; Hansen and Harlov, 2007) as well as in some types of igneous rocks (Harlov et al., 2002a,b). In either case, inclusion formation has been directly linked to alteration of the original apatite triggered by external fluids. This interpretation is supported by experiments (Harlov et al., 2002a, 2005; Harlov and Förster, 2003). Similar inclusion growth is also observed in feldspars metasomatised by (Na,K,Ca)-bearing brines (Putnis et al., 2007) and again has been documented experimentally (Norberg et al., 2011). Regions of the mineral affected by fluid-aided alteration are characterized by a pervasive, inter-connected micro- and nano-porosity, which allow fluids to infiltrate. At the same time the micro- and nano-pores provide nucleation sites for the growth of mineral inclusions. Whether or not nucleation and inclusion growth will occur is highly dependent on the level of reactivity between the fluid and the host and included mineral (cf. Harlov et al., 2002a, 2005; Harlov and Förster, 2003; Putnis et al., 2007). So far, however, the effect fluids may have regarding the chemical alteration of pre-existing mineral inclusions in areas of the host mineral chemically being altered by these same fluids has not been widely discussed in the literature.

In this study, clinopyroxene phenocryst-bearing samples are taken from nepheline clinopyroxenites associated with two Uralian-Alaskan-type complexes, Nizhnii Tagil and Kytlym, Ural Mountains, Russian Federation. These samples are investigated using scanning electron microscopy (SEM), electron microprobe (EMP) analysis, laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), cathode luminescence (CL), and Raman spectroscopy. Partial chemical alteration of the clinopyroxene and accompanying apatite inclusions is explained as a two-stage process. During the first stage plagioclase in the matrix is replaced by a symplectitic intergrowth of K-feldspar and nepheline due to the infiltration of a (K,Na)Cl-rich fluid. Conversion of the plagioclase enriches the fluid in Ca. In the second stage the now Ca-enriched fluid reacted with the clinopyroxene causing the partial chemical alteration of the host clinopyroxene and the apatite inclusions within the altered areas. Element distribution maps combined with

textural observations and the chemical analysis of mineral phases allow for a quantitative description of the replacement processes.

2. GEOLOGIC BACKGROUND

Uralian-Alaskan-type complexes or zoned mafic-ultramafic complexes are recognized as a distinctive class of mafic-ultramafic intrusions with respect to their tectonic setting, internal structure, petrology and geochemistry (e.g. Taylor and Noble, 1960; Noble and Taylor, 1960; Irvine, 1963; Himmelberg et al., 1986; Himmelberg and Loney, 1995; Pertsev et al., 2000; Batanova et al., 2005; Krause et al., 2007, 2011). These complexes are described from convergent margin settings, for example the Cordillera of Alaska and British Columbia (e.g. Taylor and Noble, 1960; Irvine, 1963; Findlay, 1969; Himmelberg et al., 1986; Nixon et al., 1990; Himmelberg and Loney, 1995), on Northern Kamchatka, Russia (e.g. Astrakhantsev et al., 1991; Batanova and Astrakhantsev, 1992; Batanova et al., 2005) and in the Ural Mountains, Russia (e.g. Levinson-Lessing, 1900; Wyssotzky, 1913; Duparc and Tikhonovitch, 1920; Noble and Taylor, 1960; Efimov and Efimova, 1967; Taylor, 1967; Efimov, 1977; Pertsev et al., 2000; Krause et al., 2007). In addition ultramafic dunite-clinopyroxenite complexes are described from within-plate geological settings in the Aldan Shield, Siberia, where they intrude the platform cover (e.g. Efimov and Tavrín, 1978; Burg et al., 2009).

In convergent margin settings like in the Cordillera of Alaska and British Columbia, on Kamchatka, and in the Ural Mountains the intrusions are aligned along narrow belts several hundreds of kilometers long. They are characterized by the zonal distribution of mafic and ultramafic rocks where a central dunite body grades outward into wehrlite, clinopyroxenite, and gabbroic lithologies and the almost complete absence of orthopyroxene-bearing rocks. Some of these complexes host a chromite-PGE mineralization.

Fifteen Uralian-Alaskan-type mafic-ultramafic complexes form a 900 km long linear belt along the 60th meridian in the Ural Mountains (Fig. 1a), the so-called “Ural platinum belt” (UPB). This belt is situated eastward of the Main Uralian Fault (MUF). It is delineated by a serpentinite-ophiolite melange, which is interpreted to trace the paleo-subduction zone of the Tagil island-arc system (Ivanov and Shmelev, 1996). Precambrian sedimentary and volcanic formations of the East-European platform occur immediately westward from the MUF. The massifs are rimmed by Ordovician and Silurian island-arc basic volcanic rocks of the Tagil zone from the east and partly in the south and north. Many of the mafic and ultramafic bodies have a narrow rim of high-grade contact metamorphic rocks. Together, with these rims, the mafic-ultramafic complexes have low temperature tectonic contacts with the surrounding greenschist-facies island-arc rocks. The composition of exsolved spinels in mafic and ultramafic rocks from Kytlym and Nizhnii Tagil indicate that: (i) irrespective of their composition all rocks were thermally equilibrated at temperatures of around 600 °C and (ii) both complexes share a similar subsolidus thermal history

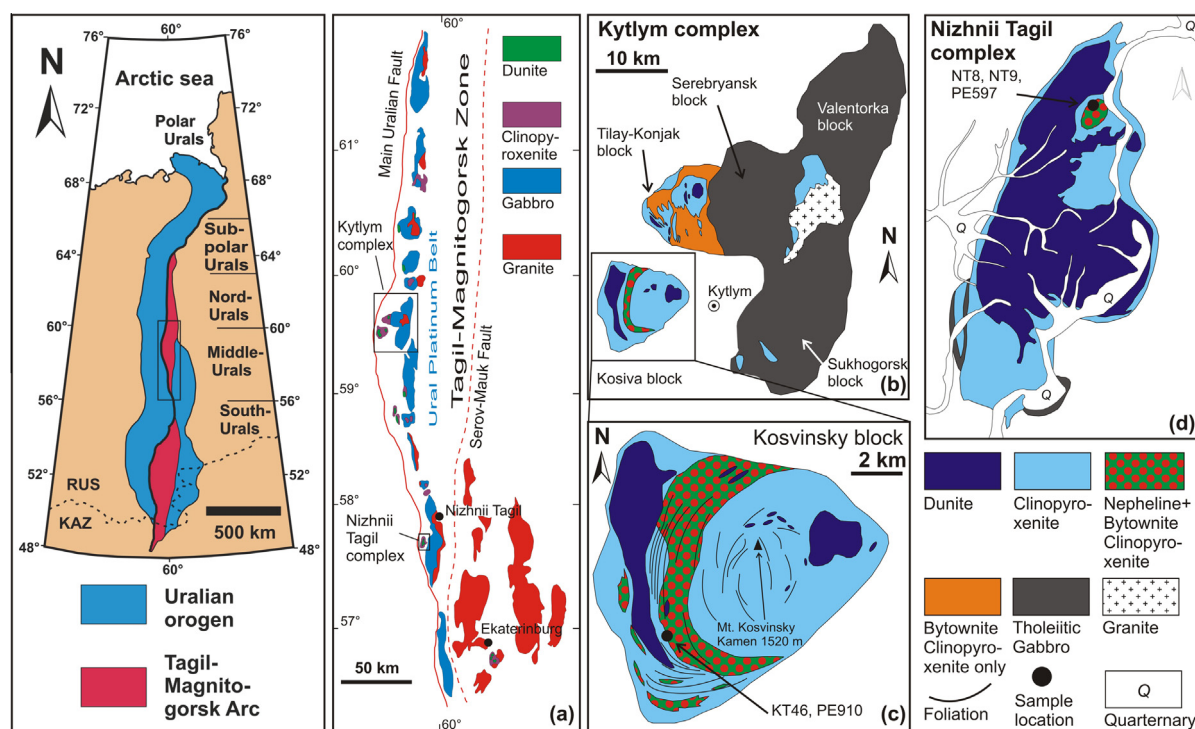


Fig. 1. Geological maps of the Ural platinum belt (a) and the Uralian-Alaskan type complexes of Kytlym (b,c) and Nizhnii Tagil (d). Geological maps are modified after Brown et al. (2006), Ivanov (1997) and Efimov and Efimova (1967).

(Krause et al., 2011). This is interpreted to reflect the thermal conditions present at the time of the intrusion.

In this study nepheline clinopyroxenites, from two Uralian-Alaskan-type complexes, Nizhnii Tagil and Kytlym, are investigated (Fig. 1). The Nizhnii Tagil Complex consists primarily of a dunite core bounded by a narrow rim of clinopyroxenite (Fig. 1c). Narrow zones of wehrlite are often developed at the contact between the dunite and clinopyroxenite (e.g. Efimov and Efimova, 1967; Savelieva et al., 1999, 2002). Mafic rocks are found in the northern part of the complex along the Zotikha and Chauzh rivers (Fig. 1d). The Kytlym Complex is a large, composite intrusive complex of mafic and ultramafic rocks (Fig. 1b). The Kosvinsky ultramafic block occurs at the southwestern edge of the Kytlym Complex. It consists of dunite, clinopyroxenite, and mafic rocks, which comprise the classic lithological association of Uralian-Alaskan-type complexes (Fig. 1c).

Some clinopyroxene-rich ultramafic rocks in Nizhnii Tagil and the western parts of the Kytlym Complex contain varying amounts of feldspar and nepheline grading into a nepheline monzonite. Similar rocks have been described from Uralian-Alaskan-type complexes in Alaska and British Columbia (Findlay, 1969; Himmelberg et al., 1986; Hammack et al., 1991; Himmelberg and Loney, 1995) and Kamchatka (e.g. Astrakhantsev et al., 1991; Kepezhinskas et al., 1993a,b; Batanova et al., 2005). These have previously been referred to as “tilaites” by Duparc and Tikhonowitch (1920). According to IUGS nomenclature (Gillespie and Styles, 1999) they are properly termed nepheline clinopyroxenites. Whole-rock geochemical analyses suggest that they crystallized from an alkaline, silica-under saturated

parental melt in a subduction-related geotectonic setting (Krause, 2008).

Five nepheline clinopyroxenite samples have been investigated for this study; NT8, NT9b, and PE597 from the northern part of the Nizhnii Tagil complex and KT46 and PE910 from the Kosvinsky block in the south western part of the Kytlym complex.

3. ANALYTICAL METHODS

3.1. Scanning electron microscopy (SEM), electron microprobe (EMP) analysis, and element mapping

High Resolution SEM images were obtained from the uncoated sample NT9b with the LEO 1530 high-resolution field emission scanning electron microscope of the Max Planck Institute for Chemistry. An acceleration voltage of 2.5 or 5.0 kV, beam current of ~20 pA, and a working distance of 2.8 mm were used. Additional SEM images were taken with the BSE detector on the FEI Quanta 600 at the Institute for Mineralogy Technische Universität Bergakademie Freiberg, Germany. An acceleration voltage of 25 kV, beam current of ~300 µA, and a working distance of 10.8 mm were used.

Polished thin sections 30 or 150 µm thick were used for analysis. Minerals were analyzed for major elements with the Jeol JXA8200 microprobe of the Max Planck Institute for Chemistry and the Jeol JXA 8900RL microprobe at the Institute of Geosciences of the University of Mainz. Natural minerals and oxides were used for calibration. Details on the standards used for calibration, measurement conditions, and the detection limits can be found in

Electronic annex EA-1. The clinopyroxenes were analyzed with an acceleration voltage of 20 kV, a probe current of 12 or 20 nA and either a focussed beam ($<1\ \mu\text{m}$) or a beam diameter of $2\ \mu\text{m}$. Fluor-chlorapatite, feldspars, and nepheline, were analyzed at an acceleration voltage of 15 kV and beam currents of 8 or 12 nA. Beam diameters varied between 1 and $5\ \mu\text{m}$. Counting times for all minerals varied between 20 and 80 s on the peak and 10–40 s on the background. Instrument drift during the analysis was corrected, if necessary, with repeated measurements of mineral standards.

Element maps of clinopyroxene were obtained with the Jeol JXA 8900RL microprobe at the Institute of Geosciences of the University of Mainz at 20 kV and 15 nA with a beam diameter of $5\ \mu\text{m}$. Chromium, Na, Al, Fe and Ti were measured with WDS spectrometers. Calcium, Mg, and Si were measured using an EDS spectrometer at counting times between 120 and 155 ms. The step size varied between 5 and $7\ \mu\text{m}$. Feldspars were mapped with both instruments. Larger sample areas (several mm in length and width) were mapped at 15 kV and 55–65 nA with a beam diameter of 2 or $5\ \mu\text{m}$, a dwell time of 20 ms and a step size between 5 and $20\ \mu\text{m}$. Detailed maps of selected feldspars were obtained at 15 kV and 30 nA using a beam diameter and step size of $1\ \mu\text{m}$ and a dwell time of 200 ms. In all cases the intensities of K, Na, Ca, Al, and Si were recorded with WDS spectrometers. Area fractions of feldspar and nepheline were calculated from gray scale converted element maps using the image analysis software ImageJ® (Abramoff et al., 2004).

3.2. Cathode luminescence imaging

Colored cathodoluminescence (CL) images were obtained with the HC1-LM cathodoluminescence microscope at the Institute of Geosciences, University of Bochum, Germany in collaboration with R.D. Neuser. Because of the beam geometry of the instrument used, only thin sections with a thickness of $30\ \mu\text{m}$ could be used for the colored CL. For comparison CL images of the $150\ \mu\text{m}$ thick sections were taken with a CL detector attached to the electron microprobe at the University of Mainz.

3.3. Confocal Raman spectroscopy

Confocal Raman spectroscopy on selected apatites was done using a Horiba Jobin Yvon LabRAM HR 800 Spectrometer at the Institute of Geosciences at the University of Mainz. The 488 nm line of a Ar-Ion Laser was used for excitation. The beam diameter was set to ca. $2\ \mu\text{m}$ and 950 lines per mm were measured. The confocal hole size was set to $100\ \mu\text{m}$ and an objective with a magnification of 50 was used. Data acquisition and spectra background subtraction were carried out using the LabSpec Software.

3.4. LA-ICP-MS (laser ablation – inductively coupled plasma mass spectrometry)

A New Wave UP193 system containing a Nd:YAG laser with 193 nm wavelength at the Max Planck Institute for Chemistry was used to determine the trace element concentrations in the clinopyroxene, nepheline and feldspars (Krause, 2008). Application of a frequency of 10 Hz and fluences between 2 and $8\ \text{J}/\text{cm}^2$, measured with the internal power meter of the UP193, produced ablation pits with diameters between 50 and $80\ \mu\text{m}$. Helium was used as the carrier gas. The ablated material was analyzed with a ThermoFinnigan Element2 sector field ICP-MS in the low resolution mode and a counting time of 20 s on the background and 80–100 s on the sample. NIST612, KL2-G, and GOR132-G glasses were used for calibration and to monitor the instrument drift during analysis. Data reduction was performed using a programmed Microsoft Excel spreadsheet. Blank-corrected count rates were calculated relative to the internal standard (^{43}Ca and ^{29}Si) in order to compensate for the intensity decrease during the ablation. The Excel routine also rejects obvious outliers.

The detection limit varies between 0.2 and 2 ppb for REE, U, Th, Hf, and Ta, between 2 and 20 ppb for Ba, Pb, Nb, Zr, and Y, and between 100 and 200 ppb for Rb and Sr. According to Jochum et al. (2006) the total analytical uncertainty is less than 5%. The analytical procedure is described in detail by Jochum et al. (2006, 2007).

EMP and LA-ICP-MS analyses (550 fluor-chlorapatite, 591 Feldspars, 146 feldspathoids, and 65 clinopyroxene) are

Table 1a
Mean plagioclase compositions (wt.%).

Sample	Locality	# anal	SiO ₂	Al ₂ O ₃	FeO	CaO	BaO	SrO	Na ₂ O	K ₂ O	Total	X_{An}	X_{Ab}	X_{Or}
NT8	Nizhnii Tagil	30	59.31 <i>0.71</i>	24.93 <i>0.38</i>	0.09 <i>0.04</i>	6.21 <i>0.58</i>	0.05 <i>0.02</i>	0.09 <i>0.04</i>	7.59 <i>0.27</i>	0.28 <i>0.23</i>	98.55	0.306	0.678	0.017
NT9b	Nizhnii Tagil	97	58.62 <i>1.47</i>	25.86 <i>1.06</i>	0.07 <i>0.03</i>	7.08 <i>1.20</i>	0.06 <i>0.02</i>	0.27 <i>0.05</i>	7.39 <i>0.62</i>	0.17 <i>0.08</i>	99.53	0.343	0.647	0.010
PE597	Nizhnii Tagil	1	57.17	27.05	0.06	8.54	0.04	0.15	6.88	0.27	100.16	0.401	0.584	0.015
KT46	Kytlym	66	59.24 <i>0.64</i>	25.51 <i>0.86</i>	0.15 <i>0.07</i>	6.67 <i>0.75</i>	0.06 <i>0.03</i>	0.11 <i>0.04</i>	6.87 <i>0.33</i>	0.76 <i>0.23</i>	99.37	0.333	0.621	0.045
PE910	Kytlym	131	56.17 <i>2.12</i>	27.23 <i>1.51</i>	0.12 <i>0.05</i>	8.84 <i>1.72</i>	0.07 <i>0.04</i>	0.48 <i>0.05</i>	5.86 <i>0.85</i>	0.75 <i>0.33</i>	99.52	0.435	0.521	0.044

1 σ – standard deviation in italics. Blank – analyzed for but not detected.

Table 1b
Mean K-feldspar compositions (wt.%).

Sample	Locality	# anal	SiO ₂	Al ₂ O ₃	FeO	CaO	BaO	SrO	Na ₂ O	K ₂ O	Total	X _{An}	X _{Ab}	X _{Or}
NT8	Nizhnii Tagil	51	63.66 <i>4.80</i>	19.37 <i>3.26</i>	0.12 <i>0.10</i>	0.70 <i>0.34</i>	0.32 <i>0.11</i>	0.17 <i>0.08</i>	2.92 <i>3.03</i>	11.64 <i>1.96</i>	98.90	0.035	0.265	0.700
NT9b	Nizhnii Tagil	75	64.05 <i>0.68</i>	19.15 <i>0.31</i>	0.13 <i>0.20</i>	0.61 <i>0.22</i>	0.27 <i>0.12</i>	0.10 <i>0.05</i>	2.54 <i>0.64</i>	12.34 <i>0.98</i>	99.18	0.030	0.231	0.739
PE597	Nizhnii Tagil	51	63.79 <i>0.33</i>	19.40 <i>0.22</i>	0.14 <i>0.20</i>	0.50 <i>0.16</i>	0.41 <i>0.09</i>	0.44 <i>0.08</i>	1.66 <i>0.47</i>	13.67 <i>0.80</i>	100.01	0.025	0.152	0.823
KT46	Kytlym	51	63.63 <i>0.69</i>	18.89 <i>0.46</i>	0.36 <i>0.28</i>	0.34 <i>0.13</i>	0.33 <i>0.11</i>	0.20 <i>0.09</i>	0.97 <i>0.35</i>	14.67 <i>0.42</i>	99.40	0.017	0.089	0.893
PE910	Kytlym	38	62.93 <i>0.58</i>	19.36 <i>0.37</i>	0.31 <i>0.35</i>	0.33 <i>0.19</i>	0.37 <i>0.23</i>	0.60 <i>0.24</i>	0.40 <i>0.26</i>	15.68 <i>0.73</i>	99.98	0.017	0.036	0.947

1σ – standard deviation in italics.

Table 1c
Mean Nepheline and Kalsilite compositions (wt.%).

Sample	Locality	# anal	SiO ₂	Al ₂ O ₃	FeO	CaO	BaO	SrO	Na ₂ O	K ₂ O	Total	X _{Ne}	X _{Ks}
NT8	Nizhnii Tagil	33	42.94 <i>0.37</i>	33.24 <i>0.25</i>	0.09 <i>0.04</i>	1.07 <i>0.82</i>	0.05 <i>0.02</i>	b.d.	15.79 <i>0.48</i>	5.66 <i>0.20</i>	98.85	0.809	0.191
NT9b	Nizhnii Tagil	35	43.27 <i>0.44</i>	33.35 <i>0.28</i>	0.11 <i>0.04</i>	1.20 <i>0.47</i>	0.05 <i>0.01</i>	b.d.	15.70 <i>0.33</i>	5.33 <i>0.40</i>	99.02	0.817	0.183
PE597	Nizhnii Tagil	42	42.76 <i>0.45</i>	34.25 <i>0.26</i>	0.15 <i>0.10</i>	1.33 <i>0.13</i>	0.05 <i>0.02</i>	0.05 <i>0.01</i>	15.52 <i>0.31</i>	5.54 <i>0.33</i>	99.66	0.810	0.190
KT46	Kytlym	33	43.12 <i>0.37</i>	33.51 <i>0.39</i>	0.39 <i>0.28</i>	1.66 <i>0.28</i>	0.05 <i>0.02</i>	b.d.	15.18 <i>0.25</i>	5.31 <i>0.22</i>	99.24	0.813	0.187
PE910	Kytlym	3	38.56 <i>0.06</i>	32.16 <i>0.25</i>	0.08 <i>0.03</i>	0.14 <i>0.16</i>	b.d.	0.06 <i>0.01</i>	0.09 <i>0.08</i>	29.06 <i>0.12</i>	100.15	0.005	0.995

1σ – standard deviation in italics, b.d. – below detection limit.

located in [Electronic annex EA-2](#). Mean EMP analyses for feldspars, feldspathoids, and fluor-chlorapatite, are given in [Tables 1a–c, and 3](#), respectively. Selected EMP- and LA-ICP-MS analyses of clinopyroxene are given in [Table 2](#).

4. PETROLOGY, MINERAL TEXTURES AND MINERAL CHEMISTRY

The principal textural feature of the nepheline clinopyroxenites is a hypidiomorphic granular texture, which is dominated by idiomorphic clinopyroxene phenocrysts up to 10 mm in diameter in a finer-grained matrix of clinopyroxene, olivine, plagioclase, K-feldspar, nepheline (all samples except PE910, which has kalsilite instead), and biotite. K-feldspar is sometimes restricted to small grains filling the pore space between the other phases (sample PE910). Accessory phases include apatite and spinel group minerals intergrown with ilmenite. These rocks are interpreted to represent orthocumulates ([Krause, 2008](#)).

A foliation is often present and can lead to a texture with alternating feldspar-nepheline and clinopyroxene-olivine-spinel-feldspar layers (sample NT9b). Occasionally the long axis of the clinopyroxene phenocrysts are oriented parallel to the foliation plane, probably reflecting an early flow texture produced by flow-banding during crystal settling.

Except for weak undulose extinction, clinopyroxene in these samples does not indicate intra-crystalline deformation or recrystallization. Feldspars often show signs of solid-state deformation including deformation lamellae in plagioclase, undulose extinction, and dynamic recrystallization. In sample NT9b, the feldspars have a lattice-preferred orientation.

The most conspicuous texture in the matrix of the nepheline clinopyroxenites is the presence of a fine-grained, symplectitic intergrowth of nepheline and K-feldspar partially to totally replacing plagioclase ([Fig. 2](#), Sample NT 9b). Plagioclase often has lobate, irregular grain boundaries with these intergrowths ([Fig. 2c](#) and [d](#)), while larger K-feldspar and nepheline grains maintain their idiomorphic to hypidiomorphic zonation ([Fig. 2e](#) and [f](#)). Under CL imaging, K-feldspar often shows a bright, idiomorphic, luminescent core (first generation) surrounded by a rim with a weaker luminescence. This rim is overgrown with a symplectitic intergrowth of K-feldspar (second generation) and nepheline. The K-feldspar in the symplectites and at the plagioclase rims has the same weak luminescence ([Fig. 2f](#)). Nepheline occurs as two different textural varieties, indicating the presence of two different generations. Hypidiomorphic chemically uniform nepheline grains represent a first generation, while xenomorphic nepheline in

Table 2
Selected analyses of Clinopyroxene (Oxides in wt.%, trace elements in ppm).

Sample	NT9b-750	NT9b-754	NT9b-765	NT9b-771	NT9b-701	NT9b-710	NT9b-727	NT9b-716	NT9b-723	NT9b-720			
Position	M	M	M	M	Po	Po	Po	Pm	Pm	Pm	Average M	Average Po	Average Pm
SiO ₂ (wt.%)	50.98	50.89	50.96	52.65	50.16	50.56	51.25	51.13	52.48	50.79	51.53	50.58	51.62
Al ₂ O ₃	5.47	6.53	5.56	4.08	5.65	5.49	5.58	3.90	3.81	3.81	4.98	5.45	4.14
Cr ₂ O ₃	0.06	0.03	b.d.	0.04	0.10	0.05	b.d.	0.08	0.07	0.06	0.05	0.09	0.06
FeO	7.06	6.31	7.24	6.80	6.33	5.96	6.78	5.81	5.80	6.31	6.66	6.35	6.11
MnO	0.19	0.23	0.18	0.17	0.21	0.17	0.24	0.15	0.15	0.12	0.21	0.17	0.17
MgO	12.81	12.25	12.72	13.57	12.61	12.80	12.72	13.68	13.88	14.15	13.08	13.00	13.84
CaO	21.51	21.62	21.67	21.76	21.93	22.98	21.40	23.12	22.99	22.92	21.84	22.60	22.78
Na ₂ O	1.44	1.45	1.29	1.35	1.27	0.84	1.35	0.62	0.70	0.68	1.25	0.96	0.78
Total	99.52	99.31	99.62	100.42	98.27	98.86	99.32	98.48	99.88	98.84	99.59	99.19	99.50
Mg/ (Mg + Fe)	0.76	0.78	0.76	0.78	0.78	0.79	0.77	0.81	0.81	0.80	0.78	0.78	0.80
Rb (ppm)	0.13	1.49	1.97	1.28	b.d.	0.04	0.86	b.d.	b.d.	b.d.	1.37	0.17	0.22
Ba	b.d.	0.04	b.d.	1.57	0.07	0.19	b.d.	0.04	0.06	0.08	1.46	0.33	0.11
Th	1.74	1.67	2.62	1.17	1.36	0.47	1.65	0.18	0.42	0.20	1.45	0.92	0.45
U	0.28	0.25	0.35	0.21	0.25	0.21	0.29	0.11	0.15	0.09	0.26	0.24	0.14
Pb	1.20	1.03	1.19	1.14	0.87	0.84	1.24	0.48	0.51	0.45	1.14	0.87	0.60
Nb	0.84	0.78	1.45	0.40	0.71	0.22	0.86	0.11	0.17	0.09	0.61	0.42	0.18
Ta	0.120	0.123	0.295	0.028	0.058	0.013	0.118	0.005	0.004	b.d.	0.075	0.037	0.010
La	15.16	14.65	20.36	12.90	10.00	6.07	16.06	4.72	4.53	3.69	13.22	8.61	5.19
Ce	44.70	44.24	63.46	35.79	30.21	19.53	47.69	15.74	14.20	12.20	39.21	26.43	16.26
Sr	98.9	89.3	84.8	107.3	243.2	304.6	96.6	330.7	290.7	285.0	165.6	262.4	287.0
Pr	6.66	6.61	9.72	5.25	4.63	3.51	7.12	2.87	2.44	2.22	5.93	4.33	2.79
Nd	28.76	28.82	41.89	22.47	21.37	18.56	30.57	15.15	12.86	11.88	26.48	21.04	14.39
Hf	4.91	3.64	14.73	2.16	2.31	1.78	4.96	1.26	1.07	1.04	3.56	2.24	1.22
Sm	7.06	7.02	10.59	5.67	5.60	5.37	7.50	4.47	3.63	3.50	6.66	5.77	4.13
Zr	201.6	162.1	618.1	85.7	90.3	41.2	201.9	30.0	25.8	23.0	134.4	65.4	29.2
Eu	2.02	2.04	2.07	1.80	1.62	1.69	2.06	1.46	1.21	1.15	1.87	1.75	1.32
Ti	2310	2454	2390	1663	3365	3888	2341	3132	2762	2651	2667	3854	2935
Gd	6.47	6.52	9.89	5.29	5.77	5.38	6.91	4.51	3.79	3.59	6.34	5.75	4.19
Tb	0.89	0.91	1.42	0.73	0.78	0.70	0.98	0.62	0.51	0.51	0.87	0.77	0.57
Dy	4.79	4.69	7.70	3.72	4.14	3.77	5.19	3.16	2.73	2.62	4.65	4.04	2.97
Y	22.7	22.5	38.8	17.2	19.4	16.5	25.1	14.1	12.2	11.6	21.7	18.3	13.3
Ho	0.94	0.91	1.55	0.66	0.78	0.69	1.01	0.59	0.49	0.49	0.89	0.76	0.55
Er	2.55	2.50	4.53	1.88	2.16	1.84	2.79	1.50	1.33	1.25	2.43	2.02	1.44
Tm	0.35	0.36	0.70	0.25	0.30	0.24	0.41	0.20	0.16	0.17	0.34	0.27	0.19
Yb	2.53	2.35	4.84	1.71	2.02	1.52	2.70	1.22	1.12	1.04	2.27	1.75	1.21
Lu	0.37	0.35	0.71	0.25	0.30	0.21	0.40	0.16	0.16	0.15	0.33	0.25	0.17

M – matrix, Po – phenocryst overprinted, Pm – phenocryst magmatic, b.d. – below detection limit.

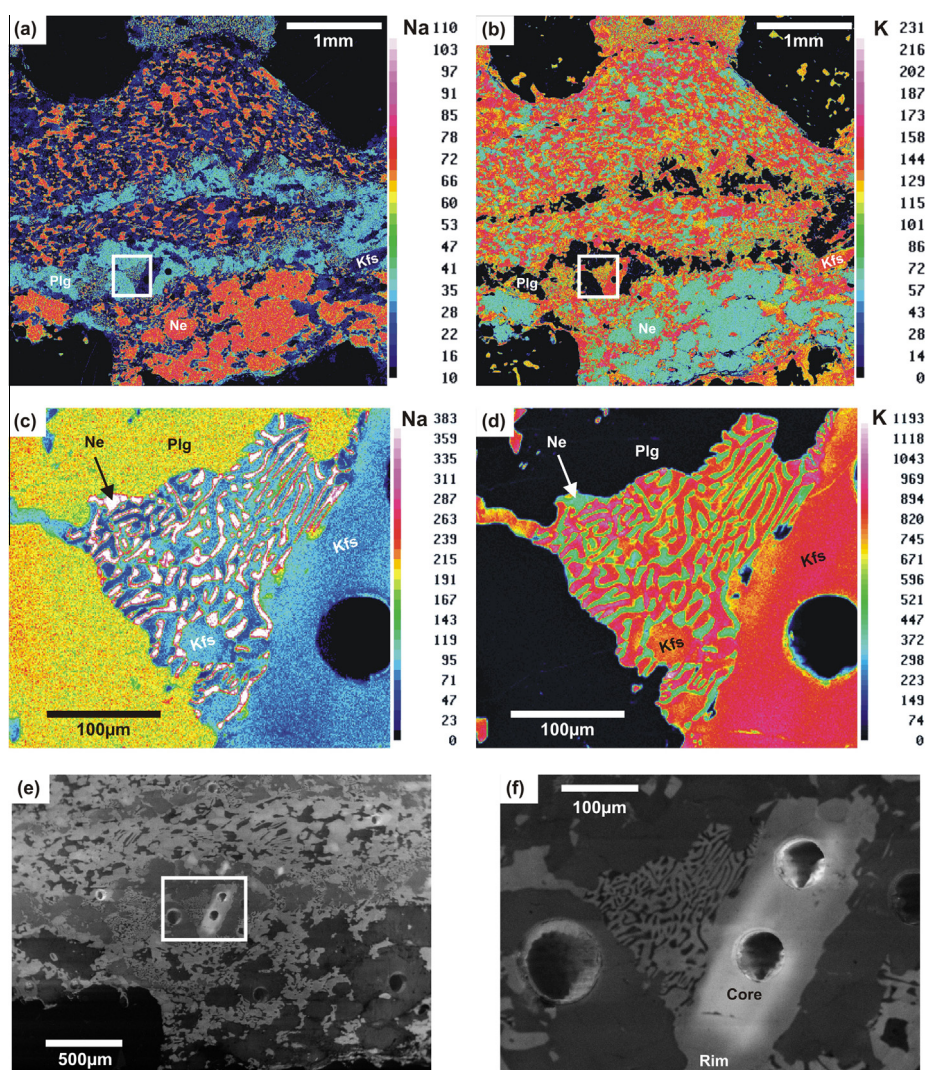


Fig. 2. Reaction textures of feldspar and feldspathoid minerals in a nepheline clinopyroxenite from Nizhnii Tagil (NT9b). X-ray element concentration maps for Na (a) and K (b) showing the mineral distribution in a felsic layer in the nepheline melanogabbro. Enlargement of the boxes in (a) and (b) for the same elements shows the symplectitic intergrowth of nepheline and K-feldspar at the interface between K-feldspar and plagioclase (c) and (d). Cathodoluminescence images of the same areas show the presence of K-feldspars with cores having a brighter luminescence surrounded by a rim and symplectitic grains with a darker luminescence (e) and (f). Note the slight compositional zonation in plagioclase and K-feldspar. Holes represent spots from LA-ICPMS analyses.

the symplectitic intergrowth with K-feldspar forms the second generation (Fig. 2e and f). In places the symplectitic intergrowth is dynamically recrystallized (Fig. 2a and b).

Fig. 3 from the same sample (NT 9b) shows xenomorphic relics of plagioclase surrounded by the symplectitic K-feldspar-nepheline intergrowths. Plagioclase is compositionally zoned and in places has an elevated An content at the contact with the symplectites (Fig. 3c and d). Close to these areas, xenomorphic chlor-fluorapatite, up to 100 µm in diameter, and fine-grained xenomorphic clinopyroxene are present (Fig. 3). The nepheline (kalsilite in sample PE910)-K-feldspar-plagioclase textures are present in variable amounts. Dimensions range from 7 mm wide (NT9b, Fig. 2a and b) to approximately 1 mm layers (NT8, PE597, KT46) to narrow rims to areas of several hundred microns (PE910).

Two different types of spinel can be found as inclusions in the clinopyroxene phenocrysts. The first type are idiomorphic spinel grains, which often show exsolutions of both an Al-Mg-rich and a Fe-Ti-rich phase. These are interpreted to represent initially homogeneous spinel inclusions which exsolved during a post-magmatic thermal equilibration at about 600 °C (Krause et al., 2011). Spinel, with compositions similar to either of the exsolved phases, are also present as hypidiomorphic to xenomorphic interstitial grains in the matrix.

The second spinel type is represented by numerous, crystallographically aligned needles of titanomagnetite. These form oscillatory or hour glass zonation patterns made up of two sets of lamellae in variable concentrations. Similar textures have also been described in clinopyroxene from the ultramafic rocks of the Alaskan-type intrusions in the

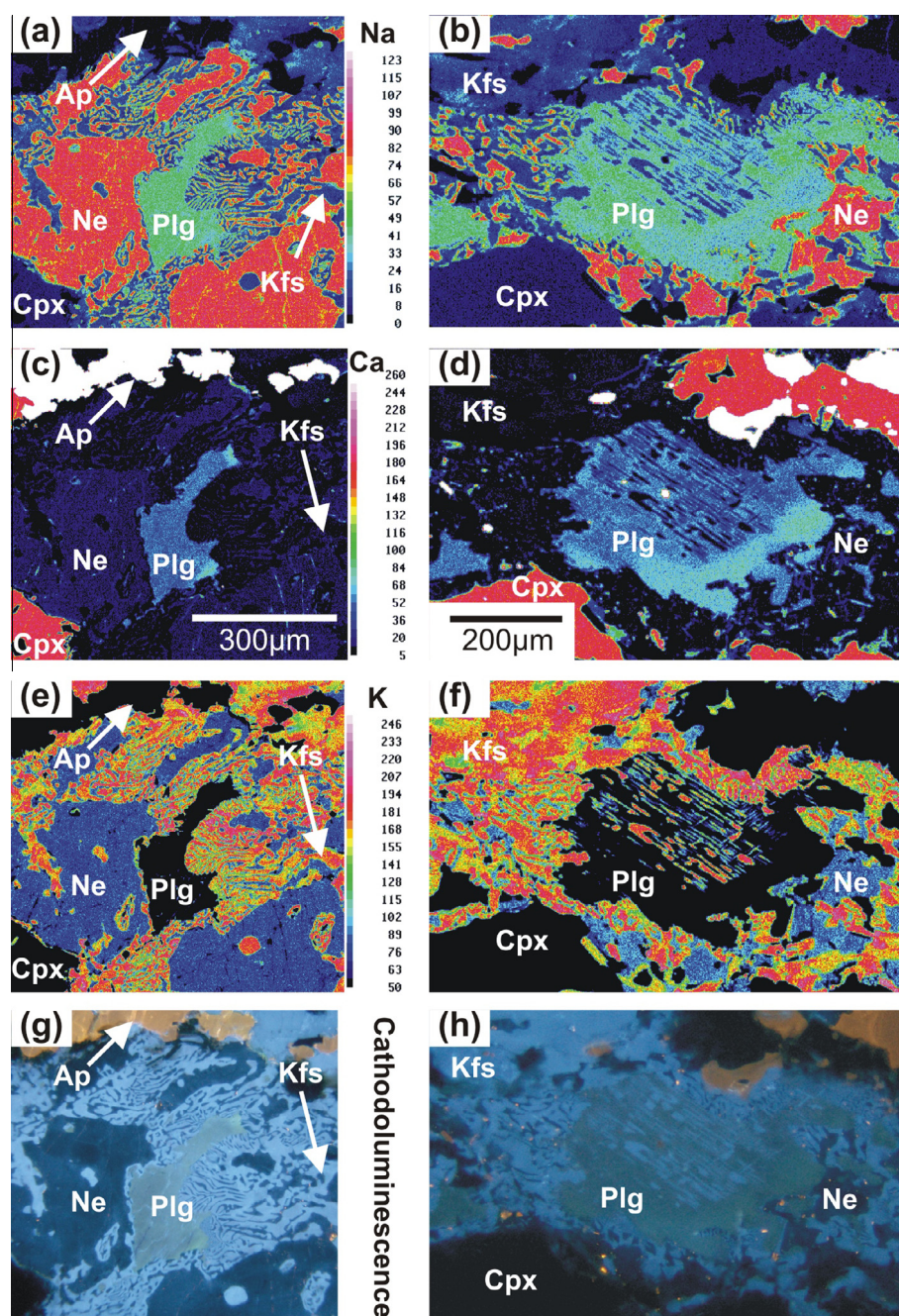


Fig. 3. X-ray element maps (a–f) and cathodoluminescence images (g,h) of relictic plagioclase replaced by a symplectitic intergrowth of plagioclase and K-feldspar and larger grains of nepheline and K-feldspar. Both areas are from sample NT9b. Larger grains of chlor-fluorapatite are often present (white areas in c and d). Note the chemical zonation of the plagioclase and the absence of nepheline in the central part of the maps on the right side indicating that nepheline is not always a product in the replacement process.

Ural Mountains (Krause et al., 2007). The textures suggest that the titanomagnetite needles were exsolved from the clinopyroxene as opposed to being incorporated during growth. The oscillatory variation in their abundance is interpreted to reflect variable amounts of Ti in the magmatically crystallized clinopyroxene.

In altered areas of the clinopyroxene, the titanomagnetite inclusions exhibit a patchy distribution pattern with areas rich in inclusions next to areas devoid of inclusions. These altered

areas often contain inclusions of biotite or exsolved spinel (Krause et al., 2011). The contact between the altered areas and the original magmatic clinopyroxene is sharp such that the oscillatory-zoned areas are truncated (Fig. 4). Towards the rim of the clinopyroxene phenocrysts and around inclusions of biotite and spinel, the lamellar titanomagnetite inclusions become less abundant and eventually disappear.

The degree of plagioclase replacement by K-feldspar and nepheline and the extent of the metasomatic overprint

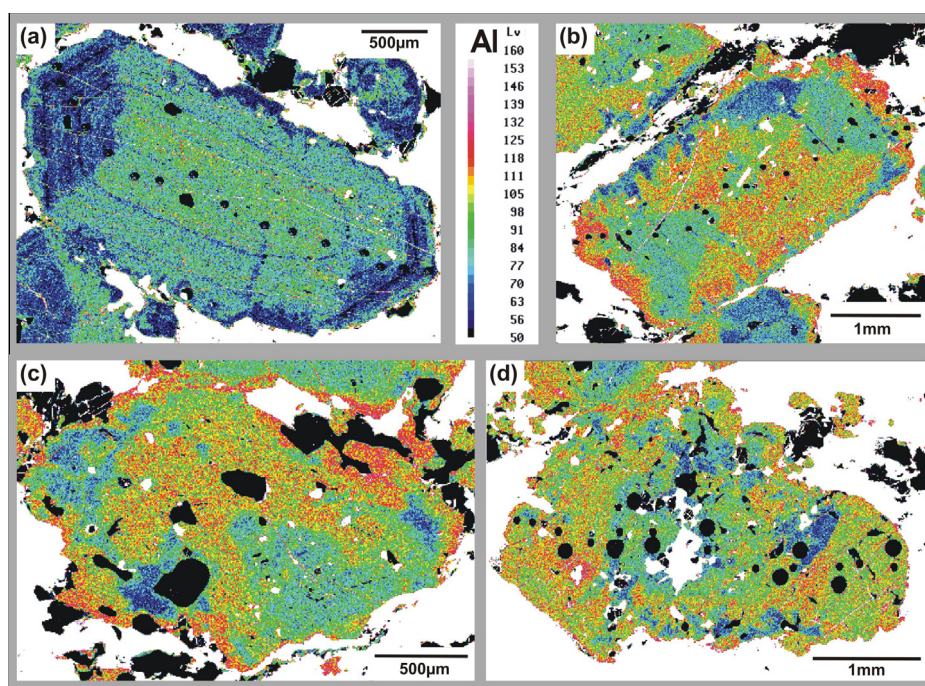


Fig. 4. X-ray element distribution maps documenting various degrees of post-magmatic overprint in clinopyroxene from a nepheline clinopyroxenite. Textures range from pristine, oscillatory, and hourglass zoned grains (a, sample PE597-Cpx3) over partially altered grains (b, sample NT8-Cpx2) to strongly altered clinopyroxenes (c and d, samples NT8-Cpx3 and NT9b-Cpx1). Note the overall lower Al content for clinopyroxene from sample PE597 if compared with the other samples (Krause, 2008).

in the clinopyroxene vary among the samples. The strongest metasomatic overprint was found in sample NT9 where only relics of the plagioclase remained and most of the clinopyroxene phenocrysts have been altered. The degree of metasomatic overprint of clinopyroxene is smaller in KT46, PE597, and NT8 and is least in PE910 where the clinopyroxene has mostly preserved its magmatic zonation. Symplectitic intergrowths of K-feldspar and nepheline are limited to the grain boundaries between the plagioclase and the other phases.

In the field no macroscopic difference between the metasomatized nepheline clinopyroxenites and other plagioclase bearing clinopyroxenites could be made. It is thus difficult to ascertain the exact geometry and degree of the metasomatic overprint in the two Uralian-Alaskan-type complexes from Nizhnii Tagil and Kytlym. However, the presence of similar overprint micro-textures in other samples from either area indicates that a significant part of the feldspar-bearing clinopyroxenites most likely experienced some metasomatic alteration (see Krause, 2008 for additional discussion).

4.1. Plagioclase, K-feldspar, and nepheline

The mean compositions of feldspar and nepheline in each sample are given in the Tables 1a–c. Plagioclase in these samples has a variable, but relatively low An content (26–62 mol.%) if compared with plagioclase from other clinopyroxene-rich ultramafic rocks in Nizhnii Tagil and the western parts of the Kytlym Complex (An = 50–

97 mol.%; Krause, 2008, Fig. 5a). Plagioclase (Or = 1 to 12) typically forms grains up to 2 mm in length in samples NT8, NT9b, KT46, and PE910, whereas in sample PE597 only a narrow interstitial rim of very small plagioclase grains, along the boundaries of the other phases, is seen. In many places plagioclase is replaced by a fine-grained, symplectitic intergrowth of K-feldspar and nepheline (Figs. 2 and 3). In these cases plagioclase often shows significant patchy compositional zoning close to the intergrowths (e.g. An = 26–48 mol.%, Fig. 3, Table 1a, Appendix 2) and has irregular lobate phase boundaries with respect to symplectitic intergrowths of nepheline and K-feldspar.

K-feldspar forms xenomorphic to hypidiomorphic grains up to 500 μm in all samples except for PE910 where a narrow rim (less than 100 μm) of small xenomorphic grains is found along the plagioclase grain boundaries (Table 1b). K-feldspar also forms symplectitic intergrowths with nepheline in all the samples (Figs. 2 and 3). K-feldspar in the samples from Nizhnii Tagil is characterized by a wide range in the Or content (Or = 53–91 mol.%) compared to Kytlym (Or = 77–99 mol.%, Fig. 5a, Table 1b). The An content remains below 8 mol.% in all samples.

Nepheline ($\text{Na}_3(\text{Na,K})[\text{Al}_4\text{Si}_4\text{O}_{16}]$) forms xenomorphic to hypidiomorphic grains up to 500 μm in length. Nepheline also occurs as a symplectitic intergrowth with K-feldspar. Both forms are present in all the samples except PE910, where instead small interstitial grains of kalsilite ($\text{K}[\text{AlSiO}_4]$) were found as narrow rims preferentially on plagioclase. The nepheline contains 17–21 mol.% of the kalsilite component. In sample PE910 the kalsilite is close

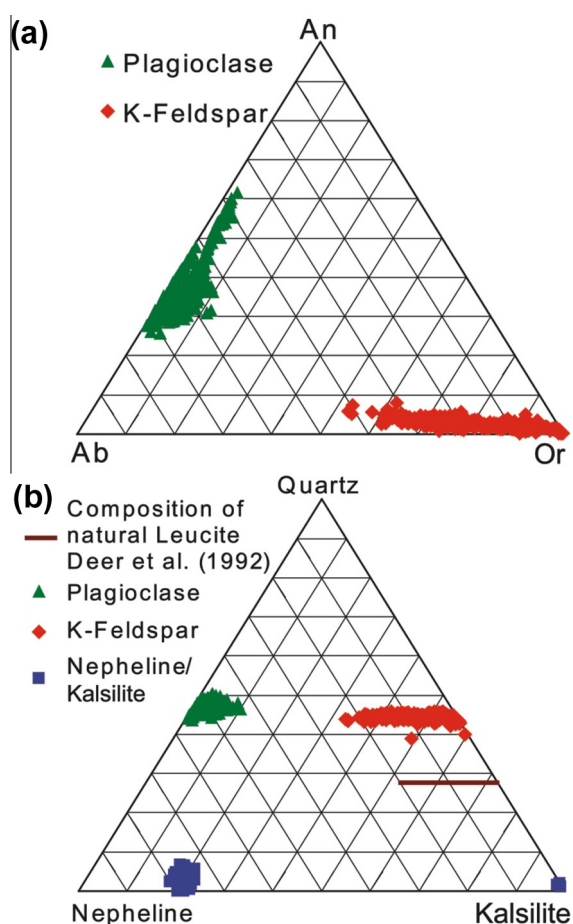


Fig. 5. Molar composition of feldspar and nepheline in anorthite-albite-orthoclase (a) and nepheline-kalsilite-quartz (b) space. Additional analyses were taken from Krause (2008). Note the presence of kalsilite instead of nepheline in sample PE910.

to the end member composition (nepheline <1 mol.%, Fig. 5b, Table 1c). BaO and SrO contents are close to or below the EMP detection limit of ~280 and ~380 $\mu\text{g/g}$ respectively (Electronic Appendix 1).

4.2. Clinopyroxene

Diopsidic clinopyroxene is the dominant mineral in the nepheline clinopyroxenites. It comprises 60–80 vol.% of the rock with the exception of sample NT9b where its fraction is ~50 vol.% (cf. Krause, 2008). It forms idiomorphic to hypidiomorphic phenocrysts up to 10 mm in diameter as well as fine xenomorphic grains in the matrix. The phenocrysts contain inclusions of fluor-chlorapatite, chlor-fluorapatite, olivine, biotite, spinel, and rare plagioclase in addition to numerous needles of exsolved titanomagnetite.

Representative clinopyroxene analyses from sample NT9b are given in Table 2. The dataset for sample NT8 can be found in Krause (2008). High Al_2O_3 and Na_2O contents ($\text{Al}_2\text{O}_3 = 2.9\text{--}6.3$ wt.%, $\text{Na}_2\text{O} = 0.5\text{--}1.6$ wt.%) and incompatible trace elements discriminate the

clinopyroxene in the nepheline clinopyroxenites from clinopyroxene in other mafic and ultramafic rocks from the Nizhni Tagil and Kytlym complexes (Table 2; Krause et al., 2007; Krause, 2008). The spatial distribution of major elements, like Al, Ti, and Cr, show a magmatic zoning pattern with hourglass and/or oscillatory zoning in some grains (Figs. 4a and 6b). This is progressively altered into a patchy, irregular element distribution pattern (Fig. 4c and d). The transition stages from this overprint process can also be observed (Figs. 4b and 6a). The contacts between the altered and magmatic areas are sharp and truncate the magmatic textures (Fig. 6a). The concentrations of the major elements change at this contact within a distance of a few microns. Al_2O_3 and Na_2O are higher in the altered areas ($\text{Al}_2\text{O}_3 = \sim 5.5$ wt.%, $\text{Na}_2\text{O} = \sim 1.0$ wt.%), if compared to the magmatic areas ($\text{Al}_2\text{O}_3 = \sim 4.1$ wt.%, $\text{Na}_2\text{O} = \sim 0.7$ wt.%), MgO decreases from ~13.8 to ~13.0 wt.% and $\text{XMg} [= \text{Mg}/(\text{Mg} + \text{Fe})]$ decreases from 0.80 to 0.78. This overprint not only affects the chemical composition of the clinopyroxene, it also modifies the abundance of the exsolved titanomagnetite needles in the clinopyroxene resulting in a patchy distribution of remobilized titanomagnetite grains. Alteration along cracks in the clinopyroxene is not seen.

As described in Krause (2008), the chemical composition of the magmatically zoned clinopyroxenes reflects fractional crystallization as well as the mixing of magmas from different sources. Based on whole rock major and trace element compositions as well as the trace element composition of clinopyroxene phenocrysts from different lithologies this mixing involves silica undersaturated alkaline and island-arc tholeiitic melts.

Sodium and Al, plus most of the trace elements, measured along profiles from a partially altered clinopyroxene phenocryst show a sudden increase in concentration, except Rb and Sr (Fig. 6c and e; Table 2), going from the original magmatic clinopyroxene into the altered clinopyroxene. As a result, Sr/Sr^* is systematically higher in the magmatically zoned part of the clinopyroxene phenocryst ($\text{Sr}/\text{Sr}^* = \sim 1.2$), if compared to the altered area ($\text{Sr}/\text{Sr}^* = \sim 0.9$, Fig. 6e and f; $\text{Sr}/\text{Sr}^* = \text{Sr}_\text{N}/(\text{Ce}_\text{N}^2 + \text{Pr}_\text{N}^2)^{0.5}$ (here N denotes concentrations normalized to the primitive mantle after Hofmann (1988)). The LREE/HREE, e.g. La/Lu, does not show a significant change (on average 33.4 ± 6 for the altered and 30.1 ± 4 for the magmatic clinopyroxene) with the exception of the outermost rim, where the high ratios, observed for the magmatic clinopyroxene rims (from La/Lu = 32 to 44), are not found on the corresponding rims of the altered clinopyroxene (La/Lu = 29–34).

At the compositional boundary between the magmatically zoned and the altered clinopyroxene a network of pores is observed in the preserved magmatic part (Fig. 7b and d). The diameter of the pores ranges from 1.5 to 0.05 μm in size and their abundance decreases outwards from the reaction front for several tens to several hundreds of microns. The presence of a porosity in the original magmatic clinopyroxene in the immediate area of the reaction front is unusual (cf. Putnis, 2009). In contrast, the altered areas show no visible remnants of porosity down to the micron scale.

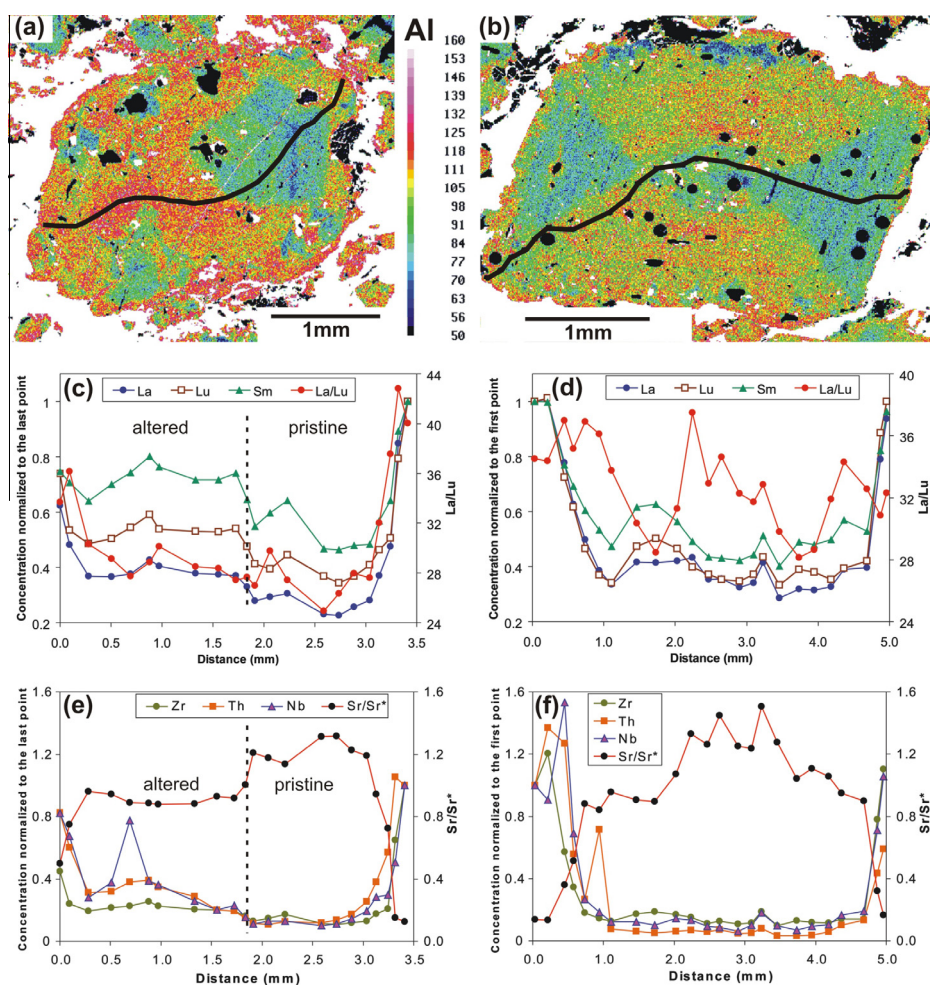


Fig. 6. Major and trace element distribution in clinopyroxene. The X-ray element distribution of a widely altered (a, sample NT9b-Cpx6) and a pristine magmatic clinopyroxene (b, sample NT8-Cpx1) is also reflected in the trace elements (c–f). White lines in (a) and (b) denote the profiles. The trace element concentrations in the profiles are normalized to the last or the first point in the profile. Note the presence of relicts of oscillatory zonation in the upper right and the lower left part of (a) and the distinct increase in the concentration of most trace elements in the altered areas (c, e). $Sr/Sr^* = Sr_N / (Ce_N^{2+} + Pr_N^{3+})^{0.5}$.

4.3. Apatite

Apatite is present as an accessory phase in all the nepheline clinopyroxenite samples and occurs as three different types (Table 3). These are (1) xenomorphic matrix grains of chlor-fluorapatite up to several hundred microns, which sometimes cluster in areas close to the symplectitic intergrowth of K-feldspar and nepheline (Fig. 3); (2) idiomorphic to hypidiomorphic inclusions of fluor-chlorapatite, usually 1–15 μm , rarely up to 150 μm in diameter, in the unaltered, magmatically zoned areas of the clinopyroxene; and (3) by 1–15 μm chlor-fluorapatite inclusions in the altered areas of the clinopyroxene.

Fluor-chlorapatite inclusions in areas of the clinopyroxene phenocrysts that have retained their magmatic zoning have moderate amounts of Cl ($F/Cl = 4$ to 8) together with high Sr and low Na_2O -contents ($Sr = 0.25$ – 1.4 wt.%, $\text{Na}_2\text{O} < 0.25$ wt.%; Table 3, Electronic annex EA-2). In contrast, chlor-fluorapatite inclusions in the altered areas

of the clinopyroxene as well as chlor-fluorapatite in the matrix are enriched in Cl ($F/Cl = 1$ to 4) and Na and depleted in Sr ($Sr = 0.03$ – 0.72 wt.%, $\text{Na}_2\text{O} = 0.03$ – 0.54 wt.%; Fig. 8, Table 3, Electronic annex EA-2).

Fluor-chlorapatite inclusions in the magmatically zoned areas of the clinopyroxene phenocrysts from Nizhny Tagil have systematically higher Sr concentrations when compared to similar fluor-chlorapatite inclusions in clinopyroxene from Kytlym (Fig. 8b). These higher Sr values appear to reflect a primary feature of the parental melt since they are also reflected in the clinopyroxene and the whole-rock chemistry (Krause et al., 2007; Krause, 2008).

Raman spectra from apatite types (1), (2), or (3) do not show any evidence for significant amounts of CO_3^{2-} . The peak at 1070 cm^{-1} ascribed to carbonate groups in biogenic fluorapatite (Klocke et al., 2007) is not present in the Raman spectra from fluor-chlorapatite in these samples suggesting that CO_2 was not present in significant amounts during their formation.

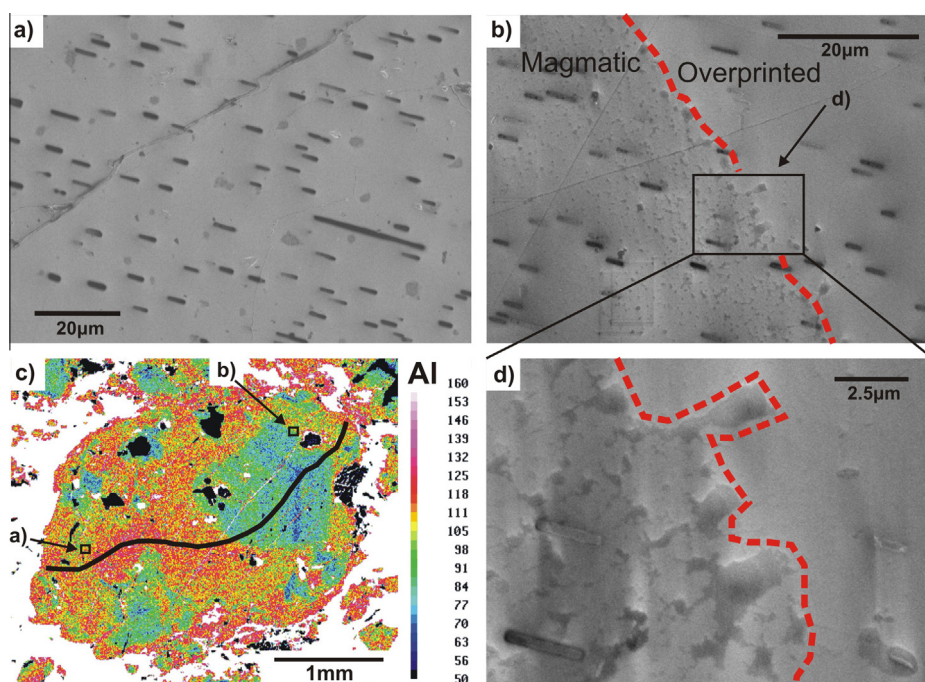
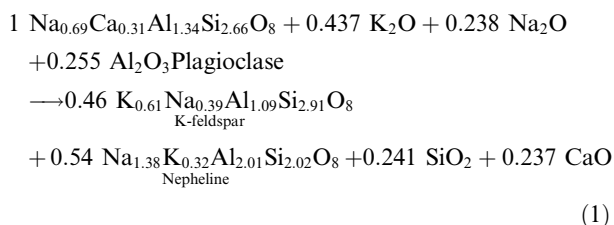


Fig. 7. High resolution SEM-images of a partially metasomatized clinopyroxene phenocryst (Sample NT9b). While metasomatized areas are devoid of a nano- to micrometer sized porosity (a) areas with a preserved magmatic zonation (b,d) show an interconnected porosity on the micrometer scale. The X-ray distribution map for Al is given for orientation (c). Note the sharp boundary between the two areas (dotted red line) and the presence of equally spaced oriented titanomagnetite inclusions.

5. DISCUSSION

5.1. Replacement of plagioclase by K-feldspar and nepheline

At some point after the crystallization of the nepheline clinopyroxenite was complete or nearly complete, a proportion of the plagioclase was replaced by K-feldspar and nepheline. Calculations involving the element distribution maps indicate that the plagioclase was replaced by 0.46 K-feldspar + 0.54 nepheline (see Section 3.1 for details of the calculation of mineral modes; note that for sample NT9b a representative analysis from a profile across a relic plagioclase grain (analysis NT9b_30 Line AB-24; Fig. 3c) was used). The feldspar and feldspathoid compositions indicate that this replacement would require the addition of K₂O, Na₂O, and Al₂O₃ and lead to an excess of CaO and SiO₂ via the following mass balance reaction:



The most likely source of K and Na was an external (K,Na)Cl brine. Such brines have been experimentally demonstrated to be extremely reactive with plagioclase (e.g. Hövelmann et al., 2010 and references therein). The initial (K,Na)Cl-rich fluid could have originated outside the

cooling cumulate body or alternatively could have been of late stage magmatic origin. The presence of late-stage magmatic K-feldspar and biotite generation, along with an elevated K content, has been reported for similar lithologies from other Alaskan-type complexes (e.g. Astrakhansev et al., 1991; Himmelberg and Loney, 1995). This suggests that the (K,Na)Cl-rich fluid was of late magmatic origin. However a detailed investigation on the origin of the fluid is beyond the scope of the present study.

Calculating the mass balance for trace elements such as LREE, Ba and Sr from Reaction (1) leads to an excess of the LREE during plagioclase break down (Fig. 9 and Table 4). The LREE excess is most pronounced for La and decreases systematically until Nd. The mass balance is slightly negative (−0.016 μg/g) which means that no Eu is consumed or liberated within the analytical error. For other trace elements such as Rb, Ba, Sr and Pb the mass balance is negative and thus an addition of these elements is required.

5.2. Partial chemical overprinting of the clinopyroxene phenocrysts

Trace elements in the matrix clinopyroxene and altered areas of clinopyroxene phenocrysts show an increase in the concentration of all measured elements except for Rb and Sr (Fig. 9 and Table 2) compared to the original magmatic areas of the clinopyroxene phenocrysts. The enrichment factors in the altered areas in clinopyroxene range from 3.8 for Ta, to values between 2 and 3 for Ba, Th, Nb, and Zr, to values of between 1.8 and 1.3 for Hf, U,

Table 3
Mean apatite compositions (wt.%).

Sample	Locality	# Anal	Textural position	P ₂ O ₅	SiO ₂	La ₂ O ₃	CaO	SrO	FeO ^a	MgO	MnO	Na ₂ O	F	Cl	H ₂ O ^b	Sum	O = (F + Cl)	Total	F/Cl
PE597	Nizhnii Tagil	35	Interstitial	41.70	0.29	0.12	54.33	0.12	0.27	0.10	0.10	0.15	2.10	2.27	0.18	101.69	1.40	100.30	0.98
				<i>0.28</i>	<i>0.27</i>	<i>0.05</i>	<i>0.41</i>	<i>0.04</i>	<i>0.17</i>	<i>0.03</i>	<i>0.03</i>	<i>0.04</i>	<i>0.25</i>	<i>0.47</i>	<i>0.07</i>				
PE597	Nizhnii Tagil	11	Inclusion in overprinted Cpx	41.60	0.36	0.12	54.26	0.19	0.36	0.13	0.10	0.13	2.32	1.92	0.17	101.63	1.41	100.23	1.37
				<i>0.44</i>	<i>0.20</i>	<i>0.06</i>	<i>0.62</i>	<i>0.09</i>	<i>0.16</i>	<i>0.09</i>	<i>0.04</i>	<i>0.07</i>	<i>0.25</i>	<i>0.62</i>	<i>0.09</i>				
PE597	Nizhnii Tagil	16	Inclusion in magmatic Cpx	41.55	0.55	0.09	54.20	0.65	0.43	0.17	0.09	0.08	2.56	1.46	0.17	101.96	1.41	100.56	2.02
				<i>0.40</i>	<i>0.41</i>	<i>0.05</i>	<i>0.47</i>	<i>0.24</i>	<i>0.15</i>	<i>0.13</i>	<i>0.03</i>	<i>0.04</i>	<i>0.33</i>	<i>0.53</i>	<i>0.12</i>				
PE910	SW- Kytlym	46	Interstitial	41.28	0.23	0.10	54.66	0.23	0.22	0.08	0.07	0.13	2.10	1.62	0.35	101.03	1.25	99.79	1.34
				<i>0.45</i>	<i>0.29</i>	<i>0.04</i>	<i>0.46</i>	<i>0.05</i>	<i>0.18</i>	<i>0.03</i>	<i>0.02</i>	<i>0.04</i>	<i>0.18</i>	<i>0.27</i>	<i>0.06</i>				
PE910	SW- Kytlym	12	Inclusion in overprinted Cpx	41.26	0.39	0.13	53.92	0.45	0.42	0.12	0.09	0.16	1.98	2.16	0.27	101.32	1.32	100.01	1.54
				<i>0.61</i>	<i>0.26</i>	<i>0.06</i>	<i>0.84</i>	<i>0.20</i>	<i>0.10</i>	<i>0.05</i>	<i>0.02</i>	<i>0.10</i>	<i>0.48</i>	<i>1.23</i>	<i>0.11</i>				
PE910	SW- Kytlym	19	Inclusion in magmatic Cpx	41.81	0.38	0.11	54.43	0.44	0.34	0.13	0.06	0.09	2.59	0.86	0.31	101.52	1.29	100.24	4.64
				<i>0.43</i>	<i>0.21</i>	<i>0.03</i>	<i>0.44</i>	<i>0.11</i>	<i>0.15</i>	<i>0.07</i>	<i>0.02</i>	<i>0.07</i>	<i>0.32</i>	<i>0.48</i>	<i>0.12</i>				
NT8	Nizhnii Tagil	81	Interstitial	41.30	0.21	0.13	53.60	0.21	0.38	0.10	0.11	0.32	1.58	2.71	0.32	100.94	1.28	99.67	0.65
				<i>0.46</i>	<i>0.14</i>	<i>0.04</i>	<i>0.37</i>	<i>0.05</i>	<i>0.21</i>	<i>0.05</i>	<i>0.04</i>	<i>0.04</i>	<i>0.25</i>	<i>0.32</i>	<i>0.06</i>				
NT8	Nizhnii Tagil	12	Inclusion in overprinted Cpx	41.22	0.32	0.10	53.21	0.41	0.43	0.11	0.11	0.34	1.61	2.72	0.30	100.81	1.29	99.52	1.19
				<i>0.48</i>	<i>0.13</i>	<i>0.04</i>	<i>0.73</i>	<i>0.20</i>	<i>0.11</i>	<i>0.05</i>	<i>0.06</i>	<i>0.08</i>	<i>0.60</i>	<i>1.12</i>	<i>0.06</i>				
NT8	Nizhnii Tagil	15	Inclusion in magmatic Cpx	41.44	0.42	0.10	53.60	0.94	0.45	0.07	0.10	0.16	2.16	1.87	0.26	101.51	1.33	100.19	1.28
				<i>0.41</i>	<i>0.32</i>	<i>0.02</i>	<i>0.76</i>	<i>0.32</i>	<i>0.15</i>	<i>0.06</i>	<i>0.05</i>	<i>0.13</i>	<i>0.29</i>	<i>0.54</i>	<i>0.13</i>				
NT9b	Nizhnii Tagil	177	Interstitial	41.13	0.23	0.12	54.12	0.10	0.30	0.09	0.11	0.32	2.06	1.57	0.38	100.53	1.22	99.30	1.38
				<i>0.49</i>	<i>0.15</i>	<i>0.04</i>	<i>0.29</i>	<i>0.04</i>	<i>0.20</i>	<i>0.03</i>	<i>0.04</i>	<i>0.06</i>	<i>0.23</i>	<i>0.27</i>	<i>0.11</i>				
NT9b	Nizhnii Tagil	46	Inclusion in overprinted Cpx	41.37	0.30	0.12	53.99	0.28	0.39	0.12	0.10	0.30	2.09	1.65	0.35	101.04	1.25	99.79	1.86
				<i>0.53</i>	<i>0.13</i>	<i>0.05</i>	<i>0.44</i>	<i>0.18</i>	<i>0.15</i>	<i>0.08</i>	<i>0.04</i>	<i>0.25</i>	<i>0.36</i>	<i>0.47</i>	<i>0.15</i>				
NT9b	Nizhnii Tagil	28	Inclusion in magmatic Cpx	41.93	0.32	0.11	54.70	0.44	0.31	0.11	0.08	0.10	2.53	0.77	0.36	101.69	1.24	100.46	3.74
				<i>0.46</i>	<i>0.11</i>	<i>0.04</i>	<i>0.41</i>	<i>0.16</i>	<i>0.07</i>	<i>0.03</i>	<i>0.03</i>	<i>0.08</i>	<i>0.35</i>	<i>0.32</i>	<i>0.19</i>				
KT46	SW- Kytlym	45	Interstitial	41.29	0.25	0.11	54.54	0.19	0.35	0.06	0.06	0.11	2.15	1.84	0.27	101.14	1.32	99.82	1.31
				<i>0.51</i>	<i>0.17</i>	<i>0.04</i>	<i>0.44</i>	<i>0.05</i>	<i>0.35</i>	<i>0.06</i>	<i>0.02</i>	<i>0.03</i>	<i>0.29</i>	<i>0.27</i>	<i>0.11</i>				
KT46	SW- Kytlym	3	Inclusion in overprinted Cpx	41.24	0.30	0.13	54.02	0.39	0.46	0.06	0.10	0.12	2.44	1.99	0.09	101.30	1.48	99.83	1.33
				<i>0.09</i>	<i>0.10</i>	<i>0.11</i>	<i>0.23</i>	<i>0.04</i>	<i>0.19</i>	<i>0.02</i>	<i>0.05</i>	<i>0.10</i>	<i>0.42</i>	<i>0.59</i>	<i>0.08</i>				
KT46	SW- Kytlym	4	Inclusion in magmatic Cpx	41.20	0.69	0.11	54.49	0.30	0.41	0.15	0.05	0.06	2.66	0.98	0.25	101.24	1.34	99.91	2.83
				<i>0.26</i>	<i>0.13</i>	<i>0.00</i>	<i>0.09</i>	<i>0.09</i>	<i>0.10</i>	<i>0.12</i>	<i>0.02</i>	<i>0.01</i>	<i>0.10</i>	<i>0.23</i>	<i>0.02</i>				

1σ – standard deviation in italics.

^a Total Fe as FeO.

^b Calculated assuming the (F,Cl,OH) site is filled.

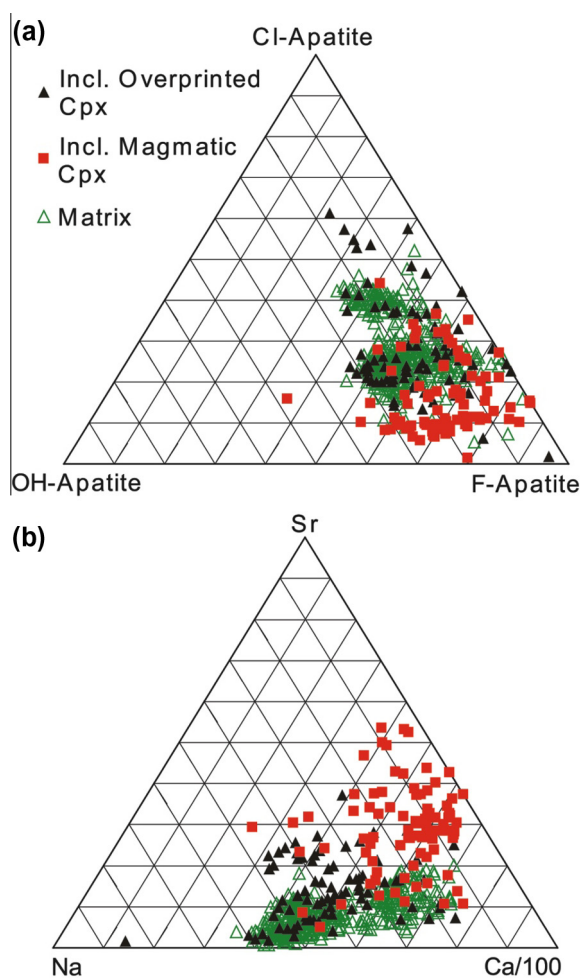
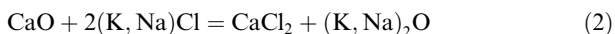


Fig. 8. Chemical composition of apatite from a nepheline clinopyroxenite in Alaskan-type complexes in the UPB. Variation of the molar proportion of fluor-, chlor- and hydroxy apatite (a); variation of Na, Sr and Ca/100 (b). Note the elevated proportions of Sr and F in the fluor-chlorapatite enclosed in the magmatically zoned clinopyroxene when compared to chlor-fluorapatite inclusions in the metasomatically altered clinopyroxene. The latter is similar in composition to apatite in the matrix.

Pb, Y, Ti, and REE, with the lowest values observed for Eu. Rubidium and Sr are depleted in the altered areas, i.e. $C_{\text{altered}}/C_{\text{magmatic}} = 0.91$ and 0.78 , respectively (Figs. 6 and 9; Table 2). This might reflect the partitioning of these elements into K-feldspar and nepheline. The relative weak enrichment of Eu in the altered areas of the clinopyroxene can be explained with the similar concentrations of Eu in plagioclase and replacing K-feldspar and nepheline.

Presuming that a (K,Na)Cl brine was indeed responsible for the partial alteration of plagioclase to K-feldspar and nepheline (Reaction (1)), Ca from the plagioclase would have been partitioned into the fluid as CaCl_2 while K and Na were being partitioned into the K-feldspar and nepheline via the following reaction:



We propose that the clinopyroxene phenocrysts were partially altered by this CaCl_2 -enriched brine concurrently with

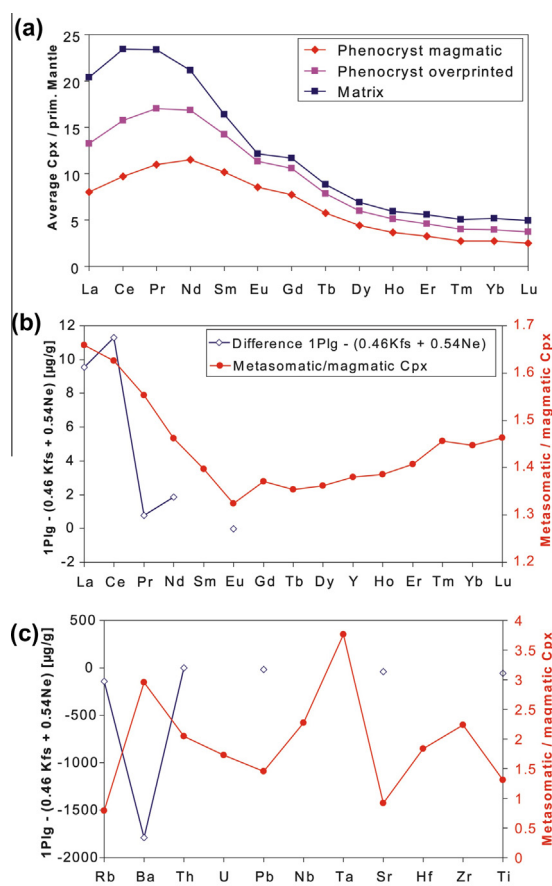


Fig. 9. Average concentrations of the REE in clinopyroxene normalized to the primitive mantle (a) and the relation between mineral reactions in the matrix and the overprint of clinopyroxene for the REE (b) and selected trace elements (c). Concentrations for the REE in the primitive mantle were taken from Hofmann (1988). The blue lines in b and c denotes the mass balance for trace elements during the decomposition of the plagioclase and the associated formation of $0.54 \text{ K-feldspar} + 0.46 \text{ nepheline}$. Positive values denote an excess of a specific element while negative values indicate that an addition is necessary. Modes are averages from 6 element maps of symplectitic intergrowths of nepheline and K-feldspar replacing plagioclase in sample NT9b. The red line is the ratio between the average element abundances of the altered and the magmatic clinopyroxene.

or shortly after the partial conversion of plagioclase to K-feldspar and nepheline. Evidence for this includes conversion of the apatite inclusions in the altered areas from fluor-chlorapatite to chlor-fluorapatite while apatite inclusions in unaltered areas (the original magmatic clinopyroxene) remain fluor-chlorapatite (Fig. 10). It has been demonstrated experimentally that fluorapatite reacts strongly with CaCl_2 -bearing fluids such that it becomes enriched in Cl relative to F (Harlow and Förster, 2003). This same set of experiments also demonstrated that in the presence of KCl or NaCl brines, Cl was partitioned out of the fluorapatite into the solution, whereas in the case of the NaCl brine experiments, Na was partitioned into the fluorapatite. During this partial alteration both the crystallo-

Table 4
Trace element contents of feldspar and nepheline.

	Plagioclase	Nepheline	K-feldspar
N	8	15	24
Rb (ppm)	8	139	164
Ba	351	1904	2421
Th	0.008	0.008	0.013
Pb	17.0	34.1	28.4
La	12.9	3.90	2.67
Ce	13.9	2.99	2.27
Sr	3177	3238	3193
Pr	0.91	0.14	0.13
Nd	2.15	0.27	0.31
Eu	0.43	0.44	0.44
Ti	134	171	219

Average concentrations were calculated from Krause (2008).

graphic orientation and primary shape of the clinopyroxene phenocrysts were preserved. This fluid could also have been responsible for the conversion of the matrix apatite to chlor-fluorapatite. A second line of evidence is the mobilization of Fe, Mg, and Ti in the altered areas as a result of the breakdown and redistribution of the titanomagnetite inclusions while at the same time titanomagnetite inclusions

in the unaltered areas preserve the original magmatic zoning. All three elements form Cl-based salts, which are highly soluble in H₂O-bearing fluids.

5.3. Proposed mechanism behind the partial chemical overprint of the clinopyroxene phenocrysts

The mechanism behind the chemical overprint of the altered areas in the clinopyroxene phenocrysts and their apatite inclusions is suggested to be a coupled dissolution–reprecipitation process (cf. Putnis, 2002, 2009; Putnis and Austrheim, 2010). Alternative mechanisms could include volume diffusion or partial resorption and subsequent overgrowth of the clinopyroxene. Volume diffusion would certainly preserve the crystallographic orientation of the clinopyroxene, but could not be responsible for the observed geometry between the overprinted and magmatic areas (Figs. 4, 6 and 7). The sharp compositional contrast along discrete compositional boundaries between the magmatic and overprinted areas of the clinopyroxene, for both the major and trace elements (Fig. 6), is definitely not characteristic of diffusion (c.f. Harlov et al., 2005, 2007, 2011; Zhang, 2010). Even if diffusion were present, the diffusion profiles of elements such as Sr, Na, Al, and

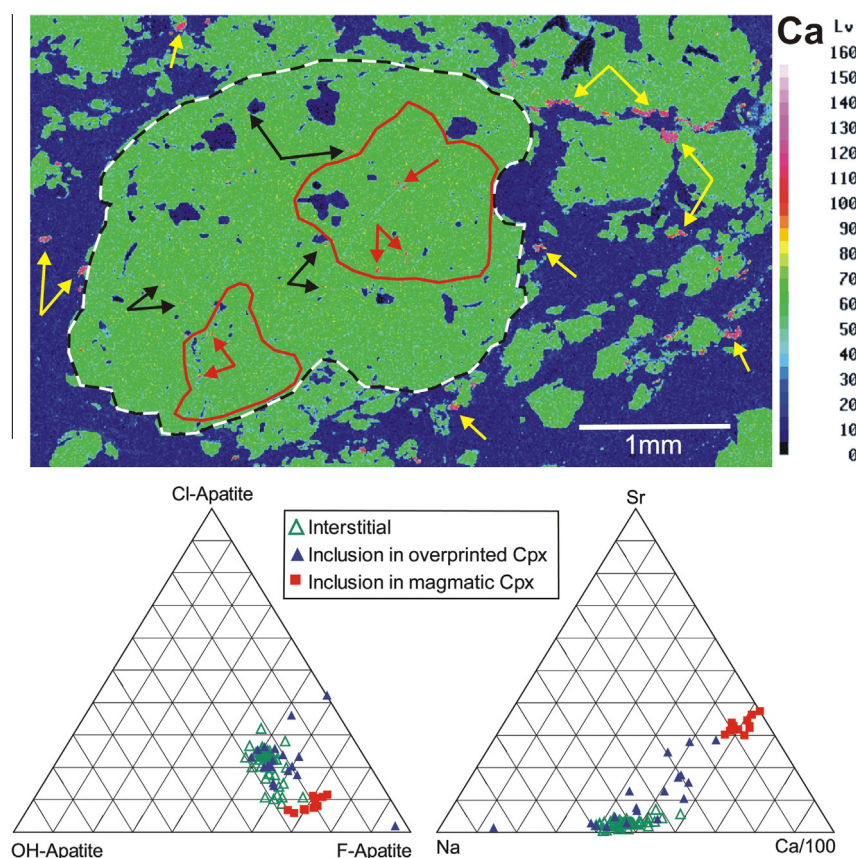


Fig. 10. Spatial distribution and chemical composition of apatite inclusions in the partially altered clinopyroxene megacrysts and apatite along the grain rim of the same clinopyroxene megacrysts. The X-ray element map of the Ca distribution (a) shows apatite enclosed in the magmatic clinopyroxene (red arrows in the area outlined in red) as well as in the altered clinopyroxene (black arrows in the area outlined in black and white) and in the matrix (yellow arrows). For comparison see also Fig. 5a. Note the different apatite compositions (b, c) in the magmatic and altered areas of the clinopyroxene and in the surrounding matrix (a).

REE, whose diffusion coefficients differ from each other by orders of magnitude, would show very different slopes in their patterns across the compositional boundary (cf. [Cherniak and Dimanov, 2010](#)). This is the case only with respect to Sr, which in contrast to the other elements decrease from the magmatic towards the overprinted area of the clinopyroxene. Lastly, and more importantly, these same diffusion coefficients indicate diffusion rates for these elements in clinopyroxene that are far too slow to explain the observed sharp compositional contrast between the altered and unaltered areas.

Partial resorption and subsequent overgrowth of the clinopyroxene would result primarily in a zonal distribution of cores of preserved primary clinopyroxene surrounded by a more or less regular rim of a secondary clinopyroxene. In contrast strongly overprinted clinopyroxene shows a patchy distribution of overprinted and primary magmatic areas (Figs. 4c and d, and 6a). Partial resorption and subsequent overgrowth is also not supported by the chemical data overall.

Fluid-aided, coupled dissolution–reprecipitation represents a chemical reaction, driven by a minimization in the Gibbs free energy ([Putnis, 2002, 2009](#); [Putnis and Austrheim, 2010](#)). In this process the reactive fluid essentially allows for a mineral phase to be replaced either by the same phase, but of different composition in equilibrium with the surrounding fluid under the prevailing P–T conditions, or by an entirely new phase. Dissolution–reprecipitation is a coupled process because the rates of both the dissolution of the original mineral phase and the reprecipitation of the new or altered mineral phase must be the same such that the two phases maintain direct contact separated only by a thin fluid film with a thickness generally on the submicron scale. This allows for material transport from the dissolving phase across the fluid-filled reaction front to the precipitating phase. Once initiated, the process can be self-perpetuating because the precipitation of the product phase allows for the continued dissolution of the parent phase into the solution (see discussion in [Andersen et al., 1998a,b](#)). This implies that the rate-controlling step, during the pseudomorphic replacement of the original clinopyroxene by a chemically and texturally altered clinopyroxene, is the rate of dissolution of the parent phase and that the activation barrier for nucleation of the product phase is low (see discussion in [Putnis, 2009](#)).

The nucleation rate is controlled by several factors. The first of these is the degree of epitaxy between the product phase and the parent surface, which, in this case, is relatively high since they are basically the same phase, i.e. clinopyroxene. Subsequently, nucleation of the product phase on the surface of the parent phase is epitaxial transferring crystallographic information from the parent to the product phase. The second factor, the fluid composition at the interface, is probably the most important factor initiating the reaction, driving the reaction, and controlling the coupling between the two phases. This implies that the rate of transport of solution species to and from the interface needs to be considered in formulating a quantitative description of the replacement mechanism. The nucleation rate of the product phase will also be controlled by the degree of supersaturation in the fluid in this boundary layer.

A consequence of this self-perpetuating dissolution–reprecipitation reaction is the migration of a reaction front through the original magmatically zoned clinopyroxene, leaving behind unzoned, chemically altered areas of the clinopyroxene. In order for this migration to occur, such that the interface between the dissolving phase and precipitating phase has contact with the surrounding fluid, there must be fluid infiltration through the precipitated phase allowing for the rapid mass transfer of Cl, F, Fe, Mg, Al, Si, and Ti over distances on the order of tens to hundreds of microns between this reaction front and the surrounding fluid. Experimental studies (e.g. [Harlov et al., 2005, 2007](#); [Hövelmann et al., 2010](#); [Norberg et al., 2011](#); also see [Putnis, 2009](#)), indicate that as the altered areas form and expand during the dissolution–reprecipitation process they should be characterized by a pervasive, interconnected nano- and micro-porosity, which would allow for fluid infiltration. Porosity development is due to a combination of molar volume change and presumed slight differences in the solubility of the parent and product phases. The parent phase is dissolved slightly faster than the product phase is precipitated resulting in a small loss of material to the fluid phase ([Putnis, 2002, 2009](#)).

Factors causing the dissolution–reprecipitation mechanism to stop include: (1) recrystallization of the re-precipitated area, which effectively obliterates the interconnected porosity, (2) some chemical change in the local system such that the fluid and parent phase are no longer mutually reactive, or (3) a drop in temperature such that the reaction rate becomes negligible (see discussion in [Putnis, 2009](#)). This normally results in a remnant porosity being frozen in as scattered micron- and nano-sized fluid inclusions and/or nano-channels. That such a fluid-filled porosity must have once existed in the altered areas of the clinopyroxene is evidenced by both the strong compositional changes in the clinopyroxene and accompanying inclusions as well as in the sharp compositional boundaries between the altered and original magmatic clinopyroxene. Simple solid-state diffusion would not be able to account for these features (see discussion in [Putnis, 2009](#); also [Putnis and Austrheim, 2010](#)). Recent studies by [Putnis \(2009\)](#), [Norberg et al. \(2011\)](#) have indicated that the interconnected porosity in the altered areas of a partially metasomatised mineral is not static but highly plastic evolving quickly over time (minutes to days) from numerous small pores to a scattering of large pores to an absence of pores.

An apparent lack of a porosity in the altered areas (at least on the micron scale) of the clinopyroxene could be the result of a coarsening and subsequent clearing away of the porosity via an Ostwald ripening process during textural equilibration ([Putnis et al., 2005](#); [Putnis, 2009](#)). In contrast, the presence of a remnant porosity along the reaction front extending some microns into the unaltered clinopyroxene suggests the partial preservation of what might be the first stages of the reaction front advancing into the unaltered clinopyroxene. Alternatively it could be the result of excess fluids along the reaction front or in the now vanished porosity of the altered clinopyroxene being forced into the unaltered clinopyroxene during the latter stages of recrystallization of the altered areas after chemical overprinting had ceased.

During coupled dissolution–reprecipitation aided alteration of the clinopyroxene phenocrysts, the fluor-chlorapatite inclusions were significantly enriched in Cl such that they were converted to chlor-fluorapatite (Fig. 10, see discussion in Section 5.2). Observations regarding the fluid-aided alteration of mineral inclusions in a host mineral are not limited to this study. For example in experiments involving partial fluid-induced alteration of fluorapatite, the initially formed monazite inclusions (<1 µm size) in the altered areas experienced Ostwald ripening to sizes of around 5 µm or more when the same exact experiment was left up for a period three times as long as the original experiment (Harlov et al., 2005). This would suggest that fluid-aided processes effecting mass transfer continued in the altered areas over the duration of the longer experiment. This phenomenon has also been observed for monazite inclusions in natural fluorapatite (see discussion in Hansen and Harlov, 2007). Fluid-aided alteration has also been observed for spinel inclusions in olivine, which have been found to equilibrate with Fe^{2+} , Mg^{2+} , and trivalent cations from an interstitial liquid present along the olivine grain boundaries (Scowen et al., 1991; Krause et al., 2011).

Overall these observations suggest that great caution must be exercised before assuming that mineral inclusions cannot be altered during later metamorphic and/or igneous processes. Instead careful attention must be paid to whatever fluid-aided alteration the rock fabric has experienced as a whole and, subsequently, to the susceptibility of host mineral and its inclusions to this alteration. If the container is susceptible to chemical alteration, presumably its contents are as well, as was this case in this study.

6. CONCLUSIONS

Nepheline clinopyroxenites from two Uralian-Alaskan-type Complexes in the Ural Mountains, Russia show ample evidence for a two-step fluid-aided metasomatic overprint. During the first step, plagioclase in the matrix was replaced by a fine-grained intergrowth of nepheline and K-feldspar. Mass balance calculations, textural observations, and experimental data suggest that a (K,Na)Cl-rich fluid was the metasomatic agent responsible. As the reaction progressed the fluid became depleted in Na and K and enriched in Ca from the plagioclase. During the second step, the original clinopyroxene megacrysts and their fluor-chlorapatite inclusions were partially overprinted by this CaCl_2 -enriched fluid, which changed the composition of the fluor-chlorapatite inclusions in the altered areas of the clinopyroxene to a chlor-fluorapatite. The originally magmatically zoned titanomagnetite inclusions in the altered areas were totally mobilized and redistributed. It also enriched the altered areas in Na, Ti, Al, REE, and Y and depleted them in Rb and Sr, while the $(\text{Mg}/\text{Mg} + \text{Fe})$ gets slightly decreased. Both the grain shape and crystallographic orientation of the clinopyroxene phenocrysts were preserved during this process. The mechanism proposed to be behind the partial alteration of the clinopyroxene and its apatite inclusions is fluid-aided coupled dissolution–reprecipitation as opposed to either volume diffusion or partial resorption and subse-

quent overgrowth. An important implication from this study is that it is important to pay close attention to the susceptibility of the host mineral to fluid-aided alteration since this can also cause the chemical alteration of the mineral inclusions within.

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APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.gca.2013.06.013>.

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