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Clinopyroxene from an alkali pyroxenite xenolith, Loučná-Oberwiesenthal Volcanic Centre, Bohemian Massif: crystal chemistry and structure

Jaromír ULRYCH, Daniel NIŽŇANSKÝ, Franz PERTLIK, Gerald GIESTER, Andreas ERTL
and Franz BRANDSTÄTTER

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Alkali pyroxenite (and ijolite) xenoliths occur in the Tertiary Loučná-Oberwiesenthal Volcanic Centre associated with the Ohře/Eger Rift. The alkali pyroxenite xenoliths represent fragments of an intracrustal complex with Sr-Nd isotope ratios consistent with mantle sources of HIMU-affinity. The crystal structure of diopside from an alkali pyroxenite xenolith with the formula $(Ca_{0.95}Na_{0.04})$ $(Mg_{0.65}Fe^{3+}_{0.13}Fe^{2+}_{0.10}Ti^{4+}_{0.10}Al_{0.01})$ $(Si_{1.69}Al_{0.31})$ O_6 and the lattice parameters $a = 9.773(2)$, $b = 8.886(2)$, $c = 5.308(1)$ [Å] and $\beta = 105.89(3)$ [°] was refined to an R-value of 0.025 for 1174 reflections. The mean interatomic distances are: within the Me1-O_6 octahedron <2.067> Å, within the Me2-O_8 polyhedron <2.498> Å. The last value reflects the occupation of this atomic position by significant amounts of Fe^{2+} and Ti^{4+}. The enlargement determined for the <T-O> bond length to 1.657 Å is in accordance with the site population for this position: $(Si_{1.69}Al_{0.31})$. The molar ratio Fe^{2+}/Fe^{3+} determined by Mössbauer spectroscopy is equal to 0.786. The Al^{IV} deficiency in T-sites of clinopyroxene of rims is negligible (up to 0.019 a.p.f.u.) restricted to sporadic local electron microprobe analyses. The presence of Fe^{3+} in the T-position of Si- and Al-poor clinopyroxenes was not confirmed by X-ray structural analyses because of its low quantity. Nevertheless, the Mössbauer spectroscopy measurements (isomer shift of 0.36 mm/s) imply that Fe^{3+} is present only in the Me1-O_6 positions.

Jaromír Ulrych, Institute of Geology, Academy of Sciences of the Czech Republic, Rozvojová 135, 165 02 Prague 6, Czech Republic, e-mail: ulrych@gli.cas.cz; Daniel Nižňanský, Department of Inorganic Chemistry, Charles University, Albertov 2030, 128 43 Prague 2, Czech Republic, e-mail: niznansk@natur.cuni.cz; Franz Pertlik, Gerald Giester and Andreas Ertl, Institute of Mineralogy and Crystallography, University of Vienna, Geozentrum, Althanstraße 14, 1090 Vienna, Austria, e-mails: franz.pertlik@univie.ac.at, gerald.giester@univie.ac.at, andreas.ertl@a1.net; Franz Brandstätter, Mineralogical-Petrographical Department, Museum of Natural History, Burgring 7, 1014 Vienna, Austria; e-mail: franz.brandstaetter@nhm-wien.ac.at (received: July 22, 2005; accepted: December 23, 2005).

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INTRODUCTION

Alkali pyroxenite and ijolite xenoliths occur in nephelinite of the Tertiary Loučná-Oberwiesenthal Volcanic Centre in the Krušné hory/Erzgebirge Mts. The alkali pyroxenite xenoliths probably represent fragments of an intracrustal, possibly layered deep intracrustal alkaline complex, overprinted by a late-magmatic phase of ijolite composition. Initial ε_{Nd} values of +3.0 and +2.3 in clinopyroxene from xenoliths and the host nephelinite respectively, indicate similar yet different sources consistent with mantle sources of HIMU-affinity (Ulrych *et al*., 2005).

Clinopyroxenes of alkali pyroxenite are often chemically zoned. The light ochreous cores (about 80–100 vol% of phenocryst) are more magnesian yet have higher silica contents and lower Al, Ti and Fe contents than the dark green-brown rims, which are more ferroan and have lower silica contents and higher Al, Ti, and Fe contents (Ulrych *et al*., 2005). Homogeneous grains in the matrix mainly resemble the rims of zoned phenocrysts. Clinopyroxenes of cores are subsilicic ferrian aluminian diopside (Table 1, No. 1), however, rims are subsilicic titanian ferrian aluminian diopside to "fassaite" (Table 1, No. 2) according to the IMA classification (Morimoto, 1988). Clinopyroxene margins can locally be deficient in Si with the entry of Fe^{3+} (up to 0.019 atoms per formula unit — a.p.f.u.) in addition to Al^{IV} into tetrahedral sites having to be assumed for rare clinopyroxene analyses (Ulrych *et al*., 2005). The postulated entry of a low amount of Fe^{3+} (calculated according to the recommendation of the IMA; Morimoto, 1988) in the tetrahedral positions of clinopyroxene is a matter of debate (Cundari and Ferguson, 1982; Mitchell *et al*., 1987; Lloyd *et al*., 1991, 1999). However, according to Stoppa *et al*. (2002), Si- and Al-deficiency in some clinopyroxene compositions actually requires Ti rather

Table 1

Representative microprobe analyses of clinopyroxene (in wt.%) from Loučná-Oberwiesenthal xenolith (sample 5A)

No.	1	2	3	4
SiO_2	44.37	42.55	45.46	44.3–46.7
TiO_2	3.77	4.08	3.69	3.5–4.0
Al_2O_3	7.50	8.33	7.47	6.9–8.2
FeO	7.66	9.17	7.56	6.9–8.3
MnO	0.17	0.31	0.13	0.10–0.15
MgO	11.36	10.68	11.81	11.2–12.2
CaO	23.71	23.51	23.99	23.9–24.1
Na_2O	0.59	0.64	0.54	0.5–0.6
Total	99.13	99.27	100.65	
TSi	1.673	1.610	1.686	
TAl	0.327	0.371	0.314	
TFe^{3+}	0.000	0.019	0.000	
Me1Al	0.006	0.000	0.013	
Me1Ti	0.107	0.116	0.103	
$Me1Fe^{3+}$	0.149	0.204	0.133	
$Me1Fe^{2+}$	0.093	0.068	0.098	
Me1Mg	0.639	0.602	0.653	
$Me2Fe^{2+}$	0.000	0.000	0.004	
Me2Mn	0.005	0.010	0.004	
Me2Ca	0.958	0.953	0.954	
Me2Na	0.043	0.047	0.039	
Sum cations	4.000	4.000	4.000	
Jadeite	0.363	0.000	0.735	
Aegirine	2.127	2.811	1.488	
CaFe Tsch	6.459	9.375	6.100	
CaTi Tsch	6.172	6.952	5.892	
CaAl Tsch	0.000	0.000	0.000	
WO	51.962	51.362	51.674	
EN	34.640	32.465	35.395	
FS	13.398	16.173	12.932	
WEF	95.156	94.563	95.661	
JD	0.197	0.000	0.383	
AE	4.647	5.437	3.956	

Analyses are recalculated using "*Minpet*" version 2.02: formula; unit normalized to 6 oxygens and recalculated to 4 cations; end-members: Tsch — Tschermak's molecule, WO — wollastonite, EN — enstatite, FS — ferrosilite, WEF — WO+EN+FS, JD — jadeite, AE — aegirine are IMA end-members for classification in the Ca-Mg-Fe quadrilateral and the jadeite-aegirine-"Quad" diagram; 1 — phenocryst core, 2 — phenocryst rim (*Cameca SX-100*, analyst A. Langrova, Praha), 3 — average, 4 — range of 12 analyses of phenocryst aggregate used for X-ray study (*ARL-SEMQ*, Wien); T — tetrahedral position, Me1 and Me2 — octahedral positions

than Fe^{3+} to enter the T-sites. As the clinopyroxenes forming the rims of phenocrysts in the alkali pyroxenite xenoliths (Ulrych *et al*., 2005) belong to titanian varieties, X-ray structural studies and Mössbauer studies were performed to ascertain the possible presence of heavy ions (Fe^{3+},Ti) in tetrahedral sites. In addition, there have been no studies of the crystal structure of clinopyroxene from deep-crustal xenoliths. Therefore, a study of the crystal chemistry and crystal structure of the clinopyroxene from a xenolith of the Loučná-Oberwiesenthal intracrustal complex was performed.

GEOLOGICAL SETTING OF THE LOUČNÁ-OBERWIESENTHAL VOLCANIC CENTRE

The Loučná-Oberwiesenthal Volcanic Centre ("Oberwiesenthaler Eruptivstock" of Reinisch, 1917; Pietzsch, 1962; Pfeiffer *et al*., 1990, and "Phonolite-Nephelinite Volcanic Centre" of Kopecký, 1988) is a remnant of a Cenozoic volcanic centre emplaced in the Saxothuringian Krušné hory Crystalline Complex (see Fig. 1). Pietzsch (1962) considered the volcanic centre to be a relict of denudation of the largest Cenozoic volcano of the Krušné hory Mts. It is situated on the northern shoulder block of the Ohře/Eger Rift near to the Krušné hory Fault Zone.

The Loučná-Oberwiesenthal Volcanic Centre comprises a major (micro)porphyritic nephelinite body (37–30 Ma), subordinate small phonolite bodies, volcanic breccias, ash tuffs and lamprophyric apophyses of the nephelinite body (Fig. 1). Abundant xenoliths of alkali pyroxenite and ijolite occur in the central part of the Loučná-Oberwiesenthal nephelinite body. They are abundant in the "bean-shaped" area between the "Na kopci/Ziroldberg Hill" and the cemetery, see Figure 1. Nephelinite occurs in association with volcanic breccias, which probably represent feeder channels. Phonolite dykes and possibly smaller stocks occur at the NW margin of the nephelinite body. A series of rocks of transitional chemical composition such as sanidine

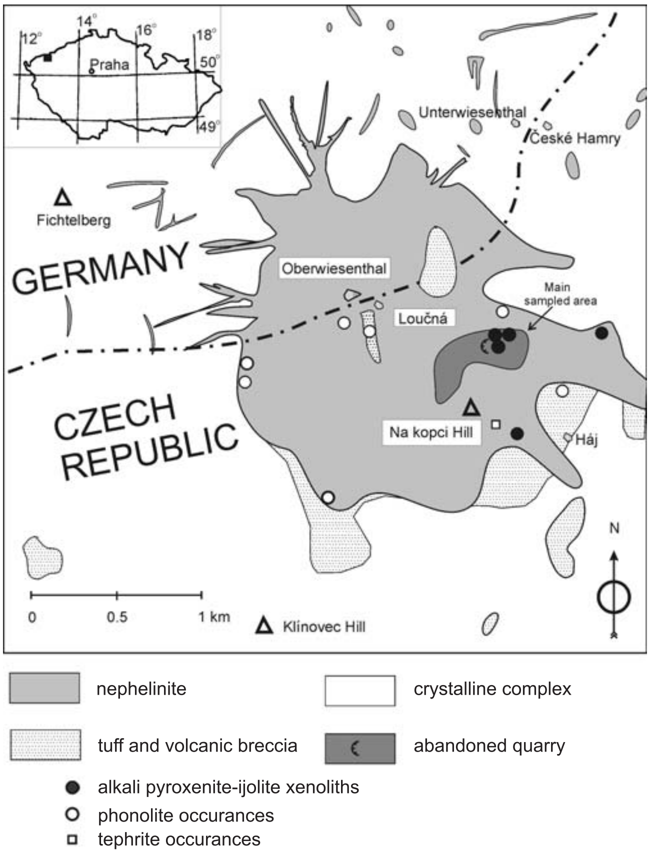

Fig. 1. Geological sketch map of the Loučná-Oberwiesenthal Volcanic Centre; compiled after Jiránek (1974) and Leonhardt (1999)

nephelinite, tephrite and phonotephrite (Reinisch, 1917; Herre, 1930; Jiránek, 1974) originated at the diffuse contact zone of with the nephelinite body. The pseudoleucite phonolite (tinguaite) dyke from Loučná is the source of the pseudoleucite megacrysts (Pivec and Ulrych, 1982; Pivec *et al*., 2004).

PETROGRAPHY OF ALKALI PYROXENITE XENOLITHS AND MINERALOGY OF THE CLINOPYROXENES

The alkali pyroxenite and ijolite xenoliths are 1 to 100 mm in size and generally subangular and in rare cases lenticular. The transitional alkali pyroxenite-ijolite xenolith types are heterogeneous with a major alkali pyroxenite and a minor ijolite component. The large variety of textures is evidence for a heterogeneous source rock with schlieren, different grain-sizes and variable proportions of felsic and mafic minerals. We are therefore concerned *de facto* with facies and not with the alkali pyroxenite and ijolite *sensu stricto*.

Petrographic characteristics of the alkali pyroxenite xenoliths show clinopyroxenite with transitions to melteigite displaying a generally coarse-grained, equigranular to porphyritic texture with grain-sizes of 1–5 mm and in some cases up to 10 mm. Some xenoliths are fractured and partly recrystallized, showing protogranular to porphyroclastic textures. The stress probably culminated after the clinopyroxene had crystallized whereas the garnet and phlogopite that crystallized at a later stage are mostly unaffected.

Euhedral to subhedral clinopyroxene makes up 52–65 modal% of the alkali pyroxenite xenoliths. It is a neutral to pale brownish green colour in thin section and shows fine oscillatory zoning. Accessory perovskite with titanian magnetite, apatite and titanite are found in subophitic relationship with clinopyroxene. Primary OH-bearing phases represented by older phlogopite and kaersutite partly altered to rhönite are restricted to a few samples. Younger phlogopite is a common accessory phase, poikilitically enclosing clinopyroxene, perovskite, titanian magnetite, apatite and schorlomite. Fine-grained feldspathoidal polycrystalline aggregates of analcime, opaques and rare glass occur interstitially usually altered to a mixture of zeolites, clay minerals and carbonates. Small vesicles are filled by analcime, Sr-chabasite, chalcedony, calcite, aragonite and strontianite.

SAMPLING AND EXPERIMENTAL METHODS

The alkali pyroxenite sample Xe-5A from Loučná is rounded (80 by 60 mm), massive, medium- to coarse-grained (3–6 mm) with a coarse-grained ijolite enclave (40 by 30 mm) in the central part. It belongs to the most mafic and geochemically primitive samples showing the following modal composition (in vol%): clinopyroxene (71), titanian magnetite (13), nepheline and analcime (9), phlogopite (2), apatite (2) and perovskite (2).

The first mineral analyses of clinopyroxene from this sample were carried out as part of a geochemical study of xenoliths of the Loučná-Oberwiesenthal Volcanic Centre (Ulrych *et al*., 2005) on a *Cameca SX-100* electron microprobe using the wavelength dispersive technique. The beam diameter was 10 µm with an accelerating potential of 15 kV. A beam current of 20 nA was measured on a Faraday cup. A counting time of 10 s was used for all elements. The standards employed were of synthetic — SiO_2, TiO_2, Al_2O_3, Fe_2O_3, and MgO — and of natural composition: e.g., jadeite, apatite, leucite, diopside, and spinel [all Kα], and barite [Lα]. The data were reduced using the X-PHI correction.

Additional quantitative chemical analyses of clinopyroxene rims (Table 1) were performed with an *ARL-SEMQ* electron microprobe at 15 kV operating voltage and 15 nA sample current, using the wavelength dispersive technique. The analyses were performed by using common natural standards: Si, Al (augite), K (adularia), Na, Al (jadeite), Cr (chromite), Fe (almandine), Ti (kaersutite), Mg (olivine), Mn (tephroite) and corrected by X-PHI corrections. The analytical results are similar to those presented by Ulrych *et al*. (2005), *cf*. the representative analyses in Table 1, No. 1, 2 and 3 and Figure 2. An average chemical composition (Table 1, No. 3) calculated from twelve new clinopyroxene analyses reveals sufficient Al to occupy the ideal two tetrahedral sites together with Si. However, some individual local analyses exhibited the same minimum tetrahedral Al deficiency, reported by Ulrych *et al*. (2005).

Crystals suitable for the X-ray work presented were checked by classical film methods. Information about the collection of X-ray data and results of structure determinations carried out with *SHELX-97* (Sheldrick, 1997) are compiled in Table 2; the resulting structural parameters are listed in Table 3. The scattering factors for neutral atoms as well as their anomalous dispersion terms were taken from the International Tables for Crystallography (1992).

Some comments about the steps of structure calculations and the refinements are necessary. From crystal chemical considerations, including the chemical analyses, the Me1 position is occupied by Mg, Ti, and Fe atoms in the ratio ~0.66 : 0.10 : 0.24. It is impossible to refine the ratio of three elements with similar atomic numbers from their scattering power by least squares calculations. Therefore the X-ray refinement, including only two atoms, yielded a Mg : Fe ratio of ~ 0.7 : 0.3. These values are in between the ratio presumed for the three elements located on this position as mentioned above.

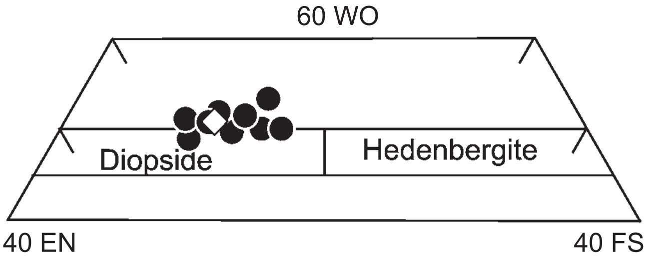

Fig. 2 Clinopyroxenes from alkali pyroxenite, Loučná (sample 5A) in the quadrilateral diagram of Morimoto (1988)

Heavy dots — analyses from Ulrych *et al*. (2005), open diamond — an average chemical composition from twelve new analyses of clinopyroxene used for this study (see Table 1); other explanations as on Table 1

Table 2

Crystal data and parameters of the X-ray single-crystal structure refinements of the clinopyroxene from Loučná-Oberwiesenthal at 295 K

Crystal data	
Crystal shape/size	cut crystal chip, 0.1mm ∅
Colour	dark green
a; *b*; *c* [Å]	9.773(2); 8.886(2); 5.308(1)
ß [°]	105.89(3)
V[Å^3]	443.3
Z	4
Space group	C2/c (15)
μ[MoKα]mm^{-1}	~3.3
Data collection	
	Nonius Kappa CCD diffractometer, MoKα radiation
Measured reflections	2697
Range of *hkl*	$\pm h, \pm k, \pm l$
2Θ [°]	80.4
Independent reflections	1387
int	0.019
Reflections with $Fo > 4\sigma(Fo)$	1174
Number of variables	54
Refinement on F^2	
$R(Fo)$; $Fo > 4\sigma(Fo)$	0.0247 (1174 data)
$R(F)$; all 1387 data	0.0342
$wR(F^2)$; all 1387 data	0.0633
$w =$	$1/[\sigma^2(Fo^2) + (0.0186P)^2 + 0.78P]$
$P =$	$[max(Fo^2,0) + 2.Fc^2]/3$
Extinction coefficient	~0.0063
Max Δ/σ	0.014
Difference Fourier [e. Å^3]	1.00 to –0.66

The ratios of occupation for the Me2 position (with Ca and Na) and T (with Si and Al) calculated from the X-ray data show large standard deviations. Nevertheless, these ratios are compatible with the results calculated from the chemical analyses.

The measurement of the Mössbauer spectra was done in the transmission mode with ^{57}Co diffused into the Rh matrix as the source moving with constant acceleration. The spectrometer was calibrated by means of a standard α-Fe foil and the isomer shift was expressed with respect to this standard at 293 K. The samples were measured at room temperature. The fitting of the spectra was performed with the help of the NORMOS program.

COMPOSITIONAL AND STRUCTURAL RESULTS

Chemical composition and structure parameters of the investigated clinopyroxene are given in Tables 1, 2 and 3, respectively. Selected interatomic bond lengths and bond angles calculated for this structure are given in Table 4.

The empirical formula of the average clinopyroxene composition with $(Ca_{0.95}Na_{0.04})$ $(Mg_{0.65}Fe^{3+}_{0.13}Fe^{2+}_{0.10}Ti^{4+}_{0.10}Al_{0.01})$ $(Si_{1.69}Al_{0.31})$ O_6 as determined by new microprobe analyses (Table 1, No. 3) shows that this clinopyroxene can be classified as subsilicic ferrian aluminian diopside . The analytical results are similar to those given by Ulrych *et al*. (2005), *cf.* the representative analyses in Table 1, No. 1, 2 and Figure 2. An average chemical composition (Table 1, No. 3) calculated from twelve new clinopyroxene analyses reveals sufficient Al to occupy the ideal two tetrahedral sites together with Si. However, some individual local analyses exhibited the same minimum tetrahedral Al deficiency reported by Ulrych *et al*. (2005).

The occupation of the Me2 site, more or less by Ca atoms (~0.98 a.p.f.u.) and the low Na content is characteristic of clinopyroxenes from alkali pyroxenite xenoliths. The <Me1-O$_6$> distance of 2.067 Å, which is relatively short compared to that of Mg-rich clinopyroxenes (Clark *et al*., 1969; Bruno *et al*., 1982), reflects the occupation of significant amounts of Fe^{3+} and Ti^{4+} at this Me1 site. The interatomic distances within the <Me2-O$_8$> polyhedron from 2.37 to 2.69 Å are within the expected range for eight coordinated Ca atoms.

The substitution of Si by Al in the tetrahedrally coordinated position leads to an enlargement of the lattice constant *c* up to 5.308 Å and a mean T-O distance of 1.657 Å. Comparable values were determined for clinopyroxenes from melilitic rocks from the Monte Vulture Volcano in Italy (Bindi *et al*., 1999) with *c* ranging from 5.294 to 5.296 Å and mean T-O distances of 1.655 Å. In these clinopyroxenes also, a significant substitution of Si by Al was described with values from 0.302 to 0.308 a.p.f.u.

Table 3

Structural parameters with e.s.d.'s in parentheses for the clinopyroxene from Loučná-Oberwiesenthal

Atom	Wyck	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Me1	4e	0	0.90596(4)	1/4	54(1)	59(1)	51(1)	0	9(1)	0
Me2	4e	0	0.30442(4)	1/4	122(1)	80(1)	84(1)	0	1(1)	0
T	8f	0.28743(3)	0.09312(3)	0.22731(6)	48(1)	53(1)	59(1)	–3(1)	13(1)	–1(1)
O1	8f	0.1137(1)	0.0871(1)	0.1384(2)	91(3)	110(3)	107(3)	–6(3)	32(3)	2(3)
O2	8f	0.3622(1)	0.2539(1)	0.3195(2)	141(3)	107(3)	117(3)	–7(3)	31(3)	–6(3)
O3	8f	0.3521(1)	0.0185(1)	0.9929(2)	99(3)	112(3)	128(3)	–38(3)	24(3)	2(3)

Wyck — number of positions and Wyckoff notation; the anisotropic displacement factors are defined as $exp(-2\pi^2 \sum_{i=1}^{3}\sum_{j=1}^{3}$ Uij hi hj a*i a*j) [Å × 10^4]; Me1 = $(Mg_{0.65}Fe^{3+}_{0.13}Fe^{2+}_{0.10}Ti^{4+}_{0.10}Al_{0.01})$; Me2 = $(Ca_{0.95}Na_{0.04})$; Ti = $(Si_{1.69}Al_{0.31})$

Table 4

Selected interatomic distances [Å] and bond angles in [°] in the structure of the clinopyroxene from Loučná-Oberwiesenthal

Me1	O2	O2’	O1	O1’	O1’’	O1’’’
O2	2.012(1)	2.982(3)	2.937(3)	2.877(3)	4.127(3)	2.974(3)
O2’	95.6(1)	2.012(1)	2.877(3)	2.937(3)	2.974(3)	4.127(3)
O1	92.4(1)	89.9(1)	2.058(1)	4.114(3)	3.072(3)	2.776(3)
O1’	89.9(1)	92.4(1)	176.6(3)	2.058(1)	2.776(3)	3.072(3)
O1’’	170.0(3)	91.7(1)	94.4(1)	83.0(1)	2.130(1)	2.789(3)
O1’’’	91.7(1)	170.0(3)	83.0(1)	94.4(1)	81.8(1)	2.130(1)

Me2	O2	O2’	O1	O1’	O3	O3’	O3’’	O3’’’
O2	2.370(1)	4.626(3)	2.937(3)	3.156(3)	4.625(3)	2.600(3)	4.165(3)	3.412(3)
O2’	154.8(1)	2.370(1)	3.156(3)	2.937(3)	2.600(3)	4.625(3)	3.412(3)	4.165(3)
O1	76.4(1)	83.2(1)	2.382(1)	2.789(3)	4.275(3)	4.554(3)	4.999(3)	3.607(3)
O1’	83.2(1)	76.4(1)	71.7(1)	2.382(1)	4.554(3)	4.275(3)	3.607(3)	4.999(3)
O3	140.3(1)	63.7(1)	120.2(1)	135.0(1)	2.547(1)	3.389(3)	2.889(3)	2.674(3)
O3’	63.7(1)	140.3(1)	135.0(1)	120.2(1)	83.4(1)	2.547(1)	2.674(3)	2.889(3)
O3’’	110.7(1)	84.5(1)	160.2(1)	90.4(1)	66.9(1)	61.3(1)	2.692(1)	4.368(3)
O3’’’	84.5(1)	110.6(1)	90.4(1)	160.2(1)	61.3(1)	66.9(1)	108.5(1)	2.692(1)

T	O2	O1	O3	O3’
O2	1.618(1)	2.782(3)	2.701(3)	2.600(3)
O1	117.6(1)	1.634(1)	2.717(3)	2.730(3)
O3	110.0(1)	110.2(1)	1.679(1)	2.674(3)
O3’	103.3(1)	110. 0(1)	104.7(1)	1.698(1)

The value for the lattice constant *c*, the identity period in the direction of the Si_2O_6 chain can further be expressed in a stretching factor defined by Liebau (1985). In the case of silicate double single chains this stretching factor *fs* was defined to *fs* = I_{chain}/2 x 2.70 (Liebau, 1985). I_{chain} = 5.308 Å is the identity period for the clinopyroxene under discussion and 2.70 a factor, half the chain period in shattuckite $Cu_5(Si_2O_6)_2(OH)_2$ with *fs* = 1 (Kawahara, 1976). The value obtained in our case is 0.983.

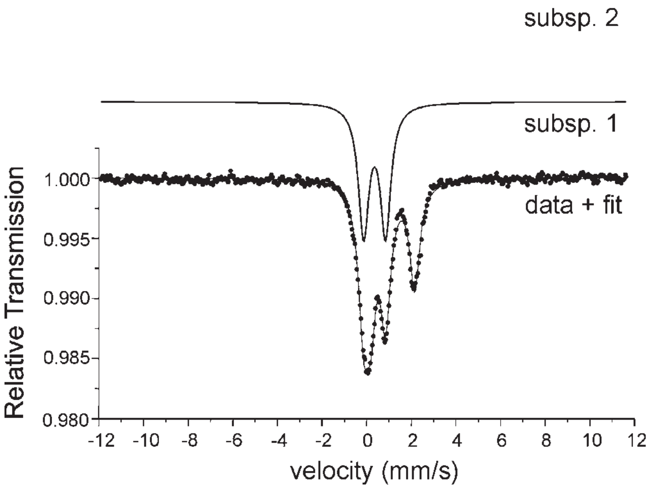

Fig. 3. Fitted Mössbauer spectra of the clinopyroxene from Loučná-Oberwiesenthal

Subsp. 1 — subspectrum 1 corresponds to paramagnetic iron Fe^{3+} in octahedral coordination, subsp. 2 — subspectrum 2 to paramagnetic iron Fe^{2+} in the same coordination

The Mössbauer spectrum, consisting of two well-defined doublets (Fig. 3), revealed the presence of both Fe^{3+} and Fe^{2+}, and confirms the results of the crystal structure investigation and crystal chemical considerations. Assuming the same recoil factor for both Fe^{3+} and Fe^{2+} (in the same crystallographic position) a molar ratio Fe^{3+}/Fe^{2+} equal to 56 : 44 was obtained (Table 5). The relative areas of spectral absorption were taken to approximate the relative abundance of the two cations. The average amount of 7.56 wt% FeO_{tot} in the clinopyroxene (Table 1) was recalculated into 4.71 wt% Fe_2O_3 and 3.33 wt% FeO.

Mössbauer data also allowed us to conclude on the site symmetry for Fe^{3+} cations. According to Ménil (1985), the usual isomer shift values for Fe^{3+} are the following: (1) 0.10–0.30 mm/s for Fe^{3+} in the tetrahedral site, and (2) 0.28–0.50 mm/s for Fe^{3+} in the octahedral site. Our Mössbauer

Table 5

Mössbauer data for the clinopyroxene from Loučná-Oberwiesenthal

	Subspectrum 1	Subspectrum 2
Isomer shift	0.36 mm/s	1.17 mm/s
Quadrupole splitting	0.98 mm/s	1.97 mm/s
Full line width at half height	0.57 mm/s	0.54 mm/s
Relative area [%]	56	44

spectroscopy measurements (isomer shift of 0.36 mm/s) suggest that Fe^{3+} is present only in the Me1-O_6 positions.

DISCUSSION

The alkali pyroxenite-ijolite xenoliths in nephelinite of the Loučná-Oberwiesenthal Volcanic Centre probably represent fragments of a buried intracrustal Tertiary alkaline complex. Two magmatic phases sourced the crystallization of the alkali pyroxenite-ijolite series: (1) early crystallization of alkali pyroxenite mafic minerals (including the cores of clinopyroxenes), (2) late crystallization of ijolitic melt injected into the alkali pyroxenite (nepheline and clinopyroxene rims). The early-crystallized clinopyroxenes show newly crystallized rims of different composition on partly resorbed phenocrysts indicating different PTX conditions of the ijolite melt crystallization (*cf.* Dal Negro *et al.*, 1985).

The Al^{IV} deficiency in T-sites in rare analyses of Si-deficient clinopyroxene of the alkali pyroxenite xenoliths (Ulrych *et al.*, 2005) was covered by Fe^{3+} ions according to the recommendation of Morimoto (1988). The average chemical composition of the clinopyroxene does not reveal this deficiency. The quantity of Al in the melt is thus mostly sufficient to cover the two tetrahedral sites but not sufficient to enter the octahedral positions.

A similar Si- and Al-deficiency in T-sites was found in clinopyroxenes from alkali clinopyroxenite xenoliths in SW Ugandan kamafugites (up to 0.08 a.p.f.u.; Lloyd *et al.*, 1991, 1999), leucite-bearing volcanics (Cundari and Ferguson, 1982; Dal Negro *et al.*, 1985) from the Roman region, Italy, and lamproites from Smoky Butte, Montana (Mitchell *et al.*, 1987). However, according to Stoppa *et al.* (2002), Si- and Al-deficiency in clinopyroxenes of kamafugites of the Umbria Latinum Ultra-alkaline district, Italy, actually require Ti, rather than Fe^{3+}, to enter the T-sites.

The Si- and Al-deficient clinopyroxenes occur in a limited number of parageneses: (1) alkali clinopyroxenites (xenoliths in kamafugite and nephelinite), and (2) leucite-bearing volcanics (kamafugite, lamproite). P-T experiments indicate that the kamafugites were in equilibrium with clinopyroxenite at a depth of >60 km. It is therefore argued that the xenoliths are fragments of a laterally variable clinopyroxenite layer in Uganda's Western Rift deep crust-mantle (Lloyd *et al.*, 1991, 1999). Similar conditions can be supposed for the buried deep intracrustal alkaline complex beneath the Loučná-Oberwiesenthal Volcanic Centre (Ulrych *et al.*, 2005). Total lithosphere thickness beneath the Bohemian Massif is 80–140 km, of which about 70–80 km are possibly formed by olivine-rich mantle lithosphere (Plomerová *et al.*, 1998).

CONCLUSION

The presence of alkali pyroxenite-ijolite xenoliths in the host nephelinite of the Loučná-Oberwiesenthal Volcanic Centre points to the existence of a buried deep crustal alkaline complex of Tertiary age with Sr-Nd isotope ratios in clinopyroxenes consistent with mantle sources of HIMU-affinity (Ulrych *et al.*, 2005).

The magmatic processes that led to the genesis of the alkali pyroxenite-ijolite series can be described by a two-phase model (with special respect to clinopyroxene crystallization):

— early crystallization of clinopyroxene±phlogopite, perovskite, apatite and titanian magnetite of alkali pyroxenite from a nephelinitic magma, leading to a residual melt of ijolitic composition.;

— back injection of the ijolitic melt into the alkali pyroxenite resulting in intermingling, and reaction with it and the crystallization of new phases (e.g., nepheline and clinopyroxene rims).

The early-crystallized clinopyroxenes show newly crystallized rims of different composition on partly resorbed phenocrysts indicating different PTX conditions of the ijolite melt crystallization in comparison to the early alkali pyroxenite portion of the nephelinite magma.

The rare negligible Al^{IV} deficiency in tetrahedral sites of rims of Si-deficient clinopyroxene phenocrysts was covered by Fe^{3+} ions on the basis of IMA-recommended calculation. However, the average chemical composition of the clinopyroxene rim does not reveal the Si- and Al-deficiency. The negligible deficiency (up to 0.019 a.p.f.u.) is restricted to sporadic local electron microprobe analyses only. The quantity of Al in the melt is thus mostly sufficient to cover the two tetrahedral sites but insufficient to enter the octahedral positions. The presence of Fe^{3+} in the T-position of Si- and Al-poor clinopyroxenes was not confirmed by the X-ray structural analyses but the Mössbauer spectroscopy (isomer shift of 0.36 mm/s) measurements leads us to the conclusion that Fe^{3+} is present only in the Me1-O_6 positions.

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