

Oscillatory-zoned crystals of the pyrochlore-group minerals from the Guaniamo kimberlites, Venezuela: first occurrence of pyrochlore in kimberlite

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Crystals of the pyrochlore-group minerals were found in kimberlites from the 'upper' part of the La Ceniza sheet, Guaniamo province, Venezuela. To author's knowledge, it is the first occurrence of pyrochlore in kimberlite. This mineral is the most common accessory mineral of carbonatites and related alkaline rocks. The Guaniamo kimberlites are highly diamondiferous. The previous studies (Sobolev *et al.*, 1998) showed uncommonly high percentage (>99%) of E-type diamonds in kimberlites of the northwestern part of the Guyana shield at Guaniamo. The rocks studied are weakly altered, coarse-porphyritic micaceous kimberlite (Kaminsky *et al.*, 2004). Porphyritic structure is due to macrocrystal-phenocrystal olivine (70-75 vol. %; size - 1-8 mm; core - Fo₉₁₋₈₉, rim - Fo₈₈₋₈₆) and phlogopite (2-5 vol.%, size - up to 5 mm) (Fig. 1). Rare xenocrysts of garnet, Mn-ilmenite, picroilmenite and chromian spinel, and peridotite microxenoliths also occur in these kimberlites (Kaminsky *et al.*, 2004).

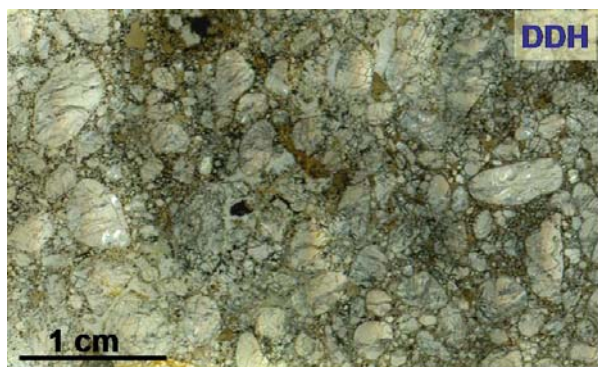


Fig.1. General view of the La Ceniza kimberlite with abundant pyrochlore-group mineral, transmitted light.

Groundmass (≈ 30 vol.%) is fine-grained and consists of microphenocrysts (size ≈ 200 μm) of zoned olivine (Fo₉₀₋₈₈) and phlogopite on the background of aggregate of zoned spinel (chromite-Ti-magnetite-magnetite), phlogopite with tetraferriphlogopite rim, dolomite, calcite, magnesite, pyrochlore, Fe-Ni-Cu-sulfides (pentlandite, chalcopyrite) and apatite (size ≈ 50-100 μm) in serpentine matrix. Moreover, secondary barite, brucite, pyrite, spongy magnetite and hematite occur in the groundmass. In general, the distribution of minerals in groundmass is not regular: some areas are

rich in silicates, whereas other areas contain abundant carbonates.

It should be noted that abundance of pyrochlore in different kimberlite samples of La Ceniza essentially varies. One specimen (DDH) contains relatively considerable amount of this mineral (0.5-1 vol. %) (Fig. 2-3), in other samples it occurs as very rare accessory phase.

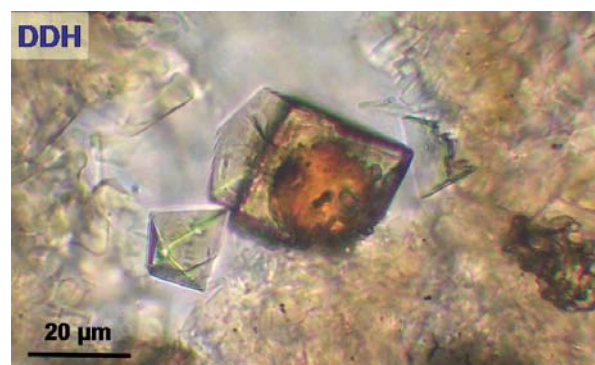


Fig. 2. Crystals of pyrochlore-group mineral in serpentine-mica aggregate, La Ceniza kimberlite, transmitted light.

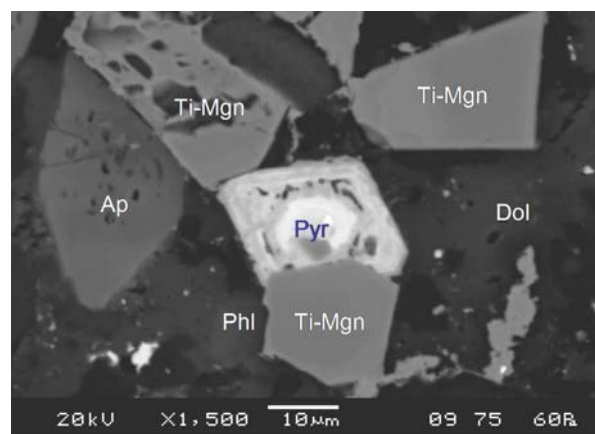


Fig. 3. Relationships of pyrochlore in kimberlite groundmass, La Ceniza, BSE image. Pyr - pyrochlore; Phl - phlogopite; Ti-Mgn - zoned spinel; Ap - apatite; Dol - dolomite.

All crystals of pyrochlore group mineral (20-50 μm) in kimberlite groundmass show fine oscillatory zoning with thickness of individual zones less than 5 μm (Fig. 3-4). Textural evidence indicates that pyrochlore crystallized relatively later than most groundmass minerals (serpentine after olivine, phlogopite, dolomite

and zoned spinel), which occur as crystalline inclusions in this mineral. The central and outer parts of the crystals of the pyrochlore-group mineral are well distinguished in transmitted light (centre - red-brown; rim - light brown) and on BSE images (Fig. 2-5). Sometimes, the boundary between these parts is decorated by crystalline inclusions, assuming interruption in crystal growth (Fig. 3, 5).

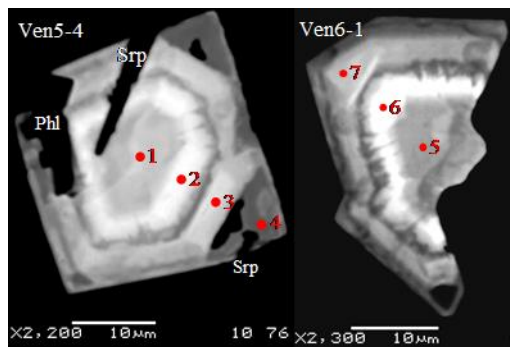


Fig. 4. Individual zoned crystals of the pyrochlore-group mineral, La Ceniza kimberlite, BSE images. Srp – serpentine.

The very broad variations in chemical composition are common of all pyrochlore crystals (in wt.%): Nb₂O₅ - 25.6-58.9; Ta₂O₅ - 0.6-10.1; ZrO₂ - 1.4-23.7; TiO₂ - 4.6-14.3; CaO - 1.6-17.5; Na₂O - 0.4-5.7; ThO₂ - 3.3-22.3; UO₂ - 0.2-8.0; LREE₂O₃ - 1.2-4.6; MnO - 0.1-1.1; BaO - 0.1-7.6; SrO - 0.0-1.0; PbO - 0.1-1.3; F - 0.6-4.5 (see also Table 1).

Table 1. Representative compositions of zoned pyrochlore crystals.

wt. %	1	2	3	4	5	6	7
	Ven5-4			Ven6-1			
	c	m1	m2	r	c	m	r
SiO ₂	0.00	0.04	0.00	0.19	0.06	0.14	0.01
TiO ₂	12.09	10.48	9.19	6.46	12.53	9.97	8.95
ZrO ₂	7.26	8.73	10.14	1.86	7.72	12.18	8.32
UO ₂	3.61	3.10	5.20	0.16	6.35	7.29	4.26
ThO ₂	12.53	14.71	13.34	4.14	10.38	17.56	12.31
SnO ₂	0.03	0.04	0.05	0.00	0.06	0.04	0.02
Nb ₂ O ₅	34.54	35.95	36.91	58.86	34.73	28.35	40.44
Ta ₂ O ₅	5.66	5.10	6.76	0.73	7.13	9.13	5.53
FeO _i	1.60	1.88	1.65	0.40	1.61	2.14	1.46
MnO	0.43	0.40	0.37	0.06	0.35	0.44	0.33
MgO	0.12	0.12	0.15	0.24	0.15	0.25	0.13
CaO	11.49	9.80	5.51	16.93	8.63	1.62	6.48
BaO	0.25	0.26	1.17	0.13	0.25	2.53	0.74
SrO	0.00	0.04	0.04	0.14	0.06	0.08	0.04
La ₂ O ₃	0.35	0.32	0.35	0.13	0.45	0.32	0.26
Ce ₂ O ₃	2.36	1.82	2.50	1.06	2.24	1.95	2.34
Nd ₂ O ₃	0.52	0.42	0.52	0.16	0.39	0.39	0.40
Na ₂ O	4.56	3.49	2.90	5.65	2.70	2.68	5.36
PbO	0.61	1.03	0.57	0.00	0.63	0.43	0.39
F	1.98	2.35	1.85	4.21	1.90	0.70	2.27
Sum	99.98	100.08	99.17	101.48	98.31	98.18	100.03
O=F ₂	0.83	0.99	0.78	1.77	0.80	0.29	0.96
Sum	99.15	99.09	98.39	99.71	97.51	97.89	99.07

WO₃, HfO₂, Yb₂O₃, Bi₂O₃ are below detection limits. c, m, r – core, middle and rim of crystal. Red numbers indicate spots on Fig. 4.

According to IMA classification for the pyrochlore group (Nb>Ta; (Nb+Ta)>2Ti, Hogarth, 1977) most of compositions from the Guaniamo kimberlite fall into the pyrochlore subgroup and may be classified as uranoan thorian pyrochlore. Some compositions are

intermediate between pyrochlore and betafite. Deviations towards microlite composition are not essential (Fig. 6).

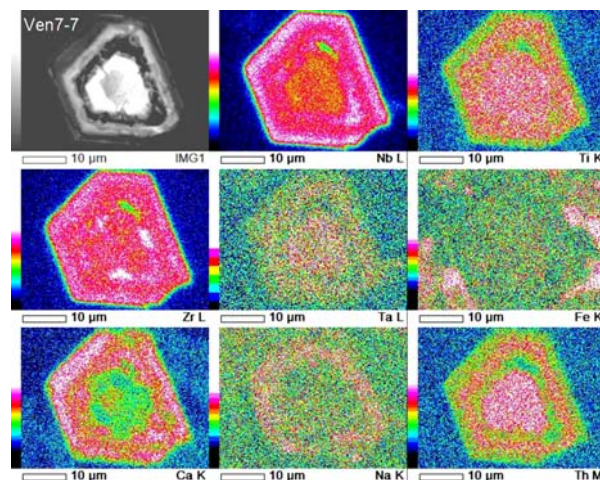


Fig. 5. Elemental mapping of individual zoned crystal of the pyrochlore-group mineral.

In general, the central zones of crystals are essentially richer in ThO₂, ZrO₂, TiO₂ and Ta₂O₅ than outer zones. Zr-rich compositions (21-23.7 wt.% ZrO₂) form individual zones or sectors in the core or near the core-rim boundary (Fig. 5).

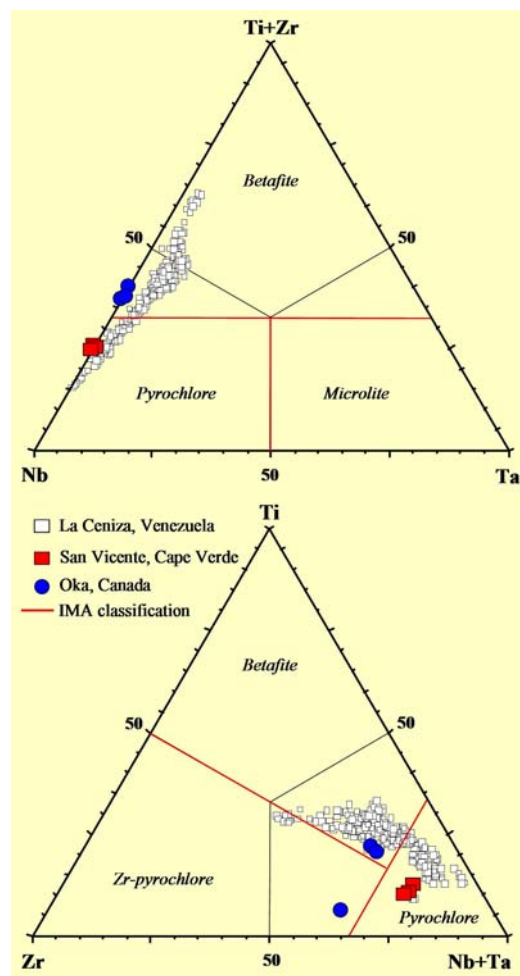


Fig. 6. Compositional variations of the pyrochlore-group mineral from the La Ceniza kimberlites in comparison with Zr-rich pyrochlore from carbonatites.

Ba-Sr-rich compositions (up to 7.6 wt.% BaO, 1.0 wt.% SrO) are confined to the outermost zones of crystals. Individual rounded segregations (up to 2 μm) of plumbopyrochlore may occur within the outer part (Fig. 7). Some zones show low totals (90-95 wt.%) due to high contents of ThO_2 and UO_2 and possible metamict nature.

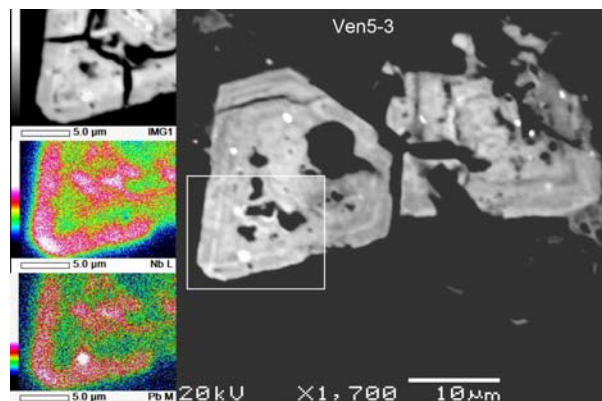


Fig. 7. Rounded inclusions of plumbopyrochlore in the outer part of zoned crystal of the pyrochlore-group mineral. BSE images and elemental mapping.

In general, the Guaniamo pyrochlore drastically differs from worldwide pyrochlores in Th-Zr enrichment. The findings of Zr-rich pyrochlore in the San Vicente carbonatite, Cape Verde (10.3 wt.% ZrO_2 , Hodgson, Le Bas, 1992), the Oka carbonatite, Canada (16.3 wt.% ZrO_2 , Zurevinski, Mitchell, 2004), and the Venezuelan kimberlite (23.7 wt.% ZrO_2) bring up possible separation of Zr-dominant subgroup within the pyrochlore group.

The appearance of the pyrochlore-group mineral is still enigmatic. Zircon, perovskite and rutile which are most common concentrators for Nb, Zr, Ta, Th, U and REE are not found in the La Ceniza kimberlites. From one

side, the presence of pyrochlore may be a specific feature of the Guaniamo kimberlites which are “anomalous” and “transitional” between Group-1 and Group-2 kimberlites according to isotopic and geochemical data (Kaminsky *et al.*, 2004). From other side, these kimberlites occur in Paleoproterozoic granitoid rocks and, consequently, contamination of these country rocks is not excluded during emplacement of kimberlite magma.

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