

# Evolution of Pyrochlore in Carbonatites: the Angola Case

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## INTRODUCTION.

Members of the pyrochlore mineral group are the most important Nb mineral, and their concentrates are produced mainly in carbonatites. The chemical composition of the group is widely variable, with a general formula  $X_2Y_2O_6(O,OH,F)$ , where  $X=Ca, Na, Ba, Sr, Pb, U, Th, Mn, REE, Fe, Sn, Bi, Sb$ ;  $Y= Nb$  (pyrochlore s.s.), Ta (microlite), Ti (betafite).

The aim of this contribution is to provide details about the changes in chemical composition of pyrochlore in carbonatite systems according: a) the different level of emplacement (plutonic to volcanic), b) the hydrothermal modifications and c) the supergenic processes.

## GEOLOGY.

We have used a model of carbonatite system the outcrops from the Lucapa structure in Angola. It is a riftogenic system produced during the Early Cretaceous, trending NE-SW and crosscutting Angola. The carbonatites are well developed at the SW part of the structure (Lapido-Loureiro, 1973; Alberti et al., 1999). As a examples of different levels of emplacement, we selected the carbonatites of the Txivira, Bonga and Catanda complexes.

The Txivira complex is the most extensive, and is emplaced in plutonic levels. Therein the carbonatites form annular structures crosscutting gabbros, ijolites, nepheline syenites and syenites; the ensemble is intruded in fenitized Precambrian granites (Matos-Alves, 1968). Some late hydrothermal events produced strong replacement of carbonatite by fluorite; in association with this replacement calcite was replaced by fine-grained dolomite and eventually ankerite.

The Bonga complex consist in concentric structure, with massive carbonatites at the center (partly replaced by ankerite carbonatites) surrounded by concentric carbonatite ring-dykes. The ensemble is crosscut by alnoite pipes. It could be produced in subvolcanic environments, as suggested by the extensive development of carbonatite breccias.

The Catanda structure comprises some deeply eroded volcanic pyroclastic carbonatite buildings, accompanied by minor carbonatite lavas and natrocarbonatites. The pyroclastic sections have in some cases a thickness of more than 100 m. Pyroclastic rocks are generally organised in cycles with graded bedding. Carbonatite agglomerates occurs at the base of the cycles, and they are composed by block fragments of fenitized granites, amphibolites and carbonatites, surrounded by a matrix of carbonate and fine-grained fragments. The upper part of the cycles is composed by poorly consolidated lapilli. The weathering of the pyroclastic rocks is very advanced. In natrocarbonatites the early nyerereite and gregoryite phenocrysts have been completely replaced by calcite.

All these outcrops have been affected by different supergene processes, comprising karstification and deep weathering.

## PYROCHLORE IN PLUTONIC CARBONATITES.

Pyrochlore in Txivira is scarce, although it is found in the primary carbonatites, the fluorite bodies and the dolomite replacements (Bambi et al., 2004). It is fine-grained (less than 1 mm in size) and euhedral, forming neat octahedrons. The crystals are generally unzoned but commonly altered. The alteration patterns are complex, producing several generations of replacements.

Primary pyrochlore is rich in F and Nb, close in composition to the pyrochlore s.s. pole. Hence, the main cation in the position Y is Nb, and Ca and Na are dominant in X; the composition is quite constant in all the massif.

On the other hand, the ratios Nb/Ta/Ti are constant, either in the unaltered carbonatites, in the fluorite bodies and in the replaced carbonatites, thus suggesting that pyrochlore crystals becomes restitic during the replacement processes leading to the development of these units. However, inside the fluorite bodies and the associated dolomitized areas the alkali content is leached and replaced by Ba, U and Th, in accordance with the content of barite and U minerals scattered into these units.

Finally, some late generations of pyrochlore produced during the weathering processes are enriched in Sr and REE (Fig. 1). These enrichments in Ba, Sr and REE are congruent with the development of supergenic minerals as REE carbonates, barite and celestine.

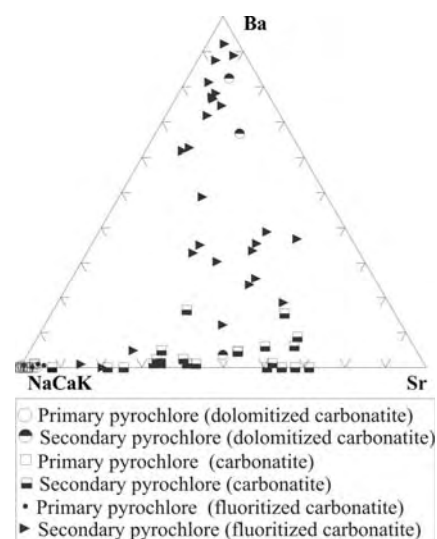


fig. 1. Composition of pyrochlore from Txivira (X position).

**palabras clave:** carbonatita, natrocarbonatita, pirocloro, Nb, Ta, Ti, U, REE, Ba, Sr, hidrotermal, supergénico, Angola.

**key words:** carbonatite, natrocarbonatite, pyrochlore, Nb, Ta, Ti, U, REE, Ba, Sr, hydrothermal, supergenic, Angola.

### PYROCHLORE IN SUBVOLCANIC CARBONATITES.

Pyrochlore content is higher in the Bonga carbonatites, in particular, at the outer part of the intrusion, in the ring dikes. Pyrochlore is euhedral, forming sharp octahedrons up to 1 cm in size, although usually has 100-300  $\mu\text{m}$  in diameter. It occurs scattered among the carbonatite, but in some cases it is concentrated in some bands, in all the cases associated with apatite and magnetite.

The chemical composition of the pyrochlore from Bonga is enriched in Ti and Ta by comparison with the pyrochlore from Txivira. Contrastingly, no significative changes are found in the X position when comparing to Txivira. Although no hydrothermal alterations are present in Bonga, the weathering trends are similar as those observed in Bonga.

On the other hand, due to extensive weathering of the massif, pyrochlore is also concentrated at the colluvial sediments around the Bonga massif. This fact produces a strong anomaly in radioactivity in the soils up to some kilometers around the massif.

### PYROCHLORE IN VOLCANIC CARBONATITES.

Pyrochlore is rare in the carbonatite pyroclasts of Catanda, since they contains a significative proportion of fragments of host rocks, whose contribute to dilute the amount of ore.

The pyrochlore content is slightly higher in the carbonatite lavas, although the crystals are very small (less than 100  $\mu\text{m}$ ) and, in many cases, are broken. Volcanic carbonatites have the highest contents of Ta found in the angolan carbonatites, and contents high as 6,4 wt% have been found in some crystals from natrocarbonatites. Despite they are generally unzoned, some primary zoning can produce outer parts strongly enriched in U and Th.

### DISCUSSION AND CONCLUSIONS.

The Ta content in pyrochlore has a slight increase from the plutonic levels of the carbonatite systems to the volcanics (Fig. 2). This could represent some kind of fractionation in the ratio Ta/Nb from the plutonic to the volcanic levels, similar as what has been classically

reported in granitic systems. In similar way, the enrichment of Ta in the natrocarbonatites of Catanda can be related with the alkaline content of these more evolved lavas.

However, the alkaline carbonatite lavas from Catanda and those of present-day eruptive carbonatites (i.e. Oldoinyo Lengai, Tanzania; Simonetti et al., 1997) are very poor in Nb-Ta, thus suggesting that the Ta content was very low in the less evolved melts. Hence, most of Nb and Ta precipitated in the deepest part of the system and, in particular, in the intermediate levels.

The high development of pyrochlore in the deep levels is congruent with the experimental data suggesting that pyrochlore tends to crystallize in magmas enriched in F (Jago & Gittins, 1993). This fact can also explain the high Nb contents in pyrochlore from Tchivira and the higher betafite content in the samples from Bonga.

The carbonatites from Txivira and Bonga are enriched in F, as indicated by the strong replacement of carbonatites by fluorite in Txivira and the high content of fluorapatite in Bonga. Hence, the wide precipitation of fluorapatite in Bonga may explain the pyrochlore enrichments in this massif. Moreover, the primary pyrochlore from both massifs contains F as the dominant additional anion in the structural formula.

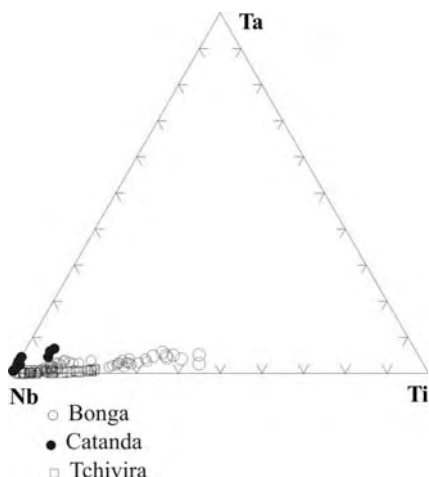


fig. 2. Evolution of the composition of pyrochlore (content of Y position) from intrusive plutonic levels (Tchivira) to intrusive subvolcanic (Bonga) to extrusive (Catanda).

The cation content in Y (Nb-Ta-Ti) of the primary pyrochlore does not changes during the subsolidus processes, and it is stable during the hydrothermal and

supergene processes. However, the alkalis of the position X can be easily removed and replaced by Ba and U-Th (in the hydrothermal stages connected with fluorization and dolomitization of the carbonatites) and by Sr and REE (in the supergene environment); the X position can have a variable degree of vacancies.

The high content in Th and U can be used for exploration of pyrochlore enrichments around the angolan carbonatite massifs, in particular, in the soils, laterites, colluvial sediments and alluvial sediments.

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