Subsolidus Processes in the Longonjo and Bailundo Carbonatites (Angola)

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INTRODUCTION

The Bailundo and Longonjo carbonatites are extremely affected by subsolidus processes leading to extensive development of iron oxide deposits. Hence, these carbonatites were considered as a target for Fe and, in less extension, P. In addition, these carbonatites are a good laboratory to study the behavior of Nb and the REE during the subsolidus processes. The aim of this contribution is to provide information about the textures and chemistry of some secondary minerals.

GEOLOGICAL SETTING

Bailundo and Longonjo carbonatite complexes are located in the Huambo province, and are among the largest carbonatite bodies in Angola. These intrusives belong to the Parana-Namibia-Angola early Cretaceous alkaline-carbonatitic province; wich is related to the break-up of Pangea (Ernst and Bell, 2010). Bailundo and Longonjo massifs are associated with the Lucapa structure, a tectonic corridor that crosses Angola trending NE-SW. Most of the carbonatites and kimberlites in Angola occur into this tectonic structure (more details in Castellano et al. 2011).

STRUCTURE

The carbonatites of Bailundo and Longonjo are hosted by Archean granitic rocks exhibiting a deep fenitization. Both ring complexes have concentric dikes around the carbonatitic core, corresponding with a plug intrusion in subvolcanic context.

The core of the structures consists of carbonatites and carbonatite breccias. Both units are crosscut by a dense network of quartz veins. These veins are 1 cm to 1 m in width and produced a strong silicification event on the carbonatites.
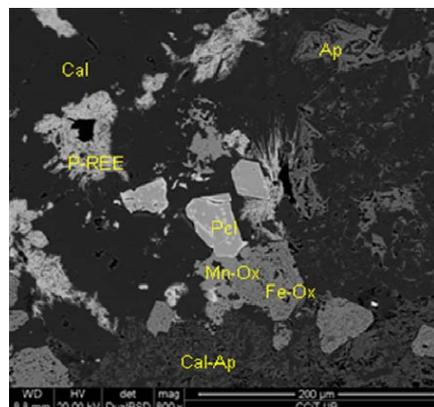

fig. 1. SEM-BSE image of a sample of an altered carbonatite from the center of the Bailundo carbonatite complex, showing primary and secondary phases. Mineral abbreviations: Pcl: pseudomorphs of euhedral primary pyrochlore, Ap: primary apatite, Cal: calcite, MnOx: secondary Mn-oxide, FeOx: secondary Fe-hydroxides pseudomorphic after magnetite crystals. Cal-Ap: fine intergrowths of secondary carbonates with secondary apatite. PREE: Late REE phosphates.

The external parts of the complexes are characterized by ring dikes, made of carbonatite breccias with a strong fenitization of the host rock.

All the carbonatites have been extremely weathered and residual clay deposits unconformably cover part of the outcrops.

PETROGRAPHY

The primary mineral assemblages have been strongly overprinted by new mineral associations produced during hydrothermal and supergenic processes. Therefore, it is difficult to reconstruct the primary mineral associations. Textural relationships of samples of NW and center of Bailundo and Longonjo massifs, suggest a primary association comprising an intergrowth of calcite and apatite crystals (Fig. 1), accompanied by accessory minerals as magnetite, primary pyrochlore, baddeleyite and pyrite.

Secondary minerals fully replace the early mineral associations. A general silicification produces milky quartz filling veins; at the same time fine-grained anhedral quartz replaces the hosting carbonates along grain rims. Hydrothermal quartz may be accompanied with fine-grained euhedral pyrochlore, ilmenorutile, barite, fluorite and abundant fine-grained secondary apatite (Fig. 1).

Sr-rich dolomite and different generations of calcite are the main component of the replaced carbonatites. Cathodoluminescence (CL) has been used to distinguish among different generations of carbonates (Fig. 2) and apatite. The EPMA analyses of these calcite crystals show that small differences in the proportions of Mn, Mg and Fe produce an important difference in CL behavior (Table 1).

Calcite	%wt Mn	%wt Mg	%wt Fe	CL
1	0.20	0.38	0.61	none
6	0.81	0.09	0.05	yellow
7	0.59	0.07	0.07	yellow
8	0.01	0.62	0.02	none

Table 1: Example of changes in CL among different generations of calcite, as related with changes in major chemical composition.

In absence of significative contents of REE elements, Mn should be the CL activator and Fe the CL quencher in these samples. However, the CL behavior of calcite could be influenced by small amounts of REE elements, which need more precise analysis to be detected. The low proportions of Sr and REEs in the analyzed samples, in any

case, suggest that all of these calcite generations are secondary.
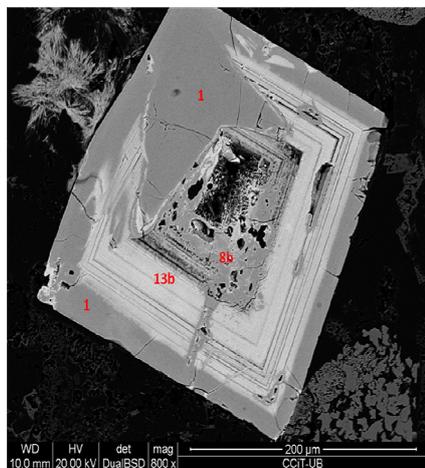

fig 2. *Complex internal texture of a pyrochlore crystal from Bailundo. A Pb-rich secondary pyrochlore (13b) replaced completely the crystal along the primary zoning, and a late generation with Ca-Na-F rich pyrochlore (1) replaces all the above generations along the grain rims and cracks. SEM-BSE image.*
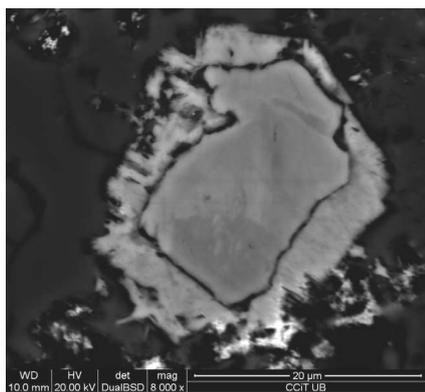

fig 3. *Nb-bearing rutile partly replaced along grain rims by goethite. Slighter areas in the rutile core correspond to Nb-rich domains. SEM-BSE image.*

Fe-Mn botryoidal hydroxides are very common and can produce large accumulations. Most of them are produced by pseudomorphic replacement of the Fe- and Mn-rich carbonates, magnetite and pyrite, and can be accompanied with a late generation of Mn-rich calcite. Large amounts of fine-grained REE phosphates and REE carbonates overgrowth these late oxides. Finally, a late generation of thin calcite veinlets cuts all the pre-existing minerals.

Nb- MINERALS

Pyrochlore from Longonjo is found as small euhedral octahedral crystals, less than 250 µm, but in Bailundo they can reach up to 1 mm in diameter. Internal texture of all of these grains is extremely

complex and has important differences with the well established alteration sequences in pyrochlores from other carbonatites in Angola and in the world (i.e., Wylliams et al., 1997; Torró et al., 2012).

Worldwide pyrochlore crystals are generally complex, and the existence of several generations has been attributed to modifications of the primary compositions, by subsolidus processes, due to the action of hydrothermal and supergenic fluids. This type of replacements produces changes mainly in the A position, and at the same time, the original F is replaced by OH. In a first stage, Na can be extracted from the structure. In a second stage, Ca can be partly or completely removed. Charge balance is achieved by introducing Ba, Pb or Sr.

In general terms, the Bailundo and Longonjo pyrochlores follow these chemical trends of alteration. However, the pyrochlore crystals from Longonjo and Bailundo have some clearly secondary pyrochlores having F-, Ca- and Na- rich compositions, close to those from the typical primary pyrochlores (fig. 2). On its turn, these "primary" pyrochlores are again replaced by the normal sequence of secondary pyrochlores.

Secondary pyrochlores are enriched in Ba in Bailundo, whereas those from Longonjo are devoid of Ba.

Nb-bearing rutile is more common in Longonjo. It occurs in discrete small anhedral grains scattered in the matrix of secondary carbonates or replacing magnetite. They are heterogeneous because of slight changes in the Nb content (Fig. 3). They are replaced by iron hydroxides.

DISCUSSION AND CONCLUSIONS

The complex sequence of alteration of pyrochlores can be explained by the repetition of subsolidus processes, perhaps because the existence of new hydrothermal events related with different pulses of carbonatite intrusions.

The source for the elements found in the secondary pyrochlores (Ba, Sr, Pb) is controversial. Large amounts of Ba and Sr could be produced during replacement of primary magmatic carbonates by hydrothermal fluids.

However, these elements could also be present in the hosting granitic rocks, and be enriched in the fluids during the fenitization processes. In this case, differences in composition between secondary pyrochlores can be explained by different degrees of interaction with the host rock. Stable and radiogenic isotope data are necessary to solve this problem.

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