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LITHOS

Lithos 104 (2008) 54-70

www.elsevier.com/locate/lithos

### Zr-rich accessory minerals (titanite, perrierite, zirconolite, baddeleyite) record strong oxidation associated with magma mixing in the south Peruvian potassic province

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Received 31 July 2007; accepted 27 November 2007 Available online 8 December 2007

#### Abstract

The Oroscocha Quaternary volcano, in the Inner Arc Domain of the Andean Cordillera (southern Peru), emitted peraluminous rhyolites and trachydacites that entrained decimetric to millimetric lamprophyric blobs. These latter show kersantite modal compositions (equal proportion of groundmass plagioclase and K-feldspar) and potassic bulk-rock compositions ( $1 < K_2O/Na_2O < 2$ ; 6.7–7.2 wt.% CaO). Kersantite blobs have shapes and microstructures consistent with an origin from a mixing process between mafic potassic melts and rhyolitic melts. Both melts did exchange their phenocrysts during the mixing process. In addition to index minerals of lamprophyres (Ba–Ti–phlogopite, F-rich apatite, andesine and Carich sanidine), the groundmass of kersantite blobs displays essenite-rich diopside (up to 22 mol%), Ti-poor magnetite microlites, Ti-poor hematite microlites and a series of Ca–Ti–Zr- and REE-rich accessory minerals that have never been reported from lamprophyres. Titanite [up to 5.3 wt.% ZrO<sub>2</sub> and 5.2 wt.% (Y<sub>2</sub>O<sub>3</sub>+REE<sub>2</sub>O<sub>3</sub>)] and Zr- and Ca-rich perrierite (up to 7.2 wt.% ZrO<sub>2</sub> and 10.8 wt.% CaO) predate LREE- and iron-rich zirconolite and Fe-, Ti-, Hf-, Nb- and Ce-rich baddeleyite (up to 5.3 wt.% Fe<sub>2</sub>O<sub>3</sub>, 3.2 wt.% TiO<sub>2</sub>, 1.5 wt.% HfO<sub>2</sub>, 1.2 wt.% Nb<sub>2</sub>O<sub>5</sub>, 0.25 wt.% CeO<sub>2</sub>) in the crystallization order of the groundmass. Isomorphic substitutions suggest iron to occur as Fe<sup>3+</sup> in all the accessory phases. This feature, the essenitic substitution in the clinopyroxene and the occurrence of hematite microlites, all indicate a drastic increase of the oxygen fugacity (from FMQ – 1 to FMQ + 5 log units) well above the HM synthetic buffer within a narrow temperature range (1100–1000 °C). Such a late-magmatic oxidation is ascribed to assimilation of water from the felsic melts during magma mixing, followed by rapid degassing and water dissociation during eruption of host felsic lavas. Thus, magma mixing involving felsic melt end-members provides a mechanism for mafic potassic melts to be oxidized beyond the HM sy

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Keywords: Potassic lavas; Essenite-rich diopside; Perrierite; Zirconolite; Baddeleyite; Andean Cordillera

#### 1. Introduction

Zirconium, a highly incompatible lithophile trace element in terrestrial rocks, may be incorporated as a major element in accessory minerals [e.g. zircon (ZrSiO<sub>4</sub>), baddeleyite (ZrO<sub>2</sub>), zirconolite (CaZrTi<sub>2</sub>O<sub>7</sub>), members of the crichtonite series (Lorand et al., 1987), pseudobrookite-group minerals (Grégoire et al., 2000) and rare alkali-zircono-silicates] or as a minor element in major minerals such as titanite [CaTi(SiO<sub>4</sub>)(O,OH,F)], ilmenite

\* Corresponding author. *E-mail address:* gabi@mnhn.fr (G. Carlier). (up to 1.1 wt.% ZrO<sub>2</sub>; Pearce, 1990; Carlier and Lorand, 2003; Seifert and Kramer, 2003) and clinopyroxene (up to 7.0 wt.% ZrO<sub>2</sub> in acmite and aegyrine; Njonfang and Nono, 2003). Baddeleyite and zirconolite were long considered to be mineralogical rarities (i. e., Lorand and Cottin, 1987; Gieré et al., 1998; Parodi et al., 1994) until they were reported in a wide variety of strongly alkaline magmatic rocks (i.e., carbonatites, kimberlites, alkaline syenites, lamproites, basalts, trachyandesites), in addition to layered mafic intrusions, diabase dykes, gabbro sills and anorthosites for baddeleyite (see Heaman and Lecheminant, 1993 and references therein) and metasomatic and metamorphic rocks for zirconolite (Gieré et al., 1998; Bellatreccia et al., 1999; Della Ventura et al., 2000; Carlier and Lorand, 2003).

In spite of their scarcity, Zr-rich accessory minerals are of great interest for igneous petrology. These are major repositories of actinides (U, Th): as such, they offer great potentiality for dating mafic rocks (Heaman and Lecheminant, 1993). They are also able to incorporate significant amounts of large ion lithophile (LILE) and high field strength elements (HFSE); thus, a precipitation of Zr-rich accessory minerals in the course of magmatic differentiation processes may deeply obliterate the incompatible to strongly incompatible behaviour of these elements. The present paper describes an unusual, Zr-rich mineral assemblage (Zr-bearing, essenite-rich diopside, Zr-rich titanite, zirconolite and baddelevite coexisting with minerals of the chevkinite group) in potassic rocks (kersantite) from a Quaternary volcano of the south Peruvian Altiplano. The kersantite that are crystallization products of ultrapotassic melt survived incomplete mixing (mingling) with peraluminous rhyolites. Usually reported to occur in miarolitic cavities (Parodi et al., 1994; Della Ventura et al., 2001 and references therein), the Zr-rich mineral assemblage belongs to the magmatic paragenesis of Altiplano kersantites. Thus, it provides additional constraints on temperature, redox conditions and fluid speciation in an ultrapotassic residual melt previously affected by magma mixing processes.

## 2. Geological setting and main petrographic features of the Oroscocha volcano

The Cenozoic magmatism in southern Peru is distributed into two magmatic arcs, the Main Arc Domain and the Inner Arc Domain (Clark et al., 1990). The Main Arc Domain consists in low-K to high-K calc-alkaline and shoshonitic suites that built up the strato-volcanoes of the Western Andean Cordillera. The Inner Arc Domain is located within the Altiplano; it is composed of small ( $\leq 50 \text{ km}^2$ ), monogenic stocks, plugs, necks, dykes, or volcanoes, which show up potassic (K) and ultrapotassic (UK) rocks (Sandeman et al., 1997; Carlier et al., 1997; Carlier and Lorand, 1997, 2003; Sandeman and Clark, 2004). The K-UK magmatism (including the calc-alkaline felsic and shoshonitic suites) is arranged into three groups of structural directions, hereafter defined as magmatic lineaments (Carlier et al., 2005, Fig. 1A). The most recent (0-2 Ma) magmatic lineament is closely associated with the still active, NW-trending Cusco and Vilcanota Fault System that divides the Peruvian Altiplano into two structural blocks referred to as the Western Altiplano and the Eastern Altiplano (Carlier et al., 2005). This lineament exposes a wide range of K-UK rocks ranging from diopside phlogopite lamproites to augite minettes, augite kersantites, hornblende-augite trachybasalts, shoshonitic lavas (30 volcanic centers) and very scarce peraluminous rhyolites and trachydacites. The two other K-UK lineaments are located within the Western and the Eastern Altiplano, respectively. At least six WNW-trending clusters of Oligocene (28-30 Ma) and Miocene (5-6 Ma) K-UK lava occurrences have been identified in the Western Altiplano: leucitites, leucite tephrites, theralites and diopside trachybasalts predominate over olivine trachybasalts. The K-UK lavas are associated with metaluminous calc-alkaline and shoshonitic suites. The Eastern Altiplano is characterized by a series of NNW-trending magmatic lineaments. Phlogopite lamproites, enstatite-phlogopite lamproites and enstatite minettes erupted 20-25 Ma ago along with peraluminous calc-alkaline felsic intrusions and pyroclastic flows, followed by rare olivine minette dykes during the upper Miocene (7.5 Ma).

The Oroscocha volcano ( $14^{\circ} 05' 48''$  W,  $71^{\circ} 22' 00''$  E, 24 km NW of Sicuani, Cusco Department, Peru; Fig. 1B) is one



Fig. 1. A — Geological sketch map of the south Peruvian Altiplano (after Carlier et al., 2005). B — details of A. 1 = leucitites, leucite-bearing tephrites, phonotephrites, tephriphonolites, and trachytes and theralites; 2 = diopside trachybasalts; 3 = olivine trachybasalts; 4 = shoshonite suites; 5 = metaluminous calcalkaline felsic intrusions; 6 = diopside sanidine phlogopite lamproites; 7 = augite kersantites; 8 = augite minettes; 9 = augite hornblende trachybasalts; 10 = high-K calcalkaline and shoshonite suites; 11 = sanidine phlogopite lamproites; 12 = orthopyroxene phlogopite lamproites; 13 = Olivine minettes; 14 = orthopyroxene minettes and shoshonites; 15 = peraluminous felsic intrusions. Straight lines indicate main magmatic lineaments.

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