Micro- and nano-scale textural and compositional zonation in plagioclase at the Black Mountain porphyry Cu deposit: Implications for magmatic processes

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ABSTRACT

Textural and compositional microscale (10–100 μm) and nanoscale (10–100 nm) zoning in a plagioclase phenocryst from a fresh, syn-mineralization diorite porphyry (Black Mountain porphyry Cu-Au deposit, Philippines) was characterized for major and trace elements using electron microprobe, laser ablation-inductively coupled plasma-mass spectrometry, and atom probe tomography. The complex plagioclase crystal (3.0 × 5.4 mm) has a patchy andesine core (An41–48 mol%), eroded bytownite mantle (An3–80 mol%), and oscillatory andesine rim (An0–51 mol%). Microscale variations with a periodic width of 50 to 200 μm were noted for most major and trace elements (Si, Ca, Al, Na, K, Fe, Mg, Ti, Sr, Ba, Pb, La, Ce, and Pr) with a ΔAn amplitude of 4–12 mol% in both the core and rim. The mantle has a distinct elemental composition, indicating the addition of hotter mafic magma to the andesitic magma. Atom probe tomography shows an absence of nanoscale variations in the andesine rim but alternating nanoscale (25–30 nm) Al-rich, Ca-rich, and Si-rich, Na-rich zones with a Ca/(Ca+Na) at% amplitude of ~10 in the bytownite mantle. The restricted variations in physiochemical parameters (H2O-rich, T = 865 to 895 °C, P = 5.3 to 6.2 kbar; fO2 = NNO+0.6 to NNO+1.1 recorded by co-precipitated amphibole) suggest microscale oscillatory zoning was likely controlled by internal crystal growth mechanisms, and not by periodic variations in physiochemical conditions. However, the uniform diffusion timescale for CaAl-NaSi interdiffusion in the mantle is far shorter than the crystallization timescale of the grain from mantle to rim, suggesting nanoscale zonation in the bytownite mantle formed by exsolution after crystallization. The occurrence of micro-scale zoning in plagioclase indicates a minimum cooling rate of 0.0005 °C/yr during crystallization, assuming an initial temperature of 880 °C, the width of 50 μm, and NaSi-CaAl interdiffusion under hydrous conditions. Assuming a formation temperature of ~675 °C for the nanoscale exsolution texture as constrained by zircon crystallization temperatures, the retention of nanoscale zoning (~28 nm) requires a minimum cooling rate of 0.26 °C/yr. Given that this is significantly faster cooling than would occur in a magma chamber, this texture likely records the post-crystallization emplacement history.

Keywords: Atom probe tomography, plagioclase zonation, microscale, nanoscale, Black Mountain porphyry Cu deposit, Philippines

INTRODUCTION

Textural and compositional zoning in plagioclase could be classified as microscale (10–100 μm) and nanoscale (10–100 nm) according to the periodic width of zonation. Characterization of such zones can provide useful information on the crystallization environment (Stamatelopoulos et al. 2000; Hattori and Sato 1996; Ginibre and Wörner 2007; Singer et al. 2016), with implications for the petrogenesis of host rocks (Haase et al. 1980; Allègre et al. 1981), metallogenesis of porphyry Cu deposits (Cao et al. 2014, 2018a, 2018b), and thermal history of related rocks (e.g., Grove et al. 1984; Liu and Yund 1992). However, the origin of micro- and nano-scale oscillatory zoning in plagioclase remains poorly understood, and the role of less well-constrained physical and chemical parameters (such as temperature, pressure, melt composition, H2O, and fO2) and post-crystallization diffusion needs to be explored. In addition, the origin of both micro- and nano-scale zonation in the same plagioclase crystal is rarely studied (Grove et al. 1983). The Baguio district (Philippines) is one of the world’s premier mineral provinces, with more than 50 Moz of Au and 6 Mt of Cu (past production + resource; Malihan and Ruelo 2009) related to