

## 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  $\mu\text{m}$ ) 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  $\times$  5.4 mm) has a patchy andesine core ( $\text{An}_{41-48}$  mol%), eroded bytownite mantle ( $\text{An}_{71-80}$  mol%), and oscillatory andesine rim ( $\text{An}_{39-51}$  mol%). Microscale variations with a periodic width of 50 to 200  $\mu\text{m}$  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  $\Delta\text{An}$  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  $\text{Ca}/(\text{Ca}+\text{Na})_{\text{at}\%}$  amplitude of  $\sim 10$  in the bytownite mantle.

The restricted variations in physiochemical parameters ( $\text{H}_2\text{O}$ -rich,  $T = 865$  to  $895$   $^\circ\text{C}$ ,  $P = 5.3$  to  $6.2$  kbar;  $f_{\text{O}_2} = \text{NNO}+0.6$  to  $\text{NNO}+1.1$  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  $0.0005$   $^\circ\text{C}/\text{yr}$  during crystallization, assuming an initial temperature of  $880$   $^\circ\text{C}$ , the width of  $50$   $\mu\text{m}$ , and NaSi-CaAl interdiffusion under hydrous conditions. Assuming a formation temperature of  $\sim 675$   $^\circ\text{C}$  for the nanoscale exsolution texture as constrained by zircon crystallization temperatures, the retention of nanoscale zoning ( $\sim 28$  nm) requires a minimum cooling rate of  $0.26$   $^\circ\text{C}/\text{yr}$ . 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