SPECIAL COLLECTION: APATITE: A COMMON MINERAL, UNCOMMONLY VERSATILE

Cathodoluminescence images and trace element compositions of fluorapatite from the Hongge layered intrusion in SW China: A record of prolonged crystallization and overprinted fluid metasomatism

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ABSTRACT

Cathodoluminescence (CL) and trace element analyses were performed for fluorapatite from the gabbro and Fe-Ti oxide ores in the upper zone of the Hongge Fe-Ti oxide-bearing, mafic-ultramafic layered intrusion in SW China. The fluorapatite is closely associated with Fe-Ti oxides and interstitial to plagioclase and clinopyroxene. The fluorapatite grains in one thin section vary from ~ 10 to 800 µm in width and \sim 50 to 1200 µm in length. Coarse-grained fluorapatite crystals (>200 in width) in the same thin section show both simple and complex CL images. The coarse-grained fluorapatite crystals with simple CL images show discontinuous, thin dark rims along grain boundaries, whereas those with complex images show clearly bright veinlets across the grains. On the other hand, fine-grained fluorapatite crystals (<200 µm in width) show complex CL images and can be divided into four types, i.e., concentric, chaotic, banded, and overall dark. The concentric type shows distinctly bright core surrounded by dark mantle that is irregularly zoned, whereas the chaotic type shows disordered bright and dark sectors in the interior with a thin dark rim. The banded type shows unevenly distributed bright and dark bands. The overall dark type shows a relatively dark and uneven image. Fluorapatite grains contain 1.84–2.74 wt% F, 0.07–0.19 wt% Cl, and 0.86–1.63 wt% OH. Coarse-grained fluorapatite grains have total rare earth elements (REE) concentrations ranging from 2278 to 3008 ppm and Sr/Y of 9 to 13. Fine-grained fluorapatite grains have relatively high REE (2242-4687 ppm) and low Sr/Y of 6 to 14 in the bright cores, sectors, and bands and relatively low REE (1881–2728 ppm) and high Sr/Y of 9 to 15 in the dark mantles, sectors, and rims under CL imaging. On the thin section scale, the bright sections under CL imaging for fine-grained fluorapatite have much higher REE contents than those for similar bright CL images for coarse-grained fluorapatite. The highly variable REE concentrations among fluorapatite grains and the sections within a single fluorapatite are attributed to a prolonged crystallization process and overprint by fluid metasomatism. The coarse-grained fluorapatite may have crystallized earlier than fine-grained fluorapatite. Then variable degrees of hydrothermal metasomatism released REE from the fine-grained fluorapatite so that diverse CL images developed in the crystals. This study reveals that magmatic apatite from a layered intrusion can be intensively modified by later-stage fluid-induced metasomatism in both trace element composition and CL image texture. Reconstruction of primary melt compositions using apatite from layered intrusions should therefore be treated with caution.

Keywords: Fluorapatite, cathodoluminescence image, trace element, fluid metasomatism, maficultramafic layered intrusion

INTRODUCTION

Apatite mainly occurs in the upper zone of layered intrusions, such as the Skaergaard intrusion in Greenland and the Bushveld complex in South Africa, and is considered as a cumulus phase during late-stage magma differentiation (Cawthorn 1994; Holness et al. 2007). Apatite can be substantially enriched in some layered intrusions and associated with Fe-Ti oxides, forming Fe-Ti-P-rich nelsonite with ~30 vol% apatite (Reynolds 1985; Von Gruenewaldt 1993; Tollari et al. 2008). The origin of apatite-rich rocks/Fe-Ti oxide ores in layered intrusions has been a matter of debate between fractional crystallization and silicate liquid immiscibility models (Reynolds 1985; Von Gruenewaldt 1993; Tegner et al. 2006; Tollari et al. 2008; Namur et al. 2012; VanTongeren and Mathez 2012). Nevertheless, the growth process of apatite itself has been relatively neglected.

Magmatic apatite commonly has a hexagonal habit when crystallizing under near-equilibrium condition (Webster and Piccoli 2015). Cumulus apatite from layered intrusions has been widely used to reconstruct the trace element compositions of the melt in equilibrium with the apatite (Tollari et al. 2008; VanTongeren and Mathez 2012; She et al. 2016).

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However, primary apatite may be intensively modified by post-crystallization processes, e.g., the trapped liquid shift effect and metasomatism by external fluids, which can cause extreme variations of the trace elements in the apatite (Harlov et al. 2002a, 2005; Harlov and Förster 2003; Cawthorn 2013). Therefore, tracing the cryptic compositional variations in apatite is significant for understanding the crystallization and overprinted post-crystallization processes in the magma chamber.

Cathodoluminescence (CL) can be activated by small amounts of trace elements in minerals, and has been used to identify episodes of mineral growth during magmatic processes (Murray and Oreskes 1997). The most common CL activators in apatite are REE and Mn, whereas Fe is a common quencher (Roeder et al. 1987; Barbarand and Pagel 2001). It has been shown that the luminescent intensity can be influenced by tens of parts per million to several weight percent variation of these elements in apatite (Filippelli and Delaney 1993; Kempe and Götze 2002).

In this paper, we present the CL images of fluorapatite from the gabbro, Fe-Ti oxide gabbro, and Fe-Ti oxide ore samples taken from the upper zone of the Hongge layered intrusion in SW China. The fluorapatite grains show diverse CL images. Combined with in situ LA-ICP-MS trace element analyses, we found that this diversity in the CL images is likely caused by variations in the REE concentrations in fluorapatite due to a prolonged crystallization process and late-stage hydrothermal metasomatism, which give further insights into the growth process of magmatic fluorapatite in a dynamic, slow-cooling magma chamber.

FLUORAPATITE IN THE HONGGE INTRUSION

The Hongge mafic-ultramafic layered intrusion is located in the Panxi region, SW China, and hosts a world-class Fe-Ti oxide deposit (Ma et al. 2003; Wang and Zhou 2013) (Fig. 1a). The intrusion is ~2.7 km thick and consists of olivine clinopyroxenite and minor wehrlite and dunite in the lower zone, clinopyroxenite and major Fe-Ti oxide ore layers in the middle zone, and fluorapatite-bearing gabbro and Fe-Ti oxide ores in the upper zone (Wang and Zhou 2013). Magnetite in the lower zone and the lower part of the middle zone is Cr- and Ti-rich magnetite, which is disseminated and commonly enclosed in olivine and clinopyroxene, whereas magnetite in the upper part of the middle zone and the upper zone is Cr-poor, Ti-rich magnetite, which is interstitial to clinopyroxene and plagioclase. The Cr- and Ti-rich magnetite in the lower and middle zones is interpreted as an early crystallized phase from less differentiated high-Ti basaltic magmas, whereas the Cr-poor, Ti-rich magnetite in the upper zone is thought to have formed from an immiscible Fe-Ti-(P)-rich melt developed from an evolved high-Ti basaltic magma (Wang and Zhou 2013).

The upper part of the upper zone is composed of gabbro, whereas the lower part is composed of Fe-Ti oxide gabbro and Fe-Ti oxide ore. Samples in this study were collected from the Luku open pit (Fig. 1b) and the sample locations are marked in the stratigraphic column of the intrusion (Fig. 1c). The boundaries between the gabbro, Fe-Ti oxide gabbro, and Fe-Ti oxide ore are sharp and characterized by an evident decrease in the proportion of Fe-Ti oxides between Fe-Ti oxide ore and Fe-Ti oxide gabbro and a sudden increase in the proportion of plagioclase between Fe-Ti oxide gabbro and gabbro. Gabbro in the upper part consists of 40-60 vol% plagioclase, 30-40% clinopyroxene, 10-15% Fe-Ti oxides, 5-7% fluorapatite, 2-3% amphibole, and <1% sulfide (Fig. 2a). On a localized scale, modal fluorapatite can be more than 10% (Fig. 2d). The Fe-Ti oxide gabbro consists of 40–60% clinopyroxene, 20–30% plagioclase, 20-30% Fe-Ti oxides, 6-8% fluorapatite, 1-2% amphibole, and 1% sulfide (Fig. 2b). Fe-Ti oxide ore consists of 40-60% Fe-Ti oxides, 30% clinopyroxene, 10% plagioclase, 4–6% fluorapatite, 1–2% amphibole, and <1% sulfide (Fig. 2c). The rocks and ores show weak to intense alteration. Plagioclase commonly experienced saussuritization and albitization and the relicts of primary plagioclase can be observed in some altered grains (Supplemental¹ Fig. 1a), whereas clinopyroxene was partly altered to amphibole (Supplemental¹ Fig. 1b).

Fluorapatite in gabbro, Fe-Ti oxide gabbro and Fe-Ti oxide ore is mostly euhedral to subhedral and shows a hexagonal or elongated shape, depending on the orientation of the grain in the thin section (Figs. 2d and 2e). Anhedral fluorapatite grains were also observed in the same thin section (Fig. 2d). Most fluorapatite grains are interstitial to clinopyroxene and plagioclase and closely associated with Fe-Ti oxides (Figs. 2d and 2e). The fluorapatite grains vary from ~10 to 800 µm in width and ~50 to 1200 µm in length (Figs. 2d and 2e). They are denoted as coarse-grained (>200 µm in width) and fine-grained (<200 µm in width) in this study. Fine-grained fluorapatite crystals (mostly <100 µm in width) are also sporadically enclosed within clinopyroxene (Fig. 3a).

Rounded pyrrhotite is occasionally enclosed in both coarsegrained and fine-grained fluorapatite (Fig. 3b). Needle-like pyrrhotite inclusion are common and have an orientation parallel to the c-axis of fluorapatite (Fig. 3c and Supplemental¹ Fig. 2). Kink bands are developed in the cross sections parallel to the c-axis of fluorapatite (Fig. 3d). Dislocation planes are distinct between the kink bands with different extinction angles (Fig. 3d).

ANALYTICAL METHODS

Cathodoluminescence imaging

CL imaging of fluorapatite was performed on carbon-coated thin sections, which were finely polished and ultrasonically cleaned to avoid possible pits and stains on the fluorapatite grain surface that may influence the CL response. CL images of fluorapatite were acquired using a Gatan MonoCL4 system installed on a Carl Zeiss SUPRA 55 SAPPHIRE field emission electron microscope at the State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry (GIG), Chinese Academy of Sciences (CAS). The CL images were all obtained using a 10 kV voltage and contrast-enhanced for better observation.

Electron microprobe analysis

Major elements in fluorapatite were analyzed using a JEOL JXA-8230 electron probe micro-analyzer (EPMA) at the Key Laboratory of Mineralogy and Metallogeny in GIGCAS. Operating conditions of 15 kV accelerating voltage, 20 nA probe current, and a 3 μ m beam were applied to the analyses for all elements. Peak and background counting times were 20 and 10 s for Ca and P, 10 and 5 s for F and Cl, 60 and 30 s for Si and S. K α line was chosen for all elements during analyses.

¹Deposit item AM-17-76028, Supplemental Figures and Tables. Deposit items are free to all readers and found on the MSA web site, via the specific issue's Table of Contents (go to http://www.minsocam.org/MSA/AmMin/TOC/2017/Jul2017_data/Jul2017_data.html).



FIGURE 1. Geological maps showing the distribution of the Emeishan large igneous province (**a**) and the distribution of major rock types in the Hongge intrusion (after Wang and Zhou 2013) (**b**), and a stratigraphic column of the Hongge intrusion showing the sample locations (**c**).

F and Cl were first analyzed during the analysis routine to minimize their loss. Analytical results were reduced using the ZAF correction routines. The standards used were fluorapatite for Ca and P, BaF₂ for F, tugtupite for Cl, diopside for Si, and pyrite for S. Relative precisions are $\pm 2\%$ for Ca, P, and F and $\pm 5\%$ for Si, Cl, and S, respectively.

Laser ablation-inductively coupled plasma-mass spectrometry analysis

In situ trace element analyses of fluorapatite were carried out using a laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) at the Key Laboratory of Mineralogy and Metallogeny in GIGCAS. The Agilent 7500a



FIGURE 2. Plane-polarized, transmitted light photomicrographs of the gabbro (sample HG1532) (**a**), Fe-Ti oxide gabbro (sample HG1539) (**b**), and Fe-Ti oxide ore (sample HG1540) (**c**) in the upper zone of the Hongge intrusion. (**d**) Close-up of **a** showing abundant fluorapatite (Ap) grains associated with Fe-Ti oxides and interstitial to clinopyroxene (Cpx) and plagioclase (Pl). Note that plagioclase is altered in local places. (**e**) Close-up of **c** showing disseminated fluorapatite grains associated with Fe-Ti oxides and interstitial to clinopyroxene.

ICP-MS instrument was coupled to a Resonetic 193 nm ArF excimer laser ablation system. Single spot ablation was adopted with a laser beam width of 31 µm. Laser energy was 80 mJ and ablation frequency was 6 Hz. Helium was used as a carrier gas. NIST SRM 610 glass was employed as an external standard and NIST SRM 612 was treated as an unknown sample. The CaO content of fluorapatite, as determined by EMPA, was used as an internal standard. Data reduction was performed using the ICPMSDataCal software (version 10.2) (Liu et al. 2008). The measured trace element concentrations of NIST SRM 610 and NIST SRM 612 and their recommended values are listed in Supplemental¹ Table 1. The relative uncertainty of the analysis is better than 10% for most trace elements.

CATHODOLUMINESCENCE IMAGE OF FLUORAPATITE

Fluorapatite grains from the gabbro, Fe-Ti oxide gabbro, and Fe-Ti oxide ore samples show similar but diverse CL images. Some coarse-grained fluorapatite grains show a simple CL image with a discontinuous, thin, dark rim along the grain boundary (Figs. 4a and 4b), whereas the other coarse grains display a complex, mosaic CL image with bright veinlets crosscutting the interior of the crystals (Fig. 4c).

Fine-grained fluorapatite shows four types of CL images, i.e., concentric, chaotic, banded, and overall dark. The concentric type shows a bright, irregular to rounded core and a clearly dark mantle in the image (Fig. 5). The dark mantle in the image is sometimes irregularly zoned (Fig. 5b). Such a concentric texture shown in the CL images (Fig. 5c), however, cannot be observed in the BSE images (Fig. 5d). The chaotic type is composed of disordered bright and dark sectors in the interior sharply bounded with a dark rim (Fig. 6). The rim is commonly <50 µm in width, but is evidently coarsened in the corner of two crystal faces

(Fig. 6). In local places, the rim is interconnected with dark veinlets that penetrate the bright and dark sectors (Fig. 6c). Rounded bright spots are occasionally preserved in both bright and dark sectors (Fig. 6b), whereas tiny amphibole inclusions (20–50 μ m in diameter) are sporadically present in the dark sectors (Figs. 6b and 6c). The banded type shows bright and dark bands unevenly distributed in the image (Fig. 7). The dark bands vary in width from ~10 to 100 μ m. The overall dark type shows heterogeneous dark sectors in the CL images but without an obvious bright core or sector (the grain on the left in Figs. 5a and 5c).

FLUORAPATITE COMPOSITIONS

Fluorapatite grains from the gabbro, Fe-Ti oxide gabbro, and Fe-Ti oxide ore samples have similar F and SO₃ contents and F/Cl, and there is no prominent variation between coarsegrained and fine-grained fluorapatite (Supplemental¹ Table 2). They contain 1.84-2.73 wt% F and 0.07-0.19 wt% Cl with F/Cl varying from 11 to 31, and contain 0.86-1.63 wt% OH (Supplemental Table 2).

Coarse-grained and fine-grained fluorapatite have similar Sr, Fe, and Mn concentrations (Figs. 8a and 8b), however, they have remarkably different REE concentrations. Coarse-grained fluorapatite grains have total REE concentrations ranging from 2278 to 3008 ppm (Supplemental¹ Table 3). They have 830–1115 ppm Ce and Sr/Y of 9 to 13, which shows a linear trend on the plot of Ce vs. Sr/Y (Fig. 8c). Cerium within a single coarse-grained fluorapatite ranges from a maximum of 1115 ppm in



FIGURE 3. Occurrence of fluorapatite in the rocks of the Hongge intrusion. (a) BSE image of fluorapatite (Ap) is associated with magnetite (Mag), ilmenite (Ilm), and pyrrhotite (Po). Note that fluorapatite has variable grain sizes in the same thin section (sample HG1540). (b) BSE image of rounded pyrrhotite inclusion enclosed within fluorapatite and a sulfide veinlet extending along fracture in the fluorapatite (sample HG1539). (c) Plane-polarized, transmitted light image of fluorapatite with abundant, elongated pyrrhotite inclusions elongated parallel to the fluorapatite *c*-axis in a topotaxial relationship. Dislocation planes are nearly perpendicular to the *c*-axis (sample HG1540). (d) Cross-polarized, transmitted light image of an elongated fluorapatite, which has kink bands with different extinction angles on two sides of the dislocation planes (sample HG1532).

the core to a minimum of 938 ppm in the rim (see the insets in Figs. 9a, 9c, and 9e).

Fine-grained fluorapatite has distinctly different REE concentrations in the bright and dark sections of the CL images. For example, the bright cores in the concentric type contain total REE ranging from 2242 to 4687 ppm with a maximum value that is nearly two times higher than those for coarse-grained fluorapatite in the same thin section. They contain 820-1692 ppm Ce and have low Sr/Y (6 to 14) relative to that for coarsegrained fluorapatite (Fig. 8c). On the other hand, the dark mantles in the concentric type contain 1981-2408 ppm REE in total (Supplementary¹ Table 3). They contain 742–872 ppm Ce, which is much lower than those for coarse-grained fluorapatite. However, they have Sr/Y (11 to 13), which is higher than those for coarse-grained fluorapatite (Fig. 8c). The dark sectors and bands in the chaotic and banded CL images have REE and Sr/Y similar to those for the dark mantles in the concentric type (Figs. 8c and 9). The overall dark type has Ce concentrations comparable with those for the dark mantles in the concentric type

(Supplemental¹ Table 3). Note that in one thin section scale of a fine-grained fluorapatite, the bright sections have higher REE than those for the dark sections in the same grain (Fig. 9). Overall, the coarse-grained fluorapatite and the CL-bright sections from the concentric type, fine-grained fluorapatite show parallel REE patterns without obvious Eu anomalies (Fig. 10).

DISCUSSION

Diverse CL images of fluorapatite due to late-stage fluid metasomatism

Fluorapatite grains from the Hongge intrusion overall have Mn concentrations lower than 250 ppm and there is no obvious difference in Mn and Mn/Fe between the bright and dark sections in the CL images (Fig. 8a). The diverse CL images of the fluorapatite are thus unlikely caused by the Mn activator and Fe quencher in the fluorapatite. Instead, it is likely that they are related to the large variation of REE in the fluorapatite (Fig. 9).

Large variations of REE within a single apatite could be



FIGURE 4. CL images for coarse-grained fluorapatite from the Hongge intrusion. (**a**) Simple image with clear dislocation planes (sample HG1539). (**b**) Simple image with clear dislocation planes and localized, discontinuous dark rims along the grain boundary (sample HG1539). (**c**) Complex image with mosaic-like sectors crosscut by bright veinlets (sample HG1540).

caused by the mixing of compositionally different magmas during its growth (Lisowiec et al. 2013) or by post-crystallization modification such as the trapped liquid shift effect and fluid metasomatism (Cawthorn 2013; Harlov 2015). Large-scaled magma mixing in the magma chamber may develop regular and concentric zonation in the apatite (Lisowiec et al. 2013), and should also be recorded in other cumulus minerals such as plagioclase. The fluorapatite in the Hongge intrusion lacks regular zoning, and no obvious zonation was observed in plagioclase, which rules out the possibility of magma mixing during the formation of the fluorapatite. The progressive growth of primary apatite from an ambient melt may produce compositional zonation, and the trapped liquid shift effect may obscure the zonation by diffusion and increase REE in the apatite (Barnes 1986; Cawthorn 2013). However this cannot explain the overall low REE in the dark rims and sectors of the CL image for the fine-grained fluorapatite in this study (Fig. 5).

It is known that hydrothermal fluids are capable of leaching REE from apatite, resulting in a substantial decrease of REE in apatite and the formation of new REE-phosphates, -silicates, -fluorides, and -carbonates in metasomatized domains (Harlov et al. 2002a; Harlov and Förster 2003; Harlov 2015; Li and Zhou 2015). Late-stage fluid metasomatism is common in iron-oxide apatite deposits, in which apatite can be partially or completely metasomatized by compositionally different fluids (Harlov et al. 2002b, 2016; Bonyadi et al. 2011; Li and Zhou 2015).

Monomineralic inclusions of calcic amphibole are common in the fine-grained fluorapatite from the Hongge intrusion. The amphibole is sometimes associated with Fe-Ti oxides and sulfides in the inclusions (Fig. 11a). The enclosed amphibole in the fluorapatite has compositions similar to the amphibole rim on the clinopyroxene and plagioclase adjacent to Fe-Ti oxides (Fig. 11b; Supplemental¹ Table 4), indicating that the amphibole may have been trapped in the fluorapatite during the late stage of magma fractionation. The presence of amphibole in fine-grained fluorapatite thus indicates that the interstitial liquid may have eventually become water-saturated and generated hydrothermal fluids during the late stage of magma fractionation.

The veinlets across the coarse-grained fluorapatite (Fig. 4c) are direct evidences for the mobility of hydrothermal fluids in the Hongge intrusion. Given the common presence of kink bands in fluorapatite, the micro-fractures crosscutting the grains may have developed due to intensive deformation and progressive compaction of overloaded crystal mush. They in turn functioned as channels to transport REE-rich fluids resulting in bright veinlets in the CL images (Fig. 4c). The orientated needle-like pyrrhotite inclusions in the fluorapatite (Fig. 3c) may be also attributed to late-stage hydrothermal activity. The pyrrhotite inclusions were likely formed by the fluid-mediated reaction, e.g., $H_2S + Fe^{2+} =$ $FeS + 2H^+$ (Broska et al. 2014). In such a scenario, the fluids leached Fe and S either from the Fe-Ti oxides and sulfides or more likely from the fluorapatite and preferentially grew the pyrrhotite inclusions parallel to the c-axis of the host fluorapatite in a topotaxial manner (cf. Pan et al. 1993; Broska et al. 2014) similar to what is seen for monazite and xenotime inclusions in apatite (cf. Harlov 2015).

Large variations in Sr/Y in a single fluorapatite or in fluorapatite grains in one thin section (Fig. 8c) are likely resulted from fluid metasomatically released Y from fluorapatite. Note that the CL-dark section for fine-grained fluorapatite has Sr/Y lower than that for the CL-bright section (Fig. 8c). This is because they have comparable Sr against highly variable Y (Supplemental¹ Table 3).

Late-stage fluid metasomatism could explain the diverse CL images for fine-grained fluorapatite in the Hongge intrusion. The fluids would have reacted with grain boundaries and decreased the REE, causing the low REE content in the dark mantle in the concentric-type CL images and in the dark rim



FIGURE 5. Concentric-type CL images of fine-grained fluorapatite from the Hongge intrusion showing that euhedral to subhedral fluorapatite grains have a bright, rounded to irregular core and dark mantle (samples HG1539 and HG1529) (**a** and **b**). The dark mantle is irregularly zoned in contrast to the overall dark type CL image (sample HG1540) (**c**). The concentric texture in the CL image is not seen in the BSE image of the same grain (**d**).



FIGURE 6. Chaotic-type CL images of fine-grained fluorapatite from the Hongge intrusion showing that bright and dark sectors are irregularly distributed (sample HG1539) (\mathbf{a} , \mathbf{b} , and \mathbf{c}) and that the dark rim penetrates the fluorapatite as veinlets (\mathbf{c} and \mathbf{d}). Note that tiny amphibole inclusions are enclosed in the veinlets (\mathbf{c}). (\mathbf{d}) Taken from sample HG1532.



FIGURE 7. Banded-type CL images of fine-grained fluorapatite from the Hongge intrusion showing dark and bright bands distributed unevenly in the flourapatite. (a) Sample HG1539 and (b) sample HG1532.



FIGURE 8. Binary plots of Mn/Fe vs. Mn (a), Ce vs. Sr (b), Ce vs. Sr/Y (c), and Th/Zr vs. U/Zr (d) for the fluorapatite in the Hongge intrusion. Note that the fluorapatite in this study has restricted Th/Zr and U/Zr, similar to those for the fluorapatite from the Bushveld Complex (VanTongeren and Mathez 2012).

and sector in the chaotic-type images relative to the bright CL cores and sectors (Figs. 9b, 9c, and 9d). The fluids would have passed through the interior of the grain and leached REE

along their path ways, leaving behind REE-contrasted sections in the grain (cf. Harlov et al. 2005). The fluids would have then percolated along micro-fractures in the grain, forming



FIGURE 9. Variation of REE within a single fluorapatite grain from the gabbro (**a** and **b**), the Fe-Ti oxide-bearing gabbro (**c** and **d**), and the Fe-Ti oxide ore (**e** and **f**). Note that the coarse-grained fluorapatite shows a restricted variation in REE, whereas the fine-grained fluorapatite shows a large REE variation. Normalization values are from McDonough and Sun (1995).

the chaotic CL image (Fig. 6). If the fluids penetrated through the grain, bright and dark bands would have developed and unevenly distributed forming banded CL images (Fig. 7). When the fine-grained fluorapatite was strongly modified by the fluids, an overall dark CL image would have formed (Fig. 5c) and the fluorapatite would have low REE concentrations relative to bright CL sections in other grains. Therefore, the diverse CL images seen for fine-grained fluorapatite reveal the



FIGURE 10. Chondrite-normalized REE patterns for fine-grained fluorapatite from the Fe-Ti oxide ore with concentric-type zoning under CL imaging and a coarse-grained fluorapatite with no obvious zoning. REE concentrations in the melt in equilibrium with the fluorapatite were calculated using the partition coefficients as Meurer and Meurer (2006). Normalization values are from McDonough and Sun (1995).

different degrees of the reaction between the fluorapatite and late-stage hydrothermal fluids.

Prolonged crystallization of fluorapatite in igneous cumulates

Coarse-grained and fine-grained fluorapatite display a good linear trend on the plot of U/Zr vs. Th/Zr (Fig. 8d), which is interpreted as the melts from which the coarse-grained and finegrained fluorapatite crystallized are co-genetic. Because U and Th have similar partition coefficients in fluorapatite and Zr is highly incompatible in fluorapatite, U/Zr and Th/Zr in the fluorapatite reflect the composition of equilibrated melt and should not change significantly during crystallization of the fluorapatite (cf. VanTongeren and Mathez 2012). The parallel REE patterns of the coarse-grained and fine-grained fluorapatite (Fig. 10) also support the idea that they crystallized from co-genetic melts.

Note that many coarse-grained fluorapatite grains have simple CL images (Figs. 3a and 3b), and have only slightly low REE in their rims (see the inset of Figs. 9a, 9c, and 9e). We therefore assume that majority of the coarse-grained fluorapatite cores may have preserved primary trace element compositions, and that the rims experienced variable degrees of fluid metasomatism. In contrast, the bright cores in some concentric-type CL images for fine-grained fluorapatite have REE up to two times higher than those for coarse-grained fluorapatite (Fig. 10), indicating that the fine-grained fluorapatite may have crystallized from an interstitial liquid with a relatively high REE. The prominent REE variations in apatite from layered intrusions may be related to liquid immiscibility (VanTongeren and Mathez 2012) or intensive differentiation of an interstitial liquid (Meurer and Meurer 2006). In the top 600 m section of the Upper Zone of the Bushveld complex, the apatite from the upper ~300 m contains REE three times higher than those for the apatite from the lower ~300 m (Van-Tongeren and Mathez 2012). The large REE interval between the apatite from the upper and lower sections is attributed to the idea that the upper and lower sections formed from immiscible Si- and Fe-rich melts, respectively (VanTongeren and Mathez 2012), even though such a model is debatable (Cawthorn 2013). However, the coarse-grained and fine-grained fluorapatite with distinctively different REE contents in the Hongge intrusion are actually present in the same thin section. Therefore, it is unlikely they were derived from a pair of conjugate immiscible melts.

In a basaltic magma system, REE are compatible in apatite with $D_{Ap/melt}$ REE ranging from ~1 to 8 (Prowatke and Klemme 2006). However, they are moderately to highly incompatible in plagioclase, clinopyroxene, and Fe-Ti oxides (Nielsen et al. 1992; Hart and Dunn 1993; Bindeman et al. 1998). Given that the major rock types in the upper zone of the Hongge intrusion are all composed of plagioclase, clinopyroxene, Fe-Ti oxides, and fluorapatite with mode of 4 to 8 vol%, the bulk partition coefficient for REE (D_{REE}^{bulk}) was calculated to be <1. The evolved interstitial liquid would therefore have REE concentration higher than the less differentiated melt. Fluorapatite, crystallized from the interstitial liquid, would then have higher REE than fluorapatite crystallized earlier from less differentiated melt. One example of this is the Stillwater complex in the United States, where the intercumulus fluorapatite in the olivine gabbro is interstitial to the silicate minerals, and the smallest fluorapatite grains have the highest REE content (Meurer and Meurer 2006). We therefore propose that the fluorapatite in the upper zone of the Hongge intrusion may have crystallized during a prolonged process. Coarse-grained fluorapatite crystallized from a less differentiated melt in cumulus stage, whereas the fine-grained fluorapatite crystallized from an evolved interstitial liquid during the last stages of crystallization. This explains why the bright areas in the CL images of the fine-grained fluorapatite have an overall higher REE content than the coarse-grained fluorapatite.

The crystallization temperature of the amphibole enclosed in fine-grained fluorapatite is estimated to range from 660 to 995 °C using the amphibole Ti content (Otten 1984) and from 712 to 926 °C using the empirical equation of Ridolfi and Renzulli (2012). This broad variation in temperature should be considered as the upper limit for the crystallization temperature of the fine-grained fluorapatite, and are supportive of the prolonged crystallization of fluorapatite even on the thin section scale. In addition, the interstitial amphibole have similar ranges of crystallization temperatures (Supplemental¹ Table 4). The intergrowth of magnetite and amphibole (Fig. 11c) indicates that the evolved interstitial liquid should be Fe- and H₂O-rich, from which finegrained fluorapatite crystallized.

A schematic model for prolonged growth of fluorapatite in the Hongge intrusion

We propose that fluorapatite in the upper zone of the Hongge intrusion experienced a prolonged crystallization process and was metasomatized by late-stage hydrothermal fluids. The coarsegrained fluorapatite represents an early-crystallized cumulus phase from a less differentiated melt (Fig. 12a). With progressive crystallization of cumulus clinopyroxene, plagioclase, fluorapatite, and Fe-Ti oxides, the interstitial liquid in the crystal mush became enriched in incompatible REE and volatiles. Fine-grained fluorapatite eventually crystallized from the interstitial liquid and was enriched in REE (Fig. 12b). At the same time, amphibole



FIGURE 11. (a) Plane-polarized, transmitted light image of brown amphibole (Amp) inclusion enclosed within a fine-grained fluorapatite from the Fe-Ti oxide gabbro. Note that magnetite (Mag) is enclosed within the amphibole inclusion. Sample HG1539. (b) Plane-polarized, transmitted light image of brown amphibole rimming along the Fe-Ti oxide, clinopyroxene, and plagioclase grains in the gabbro. (c) Plane-polarized, transmitted light image showing the irregular amphibole grained in Fe-Ti oxides. (d) BSE image of the close-up of **c** that shows the intergrowth of magnetite and amphibole.



FIGURE 12. Cartoon showing a prolonged crystallization process of fluorapatite and overprinting later fluid metasomatism responsible for the complex textures in fluorapatite seen under CL imaging.

inclusions were entrapped in some fine-grained apatite grains and amphibole rims developed in limited interstices and commonly between silicate minerals and Fe-Ti oxides (Fig. 12b). Late-stage fluid metasomatism substantially remobilized REE in the fluorapatite in different ways and left behind diverse CL patterns in the fluorapatite (Fig. 12c).

IMPLICATIONS

Cumulus fluorapatite in the upper zone of the mafic-ultramafic layered intrusions has been used to trace late-stage differentiation of the parent magma. This study, however, demonstrates that the fluorapatite grains in igneous cumulates crystallized in multiple stages during a prolonged crystallization process. Later-stage fluid metasomatism substantially modified both REE concentrations of primary fluorapatite and altered the CL texture of the fluorapatite. This study also demonstrates that a combination of CL imaging and in situ LA-ICP-MS trace element analysis is a powerful tool for unraveling the growth process of fluorapatite during crystallization of a magma chamber.

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