



Magnesium isotopic evidence for chemical disequilibrium among cumulus minerals in layered mafic intrusion

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ARTICLE INFO

Article history:

Received 6 December 2017

Received in revised form 25 January 2018

Accepted 31 January 2018

Available online xxxxx

Editor: F. Moynier

Keywords:

magnesium isotopes
kinetic isotope fractionation
chemical diffusion
compositional zoning
Baima mafic intrusion

ABSTRACT

Magnesium isotopic compositions of olivine, clinopyroxene, and ilmenite from the Baima intrusion, SW China, for the first time, are investigated to constrain the magnitude and mechanisms of Mg isotope fractionation among cumulus minerals in layered mafic intrusions and to evaluate their geological implications. Olivine and clinopyroxene have limited Mg isotope variations, with $\delta^{26}\text{Mg}$ ranging from -0.33 to $+0.05\text{‰}$ and from -0.29 to -0.13‰ , respectively, similar to those of mantle xenolithic peridotites. By contrast, ilmenites display extremely large Mg isotopic variation, with $\delta^{26}\text{Mg}$ ranging from -0.50 to $+1.90\text{‰}$. The large inter-mineral fractionations of Mg isotopes between ilmenite and silicates may reflect both equilibrium and kinetic processes. A few ilmenites have lighter Mg isotopic compositions than coexisting silicates and contain high MgO contents without compositional zoning, indicating equilibrium fractionation. The implication is that the light Mg isotopic compositions of lunar high-Ti basalts may result from an isotopically light source enriched in cumulate ilmenites. On the other hand, most ilmenites have heavy Mg isotopic compositions, coupled with high MgO concentration and chemical zoning, which can be quantitatively modeled by kinetic Mg isotope fractionations induced by subsolidus Mg–Fe exchange between ilmenite and ferromagnesian silicates during the cooling of the Baima intrusion. The extensive occurrence of kinetic Mg isotope fractionation in ilmenites implies the possibility of widespread compositional disequilibrium among igneous minerals in magma chambers. Consequently, disequilibrium effects need to be considered in studies of basaltic magma evolution, magma chamber processes, and magmatic Fe–Ti oxide ore genesis.

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1. Introduction

Investigation of layered mafic intrusions can help to understand basaltic magma emplacement and differentiation, crystal accumulation, and magmatic base and precious metal mineralization (e.g., Cr, V, Ti, Fe, and platinum group elements) in crustal magma chambers (Namur et al., 2015; Scoates and Wall, 2015). Based on two long-standing views: (1) elements diffuse very fast during magmatic processes and (2) magma chambers cool slowly during formation of mafic intrusions, it is generally assumed that cumulus minerals in magma chambers are in thermodynamic equilibrium with each other. Such an assumption is a prerequisite for using cumulus mineral compositions to evaluate

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magmatic evolution and petrogenesis of cumulate rocks as were often done. However, recent studies have found that extensive disequilibrium isotope fractionation caused by chemical diffusion widely occurs in igneous minerals and rocks (e.g., Teng et al., 2011; Chopra et al., 2012; Sio et al., 2013; Oeser et al., 2015; Pogge von Strandmann et al., 2015; Richter et al., 2016; Xiao et al., 2016; Collinet et al., 2017). For example, olivine phenocrysts from the Kilauea Iki lava lake (Hawaii) display large kinetic Mg and Fe isotope fractionations, indicative of Mg–Fe inter-diffusion between olivine and evolved melts during magma differentiation (Teng et al., 2011; Sio et al., 2013). Whether or not kinetic processes can occur among cumulus minerals in mafic magma chambers remains uncertain.

Studies of Mg isotopic compositions of cumulus minerals (olivine, clinopyroxene, and ilmenite) in layered mafic intrusions could provide key insights into whether cumulus minerals are in equilibrium or not. In this study, we find for the first time that ilmenites display extremely large Mg isotopic variation (up to 2.4‰ in $^{26}\text{Mg}/^{24}\text{Mg}$) and most times are heavier than coexisting olivine

and clinopyroxene in the Baima layered mafic intrusion, located at the central part of the Emeishan large igneous province, SW China. The extremely heavy Mg isotopic compositions of ilmenite can only result from kinetic isotope fractionation induced by Mg–Fe exchange between ilmenite and coexisting ferromagnesian silicates during the cooling of the Baima intrusion. Thus, the disequilibrium effect on cumulus minerals and rocks, which was little considered previously, should be treated seriously in investigating the petrogenesis of layered mafic intrusions.

2. Geological background and samples

The Emeishan large igneous province, derived from a ~260 Ma mantle plume, occurs in the western part of the Yangtze Block, southwest China (Fig. S1). It is predominated by widespread continental flood basalts, minor picritic lavas, and many contemporaneous mafic–ultramafic complexes and syenitic–granitic plutons (Song et al., 2001, 2008; Zhou et al., 2002; Xu et al., 2004; Zhang et al., 2006; Zhong et al., 2009). Five coeval layered mafic–ultramafic intrusions hosting world-class Fe–Ti oxide ore deposits occur in the Emeishan large igneous province central zone, namely, Taihe, Baima, Xinjie, Hongge, and Panzhihua from north to south (Panxi Geological Unit, 1984; Song et al., 2013; Chen et al., 2017). These intrusions are dated at ~260 Ma and are genetically related to the Emeishan mantle plume and the Emeishan high-Ti basaltic lavas (Zhou et al., 2002, 2008; Zhong and Zhu, 2006; Pang et al., 2008; Zhang et al., 2013).

The petrography of the Baima layered mafic intrusion (262 ± 2 Ma, Zhou et al., 2008) was presented in detail in previous studies (Panxi Geological Unit, 1984; Zhang et al., 2012, 2013; Liu et al., 2014; Chen et al., 2014; Holness et al., 2017) and is summarized briefly below. The N–S striking Baima intrusion is ~24 km long and ~1.5–6.0 km thick and dips to the west. The elongated body was surrounded by contemporaneous syenitic–granitic plutons that were emplaced into the Sinian Dengying Formation (dominated by limestone) and the Precambrian Huili group (dominated by marble and schist) (Fig. S1; Panxi Geological Unit, 1984). The Baima intrusion is characterized by medium-grained magnetite–wehrlite (Mt–wehrlite) and magnetite–troctolite (Mt–troctolite) in the Lower Zone, interlayers of fine-to-medium grained troctolite and gabbro in the Middle Zone, and fine-to-medium grained gabbro in the Upper Zone (Fig. S1; Chen et al., 2014). In addition, a few thin troctolite and gabbro are interlayered within the Mt–wehrlite and Mt–troctolite in the Lower Zone.

The Mt–wehrlite and Mt–troctolite are composed of high proportions of Fe–Ti oxides (e.g., magnetite and ilmenite, up to 70 modal%), olivine, plagioclase, and clinopyroxene, together with minor hornblende and sulfides (Fig. 1). Medium-grained ilmenite and magnetite occur as interconnected matrixes of aggregated Fe–Ti oxide grains enclosing silicates. Compared to the Mt–troctolite, the troctolite contains low contents of Fe–Ti oxides (<20%), high contents of plagioclase and olivine, as well as small abundances of clinopyroxene and hornblende. The gabbro, on the other hand, is rich in clinopyroxene and plagioclase, with <20% Fe–Ti oxide contents (Fig. 1), as well as minor olivine and/or apatite. Fine-to-medium grained and subhedral ilmenite crystals in the troctolite and gabbro are either in contact with magnetite or separated from magnetite, occurring as interstitial fillings among cumulus silicates. Micro-texture observations indicate that magnetite hosts abundant micro-intergrowths of ilmenite and hercynite while granular ilmenite has rare exsolution lamellae (Fig. 1; also see Zhang et al., 2012 and Chen et al., 2014). Moreover, both Fe–Ti oxides and silicates in the Baima intrusion are relatively fresh and little affected by post-magmatic hydrothermal alteration (e.g., Zhang et al., 2012; Chen et al., 2014).

Three Mt–wehrlites, eight Mt–troctolites, five troctolites, and four gabbros were collected from the Lower Zone and the lower

part of the Middle Zone (at Jijiping segment, Fig. S1). Eleven gabbros were sampled from the upper part of the Middle Zone and the Upper Zone (the bore hole ZK42-5 at Qinggangping segment, Fig. S1). These rocks were first crushed to 120–180 μm . Fresh olivine, clinopyroxene, and ilmenite grains were then handpicked and examined under a binocular microscope at 50 \times magnification to a purity of approximately 100%, and finally cleaned ultrasonically three times in Milli-Q water for analysis.

3. Analytical methods

3.1. Electron probe microanalysis

Chemical compositions of ilmenite and olivine were determined on polished thin sections by an EPMA-1600 electron microprobe at the State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, with the following operating conditions: Accelerating voltage: 25 kV, beam current: 10 nA, spot diameter: 10 μm . More than five spots of ilmenite core in each section were analyzed (silicate compositions were presented in Zhang et al., 2012 and Chen et al., 2014). Besides, several detailed transects of major elements of selected ilmenite and olivine crystals were measured along directions to silicates and/or Fe–Ti oxides. Natural and synthetic oxide standards from SPI Supplies, Inc., USA, were used for data calibration.

3.2. Magnesium isotope analysis

Magnesium isotopic compositions were analyzed at the Isotope Laboratory of the University of Washington, Seattle, following a slightly modified procedure after Teng et al. (2010) and Sedaghatpour et al. (2013). Briefly, approximately 5–10 mg of pure ilmenites were dissolved in a mixture of HNO_3 –HCl (~1:3) and then a concentrated HCl solution. Olivine, clinopyroxene and two international standards (DTS-1 and PCC-1) were dissolved sequentially in a mixture of concentrated HNO_3 –HF (~1:3), a mixture of concentrated HNO_3 –HCl (~1:3), and a concentrated HNO_3 solution. Magnesium purification for ilmenite and two international standards (DTS-1 and PCC-1) involves two steps of column chemistry (Sedaghatpour et al., 2013). The first step (i.e., Ti-column chemistry) was aimed to eliminate Ti from Mg using ion-exchange chromatography with Bio-Rad AG1-X8 resin (38–75 μm). Titanium was separated from Mg by 5 ml of 1 M HCl–0.5 M HF. The second step (i.e., Mg-column chemistry) was aimed to purify Mg from other matrix elements using Bio-Rad AG50W-X8 resin (38–75 μm) in 1 M HNO_3 . Samples (after the first step) dissolved in 1 M HNO_3 were loaded on the resin and Mg was eluted in 1 M HNO_3 . In contrast to ilmenite, the digested silicates as well as two international standards (DTS-1 and PCC-1, original solutions without Ti-column chemistry) were evaporated and re-dissolved in a mixture of 1 M HNO_3 and then were processed only through Mg-column chemistry as mentioned above.

The purified Mg sample solutions were measured using a Nu II MC-ICPMS in a low-resolution mode, with ^{24}Mg , ^{25}Mg , and ^{26}Mg determined simultaneously in separate Faraday cups. Magnesium isotope data are reported in δ -notation relative to the international standard DSM3: $\delta^X\text{Mg} (\text{‰}) = [({}^X\text{Mg}/{}^{24}\text{Mg})_{\text{sample}}/({}^X\text{Mg}/{}^{24}\text{Mg})_{\text{DSM3-1}}] \times 1000$, where X refers to mass 25 or 26. The long-term external reproducibility for $\delta^{26}\text{Mg}$ is better than 0.07‰ at 2 SD level (Teng et al., 2010, 2015). Data qualities were monitored by DTS-1 and PCC-1 and two well-characterized in-house standards (SC-OI and Seawater) processed as unknown samples in the same chemical and analytical procedures. All measured Mg isotopic data of these standards show excellent agreement with previous literature values (Table S1).

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