



Disequilibrium iron isotopic fractionation during the high-temperature magmatic differentiation of the Baima Fe–Ti oxide-bearing mafic intrusion, SW China



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ABSTRACT

Iron isotopic compositions of olivine, clinopyroxene and titanomagnetite of the Baima Fe–Ti oxide-bearing layered mafic intrusion, SW China, are used to investigate Fe isotopic fractionation during the formation of the Fe–Ti oxide ore bodies and to constrain the origin of silicate minerals and Fe–Ti oxides. The Baima intrusion comprises the Lower Zone of interlayered troctolite, clinopyroxenite and oxide ores and the Upper Zone of gabbros. Significant differences of Fe isotope values between olivine ($\delta^{56}\text{Fe} = -0.01$ to $+0.11\%$), clinopyroxene ($\delta^{56}\text{Fe} = +0.11$ to $+0.22\%$), and titanomagnetite ($\delta^{56}\text{Fe} = +0.20$ to $+0.31\%$) were observed in rocks and ores of the Lower Zone. Iron isotopic fractionation between olivine and clinopyroxene, olivine and titanomagnetite and clinopyroxene and titanomagnetite exhibits large variations of 0.06% to 0.22% , 0.12% to 0.27% , and 0.00% to 0.20% , respectively, suggesting disequilibrium fractionation. This disequilibrium cannot be explained by thermal or chemical gradient-induced kinetic fractionation or by possible subsolidus exsolution of granular ilmenite from titanomagnetite. Instead, it could be attributed to crystallization of silicates and titanomagnetite from two immiscible Si-rich and Fe-rich liquids. Continuous segregation of the Fe-rich liquid changed the Fe isotopic composition of the Si-rich liquid and thus the Fe isotopic compositions of olivine and clinopyroxene crystallized from it, resulting in disequilibrium Fe isotopic fractionation between them. The effect of oxygen fugacity on the crystallization order of titanomagnetite and ilmenite from the Fe-rich melts, on the other hand, gave rise to the disequilibrium Fe isotope fractionation between titanomagnetite and olivine/clinopyroxene.

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1. Introduction

In high-temperature magmatic systems, Fe isotope may fractionate during partial melting (Williams et al., 2004, 2005; Weyer and Ionov, 2007), fractional crystallization (e.g., Teng et al., 2008; Sossi et al., 2012), mantle metasomatism (e.g., Beard and Johnson, 2004; Zhao et al., 2010) and metal segregation processes (Roskosz et al., 2006; Schuessler et al., 2007). Equilibrium Fe isotopic fractionation is a function of temperature and is small at $>1000^\circ\text{C}$ (e.g., $\Delta^{56}\text{Fe}_{\text{magnetite(Mt)-olivine(Ol)}} = +0.17\%$ at 1000°C , Shahar et al., 2008). Recent investigations of Fe isotope have shown discernible fractionation during magmatic differentiation from olivine-rich cumulates to andesites (Teng et al., 2008) and from basalts to rhyolites (Schuessler et al., 2009). Enrichment of

heavy Fe isotopes in evolving magmas from the Kilauea Iki lava lake, Hawaii, and the Hekla volcano, Iceland, has been attributed to Fe oxidation states on kinetic or equilibrium isotope fractionation (Teng et al., 2008) or to crystal fractionation that removes isotopically light minerals such as olivine and pyroxenes (Schuessler et al., 2009). Sossi et al. (2012) have demonstrated that upon magnetite saturation, $\delta^{57}\text{Fe}$ values of the melt fall because of the prior partition of ^{57}Fe into magnetite (Sossi et al., 2012). Fe–Ti oxide-bearing layered mafic intrusions contain Fe–Ti oxide ores that consist of a considerable volume of magnetite, together with cumulus olivine, pyroxenes and plagioclase, and thus would be ideal for investigating high-temperature Fe isotopic fractionation in slowly cooled magma chambers.

The ~ 260 -Ma Emeishan large igneous province (ELIP) in the Panzhihua–Xichang (Panxi) region, SW China, contains several layered mafic intrusions that host economically important magmatic Fe–Ti oxide deposits (e.g., Zhong et al., 2005; Zhou et al.,

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2005, 2013; Wang et al., 2008; Pang et al., 2010; Howarth and Prevec, 2013). There are basically two schools of thoughts as to how Fe–Ti oxides were saturated. One holds the view that silicate minerals and Fe–Ti oxides were crystallized from the same ferrobasaltic magma either in one pulse (Pang et al., 2008, 2009; Shellnutt and Pang, 2012) or from repetitive magma replenishments (Bai et al., 2012; Zhang et al., 2012). The other view argues that they were crystallized from different magmas resulting from either liquid immiscibility (Zhou et al., 2005, 2013; Wang and Zhou, 2013; Liu et al., 2014a) or multiple replenishments of magmas with variable H₂O contents, titanomagnetite crystal load and volume (Howarth et al., 2013). Regardless of the mechanism, the redox state of the magma would be an important control on the crystallization sequence of mafic minerals and Fe–Ti oxides related to these large Fe–Ti oxide deposits (e.g. Reynolds, 1985; Toplis and Corgne, 2002; Ganino et al., 2008). Iron isotope of the minerals crystallized from the magma that formed the Baima intrusion, in return, may contain important information on the redox state of the magma.

The Baima deposit is the second largest Fe–Ti oxide deposit in the region. It contains conformable Fe–Ti oxide ores in the Lower Zone of the host intrusion (Zhang et al., 2012, 2013). This ~170-m-thick sequence of interlayered Fe–Ti oxide ores and Fe–Ti oxide-bearing troctolite and clinopyroxenite is ideal for investigating ore-forming processes and the evolution of the Baima magma chamber. In this paper, we report new Fe isotopic compositions of coexisting olivine, clinopyroxene and titanomagnetite from the Baima intrusion. Our objectives are (1) to investigate the extent of Fe isotope variations in high temperature magmatic system; (2) to examine the control of the crystallization sequence on Fe isotopic fractionation; and (3) to constrain the origin of the Baima Fe–Ti oxide deposit. Our study on the systematic Fe isotopic variation of co-existing Fe-bearing mineral phases in the Baima layered mafic intrusion may shed light on the processes that control high-temperature Fe isotopic fractionation.

2. Geological background

The ~260-Ma ELIP crops out over an area of 5×10^5 km² in SW China and northern Vietnam. It consists of numerous mafic–ultramafic intrusions and a volcanic succession of picrites, tholeiitic basalts and basaltic andesites varying from several hundred meters to 5 km in thickness (Chung and Jahn, 1995). These volcanic rocks are underlain by the middle Permian carbonate rocks of the Maokou Formation and are overlain by clastic sedimentary rocks of the late Permian Xuanwei Formation. Some mafic–ultramafic intrusions contain Cu–Ni–(PGE) sulfide deposits and are related to the low-Ti magma series (Zhou et al., 2008). The intrusions hosting Fe–Ti–(V) oxide deposits formed from typical high-Ti basaltic magmas of the ELIP (Zhou et al., 2008; Shellnutt et al., 2009). They are mainly distributed in the Panxi region and are exposed via N–S faulting probably active since the Early Jurassic (Chung and Jahn, 1995). The Baima intrusion is 24-km long, 2 to 6.5-km wide, and contains the second largest Fe–Ti–(V) oxide deposit in the region (Fig. 1). It includes a 150 to 300 m-thick Lower Zone of interlayered Fe–Ti oxide ores and Fe–Ti oxide-bearing troctolite and olivine clinopyroxenite, and a ~1200 m-thick Upper Zone of gabbros (Zhang et al., 2012; Liu et al., 2014a, 2014b).

3. Petrography

Fe–Ti oxide ores in the Lower Zone of the Baima intrusion include net-textured ores with >40 vol% Fe–Ti oxides and disseminated ores with 20 to 40 vol% Fe–Ti oxides. Fe–Ti oxides usually occur as interstitial phases in the spaces between cumulus olivine, clinopyroxene and plagioclase (Fig. 2(a)). Olivine is the dominant

silicate phase and makes up 10 to 30 vol% of the Fe–Ti oxide ore. It is subhedral to euhedral and varies from 1 to 1.5 mm in diameter. Plagioclase occurs as tabular laths with embayed texture and hornblende rims in contact with Fe–Ti oxides (Liu et al., 2014a). Subhedral clinopyroxene develops abundant schiller exsolution of Fe–Ti oxides. Interstitial Fe–Ti oxides include titanomagnetite, ilmenite and their exsolution product of spinel. Among them, titanomagnetite predominates in volume and contains cloth and trellis exsolution of ilmenite and aluminous spinel. Ilmenite also occurs as homogeneous granular grains. It is spectacular that small olivine grains are locally enclosed in titanomagnetite and ilmenite (Liu et al., 2014a, 2014b). Titanomagnetite and ilmenite, on the other hand, are trapped together with minor sulfide, apatite, hornblende and muscovite as multiphase mineral inclusions in olivine (Fig. 2(b)–(d), Liu et al., 2014a).

Fe–Ti oxide-bearing troctolite contains ~30 vol% olivine, ~40 vol% plagioclase, 5 to 10 vol% clinopyroxene and 10 to 20 vol% Fe–Ti oxides (titanomagnetite and ilmenite) whereas Fe–Ti oxide-bearing olivine clinopyroxenite is composed of ~35 vol% clinopyroxene, ~20 vol% plagioclase, ~25 vol% olivine, and ~10 vol% Fe–Ti oxides. Accessory minerals include hornblende, apatite and sulfides and they make up <10 vol%. These ultramafic rocks are medium-grained and isotropic. Olivine, clinopyroxene and plagioclase occur as cumulus grains, filled interstitially by Fe–Ti oxides.

4. Sampling and analytical methods

To assess the co-variations of Fe isotopes of olivine, clinopyroxene and titanomagnetite, samples (~25 × 10 × 15 cm³ in size) of one Fe–Ti oxide-bearing troctolite (sample BM341), one Fe–Ti oxide-bearing clinopyroxenite (sample BM385) and eleven disseminated or net-textured oxide ores were collected evenly from the stratigraphic column of the Lower Zone along a cross section in the Baima open pit (see location of sampling in Fig. 1).

4.1. Fe³⁺ / ∑ Fe determinations

The redox state of Fe in the bulk samples was calculated using data obtained by titration methods. Samples were decomposed in a mixture of HF and H₂SO₄. Measurement of Fe²⁺ was acquired by titration of potassium dichromate using diphenyl sulfonate as an indicator (Knop, 1924). Measurement of total Fe of the same solution was made after adding stannous chloride (a reducing agent) to an aliquot of about 10 ml. All Fe³⁺ was converted into Fe²⁺ before measurement of Fe²⁺ using the above method. Fe³⁺ is calculated by subtracting Fe²⁺ from total Fe. Fe³⁺ / ∑ Fe ratios are thus obtained.

4.2. Mineral analysis

Major element compositions of olivine and titanomagnetite were analyzed on a JEOL JXA-8100 electron microprobe (EMP) at the Key Laboratory of Isotopic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences. The analyses were carried out using a voltage of 15 kV and a beam current of 20 nA, focused to a spot of 1 μm on polished thin sections. Calibration of elemental analyses was done using multiple silicate and pure oxide standards from SPI Supplies, Inc., USA. The precisions of the trace and major element determinations were better than 5% and 2%, respectively. Matrix corrections were performed using the ZAF procedures (Jurek and Hulínský, 1980).

4.3. Fe isotope analysis

Fe isotope measurements on mineral separates, including chemistry and isotopic measurements, were performed at the CRPG-Nancy (France). A total of thirty three mineral separates from

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