American Mineralogist, Volume 105, pages 1841–1856, 2020

Magma oxygen fugacity of mafic-ultramafic intrusions in convergent margin settings: Insights for the role of magma oxidation states on magmatic Ni-Cu sulfide mineralization

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Abstract

Oxygen fugacities (f_{O_2}) of mantle-derived mafic magmas have important controls on the sulfur status and solubility of the magmas, which are key factors to the formation of magmatic Ni-Cu sulfide deposits, particularly those in convergent margin settings. To investigate the f_{O_2} of mafic magmas related to Ni-Cu sulfide deposits in convergent margin settings, we obtained the magma f_{O_2} of several Ni-Cu sulfide-bearing mafic-ultramafic intrusions in the Central Asian Orogenic Belt (CAOB), North China, based on the olivine-spinel oxygen barometer and the modeling of V partitioning between olivine and melt. We also calculated the mantle f_{O_2} on the basis of V/Sc ratios of primary magmas of these intrusions.

Ni-Cu sulfide-bearing mafic-ultramafic intrusions in the CAOB include arc-related Silurian-Carboniferous ones and post-collisional Permian-Triassic ones. Arc-related intrusions formed before the closure of the paleo-Asian ocean and include the Jinbulake, Heishan, Kuwei, and Erbutu intrusions. Post-collisional intrusions were emplaced in extensional settings after the closure of the paleo-Asian ocean and include the Kalatongke, Baixintan, Huangshandong, Huangshan, Poyi, Poshi, Tulaergen, and Hongqiling No. 7 intrusions. It is clear that the magma f_{O_2} values of all these intrusions in both settings range mostly from FMQ+0.5 (FMQ means fayalite-magnetite-quartz oxygen buffer) to FMQ+3 and are generally elevated with the fractionation of magmas, much higher than that of MORBs (FMQ-1 to FMQ+0.5). However, the mantle f_{O_2} values of these intrusions vary from ~FMQ to ~FMQ+1.0, just slightly higher than that of mid-ocean ridge basalts (MORBs) (≤FMQ). This slight difference is interpreted as the intrusions in the CAOB may have been derived from the metasomatized mantle wedges where only minor slab-derived, oxidized components were involved. Therefore, the high-magma f_{O_2} values of most Ni-Cu sulfide-bearing mafic-ultramafic intrusions in the CAOB were attributed to the fractionation of magmas derived from the slightly oxidized metasomatized mantle. In addition, the intrusions that host economic Ni-Cu sulfide deposits in the CAOB usually have magma f_{O_2} of >FMQ+1.0 and sulfides with mantle-like $\delta^{34}S$ values (–1.0 to +1.1‰), indicating that the oxidized mafic magmas may be able to dissolve enough mantle-derived sulfur to form economic Ni-Cu sulfide deposits. Oxidized mafic magmas derived from metasomatized mantle sources may be an important feature of major orogenic belts.

Keywords: Mafic-ultramafic intrusion, magmatic Ni-Cu sulfide mineralization, magma oxygen fugacity, Central Asian orogenic belt, convergent margin setting

Introduction

The oxygen fugacity (f_{O_2}) of mantle-derived mafic magmas is controlled by equilibria of Fe^{3+}-Fe^{2+} and S^{2-}-S^{6+} (Kress and Carmichael 1991; Jugo et al. 2005) and can be quantified as $\Delta\log f_{O_2}$ relative to mineral assemblage buffers. The f_{O_2} values of mafic magmas are considered to be closely related to geodynamic settings, but how they differ in different settings is still a matter of debate. In general, having $Fe^{3+}/\Sigma Fe$ and $S^{6+}/\Sigma S$ higher than the mid-ocean ridge basalt (MORB) samples, arc and back-arc basalts may have formed from relatively oxidized magmas (Wood et al. 1990; Nilsson and Peach 1993; Jugo et al. 2010; Brounce et al. 2017). It has been demonstrated that arc and back-arc basalts were derived from metasomatized mantle wedges that have been oxidized to variable degrees (Debret et al. 2016; Rielli et al. 2017; Bénard et al. 2018). It is also known that the metasomatized mantle beneath subduction zones has f_{O_2} similar to the mantle beneath the mid-ocean ridges, and it is the fractionation of metasomatized mantle-derived magmas or the interaction of hydrated magmas with ambient mantle that elevated the magma f_{O_2} (Lee et al. 2005, 2010; Dauphas et al. 2010; Tollan and Hermann 2019; Li et al. 2020).

Magmatic Ni-Cu sulfide deposits are traditionally thought to be related to the mafic magmatism induced by either mantle plumes or rifting within intraplate settings (Naldrett 2004). However, mafic-ultramafic intrusions in convergent margin settings have become targets for prospecting economic Ni-Cu sulfide deposits in recent years (Maier et al. 2008; Thakurta et al.

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0003-004X/20/0012–1841$05.00/DOI: https://doi.org/10.2138/am-2020-7351

2008; Tomkins et al. 2012; Manor et al. 2016; Song et al. 2016). The mantle sources of such intrusions are generally considered to be metasomatized by slab-derived fluids/melts (Manor et al. 2016; Song et al. 2016). The mafic magmas derived from the metasomatized mantle can be highly hydrated and oxidized with f_{O_2} being up to FMQ+6 (FMQ means fayalite-magnetite-quartz oxygen buffer) (Kelley and Cottrell 2009; Kelley et al. 2010; Gaillard et al. 2015). For example, the magma f_{O_2} of the Alaskan-type Duke intrusion in U.S.A. and the Turnagain and Mascot Ni-Cu sulfide-bearing mafic-ultramafic intrusions in Canada are calculated to be >FMQ+2 (Thakurta et al. 2008; Manor et al. 2016). The central Asian orogenic belt (CAOB) is one of the largest accretionary orogens in the world and resulted from large-scaled subduction and accretion of juvenile materials from Neoproterozoic to Paleozoic (Sengör et al. 1993; Xiao et al. 2004a, 2004b, 2009; Jahn et al. 2004). A preliminary study on the oxidation states of a few Ni-Cu sulfide-bearing mafic-ultramafic intrusions in the CAOB indicates that magma f_{O_2} values vary from FMQ+0.3 to FMQ+2.6, much higher than that of MORBs (Cao et al. 2019).

Experimental results indicate that the sulfur solubility of highly oxidized mafic magmas can be as high as 1.4 wt% with sulfur being dominant as sulfate species (S^{6+}) (Jugo et al. 2005; Jugo 2009), significantly higher than that of reduced mafic magmas with dominantly S^{2-} phases (Jugo et al. 2010; Cottrell and Kelley 2011). Therefore, the oxidized mantle source or highly oxidized, hydrated mafic magmas may be more favorable for the magmatic Ni-Cu sulfide deposits in convergent margin settings (Jenner et al. 2010; Tomkins et al. 2012; Cao et al. 2019; Wei et al. 2019). However, the linkage between magma f_{O_2} of mafic-ultramafic intrusions and Ni-Cu sulfide mineralization is not well understood. Three important issues that should be answered are: (1) do the mantle sources of the mafic-ultramafic intrusions in convergent margin settings have remarkably high f_{O_2} relative to those in intraplate settings; (2) if not, what triggers high-magma f_{O_2} of the mafic-ultramafic intrusions in convergent margin settings; and (3) what is the favorable magma f_{O_2} for the Ni-Cu sulfide mineralization in convergent margin settings?

Several Paleozoic mafic-ultramafic intrusions in the CAOB host Ni-Cu sulfide deposits with variable Ni grades and ore reserves, making up a ~4000 km long Ni-Cu sulfide mineralization belt in North China. These intrusions were dated to be Devonian to Triassic in age, some of which were emplaced in the subduction stage predating the closure of the paleo-Asian ocean, whereas others in the post-subduction, extensional stage after the closure of the paleo-Asian ocean (e.g., Yang and Zhou 2009; Qin et al. 2011; Li et al. 2012, 2015; Yang et al. 2012; Peng et al. 2013). These intrusions are ideal for unraveling the correlation between magma f_{O_2} and Ni-Cu sulfide mineralization in a convergent margin setting. In this study, we estimated the mantle and magma f_{O_2} of representative mafic-ultramafic intrusions in the CAOB that were emplaced in different ages and host variable degrees of Ni-Cu sulfide mineralization. The results indicate that most intrusions have a magma f_{O_2} much higher than that of MORBs despite the similarity in their mantle f_{O_2}. Such a feature can be further examined for the Ni-Cu sulfide-bearing mafic-ultramafic intrusions in convergent margin settings elsewhere.

Geological background

The central Asian orogenic belt is bounded by the Siberian Craton to the north and the Tarim Craton and North China Craton to the south (Fig. 1a). The belt extends for more than 7000 km from the Pacific Ocean to the Eastern Europe, making up one of the largest accretionary orogenic belts on Earth. It formed due to the closure of the paleo-Asian ocean in the Paleozoic and comprised numerous fragments of Precambrian microcontinents, Paleozoic island arcs, phiolite suites, and successions of volcanic rocks (Windley et al. 2007; Xiao et al. 2009).

The CAOB in China part is subdivided into the western and eastern segments (Zhou and Wilde 2013) (Fig. 1b). The western segment is further divided into five belts, from north to south (Fig. 1c), including: (1) the Altay orogenic belt that is bounded by the Sayan belt to the north and by the Ulungar fault and Junggar block to the south (Sengör et al. 1993; Windley et al. 2002; Xiao et al. 2009); (2) the North Tianshan orogenic belt between the Junggar block to the north and the Aqikkuduk fault to the south (Zhou et al. 2004; Qin et al. 2011; Gao et al. 2012); (3) the Central Tianshan orogenic belt between the Aqikkuduk fault to the north and the Kawabulak fault to the south (Song et al. 2013); (4) the South Tianshan orogenic belt between the Kawabulak fault to the north and the Tarim Craton to the south (Yang and Zhou 2009); and (5) the Beishan fold belt along the northeastern margin of the Tarim Craton (Xu et al. 2016). The eastern segment refers to the Xing'an-Mongolia orogenic belt in the Inner Mongolia and northeast China (Zhang et al. 2015), which consists mainly of, from north to south, the Erguna massif, Xing'an massif, Songnen-Zhangguangcai range massif, and a continental margin accretionary belt (Wu et al. 2007) (Fig. 1d).

Numerous mafic-ultramafic intrusions that contain Ni-Cu sulfide mineralization occur in the CAOB. They were emplaced mainly in two periods, one from Silurian to Carboniferous and the other from Permian to Triassic (e.g., Yang and Zhou 2009; Xie et al. 2012; Hao et al. 2014; Mao et al. 2016).

Silurian to Carboniferous mafic-ultramafic intrusions

Silurian to Carboniferous mafic-ultramafic intrusions are mainly distributed in the western segment of the CAOB and host small- to medium-sized Ni-Cu sulfide deposits (Fig. 1b). As the paleo-Asian ocean was not yet closed until Permian in the western segment (Han et al. 2007; Xiao et al. 2009), these intrusions are considered to be arc-related (Yang and Zhou 2009; Xie et al. 2012; Yang et al. 2012). Representative intrusions include the Jinbulake intrusion (ca. 430 Ma) in the central Tianshan belt (Yang and Zhou 2009; Yang et al. 2012), the Kuwei intrusion (ca. 398 Ma) in the Altay belt (Li et al. 2015), and the Heishan intrusion (ca. 356 to 367 Ma) in the Beishan belt (Xie et al. 2012).

The parental magmas of these intrusions are tholeiitic (e.g., Zhou et al. 2004; Yang and Zhou 2009; Tang et al. 2012; Xia et al. 2013; Song et al. 2013). Rocks of these intrusions have positive $\varepsilon_{Nd}(t)$ (+0.4 to +4) and initial Sr^{87}/Sr^{86} ranging from 0.704 to 0.709 (Yang and Zhou 2009; Xie et al. 2012; Yang et al. 2012). They show depleted Nb and Ta relative to large ion lithophile elements (LILE) and light rare earth elements (LREE) on the primitive mantle-normalized trace element patterns (Figs. 2a–2d), consistent with an arc-like affinity. These features were interpreted as magma generation from the depleted mantle that

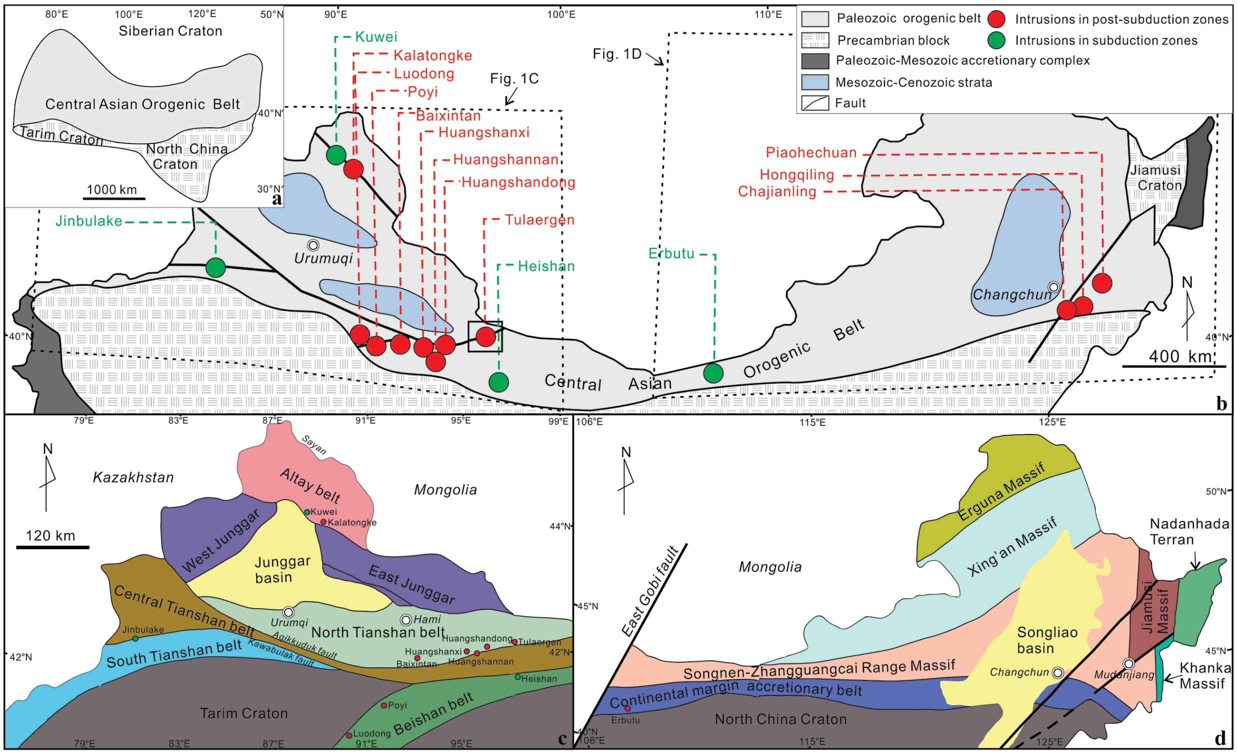

Figure 1. (**a**) The tectonic context of the Central Asian Orogenic Belt (CAOB) relative to other Cratons (modified after Jahn et al. 2000). (**b**) A simplified geological map of the CAOB (modified after Xiao et al. 2009) showing the mafic-ultramafic intrusions in the CAOB that formed in arc and post-subduction, extensional settings. (**c**) A geological map of the western segment of the CAOB. (**d**) A geological map of the eastern segment of the CAOB. (Color online.)

had been metasomatized by slab-derived fluids/melts (Yang and Zhou 2009; Xie et al. 2012; Yang et al. 2012).

The Erbutu intrusion in the eastern segment of the CAOB is an outlier. Although it is dated to be 294.2 ± 2.7 Ma, it is considered to be an arc-hosted intrusion (Peng et al. 2013). The intrusion hosts a small-sized Ni-Cu sulfide deposit, and the parental magma is boninitic (Peng et al. 2013). The intrusion is mainly composed of olivine-bearing orthopyroxenite with mineral modes quite similar to those formed from boninitic magma (Peng et al. 2013). The rocks have LREE and LILE (e.g., Ba and Rb) more enriched than those of the Jinbulake and Heishan intrusions (Figs. 2e and 2f).

Permian to Triassic mafic-ultramafic intrusions

Permian to Triassic mafic-ultramafic intrusions in the CAOB host several economic Ni-Cu sulfide deposits, including the Kalatongke intrusion (290–282 Ma) in the Altay belt (Song and Li 2009; Zhang et al. 2009; Gao et al. 2012), the Huangshandong and Huangshanxi intrusions (274–283 Ma) in the Huangshan-Jingerquan mineralized belt in the North Tianshan belt (Qin et al. 2011; Sun et al. 2013), the Tulaergen intrusion (265 ± 9.2 Ma) in the Kanggur-Huangshan shear zone in the North Tianshan belt (Zhao et al. 2017), the Poyi and Poshi intrusions (270–277 Ma) in the Beishan belt (Xue et al. 2016), and the Hongqiling No. 7 and Piaohechuan No. 4 intrusions (ca. 210–230 Ma) in the Xing'an-Mongolia belt (Wei et al. 2013, 2015) (Fig. 1b). In addition, many other intrusions in this period host potential Ni-Cu sulfide mineralization, including the Huangshannan (278 ± 2 Ma) and Baixintan intrusions (286 ± 3 Ma) in the North Tianshan belt (Mao et al. 2016; Feng et al. 2017), the Luodong intrusion (260–290 Ma) in the Beishan belt (Su et al. 2015), and the Hongqiling Nos. 1, 2, 3, 9, 32, and 33 intrusions (ca. 210–230 Ma) in the Xing'an-Mongolia belt (Hao et al. 2014).

These intrusions are considered to have formed in post-subduction, extensional settings after the closure of the paleo-Asian ocean (e.g., Jiang et al. 2009; Li et al. 2012; Sun et al. 2013; Wei et al. 2013, 2015; Mao et al. 2014, 2015). The rocks of these intrusions show arc-like trace element patterns (Figs. 3a–3d), which are attributed to the derivation from the metasomatized, depleted mantle (Xie et al. 2012; Li et al. 2012; Mao et al. 2014; Deng et al. 2015). However, the rocks of the Luodong intrusion have MORB-like, LREE-depleted trace element patterns (Figs. 3e and 3f), which may have been derived from the weakly metasomatized mantle (Su et al. 2015).

Intrusions and samples chosen for oxygen fugacity calculation

A prerequisite to using the olivine-spinel oxygen barometer is to obtain the compositions of equilibrated olivine-spinel pairs in rocks (Ballhaus et al. 1991). The mafic-ultramafic intrusions in the CAOB that have rocks containing olivine-spinel pairs include Silurian to Carboniferous Jinbulake, Heishan and Erbutu intrusions, and Permian to Triassic Baixintan, Huangshannan, Huangshandong, Huangshanxi, Poyi, Luodong, Tulaergen,

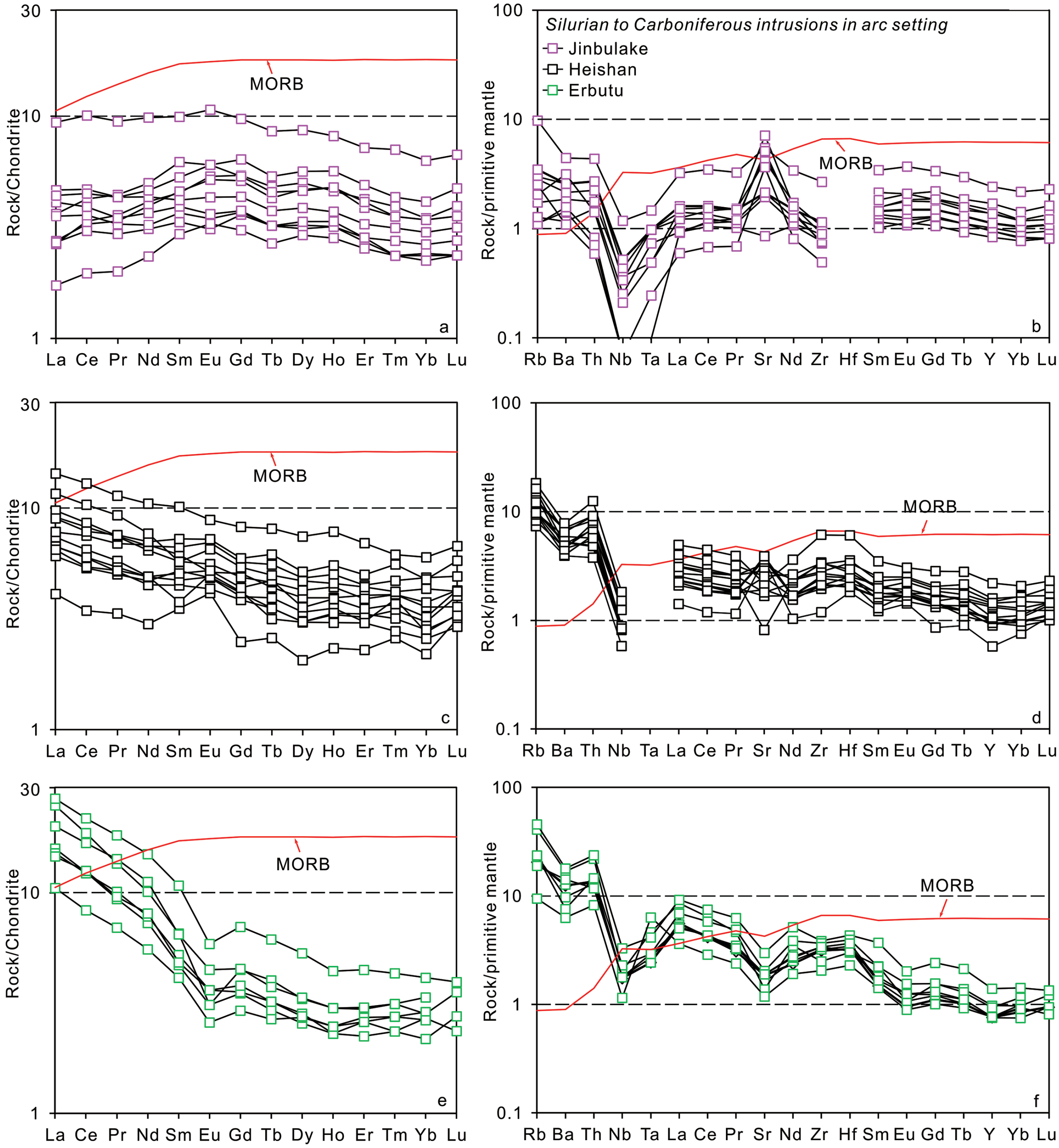

Figure 2. Chondrite-normalized rare earth element patterns and primitive mantle-normalized trace element patterns for representative mafic-ultramafic intrusions in the CAOB that were emplaced in arc settings. Data sources: Jinbulake (Yang and Zhou 2009), Heishan (Xie et al. 2012), Erbutu (Peng et al. 2013). Chondrite and primitive mantle values are from Sun and McDonough (1989). (Color online.)

Hongqiling No. 1 and No. 2 intrusions. In this study, we calculated the magma and mantle f_{O_2} values of the Jinbulake, Heishan, Erbutu, Baixintan, Huangshannan, Luodong, and Tulaergen intrusions. Together with the magma and/or mantle f_{O_2} values of the Huangshandong, Huangshanxi, and Poyi and Hongqiling No. 1 and No. 2 intrusions that were obtained in our earlier studies (Cao et al. 2019; Wei et al. 2019), an integrated framework of the magma and mantle f_{O_2} of the Ni-Cu sulfide-bearing mafic-ultramafic intrusions in the CAOB can be outlined. The results in this study are compared with the magma f_{O_2} values of the picrite in the Dali area, southwestern China, which is part of the Emeishan large igneous province (LIP) that formed within an intraplate setting. The petrography of the selected mafic-ultramafic intrusions in the CAOB and the Dali picrite in the Emeishan LIP are described in Supplemental Material[1].

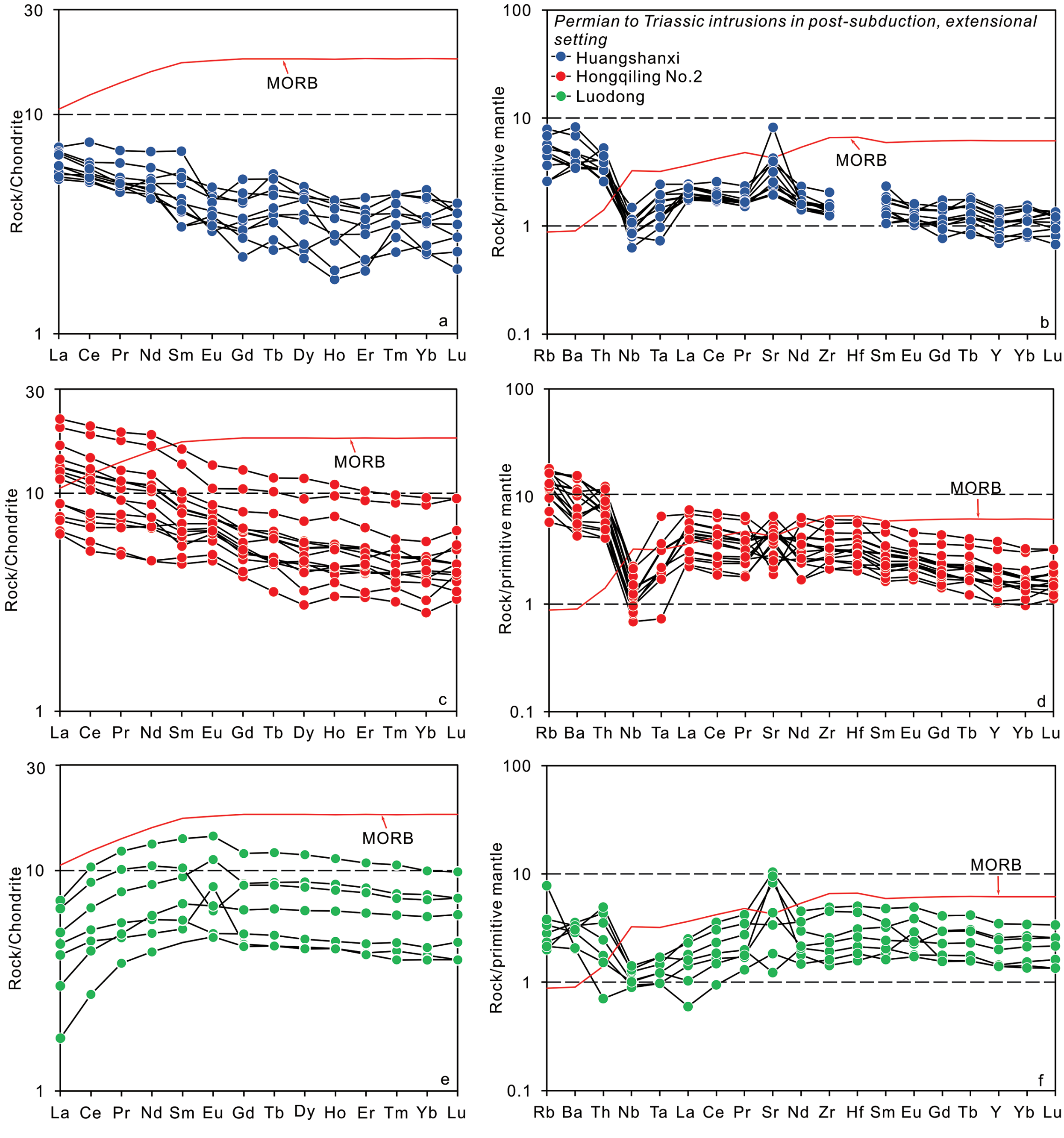

FIGURE 3. Chondrite-normalized rare earth element patterns and primitive mantle-normalized trace element patterns for representative mafic-ultramafic intrusions in the CAOB that were emplaced in post-subduction, extensional settings. Data sources: Huangshanxi (Mao et al. 2014), Hongqiling No. 2 (Wei 2013), and Luodong (Su et al. 2011). Chondrite and primitive mantle values are from Sun and McDonough (1989). (Color online.)

ANALYTICAL RESULTS

Compositions of olivine-spinel pairs in mafic-ultramafic intrusions in the CAOB

The compositions of the olivine-spinel pairs in the rocks of the selected mafic-ultramafic intrusions in the CAOB were analyzed in this study. All analytical methods are described in Supplemental[1] Information. The results of the olivine-spinel pairs are described in Supplemental Information, and the data are listed in Supplemental[1] Table S1.

A summary of spinel compositions

The spinel grains from the mafic-ultramafic intrusions in either arc or post-subduction, extensional settings in the CAOB have highly variable Cr# and XFe^{3+}. The grains from the Erbutu intrusion have the highest Cr# and the lowest XFe^{3+} among the three arc-hosted intrusions (Figs. 4a and 4b). Among the intrusions in the post-subduction, extensional settings, the spinel grains from the Baixintan, Huangshannan, and Tulaergen intrusions have relatively restricted Cr# but highly variable XFe^{3+} relative to those from the Luodong and Hongqiling No. 1 and No. 2 intrusions (Figs. 4a and 4b). In addition, the spinel grains from the Luodong intrusion has similar Cr# but relatively low and restricted XFe^{3+} compared to those from the Hongqiling No. 1 and No. 2 intrusions (Figs. 4a and 4b). The spinel grains from the Erbutu and Luodong intrusions are clustered on the plot of Mg# vs. XFe^{3+}, whereas the grains from each of the other intrusions generally show a negative trend of Mg# vs. XFe^{3+}on this plot (Fig. 4b).

The spinel grains in the Dali picrite overall have higher Mg# and Cr#, and lower XFe^{3+} than those from the intrusions in the CAOB (Figs. 4a and 4b). However, they have similar Cr# and XFe^{3+} to those from the Erbutu intrusion (Figs. 4a and 4b). They display a nearly horizontal trend on the plot of Mg# vs. XFe^{3+} (Fig. 4b), which is in contrast to the negative correlation trend for the spinel from the intrusions in the CAOB on the plot.

S isotope compositions of sulfides in mafic-ultramafic intrusions in the CAOB

The method of in situ S isotope analysis for the sulfides (pyrrhotite, pentlandite, and chalcopyrite) in the rocks of the selected mafic-ultramafic intrusions in the CAOB is described in Supplemental[1] Information. The sulfides in the wehrlite of the Jinbulake intrusion have $\delta^{34}S$ ranging from +0.3 to +1.3‰ (Table 1). The sulfides in the lherzolite of the Baixintan intrusion have $\delta^{34}S$ ranging from –0.7 to +1.2‰ (Table 1). The sulfides in the lherzolite of the Tulaergen intrusion have $\delta^{34}S$ ranging from –0.2 to +0.8‰ (Table 1). Overall, the sulfides from the three intrusions have a restricted range of $\delta^{34}S$ from –0.7 to +1.3‰. Likewise, the sulfides in the ores of three economic Ni-Cu sulfide deposits hosted in the Permian-Triassic Kalatongke, Hongqiling No. 7 and Piaohechuan No. 4 intrusions in the CAOB have $\delta^{34}S$ ranging from –1.0 to +1.1‰ (Wei et al. 2019). All of these values are similar to the $\delta^{34}S$ of MORB-type mantle (–1.5 to +0.6‰, Labidi et al. 2013, 2014) (Fig. 5). In contrast, the sulfides from the rocks of the Erbutu intrusion have $\delta^{34}S$ ranging from +5.3 to +7.5‰ (Table 1), much higher than those from other intrusions in the CAOB (Fig. 5).

Calculation results of oxygen fugacity

The oxygen fugacity of the mantle and mantle-derived mafic magmas can be calculated in four different ways, including (1) measuring $Fe^{3+}/(Fe^{3+}+Fe^{2+})$ of basalts or quenched basaltic glass (Kress and Carmichael 1991; Kelley and Cottrell 2009); (2) quantifying the partition coefficients of redox-sensitive elements (e.g., V and Cr) in the differentiation of magma (Canil 1997; Mallmann and O'Neill 2009); (3) using oxygen barometers based on the chemical equilibria between mineral pairs (e.g., olivine-spinel pair) (Ballhaus et al. 1991); and (4) calculating the ratios of redox sensitive/insensitive elements (e.g., V/Sc, Fe^t/Zn) of primary magmas (Lee et al. 2005, 2010; Mallmann and O'Neill 2009). The fourth method is exclusively used to estimate the mantle oxygen fugacity (Lee et al. 2005; Mallmann and O'Neill 2009), however, the three others are applicable to calculate the f_{O_2} of both mantle and mantle-derived magmas, depending upon whether the examined objects are mantle xenoliths (e.g., Ionov and Wood 1992), or fractionated basalts/mafic-ultramafic intrusions (e.g., Cao et al. 2019).

Mantle f_{O_2}

Given that mantle xenoliths can be directly used to calculate the mantle f_{O_2} are unavailable in the CAOB, we constrained the mantle f_{O_2} based on the relationship between the mantle f_{O_2} and the V/Sc ratios of primary magmas, an alternative method proposed by Lee et al. (2005) and Mallmann and O'Neill (2009).

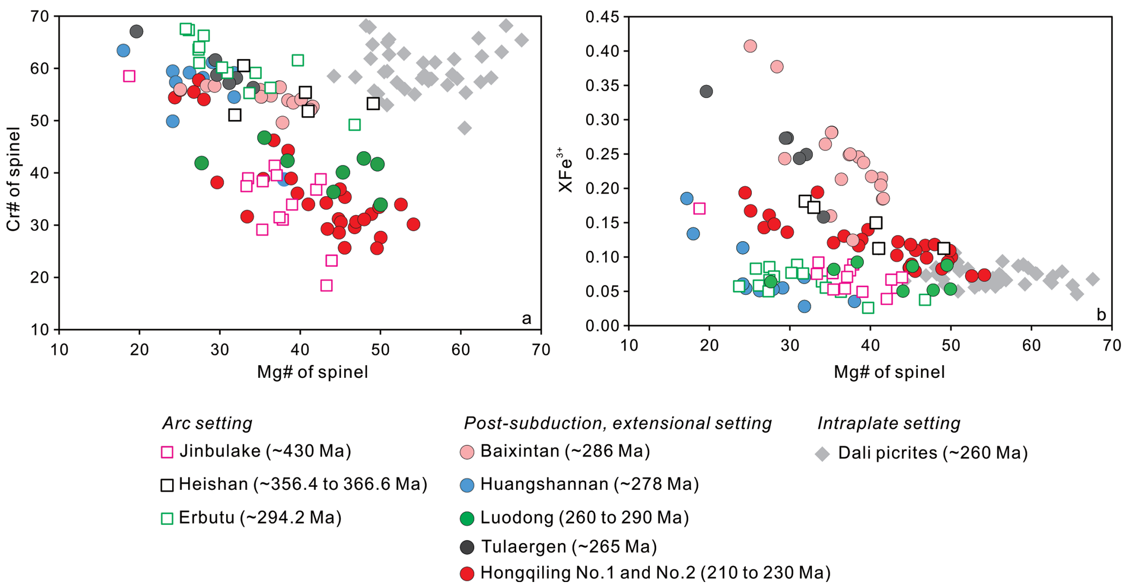

Figure 4. Plot of Mg# vs. Cr# (**a**) and Mg# vs. XFe^{3+} (**b**) for the spinel of the mafic-ultramafic intrusions in the CAOB, and the Dali picrite from the Emeishan large igneous province. Data sources: Jinbulake, Erbutu, Huangshannan, and Tulaergen intrusions (this study), Heishan intrusion (Wang 2011), Baixintan intrusion (this study; Feng et al. 2017), Luodong intrusion (Su et al. 2011), Hongqiling No. 1 and No. 2 intrusions (Cao et al. 2019; Wei et al. 2019), Dali picrite (Kamenetsky et al. 2012; Liu et al. 2017). (Color online.)

Table 1. S isotopic compositions of the sulfides in the rocks from the Jinbulake, Erbutu, Baixintan, and Tulaergen intrusions in the Central Asian Orogenic Belt

Analysis no.	Sample no.	Sulfides	δ^{34}S‰ (V-CDT)
	Jinbulake intrusion		
1	QB-13	pyrrhotite	0.6
2	QB-13	pyrrhotite	0.3
3	QB-13	pyrrhotite	0.0
4	QB-13	pyrrhotite	0.5
5	QB-13	pyrrhotite	0.9
6	QB2-102	pyrrhotite	0.9
7	QB2-102	pyrrhotite	0.8
8	QB2-102	pyrrhotite	0.8
9	QB2-102	pyrrhotite	1.3
10	QB2-78	pyrrhotite	0.1
11	QB2-78	pyrrhotite	0.2
12	QB2-78	pyrrhotite	0.7
13	QB2-78	pyrrhotite	0.5
14	QB-43	pyrrhotite	0.3
15	QB-43	pentlandite	0.3
16	QB-43	pentlandite	0.3
17	QB-43	pyrrhotite	0.6
18	QB-43	pyrrhotite	0.7
19	QB-43	pentlandite	0.6
20	QB-43	pyrrhotite	0.7
21	QB-65	chalcopyrite	0.9
22	QB-65	chalcopyrite	0.9
23	QB-65	pyrrhotite	0.6
24	QB-65	pyrrhotite	0.4
25	QB-65	chalcopyrite	1.3
26	QB-65	pentlandite	0.7
27	QB-65	pyrrhotite	0.9
28	QB-65	pyrrhotite	0.6
	Erbutu intrusion		
1	18EBT-10	pyrrhotite	7.5
2	18EBT-10	pyrrhotite	7.4
3	18EBT-10	chalcopyrite	7.3
4	18EBT-10	chalcopyrite	5.9
5	18EBT-11	chalcopyrite	6.7
6	18EBT-11	pentlandite	6.2
7	18EBT-11	pentlandite	6.0
8	18EBT-11	chalcopyrite	6.7
9	18EBT-11	chalcopyrite	6.9
10	18EBT-11	pentlandite	6.2
11	18EBT-11	pentlandite	6.7
12	18EBT-11	chalcopyrite	6.9
13	18EBT-11	pentlandite	6.4
14	18EBT-11	pentlandite	5.9
15	18EBT-11	pentlandite	6.2
16	18EBT-11	pyrrhotite	6.2
17	18EBT-11	pyrrhotite	6.4
18	18EBT-5	pentlandite	5.5
19	18EBT-5	pentlandite	5.5
20	18EBT-5	pyrrhotite	5.8
21	18EBT-5	pyrrhotite	5.3
22	18EBT-5	pyrrhotite	5.6
23	18EBT-5	chalcopyrite	6.0
24	18EBT-5	pentlandite	6.0
25	18EBT-5	pentlandite	5.6
	Baixintan intrusion		
1	19BXT-4	chalcopyrite	0.4
2	19BXT-4	chalcopyrite	0.3
3	19BXT-4	pyrrhotite	-0.1
4	19BXT-4	pyrrhotite	0.5
5	19BXT-4	chalcopyrite	1.1
6	19BXT-6	pyrite	0.7
7	19BXT-6	pyrite	0.5
8	19BXT-6	pyrite	0.6
9	19BXT-14	chalcopyrite	0.6
10	19BXT-14	chalcopyrite	0.1
11	19BXT-14	pyrrhotite	-0.7
12	19BXT-14	pyrrhotite	0.1
13	19BXT-ZK-15	chalcopyrite	1.2
14	19BXT-ZK-15	pyrrhotite	0.0
15	19BXT-ZK-15	chalcopyrite	–0.4
16	19BXT-ZK-15	chalcopyrite	0.2
17	19BXT-ZK-15	chalcopyrite	–0.1
18	19BXT-ZK-15	pentlandite	–0.3
19	19BXT-ZK-15	pentlandite	–0.4
	Tulaergen intrusion		
1	TLEG-16	pyrrhotite	0.5
2	TLEG-16	pyrrhotite	0.9
3	TLEG-16	pyrrhotite	0.3
4	TLEG-16	pentlandite	0.4
5	TLEG-16	pyrrhotite	0.3
6	TLEG-19	pyrrhotite	0.2
7	TLEG-19	pyrrhotite	–0.2
8	TLEG-19	pyrrhotite	0.3
9	TLEG-19	pyrrhotite	0.4
10	TLEG-26	chalcopyrite	0.5
11	TLEG-26	pyrrhotite	0.2

Because V is sensitive to redox and Sc is not, the V/Sc ratio of primary magma is mainly governed by f_{O_2} during partial melting of a given mantle lithology (Lee et al. 2005; Mallmann and O'Neill 2009) and is not affected by temperature and pressure (Canil and Fedortchouk 2001; Li 2018). In addition, the V/Sc ratio of basaltic magma is not sensitive to the crystallization of olivine (Lee et al. 2005; Mallmann and O'Neill 2009), the V/Sc ratio of the melt in equilibrium with the most primitive olivine in a mafic-ultramafic intrusion can be taken as the ratio of primary magma, particularly if olivine is the only cumulus phase. Therefore, we selected the samples from the Heishan, Huangshannan, Luodong, Poyi, and Hongqiling No. 2 intrusions in the CAOB that contain high-Fo olivine (Fo = 86 to 90) as the only cumulus phase, the obtained V/Sc ratio of the melt in equilibrium with the olivine is analog to the V/Sc ratio of the primary magma of the intrusion.

As olivine is the only cumulus phase in the rocks, the concentrations of V and Sc of the melt can be calculated using the mass-balance equation (Godel et al. 2011):

$$C_{WR}^{V,Sc} = F_{Ol} \times C_{Ol}^{V,Sc} + (1 - F_{Ol}) \times C_{Liq}^{V,Sc} \quad (1)$$

where $C_{WR}^{V,Sc}$ and $C_{Ol}^{V,Sc}$ is the concentrations of V and Sc in the bulk rock and cumulus olivine, respectively. The fraction of olivine (F_{Ol}) can be estimated in two ways; one is to analyze the backscattered electron (BSE) images or scan thin sections of the samples, the other is to use the mass balance of whole-rock MgO and FeO contents combined with the olivine-liquid exchange coefficient (Kd) (Li and Ripley 2011). In this study, we integrated the two ways to obtain the F_{Ol} and then calculated the concentrations of V and Sc in the melt ($C_{Liq}^{V,Sc}$) based on Equation 1 (Supplemental[1] Table S2).

The V/Sc ratios of primary magmas would increase slightly with the degree of partial melting of the mantle at a given mantle f_{O_2} when it is ≤FMQ, but would decrease significantly when it is >FMQ (Lee et al. 2005) (Fig. 6). Therefore, the degree of partial melting of the mantle should be considered when the V/Sc ratio of a primary magma is used to calculate mantle f_{O_2}. Mafic magmas in subduction zones are generally produced by higher degrees of partial melting of the mantle (e.g., up to 15–20%, Kelley et al. 2006) than those in the mid-ocean ridges (~10%, Bottinga and Allegre 1976). The degrees of partial melting of the mantle are thus set to be 15 to 20% for the intrusions in the CAOB, and the obtained mantle f_{O_2} of the Heishan, Huangshannan, Luodong,

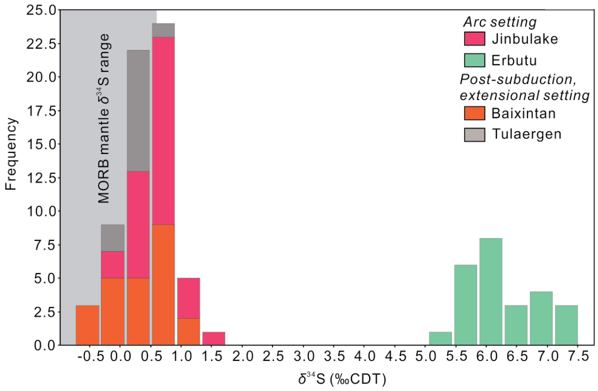

Figure 5. Histogram of δ^{34}S values of sulfides from the Jinbulake, Erbutu, Baixintan, and Tulaergen intrusions in the CAOB. The δ^{34}S values of MORB-type mantle are from Labidi et al. (2014). (Color online.)

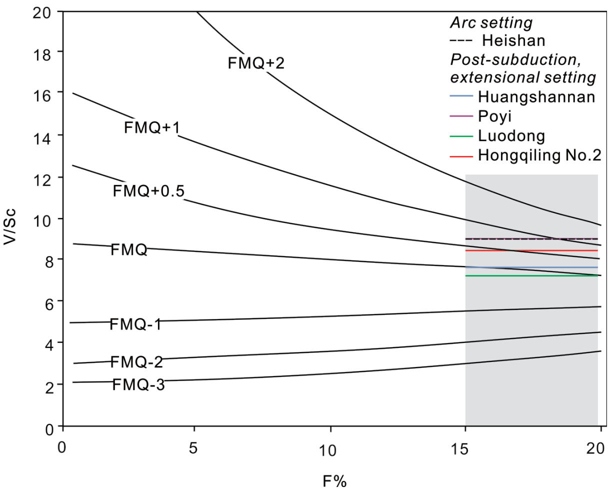

Figure 6. Variation of V/Sc of the primary magma against the degrees of partial melting (F) at a given f_{O_2} (Lee et al. 2005). It is assumed that the mafic-ultramafic intrusions in the CAOB were derived from magmas produced by ~15 to ~20% of partial melting (indicated by the gray shaded area) of the mantle wedge in the spinel stability field. (Color online.)

Poyi, and Hongqiling No. 2 intrusions is ~FMQ+1.0, ~FMQ, ~FMQ, ~FMQ+1.0, and ~FMQ+0.5, respectively (Fig. 6).

In our previous study, the mantle f_{O_2} of the Poyi and Hongqiling No. 2 intrusions was estimated to be FMQ+0.3 and FMQ+0.5, respectively, using the olivine-spinel oxygen barometer (Cao et al. 2019). As the chemical data of the spinel from the Poyi intrusion in that study were collected from the literature and the $Fe^{3+}/\Sigma Fe$ of the spinel was not corrected, the obtained mantle f_{O_2} was likely underestimated by ~0.6 log unit (Cao et al. 2019), so the mantle f_{O_2} of the Poyi intrusion could be ~FMQ+0.9. Therefore, the mantle f_{O_2} of the Poyi and Hongqiling No. 2 intrusions obtained in two different ways are quite consistent with each other.

Magma f_{O_2}

The magma f_{O_2} of the mafic-ultramafic intrusions in the CAOB was acquired by two methods; one is based on the olivine-spinel oxygen barometer (Ballhaus et al. 1991), the other is based on V partitioning in olivine (Canil 1997; Shishkina et al. 2018).

Olivine-spinel oxygen barometer. The oxygen fugacity of magmas was calculated using the olivine-spinel oxygen barometer given by Ballhaus et al. (1991):

$$\log_{10} f_{O_2}(\Delta QFM) = 0.27 + 2505/T - 400\,P/T - 6\log(X^{Ol}_{Fe}) - 3200(1 - X^{Ol}_{Fe})^2/T + 2\log(X^{Spl}_{Fe^{2+}}) + 4\log(X^{Spl}_{Fe^{3+}}) + 2630(X^{Spl}_{Al})^2/T \quad (2)$$

where P is pressure in GPa, T is temperature in K, X^{Ol}_{Fe} is molar $Fe^{2+}/(Fe^{2+}+Mg^{2+})$ in olivine, $X^{Spl}_{Fe^{3+}}$ is molar $Fe^{3+}/\Sigma R^{3+}$ in spinel, X^{Spl}_{Al} is molar $Al/\Sigma R^{3+}$ in spinel, and $X^{Spl}_{Fe^{2+}}$ is molar $Fe^{2+}/(Fe^{2+}+Mg^{2+})$ in spinel. Olivine grains in the samples from the intrusions in the CAOB have Fo contents varying from 82 to 90, with most being >84 (Supplemental[1] Table S1), and those from the Dali picrite have Fo contents varying from 82 to 92 (Kamenetsky et al. 2012; Liu et al. 2017), which are all applicable to the equation. The pressure was calculated using the clinopyroxene geobarometer given by Nimis and Ulmer (1998) (Supplemental[1] Table S1). The $Fe^{3+}/\Sigma Fe$ of the spinel from the Jinbulake, Erbutu, Baixintan, Huangshannan, and Tulaergen intrusions is corrected based on the EPMA data obtained in this study, whereas the $Fe^{3+}/\Sigma Fe$ of the spinel from the Heishan, Luodong intrusions and Dali picrite cannot be corrected as the EPMA data were collected from the literature. The magma f_{O_2} calculated using uncorrected $Fe^{3+}/\Sigma Fe$ of the spinel is 0.2 to 0.6 log units lower than that using corrected $Fe^{3+}/\Sigma Fe$ (Cao et al. 2019). However, the bias becomes smaller with increasing f_{O_2}, which is <0.4 log units when f_{O_2} is >FMQ+1, and is <0.2 log units when f_{O_2} is >FMQ+1.5 (Cao et al. 2019).

The accuracy of the results depends on whether or not the olivine-spinel pairs in the rocks are in chemical equilibrium (Ballhaus et al. 1991). The spinel grains in this study overall are euhedral, fresh, and homogeneous, and they are commonly enclosed within olivine (Supplemental[1] Fig. S1c). Textures showing chemical disequilibrium, such as complex zoning, embayment, symplectite, and sieve texture, are not observed in both minerals. In addition, the olivine-spinel pairs in the rocks from the intrusions in the CAOB overall have $\ln Kd^{Ol\text{-}Spl}_{Mg/Fe}$ positively

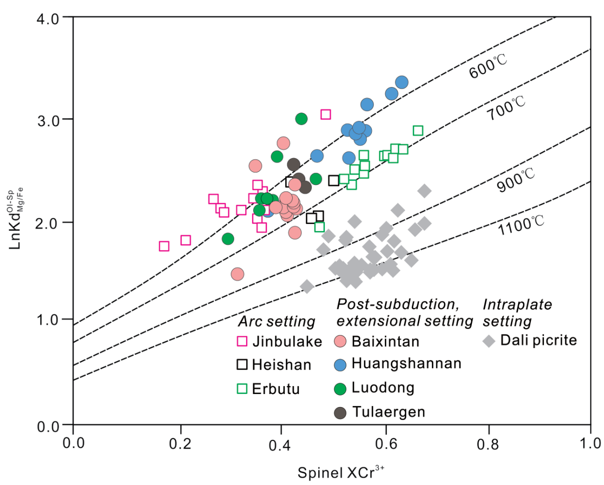

Figure 7. Plot of XCr^{3+} of spinel vs. $\ln Kd^{Ol\text{-}Spl}_{Mg/Fe}$ for the mafic-ultramafic intrusions in the CAOB, and the Dali picrite in the Emeishan large igneous province. Data sources are the same as those in Figure 4. (Color online.)

correlated with XCr^{3+} [molar $Cr^{3+}/(Fe^{3+}+Cr^{3+}+Al^{3+})$] along the equilibrium lines between 600 and 700 °C (Fig. 7), indicating that the olivine-spinel pairs reached chemical equilibrium. The temperatures of the equilibrium lines on Figure 7 were estimated from the experimental data related to the reciprocal reaction ($FeCr_2O_4 + MgAl_2O_4 \leftrightarrow MgCr_2O_4 + FeAl_2O_4$) in spinel (Liermann and Ganguly 2003), which are consistent with the equilibrium temperatures calculated using the olivine-spinel thermometer given by Ballhaus et al. (1991) (Supplemental[1] Table S1). It is noted that the obtained temperature values are the closure temperatures of Mg-Fe^{2+} diffusion between olivine and spinel on subsolidus cooling, which are lower than the crystallization temperature of minerals (Kamenetsky et al. 2001). However, the f_{O_2} could be only elevated by ~0.2 log units due to subsolidus Mg-Fe^{2+} equilibrium between the olivine-spinel pairs (Birner et al. 2018). Therefore, the f_{O_2} values obtained using the closure temperatures of the olivine-spinel pairs can be taken as the magma f_{O_2} of the intrusions.

Using the Equation 2, we obtained the magma f_{O_2} of the Jinbulake, Heishan, Erbutu, Baixintan, Huangshannan, Luodong, and Tulaergen intrusions, which ranges from FMQ+1.2 to FMQ+2.6, FMQ+1.3 to FMQ+2.3, FMQ-0.1 to FMQ+1.2, FMQ+1.3 to FMQ+3.0, FMQ+0.6 to FMQ+2.6, FMQ+0.3 to FMQ+1.7, FMQ+2.5 to FMQ+2.9, respectively (Supplemental[1] Table S1; Fig. 8a). Although the values for the Heishan and Luodong intrusions were calculated using uncorrected $Fe^{3+}/\Sigma Fe$ of the spinel, the upper values should be reliable (cf. Cao et al. 2019). These data, together with the magma f_{O_2} of the Huangshandong, Huangshanxi, Poyi, and Hongqiling No. 1 and No. 2 intrusions obtained in our earlier studies (Cao et al. 2019; Wei et al. 2019), display a negative correlation between the magma f_{O_2} and the Fo contents of olivine, except for the Erbutu intrusion (Fig. 8b).

The olivine-spinel pairs from the Dali picrite plot between the equilibrium lines at 900 and 1100 °C (Fig. 7). The magma f_{O_2} of the Dali picrite varies from FMQ+0.2 to FMQ+0.8 (Fig. 8a). Given that the uncorrected $Fe^{3+}/\Sigma Fe$ of the spinel was used in

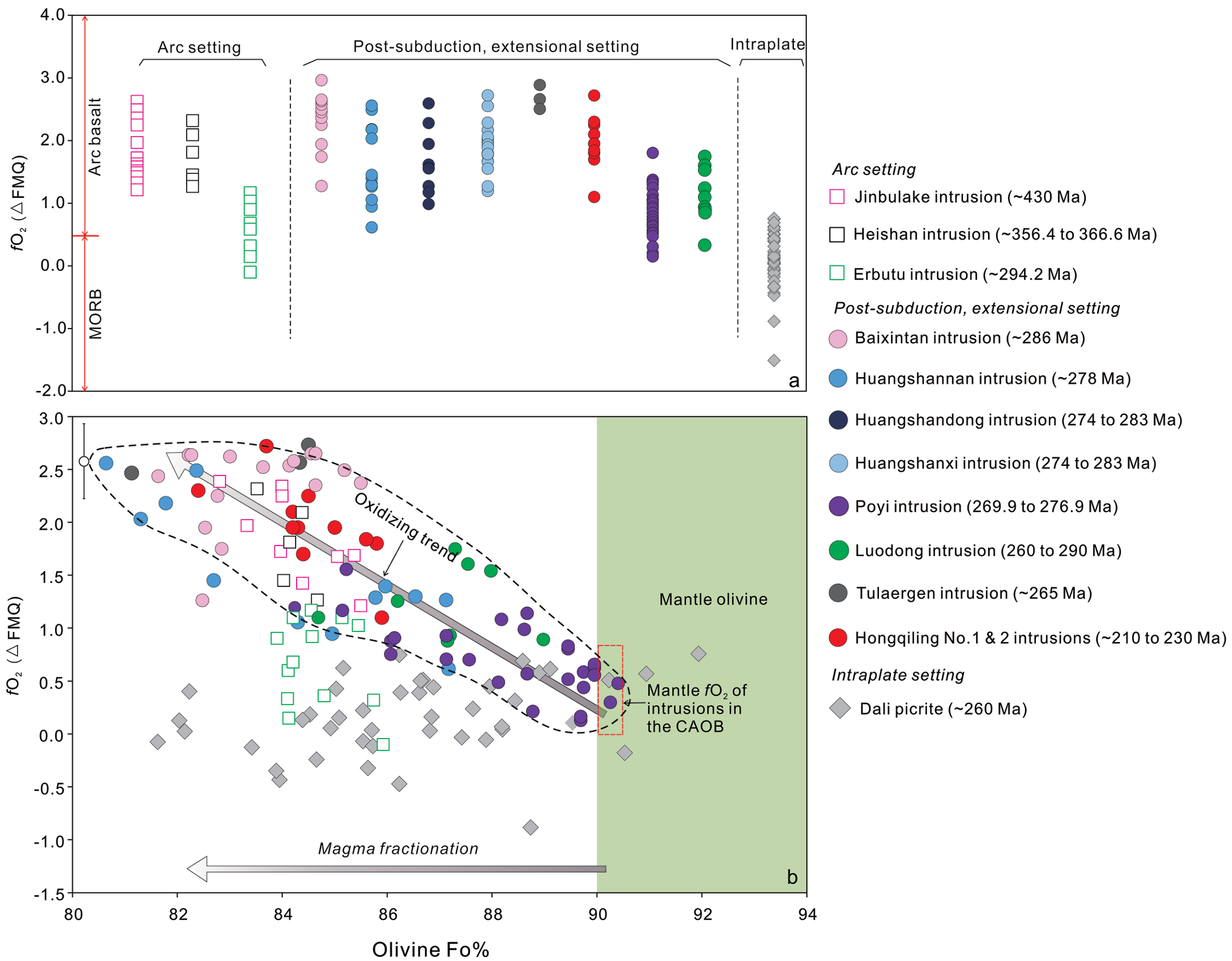

FIGURE 8. (**a**) Comparison of the estimated magma f_{O_2} of the mafic-ultramafic intrusions in the CAOB and the Dali picrite in the Emeishan large igneous province with the f_{O_2} of MORBs (FMQ-1 to FMQ+0.5) and arc basalts (FMQ+0.5 to FMQ+6). Data sources: MORBs (Cottrell and Kelley 2011; Zhang et al. 2018), arc basalts (Woodland et al. 2006). (**b**) Plot of the magma f_{O_2} vs. the Fo contents of olivine for the mafic-ultramafic intrusions in the CAOB and the Dali picrite in the Emeishan large igneous province. The error bars in **b** represent the uncertainty (FMQ±0.4) of calculated magma f_{O_2} based on the olivine-spinel oxygen barometer (cf. Ballhaus et al. 1991). The dashed line outlines the data for the intrusions with tholeiitic, parental magmas. (Color online.)

the calculation, the results could be underestimated by ~0.6 log units in this case (cf. Cao et al. 2019). However, even if the bias is considered, the magma f_{O_2} of the Dali picrite is still much lower than the magma f_{O_2} of the mafic-ultramafic intrusions in the CAOB (Fig. 8a).

Vanadium partitioning in olivine (D_V^{Ol}). Experimental results demonstrated that the partition coefficient of V between olivine and melt will decrease with elevated magma f_{O_2} (e.g., Canil 1997, 2002; Mallmann and O'Neill 2013; Laubier et al. 2014; Shishkina et al. 2018). This relationship was used to calculate the magma f_{O_2} of hydrous arc basalts (Shishkina et al. 2018), i.e.,

$$\Delta FMQ = -3.07 \times \log D_V^{Ol} - 3.34 \quad (3)$$

A common way to measure D_V^{Ol} is to acquire the V concentration of melt inclusion and host olivine in basalts. However, melt inclusions trapped in the olivine of cumulates are difficult to be find and analyze as they are usually very small. We therefore chose an alternative protocol to estimate the D_V^{Ol}.

V and Sc are highly incompatible to olivine and have similar diffusivities between olivine and trapped liquid in crystal mush (Locmelis et al. 2019); the V/Sc ratio of olivine is thus hardly affected by the trapped liquid shift effect. In addition, the V/Sc ratio of olivine is resistant to post-magmatic overprints, crustal contamination, and crystallization of small amounts of spinel (<5%) (Lee et al. 2005; Locmelis et al. 2019). Nevertheless, we tried to analyze the cores of the best-preserved olivine grains in each sample to warrant that the primary V/Sc ratio of olivine is acquired. In theory, the V/Sc ratio of olivine can be calculated using the equation:

$$\left(\frac{V}{Sc}\right)_{Ol} = \frac{D_v^{Ol} \times V_{Liq}}{D_{Sc}^{Ol} \times Sc_{Liq}} \quad (4)$$

Since D_{Sc}^{Ol} is constant at ~0.2 (Villemant et al. 1981; Sun and Liang 2013), Equation 4 can be simplified as the equation:

$$\left(\frac{V}{Sc}\right)_{Ol} = \frac{D_v^{Ol} \times V_{Liq}}{0.2 \times Sc_{Liq}} \quad (5)$$

D_V^{Ol} can be then acquired through the equation:

$$D_v^{Ol} = 0.2 \times \frac{\left(\frac{V}{Sc}\right)_{Ol}}{\left(\frac{V}{Sc}\right)_{Liq}} \quad (6)$$

If Equation 6 is combined with Equation 3, the magma f_{O_2} can be calculated by the equation:

$$\Delta FMQ = -3.07 \times \log\left[0.2 \times \frac{\left(\frac{V}{Sc}\right)_{Ol}}{\left(\frac{V}{Sc}\right)_{Liq}}\right] - 3.34 \quad (7)$$

Although V and Sc are highly incompatible in both olivine and orthopyroxene, Sc is more compatible to clinopyroxene than V (Canil 2002). $(V/Sc)_{Liq}$ would vary slightly when olivine and/or orthopyroxene are on liquidus but increase significantly when clinopyroxene is on liquidus during the fractionation of mafic magmas (Laubier et al. 2014). Most samples in this study contain olivine and/or orthopyroxene as major cumulus minerals (Supplemental[1] Fig. S1), except for those from the Jinbulake intrusion. Therefore, $(V/Sc)_{Liq}$ can be referred to the V/Sc ratio of the primary magma for each intrusion in the CAOB (Supplemental[1] Table S2), and then the magma f_{O_2} of the intrusions can be directly calculated using Equation 7 (Supplemental[1] Table S3).

Comparison of the results based on the two methods. The obtained magma f_{O_2} values based on the two methods are consistent with each other within uncertainties (Fig. 9a). The V/Sc ratios of the olivine from the Erbutu, Huangshannan, Hongqiling No. 1 and No. 2 intrusions generally decrease with increasing magma f_{O_2} values that were obtained based on the olivine-spinel oxygen barometer (Fig. 9b), indicating that the magma f_{O_2} values in this study are reliable (cf. Canil 1997, 2002; Mallmann and O'Neill 2013; Laubier et al. 2014; Shishkina et al. 2018).

In summary, the magma f_{O_2} values of the arc-hosted Jinbulake and Heishan intrusions are comparable to those of the post-collisional Baixintan, Huangshandong, Huangshanxi, Huangshannan, Tulaergen, Hongqiling No. 1 and No. 2 intrusions. The magma f_{O_2} values of the mafic-ultramafic intrusions in the CAOB overall have a range similar to those of arc basalts (FMQ+0.5 to FMQ+6; Woodland et al. 2006), much higher than those of MORBs (FMQ-1 to FMQ+0.5; Cottrell and Kelley 2011; Zhang et al. 2018) (Fig. 8a). The magma f_{O_2} values of the Erbutu, Poyi, and Luodong intrusions are lower than that of other intrusions in the CAOB and overlap the upper f_{O_2} limit of MORBs (Fig. 8a). In contrast, the magma f_{O_2} values of the Dali picrite are basically within the range of MORBs (Fig. 8a).

Discussion

The magma f_{O_2} of mafic-ultramafic intrusions in convergent margin settings could be controlled by complex factors such as the oxidation and fertility states of the metasomatized mantle sources (e.g., Rielli et al. 2017) and magmatic processes (e.g., Lee et al. 2005). Our results indicate that metasomatized mantle sources of the mafic-ultramafic intrusions in the CAOB overall are slightly oxidized compared with that of MORBs, and the elevated magma f_{O_2} of the intrusions in both arc and post-subduction, extensional settings is mainly attributed to the fractionation of hydrated magmas derived from the metasomatized mantle.

Mantle f_{O_2} of the mafic-ultramafic intrusions in the CAOB

The arc-related Heishan intrusion and post-collisional Huangshannan, Poyi, Luodong, and Hongqiling No. 2 intrusions have mantle f_{O_2} values ranging from ~FMQ to ~FMQ+1.0 (Fig. 6), slightly higher than the mantle f_{O_2} (≤FMQ) of MORBs (Frost and McCammon 2008; Kelley and Cottrell 2009, 2012; Rielli et al. 2018a), but much lower than the mantle f_{O_2} of arc basalts (e.g., FMQ+1 to FMQ+3, Woodland et al. 2006; Ballhaus 1993). These results indicate that the mantle sources of mafic-ultramafic intrusions in the CAOB are not highly oxidized as supposed for the subarc mantle. In addition, the mantle f_{O_2} is much lower than the magma f_{O_2} of these intrusions (Fig. 8b), the high-magma f_{O_2} of the intrusions in the CAOB is thus not governed by the oxidation state of the mantle source alone.

The oxidation of the subarc mantle is attributed to the trans-

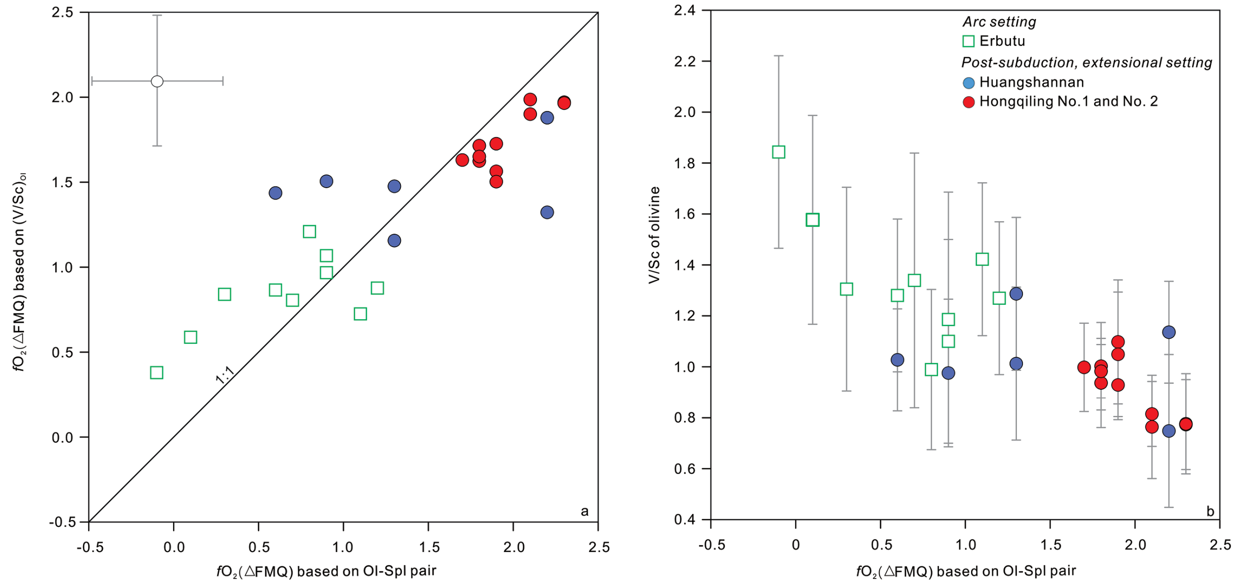

FIGURE 9. (**a**) Comparison of the magma f_{O_2} calculated based on olivine-spinel oxygen barometer and the partitioning of V in olivine showing the good agreement of the results obtained by two different methods. The error bars represent the uncertainty of magma f_{O_2} calculated based on the two methods. (**b**) Plot of the magma f_{O_2} calculated based on the olivine-spinel oxygen barometer vs. the V/Sc of olivine. There is an overall negative relationship between the magma f_{O_2} and the V/Sc of olivine. The error bar represents 1σ (standard deviation) of the measured V/Sc of olivine. (Color online.)

portation of highly oxidized, CO_3^{2-}-, SO_4^{2-}-, or Fe^{3+}-rich fluids to the subarc mantle during subduction (Mungall 2002; Evans 2006; Evans et al. 2012; Debret et al. 2016; Pons et al. 2016; Debret and Sverjensky 2017; Rielli et al. 2017). However, this process depends on the subduction depth and temperature (Tomkins and Evans 2015). Modeling results indicate that sulfate tends to be released at shallower subduction zone depths and relatively low temperatures, whereas sulfide tends to be released at deeper subduction zone depths and relatively high temperatures (Tomkins and Evans 2015). The mafic-ultramafic intrusions in the CAOB are considered to have been derived from partial melts of the mantle wedge in the spinel stability field (e.g., Zhang et al. 2016). It is likely that only minor slab-derived, oxidized components were involved in the mantle wedge at this depth. In addition, the mantle sources of these intrusions in the CAOB are considered to have experienced interaction of the depleted lithospheric mantle with upwelling asthenospheric materials due to slab break-off (Han et al. 2010; Li et al. 2012; Xie et al. 2012; Wei et al. 2013; Mao et al. 2014, 2016; Deng et al. 2015). This process may also dilute the oxidized components in the mantle wedge because asthenospheric materials are typically more reduced than the lithospheric mantle by ~1 log unit (Wood et al. 1990). Therefore, the mafic-ultramafic intrusions in the CAOB overall have mantle f_{O_2} values slightly higher than that for the mantle of MORBs.

Fractionation of hydrated magmas derived from metasomatized mantle sources

Experimental results indicate that the fractionation of olivine and clinopyroxene may slightly increase the $Fe^{3+}/\Sigma Fe$ of magmas and have a limited effect on the oxidization states of magmas (Cottrell and Kelley 2011; Kelley and Cottrell 2012). However, water in silicate magmas can play an efficient "catalyst" to promote the oxidation states of magmas if it is partially dissociated and loses H^+ at high temperatures (Carmichael 1991; Cornejo and Mahood 1997), or exsolved from the melt that carried more Fe^{2+} than Fe^{3+} (Bell and Simon 2011). Mafic magmas tend to become more hydrous with fractionation because volatiles (e.g., H_2O) are essentially incompatible to olivine and clinopyroxene. Therefore, the fractionation process could significantly elevate the oxidation states of hydrated, mafic magmas.

The mafic-ultramafic intrusions in the CAOB contain abundant hydrous minerals such as amphibole and phlogopite (e.g., Deng et al. 2014; Su et al. 2011; Xie et al. 2012; Wei et al. 2013, 2015). On the plot of Alz (percentage of tetrahedral sites occupied by Al) vs. TiO_2, the clinopyroxene from the intrusions in the CAOB has Alz/Ti scattered along the arc cumulate trend, in contrast to the low Alz/Ti of the clinopyroxene from the sulfide-bearing mafic-ultramafic intrusions in the Emeishan LIP (Fig. 10). The high-Alz values of the clinopyroxene from the CAOB are attributed to the idea that more Al would enter the tetrahedral site of clinopyroxene with increasing H_2O content of melt (cf. Loucks 1990). This is consistent with an interpretation that the parental magmas of the intrusions in the CAOB may be hydrated due to the derivation from the mantle sources metasomatized by slab-derived melts/fluids. There is an overall negative correlation between the magma f_{O_2} and the Fo contents of olivine for the intrusions in the CAOB (Fig. 8b), showing that the magmas became more oxidized with fractionation. Therefore, the H_2O content of magmas derived from the metasomatized mantle and relative degrees of the fractionation of magmas are likely two key factors controlling magma f_{O_2} of the mafic-ultramafic intrusions in convergent margin settings.

The Erbutu intrusion is an exceptional case as the olivine grains of the intrusion have Fo contents comparable with those for the olivine of the Jinbulake and Heishan intrusions, but the intrusion has much lower magma f_{O_2} than the latter two intru-

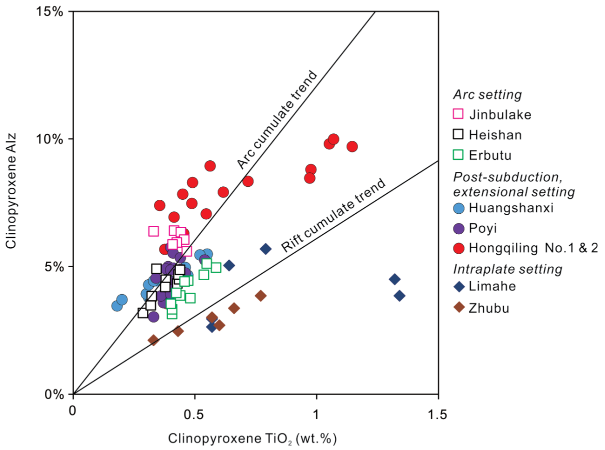

Figure 10. Plot of Alz (percentage of tetrahedral sites occupied by Al) vs. wt% TiO_2 of clinopyroxene from the mafic-ultramafic intrusions in the CAOB and the Emeishan large igneous province. The trends of the arc and rift cumulate are modified after Loucks (1990). (Color online.)

sions (Fig. 8b). The parental magma of the Erbutu intrusion is thought to be boninitic that may have been emplaced early in the subduction history (cf. Jian et al. 2010; Peng et al. 2013). As the oxidation of the mantle wedge by the metasomatizing agents could occur after subduction initiation in 1 Ma. (cf. Brounce et al. 2015), it is likely that the mantle source of the Erbutu intrusion is relatively reduced; thus the magma f_{O_2} of this intrusion is lower than that of other intrusions in the CAOB for a given degree of fractionation of magma.

Magma f_{O_2} constraints for Ni-Cu sulfide mineralization in convergent margin settings

Experimental results show that the sulfur solubility in silicate magmas could increase by an order of magnitude if the magma f_{O_2} increases from FMQ+0.5 to FMQ+1.5 (Luhr 1990; Jugo et al. 2005, 2010; Jugo 2009). Mantle-derived mafic magmas in intraplate settings usually have magma f_{O_2} values ranging from FMQ-1 to FMQ+0.5 and could dissolve a maximum of ~1500 ppm S (cf. Wood et al. 1990; Jugo et al. 2010), therefore the formation of economic Ni-Cu sulfide deposits often requires the addition of external crustal sulfur into the magmas (e.g., Li et al. 2001; Ripley and Li 2003; Barnes and Lightfoot 2005; Wang et al. 2006; Mungall and Naldrett 2008; Keays and Lightfoot 2010; Taranovic et al. 2018). For instance, the Ni-Cu sulfide deposits in the Emeishan LIP and the Jinchuan Ni-Cu deposit formed in a rifting setting have magma f_{O_2} overlapping with the range of MORBs, and the sulfides from the deposits have highly variable $\delta^{34}S$ (–4 to +8‰, Fig. 11), indicating substantial addition of external crustal sulfur in the formation of these deposits (Ripley et al. 2005; Duan et al. 2016; Wang et al. 2018).

In contrast, the mantle-derived mafic magmas in convergent margin settings have f_{O_2} values ranging from FMQ+0.5 to FMQ+3 (Fig. 8a) and could dissolve ~1800 to ~13 000 ppm S (Jugo et al. 2010), much higher than the S solubility of the magmas in intraplate settings. In addition, the sulfides from the Ni-Cu sulfide-bearing mafic-ultramafic intrusions in the post-subduction, extensional setting in the CAOB have $\delta^{34}S$ values (–1.0 to +1.3‰) nearly identical to that of the MORB mantle (Fig. 11), despite the large $\delta^{34}S$ range (–10.0 to +5.4‰) of the sulfides from the metasomatized mantle xenoliths (Rielli et al. 2018b). This was interpreted as evidence that the magmas of the Ni-Cu sulfide-bearing mafic-ultramafic intrusions in the CAOB contain dominantly mantle-derived sulfur with trivial additions of external crustal sulfur (Wei et al. 2019). Therefore, the high-magma f_{O_2} and the MORB mantle-like $\delta^{34}S$ of the mafic-ultramafic intrusion in the CAOB indicate that highly oxidized, mantle-derived magmas may be capable of dissolving enough mantle-derived sulfur to form magmatic Ni-Cu sulfide deposits so that the addition of external crustal sulfur is not al-

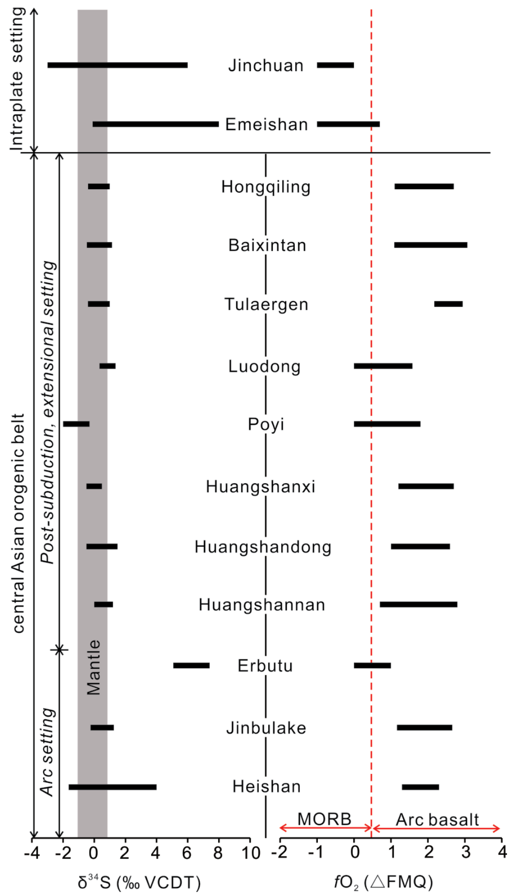

Figure 11. Comparison of $\delta^{34}S$ values of sulfides and magma f_{O_2} among the mafic-ultramafic intrusions in the CAOB, the Jinchuan Ni-Cu sulfide deposits in the southern margin of the North China Craton, and the Ni-Cu sulfide deposits in the Emeishan large igneous province. The mafic-ultramafic intrusions in the CAOB overall have f_{O_2} > FMQ+1 and $\delta^{34}S$ similar to the MORB mantle value (–1.6 to +0.6‰; Labidi et al. 2013, 2014), whereas the Ni-Cu sulfide deposits in the intraplate settings have relatively low f_{O_2} and high $\delta^{34}S$ of sulfides. Data sources: Jinbulake, Erbutu, Baixintan, and Tulaergen intrusions (this study), Heishan intrusion (Xie et al. 2014), Hongqiling No. 7 intrusion (Wei et al. 2019), Luodong intrusion (Su et al. 2015), Poyi intrusion (Xia et al. 2013), Huangshannan intrusion (Zhao et al. 2016), Huangshandong and Huangshanxi intrusions (Wang et al. 1987), Jinchuan intrusion (Ripley et al. 2005; Duan et al. 2016), and the intrusions in the Emeishan large igneous province (Wang et al. 2018). (Color online.)

ways necessary in such cases. In addition, the mafic-ultramafic intrusions in the CAOB that have sulfides with mantle-like $\delta^{34}S$ values generally have magma f_{O_2} > FMQ+1, whereas the Erbutu intrusion that has sulfides with the highest $\delta^{34}S$ values has magma f_{O_2} < FMQ+1 (Fig. 11), we thus consider that the mantle-derived mafic magmas with f_{O_2} greater than ~FMQ+1.0 may be able to dissolve sufficient mantle-derived sulfur to form important Ni-Cu sulfide deposits in convergent margin settings (cf. Rielli et al. 2018a).

On the other hand, the formation of economic Ni-Cu sulfide deposits from the highly oxidized, mantle-derived magmas depends on how the magmas can be reduced to reach sulfide saturation so that the sulfide melts can be segregated from the magmas (Tomkins et al. 2012). This can be examined by comparing the f_{O_2} between the parental magmas prior to sulfide saturation and the magmas concurrent with sulfide saturation (e.g., Wei et al. 2019). The magma f_{O_2} obtained by the olivine-spinel oxygen barometer in this study can represent the parental magma f_{O_2} before sulfide saturation. The f_{O_2} of the magmas concurrent with sulfide saturation for the intrusions in the CAOB were estimated using Fe-Ni exchange between olivine and sulfide liquid (e.g., Feng et al. 2017; Mao et al. 2018; Wei et al. 2019). As shown in Figure 12, the magma f_{O_2} at sulfide saturation is considerably lower than the f_{O_2} of parental magmas for each intrusion, indicating that the oxidized magmas were indeed reduced with the sulfide saturation of magmas. A possible way to trigger the reduction is the crystallization of magnetite (Jenner et al. 2010). However, this mechanism does not appear as the driver of magma reduction in the CAOB because the examined rocks in this study contain little magnetite. Alternatively, the reduction of oxidized magmas can be triggered by the addition of organic-carbon or graphite-rich sedimentary rocks, which was evidenced by the C isotope studies on a few intrusions in the CAOB (e.g., Wei et al. 2019) and the O isotope studies of the olivine in the lower zone of the Huangshanxi intrusion (Mao et al. 2019).

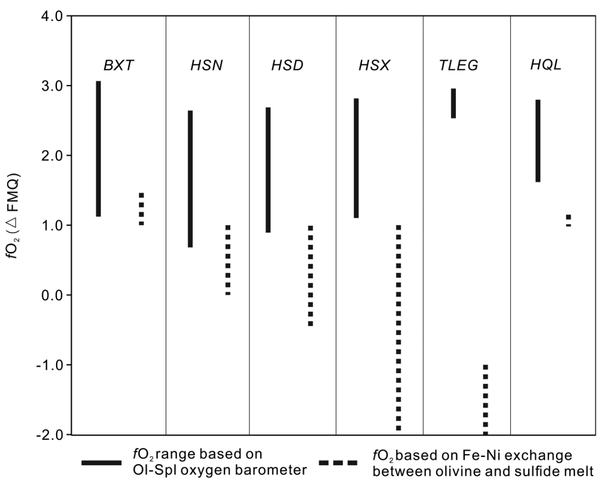

Figure 12. Comparison of magma f_{O_2} values calculated based on the olivine-spinel oxygen barometer with those calculated based on the Fe-Ni exchange between olivine and sulfide melt for the Baixintan (BXT), Huangshannan (HSN), Huangshandong (HSD), Huangshanxi (HSX), Tulaergen (TLEG), and Hongqiling No.1 (HQL) intrusions in the CAOB. The values based on the Fe-Ni exchange between olivine and sulfide liquids are much lower than those based on the olivine-spinel oxygen barometer.

Implications

Most Ni-Cu sulfide-bearing mafic-ultramafic intrusions in the central Asian orogenic belt (CAOB) have magma f_{O_2} values (FMQ+0.5 to FMQ+3) much higher than that of MORBs (FMQ-1 to FMQ+0.5), consistent with the global observation that the mafic-ultramafic intrusions emplaced in convergent margin settings have relatively high-magma f_{O_2} values. In contrast, the mantle f_{O_2} of these intrusions ranges from FMQ to ~FMQ+1.0, just slightly higher than that of mid-ocean ridge basalts (MORBs) (≤FMQ). Because the amounts of oxidized components that were added to the metasomatized mantle wedges generally decrease with the depth of the mantle wedges in convergent margin settings, the slightly oxidized mantle source of the intrusions in the CAOB is likely related to the limited amounts of slab-derived, oxidized components added to mantle wedges and relatively deep mantle wedges where the partial melting occurred. The negative correlation of the magma f_{O_2} and the Fo contents of the olivine of the intrusions in the CAOB indicates that the magma f_{O_2} could be elevated with the fractionation of hydrated, mafic magmas derived from metasomatized mantle sources. In addition, the mafic-ultramafic intrusions that host economic Ni-Cu sulfide deposits in the CAOB usually have sulfides with mantle-like $\delta^{34}S$ (–1.0 to +1.1‰) and magma f_{O_2} > FMQ+1, indicating that the relatively oxidized magmas may be capable of dissolving enough mantle-derived sulfur to form economic Ni-Cu sulfide deposits in convergent margin settings. The sulfide saturation of the oxidized, mafic magmas may be triggered by the addition of organic-carbon or graphite-rich sedimentary rocks into the magmas. Therefore, our results imply that the addition of external crustal sulfur is not compulsory to trigger the sulfide saturation of highly oxidized, mantle-derived mafic magmas and the formation of economic Ni-Cu sulfide deposits in convergent margin settings, although it is very important in the formation of giant Ni-Cu sulfide deposits such as those at Noril'sk in Russia (Ripley and Li 2013).

Acknowledgments and Funding

S. Yang provided the samples of the Jinbulake intrusion and B. Su shared the EPMA data for the olivine and spinel of the Luodong intrusion. Constructive reviews by A. Tomkins and an anonymous reviewer have greatly improved the quality of this manuscript. This work was supported by grants from the National Natural Science Foundation of China (No. 41730423 and 41902077), and China Postdoctoral Science Foundation Grant (No. 2019M653103).

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Manuscript received November 1, 2019
Manuscript accepted May 1, 2020
Manuscript handled by Julie Roberge

Endnote:

[1]Deposit item AM-20-127351, Supplemental Material and Tables. Deposit items are free to all readers and found on the MSA website, via the specific issue's Table of Contents (go to http://www.minsocam.org/MSA/AmMin/TOC/2020/Dec2020_data/Dec2020_data.html).