Redox state of southern Tibetan upper mantle and ultrapotassic magmas

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Abstract

The redox state of Earth’s upper mantle in several tectonic settings, such as cratonic mantle, oceanic mantle, and mantle wedges beneath magmatic arcs, has been well documented. In contrast, oxygen fugacity ($fO_2$) data of upper mantle under orogens worldwide are rare, and the mechanism responsible for the mantle $fO_2$ condition under orogens is not well constrained. In this study, we investigated the $fO_2$ of mantle xenoliths derived from the southern Tibetan lithospheric mantle beneath the Himalayan orogen, and that of postcollisional ultrapotassic volcanic rocks hosting the xenoliths. The $fO_2$ of mantle xenoliths ranges from $\Delta$FMQ = +0.5 to +1.2 (where $\Delta$FMQ is the deviation of log $fO_2$ from the fayalite-magnetite-quartz buffer), indicating that the southern Tibetan lithospheric mantle is more oxidized than cratonic and oceanic mantle, and it falls within the typical range of mantle wedge $fO_2$ values. Mineralogical evidence suggests that water-rich fluids and sediment melts liberated from both the subducting Neo-Tethyan oceanic slab and perhaps the Indian continental plate could have oxidized the southern Tibetan [...]
Redox state of southern Tibetan upper mantle and ultrapotassic magmas

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ABSTRACT

The redox state of Earth’s upper mantle in several tectonic settings, such as cratonic mantle, oceanic mantle, and mantle wedges beneath margin arcs, has been well documented. In contrast, oxygen fugacity ($f_{O_2}$) data of mantle xenoliths under orogens worldwide are rare, and thus the redox condition of the upper mantle beneath orogens is not well constrained. In this study, we investigated the $f_{O_2}$ of mantle xenoliths derived from the southern Tibetan lithospheric mantle beneath the Himalayan orogen, and that of postcollisional ultrapotassic volcanic rocks hosting the xenoliths. The $f_{O_2}$ of mantle xenoliths ranges from $\Delta F_{MQ} = +0.5$ to $+1.2$ (where $\Delta F_{MQ}$ is the deviation of log $f_{O_2}$ from the fayalite-magnetite-quartz buffer), indicating that the southern Tibetan lithospheric mantle is more oxidized than cratonic and oceanic mantle, and it falls within the typical range of mantle wedge $f_{O_2}$ values. Mineralogical evidence suggests that water-rich fluids and sediment melts liberated from both the subducting Neo-Tethyan oceanic slab and perhaps the Indian continental plate could have oxidized the southern Tibetan lithospheric mantle. The $f_{O_2}$ conditions of ultrapotassic magmas show a shift toward more oxidized conditions during ascent (from $\Delta F_{MQ} = +0.8$ to $+3.0$). Crustal evolution processes (e.g., fractionation) could influence magmatic $f_{O_2}$, and thus the redox state of mantle-derived magma may not simply represent its mantle source.

INTRODUCTION

The redox state of Earth’s upper mantle controls partial melting, the valence state of multivalent and chalcophile elements, and the speciation of volatiles, and therefore it strongly affects subsequent mantle generation, orogenic processes, and atmospheric evolution (e.g., Frost and McCammon, 2008). The oxygen fugacity ($f_{O_2}$) of the upper mantle in several tectonic settings has been well documented by mantle-derived magmas and mantle peridotites (e.g., xenoliths, orogenic massifs), particularly using $\Delta F_{MQ}$, which is the deviation of log $f_{O_2}$ from the fayalite-magnetite-quartz buffer. For instance, typical cratonic mantle ($\Delta F_{MQ} = -4$ to $-2$; Frost and McCammon, 2008) and oceanic mantle ($\Delta F_{MQ} = -1.2$ to $-0.4$; Bézos and Humbler, 2005) are generally reduced. Mantle wedges beneath margin arcs are relatively oxidized (e.g., $\Delta F_{MQ} = +0$ to $+3$; Bénard et al., 2018, and references therein). In contrast, the $f_{O_2}$ data of upper mantle beneath orogens worldwide are rare and indicate a broader range of variability ($\Delta F_{MQ} = -4.5$ to $+2.6$; Foley, 2010). The mechanism responsible for the orogenic mantle $f_{O_2}$ condition is not well constrained, except for a few studies based on orogenic peridotite massifs (e.g., Woodland et al., 2006, and references therein). However, orogenic peridotite massifs were tectonically emplaced into the crust at convergent margins. Compared to mantle xenoliths, their original geodynamic setting cannot be exactly constrained (Menzies and Dupuy, 1991). Moreover, mantle structures and $f_{O_2}$ conditions may be obscured by deformation and metamorphic recrystallization during tectonic emplacement (Bodinier and Godard, 2014). The Himalayan-Tibetan orogen, created by the collision between India and Asia after subduction of the Neo-Tethyan oceanic slab (e.g., Mo et al., 2007), is arguably one of the youngest collisional belts on Earth. In the southern margin of the Tibetan Plateau (Lhasa terrane; Fig. 1), lithospheric mantle xenoliths have been entrained by postcollisional ultrapotassic volcanic rocks (UVRs) in the Saililu area (Zhao et al., 2008; Liu et al., 2011). The UVRs were derived from low-degree partial melting of the highly metasomatized Tibetan upper mantle during the Miocene (Turner et al., 1996; Miller et al., 1999; Zhao et al., 2009; Guo et al., 2015). Volcanic rock–hosted mantle xenoliths are commonly considered to preserve the physicochemical features of their mantle source (Coltorti and Grégoire, 2008), and therefore the mantle xenoliths in southern Tibet may provide insights into the $f_{O_2}$ condition of the upper mantle beneath the Himalayan-Tibetan orogen.

Here, we report for the first time: (1) $f_{O_2}$ values of lithospheric mantle xenoliths from southern Tibet; and (2) $f_{O_2}$ values of ultrapotassic volcanic magmas and their variation during ascent. The main objectives of this study were to identify the redox state of the southern Tibetan upper mantle and reveal the $f_{O_2}$ evolution of mantle-derived magmas along the path from mantle source to shallow crust.

GEOLOGICAL SETTING

The Lhasa terrane in southern Tibet is bounded by the Indus–Yarlung Zangbo suture (YSS) to the south and the Bangong-Nujiang suture (BNS) to the north (Fig. 1A). The final closure of the Neo-Tethys Ocean and collision of India with Asia along the southernmost margin of the Lhasa terrane occurred during the early Cenozoic (ca. 65–55 Ma; Leech et al., 2005; Mo et al., 2007). After the collision, the Lhasa terrane in the Himalayan-Tibetan orogen became part of a postcollisional setting. Recent geophysical studies (Zhao et al., 2011) have suggested that the Indian continental plate subducted northward beneath the Tibetan Plateau after collision (e.g., since the Eocene; Leech et al., 2005). Since the
mid-Oligocene, postcollisional magmatism has been widespread in the Lhasa terrane, mainly consisting of ca. 25–8 Ma potassic to ultrapotassic volcanic rocks and ca. 21–12 Ma adakite-like intrusions (Fig. 1A; Yang et al., 2016).

The UVRs reported here were collected from the Sailipu, Chazi, and Mibale areas (Fig. 1A). These samples show porphyritic textures, with the main phenocrysts (0.2–0.8 mm in size) being olivine, clinopyroxene, phlogopite, and sani-
dine (Figs. S2A–S2C). Some of the subhedral clinopyroxenes in these samples are enclosed or poikilitically enclosed in olivine pheno-
crys (Fig. S2D), suggesting their simultaneous crystallization. The proportion of olivine phenocrysts gradually decreases from the most mafic trachyandesite to the most silicic trachy-
chondite in the Sailipu area (Fig. 1; Fig. S4). They display a porphyroclastic texture, with larger grains (0.1–1 mm) of olivine, orthopyroxene, clinopyroxene, and phlogopite, and a few fine-
gained (<50 μm) spinel and apatite grains (Fig. S5A). Clinopyroxenes show embayed texture filled by orthopyroxene (Fig. S5B), suggesting disequilibrium between the two pyroxene types. Orthopyroxenes in lherzolite xenoliths host tiny two-phase melt inclusions, composed of silicate glass (<50 μm) and CO₂ + N₂ gas bubbles (Figs. S3G–S3J). These melt inclusions are isolated without healed fracture trails (Figs. S3G and S3I). Phlogopite is the only hydrous mineral phase. Spinel in the lherzolite is Cr-rich and often occurs as inclusions in large crystals (Figs. S5A–S5C). Detailed descriptions of lherzolite xenoliths can be found in the Supplemental Material.

METHODS AND RESULTS

The oxabarometer of Ballhaus et al. (1991) was used to calculate the fO₂ of lherzolite xenoliths based on olivine-spinel pairs (Fig. S5C). The ferric iron content of spinel in lherzolite xenoliths was determined by electron microprobe analysis (EMPA), because the very small size and volume of the spinel (Fig. S5) were not suitable for the Mössbauer spectroscopy analysis. Due to the disequilibrium texture of the two pyroxenes in lherzolite xenoliths (Fig. S5B), the single-clinopyroxene thermometer and barometer (Nimis and Taylor, 2000; Putirka, 2008; see Equations 1 and 2 in the Supplemental Material) were used to calculate temperature (T) and pressure (P), respectively. For compari-
son, results calculated by other thermometers are also provided in Table S2. Olivine phenocrysts in all UVRs were used to calculate fO₂ by the DfO₂/oxym (oximeter) of Mallmann and O’Neill (2003). The whole-rock compositions were used as the melt compositions. The primary melt may have higher V content than whole rock because V is a compatible element, which may lead to a slight underestimation of the fO₂ (Equation 6 in the Supplemental Material). Clinopyroxene inclusions in olivine phenocrysts were used to calculate crystallization T and P of host olivines by the clinopyroxene–liquid thermobarometer (Putirka et al., 2003; see Equations 3 and 4 in the Supplemental Material). Detailed methods of all calculations and error estimations are given in the Supplemental Material.

On the basis of 60 sets of EMPA data, calculated T, P, and ΔFMQ values of lherzolite xenoliths were 1316–1355 °C, 1.7–2.1 GPa (corresponding to a continental paleodepth of 64–79 km), and +0.5 to +1.2, respectively (Fig. 2; Tables S1 and S2).
Several factors could influence the calculated $f_{O_2}$ results, such as crystal-chemistry, $T$-$P$ condition, and hydrothermal alteration. For example, Fe$^{3+}$-Cr substitutions are more favorable than Al$^{3+}$-Cr substitutions in spinel, which could lead to a positive correlation between Fe$^{3+}/\Sigma$Fe$_{spinel}$ and Cr/(Cr + Al) ratios in spinel (e.g., Bénard et al., 2018). However, a plot of Fe$^{3+}/\Sigma$Fe$_{spinel}$ versus Cr/(Cr + Al) showed no positive correlation (Fig. S6), which means no crystal-chemical effects influenced the Fe$^{3+}/\Sigma$Fe$_{spinel}$ ratios and $f_{O_2}$ calculation.

Based on the expression of Ballhaus’s oxygen barometer (Equation 5 in the Supplemental Material), a variation of ±1 GPa and ±100 °C can result in a maximum ΔFMQ error of ±0.25 and ±0.13, respectively (see similar errors in Woodland et al., 1996). Therefore, the narrow T-P variation of lherzolite xenoliths (1316–1355 °C; 1.7–2.1 GPa) cannot significantly influence $f_{O_2}$ calculation.

As olivine-spinel pairs used for calculation were selected in the core of olivines without zoning (Fig. S5C), and samples used here were sufficiently fresh (Figs. S4 and S5), late-stage hydrothermal alteration is also unlikely to have affected the calculation.

Among UVRs, the most mafic Sailipu trachyandesite recorded the highest $T$ of 1191–1236 °C and $P$ of 1.1–1.5 GPa (43–56 km paleodepth; 10 EMPA spots; Fig. 2; Table S2) and the lowest ΔFMQ values of +0.8 to +1.3 (10 laser-ablation–inductively coupled plasma–mass spectrometry [LA-ICP-MS] spots; Fig. 2; Table S3).

Calculated $T$ and $P$ values of the Chazi trachyandesite were 1124–1137 °C and 0.7–0.8 GPa, respectively (25–31 km paleodepth; 5 EMPA spots; Fig. 2; Table S2), and ΔFMQ values ranged from +1.3 to +2.0 (5 LA-ICP-MS spots; Fig. 2; Table S3).

By contrast, the most silicic Mibale trachyte yielded the lowest $T$ (1058–1061 °C) and $P$ (0.40–0.43 GPa, 15–16 km paleodepth; 4 EMPA spots; Fig. 2; Table S2) and the highest ΔFMQ values of +1.9 to +3.0 (6 LA-ICP-MS spots; Fig. 2; Table S3).

**DISCUSSION**

**Causes of the Oxidized State of Southern Tibetan Lithospheric Mantle**

The mantle xenoliths reveal that the southern Tibetan lithospheric mantle was oxidized (ΔFMQ = +0.5 to +1.2) in the Miocene. It is markedly more oxidized than the Coreil (ΔFMQ = −4 to −2) and oceanic mantle (ΔFMQ = −1.2 to −0.4) and falls within the typical $f_{O_2}$ range of oxidized mantle wedge (ΔFMQ = 0 to +3). This oxidized state of the southern Tibetan lithospheric mantle is consistent with the occurrence of oxidized volatile species of CO$_2$ and N$_2$ (Figs. S3G–S3J), which are thought to indicate oxidized mantle conditions (above FMQ; Green et al., 1987; Li et al., 2013).

The metasomatism of oxidizing melts and fluids released from a subducted seawater-altered slab is commonly considered to be the most likely agent that could oxidize the mantle wedge (e.g., Bénard et al., 2018). The upper mantle beneath the Himalayan-Tibetan orogen experienced a continuous slab-related metasomatic process from subduction to collision during ca. 210–65 Ma (Zhu et al., 2011). Although oceanic subduction was not occurring during the Miocene in this area, the former subduction of the Neo-Tethyan oceanic slab could have modified the redox state of the southern Tibetan lithospheric mantle. The low Mg$_2$(Mg + Fe) ratios (0.35–0.49; Table S1) in spinel are indicative of iron enrichment, a trend commonly associated with metasomatic effects (Perini et al., 2006). The porphyroclastic and disequilibrium mineral textures in lherzolite xenoliths, especially the reaction texture of spinel with clinopyroxene (Fig. S5B), indicate metasomatism by Si- and alkali-rich melt/fluid derived from a subducted slab (e.g., Shaw et al., 2006). In addition, olivines in the lherzolite xenoliths are rich in highly incompatible elements, such as Ba, K, and Th (Fig. S7). Since Ba and K are water-mobile elements, and Th appears only to be mobilized in sediment melts (Woodhead et al., 2001), their enrichments imply the metasomatic agent was a water-rich and sediment melt–derived source, respectively. Melt extractions from the mantle lherzolite would result in the depletion of these elements rather than in such enrichments. Later interactions between lherzolite xenoliths and the host magma during ascent are unlikely to have caused the observed incompatible element enrichments because contents of these elements in olivine phenocrysts of host trachyandesite are much lower than those in olivines of the lherzolite xenolith (Fig. S7; Table S6). Hence, the interaction between lherzolite and slab-derived melt/fluid during metasomatism probably resulted in the enrichment of incompatible elements in the mantle source.

Furthermore, the Fe$_2$O$_3$/FeO ratios of the Cenozoic lower-crustal rocks display roughly positive correlations with Ba/La and Th/Yb ratios (Zhang et al., 2019; Figs. S8B and S8C; Table S7). This implies that water-rich fluids and sediment melts liberated from the Indian continental plate since ca. 65 Ma (Yang et al., 2016) could have also oxidized the southern Tibetan lower crust and the underlying lithospheric mantle.

**Redox Variation of Ultrapotassic Volcanic Magmas**

There is a long-standing debate on whether the redox state of mantle-derived magmas represents that of their mantle sources or not (e.g., Kelley and Cottrell, 2012). In this study, we found that the most mafic host trachyandesitic magma formed at a paleodepth (43–56 km) close to that of the lherzolite xenoliths (64–79 km; Fig. 2B), and it has a similar oxidation state (ΔFMQ = −0.8 to +1.3) to that of the lherzolite xenoliths (ΔFMQ = +0.5 to +1.2; Fig. 2B), implying inheritance of the oxidized signature from the mantle source. However, the $f_{O_2}$ of the ultrapotassic volcanic magmas shows a shift toward more oxidized values above 48 km (i.e., the average formation depth of the most mafic trachyandesitic magma; Table S2; Figs. 2B and 2C), implying that $f_{O_2}$ was modified during crustal evolution of the magma. Common factors that could influence the $f_{O_2}$ of mantle-derived magmas include changing T-P conditions, assimilation, crystal fractionation, and degassing (e.g., Lee et al., 2005). Variations in T-P conditions would not exert significant controls on the magmatic $f_{O_2}$ because the $D_{O_{liq-melt}}$ oxygen barometer is not P-sensitive (Equation 6 in the Supplemental Material), and a variation of ±100 °C only causes a maximum $f_{O_2}$ variation of ±0.25 log units.

The similar Sr-Nd-Pb-Os isotopes and trace-element ratios of the trachyandesite and trachyte (Tables S4 and S5; data are from Zhao et al., 2009; Liu et al., 2014; Guo et al., 2015) indicate that these ultrapotassic volcanic magmas have experienced similar assimilation degrees during ascent. Therefore, the lack of obvious correlation between $f_{O_2}$ and assimilation proxies suggests that assimilation is not a significant factor.

Degassing of volatile species has long been suggested to affect magmatic $f_{O_2}$, particularly degassing of reduced-type volatile species (e.g., H$_2$, CH$_4$, H$_2$S; Moussallam et al., 2016). However, the fact that mineral inclusions coexist with CO$_2$ and N$_2$ gas bubbles (Figs. S3A–S3F) suggests that gases were trapped during crystallization of host phenocrysts at magmatic temperature. Thus, degassing of these oxidized type gases cannot account for the elevated $f_{O_2}$.

In contrast, the oxidized trend of the ultrapotassic volcanic magmas matches the decreasing proportions of olivine, ilmenite, and sulfide, and the increasing proportions of magnetite from trachyandesite to trachyte (Figs. S2D–S2F). The early segregation of reduced minerals, such as ilmenite and sulfide inclusions enclosed in early crystallized phenocrysts (Figs. S2G–S2I), could have caused oxidation of the residual magma by consuming reduced ions (e.g., Fe$^{2+}$ and S$^2$).

Thus, the $f_{O_2}$ conditions of the evolved ultrapotassic volcanic magmas do not simply reflect their mantle source but were affected by subsequent crustal evolution processes (e.g., fractionation).

**ACKNOWLEDGMENTS**

We thank C. Ballhaus and C. Perinielli for guidance with the calculations, and L. Danyushchevsky and M. Harlaux for experimental analyses. This work was funded by the National Natural Science Foundation of China (91955207, 41825005) and the National Key Research and Development Project of China (2016YFC0600305). We acknowledge editor Gerald...
Dickens for handling, and three anonymous review

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