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High-pressure experiments provide insights into the Mantle Transition Zone history of chromitite in Tibetan ophiolites

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ABSTRACT

The chromitites in the Luobusha ophiolite (Tibet) have been proposed as messengers from the deep mantle. The exsolution of diopside, $MgSiO_3$ and coesite in chromite from these bodies has been used to argue that the chromite previously existed as a phase with the $CaFe_2O_4$ structure (idealized composition $(Mg, Fe)(Cr, Al)_2O_4$), an indicator of Mantle Transition Zone (MTZ) conditions. However, evidence about the stability of the $CaFe_2O_4$-structured phase and its formation mechanism are limited. Here we present experimental evidence for the depth of metamorphism and subsequent petrogenesis of the podiform chromitite. The $CaFe_2O_4$-structured phase was observed at ∼14–18 GPa, and can contain several weight percent of CaO and SiO_2. Partial-melting experiments show that chromite cannot be formed through direct crystallization in the MTZ. Therefore, we suggest that the Tibetan chromitites formed under shallow conditions, were then subducted, and were metamorphosed near the top of MTZ. During the tectonics/buoyancy-driven ascent of the enclosing peridotites, the $CaFe_2O_4$-phase transformed to chromite at depths of ∼400 km, accompanied by the simultaneous exsolution of diopside and other phases, which were then preserved during transportation to shallow depths. These observations provide a new window into the processes of mantle geodynamics, and constraints on mantle convection in major collision zones.

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1. Introduction

Podiform chromitites in the Luobusha ophiolite (southeastern Tibet) are typically lens-shaped and surrounded by dunite envelopes, enclosed in well-preserved depleted harzburgites. The chromitites consist mainly of chromite, associated with forsterite ± diopside. Most chromite grains are chemically homogeneous and have high Cr# (molar $Cr/Cr + Al$) and Mg# (molar $Mg/Mg + Fe$) of ∼0.7–0.8 and ∼0.70–0.76, respectively (e.g., Zhou et al., 2014; Zhang et al., 2016). Previous studies have shown that these chromitites can be explained by interaction between mantle peridotite (especially harzburgite) and melt in the upper mantle (less than ∼30 km depth) (Arai and Yurimoto, 1994; Zhou et al., 1996; Arai, 1997), or partial melting of mantle peridotite and crystal fractionation at shallow depths (Jin et al., 1996; Edwards et al., 2000), or mixing of mafic magmas (González-Jiménez et al., 2014). However, discoveries of ultrahigh-pressure (UHP) mineral inclusions (e.g., coesite, diamond) within the chromitites have suggested a much deeper origin for both the chromitites ("UHP chromitites"),

and their host rocks (no less than ∼120 km) (Yang et al., 2007). Recent studies have also revealed numerous exsolution lamellae of diopside and an $MgSiO_3$ phase within chromites in the podiform chromitites from Tibet and Oman (Yamamoto et al., 2009; Miura et al., 2012; Satsukawa et al., 2015). Previous experimental studies have shown that only trace amounts of SiO_2 (less than ∼1 wt%) can be incorporated into chromite at pressures less than 6 GPa and temperature ranges of 1000–1500 °C (Brey et al., 1999; Klemme and O'Neill, 2000; Girnis et al., 2003). Recent experimental studies also show no obvious increase of SiO_2 in chromite with pressure up to 12 GPa at 1400–1600 °C (Xu, 2011; Jin et al., 2014; Wu et al., 2016). Thus, the exsolution of diopside ($CaMgSi_2O_6$), $MgSiO_3$ and coesite/quartz in chromite may suggest the previous existence of a $CaFe_2O_4$-phase (CF phase, idealized composition $(Mg, Fe)(Cr, Al)_2O_4$), stable at pressures of >12.5 GPa (Chen et al., 2003), which was then replaced by chromite with exsolution of diopside and other phases during mantle upwelling (Yamamoto et al., 2009; Arai, 2013; McGowan et al., 2015). However, little is known about the stability field of the CF phase at realistic mantle temperatures, and how much CaO and SiO_2 can be incorporated into chromite and its high-pressure polymorphs.

Recent experimental studies by Ishii et al. (2014, 2015) have shown that in the $FeCr_2O_4$ system the CF phase can only be ob-

served at pressures above ∼17–18 GPa and temperatures below 1300 °C. However, the temperature at the base of the upper mantle is thought to be ∼1400 °C (Ito and Katsura, 1989), and the temperature of a mantle plume rising adiabatically from these depths is thus ∼200 °C higher than normal upper mantle (Herzberg et al., 2007). Thus, whether the observed diopside, $MgSiO_3$ and coesite exsolution within chromite can be thought of an indicator of a Mantle Transition Zone (MTZ) origin is debatable.

In this study, we use new experimental data in the magnesiochromite + diopside system to constrain the depth of origin of the Tibetan chromitites. Here, magnesiochromite, instead of natural chromite (with small amounts of iron), was used as the starting material; iron was omitted to avoid complexity. This system is relevant because mineral separates of these chromitites contain abundant large (50–250 μm) grains of diopside with crystal faces controlled by chromite, implying equilibration in a diopside-rich system (Griffin et al., 2016; Zhang et al., 2016). We have observed the formation of the CF phase at pressures corresponding to the top of the MTZ. The solubility of CaO and SiO_2 in magnesiochromite and its high-pressure polymorphs provides direct experimental constraints on the depth of metamorphism of the UHP chromite. Furthermore, partial-melting experiments in the pyrolite + chromite system have been used to test petrogenetic models for the UHP chromite.

2. Methods

2.1. Starting materials

Two types of magnesiochromite [$Mg(Cr_{1.5}Al_{0.5})O_4$ and $MgCr_2O_4$] were prepared from stoichiometric mixtures of reagent grade MgO, Cr_2O_3 and Al_2O_3. Cr# of the starting magnesiochromite [$Mg(Cr_{1.5}Al_{0.5})O_4$] was set at 0.75, consistent with that of the natural chromite from Luobusha (Zhou et al., 2014; Zhang et al., 2016). The oxide mixtures were first crushed and mixed to form fine powders, and then heated at 1000 °C for 24 h. After heating, the products were confirmed to consist of single phases by observations in a field-emission scanning electron microscope (FE-SEM), fitted with an energy-dispersive spectrometer (EDS). $CaMgSi_2O_6$ glass was synthesized from a mixture of $CaCO_3$, MgO and SiO_2 with a 1:1:2 molar ratios by heating at 1350 °C for 0.5 h. Three starting materials, *Mixes A*, *B* and *C*, were synthesized and used in the present study. *Mixes A* and *B* were synthesized by mixing 90 mol.% $Mg(Cr_{1.5}Al_{0.5})O_4$ + 10 mol.% $CaMgSi_2O_6$, and 95 mol.% $Mg(Cr_{1.5}Al_{0.5})O_4$ + 5 mol.% $CaMgSi_2O_6$, respectively. *Mix C* was synthesized by mixing 90 mol.% $MgCr_2O_4$ + 10 mol.% $CaMgSi_2O_6$. The two types of magnesiochromite [$Mg(Cr_{1.5}Al_{0.5})O_4$ and $MgCr_2O_4$] and $CaMgSi_2O_6$ glass were first crushed and ground into very fine powder (grain size ∼<5 μm) separately, and then ground together in alcohol with an agate mortar to produce homogeneous mixtures.

The pyrolite + chromite starting materials were synthesized by mixing 95 wt% pyrolite + 5 wt% chromite (*PC-A*) and 90 wt% pyrolite + 10 wt% chromite (*PC-B*), respectively. The pyrolite was synthesized by mixing approximately 53 wt% olivine + 31 wt% enstatite + 14 wt% clinopyroxene + 2 wt% spinel. The average chemical composition of this synthetic pyrolite is (in wt%): SiO_2 = 46.29, TiO_2 = 0.09, Al_2O_3 = 3.87, Cr_2O_3 = 0.51, MgO = 38.67, CaO = 3.09, MnO = 0.12, FeO = 7.17, Na_2O = 0.18 and K_2O = 0.01. The chromite was hand-picked from a natural chromitite sample from Luobusha, Tibet. Its average chemical composition is (in wt%): SiO_2 = 0.07, TiO_2 = 0.24, Al_2O_3 = 10.33, Cr_2O_3 = 59.96, FeO = 11.98, MnO = 0.22, MgO = 16.74, ZnO = 0.14 and NiO = 0.25, with Cr# of 0.76 and Mg# of 0.79. Detailed microscopic study did not show any pyroxene or coesite exsolution lamellae in the chromite grains (Xu, 2011; Wu et al., 2016).

2.2. Experimental procedures

High-pressure, high-temperature (HPHT) experiments were carried out in a 1000-ton Walker type multi-anvil press at the Laboratory for the Study of the Earth's Deep Interior (SEDI-Lab), China University of Geosciences. Cell assemblages with 10 and 8 mm octahedral edge lengths and 5 and 3 mm truncation edge lengths, respectively, were used (10/5 and 8/3 cell assemblies). The detailed descriptions and pressure calibrations of the cell assemblies were reported by Zhang et al. (2013). A type C thermocouple was used to measure the temperature at the center of the furnace. The estimated temperature gradient across the sample length was no more than ∼25 °C.

2.3. Data analysis

After recovery, Pt capsules containing the samples were embedded in epoxy resin and polished to expose the center of the charges. A field-emission scanning electron microscope (Quanta 2000-type) (FE-SEM), fitted with a LINK EDS detector, was used to study the microstructure of the recovered samples. Micro-Raman spectrum and electron-backscattered diffraction (EBSD) were used to identify phases in the recovered charges. Quantitative compositional analyses were conducted with an electron probe microanalyzer (EPMA, JXA-8100) at the Key Laboratory of Submarine Geosciences, State Oceanic Administration, China, using an accelerating voltage of 15 kV, a beam size of 1.0–2.0 μm, and a beam current of 20 nA.

3. Results

Details of the experimental conditions and run products are summarized in Tables 1 and 2. Quantitative compositional data for minerals are listed in Tables S1 and S2 (see supplementary material). Raman spectra of magnesiochromite and its high-pressure polymorphs are shown in Fig. 1. We observed one characteristic excitation peak of magnesiochromite [idealized composition $Mg(Cr, Al)_2O_4$] at 697 cm^{-1} in the Raman spectrum, in contrast to the two strong peaks of the CF phase [idealized composition $Mg(Cr, Al)_2O_4$] at 628 and 658 cm^{-1}. Two strong bands at 574 and 643 cm^{-1} can be assigned to the mLd phase [modified ludwigite-type phase, idealized composition $Mg_2(Cr, Al)_2O_5$], in comparison to the one strong peak of the CT phase [$CaTi_2O_4$-structured phase, idealized composition $Mg(Cr, Al)_2O_4$] at 626 cm^{-1}. These results were further confirmed by EBSD analyses, which can be indexed in the space groups *Fd3m*, *Pnma* and *Pbam* for magnesiochromite, the CF phase and the CT phase respectively.

3.1. Phase relations

3.1.1. $MgCr_{1.5}Al_{0.5}O_4$ + $CaMgSi_2O_6$ (mixes A and B)

We conducted a series of experiments in the system $MgCr_{1.5}Al_{0.5}O_4$ + $CaMgSi_2O_6$ over pressure ranges of 12–21 GPa, at 1400 and 1600 °C (Table 1). Microstructures of representative run products are shown in Figs. 2a–b. The obtained phase relations are presented in Fig. 2c. At a pressure of 12 GPa and temperatures of 1400 and 1600 °C, the starting materials were transformed into assemblages consisting of magnesiochromite + eskolaite (Cr_2O_3) + garnet. When pressure was increased to 14 GPa, the CF phase was observed in contact with garnet (Figs. 2a, b), and is stable up to at least 18 GPa. These observations indicate that garnet (or another silicate phase?) can catalyze the formation of the CF phase. Magnesiochromite can be preserved up to ∼16 GPa, coexisting with the CF or the mLd phase. The assemblage mLd phase + eskolaite, which formed by the de-