



Experimental constraints on the formation of the Tibetan podiform chromitites



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ABSTRACT

The discovery of diamonds and highly reduced minerals in podiform chromitites, which have generally been interpreted as magmatic rocks formed from partial melts of upper mantle peridotites under low-pressure conditions, has raised many questions about the origin of these enigmatic bodies.

In order to provide experimental constraints on the formation and emplacement of podiform chromitites in ophiolites, we carried out a number of multi-anvil experiments in the magnesiochromite + SiO₂ system at temperatures of 1000–1600 °C and pressures of 5–15 GPa. The experimental results demonstrate that magnesiochromite is stable up to 14 GPa and decomposed into eskolaite (Cr₂O₃) together with a quenchable modified ludwigite-structured phase [(Fe, Mg)₂(Al, Cr)₂O₅] at higher pressures, thus placing an approximate maximum depth for chromite crystallization and/or metamorphism. This depth corresponds to the top of the mantle transition zone (MTZ) at 410 km. The ludwigite-structured post-chromite phase has significant implications for understanding phase transformations and Cr incorporation/partitioning of minerals in the MTZ. On the basis of our results, we propose a multi-stage model for the formation of podiform chromitites that incorporates the geochemical, textural and mineralogical features of these bodies.

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1. Introduction

Podiform chromitites are generally lenticular bodies of massive to disseminated chromite typically hosted in mantle peridotites in ophiolites. Most such chromitites are surrounded by envelopes of dunite, a few centimeters to a few meters wide, which show clear evidence of formation by melt-rock reaction (Arai, 1997; Zhou et al., 1996). Based on their textures and compositions, podiform chromitites have been interpreted as magmatic rocks formed under low-pressure conditions in the upper mantle (<30 km deep) by magma mingling and melt-rock reaction (Arai, 1997; Ballhaus, 1998; Edwards et al., 2000; Zhou et al., 1996).

However, the discovery of ultrahigh pressure (UHP) minerals, such as micro-diamonds, coesite and moissanite (Yang et al., 2007) and highly reduced native elements and metallic alloys (Bai et al., 2000; Robinson et al., 2004) in podiform chromitites in the Luobusa ophiolite of Tibet, suggests that these enigmatic bodies have a much deeper origin. A deep origin is also suggested by the discovery of coesite and clinopyroxene exsolution lamellae in magnesiochromite grains from the same ophiolite (Yamamoto et al., 2009).

In general, exsolution of a mineral phase is caused by a decrease in solubility due to a change in oxygen fugacity (Buddington and Lindsley, 1964), cooling (Moseley, 1984) or decompression (Dobrzhinetskaya et al., 1996) upon exhumation of the host mineral. Thus, the presence of coesite and clinopyroxene lamellae in magnesiochromite grains indicates a much higher SiO₂ solubility for chromite at ultrahigh pressures. However, previous experimental studies have shown no obvious increase of SiO₂ solubility in chromite at 0.5–6 GPa. For example, using the system MgO–Al₂O₃–SiO₂–Cr₂O₃ (MASCr), Klemme and O'Neill (2000) found that only 0.3–1.2 wt% SiO₂ can be incorporated into spinel at pressures of 0.5–4 GPa and temperatures of 1300 °C–1500 °C in the resulting spinel + orthopyroxene + olivine assemblage. Likewise, Giris et al. (2003) found only 0.15–0.7 wt% SiO₂ in magnesiochromite coexisting with garnet, orthopyroxene and forsterite at pressures of 3–6 GPa and temperatures of 1000 °C–1500 °C. In another experiment, Brey et al. (1999) showed that spinel in the FeO–MgO–Al₂O₃–SiO₂–Cr₂O₃ (FMASCr) system contains 0.2 to 0.8 wt% SiO₂ at pressures of 3–5 GPa and temperatures of 1200 °C–1500 °C. They also noted that the SiO₂ content correlated positively with increasing temperature.

In order to investigate the stability field of chromite in the mantle and to quantify the exsolution mechanism of coesite in chromite grains, we undertook a series of multi-anvil experiments in the magnesiochromite + SiO₂ system. We added SiO₂ into the system because various forms of SiO₂ are present in the upper mantle as

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indicated by the coesite lamellae in chromite grains (Yamamoto et al., 2009), as well as intergrowths of coesite and kyanite in the Luobusa chromitites (Yang et al., 2007).

2. Experimental and analytical techniques

The starting materials for all experiments were mechanical mixtures of 90 wt% natural magnesiochromite and 10 wt% pure SiO₂ (Table 1). The magnesiochromite (Mg_{0.79}, Fe²⁺_{0.21})_{1.00}(Al_{0.42}, Cr_{1.50}, Fe³⁺_{0.10})_{1.98}O₄, which has a Mg# of 79 and a Cr# of 76, was separated from sample T97-102 collected from the No. 28 ore body of the Luobusa ophiolite, Tibet. It is composed of >95% massive magnesiochromite with a few silicate minerals (e.g. olivine and orthopyroxene) filling the narrow interstices between grains. The chemical composition of this magnesiochromite is quite similar as that reported in Yamamoto et al. (2009). The magnesiochromite was crushed to small particles about 1 mm in diameter and handpicked under a binocular microscope to ensure that they contained no inclusions or adhering material. The handpicked grains were then ground to a very fine powder and mixed with pure SiO₂ in ethanol. The average grain size of the starting material was about 8 μm, as determined by scanning electron microscopy (SEM), and the composition was homogeneous as indicated by electron microprobe analysis (Table 1). Detailed microscopic study did not show any coesite and clinopyroxene exsolution in these grains.

The high P–T experiments were carried out using the multi-anvil apparatus at the Geophysical Laboratory, Carnegie Institution of Washington, and the State Key Laboratory of Geological Processes and Mineral Resources (GPMR), China University of Geosciences, Wuhan. Two cell assemblies, 10/5 and 18/11 (octahedron edge length/truncated edge length), were used in the experiments under pressures higher and lower than 8 GPa, respectively. Rhenium foil and graphite were used as heaters for the 10/5 and 18/11 assemblies, respectively, with Al₂O₃ sleeves separating them from the capsules and ZrO₂ insulators lowering heat loss. For all runs, samples were sealed in platinum capsules. Temperatures were measured with a W5%Re–W26%Re (Type C) thermocouple at the center and were controlled within ±1 °C of the target temperature. The pressure and temperature calibrations of the cell assemblies have been described by Bertka and Fei (1997), Wu et al. (2012) and Zhang et al. (2013). All experiments were first automatically pumped to the desired pressure, and then heated at a rate of 100 °C/min to the target temperature. They were kept at the desired pressure–temperature conditions for specific periods of time (Table 2) and then quenched to ambient conditions.

All recovered samples were embedded in epoxy for electron microscopy and microprobe analysis. Mounts were polished in several steps using sand paper of different grain size, with the final polish being performed with 0.3 μm polishing powder. The phase relations were obtained from detailed studies of backscattered electron images (BSE) using a JEOL 6500F Field Emission SEM. The compositions of the phases were determined with a JEOL JXA-8900 super microprobe at the Geophysical Laboratory, operating at 15 kV with a 30 nA beam current. The analyses were recalculated by the ZAF procedure provided by JEOL. Pure Fe₃O₄, ZnS, MgCr₂O₄ and TiO₂, as well as natural spinel, spessartine and Ni-olivine were used as standards. Only analyses with totals between 98

Table 2
Experimental conditions and run products.

Run number	P (GPa)	T (°C)	Duration (h)	Products
PR841	5	1000	48	Chr + Grt + Esk + Opx
PR839	5	1200	48	Chr + Grt + Esk + Opx
PR854	5	1400	24	Chr + Grt + Esk + Melt
PR848	5	1600	24	Chr + Grt + Esk + Melt
PR856	8	1400	24	Chr + Grt + Esk
PR851	8	1600	10	Chr + Grt + Esk + Melt
M-1135	12	1400	24	Chr + Grt + Esk
M-1132	12	1600	24	Chr + Grt + Esk
M-1136	14	1400	24	Chr + Grt + Esk
R0030	14	1600	13	Chr + Grt + Esk + pCP
R0028	15	1400	24	pCP + Grt + Esk
M-1134	15	1600	24	pCP + Grt + Esk

Mineral abbreviations: Chr, chromite; Grt, garnet; Esk, eskolaite; Opx, orthopyroxene; pCP, post-chromite phase.

and 101 wt%, and which yielded appropriate stoichiometry for the various phases, were accepted.

An initial set of 10 runs was completed at the Geophysical Laboratory (labeled PR and M in Table 2). Because run M-1134 resulted in the decomposition of chromite and the formation of a post-chromite phase, two additional runs (R0030 and R0028) were later undertaken at the GPMR Lab in Wuhan to confirm this reaction and to place tight constraints on the temperatures and pressures at which it occurred (Table 2).

3. Experimental results

3.1. Phase relations

We conducted a total of twelve runs, four at 5 GPa and two each at 8, 12, 14 and 15 GPa with temperatures ranging from 1000 °C to 1600 °C (see Table 2 for the experimental conditions and mineral assemblages produced in each run). Representative backscattered electron (BSE) images of the run products are shown in Fig. 1. All the added silica was reacted to form silicate phases or dissolved into the coexisting minerals. No separate SiO₂ phases were observed in the run products at all investigated P–T conditions.

At a pressure of 5 GPa in the temperature range of 1000 °C–1200 °C, the starting material was transformed into an assemblage consisting of magnesiochromite + garnet + eskolaite + orthopyroxene (Fig. 1a). In the first run at 1000 °C for 24 h, the grain boundaries were irregular and the magnesiochromite grains displayed considerable core-to-rim compositional variations, indicating that the run time was insufficient to achieve equilibrium. This run product was not considered further and the run time was increased to 48 h at 1200 °C. The longer run time at higher temperature produced generally homogeneous magnesiochromite crystals with straight or flat grain boundaries, coexisting with garnet, orthopyroxene, and eskolaite. The garnet grains also contain inclusions of magnesiochromite, orthopyroxene and eskolaite (Fig. 1a). At 8 GPa and 1400 °C the orthopyroxene completely reacted with eskolaite to produce garnet, resulting in an assemblage composed of chromite + garnet + eskolaite. The garnet formed under

Table 1
Chemical composition of starting materials (wt%).

Starting material	SiO ₂	TiO ₂	Al ₂ O ₃	Cr ₂ O ₃	FeO	MnO	MgO	ZnO	NiO	Total
Magnesiochromite	0.07	0.24	10.33	59.96	11.98	0.22	16.74	0.14	0.25	99.95
SiO ₂	99.99									99.99
90%Chr + 10%SiO ₂	10.06	0.22	9.30	53.96	10.78	0.20	15.07	0.13	0.23	99.95

Iron is reported as FeO.

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