

# Tibetan chromitites: Excavating the slab graveyard

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## ABSTRACT

**Podiform chromitites enclosed in depleted harzburgites of the Luobusa massif (southeastern Tibet) contain diamond and a highly reduced trace-mineral association. Exsolution of diopside and coesite from chromite suggests inversion from the Ca-ferrite structure in the upper part of the mantle transition zone (>400 km). However, the trace-element signatures of the chromites are typical of ophiolitic chromitites, implying primary crystallization at shallow depths. Os-Ir nuggets in the chromitites have Re-Os model ages ( $T_{RD}$ ) of  $234 \pm 3$  Ma, while  $T_{RD}$  ages of in situ Ru-Os-Ir sulfides range from 290 to 630 Ma, peaking at ca. 325 Ma. Euhedral zircons in the chromitites give U-Pb ages of  $376 \pm 7$  Ma,  $\epsilon_{Hf} = 9.7 \pm 4.6$ , and  $\delta^{18}O = 4.8\text{‰} - 8.2\text{‰}$ . The sulfide and zircon ages may date formation of the chromitites from boninite-like melts in a supra-subduction-zone environment, while the model ages of Os-Ir nuggets may date local reduction in the transition zone following Devonian subduction. Thermo-mechanical modeling suggests a rapid ( $\leq 10$  m.y.) rise of the buoyant harzburgites from >400 km depth during the early Tertiary and/or Late Cretaceous rollback of the Indian slab. This process may occur in other collision zones; mantle samples from the transition zone may be more widespread than currently recognized.**

## INTRODUCTION

Ophiolitic chromitites are bodies of Cr-rich spinel precipitated from mafic melts near the oceanic crust–mantle boundary, or less commonly, in the lowermost crust. The inferred parental magmas typically have island-arc characteristics, suggesting that the chromitites originated in extensional zones developed during subduction (González-Jiménez et al., 2014a, 2014b). However, chromitites in some ultramafic complexes from Tibet, the Polar Urals, and Myanmar (Yang et al., 2007, 2014) contain a super-reducing ultrahigh-pressure (SuR-UHP) mineral association derived from >400 km depth (Yamamoto et al., 2009; González-Jiménez et al., 2013; Arai, 2013). In chromitites from the Luobusa peridotite massif (Tibet), the SuR-UHP association includes microdiamonds, found both in mineral separates (Bai et al., 1993) and in situ (e.g., Yang et al., 2014), as well as native metals (Cr, Si, Ti, Fe, Cr, Ta), alloys (Ni-Fe-Cr-C, Fe-Ti-Si, Cr-Fe, platinum group elements), moissanite (SiC), and Cr<sup>2+</sup>-bearing chromite (see Arai [2013] for a comprehensive list). Chromite contains exsolved inclusions of pyroxenes, coesite, and other phases, implying inversion from the high-pressure Ca-ferrite structure (Yamamoto et al., 2009). Higher

Fe<sup>3+</sup>/ΣFe in more massive chromites is interpreted to be produced by disproportionation of Fe<sup>2+</sup> during the polymorphic inversion at depth, reflecting a greater affinity for Fe<sup>3+</sup> in the UHP Ca-ferrite structure (Ruskov et al., 2010).

The Luobusa chromitites are volumetrically minor domains (<1% by volume) within a highly depleted harzburgite-dunite massif. Previous studies of Luobusa peridotites (e.g., Malpas et al., 2003) concluded that they were typical of ophiolitic settings, with chromitites generated near the oceanic crust–mantle boundary in mid-ocean-ridge or supra-subduction-zone (SSZ) environments. However, the Luobusa peridotites lack a clear crust–mantle transition as found in ophiolites such as Troodos (Cyprus) or Oman (Liu et al., 2010). While they may once have been part of a section of oceanic mantle, the current designation of the peridotites as “ophiolites” may be misleading. Attempts to reconcile these findings with the presence of the SuR-UHP trace-mineral associations have argued that the chromites crystallized at great depths, trapping UHP phases, and then were carried up in asthenospheric melts and emplaced at shallow depths (e.g., Xiong et al., 2014; Yang et al., 2014; Zhou et al., 2014). However, this mechanism does not explain the occurrence of diamonds and other members of the SuR-UHP association in the host peridotites (Yang et al., 2014).

We present compositional data for the chromitites that substantiate their origin under shallow-mantle conditions, and new Re-Os and U-Pb

ages constrain the age of formation of the host chromitites to older than or equal to 375 Ma, much older than previously suggested. We integrate this new information with previously published data to construct a pressure-temperature ( $P$ - $T$ ) history for the chromitites; thermo-mechanical dynamic modeling is used to test a mechanism for the extraction of these highly depleted peridotites from the mantle transition zone (TZ) and their emplacement to shallow levels.

## LUOBUSA CHROMITITES

A detailed discussion of the geology and petrology of the Luobusa chromitites is given by Shi et al. (2007).

The chromite grains from the studied chromitites contain exsolved needles or grains of diopside, enstatite, diopside + olivine, FeC, diopside + SiO<sub>2</sub>, and SiO<sub>2</sub> with preferred orientations (section 3 in the GSA Data Repository<sup>1</sup>). Yamamoto et al. (2009) identified the SiO<sub>2</sub> phase as coesite, and interpreted the exsolution assemblage as evidence of pressures >12.5 GPa, near the top of the TZ; as the relevant experiments (Chen et al., 2003) were done at 2000 °C, this represents a minimum depth. Under these conditions, chromite inverts to the orthorhombic Ca-ferrite structure, which accommodates ions such as Ca and Si, derived from coexisting silicates (Kojitani et al., 2007), as well as Fe<sup>3+</sup>. Yamamoto et al. (2009) argued that the oriented inclusions exsolved when chromite inverted to the spinel structure during ascent to the surface.

The Luobusa chromitites also host abundant inclusions of Os-rich platinum-group minerals (PGMs), similar to mantle-hosted ophiolitic chromitites elsewhere (see González-Jiménez et al., 2014a). In situ PGMs occur as single euhedral crystals or, more commonly, polyphase inclusions with diopside and NiS (Fig. DR4.1.1 in the Data Repository). The negative-crystal chromite faces of the diopside grains suggest that they exsolved from the chromite as described above.

Zircons separated from a Luobusa chromite show idiomorphic habits with complex morphologies and prismatic inclusions of fluorapatite. Cathodoluminescence images show strongly marked, narrow oscillatory zoning. These zircons are similar to those included in chromite from chromitites in the Finero Com-

<sup>1</sup>GSA Data Repository item 2015066, analytical methods and results, is available online at [www.geosociety.org/pubs/ft2015.htm](http://www.geosociety.org/pubs/ft2015.htm), or on request from [editing@geosociety.org](mailto:editing@geosociety.org) or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

plex, Italy (Grieco et al., 2001). The same mineral separate yielded two 40  $\mu\text{m}$  diamonds with cubo-octahedral morphology, typical of the diamonds found previously in Luobusa chromitites.

## ANALYTICAL METHODS

Details of analytical methods and results are given in the Data Repository. Elemental and isotopic analyses were conducted at the Geochemical Analysis Unit, CCFS, Macquarie University, Australia.  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratios were analyzed by Mössbauer spectroscopy at Bayerisches Geoinstitut, Germany. Oxygen isotopes of zircons were analyzed by ion microprobe at the China Academy of Sciences, Beijing, China.

## RESULTS

Figure 1 shows the trace- and major-element signatures of Luobusa chromitites normalized to the composition of chromite crystallized from mid-oceanic-ridge basalt; these are compared with mean values for chromitites from the Antalya ophiolite (Turkey), which shows no evidence of a UHP history, and for chromite in boninitic lavas (Pagé and Barnes, 2009).

In situ analyses of laurite grains in chromitite give Re-depletion model ages ( $T_{\text{RD}}$ ) of ca. 290–630 Ma, with a pronounced peak at ca. 325 Ma (Fig. 2A). One older  $T_{\text{RD}}$  (1.9 Ga) is consistent with some older Re-Os whole-rock model ages previously reported from the Luobusa complex (Shi et al., 2012).

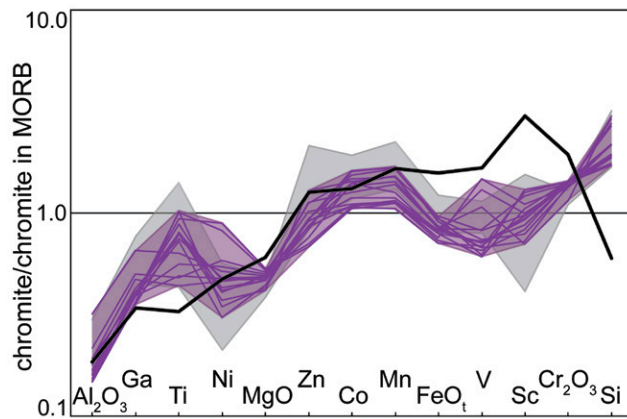
U-Pb dating of the euhedral zircons yields a concordia age of  $376 \pm 7$  Ma (Fig. 2B). The zircons have juvenile Hf-isotope compositions ( $\epsilon_{\text{Hf}} = 9.7 \pm 4.6$ ; maximum crustal model age of ca. 440 Ma; Fig. 2A).  $\delta^{18}\text{O}$  values range from 4.8‰ to 8.2‰ relative to standard mean ocean water, and show a weak negative correlation with  $\epsilon_{\text{Hf}}$ .

The zircons have trace-element compositions typical of crustal zircons (Table DR5.2.1 in the Data Repository; Belousova et al., 2002), with high concentrations of Y (1200–5000 ppm), U (400–1000 ppm), and Th (140–750 ppm), moderate heavy rare earth element (HREE) enrichment (Yb/Sm mainly from 12 to 90), and small negative Eu anomalies. The relatively high U/Yb ratios plot outside the field for ocean-crust zircon (Grimes et al., 2007). Their trace-element contents suggest derivation from plagioclase-bearing, low- $\text{SiO}_2$  intermediate to mafic magmas.

$\text{Fe}^{3+}/\Sigma\text{Fe}$  of chromite from two massive chromitites is higher ( $32 \pm 5\%$ ) than that of the associated nodular chromite ( $24 \pm 2\%$ ).

## DISCUSSION

The trace- and major-element signatures of massive and nodular chromitites from Luobusa and Antalya are indistinguishable from those of boninitic chromitites, and are similar to those of most ophiolitic chromitites (González-Jiménez et al., 2013). Depletion of redox-sensitive elements (V and Fe) compared with their abundances in



**Figure 1.** Plots of major-element oxides and trace elements (normalized to mid-oceanic-ridge basalt [MORB] chromite; Pagé and Barnes, 2009) for chromites from Luobusa, Tibet (purple), the Antalya ophiolite complex, Turkey (gray), and chromite hosted in boninite-lavas from Bonin Island, Japan (black; Pagé and Barnes, 2009). Luobusa chromites have Cr# 0.60–0.78 and Mg# 0.58–0.73; Antalya (Turkey) chromites have Cr# 0.59–0.73 and Mg# 0.55–0.69.

boninitic chromite may be related to differences in redox conditions between the upper mantle and crust, or to oxidation of boninite magmas during ascent (Pagé and Barnes, 2009). The host peridotites were not obviously oxidized during the formation of the chromitites, suggesting that the melts were confined to the dunite channels that host the chromite (González-Jiménez et al., 2013). These data suggest that the Luobusa chromites crystallized from typical arc-related melts at shallow depths; their trace- and major-element compositions were apparently unaffected by the later subduction.

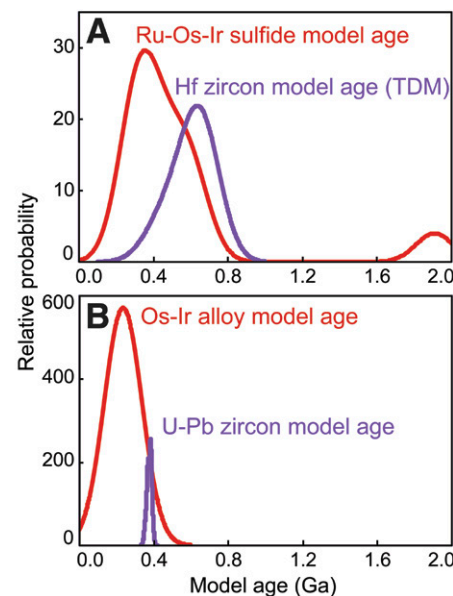
However, the exsolution of diopside, coesite, enstatite, and FeC in the Luobusa chromites requires equilibration between spinel and silicates under UHP conditions in the TZ. While previous studies observed these exsolution features only in massive chromitites, Yamamoto et al. (2009) observed exsolution features in nodular chromitite, and we have found these features

also in disseminated chromitite. This appears to exclude the possibility that the nodular and disseminated chromite are secondary products formed by interaction of the massive chromitite with the host peridotite during its upwelling (Ruskov et al., 2010). It therefore appears most likely that exsolution of Ca- and Si-bearing phases occurred when the chromitite (and peridotite) left the TZ and the orthorhombic Ca-ferrite polymorph (stable at  $P > 12.5$  GPa; Chen et al., 2003) inverted to the cubic spinel structure.

Another feature consistent with polymorphic inversion is the higher  $\text{Fe}^{3+}/\Sigma\text{Fe}$  observed in more massive chromitites. Experimental studies have suggested that disproportionation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+} + \text{Fe}^0$  occurs at depth and subsequently  $\text{Fe}^{3+}$  is stabilized in HP polymorphs with unusually high affinities for  $\text{Fe}^{3+}$ , despite the low oxygen fugacity ( $f_{\text{O}_2}$ ) conditions (see McCammon, 2005).

The simplest explanation for the coexistence of shallow-crystallization trace-element patterns and SuR-UHP mineral inclusions in the chromitites seems to be that a volume of peridotite containing the chromitites was subducted from shallow depths to the TZ during the Devonian, and then subsequently exhumed in the Yarlung-Zangbo suture zone (YZSZ) (Arai, 2010).

Whole-rock Os-isotope analyses of the harzburgites hosting the Luobusa chromitite deposits give a range of  $T_{\text{RD}}$  model ages from 1.5 Ga to  $>2.2$  Ga, indicating that the protoliths of the peridotites may be derived from ancient subcontinental lithospheric mantle (Shi et al., 2012). The  $T_{\text{RD}}$  model ages of the laurite inclusions provide some constraint on the crystallization of the chromitites; the homogenization of Os isotopes during the genesis of chromitites appears in many cases to produce model ages that approximate the crystallization age (González-Jiménez et al., 2014b). In this case, the peak of  $T_{\text{RD}}$  ages of ca. 325 Ma (Fig. 2) probably represents a minimum estimate for the formation of the chromitites. The spread observed for  $T_{\text{RD}}$  model ages in the laurite grains from Luobusa may reflect incomplete homogenization of Os isotopes during mixing of numerous batches of melts in the



**Figure 2.** Model age ranges for laurite Os and zircon Hf (A), and Os-Ir alloys (Shi et al., 2007) and zircon U-Pb (B). Analytical uncertainties are expanded to uniform 0.1 Ga.

open system represented by the dunite channels in which the chromitites were formed (González-Jiménez et al., 2014a, 2014b).

Robinson et al. (2014) obtained secondary ion mass spectrometry ages for zircons, separated from large chromitite samples, both younger and older than the emplacement age (ca. 130 Ma?) of the Luobusa ophiolites. However, most of these zircons are rounded to anhedral, suggesting that they are xenocrystic. In contrast, the euhedral morphology and typically magmatic zoning of the zircons reported here (Fig. DR5.1.1), and the existence of a single age population in a single hand specimen, make it unlikely that they are xenocrysts. The positive  $\epsilon_{\text{Hf}}$  of the zircons indicates derivation from juvenile, mantle-derived melts. However, the moderate spread in both  $\epsilon_{\text{Hf}}$  and  $\delta^{18}\text{O}$  (Fig. DR5.4.1; Table DR5.4.1) and a mean  $\delta^{18}\text{O}$  higher than the mantle range ( $5.3\text{‰} \pm 0.3\text{‰}$ ) suggest mixing between mantle-derived melts and a crustal component, the mechanism proposed by González-Jiménez et al. (2014b) for precipitation of chromitites in SSZ fluid-melt systems. Their inferred crystallization age (ca. 375 Ma) therefore is interpreted as recording the formation of the chromitite under low-pressure conditions.

The preservation of the U-Pb ages under UHP conditions may be related to the relatively small unit-cell volume of the Luobusa zircons (Yu et al., 2001). This may slow Pb diffusion and raise the U-Pb closure temperature (Yamamoto et al., 2013).  $\text{ZrSiO}_4$  transforms to a scheelite structure at 15 GPa and 900–1000 °C (Tange and Takahashi, 2004). However, no data exist for zircons with the high levels of Hf and HREE found in our samples. These elements may stabilize the zircon structure to pressures closer to the zircon  $\rightarrow$   $\text{ZrO}_2$  + stishovite transition at  $\sim 20$  GPa ( $>1300$  °C).

The model ages of  $234 \pm 3$  Ma obtained by Shi et al. (2007) for Os-Ir nuggets separated from the Luobusa chromitites (Fig. 2B) were interpreted as being produced by melting and homogenization of large volumes of fertile, convective upper mantle. If this is correct, the model ages could record the residence of the harzburgites together with more fertile mantle in the TZ. Infiltration of highly reducing fluids in the TZ (related to the SuR-UHP assemblage) could desulfurize laurites to Os-Ir alloys while modifying and homogenizing their original  $^{187}\text{Os}/^{188}\text{Os}$  signatures. The porous textures of the Os-Ir alloys (Shi et al., 2007) are a typical feature of such desulfurization (e.g., Bai et al., 2000; Shi et al., 2007; González-Jiménez et al., 2014b, and references therein). A similar process has been described in laurites from the metamorphosed chromitites of the Dobromirski ultramafic massif, Bulgaria (González-Jiménez et al., 2012).

The problem of exhuming the peridotite massif from the TZ has been addressed by thermo-mechanical modeling of the dynamics of the Indian plate (section 6 in the Data Reposi-

tory). This model, based on the work of Afonso and Zlotnik (2011), demonstrates that highly depleted (buoyant) harzburgite volumes can be carried up from the TZ in response to slab rollback in a collisional setting. Such exhumation of deep-mantle material in the fore-arc side of a subduction system is a result of the initial steepening and subsequent rollback of the slab; this produces large-scale passive upwelling, which rapidly develops into a self-maintained low-viscosity channel. The relatively high velocities ( $\sim 6\text{--}8$  cm yr $^{-1}$ ) generated in this channel could bring material from the TZ to the uppermost mantle in  $\lesssim 10$  m.y., provided the subduction system remains active for at least that long. The bodies of harzburgite being carried by the upwelling mantle contain  $<1$  vol% chromitite; it is unlikely that the chromitite would develop the body forces necessary to separate from its host. The generally low degree of deformation in the bodies on which research attention has been focused can be explained by the relative ductility of the surrounding asthenospheric mantle, acting as a lubricant and protecting the upwelling harzburgite.

This rapid upwelling, followed by rapid cooling as the peridotites rise to shallow levels, can help to explain the preservation of several high-pressure features, such as the diamonds, the exsolution structures in the chromites, the high  $\text{Fe}^{3+}$  contents of the more massive chromitites (Ruskov et al., 2010), and the diverse phases of the SuR-UHP mineral association.

The different ultramafic massifs in the YZSZ contain a variety of lithologies, and appear to have been emplaced as discrete units from the mid-Jurassic to the mid-Cretaceous (Hébert et al., 2012). There seems to be general agreement that the final emplacement of the peridotites into the crust occurred at ca. 65 Ma (e.g., Liu et al., 2010), but many may have “surfaced” much earlier, allowing them to acquire a crust of sediments and minor volcanic rocks, without the sheeted dikes and gabbroic piles characteristic of typical ophiolites. The rapid upwelling of hot mantle material, as in the model presented here, would deliver large amounts of heat to shallow levels, and may have been involved in the generation of the neighboring Gangdese batholith, which experienced its major granitic magmatism during the Paleocene–Eocene (65–40 Ma; Ji et al., 2009).

If these interpretations are correct, the Luobusa peridotites were in a SSZ setting at 375–350 Ma, and then were subducted to reside in the TZ, possibly for  $>150$  m.y. It appears unlikely that the chromitites were, as previously suggested, generated at spreading centers in the Neo-Tethys ocean, or in the back-arc system related to the India-Asia collision.

## CONCLUSIONS

Compositional data and radiometric ages suggest that chromitites in the Luobusa peridotite

initially crystallized under shallow conditions ( $\lesssim 30$  km) in a continental-margin supra-subduction-zone environment at 375 Ma or before. A segment of this lithospheric mantle containing the chromitites was then subducted to the upper part of the TZ by at least ca. 235 Ma. Here, the chromitite structure inverted to the Ca-ferrite structure, and SuR-UHP phases formed by reaction of reducing fluids with the chromitite and its host peridotite. After a TZ residence of  $\geq 150$  m.y., a massif of buoyant, depleted lithospheric material was emplaced back to shallow depths, with chromite inverting back to the spinel structure. Dynamic modeling suggests that the rise of the peridotite from  $>400$  km depths was rapid ( $\lesssim 10$  m.y.), and occurred during rollback of the Indian slab or an immediate precursor. This may be a recurring geodynamic process that occurs in collision zones of this nature globally. Mantle samples from the TZ thus may be more widespread than generally realized, and provide a prime target for further research into subduction and deep-mantle processes.

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