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## Metals in Podiform Chromitite of Mantle Section of the Tibetan Ophiolite: What Do We Learn From Them?

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Ophiolitic podiform chromitites for a long time have been considered as “cumulates” formed by harzburgite-melt interaction and related melt mixing at the upper part of the suboceanic mantle to the Moho transition zone. Within many existing concepts, which are in a focus of this workshop, there is one suggesting that some portion of chromitites originate from deep mantle, where Cr-spinel was represented by its high-pressure polymorph with Ca-ferrite ( $\text{Ca}^{2+}\text{Fe}^{3+}_2\text{O}_4$ ) structure, or these high-pressure chromitites are products of mantle recycling containing relicts of ultrahigh pressure minerals. Unusual accessory minerals in podiform chromitite are: diamond, Fe-Ti alloy, FeO, TiO,  $\text{FeTiSi}_2$  – zangoite, coesite pseudomorphous after stishovite, TiN - osbornite, cBN - qingsongite,  $\text{TiO}_2$  II, Cr-spinel, with exsolution of coesite and diopside (a precursor is CF type of Cr-spinel) that require depth of > 250–380 km for their formation.

We have recently made a progress in studying valence of Cr in Cr-spinel from massif chromitite ore, and metals in the sample where we previously found cBN, TiN and Fe-Ti-silicide. We have studied chromium spinel [(wt%):  $\text{TiO}_2 = 0.30$ ,  $\text{Al}_2\text{O}_3 = 11.15$ ,  $\text{Cr}_2\text{O}_3 = 59.66$ ,  $\text{FeO} = 12.27$ ,  $\text{MnO} = 0.18$ ,  $\text{MgO} = 15.97$ ,  $\text{NiO} = 0.16$ ] with synchrotron assisted XANES technique (Brook Haven National Laboratory) to determine valences of chromium. The XANES studies revealed presence of ~7% of  $\text{Cr}^{+2}$ . Although the valence and behavior of Cr in deep mantle has not been studied extensively, with the synchrotron XANES studies we have found possible additional confirmation that the  $\text{Fe}^{3+}/\sum\text{Fe} = 0.42$  in Cr-spinel is related to  $\text{Fe}^{2+}$  disproportionation caused by high pressures. The phenomenon of pressure-induced crystallographic

stabilization of  $\text{Fe}^{3+}$  via disproportionation of  $\text{Fe}^{2+}$  into  $\text{Fe}^{3+}$  and precipitation of FeO (e.g., Frost et al., 2004) implies a low  $f_{\text{O}_2}$  rather than a high  $f_{\text{O}_2}$ . Otherwise, at such a high level of  $\text{Fe}^{+3}$ , one would expect to have only  $\text{Cr}^{+3}$  cations in the Cr-spinel structure. Upon decompression and stabilization of upper-mantle minerals with abundant  $\text{Fe}^{2+}$  sites, the  $\text{Fe}^{3+}$  and FeO react in the reverse direction of the  $\text{Fe}^{2+}$  disproportionation (Frost et al., 2004):  $2\text{Fe}^{3+} + \text{FeO} \rightarrow 3\text{Fe}^{2+}$ . If all FeO were to be consumed, the  $f_{\text{O}_2}$  would rise to the observed values of the upper mantle. However, in our sample, inclusions of FeO are found in coesite and in chromite. Therefore, this strongly support that such a reaction may have occurred in a high-pressure polymorph of chromite, with CF structure at depth ~380 km in the upper mantle.

Another evidence of highly reduced conditions is presence of TiO in association with the mineralogical assemblage of c-BN, TiN, FeTi and  $\text{FeTiSi}_2$ . TEM studies showed that native Ti in the sample of interests, is alpha-Ti (hexagonal symmetry) which synthetic analogues, exists in the wide range of temperatures (0~900°C) and pressures (0.1~8 GPa). Mineral zangoite -  $\text{FeTiSi}_2$  is a low pressure and high-temperature phase, although no experimental data at high pressures are available. There is no doubt, that exotic mineralogy in Tibetan chromitites, particularly nitrides and metals are important indicators of both high P and/or only high T conditions; they were crystallized in mantle transition zone regions with very low  $f_{\text{O}_2}$ . However, further search for samples with clear (“in-city”) relationships between host rock-forming minerals and exotic minerals should not be ignored.

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