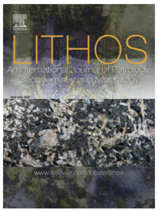
Lithos 262 (2016) 213–231

Contents lists available at ScienceDirect

Lithos

journal homepage: www.elsevier.com/locate/lithos



# Skarn formation and trace elements in garnet and associated minerals from Zhibula copper deposit, Gangdese Belt, southern Tibet

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## ARTICLE INFO

*Article history:*
Received 16 April 2016
Accepted 10 July 2016
Available online 20 July 2016

*Keywords:*
Zhibula
Gangdese belt
Southern Tibet
Garnet
Trace element substitution

## ABSTRACT

Trace element concentrations in garnet and associated minerals from the mid-Miocene Zhibula Cu skarn, Gangdese Belt, Tibet reflect a diversity of local environments, evolving fluid parameters and partitioning with coexisting minerals. Exoskarn occurs as massive but narrow intervals within a Lower Jurassic volcano-sedimentary sequence containing limestone, the main skarn protolith. Endoskarn is present at the contact with mid-Miocene granodiorite dikes. Prograde skarn associations are garnet-dominant but also include diopside-dominant pyroxene in variable amounts. Garnet compositions in exoskarn change from andradite (And)- to grossular (Gr)-dominant from the massive intervals to bands/lenses within marble/tuff, but not in endoskarn. In both cases however, associations at the protolith contact include anorthite and wollastonite, both indicative of skarnoid or distal (relative to fluid source) skarn formation. Exoskarns also contain vesuvianite. Retrograde clinozoisite, actinolite and chlorite replace pre-existing skarn minerals. Garnet displays brecciation and replacement by Al-richer garnet. Depending on partitioning among coexisting minerals, chondrite-normalised REY (REE + Y) fractionation trends for garnet depict endo- to exoskarn diversity, the dominance of And- vs. Gr-rich garnet (in turn related to proximal-to-distal relationship to fluid source), as well as prograde-to-retrograde evolution in the same sample. A strong variation in Eu-anomaly, from positive to negative, in And-dominant garnet can be correlated with variation in salinity of ore-forming fluids, concordant with published fluid inclusion data. Trends depicted by And- and Gr-dominant garnets are consistent with published data from skarns elsewhere, in which the dominant substitution mechanism for REY is YAG-type. Zhibula garnets are enriched in a range of trace elements less commonly reported, including W, Sn, and As, but also Mo (as high as 730 ppm), an element seldom analysed for in silicates. Molybdenum, W, and Sn display excellent co-correlation and shared zonation patterns on LA–ICP–MS maps of garnet, indicating substitution in the crystal lattice. As well as assisting in interpreting skarn evolution in time and space, and providing constraints on ore genesis, the trace element data for garnet explain the range of colours observed. The discovery of garnets carrying significant concentrations of W, Sn and Mo is a valuable finding that deserves evaluation in post-collisional skarns elsewhere, and is potentially of critical significance in prospecting. Together with a conspicuous trace ore mineral signature, garnet compositions at Zhibula support a genetic connection and sharing of ore-forming fluids between the skarn and the Qulong porphyry Cu-Mo deposit, 2 km to the north. Within the Gangdese belt, or in analogous settings elsewhere, the presence of deep-seated porphyry mineralization beneath exposed skarns could be tested for by studying garnet chemistry. As more data become available, such trace element signatures could be viable tools for distinguishing barren from mineralized skarn systems.

## 1. Introduction

Garnet, typically the main component of skarn mineralization, is a highly refractory mineral that incorporates a broad range of trace elements at concentrations measurable by laser-ablation inductively-coupled plasma mass spectrometry (LA–ICP–MS) (Gaspar et al., 2008; Ismail et al., 2014; Peng et al., 2015; Smith et al., 2004; Zhai et al., 2014). This makes garnet an attractive target to constrain ore-forming

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http://dx.doi.org/10.1016/j.lithos.2016.07.010

processes and derive constraints on the sequence of mineralizing events.

In this contribution, we address the mineralogy of the mid-Miocene Zhibula Cu skarn, Gangdese Belt, Tibet (Li et al., 2005; Xiao et al., 2011; Xu et al., 2014, 2016a, 2016b; Yao et al., 2015). Zhibula is a relatively recent discovery in a frontier mineral province of increasing economic significance. The relationships with distinct protoliths, and relative lack of deformation in the area, make it a suitable study case to understand the mineralogical and geochemical response to evolving conditions during skarn formation. We set out to show that the distribution of trace elements, including rare earth elements and yttrium (hereafter REY) in garnet and associated minerals, including pyroxene, vesuvianite and clinozoisite, evolves systematically in both space and time. At Zhibula as in most other skarns, individual garnet grains record multiple events, and are characteristically composed of zones of different colours (Xu et al., 2014, 2016a). We show here that these colour variations are linked to variation in both major and trace elements, and do not reflect a simple prograde to retrograde evolution. We also set out to address trace element partitioning between garnet and co-existing minerals and determine whether the concentrations of trace elements less commonly reported in garnet, including the 'granitophile' elements W, Sn and Mo, can be valuable in constraining skarn-forming processes, and how these may be incorporated and retained within the garnet structure. A further objective is to demonstrate relationships and commonality of ore-forming fluids between skarn and contemporaneous porphyry-style mineralization. The recognition of evidence preserved in skarn garnet for underlying porphyry mineralisation at depth has considerable potential value for mineral exploration in complex, challenging terranes such as the Gangdese Belt and elsewhere.

## 2. Geological background

Indian–Asian continental collision in the early Tertiary, and subsequent northwards movement of the Indian continent created the Himalayan–Tibetan plateau (Fig. 1a; Dewey and Burke, 1973; Yin and Harrison, 2000). The Lhasa terrane is divided into the northern Lhasa, central Lhasa, and southern Lhasa subterranes, which are separated from one another by the Shiquan River–Nam Tso Mélange Zone (SNMZ), and Luobadui–Milashan Fault (LMF) (Fig. 1b; Zhu et al., 2009). Sedimentary cover in the southern Lhasa subterrane is dominated by clastic sedimentary rocks, basalts, and silicic volcanic rocks of Lower Jurassic Yeba Formation, Upper Jurassic–Cretaceous volcano–sedimentary strata (Pan et al., 2004; Zhu et al., 2008), and the Paleogene Linzizong volcanic succession (Mo et al., 2008).

The Gangdese belt, host for mineralization described in this contribution, is located to the east of the 1000 km-long Gangdese tectonic–magmatic belt in the southern Lhasa sub-terrane, which underwent a complex tectonic evolution from Jurassic to Cretaceous Neo-Tethyan oceanic subduction, through Cenozoic Indian — Asian continental main-collision, to late-collision, and post-collision stages (Hou et al., 2004, 2011; Yin and Harrison, 2000; Zheng et al., 2015). Multiple episodes of magmatic activity occurred during this period, including events during the Early Cretaceous (130–100 Ma), Late Cretaceous (100–80 Ma), Paleocene to Eocene (65–41 Ma), and Oligocene to Miocene (33–13 Ma) (Wen et al., 2008; Zhu et al., 2011). Post-collisional granitoids emplacement occurred between 26 and 13 Ma, peaking at 16 ± 1 Ma (Chung et al., 2009; Hou et al., 2004; Zheng et al., 2004). These intrusive bodies are associated with a large number of Miocene porphyry Cu–Mo deposits. Their distribution within the belt is close to EW-trending, whereas the main ore-controlling structures are compound NE-trending fracture zones with multiphase and inherited characteristics (Zheng et al., 2004). Porphyry and skarn deposits are the most important mineralization types in this belt. Significant resources include the Xiongcun Cu–Au porphyry (>2.4 Mt Cu, >200 t of Au metal; Lang et al., 2014), Qulong Cu–Mo porphyry deposit (10 Mt of Cu and 0.44 Mt of Mo metal; 16 Ma, Zheng et al., 2015), and Jiama Cu–Mo–Au–Ag–Pb–Zn porphyry–skarn deposit (5 Mt of Cu, 0.55 Mt of Mo, 105 t of Au, 7000 t Ag, and 0.56 Mt of Pb + Zn metal; 15 Ma, Tang et al., 2011) (Fig. 1b).

## 3. Ore deposit geology

The Cu skarn at Zhibula is one of the smallest in the region with a resource of only 0.32 Mt Cu metal at an average grade of 1.64% (Li et al., 2012). The Zhibula deposit is located just 2 km south of the larger Cu–Mo porphyry deposit at Qulong (Fig. 1c). The Zhibula skarn has an E-W strike of ~3 km, and is hosted within the Yeba Formation, a volcano-sedimentary sequence formed during the Early to Middle Jurassic (U–Pb zircon age of 174.4 ± 1.7 Ma; Dong et al., 2006). The lithologies in the Yeba Formation are sub-vertical but with a sub-fold, syncline and faulted structure within the deposit area (e.g., Wang et al., 2015). Such deformation is attributed to geological events associated with Neo–Tethyan oceanic subduction in the Late Cretaceous (94–85 Ma), followed by Indian — Asian continental collision during the Eocene (50 Ma; Zhong et al., 2013). The lithology includes both intermediate rocks and felsic tuffs interbedded with lavas, volcanoclastic rocks, meta-sandstone and limestone (Yang et al., 2009). Zhibula deposit is hosted within the intermediate member that comprises limestone beds of variable thickness, from a few metres up ~100 m. The tuffs are recognised as being modified during either regional metamorphism at greenschist facies (Zhong et al., 2013), or by contact metamorphism (and thus named as 'felsic-hornfels', 'spotted-' and 'biotite-hornfels'; Wang et al., 2015).

Two groups of faults are present within the mine area: (i) WNW-trending, sub-vertical (70–85° dip) thrust faults which are considered to control the geometry of the orebodies as layers and less commonly lenticular bodies; and (ii) NW-trending and subparallel faults, considered to post-date the mineralisation (Fig. 2a). In detail, the orebodies also include breccias and fault gouge filling of both skarn and mineralization (Li et al., 2012). Mineralisation is closely associated with skarns, of which garnet skarn is the most abundant (e.g., Xu et al., 2014). The skarn has recently been recognised to comprise a more complex assemblage of minerals, including pyroxene, epidote and wollastonite together with garnet (Xu et al., 2016a). An orefield-scale zonation based upon variation in garnet colour is also suggested (Xu et al., 2014, 2016a). The ore consists of Cu–Fe-sulphides (chalcopyrite, minor bornite and chalcocite), minor molybdenite, sphalerite and galena, all of which are associated with either pyrrhotite and/or pyrite (e.g., Wang et al., 2015; Xu et al., 2016a).

Xu et al. (2016a) provide constraints for skarn and ore formation based upon fluid inclusions data, including fluid inclusions hosted by garnet, epidote, quartz and calcite, as well as the stable isotope signatures of sulphides, garnet, calcite and quartz. Fluid inclusion data indicate that skarn formation, from prograde to retrograde, is characterised by two distinct fluids: (i) high-temperature (405–667 °C), high salinity (up to 44.0 wt% NaCl equiv.); and (ii) lower temperature (194–420 °C) and moderate salinity (10.1–18.3 and 30.0–44.2 wt% NaCl equiv.). Stable isotope data: $\delta^{34}S$ ($-0.1$ to $-6.8$‰); $\delta D_{H2O}$ ($-91$ to $-159$‰); and $\delta^{18}O_{H2O}$ (1.5 to 9.2‰), confirm skarn and ore-forming fluids as magmatic-hydrothermal (Xu et al., 2016a). She et al. (2005) reached similar conclusions on the source of fluids in a comparative isotope study of several deposits including Zhibula and Qulong.

In the Zhibula orefield, intrusions that can be related to skarn mineralisation are scarce, and occur only as narrow dikes or apophyses of monzogranite and granodiorite, no more than a few metres wide, intersected in drillholes below >400 m. There is an overlap in zircon U–Pb ages obtained on Early to Middle Miocene post-collisional granitoids from Qulong (SHRIMP, 16.38 ± 0.40 Ma, Wang et al., 2006) and Zhibula (SIMS, 16.9 ± 0.3 Ma, Xu et al., 2016b) implying that the deposits are genetically related to the same event.