Growth of hydrothermal baddeleyite and zircon in different stages of skarnization

WEN WINSTON ZHAO¹, MEI-FU ZHOU¹,*, AND WEI TERRY CHEN²

¹Department of Earth Sciences, The University of Hong Kong, Pokfulam Road, Hong Kong, China
²State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, China

ABSTRACT

Both prograde and retrograde skarns from the Tengtie iron deposit, South China, contain rounded, euhedral, and anhedral zircon grains. Rounded grains were originally derived from detritus in carbonate rocks and were incorporated into the skarns. Euhedral and anhedral crystals are intergrown with various skarn minerals and are clearly hydrothermal in origin. These hydrothermal grains have low (Sm/La)₀ ratios and high La contents relative to typical magmatic ones and display flat LREE and subdued flattening of HREE chondrite-normalized patterns, similar to those of zircon crystallized from Zr-saturated fluids. Prograde skarns also contain baaddeleyite rimed by zircon, which record a period of low Si activity during prograde skarnization relative to original magmatic-hydrothermal fluids. Hydrothermal zircon grains from Tengtie have variable Eu anomalies and slightly positive Ce anomalies, indicating that they may have crystallized from highly heterogeneous, but generally reducing fluids. They have low δ¹⁸O values (~5.1 to ~2.7 ‰), suggesting the involvement of meteoric fluids. Fluorine-rich fluids played an important role in remobilizing and transporting some high field strength elements (HFSE), including Zr, from the host granites into the skarn system. Reaction between HFSE-bearing fluids and carbonate rocks at the prograde stage decomposed F complexes to deposit HFSE-rich skarn minerals and baraddeleyite. At the retrograde stage, alteration of the HFSE-rich skarn minerals released HFSE, including Zr and Sn, consequently producing a mineral assemblage of zircon, cassiterite, and retrograde skarn minerals. Dating results of zircons from the Tengtie skarn system by SIMS indicates roughly less than several million years duration for skarnization. Our study indicates that Zr was not only mobile locally under favorable conditions, but was also readily transported and deposited in different stages of skarnization.

Keywords: Baddeleyite, zircon, oxygen isotope, U-Pb geochronology, skarnization, HFSE

INTRODUCTION

Being one of the high field strength elements (HFSE), zirconium (Zr) has long been considered to be immobile during metamorphism or alteration (e.g., Ague 1994, 2003, 2011; Bebout et al. 1999; Breeding et al. 2004; Penniston-Dorland and Ferry 2008), and it is widely used for petrogenetic studies (e.g., Pearce and Cann 1973; Floyd and Winchester 1975; Drummond et al. 1996; Pearce 1996, 2008; Solar and Brown 2001; Ernst and Buchan 2003). However, an increasing body of evidence has shown that Zr can be mobilized by hydrothermal fluids and re-deposited as hydrothermal Zr-bearing minerals (e.g., Kerrich and King 1993; Nesbitt et al. 1999; Hoskin 2005; Pettke et al. 2005; Geissler et al. 2007; Lawrie et al. 2007; Pelliter et al. 2007; Kusiai et al. 2009; Toscano et al. 2014; Deng et al. 2015).

Skarns typically exhibit a temporal evolution with early-formed high-temperature phases precipitated from magmatic fluids overprinting isochemical thermal metamorphic marble and hornfels, in turn variably replaced by late low-temperature assemblages involved in meteoric and/or basinal fluids (Einaudi et al. 1981; Meinert et al. 2005; Rubenach 2013). Some studies have reported hydrothermal Zr-bearing minerals in contact zones between igneous rocks and carbonate sedimentary rocks (e.g., Gieré 1986; Rubin et al. 1989, 1993; Gieré and Williams 1992; Moine et al. 1998; Deng et al. 2015). Specifically, hydrothermal zircons in these skarns show various morphologies, and sometimes contain skarn mineral inclusions (e.g., Rubin et al. 1989; Deng et al. 2015). Furthermore, Rubin et al. (1993) proposed that leaching of igneous source rocks by F-rich hydrothermal fluids could be the major control on the precipitation of zircon in associated skarn assemblages. Recently, Deng et al. (2015) analyzed hydrothermal zircon by LA-ICP-MS showing a genetic relationship between iron skarn mineralization and the coeval magmatism. However, it remains unclear whether Zr-bearing minerals can form during different stages of skarnization, and what controls the growth of these minerals corresponding to the skarnization. Moreover, understanding the formation of Zr-bearing minerals in skarns can place significant constraints on the mechanism of mobilization, transportation, and deposition of Zr, and the fluid evolution of skarn systems, not only because of their presence, but also because they would be precisely dated using the U-Pb isotopic system to place tight temporal constraints on the timing of the ore-forming hydrothermal system if high precision of techniques were achieved.

Here, we report findings of hydrothermal baddeleyite and zircon in mineralized skarns from the Tengtie iron deposit,