Possible new Ca-REE-Bi phosphate minerals from a tungsten-rich calcilicate skarn, Sierra Nevada Mountains, California

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ABSTRACT

Scanning electron microscope and electron microprobe analyses of 3 to 15 μm diameter grains present within a garnet-quartz granofels from a tungsten skarn reveal the possible existence of at least two new rare earth element (REE)-bearing phosphate phases: Ca(Ce,La,Bi,Nd)₆[(P,As)O₄]₂(OH)₂ and Ca(La,Ce,Nd,Pr,Bi)₂[(P,As)O₄]₂(OH)₂. The analyzed REEs constitute up to 50 wt% of the phases; bismuth oxide contents range from 4.1 to 16.1 wt%. Structural data has proved impossible to obtain from these tiny grains, presumably due to radiation damage by thorium decay. These potentially new phosphate minerals are present within alteration assemblages of REE-rich epidote crystals, as well as along grain boundaries and cracks cross-cutting the quartz-garnet host rock. Association with the zoelite brebsterite-Ba suggests that these hydroxyl phosphates formed during water-rich, low-temperature, retrograde mineralization in the skarn environment.

Keywords: Phosphate mineral, rare earth element, bismuth, Sierra Nevada, tungsten, skarn

INTRODUCTION

A detailed mineralogic examination of samples collected from a small tungsten mine in the western foothills of the Sierra Nevada Mountains in California reveals the possible presence of various new minerals. In particular, distinct phosphate phases containing various abundances of the REE, bismuth, and hydroxyl appear to coexist along grain boundaries and cracks, as well as within alteration assemblages replacing epidote cores (Berekian 2008). Structural data have proven impossible to collect; moreover, the collection of high-quality chemical data is challenged by the small grain size (<15 μm). In this paper, we present chemical data that may help define two new REE-rich phosphate phases. REE-phosphates include monazite, xenotime, and varieties of apatite (Pan and Fleet 2002; Spear and Pyle 2002); naturally occurring bismuth-bearing phosphates have also been identified. REE-bearing calcium-bismuth phosphors have been synthesized (Jiao et al. 2013) but naturally occurring REE-bearing phosphates having high bismuth contents are currently unknown.

Calcilicate-hosted skarns are scattered throughout the Sierra Nevada batholith, having formed where Mesozoic are plutons intruded Neoproterozoic to early Mesozoic carbonate rocks present along the southwestern margin of Laurentia (Newberry 1980, 1998). Skarn formation is characterized by an initial period of prograde metamorphism to temperatures of ~400–650 °C (Stage 1); a period of thermal equilibration between host rock and intruding pluton (Stage 2); followed by retrograde mineralization (Stage 3) marked by the invasion of meteoric and/or metamorphic fluids that promote cooling and the precipitation of metals (Einaudi et al. 1981; Corbett and Leach 1998). Some Sierra Nevada skarns host ore deposits that have proven to be economically viable, most significantly the Pine Creek mine from which more than 16 million tons of tungsten-bearing ore (0.6% WO₃) and 31 thousand tons of molybdenum and copper were extracted (Newberry 1982; Kurtak 2007). Sierra Nevada skarns were first mined for tungsten during World War I, with production resuming during both World War II and the Korean War (Krauskopf 1953; Newberry 1980). Production in Sierra Nevada skarns continued at decreased levels until 1990 when cheaper, foreign sources of tungsten became available (Kurtak 2007).

The Consolidated Tungsten Mine (CTM), located in the western foothills near the northern edge of Tulare Co., produced ~17 thousand tons of tungsten-bearing ore (~2% WO₃) between 1941 and 1957 (Krauskopf 1953). Of the Sierra Nevada tungsten mines, the CTM was among the top 20 producing mines by tonnage, although it was not one of the largest mines geographically (Newberry 1980). The CTM skarn (11S 31096E0, UTM 4056628N) formed in the aureole surrounding a 163 ± 1.5 Ma granodiorite pluton intruded into the northeastern tip of the Lake Kaweah pendant (Clemens-Knot 2013). Based on mineral assemblages and chemistries, CTM skarn formation is estimated to have occurred at temperatures less than 700 °C, pressures of ~3–4 kbar, low XCO₂, and low fO₂ (Newberry 1980; Berekian 2008).

METHOD

Newberry (1980) mapped and described mineral assemblages defining the lithologic zonation within the CTM skarn. The mine is currently sealed, so samples of tremolite-diopside-epidote-quartz-garnet granofels, characteristic of the inner skarn, were collected with landowners permission from the tailings pile (Berekian 2008). Although tailings are expected to be poor in ore minerals, rare scheelite crystals surrounded by thin calcite rims were observed. Multiple grains of the