Manganiferous pyroxenes and pyroxenoids from three Pb—Zn—Cu skarn deposits

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Abstract. Samples from the Pb—Zn—Cu skarns of M. Civillina (Italy), Valle del Temperino (Italy), and Empire Mine (New Mexico, USA) have been analysed for their pyroxenes and pyroxenoids. The samples were collected immediately adjacent to the marble-skarn replacement front. All contain manganiferous pyroxenoids and manganese-rich Ca-pyroxenes. The pyroxenes from each deposit form distinct groups of compositions within the diopside-hedenbergite-johannsenite triangle, with no apparent miscibility gap. Diopside contents usually are below 15 mole percent. Fibrous bustamite occurs as monomineralic zones in the Empire and in the Temperino deposit. Although rhodonite may be a primary phase in some samples from the Empire Mine, it is commonly of secondary origin in the Empire Mine and in the Civillina deposit. Its formation from manganiferous clinopyroxenes is either due to increasing Mn activity in the hydrothermal skarn solution or to higher X(CO₂) in the vapour phase. When rhodonite is formed within clinopyroxenes as submicroscopic lamellae that eventually replace the whole host crystal, resulting compositions lie in the miscibility gap between rhodonite and bustamite. Textural relations indicate the replacement reaction: johannsenite + CO₂ = rhodonite + calcite + quartz. Equilibrium temperatures for this reaction have been calculated by using estimated thermochemical data for johannsenite, giving a T(eq) = 385 °C for X(CO₂) = 0.1 at P(tot) = 1 kbar. Taking into consideration the reduced activity of Mn in rhodonite and of Ca in calcite, both buffered by the johannsenite, the temperature is increased for about 15 °C at X(CO₂) = 0.01. At lower temperatures, where johannsenite is stable, the X(CO₂) is confined to values below 0.01. Despite the mineralogical similarities of the three deposits differences in the development of the manganiferous skarns can be depicted.

Introduction

Several studies on pyroxene skarn mineralogy have shown that the composition of the clinopyroxenes is related to the associated ore minerals (Einaudi et al. 1981; Meinert 1980). Manganiferous clinopyroxene-andradite-Mn pyroxenoid-assemblages are typical for Pb—Zn—Cu skarns. To gain more detailed information on the extent of Mn clinopyroxene solid solutions and their paragenetic relationships with manganiferous pyroxenoids and other coexisting skarn minerals, a number of Mn-rich samples from three different Pb—Zn skarns were investigated by standard optical methods, electron microprobe analysis, and SEM techniques.

Samples have been collected at the following deposits, classified as calcic replacement skarns: (a) Valle del Temperino near Campiglia Marittima (Tuscany, Italy, = VT samples), (b) the Empire Mine near Santa Rita (New Mexico, USA, = Em samples), and (c) Monte Civillina (Venetia, N-Italy, = Mn 26 samples). Some additional samples were collected on the dumps of the Princess Mine near Santa Rita (= Pr samples).

Geologic setting of the deposits

Empire Mine (and Princess Mine)

The mineralogy and geology of the Pb—Zn—Cu skarn deposits around the Hanover-Fierro pluton in New Mexico have been described by Schmitt (1939), Jones et al. (1967), and Hernon and Jones (1968), and others. The two mines, which have been mined quite extensively, are situated along the south-western border of the Hanover-Fierro pluton within the limestones of Mississippian to Pennsylvanian age. Skarn and ore mineralization are located along faults and dikes of post-pluton age. Schmitt’s (1939) description of the geology and mineralogy of the Pewabic Mine also largely applies to the nearby Empire Mine. A short description of the skarn mineral assemblages of the Empire Mine with some genetic considerations was given by Burt (1978). Clinopyroxenes from less manganiferous portions of the skarn at the Empire Mine and at Temperino have been analysed by Allen and Fahey (1957) and Burton et al. (1982). The samples for the present study were taken in the area called Annie Fox Quarry, where irregular skarn bodies occur along and within the crystalline limestone. With two exceptions (Em 12 and 13), only samples from the immediate contact between the skarn and the marble were chosen for microprobe analyses because the most manganiferous phases are present right along the skarn-marble replacement front (Burt 1978).

Monte Civillina

The only detailed study on the Civillina skarn was published by Schiavinato (1953), who also gave an analysis of rather pure johannsenite that was previously reported as bustamite. Several small skarn bodies were formed within Anisian limestones (“Calcare di Monte Spitz”) in the vicinity of Ladinian volcanic dikes in the sediments. They form
small irregular masses that are not in direct contact with the volcanic rocks. No direct relationship of the skarn bodies to faults or dikes have been recognized. The area has been mapped and described by Barbieri et al. (1980), who report at least three different Mn skarn bodies.

Valle del Temperino

The deposit of Valle del Temperino has been known for its attractive aggregates of radiating and spherical clinopyroxene which were originally taken for bustamite (Aloisi 1926). The ore bearing skarn bodies near Campiglia Maritima lie within Liassic crystalline limestones which have been intruded by Mio-Pliocene acid rocks. The Valle del Temperino skarn, where all the samples were taken from, is spatially related to NW-SE striking porphyritic monzonitic dikes. The geology and zoning of the skarn body has been described by Giamlini (1955) and by Tanelli (1977). More recent studies (Tanelli 1977; Corsini et al. 1980) are mainly concerned with the ore minerals. Clinopyroxene skarns enriched in manganese were collected in blocks containing both skarn and marble. They form radiating masses of varying color with lenses of pinkish pyroxenoids.

Description of samples

Empire Mine (and Princess Mine)

Most samples show a small-scale zonation with an andradite-clinopyroxene-bustamite-rhodonite sequence of mainly monomineralic layers towards the replacement front (Fig. 1). The zones are usually only a few millimetres thick. Bustamite and/or rhodonite may occasionally be missing and andradite zones may occur next to the bustamite zone (see also Burt 1978). Ore minerals (sphalerite, pyrite, galena) are enriched in the clinopyroxene zones. Unfortunately large portions of the skarns have been altered to carbonate to various degrees by post-skarn processes. This often hindered the determination of the primary mineral assemblages and no chemical analyses could be obtained. However, primary textures usually are preserved due to pseudomorphic replacement of the silicate phases.

Microscopic description

Clinopyroxene: The colorless crystals have four habits: short unoriented prisms; blades with no preferred orientation; elongated prisms oriented towards the contact; and aggregates of radiating clusters. Twinning of the crystals is common in samples from the Princess Mine. Altered clinopyroxene aggregates are preserved as “ghost structures” in andradite grains. These textures indicate at least two generations of both andradite and clinopyroxene. The clinopyroxenes are commonly replaced by rhodonite and late calcite. Andradite and sphalerite form thin zones or are scattered within clinopyroxene and bustamite zones.

Bustamite: The bustamite forms thin-prismatic to fibrous radiating aggregates oriented towards the skarn replacement front. Bladed crystals with random orientations are less common. In thin section bustamite is usually colorless, although slight coloration due to a fine pigmentation may occur. In zones with densely intergrown fibrous bustamite, clusters of coarse platy bustamite crystals occur. These coexist with magnetite and quartz, and contain numerous small, elongate solid inclusions (exsolution?). Bustamite is not observed coexisting with rhodonite.

Rhodonite: Rhodonite is found primarily adjacent to the contact either as idiomorphic crystals coexisting with calcite and quartz or intergrown with clinopyroxene showing replacement phenomena. The grains are pinkish in hand specimen, but colorless in thin section. It commonly shows anomalously blue birefringence. Twinning is frequent and the extinction often cloudy.

Andradite: Andradite is present either as euhedral crystals forming monomineralic zones or as relics included in pyroxene or bustamite. The garnets are commonly birefringent, especially along the edges. Their color is yellow, but colorless cores with inclusions of bladed or fibrous crystals may occur, possibly indicating replacement of earlier clinopyroxene and wollastonite. No microprobe analyses could be obtained of these included phases because of their complete alteration. Other textures indicate a later replacement of garnet by clinopyroxene (Fig. 2 a), although the inclusions suggest an earlier replacement of the clinopyroxene. No obvious paragenetic relationships seem to exist between andradite and rhodonite. However, bustamite frequently has overgrown the garnet. The decomposition of andradite into a pseudomorph composed