A Model for the Genesis of Distal Zinc Skarns based on data for the Mochito Deposit, Honduras

I.M. Samson*
Earth and Environmental Sciences, University of Windsor, Windsor, Ontario, Canada
Iain.Samsonl@gmail.com

A.E. Williams-Jones
Earth and Planetary Sciences, McGill University, Montreal, Québec, Canada.

K. Ault
Aurum Exploration, Kells, County Meath, Republic of Ireland.

J.E. Gagnon
Earth and Environmental Sciences, University of Windsor, Windsor, Ontario, Canada.

B.J. Fryer
Earth and Environmental Sciences, University of Windsor, Windsor, Ontario, Canada.

Summary

This work develops a model for the genesis of zinc skarns based on a combination of petrographic, whole-rock geochemical, isotopic and fluid inclusion (including microthermometric, GC and LA-ICPMS) data from the Mochito deposit in Honduras. These data are used in conjunction with thermodynamic modeling of phase relationships and ore mineral solubility to show that, contrary to conventional wisdom, distal zinc skarns form from dominantly magmatic rather than mixed magmatic and formational fluids, that ore deposition and skarn formation are penecontemporaneous. Ore deposition occurs at high fluid/rock ratios in response to the sharp increase in pH that occurs during interaction of the fluids with limestone.

Introduction

Distal zinc skarns pose an important challenge not presented by other skarn types because, in many cases, there is no apparent association with felsic intrusions and consequently the widely held view that skarn-forming fluids are dominantly magmatic may not apply. Indeed, it seems reasonable to expect, as a number of studies have suggested, that external fluids, e.g., meteoric waters or basinal brines, become increasingly important, and even dominant, with increasing distance from the potential igneous source. In this work, we address this issue of the nature of the ore-forming fluid using LA-ICPMS analyses of fluid inclusions from the Mochito deposit in Honduras and, in combination with other geochemical data and thermodynamic calculations, develop a model for zinc skarns that calls for penecontemporaneous skarn formation and ore deposition by magmatic fluids in response to interaction with limestone.

Mochito Geology and Geochemistry

The Mochito deposit, Honduras, is a distal Zn-Pb-Ag skarn in which the economic mineralization (sphalerite and subordinate argentiferous galena) takes the form of mantos and chimneys dominated by garnet and pyroxene that replaced limestone and a mixed limestone-siliciclastic unit (mainly pyroxene), both of Late Cretaceous age. Except for a few variably altered, unmineralized diabase dykes, evidence of igneous activity is conspicuously absent. The nearest felsic igneous rocks, volcanics, outcrop ~13 km from the deposit. Early skarn, and skarn proximal to faults, consists dominantly of garnet that evolved from grandite with an average composition of Ad_{55} to andradite ($>Ad_{90}$), whereas the later skarn or skarn that developed distal from faults is composed mainly of pyroxene with an average composition of Hd_{70}. Deposition of these minerals was accompanied by magnetite, pyrrhotite, sphalerite and galena. Sphalerite in

garnet skarn is a low iron variety, whereas in pyroxene (the bulk of the sphalerite) and massive magnetite or pyrrhotite, it is enriched in iron.

Analyses of the whole-rock chemistry show that formation of grandite skarn involved large additions of all major elements, except Ca and K (present in very low concentrations) and most trace elements, whereas formation of andradite skarn involved losses of most of these elements, the notable exceptions being Ca and Fe, which were added. Mass changes in pyroxene skarn were not evaluated because of the heterogeneous nature of the precursor.

Primary fluid inclusions in grandite and associated low-iron sphalerite are interpreted to have been trapped at ~370 °C, based on their homogenization temperatures and isochoric projections to 500 bars, the assumed pressure obtained from stratigraphic reconstruction. These inclusions have a mean salinity of 14 wt.% NaCl eq. By contrast, primary inclusions in pyroxene and high-iron sphalerite were trapped at ~400 °C and have a mean salinity of 5 wt.% NaCl eq. The relatively opaque nature of the andradite prevented observation of fluid inclusions. Although there was no microthermometric evidence of the presence of incondensable gases, small proportions of CO_2, CH_4 and N_2 were detected by gas chromatographic analyses of the fluids released by crushing small samples of the host mineral. Carbon dioxide was the principal incondensable gas, with a mole fraction of 0.001. Based on LA-ICPMS analyses of individual fluid inclusions, Na and Ca were the principal metals in the fluids, followed by K and Mn (the data for Fe are highly variable). However, the proportions of Na and Ca vary greatly with the host mineral. The proportion of Ca is highest in inclusions in grandite, up to 90% of the cation total, whereas it is much lower in fluid inclusions hosted by low-iron sphalerite (< 60% of the cation total). Many sphalerite-hosted inclusions contain no detectable Ca. The proportion of K is less variable, being typically on the order of 10 to 20% of the cation total. Mean concentrations of the ore metals, Zn, Pb and Ag, for all grandite and sphalerite-hosted fluid inclusions were, 6,000, 900 and 50 ppm, respectively.. Statistically meaningful numbers of fluid inclusions were not analyzed in the other minerals.

Analyses of phase equilibria and related thermodynamic calculations indicate that the log fO_2 during the grandite and pyroxene skarn stages was >-30.3 and <-30.2, respectively. The pH during the grandite stage was ~5.0. In the absence of reliable data on the bulk fluid chemistry, a pH for the pyroxene stage could not be estimated. The Si content of the fluid is estimated to have been between 230 and 460 ppm, which, when related to the mass of Si added during grandite skarn formation, corresponds to a fluid:rock ratio of between 500:1 and 1000:1. Calculations of the solubility of sphalerite, galena and argentite based on the determined physicochemical characteristics of the putative ore fluid indicate that the ore metals were transported dominantly as chloride complexes and deposited primarily in response to an increase in pH.

Genetic Model

A model is proposed in which relatively oxidizing hydrothermal fluids exsolving from a magma at a depth of > 4 km interacted with limestones in the Mochito Graben during an episode of mid-Tertiary intra-plate extension. These fluids, which initially were moderately saline but became progressively more dilute due to crystallization of the magma, rose up faults created by the extension, and were cooled by the overlying sedimentary succession. Early skarn formed at comparatively low temperature (~ 370 □C) in an environment of high fluid flux proximal to the faults and was dominated by grandite because of the oxidizing nature of the fluids. With continued heating of the rocks by subsequent pulses of fluid, temperature increased and the locus of interaction expanded into unaltered graphite-bearing limestone distal to the faults, where lower fluid/rock ratios promoted buffering of the fluid to lower fO_2 and formation of pyroxene skarn. Ore mineral deposition, which began during formation of grandite skarn and

continued after formation of pyroxene skarn, occurred in response to the sharp increase in pH that accompanied neutralization of the fluid by limestone, and was dominated by low iron sphalerite. Galena, which was subordinate to sphalerite because of the much lower content of Pb of the fluid, incorporated significant Ag in its structure as a result of the failure of the fluid to saturate with argentite. Deposition of ore minerals reached a maximum after temperature had increased to ~400 °C and hydrothermal activity was focused in the lower fluid/rock ratio regime of pyroxene skarn formation, where lower fO_2 promoted the precipitation of iron-rich sphalerite.