

The origin of metasomatic fluids in skarns from La Maladeta (Central Pyrenees, Spain): C, O, H, S and Sr isotope compositions

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Introduction The origin of fluids involved in skarn formation has been of great interest to economic geologists for many years. It has been shown recently that some skarns contain significant amounts of precious metals, emphasizing their importance as gold prospects. Insights into the mechanisms that control the presence or absence of precious metals in such bodies can be obtained by comparing the geochemistry of barren and gold-bearing skarns from a given area. Apart from economic considerations, skarn mineralization provides important information on paleohydrological systems in certain parts of the Earth's crust. The present investigation is focussed on the stable and radiogenic isotope geochemistry of skarns from La Maladeta, Spain.

Geology The skarns investigated are spatially associated with the Maladeta batholith, a late Hercynian igneous complex with a Rb/Sr isochron age of 277 ± 7 Ma (Michard Vitrac *et al.*, 1980). The batholith comprises granodioritic rocks and subordinate gabbro-norites and two-mica granites and is situated in the central segment of the Pyrenean Axial Zone (Arán and Benasque Valleys, Spain). These magmas intruded Paleozoic rocks ranging from Cambrian and Ordovician to Carboniferous age although most of the rocks outcropping along the northern and southern flanks are Devonian limestones and marls. A thermal contact aureole more than 300-m wide overprinted previous effects of low grade (greenschist facies) regional metamorphism in this area. Peak contact metamorphism conditions were about 625°C and 2.5–3.5 kbar and these figures provide an upper P–T limit for skarn formation at La Maladeta (Delgado *et al.*, 1993a). Tectonic features of the area are related to the complex geologic history of the Pyrenees: pre-intrusive polyphase folding and E–W thrusting events of Hercynian age and the later E–W thrusting that gave rise to the physiographically

distinctive Pyrenean Range in Alpine time.

Skarns Along the northern contact of the Maladeta batholith there are several dozen skarns with sizes ranging from meters to tens of meters. Among them, three well-exposed and mineralogically distinct skarns were selected to compare their physical-chemical conditions of formation: Sarraera, Arties and Escunyau. These three skarns are assumed to be coeval and are located in a restricted area that extends less than 2 km along the contact of the pluton. The skarns are classical W-bearing, calcic, reduced, hedenbergitic skarns (Einaudi *et al.*, 1981) which are widespread throughout the Pyrenees. Their evolution may be divided into two major stages: (1) the development of a thick, monomineralic hedenbergitic zone (up to 45 m), and (2) formation of characteristic hydrated silicate phases together with sulfides and carbonates. The second stage accounts for much of the macroscopic differences observed between skarns: in the barren skarns at Arties and Escunyau, the second stage is characterized by the presence of axinite (B-rich silicate) and a significant lack of sulfides whereas in the Au-bearing skarn at Sarraera, axinite is absent and sulfides (mainly arsenopyrite and pyrrhotite) are volumetrically important.

Physical-chemical conditions of formation Detailed studies of mineralogy and phase equilibria were conducted in a search for identifiable characteristics that would distinguish the gold-bearing skarn from the other two. The oxidation state of the metasomatic fluid in all three skarns followed a common redox path, between NNO and QFM for a temperature interval from 625°C to 300°C. Sulfur fugacities were about 10^{-8} to 10^{-10} bar in the temperature range from 500 to 325°C. Volatile fluid speciation calculated from these ranges of f_{O_2} and f_S , show that the most important fluid species is H_2O with CO_2 and H_2S the most important carbon- and sulfur-bearing species, respectively. A

near neutral pH is constrained by the presence of muscovite + quartz + K-feldspar as a common assemblage in the three skarns. Fluid inclusion studies are seriously hampered by the intense alpine tectonization of the skarns, but the data at hand indicate a saline brine (22–34 wt.% eq. NaCl) system dominated by the binary NaCl–H₂O (Delgado, 1993; Delgado *et al.*, 1993b). The above measurements and calculations effectively rule-out changes in the prime intensive variables as an explanation for gold mineralization in the skarn at Sarraera and the absence of gold at Arties and Escunyuau.

Stable isotope compositions Fluids that would have been in C, O and S isotope equilibrium with minerals from the Sarraera skarn are all enriched in the heavy isotopes of these elements relative to solutions that would have been in equilibrium with minerals in the Arties and Escunyuau skarns. Some of the isotopic differences are small but nonetheless distinctive ($\delta^{34}\text{S}_{\text{Fluid}}$ between –1 and 2‰ in Arties and Escunyuau, and between 2 and 4‰ in Sarraera) and others are larger ($\delta^{18}\text{O}_{\text{Fluid}}$ between 6.5 and 9‰ in Arties and Escunyuau and between 9 and 11.5‰ in Sarraera). There are two apparent explanations for these data: (1) temperatures of mineral formation were significantly different in the different skarns and (2) the skarns formed in the presence of isotopically distinct fluids. The first possibility may be excluded if we consider that identical minerals from the three skarns which formed at the same temperature or over what should have been a very narrow temperature range are isotopically different. In the second case, the fluids responsible for Sarraera mineralization were consistently enriched in the heavier isotopes and presumably had a different origin and/or exchanged with different wall rocks prior to precipitating the skarn minerals. The most reasonable explanation of such isotopic data is existence of more than one fluid phase within the thermal contact aureole of the Maladeta batholith, on the scale of our study.

The hydrogen isotope composition of fluids calculated to be in equilibrium with the second-stage skarn minerals are very similar in all three skarns. As a consequence of possible greater susceptibility of the hydrogen isotopes to exchange processes and/or appropriate water/rock ratios, the last fluid present in the large system may have exchanged hydrogen isotopes with the hydrous minerals throughout the entire suite of skarns examined while leaving the other isotopic systems intact. The δD values of –20 to –35‰ for these fluids are heavier than those of typical magmatic fluids of but lighter than those

expected from dehydration of the regional metapelites. Few stable isotope studies have been undertaken to characterize the isotopic composition of Pyrenean rocks on a regional scale, making predictions about the sources of the fluids difficult. The observed range of values, however, is likely to reflect igneous or mixed igneous/metamorphic fluids. Single isotopic systems are not compatible with the compositions observed and most probably reflect mixing of fluids and/or variable exchange of fluids with distinct wall rocks. The tendency of the Sarraera fluids to be enriched in heavy isotopes of S, C and O may well reflect exchange with and/or significant fluid derivation from the metasedimentary rocks.

Strontium isotope compositions Strontium isotope analyses of second stage carbonates of the three skarns provide additional constraints on the fluid genesis as they reflect the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the fluids without fractionation effects due to temperature or any other physical-chemical process. On combining Sr and O isotope compositions for all the studied skarns as well as the potential end-member fluid sources, an interesting picture emerges. According to the initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the three main igneous lithologies of the batholith (Michard Vitrac *et al.*, 1980), the major source of strontium for the fluid appears to be the granodioritic rocks, with almost no contribution from the two-mica granites and gabbro-norites. Moreover, it appears that the fluids responsible for all the skarns studied had an important magmatic component, much more developed in the Arties and Escunyuau skarns than in the Sarraera skarn where a less radiogenic Sr and higher $\delta^{18}\text{O}$ source is indicated. If two-mica granites or gabbro-norites would have contributed a substantial proportion to the mineralizing fluid in Sarraera, we would expect more radiogenic strontium isotope ratios and if that were the case of gabbro-norites, we should see lower $\delta^{18}\text{O}$ values. The most plausible source that is compatible with the oxygen and strontium isotope ratios of Sarraera minerals compared with those from Arties and Escunyuau are the Devonian metacarbonates (marls and limestones) which are widespread throughout the region. However, we can not disregard the more-or-less important contribution of metapelitic rocks whose volume is not apparent in outcrops. This conclusion is in agreement with the work of Cardellach *et al.* (1992) who suggested a relation between Hercynian metasedimentary rocks (particularly those with As-Au anomalies) and late Hercynian As-Au rich veins and skarns.