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Geochemistry of zoned garnets from the San Pedro mine, Santa Fe County, New Mexico

by *Charles G. Lee* and *W. W. Atkinson, Jr.*, Department of Geological Sciences, University of Colorado, Boulder, CO 80309

Abstract

The San Pedro mine, in north-central New Mexico, contains chalcopyrite-bearing garnetite skarn as replacements of 14 favorable carbonate beds. Mineralization is concentrated along or near marble line boundary surfaces between garnet and marble in each bed, such that orebodies are arranged in a manto configuration, stacked one above another.

Early high-temperature contact metamorphism resulted in the formation of iron-poor calc-silicates in marble and grossularitic garnet (gr) in interbedded orbicular hornfels. Subsequent infiltration of an iron, silica, and metal-bearing magmatohydrothermal fluid caused the metasomatic replacement of marble by massive garnet-chalcopyrite skarn. This main stage of disseminated ore deposition and skarn formation was in turn followed by a low-temperature skarn-destructive phase involving the entry of meteoric water into the hydrothermal system, which produced a quartz-calcite-hematite-chlorite-chalcopyrite alteration assemblage and second-generation garnet veinlets and vug linings.

Microprobe analysis of some zoned and unzoned San Pedro garnets provides an important insight into the nature of short- and long-term variation in hydrothermal fluid chemistry. Early main-stage first-generation garnets have andradite cores and zoned rims. The rim zones alternate between purely andraditic and more grossularitic (up to 9 mole percent Al) compositions. This pattern of oscillatory zoning is present to a much greater degree in the cross-cutting second-generation vein garnets (up to 45% Al). Unzoned garnet present in orbicular hornfels has an extremely high Al content, containing up to 81 mole percent grossular (81% Al).

Although variation of many factors could be responsible, a likely cause of a shift to more aluminous garnet compositions is a decrease in CO_2 in hydrothermal fluid, caused by boiling. Another possibility is a change from lithostatic to hydrostatic pressure accompanied by fracturing. Finally, an influx of meteoric water may also have been involved.

General geology

The San Pedro mine, which contains a small copper-bearing skarn, is located in the San Pedro Mountains of north-central New Mexico. The mountain range belongs to the set of intrusive centers that make up the 25-mile-long north-trending San Pedro–Ortiz porphyry belt. From north to south the centers are known as La Cienega, Los Cerrillos, the Ortiz Mountains, the San Pedro Mountains, and South Mountain. The Sandia uplift lies to the southwest of the porphyry belt, and the Sangre de Cristo Mountains lie to the northeast. The belt lies about 12 mi from the eastern edge of the Rio Grande rift (Fig. 1).

Except for the younger La Cienega intrusion, the porphyry belt appears to be Oligocene in age based on K–Ar dates of 38 to 26 m.y. for the contemporaneous Espinaso ☞

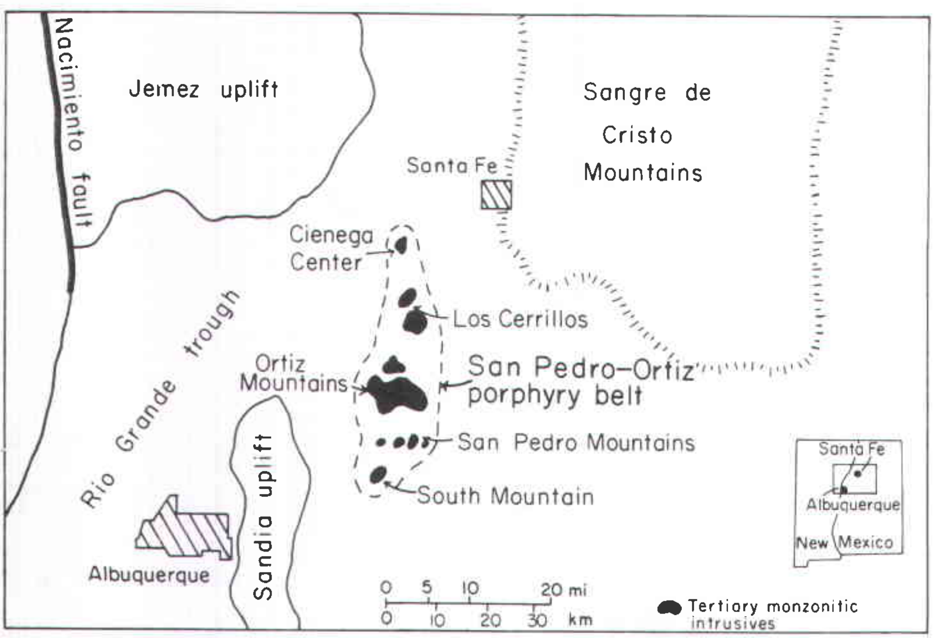

FIGURE 1—Index map of north-central New Mexico showing location of the San Pedro Mountains, from Atkinson, 1976.

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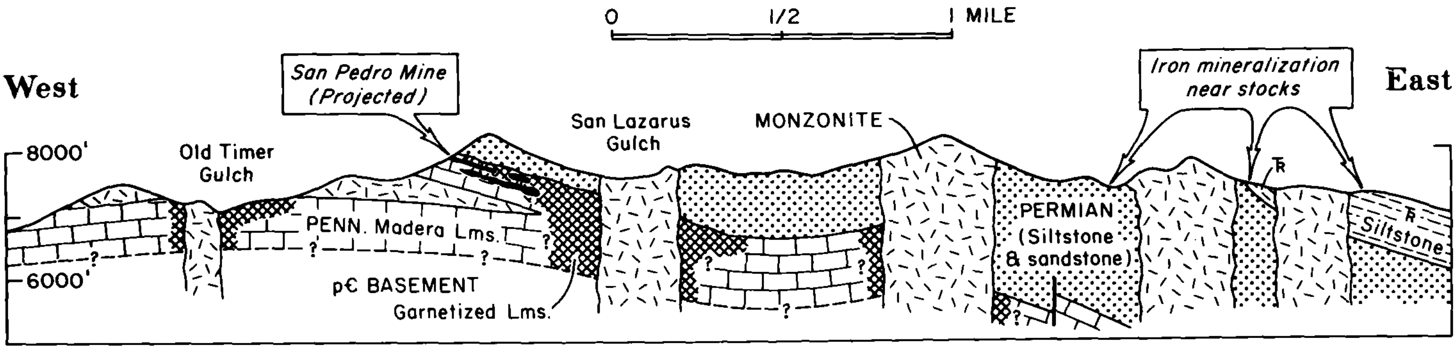

FIGURE 2—Geologic cross section of the San Pedro Mountains, Santa Fe County, New Mexico, generalized from Atkinson, 1976.

volcanics, which erupted from vents in the Cerrillos and Ortiz Mountains areas (Kautz et al., 1981). The intrusive rocks of the belt as a whole and of the San Pedro Mountains in particular tend to be rather homogeneous monzonitic porphyries. The source of the mineralization at the San Pedro mine was probably the San Lazarus stock, a composite pluton made up of porphyritic monzonite and quartz monzonite containing molybdenum-bearing quartz veinlets.

Sedimentary rocks dip about 14° to the east in the San Pedro mine area, where the mineralization is hosted by the upper part of the Pennsylvanian Madera Formation, a sequence of alternating shale and carbonate beds. Massive and disseminated mineralization occurs in replacements of 14 chemically receptive limestone beds separated by barren shale. This favorable series is 270 ft thick, and is sandwiched between an underlying monzonite porphyry sill and an overlying rhyolite sill.

Hydrothermal fluid expelled from the adjacent San Lazarus stock was constrained to flow between the pre-existing sills and through the favorable series, which resulted in the metasomatic replacement of limestone/marble beds by garnet-chalcopyrite skarn (Fig. 2). Shale units were simultaneously converted to diopside-plagioclase-quartz hornfels. Sharply defined marble line boundary surfaces mark the position of the metasomatic front and separate skarn from marble within each limestone bed. Mineralization is concentrated along and near these marble line boundaries, with ore grades decreasing rapidly from the skarn–marble contacts into the skarn, toward the source of mineralization. Ore generally does not extend more than 200 ft inward from the marble lines and does not occur in marble. At San Pedro, this style of mineralization has produced a stack of skarn-hosted, marble-line orebodies, each of which has a manto configuration.

San Pedro skarn

The character of a given skarn-type ore deposit is the result of the interplay of many factors, such as the chemistry of the mineralizing hydrothermal fluid and its evolution through time, the establishment of localized activity gradients, host rock composition and permeability, volatile composition, temperature, pressure, and the relative importance of metamorphic and metasomatic processes (Einaudi et al., 1981). Most skarns appear to go through a similar set of developmental stages as a result of variation through time in the relative impact of these factors. Metamorphic effects generally precede metasomatic ones, with late-stage alteration being overprinted onto them both, which produces distinctive patterns of mineralogical zonation and alteration (Rose and Burt, 1979).

At San Pedro, early contact metamorphism of impure limestone and/or dolomite resulted in formation of light-colored calc-silicates such as tremolite, diopside, and wollastonite. This was followed by two periods of mineralization. Disseminated ore was deposited first as Fe, Si, and metal-bearing fluids infiltrated the carbonate beds, resulting in formation of massive garnetite skarn and early chalcopyrite deposition. Late skarn destruction and ore redistribution produced vuggy ore. Here, garnet destruction and alteration associated with the entry of meteoric water into the hydrothermal fluid produced a quartz-hematite-calcite-chlorite-chalcopyrite mineral assemblage. The vugs containing these minerals are lined almost invariably with euhedral garnet. Cross-cutting, second-generation garnet veinlets also were produced during this stage of genesis. Finally, argillic alteration occurred, forming talc, chlorite, montmorillonite, sericite, quartz, and limonite. Typically, temperatures for the formation of skarns have been found to be 500–700°C for early contact metasomatism, 400–600°C for garnet skarn, and 200–400°C for the late hydrous alteration phase (Rose and Burt, 1979; Einaudi et al., 1981). It is expected that temperatures yet to be determined on San Pedro rocks will fall in these ranges. The resulting San Pedro deposit exhibits the following zonation from the inside outward: garnetite skarn/vuggy ore with argillic alteration; garnetite skarn/vuggy ore; marble line with garnetite skarn and disseminated ore; marble ± wollastonite–diopside–tremolite; and unaltered limestone/dolomite.

Interaction between the infiltrating hydrothermal fluid and the host limestone/marble is responsible for skarn formation and mineralization. Therefore, it is clear that the thermochemical character of the hydrothermal solution must have varied considerably over time and distance to have produced such a complex pattern. Some insight into the nature of local and temporal variation in fluid chemistry at San Pedro may be obtained through detailed microprobe analysis of some zoned and unzoned garnets.

Garnet analyses

All the San Pedro garnet analyses were performed at the University of Colorado with a MAC–25 electron microprobe using a Kevex energy dispersive system at an operating voltage of 15 kV, a 2-micron beam diameter, a sample current of 200 microamps, and 100-second count times. Standards employed were wollastonite for Ca and Si, andradite garnet for Fe, and augite and garnet for Al. Corrections were made using the Magic IV computer program (Colby, 1968). Cr, Mg, and

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Mn were not determined because of an interest in Fe–Al variation and the lack of measurable amounts of these elements. Traces of Mn were found in San Pedro garnets.

Three samples chosen from drill core were analyzed at 60 points by microprobe. Of these, sample R–15 (673 ft) contains skarn garnets. Contact–metamorphic garnets present in samples R–15 (676 ft) and R–15 (773.5 ft) occur in orbicules in the interbedded hornfels. In all cases, San Pedro garnets are of the andradite (ad)–grossular (gr) solid solution series ($Ca_3Fe_2Si_3O_{12}$–$Ca_3Al_2Si_3O_{12}$). Table 1 presents representative analyses of San Pedro garnets.

In sample R–15 (673 ft) two generations of metasomatic garnet are present. The first-generation garnet grains contain yellow-brown isotropic cores bounded by zoned rims, consisting of oscillatory zones of yellow, isotropic garnet, alternating with paler, weakly anisotropic zones. Twenty-one points were analyzed in a traverse across a first-generation garnet (Figs. 3, 4A). The core (C) is nearly pure andradite (Xad = 100 mole percent; Xgr = 0%), as are the yellow, isotropic zones in the rim (R). The weakly anisotropic zones contain up to 9 mole percent grossular. Although the precise nature of chemical variation within zones cannot be resolved with the spacing of analyses used, the correlation between anisotropic garnet and the presence of aluminum is clear.

The massive first-generation garnet is cut by grossular-rich second-generation garnet veins (V; Fig. 4B). Locally, the second-generation garnet cements a breccia of the first. The second-generation garnet is strongly anisotropic, showing sector twinning and weak to strong oscillatory zoning. Birefringence varies from 0.003 to 0.015, attaining first-order red colors. In some veins, an isotropic band that has sharp boundaries with the anisotropic garnet is present. Other sharp changes in birefringence are present locally, but in general, changes are smooth but nonsystematic.

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TABLE 1—Representative garnet analyses in weight percent. **A**, first-generation, core andradite, sample R–15 (673 ft); **B**, first-generation, rim garnet, sample R–15 (673 ft); **C**, second-generation, vein garnet, sample R–15 (673 ft); **D**, garnet in hornfels orbicule, sample R–15 (676 ft); * the low total may be accounted for by the presence of H_2O in hydrogrossular, as indicated by loss on ignition; **Xgr**, mole percent grossular.

oxide	A	B	C	D
SiO_2	36.26	36.41	37.38	37.15
Al_2O_3	0.00	0.91	5.11	14.02
Fe_2O_3	29.75	28.12	22.20	5.91
CaO	34.32	34.28	36.04	34.87
Total	100.33	99.72	100.73	91.95*
	No. of ions per 24 oxygens			
Si	6.091	6.115	6.083	6.229
Al	0.000	0.180	0.980	2.772
Fe	3.761	3.554	2.719	0.746
Ca	6.177	6.169	6.285	6.265
Xgr	0.000	0.048	0.265	0.788

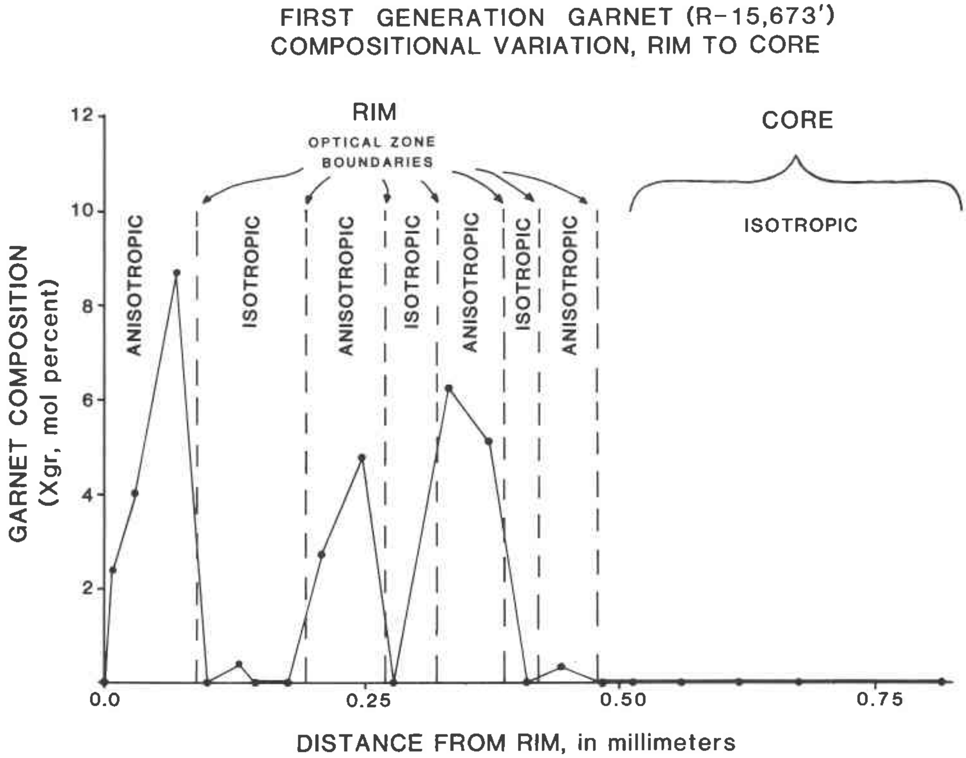

FIGURE 3—Microprobe analyses of first-generation garnet, zoning profile, and mole percent grossular (Xgr) plotted, versus distance from rim edge, in mm. Boundaries between isotropic and anisotropic optical zones indicated by vertical dashed lines.

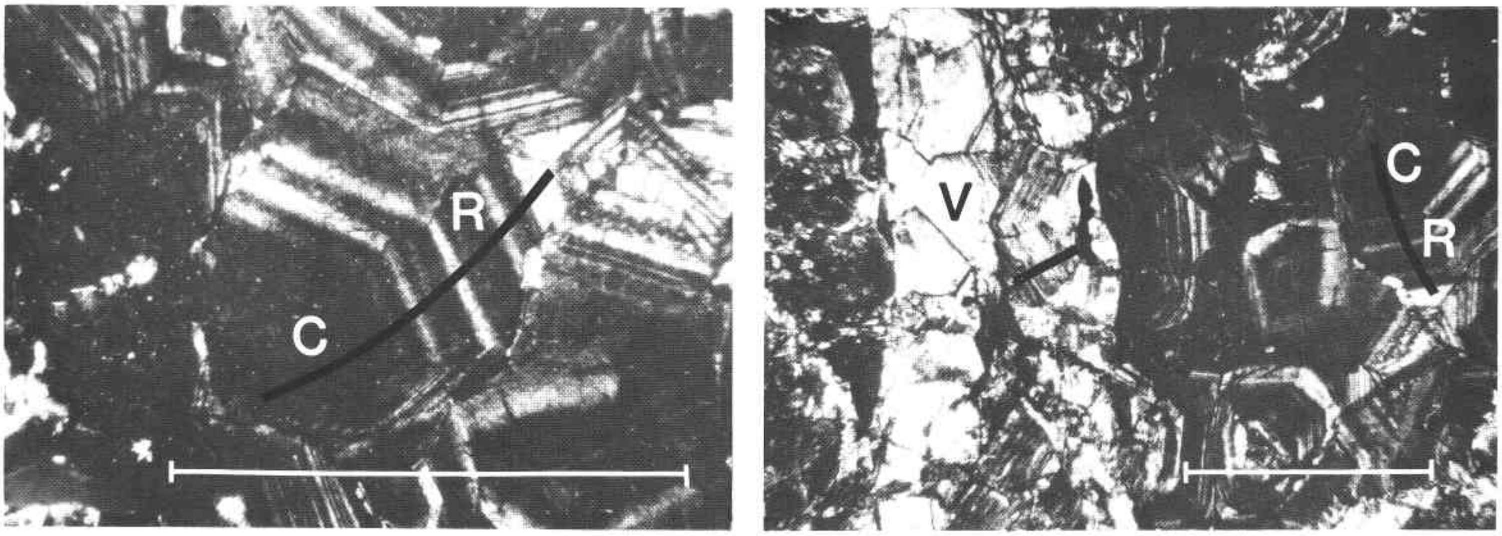

FIGURE 4—Photomicrographs of San Pedro garnets. Sample R–15 (673 ft); crossed polarizers; length of each white scale bar equals 1 mm. **A**, First-generation garnetite, showing isotropic andradite cores (**C**) and zoned rims (**R**); **B**, Second-generation garnet vein (**V**) cutting first-generation garnetite. Note the highly birefringent nature of the vein material. The location of probe traverses are shown by heavy solid lines.

A traverse across one vein garnet (Fig. 5) was analyzed at 18 points, revealing oscillatory compositional zoning of a much greater amplitude and higher frequency than that of the first-generation garnet. Zones at the center of the vein are very andradite-rich (Xgr = 2.5 mole percent), but these give way toward the vein wall to highly aluminous compositions as the Al content of the garnet quickly attains its maximum (Xgr = 45 mole percent), then falls off erratically with the amplitude of its variation being as much as 25 mole percent, eventually coming down to much lower values (21–22%) near the vein walls. The mean grossular content for vein garnets is 25.7%, as opposed to a value of 2.0% for the first-generation garnet (*see* Fig. 6).

Harris and Einaudi (1982) have documented a style of garnet compositional zoning for calcic, Fe-rich skarn at Yerington, Nevada, which is similar to that found at San Pedro. These authors note the presence of grossularitic veinlets cutting early garnet having isotropic andraditic cores and aluminous and compositionally variable rims. This same pattern is shown clearly by the analysis of first- and second-generation garnets in sample R–15 (673 ft; *see* Figs. 3 and 5).

Sweeney (1980) has studied skarn garnet in the Bingham district, Utah, and has found it to be very similar in nature to the first-stage garnet at San Pedro. Bingham garnet is mostly nearly pure andradite, with a few thin aluminous zones present in each crystal. The zoning was found to exist on a very fine scale, with many thin zones only a micron or two wide. Anisotropic garnet also correlated with Al content, although the maximum grossular component was no more than 30%.

Alteration of massive vein wall garnet to a mixture of chlorite, hematite, calcite, and quartz occurs in places along the vein itself and in patches scattered throughout the skarn. Elsewhere, fresh first-generation andradite dominates. Remnant garnet in the altered patches has an Al content that is only slightly lower than the Al content of the vein garnet itself (*see* Fig. 6; maximum = 25.3 mole percent, mean = 19.9 mole percent), which suggests that the composition has been altered by diffusional exchange.

The garnets found in orbicules in hornfels were probed in two samples: R–15 (773.5 ft) and R–15 (676 ft). The results of the analysis show that these unzoned garnets are distinctive by virtue of their highly aluminous compositions. The mean grossular contents for samples R–15 (773.5 ft; 3 analyses) and 676 ft; 7 analyses) are 53.7 and 81.3 mole percent, respectively.

Interpretation and conclusions

The compositions of the garnets found in orbicules in hornfels are the most aluminous found at San Pedro. The unzoned character of these garnets and their very high Al contents suggest that the hornfels environment of formation was relatively unaffected by the

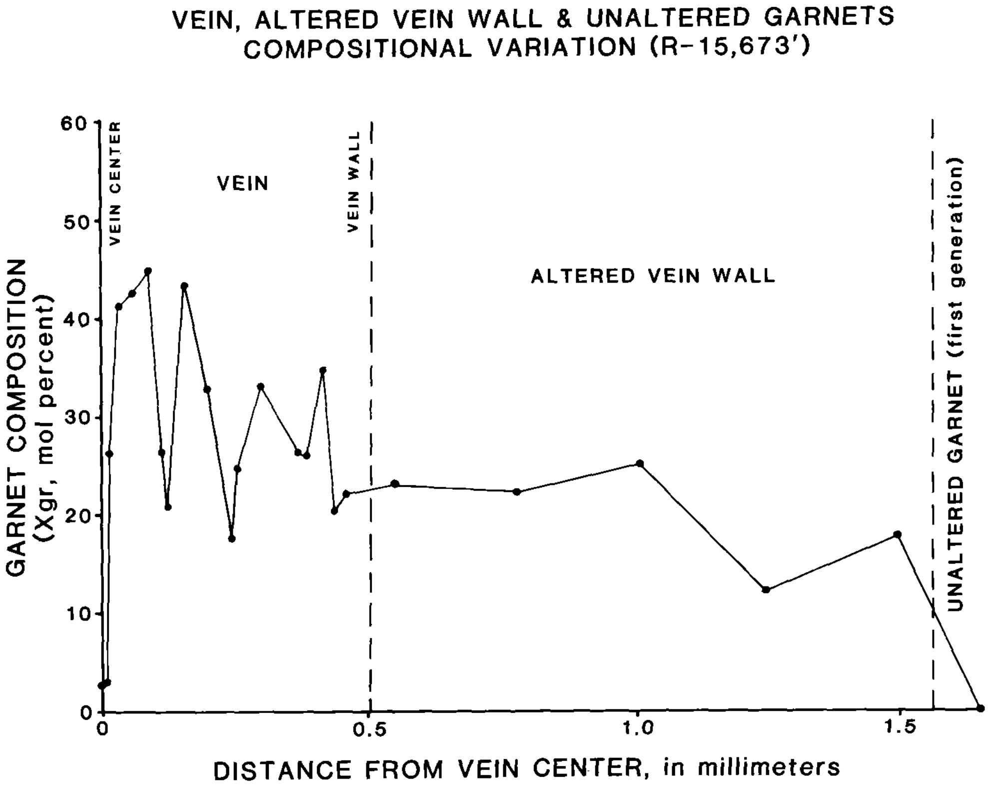

FIGURE 5—Microprobe analyses of second-generation vein, first-generation altered vein wall, and first-generation unaltered garnet zoning profiles. Mole percent grossular (Xgr) is plotted versus distance from vein center. Boundaries between zones are indicated by vertical dashed lines.

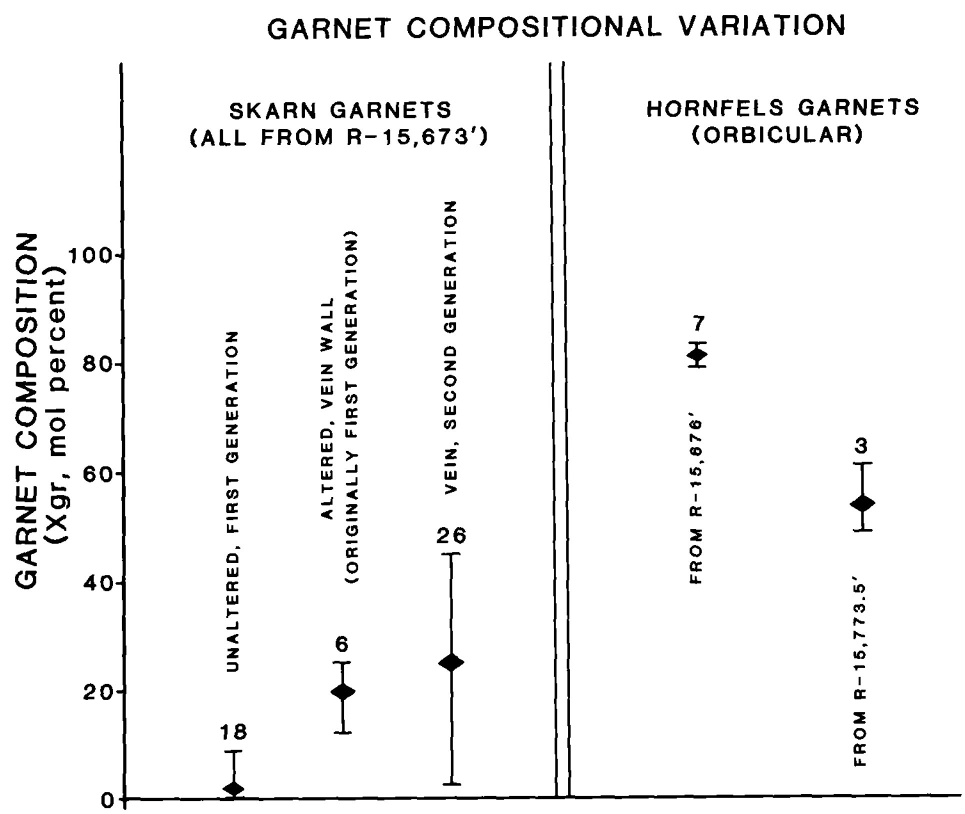

FIGURE 6—Microprobe analyses, garnet compositional range, mole percent grossular (Xgr), and skarn and hornfels varieties. Bars indicate range and diamonds represent mean values for each garnet type. Numerals placed above upper bar show the number of analyses performed on each variety.

infiltrating hydrothermal fluid responsible for the deposition of the skarn garnets. The orbicules must have had a locally derived composition and a metamorphic rather than metasomatic origin.

Tracy (1982) defined growth zoning as zoning developed in a mineral because of a continuous or discontinuous change in the composition of material supplied to the growing surface of the crystal. Negligible rates of solid-state diffusion are also required to preserve such zoning. Skarn formation results from interaction between an infiltrating hydrothermal fluid and carbonate host rocks over a wide range of temperatures (200–700°C). Garnet zoning shows that the composition of that solution varies over time and with distance from its source. Details of this variation are provided by analysis of the growth-zoned garnets present in the San Pedro skarn.

First-generation garnets have andradite cores and zoned rims. The rim zones alternate abruptly between purely andraditic and more grossularitic (up to 9 mole percent Al) compositions. Therefore, compositional differences as expressed by the oscillatory zoning observed in the first-generation garnet rims reflect short-term variation in the composition of the hydrothermal fluid.

Without more information, it is not possible to suggest exactly what controls the composition of the solution depositing the garnet. It is likely that it was largely a hypersaline fluid exsolved by an igneous source, probably buffered at its source by igneous minerals in deeper rocks. After it left the source, it may have mixed with unknown amounts of meteoric or connate water and traversed underlying sedimentary rocks and Precambrian basement rocks affected to unknown degrees by contact metamorphism and the early portions of the mineralizing fluid. The chemistry of such solutions is complex. The stability of andradite vs. grossular is affected not only by such obvious factors as the Fe/Al ratio, but by activities of species that would affect the Fe^{3+}/Fe^{2+} ratio, such as fo_2, fs_2, pH, and others.

Sweeney (1980) has proposed a mechanism for producing zoned ad–gr garnets based on T–X_{CO_2} relations. In Figure 7, the lowermost T–X_{CO_2} stability curve for grossular lies at higher temperatures than that for andradite, requiring higher temperatures, and/or lower X_{CO_2} to stabilize grossular. Calculated curves for intermediate solid solutions lie between the two curves. An earlier study of fluid inclusions at Bingham by Moore and Nash (1974) showed that hydrothermal solutions underwent a change in pressure from lithostatic to hydrostatic during the period of ore deposition. Sweeney showed that such an event could change conditions from those depositing pure andradite to those depositing grossular-rich garnet. She also examined the lowering of X_{CO_2} by boiling as a mechanism for the shift to more grossular-rich compositions. For high values of X_{CO_2} boiling would have little effect. However, Einaudi et al. (1981) report that,

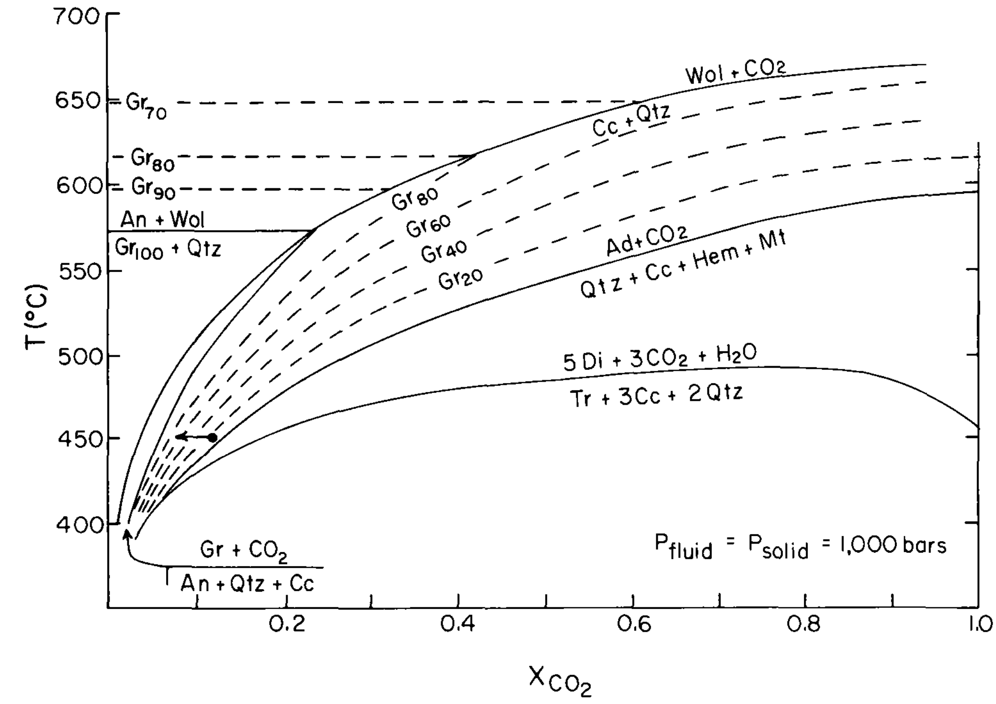

FIGURE 7—T–X_{CO_2} diagram. Dashed lines represent the position of the garnet univariant boundaries as a function of variation in aluminum content, where Gr_{100} is pure Ca–Al garnet (grossular), Ad is pure Ca–Fe garnet (andradite), and Gr_{20}, Gr_{40}, Gr_{60}, Gr_{70}, Gr_{80}, and Gr_{90} are andradite-grossular solid solutions. The arrow indicates the rapid shift toward grossularitic compositions expected to result from isothermal boiling of the hydrothermal fluid. Adapted from Sweeney, 1980.

in most skarns, X_{CO_2} values vary from initial values of 0.2 to later values of 0.05. At low CO_2 concentrations, boiling would reduce CO_2 quickly, and solutions would shift rapidly into the field of grossularitic garnet (*see* Fig. 7). Studies of fluid inclusions in the Bingham district (Moore and Nash, 1974; Starkins, 1983) indicate extensive boiling at temperatures less than 500°C, under which boiling would easily reduce CO_2 content to stabilize grossular.

It must always be borne in mind, of course, that with many variables involved, other factors may cause the changes. For example, pulses of higher temperature fluids could be responsible. Meteoric water might also enter with a low CO_2 content.

At San Pedro, a period of fracturing and local brecciation preceded the change from first- to second-stage garnet. A rapid survey of fluid inclusions in thin sections indicated that vapor-rich and coexisting liquid-rich inclusions are indeed present in garnet, which suggests that solutions did boil, although they are so sparse that they cannot yet be related to specific events. Release of pressure and consequent boiling accompanying fracturing may therefore have been important.

In general, during the late destructive stage of skarn evolution, temperatures are greatly reduced, pH decreases, release of hydrothermal fluid from the magmatic source may be restricted, and dilution of the fluid by the entry of meteoric water is expected (Einaudi et al., 1981). The result is garnet-destructive alteration and sulfide redistribution. Such events are apparent at San Pedro. We expect that dilution of the hydrothermal fluid by meteoric water causes an extreme decrease in the activity of the chloride ion (Cl^-). The reduced availability of this important complexing agent could greatly lessen the ability of the hydrothermal fluid to carry ferric iron, without affecting Al solubility (Barnes, 1979). Garnet nucleated from such a fluid would be grossularitic rather than andraditic. The formation of second-generation garnet veins and vuggy garnets (associated with vuggy ore) may have occurred in this manner at San Pedro. The second-generation vein garnet is very aluminous (up to 45 mole percent grossular), shows oscillatory zoning, and cuts first-generation garnetite. Here again, the oscillatory nature of the zoning may have been due to the episodic release of fluid from the cooling magmatic source.

In places, metasomatic exchange between this fluid and previously deposited vein-wall garnet may have altered the original (first-generation) garnets to the extent that they approach the compositions of the vein garnets themselves. These altered vein-wall garnets show elevated Al contents and contain patches of fine-grained chlorite-calcite-specular hematite, an assemblage typical of the garnet-destructive stage of skarn formation. The lack of pervasive alteration of first-generation garnet by fluids of the second generation may indicate that meteoric water influx was restricted. Alternatively, the alteration process may have been aborted by loss of fluid pressure due to fracturing as shown by the cross-cutting alteration along garnet veins. The structural setting of the San Pedro deposit between two thick sills may have enhanced early Fe-rich skarn formation but also

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may have limited the circulation of meteoric water during the skarn-destructive stage.

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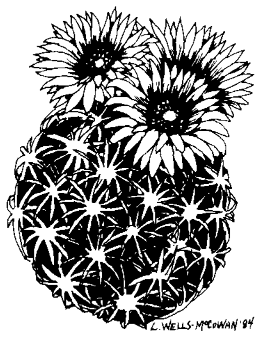

Pincushion cactus

Preliminary report on the vertebrate fauna of U-Bar Cave, Hidalgo County, New Mexico

by *Arthur H. Harris*, Curator of Vertebrate Paleobiology, University of Texas (El Paso), El Paso, TX 79968

Introduction

Current excavations in southwestern New Mexico are producing a major late Pleistocene vertebrate assemblage that is adding greatly to our knowledge of the biota and past ecology of the state. Since December 1983, evidence of more than 90 vertebrate taxa has been produced in U-Bar Cave. The complexity and extent of the cave deposits and faunas will require an extensive period of study; however, the importance of the early findings to understanding the Pleistocene biology of New Mexico is such that these preliminary data should be made available now.

U-Bar Cave (site LA 5689) is in the U-Bar Limestone (Cretaceous) about 6 mi from the Mexican border in the "boot heel" of southwestern New Mexico. The altitude is about 5150 ft. The cave is surrounded by Chihuahuan desertscrub mixed with Upper Sonoran woodland elements. The main chamber of the cave (Fig. 1) is about 315 ft long and averages about 50 ft wide.

The cave has produced archaeological material since about 1935 (Lambert and Ambler, 1961), and it was the site of formal excavations by Lambert and Ambler in 1960. They considered the archaeological material as most probably assignable to the Animas Phase of the Casas Grandes culture, with a likely date

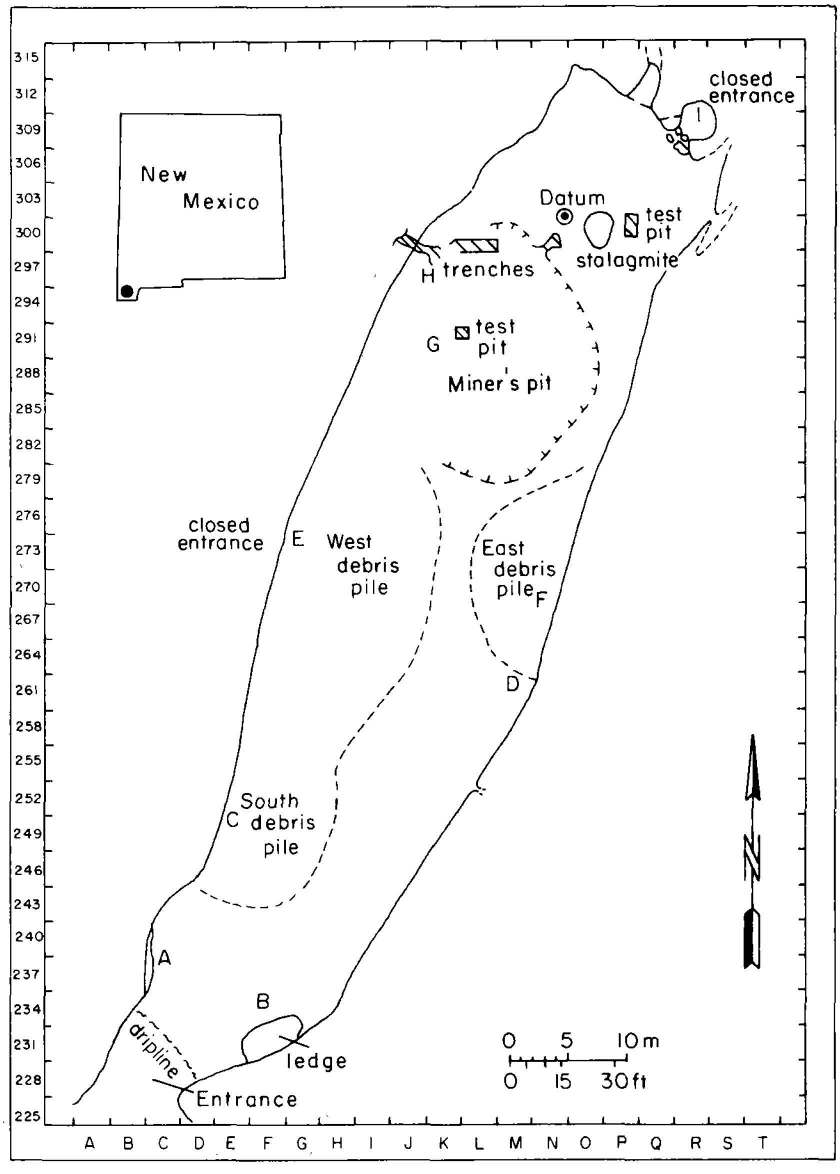

FIGURE 1—Sketch map of U-Bar Cave showing grid system, features, and regions referred to in the text.