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MINERALOGY AND PETROLOGY OF SKARN DEPOSITS

ABSTRACT. — Pyrometamorphic or skarn deposits are high temperature hydrothermal ore deposits of world-wide distribution (usually in orogenic belts) which are important sources of Fe, Cu, Zn, W, and other metals. The characteristic feature of these deposits is the gangue, a coarse-grained, generally dark-weathering mixture of calcium and magnesium silicates, which has variously been termed skarn or tectite. Skarn deposits most typically are found replacing limestone or dolomite beds adjacent to and above granitic intrusives. They appear to be formed by postmagmatic, ascending, iron-rich hydrothermal solutions, probably at shallow depths within the earth's crust. The skarn silicates themselves seem to be deposited earlier than most of the oxide or sulfide ores, and in a given deposit there is usually much skarn that is barren of economic mineralization. Skarns replacing pure limestones can be termed Ca-Fe-Si skarns, although sometimes there is considerable Mn^{2+} substituting for Fe^{2+} . The dominant skarn silicates in this case are andraditic garnet and/or hedenbergitic clinopyroxene.

Skarns may be distinguished from mineralogically similar calc-silicate metamorphic rocks in that they are metasomatically zoned, coarse-grained, distinctly Fe-rich, and often mineable for their base or precious metal content. In this regard, skarn deposits bear a unique relation to the so-called « porphyry copper » deposits. This relation is that where intrusives containing disseminated copper-molybdenum mineralization contact limestone, skarn deposits are nearly always present, but (unfortunately for prospectors) most intrusives associated with skarn deposits are themselves barren of economic mineralization.

To aid in understanding the various processes which occur during the formation of Ca-Fe-Si skarn deposits, a theoretical study has been made of mineral stabilities and compatibilities in the eleven-component model system Ca-Fe-Si-C-O-S-H-F-Zn-Cu-W. Reactions in this model system clarify many previously unexplained phenomena observable in skarns, and also explain some characteristics of carbonatites, greisen and vein tungsten deposits, and metamorphosed ferruginous marbles and iron formations.

Introduction: terminology

« Skarn » is an old Swedish mining term for the gangue minerals associated with Precambrian magnetite and sulfide deposits. These minerals were predominantly calcium and magnesium silicates. By the time of V. M. Goldschmidt's classic memoir « Die Kontaktmetamorphose im Kristianiagebiet » (1911), the word « skarn » was generally used in northern Europe for the silicates associated with ore replacing limestone and dolomite near igneous contacts.

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In 1919 F.L. Hess, an American who worked with tungsten and molybdenum deposits, coined his own word «tactite» for such rocks. This term has found limited acceptance in the geologic literature of North America, although it appears to be synonymous with skarn as used by Goldschmidt (1911).

«Skarn deposit» is a term I and others have used for one deposits possessing skarn as a gangue. In older literature these deposits are described by one or more of the following terms:

contact
 contact metamorphic
 contact metasomatic
 contact pneumatolytic
 hydrothermal metamorphic
 pyrometasomatic
 igneous metamorphic.

Most of these genetically-oriented terms are, for one reason or another, misleading. For example, the terms «contact» and «igneous» are misleading because these deposits can occur along veins or sedimentary contacts, rather far from an igneous contact. The term «metamorphic» is misleading because the deposits are distinctly metasomatic. The term «pyrometasomatic», coined by Lindgren (1922) to imply metasomatism at high temperatures, is also misleading. The reason is that close to the earth's surface and in the presence of CO₂-poor fluids, skarn silicates can form at quite low temperatures (zeolites being an extreme example). Thus the only truly distinctive feature of these deposits is not the metals mined, nor the presence of an intrusive, but rather the gangue, termed skarn.

Occurrence and importance

Skarn deposits are of worldwide distribution, generally in orogenic belts. They range in age from Precambrian to late Tertiary, with most economically important deposits being relatively young. (Skarn formation is presumably a fairly near-surface phenomenon, so that erosion has removed many older deposits).

As of this writing, I have visited nearly 100 skarn and related deposits in the U.S.A., Canada, Mexico, Peru, Japan, France, Italy, Greece, Bulgaria and Romania. My interest in skarn deposits results from several considerations (listed more or less in random order).

1. They are important sources of Fe, Cu, Zn, W, Mo and other metals, as well as of the industrial minerals asbestos, magnesite, talc and wollastonite.

2. They are closely associated genetically and spatially with intrusive igneous rocks. Historically, they provided one of the strongest arguments for W. Lindgren's «magmatic» theories of ore deposition.

3. They are closely associated genetically and spatially with other types of ore deposits, such as porphyry copper and greisen deposits.

4. Their intimate admixture of iron-rich skarn minerals and ore minerals implies that skarns may provide natural examples of the laboratory processes of sulfidation and oxidation.

5. They are essentially retrogressive; that is, they form with falling temperature. This feature promotes the formation of mineral assemblages of low variance. Several « facies » or phases of skarn formation can be studied in a single hand specimen or thin section.

6. They are generally coarse-grained and the minerals are strongly colored. This features is convenient for the study of textures and zoning in hand specimen.

Distinguishing characteristics

How may skarn be distinguished from mineralogically similar rock types such as calc-silicate hornfels? In the first place, as recognized by Goldschmidt (1911), skarns tend to be distinctly more coarse-grained than hornfelses. Skarn garnets commonly exceed 2-3 cm in diameter, and clinopyroxene crystals are 10 cm or more long. This coarse grain size is presumably indicative of crystal growth from high temperature, mineral-rich fluids (cf. the giant crystals in pegmatites).

A second characteristic is that skarns consist of minerals with distinctive colors (especially, weathering colors) and chemistry. The garnets in skarn tend to be andradite rather than grossular, and the clinopyroxenes hedenbergite or johannsenite rather than diopside. This enrichment in Fe and Mn generally causes skarns to be dark-weathering. Enrichment in « pneumatolytic » elements, such as B (in axinite, datolite and other borosilicates and borates) and F (in fluorite, apophyllite, humite-group minerals, micas and amphiboles), is also common.

Thirdly and most distinctively, skarns tend to be metasomatically zoned around the presumed passageways of hydrothermal fluids — igneous contacts, sedimentary contacts, faults and fissures. In hornfelses, in contrast, the calc-silicate distribution is strictly controlled by bedding and by original chemical inhomogeneities in the rock.

An indication of metasomatic zoning in skarns is that skarns typically consist of a sequence of more-or-less monomineralic bands that replace each other across sharp boundaries. This original zoning may be partly obscured by cross-cutting late hydrothermal alterations, but it is still generally recognizable. The abundance of late hydrothermal alteration is itself a distinctive feature of skarns as contrasted with hornfelses.

Lastly, an obvious distinctive feature of skarns is their association with the mineable ores contained within them.

Classifications

Skarn deposits have been classified by scale, by structure, by the rock replaced, and by the metals mined. Classifications have also been attempted based on the processes of skarn formation (e.g. Zharikov, 1970).

Scale

By scale, skarns can be divided into two categories, reaction skarns and replacement (ore) skarns. Small «reaction skarns» (Magnusson, 1936), which have also been termed «skarns of the first kind», «local exchange skarns», «(bimetasomatic) diffusion skarns» (cf. Korzhinskii, 1964-1965; Phan, 1969) and «calc-silicate bands» (Vidale, 1969) are generally the products of high grade regional metamorphism (cf. Thompson, 1975; Brady, 1977). Related «primary skarns» (Tilley, 1951) or «skarns of the magmatic stage» (Pertsev, 1974) can form by direct reaction between an intrusive and carbonate wall rocks (especially dolomites), but these are also small.

The skarns considered in this report belong to the second category, «skarns proper», «skarns of the second kind», «secondary skarns», «replaced skarns», «ore skarns» (Watanabe, 1960), or «skarns of the postmagmatic stage» (Pertsev, 1974).

The scale of «reaction skarns» can range from millimeters to meters, whereas the scale of «replacement skarns» ranges from meters to hundreds of meters or more. Gradations between the two types obviously exist and in fact are common.

Mass transport for formation of the first type of skarn above was presumably by diffusion of components through a slowly-moving or stagnant pore fluid. For the second type considerable mass transport by fluid flow must also have been involved. «Infiltration metasomatism» is the name given to the process that occurs when the rate of fluid flow exceeds the rate of diffusion of components through that fluid. For mathematical reviews of the processes of metasomatism by infiltration and, especially, by diffusion, consult e.g. Korzhinskii (1970), Fletcher and Hofmann (1974), Fletcher and Vidale (1975), Frantz and Mao (1976), Hofmann (1972), Joesten (1977) and Weare et al. (1976).

Structure

Replacement skarns can be classified according to their structural relations to an intrusive (Burt, 1972 a). Most skarns, as exposed on the earth's surface, occur replacing carbonate rocks adjacent to a small intrusive body. This may be called the «normal» or «skarn around intrusive» configuration, as at the Antamina copper deposit, Peru. Other skarns occur replacing roof pendants or xenoliths in a large intrusive batholith. This may be called the «inverse» or «intrusive around skarn» configuration, as at the Tintaya copper deposit, Peru. Finally, some skarns occur along veins far from an exposed intrusive (presumably one

exists at depth). This may be called the «no intrusive» or «skarn along a vein» configuration, as at the Chupa Zn deposit, Peru.

The above categories roughly correspond in order to the «bimetasomatic», «infiltrational frontal» and «contact infiltrational exoskarn, vein type» categories of Zharikov (1970, p. 627-629).

Rocks replaced

Replacement skarns can also be classified according to the types of rock they replace. «Exoskarns» are those skarns that replace carbonate rocks; «endoskarns» are those that replace an intrusive or other aluminous rock. Exoskarns are generally much more extensive than endoskarns, and they carry most of the ore. In cases where this dual classification breaks down, Russian authors designate the type of rock being replaced by the prefix «apo-», as in «apo-skarn greisen» (greisen replacing skarn).

Exoskarns can be further classified according to the type of carbonate rock being replaced. Skarns replacing dolomites tend to be Mg-rich, with minerals such as forsterite, serpentine, phlogopite, and humite-group minerals, and so are termed magnesian skarns (cf. Shabynin, 1973; 1974). Skarns replacing more-or-less pure carbonate rocks tend to be more Ca-rich, with minerals such as andradite, hedenbergite, ilvaite, and johannsenite, and are termed limy or calcic skarns. Neglecting Mn, Mg, and Al, I have termed this latter category «Ca-Fe-Si skarns» because of their dominant Ca-Fe silicate mineralogy (Burt, 1972 a).

Russian authors (e.g. Korzhinskii, 1964; Shabynin, 1974; 1975) sometimes describe calcic skarns replacing magnesian skarns («apo-magnesian limy skarns») but I have not seen this feature described in North America.

Replacement of impure carbonate-bearing rocks can yield extremely complex skarn mineral assemblages. Fine-grained dense garnet hornfels formed by such replacements are sometimes termed «skarnoid» by Russian authors.

Metals

The most pragmatic classification of skarns is by contained metals. The commonest metals of economic importance are Fe (magnetite or, rarely, specularite), Cu (chalcopyrite, bornite, and other sulfides), Zn (sphalerite), and W (scheelite).

In this regard, Korzhinskii (1965; 1965) has noted that magnetite replacement deposits in limestone seem to be post-skarn (otherwise the Fe would be combined into Ca-Fe silicates), whereas in dolomite magnetite can form at the same time as coexisting magnesian silicates.

Other correlations between Cu, Zn, and W ore and gangue minerals in skarn deposits have been summarized elsewhere (Burt, 1972 a, c, d).

Stages of formation

The formation of a typical skarn deposit seems to involve a number of stages, as revealed by textural and spatial relations among the minerals (Burt, 1972 a). For convenience of discussion, five separate stages are separated below; in nature the transition from skarn formation to skarn destruction is presumably continuous. The temperatures listed are only intended to be representative.

1. Intrusion of an intermediate to granitic magma occurs at 900-700° C, probably at shallow depths (perhaps ranging from tens or hundreds of meters to several kilometers). Rarely, the intrusive may be mafic (diabase, gabbro, or syenite), especially at iron deposits.

2. Contact metamorphism (dehydration and decarbonation) of the country rocks occurs at 700-500° C, and results in a volume decrease (« ground preparation »). Crystallization of the intrusive proceeds to completion.

3. Early anhydrous zoned skarn formation occurs at 600-400° C, due either to the release of iron and silica-rich fluids from the magma, or to the arrival of fluids from a deeper source. In limestones, the dominant early skarn minerals are commonly garnet and/or clinopyroxene; in dolomite forsterite and/or phlogopite.

4. Metalliferous ore deposition commences at 500-300° C, as skarn formation continues. Scheelite and oxides generally appear to be earlier than associated sulfides. Ore deposition is confined to earlier-formed skarn, some of which remains barren.

5. Late hydrothermal alteration occurs at 400-200° C or lower, with destruction of early anhydrous skarn minerals and continued ore deposition. Serpentine replaces forsterite, and calcite, magnetite, hematite, quartz, pyrite, ilvaite, chlorite, and other minerals replace garnet and clinopyroxene.

During stages 4 and 5 above the ore-bearing fluid presumably changes from magmatic to convective meteoric (cf. Taylor, 1974). Silicate minerals characteristic of the latest hydrothermal phases of skarn formation include babingtonite, nontronite, apophyllite, stevensite, thaumasite, and various zeolites.

Mineralogy: a model

The minerals of skarn deposits could concisely be described as most of those in the system K-Na-Ca-Fe-Mg-Mn-Al-Si-C-O-H-S-As-F-Cl-B-Sn-Be-W-Mo-Cu-Zn-Pb-Ag-Au, and even then I have probably omitted a few such as P, U, Ti, Co, and Pt. Metamorphic petrologists, working with a far smaller group of elements, have found it necessary to idealize calc-silicate mineral equilibria into simple model systems such as CaO-MgO-SiO₂-CO₂-H₂O. The results (summarized in part by Kerrick, 1974 and Hewitt and Gilbert, 1975) work quite well for some metamorphic rock types. They give, at best, a very incomplete representation of skarn mineral compositions and equilibria.

The mineralogical model system that I chose (Burt, 1972 a) for skarn deposits

in limestone is Ca-Fe-Si-C-O-S-H-F-W-Cu-Zn. The first three elements are for the Ca-Fe silicates, the next five are for volatiles such as CO₂, H₂O, H₂S, and HF, and the last three are (with Fe) the major ore metals. My justification for omitting the rock forming elements Mg, Mn, and Al is that they merely « dilute » the Ca-Fe silicates andradite and hedenbergite.

Some skarn and related minerals in the system above are listed in Table 1. Many of the silicates in this table are actually quite rare; the most common ones, in addition to quartz, are probably andradite (garnet) with Fe³⁺, hedenbergite (clinopyroxene) with Fe²⁺, ilvaite (sorosilicate with both Fe²⁺ and Fe³⁺), and wollastonite. The last two minerals never occur together, contrary to a diagram given by Liou (1974, p. 1023).

Skarn garnets are rarely pure andradite. One of their most interesting features in thin section is their alteration of isotropic and anisotropic zones in a beautiful geometric pattern (cf. Wright, 1915; Verkaeren, 1971; Lessing and Standish, 1973). Sector zoning is commonly evident, as is a selective replacement of the anisotropic zones by hydrothermal calcite and other minerals. The alternating zones presumably indicate fluctuating fluid compositions during garnet growth. An explanation for the anisotropy of the Al-rich zones has recently been offered (Takeuchi and Haga, 1976).

Skarn facies

The minerals in Table 1 are stable over different conditions of temperature, pressure, and volatile fugacities. Differences in the stabilities of various minerals and mineral assemblages can be used to define the facies of iron-rich skarn formation (Burt, 1971 a; 1972 a).

Volatile fugacities and temperature commonly play inverse roles in determining which facies is stable. For example, at a given pressure wollastonite is stable at higher temperatures than calcite plus quartz, but it can form at quite low temperatures if the fluid is sufficiently depleted in CO₂ (cf. Greenwood, 1967; Kerrick, 1974). Fluid inclusion and other evidence suggests that skarn-forming fluids are commonly depleted in CO₂, and thus skarn formation can proceed at relatively low temperatures.

The facies of skarn formation can be presented extremely concisely on mineral stability diagrams. For the facies of early anhydrous skarn formation, the model system Ca-Fe-Si-C-O was chosen (Burt, 1971 a). The minerals considered were graphite, magnetite, hematite, calcite, siderite, quartz, hedenbergite, wollastonite, fayalite and andradite.

Natural assemblages and mineral incompatibilities (assemblages never observed) suggested Figure 1 as the stable configuration of the isobaric, isothermal μO_2 - $2\mu\text{CO}_2$ diagram for skarn facies. (The symbol μ designates the chemical potential,

proportional to the logarithm of the fugacity). Later limited experimental work (Gustafson, 1974; Liou, 1974) is consistent with this interpretation of the stability

TABLE 1

Some typical skarn minerals in the system Ca-Fe-Si-C-O-S-H-F-Zn-Cu-W
Minerals in parentheses are exceedingly rare in skarns

Mineral	Abbreviation	Formula
Elements		
Graphite	Gra	C
Sulfides		
Bornite	Bn	Cu_3FeS_4
Sphalerite	Sf	$(\text{Zn}, \text{Fe})\text{S}$
Pyrrhotite	Po	Fe_{1-x}S
Cobanite	Cb	CuFe_2S_3
Chalcopyrite	Cp	CuFeS_2
Pyrite	Fy	FeS_2
Oxides		
Magnetite	Mag	Fe_3O_4
Hematite	Hem	Fe_2O_3
Halide		
Fluorite	Flu	CaF_2
Carbonates		
Calcite	Cal	$(\text{Ca}, \text{Fe})\text{CO}_3$
Siderite	Sid	$(\text{Fe}, \text{Ca})\text{CO}_3$
Sulfates and Tungstates		
Anhydrite	Ahy	CaSO_4
(Ferberite)	Fr	FeWO_4
Scheelite	Sch	CaWO_4
Silicates		
Quartz	Qtz	SiO_2
Ferroactinolite	Fac	$\text{Ca}_2\text{Fe}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$
Hedenbergite	Hed	$\text{CaFeSi}_2\text{O}_6$
Wollastonite	Wol	CaSiO_3
Ferrobustamite	Fbs	$(\text{Ca}, \text{Fe})_3\text{Si}_3\text{O}_9$
Xenotilite	Xon	$\text{Ca}_6\text{Si}_6\text{O}_{17}(\text{OH})_2$
Babingtonite	Bab	$\text{Ca}_2\text{Fe}^{2+}\text{Fe}^{3+}\text{Si}_3\text{O}_{14}(\text{OH})$
Ilvaite	Ilv	$\text{CaFe}^{2+}_2\text{Fe}^{3+}\text{Si}_2\text{O}_7(\text{OH})$
Rankinite/Kilchoanite	Rnk	$\text{Ca}_3\text{Si}_2\text{O}_7$
Tillyite	Til	$\text{Ca}_3\text{Si}_2\text{O}_7(\text{CO}_3)_2$
Cuspidine	Cus	$\text{Ca}_4\text{Si}_2\text{O}_7\text{F}_2$
(Fayalite)	Fay	Fe_2SiO_4
(Kirschsteinite)	Kir	CaFeSiO_4
Larnite/Bredigite / Shannonite	Lar	Ca_2SiO_4
Spurrite	Spr	$\text{Ca}_3\text{Si}_2\text{O}_8(\text{CO}_3)$
Andradite	And	$\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$

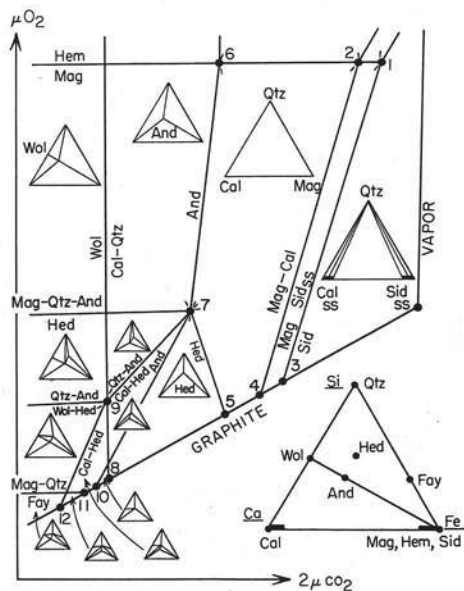


Fig. 1. — Schematic isobaric, isothermal μO_2 - $2\mu\text{CO}_2$ diagram for the facies of Ca-Fe-Si skarns (after BURT, 1972 a).

relations. Shimazaki and Yamanaka (1973) suggest, however, that an iron-poor ferrobustamite of approximate composition $\text{Ca}_5\text{FeSi}_6\text{O}_{18}$ should be stable between CaSiO_3 and $\text{CaFeSi}_2\text{O}_6$. If so, the diagram will have to be slightly modified.

The facies diagram shows that andradite and hedenbergite are both stable under low CO_2 or high temperature conditions. Under such conditions, hedenbergite is stable in relatively reducing fluids and andradite in relatively

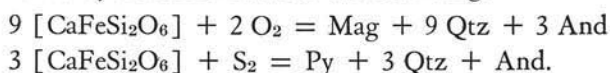
oxidizing fluids. Under intermediate oxygen potentials, both minerals can coexist. (Solid solution in nature greatly enlarges their field of coexistence). Wollastonite is stable at rather extremely low CO_2 or high temperature conditions. At any temperature, the minimum oxygen potential is that determined by graphite. Fayalite does not occur in skarns because it is incompatible with calcite.

Under low temperature or high CO₂ conditions, andradite and hedenbergite both yield to calcite-quartz-magnetite (or hematite) assemblages, corresponding to magnetite replacement deposits in limestone. Under very low temperature or high CO₂ conditions, siderite-quartz-calcite assemblages appear, corresponding to siderite-jasperoidal silica replacement deposits in limestone.

The above discussion does not consider the water-bearing phases ilvaite, ferroactinolite, and babingtonite. Ilvaite stability relations were deduced by Bartholomé and Dimanche (1967) and later modified slightly (Burt, 1971 b; 1972 a). These papers show that ilvaite is stable under fairly reducing, iron-rich, hydrous (low temperature) conditions. Ferroactinolite is stable under extremely reducing hydrous conditions, and babingtonite under extremely hydrous, low CO₂ conditions (typically with zeolites).

The influence of fluorine on skarn facies is of interest, especially as regards the relation of skarns to greisens. If the fictive «exchange operator» F₂O₋₁ is used (defined by the relation $\mu_{F_2O_{-1}} = 2\mu_{HF} - \mu_{H_2O}$), skarn equilibria involving calcite and CO₂ are almost completely exchangeable for greisen equilibria involving fluorite and F₂O₋₁ (Burt, 1972 c). Similarly, at very high temperatures, reactions involving tilleyite and spurrite are exchanged for those involving cuspidine. The presence of siderite, as well as fluorite, in many greisen deposits suggests that CO₂ and HF fugacities were both high during their formation.

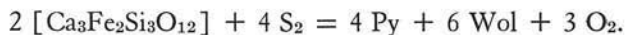
Finally, the influence of sulfidation and oxidation equilibria are of interest, insofar as these equilibria can be related to processes of ore deposition (Burt, 1972 d). The hedenbergite component of clinopyroxene controls the potential of O₂ and S₂ to low levels by reactions such as the following:



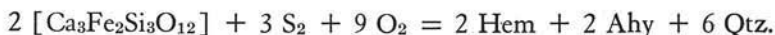
If water is added, ilvaite can participate in reactions such as:



The andradite component of garnets is stable over a somewhat wider range of conditions. Under high μ_{S_2} and low μ_{O_2} it breaks down to pyrite plus wolastonite:



Under high μ_{S_2} and μ_{O_2} conditions it breaks down to hematite (or pyrite)-anhydrite-quartz assemblages:



Anhydrite-bearing assemblages are rare in skarns, probably due to the relatively high low temperature solubility of anhydrite.

In any case, early-formed Ca-Fe-Si skarn minerals are seen to be capable of chemically modifying later fluids that pass through them. This modification could promote ore deposition.

Metasomatic zoning

Ca-Fe-Si skarns

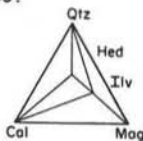
Metasomatic zoning is a distinctive feature of skarn deposits. Individual early-formed skarn zones generally consist of essentially one or two minerals. A single sequence of zones tends to occur through a given deposit or group of deposits, although locally the width of individual zones may vary considerably, and some zones may be missing in places.

Zoning Sequence: Mag/Ilv/Hed/Cal

A. System: Ca-Fe-Si-C-O-H

B. Externally-controlled variables:
T, P, μ_{O_2} , μ_{CO_2} , μ_{H_2O}

C. Facies diagram:



D. μ_{Ca} - μ_{Fe} - μ_{Si} diagram:

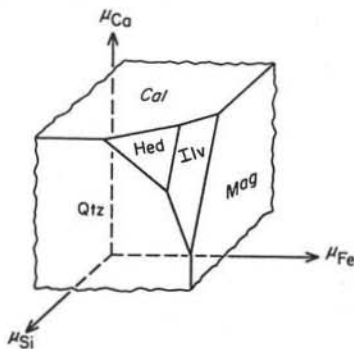


Fig. 2. — Chemical potential and related diagrams for the skarn zoning sequence magnetite/ilvaite/hedenbergite/marble (after BURT, 1972 a).

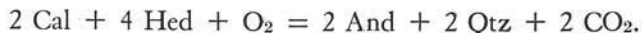
Bartholomé and Evrard, 1970). The fact that in places at Temperino a quartz zone occurs between hedenbergite and limestone is also consistent with the model.

Models such as Figure 2 imply the simultaneous development of all major zones, as the result of chemical potential gradients set up between iron and silica-rich solutions and limestone host rocks. The inner zones continuously replace the outer ones. In nature, the early-formed zoning sequences are modified as mineral compatibilities and stabilities change with changing temperatures and fluid compositions. The hedenbergite/marble contact is a good place to look for such changes, as

Models for skarn zoning based on chemical potential diagrams were first developed by D. S. Korzhinskii (1959 and earlier papers). J. B. Thompson, Jr. (1959) presented an equivalent geometrical approach. I have applied these models to Ca-Fe-Si skarn deposits (Burt, 1972 a; 1974); what follows is a brief summary of this approach (cf. Grant, 1977; Joesten, 1977).

During the formation of replacement skarns, mass transport presumably occurs both by infiltration of fluid along fractures and by diffusion away from these fractures. I have assumed, in using chemical potential diagrams, that the results will look predominantly like diffusion, with fluid motion tending merely to «spread the zones out» over larger distances (cf. Fletcher and Hofmann, 1974). This approach appears to work, and Figure 2 is an example. This figure is based on the classic exoskarn zoning sequence magnetite/ilvaite/hedenbergite/limestone at Temperino, Tuscany, Italy (Vom-Roth, 1868;

hedenbergite plus calcite can become unstable by reactions such as the following:



By searching, I have discovered local millimeter-thick bands of andradite at the hedenbergite/marble contact at Campiglia Marittima, Tuscany.

Solid solutions

The above simple zoning model neglects the fact that skarn minerals in nature are solid solutions. This feature generally expresses itself in skarn zoning sequences by a regular change of mineral compositions in each zone. Numerous studies show that andraditic garnet tends to be enriched in Fe away from the intrusive, and hedenbergitic clinopyroxene further out is commonly enriched first in Fe and then in Mn as the limestone is approached.

The cation enrichment sequence in skarn clinopyroxenes, namely Mg-Fe-Mn, is apparently the inverse of the order of preference of clinopyroxenes for the cations Mg, Fe, and Mn (as suggested by the decreasing thermal stabilities of the endmembers diopside, hedenbergite, and johannsenite). A possible interpretation is that fluids passing through a clinopyroxene zone are depleted first in Mg and then in Fe, so that finally only Mn remains to form johannsenite near the unreplaced limestone.

Related deposits

Some skarn deposits appear to be genetically and spatially related to « porphyry copper » or to greisen deposits. Skarns are also mineralogically related to (i.e. similar to) carbonatites, magnetite-apatite-amphibole deposits, metamorphosed calcareous iron formations, and metamorphosed manganese-rich deposits.

Skarn deposits bear a unique relation to the so-called « porphyry copper » deposits (Burt, 1972 a). This relation is that where an intrusive containing disseminated copper mineralization contacts limestone, skarn deposits are always present. The converse is definitely *not* true - many intrusives associated with copper or zinc-bearing skarns are barren of economic mineralization. The implication is that formation of a porphyry copper deposit requires more specialized conditions than formation of a skarn orebody. These conditions may involve the metal and volatile content of the magma, the depth of emplacement, or other factors.

Some skarn deposits are associated with greisen deposits, in which case they commonly contain considerable fluorite (Sainsbury, 1964). Well-known U.S. examples are the Be-W deposit at Iron Mountain, New Mexico (Jahns and Glass, 1944) and the Sn-Be deposits of the Central York Mountains (Lost River district), Seward Peninsula, Alaska (Sainsbury, 1969).

Greisen is occasionally reported as replacing skarn (the « apo-skarn greisens » of Soviet writers); the implication is that greisen formation occurs at lower tem-

peratures than skarn formation. Recent considerations of W, Be, and Sn mineral stabilities in skarns and greisens (Burt, 1972c; 1975; 1978) indicate that greisens are characterized by higher potentials (or fugacities) of acid volatiles than skarns.

The mineral assemblages of skarns resemble those of carbonatites (Heinrich, 1966) and some iron-rich carbonatites, such as those at Iron Hill, Colorado, were initially mistaken for skarns (Singewald, 1912). Nevertheless, in comparison with skarns, carbonatites have a distinct origin as a carbonate magma. Their geochemical characteristics, including their high titanium and rare earth contents, are also distinctive. Hedenbergite has never been reported from a carbonatite.

Some «skarn» magnetite deposits may be genetically related to the magmatically-derived magnetite-apatite-amphibole deposits of the Pacific coast (Park, 1972), but the relation, if any, requires clarification.

The mineral assemblages of metamorphosed calcareous iron formations (Klein, 1973) are similar to those of skarns. A distinction involves the behavior of oxygen. During the early stages of skarn formation, μO_2 appears to be «externally» controlled by through-going solutions. In metamorphosed iron formations, in contrast, μO_2 appears to be «internally» controlled by the local mineral assemblages themselves (cf. Zen, 1963; Vidale and Hewitt, 1973). The most common local control is perhaps finely divided graphite, in part the product of the metamorphic breakdown of siderite. The highest grades of metamorphism in such rocks sometimes produce a rock called eulysite, containing fayalite (Burt, 1972b). Neither fayalite, nor the hydrous lower temperature iron silicates greenalite, minnesotaite, and greenalite, typically occur in skarns.

Finally, the mineral assemblages of skarn deposits resemble those of metamorphosed manganese-rich deposits, including Langban, Sweden (Moore, 1970), Franklin, New Jersey (Fron del, 1973), and various deposits in Japan (Watanabe et al., 1970). These deposits, in addition to being much more varied mineralogically than most skarns, lack the typical metasomatic character of the replacement skarns here discussed. Some of the zoned manganese deposits in Japan are, however, excellent examples of reaction skarns.

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