

Banded skarns, an example of geochemical dissipative structure

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Abstract

Banded skarns are metasomatic rocks produced by oscillatory precipitation on a centimetre scale. These rocks result from the transformation of homogeneous carbonate materials by aqueous fluids under metamorphic conditions. After reviewing ordinary, unbanded zoning in skarns and the evolution of this zoning, descriptive elements of banded skarns are identified. It is proposed that banded skarns occur mainly at the rare moment when different minerals (or groups of minerals) compete for the same zone of the metasomatic column. A qualitative preliminary model explaining the appearance of oscillatory precipitations is outlined. Banded skarns are an example of geochemical dissipative structure, showing the onset of self-organization because of the interplay of competitive phenomena inside the system, and not because of external template.

Keywords: banded skarns, oscillatory precipitation, dissipative structure

1. Introduction

Skarns are coarse-grained calc-silicate metasomatic rocks that develop from carbonates under metamorphic conditions, through the operation of pervasive aqueous hot (hydrothermal) solutions (Einaudi et al., 1981). Some of these rocks may be banded, in the sense that the metasomatic minerals are deposited in the form of alternating or oscillatory strata of centimetre wave length ; and they develop at the expense of starting materials (marbles) that may be homogeneous (Guy, 1981).

The purpose of this paper is to give an introduction to an understanding of these structures, through description and qualitative discussion of some natural examples, as a basis for further more quantitative studies. The temporal evolution of zoning patterns in skarns and the situation of banded skarns within this evolution will be stressed.

2. Ordinary zoning and evolution of zoning in skarns

The fluids responsible for the chemical transformation of (mainly) carbonate materials may be rich in silica, iron, manganese, and possibly aluminium and other elements. The conditions are metamorphic, in that temperatures are in the range of several hundreds of degrees Celsius, pressures are several hundreds of bars to 1 or 2 kilobars (Einaudi et al., 1981, Einaudi and Burt, 1982). Because of their mode of formation, the minerals in skarns combine elements from the carbonates, such as calcium, with others added by the external fluid, such as silica, iron, aluminium. Thus these minerals are mainly calc-silicates such as garnet (grandite solid solution : $\text{Ca}_3(\text{Al,Fe})_2\text{Si}_3\text{O}_{12}$), clinopyroxene solid solution ($\text{Ca}(\text{Fe,Mg})\text{Si}_2\text{O}_6$), calcic amphibole (solid solution $\text{Ca}_2(\text{Mg,Fe})_5(\text{OH})_2\text{Si}_8\text{O}_{22}$), ilvaite ($\text{CaFe}_2^2\text{Fe}^3\text{O}(\text{OH})\text{Si}_2\text{O}_7$), epidote ($\text{Ca}_2(\text{Al,Fe})\text{Al}_2\text{Si}_3\text{O}_{12}$) and so on. One may also encounter other minerals, and particularly economic minerals (skarns may be ores of tungsten, tin, iron, copper and other metals). Skarns usually form decimetric to metric sized veins within

marbles, or metric to decametric-sized lens-shape bodies along lithologic discontinuities, between marbles and other rocks (granites, schists...), that have guided the aqueous solutions.

One characteristic feature of ordinary skarns is the pattern of zoning some may have. For instance transformation of marble A may be made through different steps in space separated by sharp fronts defining zones B, C, D and so on. In Fig. 1, two zones (hedenbergitic clinopyroxene and granditic garnet) develop in a calcitic marble.

These features are best explained by hypothesizing that the different fronts of transformation induced by a pervading metasomatic fluid, simultaneously progress at different speeds, the first front progressing faster than the second, and so on. This type of phenomenon has been studied by Korzhinskii (1970), who proposed a model based on local chemical equilibrium (no kinetics, no diffusion), and developed by several other workers including the present author (e.g. Guy, 1984, 1988, 1993, Guy et al., 1984). In the example of Fig. 1, one part of the starting marble has thus been converted first to pyroxene and then to garnet. This collection of zones of synchronous growth is called a metasomatic column.

Another feature of ordinary skarns that is less appreciated is the hypothesized evolution with time of the zonation itself (Guy, 1988). In a given skarn deposit, different types of zonings may form from the same starting material. In figure 2, another zoning of a skarn developing in calcitic marble has been portrayed : marble / ilvaite / andraditic garnet. A simple explanation for this variety of zonings is that they have been produced under different physical and/or chemical conditions i.e. by different activities of the mobile components in the fluid. When we compare zoning 1 (Fig. 1) and zoning 2 (Fig. 2) one (or several) parameter(s) must have changed and ilvaite has replaced hedenbergite.

The transformation of dolomites (calcium-magnesium carbonates) shows conspicuous evolution of zoning (e.g. Bucher-Nurminen, 1981, Dubru, 1986, Guy, 1988), and the paragenetic studies indicate that one important factor governing these changes is the decrease of temperature during the history of skarn

development. The evolution of zoning may be portrayed on diagrams such as figure 3, where different metasomatic columns are represented and substitute for one another along the vertical axis.

3. Banded skarns

Ordinary zoning generally shows a succession of zones A, B, C and so on ; sometimes, rather infrequently, we observe that the skarns are banded (Fig. 4) : the new minerals are disposed in oscillatory precipitations B-D-B-D and so on, even though the starting material may be homogeneous ; B and D may be two minerals or two groups of minerals. The examples are many. In Fig. 4.1, one can see a schematic example drawn as a synthesis of personal and literature observations : a banded skarn is developed in homogeneous marble. The ribbons of the banded skarn are a few millimetres to centimetres in width ; they are parallel to the main front of the marble transformation, or they may form orbicular structures around remnants of marbles, independantly of the lithology of the marble. These structures most often appear on the marble side but they may also appear inside the skarn as well. When they start to develop on the marble side, their evolution inside the skarn may have different forms in which either one of the two minerals in the alternation predominates, or a third mineral (or groups of minerals) forms a new zone as illustrated in figures 4.2 and 4.3. Figures 4.4 and 4.5 show photographs of banded skarns of these kinds.

Banded skarns were first described at the beginning of the century, and many new examples are found in more recent publications. We need give only a few examples. Knopf (1908) described banded structures in the tin skarns of the Seward Peninsula (Alaska). The skarns developed in a Paleozoic sedimentary sequence in the vicinity of Mesozoic granitic intrusions. The main skarns consist of massive garnet and idocrase rocks that cross cut the calcareous beds of the sequence. At the border of the main skarns the recurrent alternations can form orbicular structures and veins, that are an extension of the skarns into the marbles ; the alternations show white and black strips, of millimetric thickness. The

orbicular structures have a spheroidal shape like onion skins with the same type of alternation as the veins. The white strips are fluorite with possible calcic plagioclase, the black strips are made of magnetite, hornblende and idocrase with accessory garnet and pyroxene. More rarely, strips of garnet + pyroxene alternate with magnetite.

Other descriptions are reported in the literature : Trustedt (1907) and Jahns (1944) describe quite similar alternations in an identical context (skarn developing in marbles). In the second case these are thin alternations of magnetite and silicates, associated with fluorite. Other examples are given in table 1.

Such phenomena have been observed elsewhere (Guy, 1981, 1988) : in the Empire Mine (New Mexico) and at Rio Marina and Calamita (Elba Island), the skarns are made of centimetric alternations of hedenbergitic clinopyroxene and ilvaite (figure 4.4) giving beautifully banded rocks developed within homogeneous marbles, similar to that portrayed in figure 4.1. At San Leone (Sardinia), the clear bands of andradite and the dark bands of magnetite + quartz are particularly conspicuous (figure 4.5).

4. The genesis of banded skarns

The formation of banded skarns must be understood in the context of ordinary skarns. Their genesis mainly involves transport and chemical reaction. As already stated by Knopf, the geometric connection between the banded veins and orbicules and the massive skarns of which they are an extension, is an indication of the similarity of formation of all the rocks ; according to Knopf, all result from the action of fluids emanating from the nearby granite and infiltrating through the calcareous wall-rock.

In this sense, a possible explanation for the banding would entail an oscillation of the composition of the metasomatic fluid or an oscillation of the fracturing of the system, as proposed by various workers (see table 1). These

explanations will not be considered here since, 1) they are very unlikely, and 2) since other explanations may be put forward to understand the oscillating and non-oscillating patterning within a unified framework.

The first step is to understand the time of formation of banded structures. An important feature noticed by Jahns (1944) strongly suggests that in the course of the temporal evolution of hydrothermal deposits, where some minerals (or "alteration minerals") may develop at the expense of previously formed minerals (or "primary minerals"), the banded skarns seem to develop at the intermediate time when primary and alteration minerals are "equivalent". This statement is based on the following reasoning.

So far as the minerals involved in an alternating structure are concerned, one most often observes that some (one type of strata) belong to the group of "primary mineral" of usual skarns, whereas others (second type of strata) belong to the group of "alteration minerals" of usual skarns. The textures of the rocks that display such oscillatory precipitation are original, and the two groups of minerals are on the same level ; they appear to be equivalent of competing with each other and none grows from alteration of the other. We can give the example of pyroxene (a mineral of the first group) and ilvaite (a mineral of the second group) that can be found in oscillatory patterns or also of andradite (first group) and of the assemblage magnetite, calcite and quartz (second group). The example of forsterite or diopside and magnetite that can form banded skarns in dolomites is also of the same type. The role of fluorite, together with silicates, in certain banded structures described in the literature, can be understood in the same scheme.

In keeping with these observations on the evolution of zoning in skarns, we have inferred that the physical parameters (pressure and temperature) and the chemical parameters (composition of the fluid at its source) could evolve during the history of a deposit (we are speaking here of a monotonous, non-oscillating evolution), and that the stability field of primary minerals could be overstepped, whereas the stability field of other alteration minerals (that can then develop at the

expense of the first) could be reached. But if for any reason the parameters stay close to the equilibrium conditions of both types, primary and alteration minerals, while the fluid is still entering the system and transforming the original rock, we are led to a critical situation in the sense that one does not know in advance which of the two types of minerals will develop, since they are equivalent with respect to the zoning. In figure 3, this critical situation corresponds to the dotted line that stays along the border between phases B and D. In such a situation a loss of stability may occur, in the sense that the ordinary evolution that produces the non-repetitive zoning (here A / B / C) may be upset ; small fluctuations of the parameters may cause precipitation of one phase for another (here B or D). In short, according to natural observations, this seems to be one case in which oscillations develop. In that case of oscillatory precipitation of the primary and alteration minerals the usual terminology becomes misleading since the two types of minerals precipitate contemporaneously.

5. Discussion

Let us go a little further and discuss a qualitative model trying to give a preliminary account for the banding of skarns. In the critical situations we have described in the preceding section, second order effects (effects of the supersaturation threshold necessary for nucleation, of crystal-growth kinetics, and of diffusion) may be important and even dominant. Different authors (cf table 1) have compared the banding structures to that of Liesegang rings, stressing the role of diffusion ; in that respect they have already dismissed the action of an external template to explain the oscillation. Recently, several models have been put forward to explain the onset of oscillations in geological systems and particularly in fluid-rock interaction ; these are reviewed by Ortoleva et al. (1987a). In our case, the problem of banded skarns is original in that the model must account at the same time for 1) a periodic precipitation of the two alternating phases or groups of phases, taken one by one, during the dissolution of the starting material, and 2) for an organized competition between the two new phases so that their precipitation is shifted by one wave-length. For clarity, this can be explained by a combination of two end-member processes.

1) The supersaturation / nucleation / depletion cycle discussed by Ortoleva et al. (op. cit.) must be invoked in the periodic precipitation of one phase. In this phenomenon, the pervading reacting fluid dissolves the phases contained in the starting material causing an increase in the concentration of the chemical component contained therein. In addition to these components, the building of the new phases involves other components brought into the system by the inflowing fluid. A finite supersaturation is needed to begin nucleation of the new phases ; crystal growth of the phase locally impoverishes the medium in the chemical components including those taken from the starting material ; the possible nucleation of a new crystal is then possible only downstream where the concentration of the chemical components induced by dissolution of the initial minerals has reached the proper value for supersaturation, and this can explain the oscillatory precipitation of one phase.

2) The skew-synchronicity of the two precipitation processes may be accounted for by their coupling via aqueous species involved in the mass balance, the mass action laws, and the kinetics of crystal growth. As is well known, the rate of mineral growth or dissolution is limited by surface attachment. Since the two phases precipitate in approximately the same amounts and in oscillation together, the temporal laws for their precipitation must, as a first approximation, be the same. A coupling of the precipitations of the two phases may take place because of the instability of the precipitation in equal amounts of the two phases or groups of phases coupled : if there is any slight difference in surface area of the two phases, all other parameters being equal, including the number of nucleated grains, then the mineral having the larger surface area will grow faster than the other. The interstitial fluid will then be impoverished in the chemical components necessary to build the first phase until the system jumps to a more abundant development of the second mineral and so on. Because of the nucleation threshold discussed above, the precipitation of one mineral may be completely repressed in the domain where the other mineral precipitates. This may in brief account for the appearance of oscillatory precipitation. This discussion must be assessed by a more quantitative (numerical) approach.

In the model proposed here, the oscillations maintained provided the inlet fluid continues to bring in chemical components at the right speed to keep up with the growth of crystals. There is thus a critical value for the inlet velocity with respect to the kinetic rate and diffusion constants. If fluid velocity is too fast, the composition of the in-coming fluid is imposed everywhere and local disequilibrium allowing for the oscillations is no longer possible. We then return to the Korzhinskii's model (1970) for the propagation of fronts. It is also necessary that the composition of the inlet fluid is such that two minerals or groups of minerals may be stable together and so as a whole precipitate in the same time.

Other models may be envisaged to explain banding. Oscillations may appear with diffusion coefficients non-linearly dependant on concentration (Hazewinkel et al., 1985), in non-ideal system (Li Ru sheng, 1981), and in the framework of hyperbolic systems of equations (Bonnefille, 1987). In the last case, fronts and oscillations are treated only with an equilibrium formulation and without diffusion, whereas these features are more usually treated in terms of the kinetics of the chemical reactions and with diffusion. As a solution of the more general equation that could be written for such problems and involve diffusion, advection and chemical kinetics terms, several types of behaviours may be observed according to the importance of the different terms and the values of the parameters : fronts (Ortoleva et al., 1986), oscillations, combinations of both, and even chaotic behaviour. One will find in Nicolis and Prigogine (1977), or in Pacault and Vidal (1982), general features of the models that may account for the appearance of oscillatory chemical "waves". The instability effect of surface attachment evoked here has been termed autocatalysis by some workers : Slin'ko and Slin'ko, 1978, Chaix, 1983, Gruffat et Guy, 1984. There is some analogy with the model proposed by Haase et al. (1980) to explain the oscillatory zoning of feldspar.

In conclusion, one must set the problem of the oscillatory precipitations in the overall context of where ordinary skarns are formed. Without pretending to offer a general explanation for banded skarns, it may be recalled that, in the qualitative model proposed, the critical condition responsible for the oscillations must be defined at the same time by 1) the magnitude of the transport parameters (fluid velocity, diffusion coefficient) compared to that of kinetics and 2) by the concentrations of the components in the fluid : 1) transport must not be too fast as compared to kinetics : this is in agreement with observation that oscillatory structures preferentially develop in places where advective transport seems to play a minor role, as at the borders of veins, around blocks that are completely surrounded by veins, or within thick skarns where pressure gradients must have been small ; 2) it is necessary that the concentrations of the components in the fluid lie close to the value where several phases may co-exist in chemical equilibrium, or rather, may compete for the same zone with respect to the dynamic development of the metasomatic column (this may occur only at particular times during the skarn evolution).

Banded skarns are a beautiful example of geochemical self-organization in the sense that the organization must not be due to oscillating boundary condition but to the interplay of competitive phenomena within the system. Speaking of these self-organized structures, the equivalent term of dissipative structures (Prigogine) has been used (Guy, 1981), in the sense that their formation is manifested in a system that is out of equilibrium, with a dissipation of energy, and with feed-backs. Similar structures have been studied on a quantitative basis by Ortoleva et al. (1987 a and b). The ordinary zoning of skarn wherein the concentrations of components are organized into different domains separated by sharp fronts is already an example of self-organization (Guy, 1988).

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Captions for figures

Figure 1

An example of skarn development within a marble, showing metasomatic zoning : marble (A) / pyroxene (B) / garnet (C). One will notice the constancy of the order of the metasomatic zones (marble, then pyroxene, then garnet) wherever they develop, in veins or veinlets, around marble remnants or in massive skarns. Arrows indicate the supposed direction of the metasomatic fluid. Width of zone B may be centimetric to metric.

Zoning of this type is described in many skarn deposits (e.g. Soler, 1977, Burt, 1972).

Figure 2

Another example of metasomatic zoning in skarns developed on pure marble : marble (A) / ilvaite (D) / garnet (C). Width of zone D may be centimetric to metric.

Zoning of this type has been observed in the Empire Mine (New Mexico) (cf Burt, 1978).

The choice of the letters A, B, C, D has been made consistent between the different figures.

Figure 3

The evolution of metasomatic zoning. A possible explanation for the variety of zoning patterns that develop on the same starting material (such as zonings 1 and 2 on figures 1 and 2) is to suppose that some parameters have changed during skarn evolution (time is along the vertical axis) and that zoning (1) A / B / C is replaced by zoning (2) A / D / C (distance is along the horizontal axis), because mineral B is no longer stable and is replaced by mineral D.

As will be discussed in the following, we will suppose that when the transformation operates in conditions close to the boundary between B and D (dotted line), the zoning may be oscillatory : A / B-D-B-D and so on / C or A / B-

D-B-D and so on / B (or D) (oscillatory zoning of this sort is illustrated in figures 4.1 to 4.5).

We can give many examples where this situation may occur, although clear evidence of evolution of zoning in a skarn deposit is not common. (B,D) couples may be (pyroxene, ilvaite), (pyroxene, amphibole), (garnet, magnetite + quartz), (forsterite, magnetite), (diopside, magnetite) and so on.

We suppose in this picture that the changes in the physical and/or chemical conditions that take place along the vertical axis are slower than the time necessary to create a single zoning pattern developing along the horizontal axis ; the horizontal arrow in the figure shows the direction of fluid movement during an interval of time when the conditions did not change much and were close to the boundary between two zoning systems. In this situation, we suppose that the spatial zoning is not merely that indicated by the arrow (A / D / B / C) but that there is an oscillation between B and D. The change in the zoning is sometimes defined by the disappearance of one zone, such as B in the A / B / C zoning pattern (this situation is different from that portrayed in the figure). If then the conditions are maintained in the vicinity of the triple point A B C, we may expect an oscillation between B and C phases. In that case the oscillatory zoning may involve minerals that may in other cases be involved in the same zoning pattern. In skarns we may for instance observe the disappearance of wollastonite from the sequence calcite / wollastonite / hedenbergite, with the later zoning calcite / hedenbergite. The oscillation between hedenbergite and wollastonite is then expected (it has been observed by numerical simulation, Ortoleva and Guy, pers. obs.).

Figure 4 Banded skarns

Figure 4.1

An example of banded skarn : skarn develops in an homogeneous marble. It is banded in the sense that the metasomatic minerals B and D are precipitated alternatively forming oscillatory structures B-D-B-D... The ribbons are parallel to the main transformation front, in the external part of the skarn or around remnants of marbles.

This may apply to the ilvaite + pyroxene banded skarns of Rio Marina (Elba Island, Italy, Guy, 1981) (see also figure 4.4).

Figure 4.2 and 4.3

Two idealized cross-sections of banded skarns : in 4.2 mineral B dominates in the inner part of the skarn (as it is in the case in Rio Marina where B = hedenbergite dominates). In 4.3 another mineral or zone, C, develops at the expense of the "zone" B-D-B-D. This is the case in some other deposits.

Figure 4.4

Photograph : ilvaite : pyroxene banded skarn (Rio Marina, Elba Island, Italy) seen in thin section. The ilvaite bands, in black, alternate with hedenbergitic pyroxene (with interstitial quartz and calcite). Notice the radial texture of ilvaite within a "stratified" distribution. This is also the case for hedenbergite, though less distinctly. On this sample, the ilvaite bands are 2 to 3 millimetres thick, the hedenbergite ones 4 to 6 millimetres. In other parts of the skarns, the bands may reach one centimetre.

Figure 4.5

Photograph : banded skarn in San Leone (Sardinia, Italy) : alternations of andraditic garnet (light) and magnetite + quartz (dark). The garnet bands are 2 to 5 mm thick, and the magnetite + quartz bands are 5 to 15 mm thick (Guy, 1981, 1988).

TABLES

TABLE 1

Banded skarns in the literature.

A few examples are given here, together with some comments. Additional examples include : Zimmernink, 1985 (Fe-sphalerite / calc-silicates, in Santander, Peru) ; Shabynin, 1977 (banded skarns and greisens) ; Alexandrov, 1982 (banded magnesian skarns) ; Guy, 1988 (forsterite / magnetite and diopside / magnetite at Traversella, Italy) ; Meinert, 1982, in which case the template of replaced argillaceous layers is recognized; one will also find in Kwak and Askins (1981) and in Kwak (1987) a review on what they call "wrigglite" (i.e. banded skarns).

Skarn minerals may also exhibit oscillatory zoning : garnets (e.g. Verkaeren, 1971, Zimmernink, 1985), epidote (pers. observations of the author) and so on.