The scheelite-skarn of Salanfe (Valais, Switzerland)

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(Valais, Switzerland)

by *Massimo Chiaradia*[1]

Abstract

New data on geology, metamorphism, mineralogy and formation mechanisms of the scheelite-skarn of Salanfe are presented. The skarn, situated in a metasedimentary sequence of possible Pre-Cambrian age in the Aiguilles Rouges massif (Swiss Alps), was formed during a Late Variscan high temperature metamorphic event. Skarn mineralogy shows a typical evolution from a metamorphic stage to ore skarn stages (prograde and retrograde). In the retrograde stage of the ore skarn, pyroxene is replaced by hydrated minerals (chlorite, epidote, amphibole) or by the association hematite-calcite-quartz depending on the distance from the marble. The main ore minerals are scheelite, arsenopyrite and gold. Two scheelite generations have been recognized on the basis of mineralogical associations and trace element (Fe and Mn) concentrations. Skarn formation mechanisms and fluid evolution are investigated with the aid of activity-activity diagrams. The existence of two scheelite generations is interpreted as a result of the favourable interaction between particular fluid conditions (established in a given moment or in a given portion of the skarn) and the mechanism of W precipitation from the most common W-transporter complexes.

Keywords: Skarn, scheelite, pyroxene zone, fluid evolution, Salanfe, Valais, Swiss Alps.

1. Introduction

The W–As–Au skarn of Salanfe (Valais, Switzerland) was worked for arsenic and gold during the first forty years of this century when about 700 tons of arsenic and 55 kg of gold were extracted (RICKENBACK and VON KAENEL, 1953; WOODTLI et al., 1987). In the seventies, discovery of scheelite (FREY and VON RAUMER, 1977), with local concentrations of more than 1% WO_3 (WOODTLI et al., 1987), renewed the scientific and economic interest of the site.

2. Geologic setting

The scheelite-skarn of Salanfe is situated in the crystalline basement of the Aiguilles Rouges massif (Helvetic realm of the Swiss Alps). The general geologic setting of this region is well defined in various papers (VON RAUMER, 1981, 1984a, 1984b, 1987, 1988; JOYE, 1989). In the Salanfe area, in particular, the metamorphic sequence is composed of three units with distinct lithological and deformational characteristics (Fig. 1):
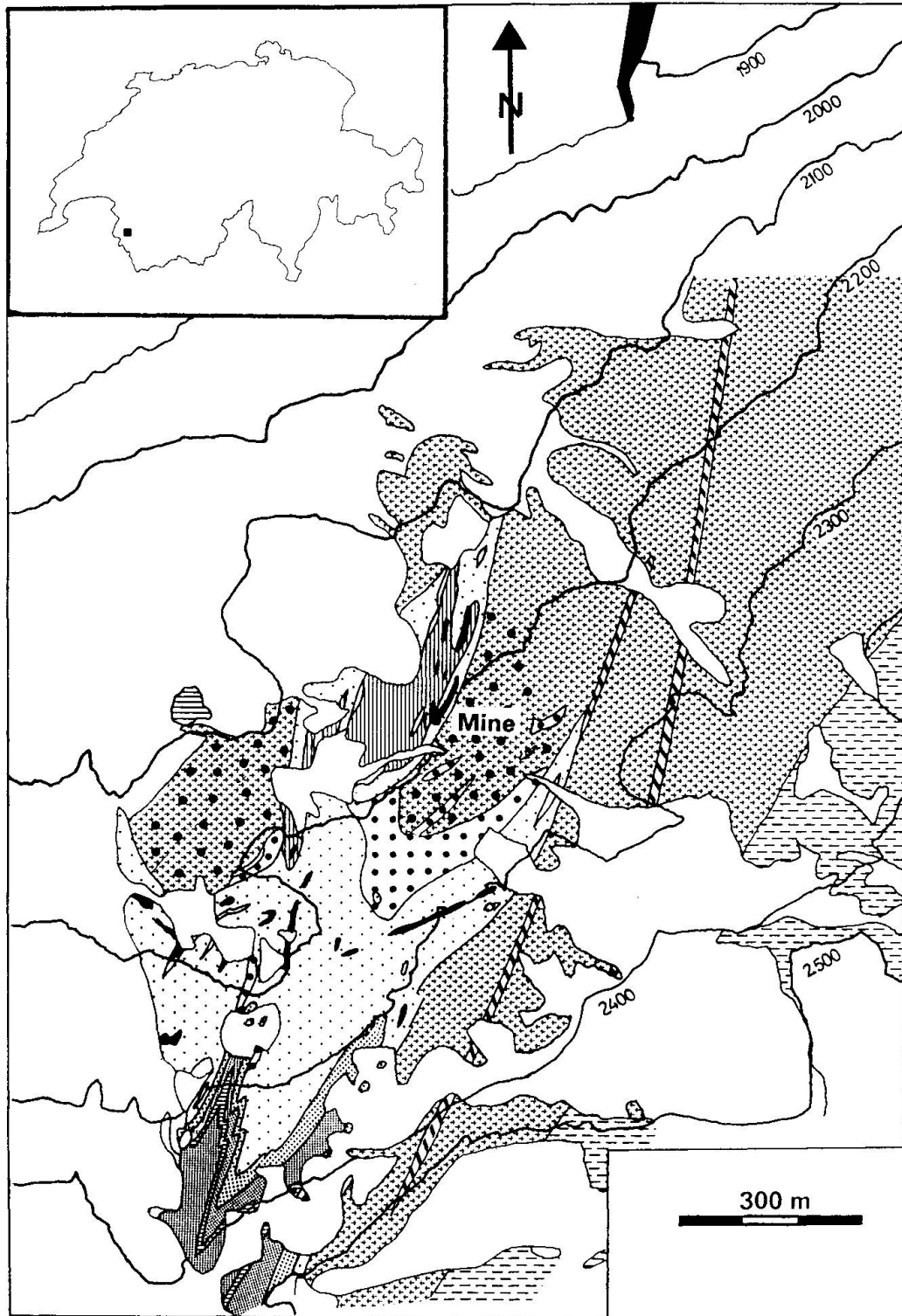
1. metagreywackes with calc-silicate lenses and intercalations of graphite-bearing dolomite marbles, quartzites and graphitic quartzites ("Varied Gneiss Unit"; Pre-Cambrian?). This unit underwent three main deformational events of pre-Alpine age (according to VON RAUMER, 1987);

2. granitic to granodioritic orthogneisses (Early Paleozoic?). They are affected by two main pre-Alpine deformational phases (D2, D3; see VON RAUMER, 1987);

3. acidic orthometamorphites (fine-grained gneiss and augen-gneiss, Early Paleozoic?). Also this unit is affected by only two pre-Alpine deformational events (D2, D3; see VON RAUMER, 1987).

During Late Variscan, between D2 and D3 events, a static high temperature metamorphism (VON RAUMER, 1987) produced a sillimanite-

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
Fig. 1   Geologic map of the Salanfe area.

biotite-K-feldspar paragenesis in the metagrey-wackes, local diatexis in the orthogneisses and the formation of a small garnet-bearing leucogranite (Fig. 1).

Microstructural evidences, such as static crys-tallization of metasomatic phases on the S2 planes of schistosity as well as on the axes of the F3 microfolds in the metagreywackes, show that also skarn formation occurred between D2 and D3 and continued up to the beginning of D3.

3. The host rock

The "Varied Gneiss Unit" is composed of meta-greywackes with local intercalations of mica-schists, quartzites and graphite-bearing dolomite marbles (Fig. 1). Calc-silicate lenses are wide-spread throughout the series, but they are partic-ularly concentrated in proximity to the marble lenses.

The mineralogy of the metagreywackes is rather uniform: biotite, muscovite, quartz, K-feldspar, plagioclase (anorthite$_{35}$ by optical deter-mination), titanite, apatite, zircon ± tourmaline ± garnet ± sillimanite.

Calc-silicate lenses have centimetric to deci-metric thickness. They are composed of garnet (grossulare$_{84}$-almandine$_{16}$), Ca-pyroxene (diop-side$_{60}$-hedenbergite$_{39}$-johannsenite$_{1}$), quartz, com-pletely sericitized plagioclase and K-feldspar. A rough zonation can be recognized in places with garnet prevailing over pyroxene in the cores and vice-versa in the outer zones of the lenses.

The high temperature associations of the calc-silicate lenses and of the metagreywackes and the curve of first melting (for which an X$_{H_2O}$ = 0.85 has been chosen) allow the definition of the P-T con-ditions of the high temperature event: tempera-tures of about 700 °C and pressures of at least 4 kbars are the obtained values. This result is in good agreement with that of the P-T-t path established by JOYE (1989) and by SCHULZ and VON RAUMER (in press) for the paragneisses of the Aiguilles Rouges massif.

4. The skarn

Skarns are present at the contact marble-para-gneiss only where this contact is situated in close proximity to the leucogranite. Fluids exsolving from the leucogranite are hence regarded to as the most probable responsible for the skarn building processes.

At the Robert mine, the most important site for the mineralization, two skarn horizons have
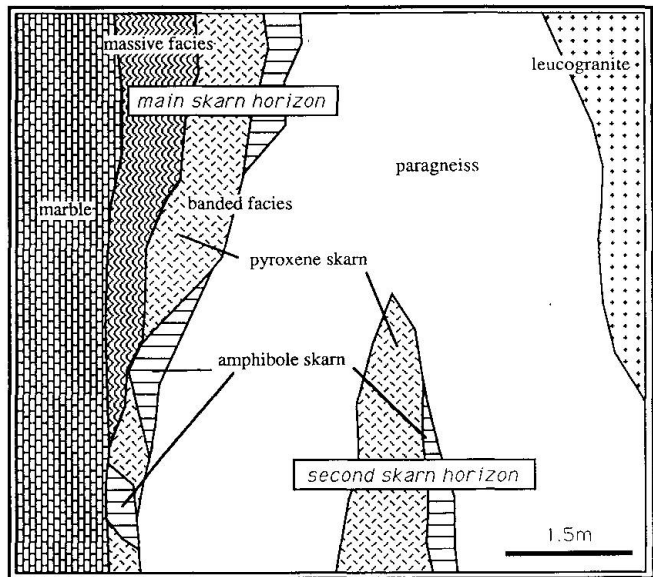
Fig. 2   Sketch of the two skarn horizons present at the Robert mine. For explanations see the text.

been identified (Fig. 2): a main horizon at the contact with the marble lense and, few metres away, a second horizon in a zone formerly char-acterized by the alternance of thin carbonatic layers and paragneisses. Both exhibit a minera-logical primary zonation with a poorly developed (or lacking!) amphibole zone on the gneiss side and a pyroxene zone on the marble side (Fig. 2). For simplicity we will deal here only with the main skarn horizon which is representative also of the features of the second one.

4.1. THE AMPHIBOLE ZONE

Amphibole skarn is composed of actinolitic to Mg-hornblendic amphibole, calcite, quartz, plagioclase, titanite and apatite. Retrograde re-placement of amphibole by chlorite is frequently observed. Ore minerals are absent.

4.2. THE PYROXENE ZONE

This zone, which is the most important one for the mineralization, presents the superposition of dif-ferent stages succeeding each other in time:

– a metamorphic stage characterized by the crystallization of diopsidic pyroxene (Fig. 3), ti-tanite ± quartz ± plagioclase ± calcite;

– an ore skarn stage which can be subdivided in a prograde and a retrograde phase:
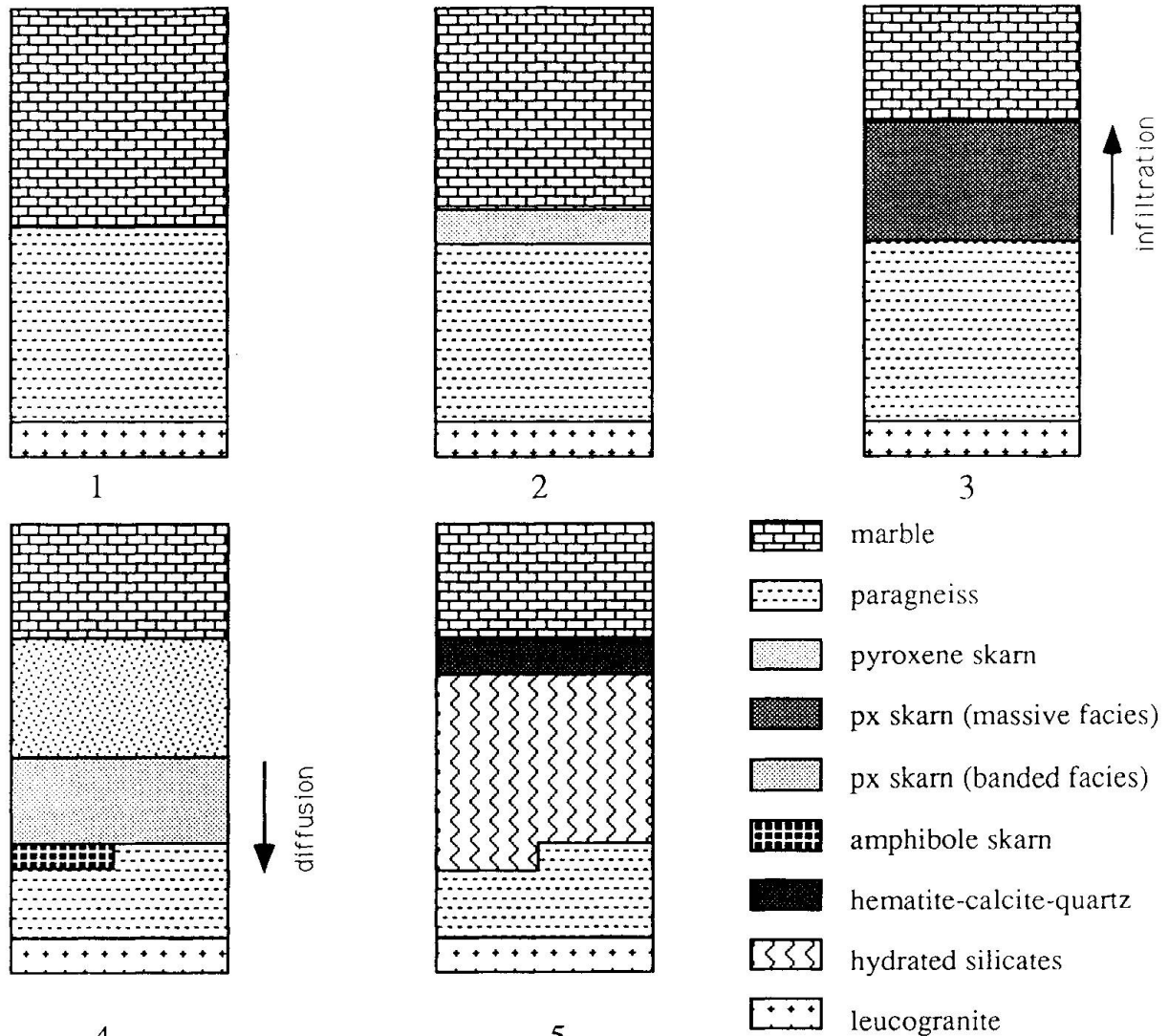
Fig. 3   Evolution of the skarn formation process in the main horizon: 1 = pre-metasomatic stage; 2 = metamorphic stage of the skarn; 3 = infiltration metasomatism during the prograde ore stage of the skarn (formation of the massive facies); 4 = diffusion metasomatism during the prograde ore stage of the skarn (formation of the banded facies); 5 = retrograde stage of the ore skarn. Abbreviation in the legend: px = pyroxene.

a) the prograde phase is characterized by the crystallization of diopsidic to hedenbergitic pyroxene (Fig. 4; nomenclature after MORIMOTO, 1988) and very abundant scheelite. Other minerals associated with this stage are a boron-silicate with a danburite-like structure – but with relevant contents of Al_2O_3 (21%) and FeO (10%) –, ilmenite (replacing titanite), sulphide minerals ± quartz ± calcite. The mineral association of the prograde ore skarn is typical of a reduced skarn type, i.e. poor or lacking in Fe^{+++}-bearing mineral phases (EINAUDI et al., 1981). This is probably related to the presence of abundant carbonaceous matter in the marble which acted as a buffer for the a_{O_2} of the fluids. From a textural point of view

the pyroxene zone can be furtherly subdivided in two facies:

– a massive facies on the marble side;
– a banded facies on the gneiss side.

The massive facies is formed by a monomineralic hedenbergite-skarn with isotropic texture; the boron-silicate, plagioclase, quartz and calcite are the accessory minerals. The pyroxene composition is constant throughout the zone and characterized by high Fe contents (hedenbergite$_{95}$). This facies has overprinted the marble so that it represents a skarn after marble (KWAK, 1987; see below). Closer to the gneiss, skarn portions of few cm^3 have been individuated, composed of Mg-rich pyroxene (diopside$_{70}$). The contact between these

Fig. 4 Compositions of the skarn clinopyroxene: circles = pyroxene of the metamorphic stage; squares = pyroxene of the ore skarn.

zones and the Fe-rich pyroxene skarn hosting them is abrupt. The Mg-pyroxene zones can be interpreted as the remnants of the metamorphic stage included in the ore skarn of the following stage. These zones are no longer present in the skarn portions situated closer to the marble contact, showing that the latter were built up during the ore skarn stage (see later).
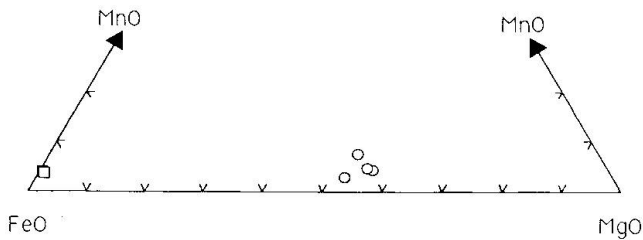
The *banded facies* is characterized by an alternance of monomineralic horizons composed of pyroxene and of polymineralic layers formed by quartz-plagioclase-pyroxene. The pyroxene composition is, in both cases, diopsidic (MORIMOTO, 1988), but with higher Fe-contents in the pyroxene of the monomineralic horizons (hedenbergite$_{48}$) than in that of the pyroxene-quartz-plagioclase layers (hedenbergite$_{42}$);

b) the retrograde stage can be subdivided in two subphases: initial and final. The initial subphase consists of a limited replacement of pyroxene by the associations magnetite-calcite-quartz and/or actinolite-calcite-quartz. In the final subphase a complete replacement of pyroxene occurs with quite distinct features depending on the position of the skarn with respect to the contact with the marble:

– close to this contact the pyroxene is almost entirely substituted by the association hematite-calcite-quartz;

– on the gneiss side the pyroxene is replaced by hydrated silicate minerals such as chlorite, epidote, green biotite and amphibole.

5. Skarn formation processes

Some conclusions on the skarn formation processes can be drawn on the basis of the above data. A scheme of this evolution is given in figure 4:

1) The skarn of the metamorphic stage was formed in consequence of limited diffusional processes (KORZHINSKII, 1965; KORZHINSKII, 1968) at the contact marble-paragneiss in response to

the high temperature regional metamorphism post-D2 and pre-D3. This is supported by the Fe-poor composition of the pyroxene (which is typical of a diffusion process, see KWAK, 1987) and by the limited spatial extension of the skarn related to this stage (see above; FONTEILLES, 1978; Fig. 4).

2) The skarn of the ore stage is built up by the fluids coming from the cooling leucogranite magma. The following succession of events is proposed to explain the existence of the massive and of the banded facies:

The skarn formation process in the ore stage begins with the onset of an infiltration front which comes from the leucogranite and gradually approaches the marble-gneiss contact. We admit (according to KWAK, 1987) that the metasomatic fluid in this case is charged with some elements like Fe, Si, B and W. The fluid does not react with the paragneiss during its advancing movement but when it comes in contact with the marble it reacts with the carbonate. Decarbonation reactions occur at this stage (see also KWAK, 1987). Causing the departure of the CO_2 from the system, they release Ca and Mg of the dolomitic marble to react with the elements transported by the metasomatic fluid (Fe, Si, W, B). Hedenbergite, Ca–Fe boron-silicate and scheelite result from this interaction. The metasomatic front continues its advancing movement into the marble favoured by the pressure gradient established as a consequence of the increased porosity in the marble owing to decarbonation reactions. The advancing movement of the front goes on and forms the massive skarn facies until conditions of equilibrium between the fluid (progressively impoverished in its "exotic" compounds as the reactions with the carbonate proceed) and the marble are reached. The constant composition of pyroxene throughout the massive zone (see above) supports the origin of this facies by an infiltrational metasomatism (KORZHINSKII, 1965; KORZHINSKII, 1968; FONTEILLES, 1978).

At this moment the rock volume comprised between the head of the metasomatic front and the leucogranite is permeated with a fluid phase which joins two environments in chemical disequilibrium: the marble (Ca and Mg rich) and the paragneiss (Si, Al and Fe rich). The onset of a diffusional metasomatic front, with an advancing movement in an opposite direction with respect to that of the above infiltrational front, is now possible. Then, fluids charged with Ca and Mg diffuse from the marble into the paragneiss and, reacting with this rock, form the diopsidic pyroxene of the banded facies (see above). The Mg-rich composition of this pyroxene supports the idea of a metasomatic transport of Mg from the marble towards
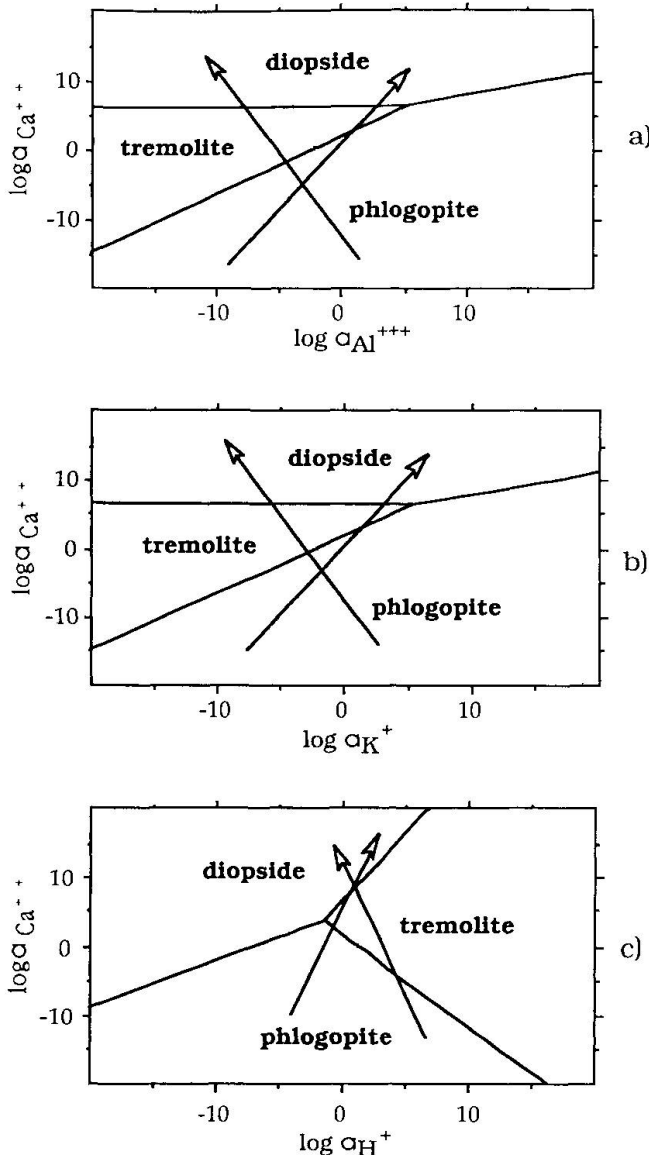
Fig. 5 Activity-activity diagrams for Ca^{++} versus Al^{+++} (a), K$^+$ (b) and H$^+$ (c). The diagrams show that the geometric zonation gneiss – amphibole skarn – pyroxene skarn (here represented by phlogopite, tremolite and diopside as significant minerals of each zone) is related to a strong a$_{Ca++}$ increase in the fluids approaching the marble. The arrows correspond to two arbitrarily chosen paths of the fluid responsible for the zonation, indicating that the transition from phlogopite to tremolite to diopside occurs always by an increase in a$_{Ca++}$ while a$_{Al+++}$, a$_{K+}$ and a$_{H+}$ can either increase or decrease. Reaction curves were calculated using MacII-PTAX computer program described on Macintosh by J. Lieberman (Institute of Earth Sciences – The Hebrew University of Jerusalem). Thermodynamic data for minerals are from BERMAN (1988); thermodynamic data for aqueous species are from HELGESON et al. (1981).

the gneiss. Moreover, the variation of pyroxene composition within the banded facies (passing from the mono- to the polymineralic horizons,

hence within very limited distances) shows that diffusion was the metasomatic process responsible for the formation of this facies (see FONTEILLES, 1978).

In summary, the pyroxene zone of the Salanfe skarn was formed by two distinct metasomatic processes: infiltration was responsible for the formation of the massive facies, diffusion for the formation of of the banded facies.

Diffusion was responsible also for the formation of the amphibole zone. The transition from pyroxene to amphibole zone and finally to paragneiss is easily comprehensible from figure 5 which shows that the stability fields for the three minerals, diopside, tremolite, phlogopite, considered as representative, respectively, of the pyroxene zone, the amphibole zone and the paragneiss are characterized by decreasing a$_{Ca++}$ in the fluids. This means that the transition from the pyroxene to the amphibole zone is a consequence of the progressive calcium impoverishment in the fluids diffusing from the marble towards the gneiss due to calcium precipitation as pyroxene in the gneiss portions closer to the marble (see also VAN MARCKE DE LUMMEN and VERKAEREN, 1986).

The scarce development of the amphibole zone can be related to high activities of Al^{+++} and K$^+$ and/or to low activity of H$^+$ in the fluids of the prograde stage (see Fig. 5). In particular, the low a$_{H+}$ could have played an important role in our case. Indeed, the activity of free hydrogen ions must be low at the high temperatures (700 °C) at which prograde skarn formation occurs, because, under these conditions, the dielectric constant of water is very low thus favouring the stability of ionic compounds such as HCl and HF (BRIMHALL and CRERAR, 1987). Hence, the absence of a well developed primary amphibole zone indicates the absence of an important thermal gradient (or, in other words, high temperature conditions throughout the skarn). This fact suggests that skarn formation, even if strictly related to the leucogranite, was somehow controlled by the regional high temperature metamorphic event post-D2 and pre-D3 with which leucogranite emplacement is associated.

3) The geometry of the present day skarn is the result of the prograde ore stage. In the retrograde stage some portions of the skarn previously formed undergo more or less important replacements but no new skarn portions are built up. The variable mineral overprint of the retrograde stage on the prograde skarn is shown, as already reported, by the presence of two distinct parageneses depending on their distance from the contact with the marble. This variability, which occurs within very limited spatial portions of the skarn,
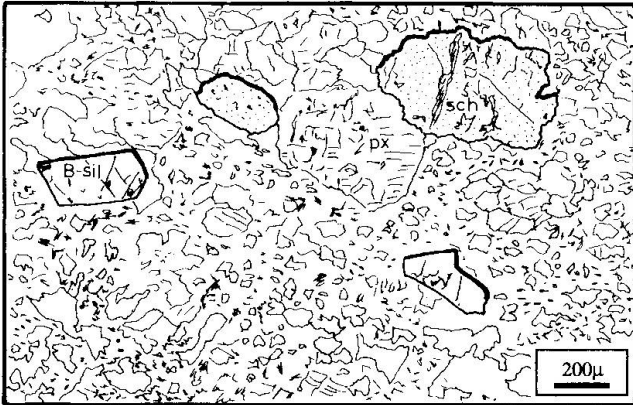
Fig. 6 First generation scheelite is associated with hedenbergite and the boron-silicate of the prograde ore stage. Abbreviations: px = pyroxene; sch = scheelite; B-sil = boron silicate.
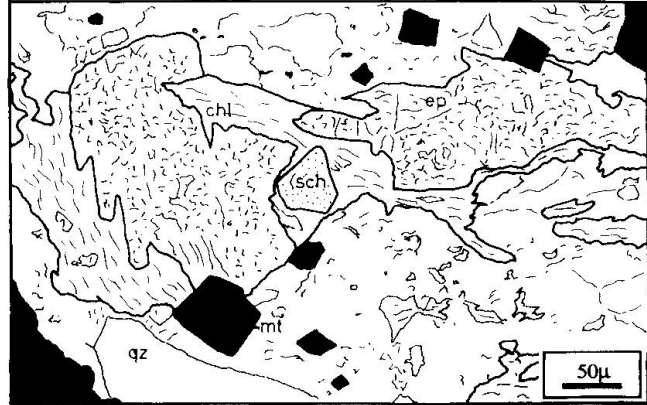

Fig. 7 Second generation scheelite is associated with epidote and chlorite of the retrograde ore stage in the skarn portions situated far from the marble. Abbreviations: sch = scheelite; ep = epidote; chl = chlorite; qz = quartz; mt = magnetite.

indicates that fluid circulation was very limited at this stage and that fluid composition was strongly controlled by the lithologies it came in contact with.

6. The scheelite mineralization

RICKENBACH and VON KAENEL (1953) report the following minerals in the skarn at Salanfe: löllingite, arsenopyrite, pyrite, galena, sphalerite, magnetite, hematite, pyrrhotite, chalcopyrite, fahlore, bismuthinite, As–Bi sulphosalts, native gold, native bismuth, native arsenic, bornite, covelline, cubanite and silver minerals in galena.

This paper deals only with the features of the scheelite mineralization, those of the sulphide minerals being object of a next study.

Two generations of scheelite have been recognized on the basis of mineralogical associations and trace element contents (see below):

– a first generation of scheelite is associated mainly with the hedenbergite and the boron-silicate mineral of the prograde ore stage (Fig. 6). It is concentrated in a high grade belt at the contact with the marble or in the marble itself;

– a second generation of scheelite precipitates only far from the marble in the retrograde stage of the ore skarn, associated with hydrated silicate minerals which derived from the break-down of the pyroxene (Fig. 7).

The presence of two distinct generations of scheelite, separated both in space and in time, can be explained by taking into account the mechanisms of tungsten transport and deposition on one

side and the fluid evolution on the other. In fact the precipitation of W as scheelite results from the interaction between favourable fluid conditions and the deposition mechanism of the W transported as a given complex. As the fluid composition changes continuously throughout the skarn history, favourable fluid conditions will be established only in some limited periods of the skarn building process.

At high temperatures (like those related to first generation scheelite deposition) tungsten is mainly transported as H_2WO_4, or as WO_2Cl_2 if sufficiently high salinities are present in the mineralizing fluid (FOSTER, 1977). Tungsten precipitation as scheelite from such complexes is favoured by high $a_{Ca^{++}}$ and low a_{H^+} (WESOLOWSKII, 1984) as shown, for instance, by a reaction of this kind

$$H_2WO_4 + Ca^{++} + CO_3^{2-} \rightarrow CaWO_4 + H_2O + CO_2.$$
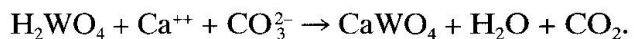
We can argue that W precipitation in the prograde stage is essentially the result of the enormous increase of $a_{Ca^{++}}$ in the fluids close to the marble as demonstrated by the fact that scheelite of the first generation is strongly concentrated in a belt at the skarn-marble contact.

A study of the fluid evolution through skarn development is necessary to understand the precipitation process of the second generation scheelite. In the a_{O_2}-a_{CO_2} diagram (Fig. 8) the field of the prograde ore stage and those of the two different final retrograde stages are defined. During the final retrograde stage higher a_{O_2} and a_{CO_2} conditions prevailed on the marble side than on the gneiss side. A possible explanation to this
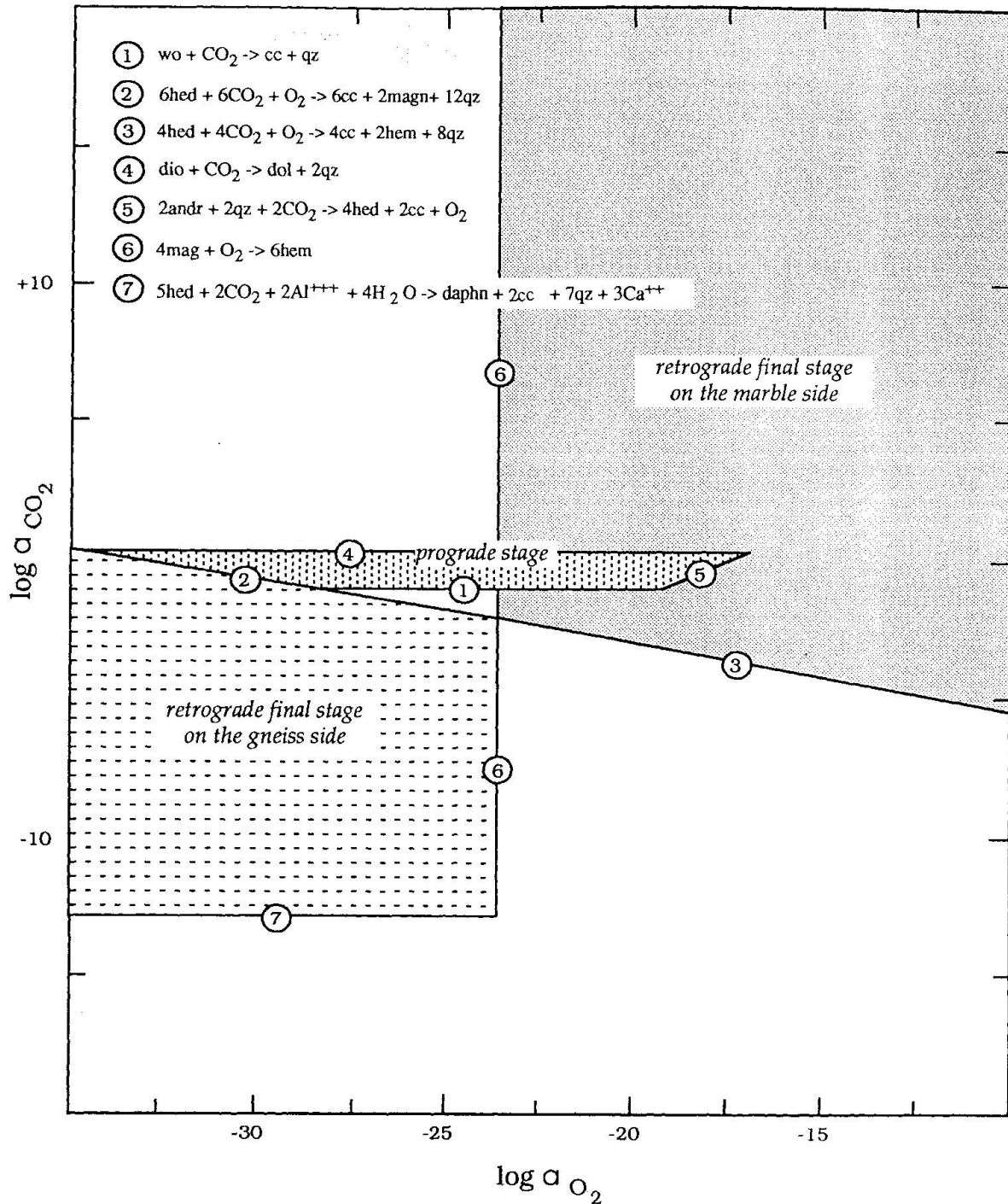
① $wo + CO_2 \rightarrow cc + qz$

② $6hed + 6CO_2 + O_2 \rightarrow 6cc + 2magn + 12qz$

③ $4hed + 4CO_2 + O_2 \rightarrow 4cc + 2hem + 8qz$

④ $dio + CO_2 \rightarrow dol + 2qz$

⑤ $2andr + 2qz + 2CO_2 \rightarrow 4hed + 2cc + O_2$

⑥ $4mag + O_2 \rightarrow 6hem$

⑦ $5hed + 2CO_2 + 2Al^{+++} + 4H_2O \rightarrow daphn + 2cc + 7qz + 3Ca^{++}$

+10

$\log a\ CO_2$

retrograde final stage on the marble side

⑥

④ *prograde stage* ⑤

② ①

③

retrograde final stage on the gneiss side

⑥

-10

⑦

-30   -25   -20   -15

$\log a\ O_2$

Fig. 8 In this a_{CO_2}-a_{O_2} diagram the stability fields of the prograde ore and of the two differentiated retrograde ore stages are drawn. Fields are limited by the reactions reported in figure 8. The prograde stage is limited by the absence of wollastonite concerning the lower limit of a_{CO_2}, by the formation of diopside at the expense of dolomite concerning the upper limit of a_{CO_2} and by the absence of andradite concerning the upper limit of a_{O_2}. In the retrograde stage higher a_{CO_2} and a_{O_2} conditions are present closer to the marble than to the gneiss. The field of the retrograde stage on the marble side is limited by the replacement of pyroxene by the association hematite-calcite-quartz concerning the lower limit of a_{CO_2} and by the transformation of magnetite into hematite concerning the lower limit of a_{O_2}. The field of the retrograde stage on the gneiss side is limited by the transformation of hedenbergite into magnetite-calcite-quartz concerning the upper limit of a_{CO_2} and by the stability of magnetite instead of hematite concerning the upper limit of a_{O_2}. Reaction curves were calculated using the MacII-PTAX and GridLoc computer programs described on Macintosh by J. Lieberman (Institute of Earth Sciences – The Hebrew University of Jerusalem). Thermodynamic data for minerals are from BERMAN (1988); thermodynamic data for aqueous species are from HELGESON et al. (1981). Abbreviations: wo = wollastonite; cc = calcite; qz = quartz; hed = hedenbergite; magn = magnetite; hem = hematite; dio = diopside; dol = dolomite; andr = andradite; daph = daphnite.

differentiated fluid character could be the decomposition of dolomitic marble:

$$CaMg(CO_3)_2 \rightarrow CaCO_3 + CO_2 + {}^1/_2O_2 + Mg^{++}.$$
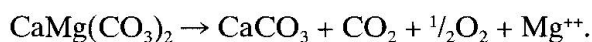
This reaction is documented by the constant presence of a calcitic belt replacing dolomitic marble at the contact with those portions of skarn which retrograded to the hematite-calcite-quartz association. The reaction could explain the higher a_{O_2} and a_{CO_2} conditions in proximity to the marble. We have already reported that, in the retrograde stage, W precipitates as scheelite only in the portions of the skarn situated far from the marble where low a_{CO_2} prevailed. This can be explained by the fact that the high a_{CO_2} in the fluids close to the marble buffered all the Ca^{++} ions resulting from the pyroxene break-down by precipitating them as calcite and thus preventing scheelite deposition. On the contrary, far from the marble a_{CO_2} was not sufficiently high to buffer all the Ca^{++} ions, part of which remained at disposal for scheelite precipitation (provided that W was still present in the solutions at this stage). A time-crystallization scheme which summarizes the mineral evolution of the Salanfe skarn through its different stages is given in figure 9.

Microprobe analyses of scheelite were carried out at the Institute of Mineralogy and Petrography of the University of Bern using a CAMECA-SX 50 microprobe. The analytical conditions were: a) for W and Ca, accelerating voltage 15 kV, regulated current 20 nA, fixed analysis time 15 sec.; b) for trace elements (Mo, Fe, Mn, Mg,
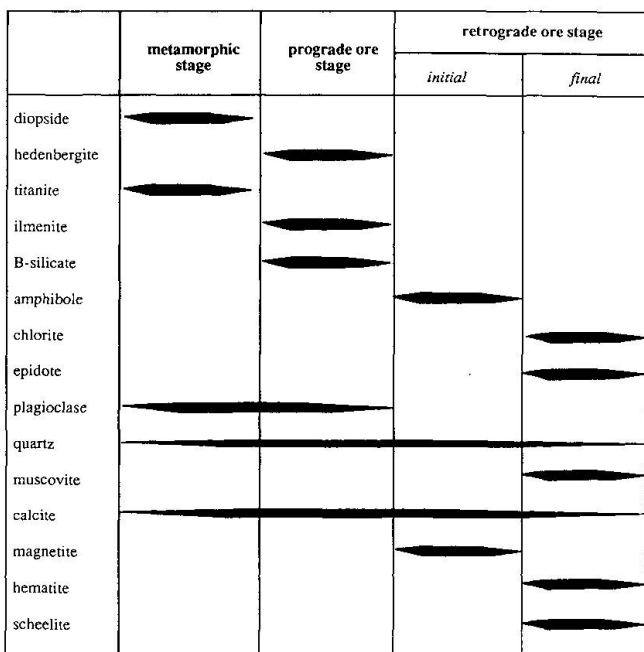
Tab. 1 Microprobe analyses of scheelites.

	scheelite I in the clinopy-roxene skarn (mean of 24 analyses)	scheelite II in the clinopy-roxene skarn (mean of 3 analyses)	scheelite I in the marble (mean of 14 analyses)	scheelite II in the marble (mean of 4 analyses)
CaO	19.313	19.347	19.603	19.930
WO$_3$	81.651	83.106	82.340	80.827
Al$_2$O$_3$	0.004	0.005	0.010	0.005
SiO$_2$	0	0	0	0
MnO	0.009	0.012	0.005	0.016
FeO	0.022	0.120	0.012	0.390
MgO	0.006	0.024	0.002	0.039
Ga$_2$O$_3$	0.050	0.053	0.022	0.043
Nb$_2$O$_5$	0.030	0.003	0.020	0.012
Total	101.085	102.670	102.014	101.262

Al, Si, Ga, Nb), accelerating voltage 15 kV, regulated current 50 nA, fixed analysis time 100 sec. (RAMSDEN and FRENCH, 1990). The standards used were a natural scheelite for W and Ca and natural silicates for trace elements. Slight enrichments in Fe and depletions in Mn are seen passing from the first to the second generation scheelites belonging to the skarn (Tab. 1 and Fig. 10). Scheelite precipitates also within the marble as rims of small crys-
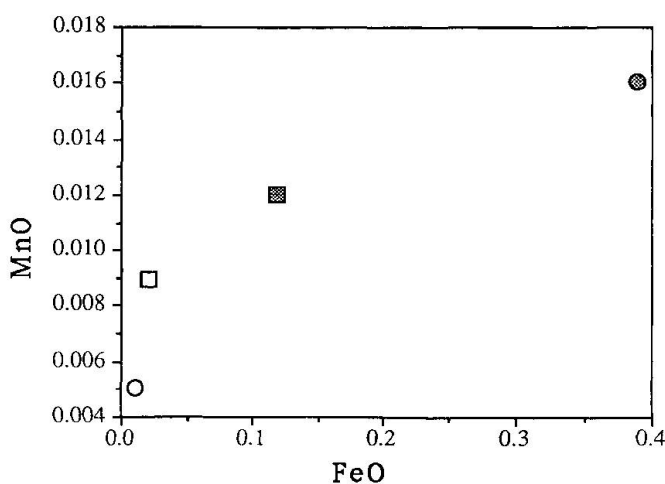
Fig. 9   Time-crystallization table summarizing the mineral evolution through the different stages of the skarn.

Fig. 10 MnO and FeO contents in scheelites of the first and of the second generation in the skarn and in the marble: scheelites of the second generation are slightly enriched in Mn and strongly in Fe in comparison to scheelites of the first generation. These enrichments are particularly strong in the second generation scheelites present in the marble. Data are from table 1. Symbols: ○ = scheelite of the first generation in the marble (mean of 24 analyses); □ = scheelite of the first generation in the skarn (mean of 3 analyses); ▨ = scheelite of the second generation in the skarn (mean of 14 analyses); ◉ = heelite of the second generation in the marble (mean of 4 analyses).
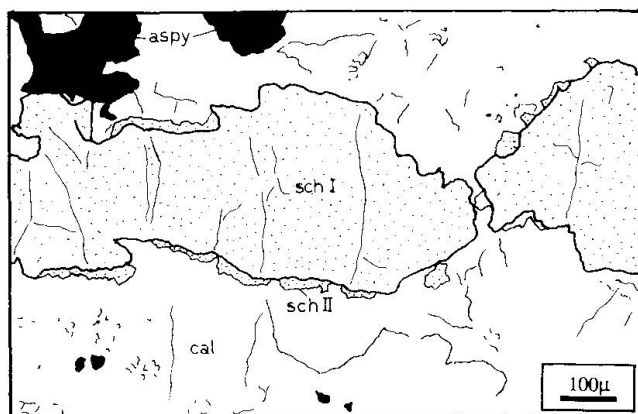
Fig. 11 A late generation of scheelite crystallizes as rims of small idiomorphic crystals around elements of first generation scheelite in the marble portions situated at the contact with the skarn. Abbreviations: schI = scheelite of the first generation; schII = scheelite of the second generation; cal = calcite; aspy = arsenopyrite.

tals (few tens of microns) around first generation elements (Fig. 11). These rims are always in geometric link with microfractures filled by chlorite. This scheelite could represent an episode of W precipitation even later than that we have previously ascribed to the second generation scheelite in the skarn. This is indirectly supported by the fact that we find this scheelite in the marble hence in an environment which, for what reported above, was not favourable to scheelite precipitation in the retrograde stage (because of the high a_{CO_2} conditions: see above). Indeed we can suppose that this scheelite belongs to a later stage when also close to the marble a_{CO_2} had decreased as a consequence of the continuous precipitation of calcite in the association calcite-hematite-quartz. Microprobe analyses on these scheelites show that they display a sensible enrichment in Fe with respect to the first and to the second generation scheelites of the skarn (Fig. 10), supporting their later genesis. Molybdenum contents in all the scheelites are always below the detection limit of 100 ppm: low molybdenum contents are typical of scheelites associated with reduced-type skarns (KWAK, 1987). On the contrary, gallium is often present in relevant concentrations (500–600 ppm) probably as a consequence of the identity of its ionic radius with that of tungsten.

7. Conclusions

This paper has put in evidence that the scheelite-skarn of Salanfe was built by two different metasomatic processes (infiltration and diffusion): in-

filtration was responsible for the formation of the massive facies and of the mineralization while diffusion was responsible for the formation of the banded facies and of the badly developed amphibole zone. A limited fluid circulation resulted in a high variability of the fluid composition even within very limited spatial portions. This fact had a great influence in the precipitation processes of W as scheelite which seems to be heavily conditioned by local fluid-rock interactions. Moreover this study has enhanced that also a_{CO_2}, besides other factors usually reported in the literature (T, $a_{Ca^{++}}$, a_{H^+}, ionic strength), is an important factor in the control of W precipitation as scheelite.

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