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Sedimentary protoconcentrations as a source of tungsten in the W–As–Au skarn of Salanfe (Aiguilles Rouges Massif, Switzerland)

by *Massimo Chiaradia*[1]

Abstract

The W–As–Au skarn of Salanfe is a stratiform epigenetic mineralization situated at the contact between dolomitic marble lenses and paragneisses (Early Paleozoic or Upper Proterozoic) in the crystalline basement of the Aiguilles Rouges Massif (Helvetic domain of the Alps). In this area the basement is composed, besides the paragneisses, of orthometamorphites of granitoidic composition. The skarn was formed during Late Variscan by the fluids released from a garnet bearing leucogranite issued from the in situ melting of former granitic gneisses. Trace elements show that neither the orthometamorphites nor the leucogranite display anomalous contents in W. On the other side, paragneisses are slightly anomalous in W, Au, Ba, Zn and V. Ba, Zn and V show a good correlation with the H_2O content of the paragneisses. This makes reasonable the supposition that these metals were adsorbed on clay minerals during the deposition of the sedimentary series. A similar process of concentration can be envisaged for W which is highly concentrated (up to 500 ppm) in the biotites of the paragneisses. These anomalies indicate that the metasedimentary series was a potential supplier of the metals for the skarn ore. Metals were possibly leached from the paragneisses by the fluids coming from the leucogranite, transported and finally deposited at the contact with the marble lenses. Simple calculations can demonstrate that the rock volume of the paragneiss sequence involved by the fluid circulation was large enough to furnish the W supply to the skarn ore at the nowadays measured concentrations.

The definition of the primary source of the metals present in this mineralization is also discussed. Some arguments indirectly support the existence of an exhalative activity somewhere in the depositional basin or close to it as the primary source of the metals. By this way metals mixed up with the detrital sediments and were diluted within the series giving rise to their general high background in the paragneisses. Stronger enrichments occurred in some horizons which reflected particular conditions of sedimentation (graphitic schists and quartzites) more favourable to metal deposition.

Keywords: skarn, tungsten protoconcentrations, remobilization, geochemistry, Aiguilles Rouges Massif, Western Alps.

Geologic setting

The W–As–Au skarn of Salanfe (first described by Rickenbach and von Kaenel, 1957 and afterwards by Frey and von Raumer, 1977 and by Chiaradia, 1993a and Chiaradia, 1993b) is situated in the crystalline basement of the Aiguilles Rouges Massif which consolidated during the Variscan orogeny (von Raumer, 1984a; von Raumer, 1984b; von Raumer, 1987; von Raumer and Neubauer 1993; von Raumer et al., 1993). In the Salanfe area the basement is composed, from SE to NW, of the following lithological units (Fig. 1): granodioritic orthogneisses; granitic orthogneisses passing to anatexites in some places; fine-grained orthogneisses with an intercalation of white-mica schists; tonalitic augen-gneiss; paragneisses with intercalations of quartzites, graphitic schists and marbles; garnet-bearing leucogranite.

All these units have suffered a complex and differentiated metamorphic-deformational history during the Variscan orogeny. The paragneisses and their intercalations are the only unit that displays three different deformations (D1, D2, D3); for this reason they are supposed to be the

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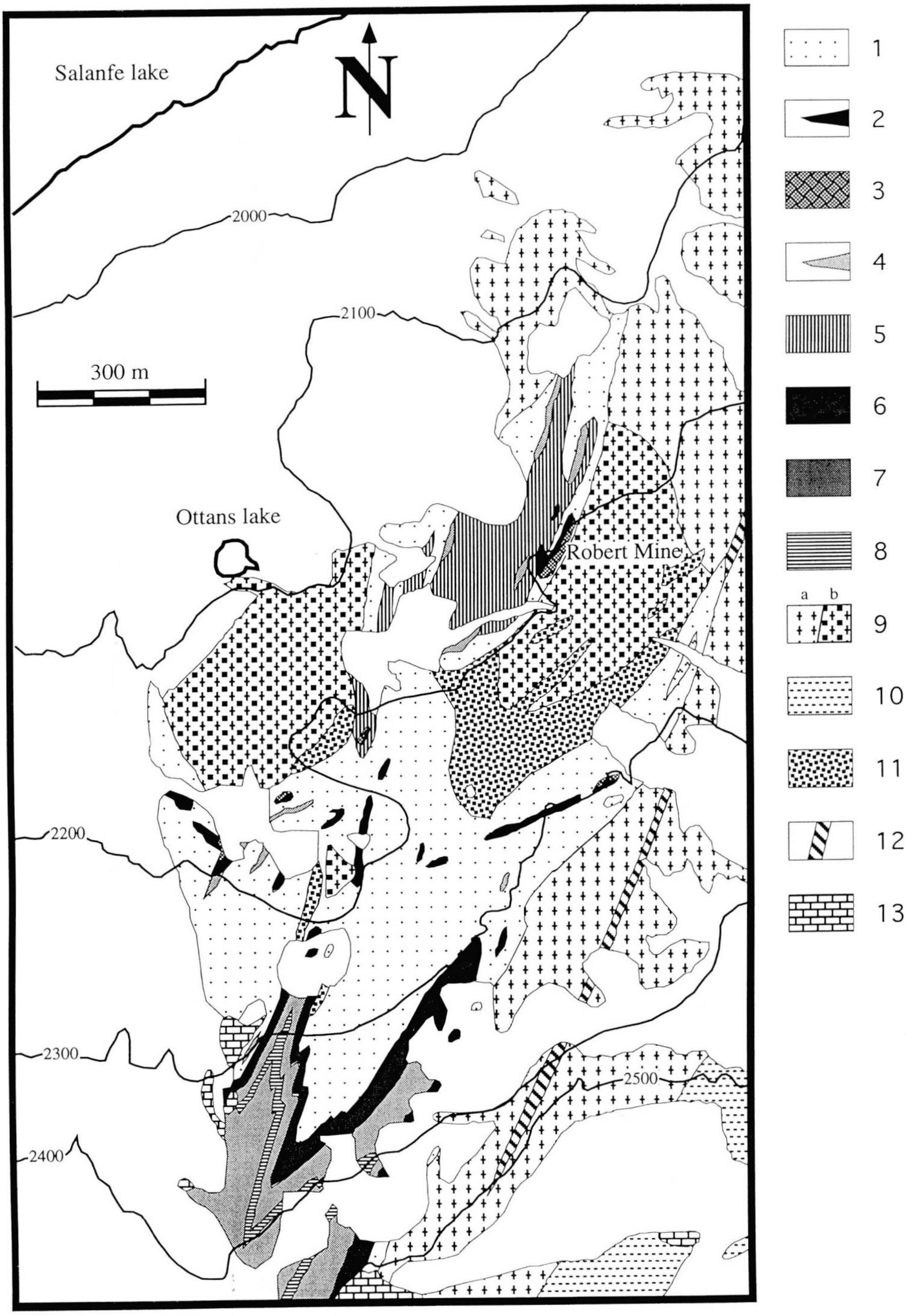

Fig. 1 Geologic map of the Salanfe area. Legend: 1 = metagreywackes; 2 = marbles; 3 = skarns; 4 = quartzites; 5 = micaschists; 6 = tonalitic augen-gneiss; 7 = tonalitic fine-grained orthogneiss; 8 = white micaschist; 9a = granitic orthogneiss; 9b = anatectic orthogneiss; 10 = granodioritic orthogneiss; 11 = leucogranite; 12 = rhyolitic dykes; 13 = Triassic cover.

oldest unit of the outcropping basement. The granodioritic and granitic orthogneisses as well as the fine-grained orthogneisses and the augengneisses suffered only the two late events (D2 and D3). They are thought to represent intrusions into the paragneisses after the D1 event (CHIARADIA, 1993b). The leucogranite is slightly and only locally affected by the D3 event. Structural observations indicate that leucogranite formation is related to a static high temperature event that occurred between D2 and D3. This event produced the total melting of a portion of the granitic orthogneisses and a partial melting of the surrounding portions (anatexites: Fig. 1). Quite high temperature conditions lasted then until the beginning of the dynamic D3 event. The D3 event affected the leucogranite with a solid state deformation only in those portions which had undergone a cooling fast enough to bring them in a partially solid state (like apophyses); on the other side it obliterated all the previous deformations in the anatexites.

Geochemistry, structural relationships and sedimentologic facies associations (for the paragneisses) have been used to reconstruct the geodynamic environment of formation of the different units.

The geochemistry of the paragneisses indicates that they were originally greywackes and lithic sandstones (CHIARADIA, 1993b; FONTEILLES, 1976; Fig. 2: geochemical data available from the author). Greywackes and lithic sandstones can be found in turbiditic sequences of the flysch type (PETTIJOHN et al., 1984). However, their association with dolomitic limestones and graphitic schists relates them to rather shallow anoxic basins particularly developed in back arc environment during Proterozoic time (CONDIE, 1982). Geochemistry of metabasic rocks outcropping in the Lake Emosson region, few kilometres north of Salanfe, within a series comparable to that of the Salanfe region, indicates an intracontinental basin environment (VON RAUMER et al., 1990).

The four different groups of orthogneisses of the Salanfe area (granodioritic, granitic, fine-grained and augen-gneiss) have all intruded the paragneiss sequence after D1 and before D2. Geochemistry of all these groups indicates a volcanic arc environment for their emplacement (Fig. 3; PEARCE et al., 1981; data available from the author). Petrographic differences among the different groups as well as differences in the major and minor element geochemistry point out that they belong probably to different phases of a unique magmatic cycle (CHIARADIA, 1993b): granitic and granodioritic gneisses are coarse-grained and contain enclaves which suggest an intrusive origin for them. Their lower Nb and higher Cr contents, in comparison with the fine-grained and augen-gneisses, plead for their derivation from a less evolved source (CHIARADIA, 1993b). Besides the difference in Nb and Cr contents, the fine-grained and augen-gneisses are more basic in composition (tonalitic) when compared to the granodioritic and granitic gneisses (CHIARADIA, 1993b); moreover their structures do not have elucidate so far whether their origin is intrusive or effusive.

The leucogranite is a typical syncollisional granite (Fig. 3). Both geochemical trends and structural observations (spatial relationships) indicate that it originated from the in situ melting of the granitic orthogneiss (CHIARADIA, 1993b).

On the basis of these structural and geochemical data the geologic evolution of the Salanfe region can be summarized as follows:

1) sedimentation of a detritic (flysch-like?) sequence represented by greywackes with intercalations of lithic sandstones, quartzites, pelites and carbonates. The age of this series is probably Early Cambrian or Upper Proterozoic on the basis of comparisons with similar series outcropping elsewhere in the Alps and in other pre-Mesozoic

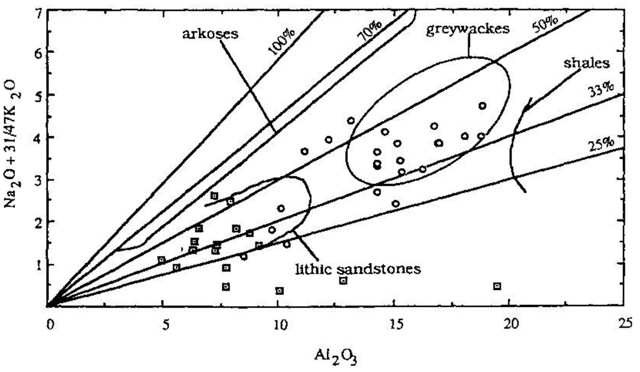

Fig. 2 Fonteilles' diagram showing the original sedimentary lithologies corresponding to the nowadays paragneisses (after FONTEILLES, 1976).

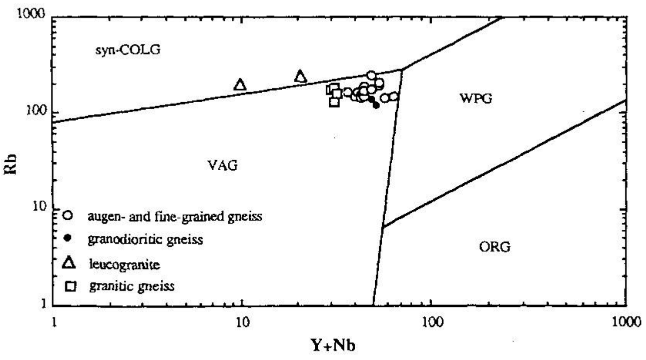

Fig. 3 Diagram showing a volcanic arc environment for the emplacement of the orthometamorphites and a syn-collisional environment for the leucogranite (from PEARCE et al., 1984).

crystalline massifs of Europe (VON RAUMER, personal communication); the sedimentation occurred in an intracontinental basin, possibly in a back-arc basin;

2) first deformational event (D1) with development of a S1 schistosity;

3) polyphasic intrusion of magmatic bodies of granitic-granodioritic and of tonalitic composition in a volcanic arc environment;

4) second deformation event (D2) with development of a S2 schistosity. The first two deformation events correspond to the subduction and to the nappe stacking stages of the Variscan orogeny according to VON RAUMER (1987);

5) high temperature static event with widespread anatexis in the central and south-western part of the area (Fig. 1); formation of a garnet-bearing leucogranite from the diatexis of the granitic orthogneiss. This event corresponds to the rise of the geotherms in the final stages of the collision (VON RAUMER, 1987);

6) third deformation event (D3) which is continuous with the static event and is characterized by an initial high temperature ductile shear. Shearing continues then at progressively lower temperatures. This event corresponds to the onset of a strike-slip regime at a regional scale (VON RAUMER, 1987).

Skarn formation

Skarns are present at the contact between marble lenses and paragneisses only where this contact is in close proximity to the garnet bearing leucogranite or to the anatectic portions of the granitic orthogneiss (Fig. 1). They develop at the expenses both of the marble (massive facies) and of the paragneisses (banded facies). Only the massive facies is carrier of mineralization. The following structural and geochemical arguments plead for a skarn formation strictly bound to the fluid exsolved from the leucogranite during its cooling stage:

1) the spatial relationship between skarn and leucogranite: where marble lenses are far from the leucogranite (more than a ten of metres) they are not transformed into skarns (see Fig. 1);

2) the presence of skarns only on the marble side facing the leucogranite showing the unidirectional provenance of the fluids from the magmatic body (Fig. 1);

3) the static crystallization of metasomatic phases (pyroxene, amphibole) at the expense of biotites defining the S2 schistosity planes in the gneissic portions of the skarn (banded facies) which shows that skarn formation occurred in correspondence with the emplacement of the leucogranite (after D2 and before D3);

4) the similar REE spectra of the massive skarn facies and of the leucogranite (CHIARADIA, 1993b) showing the imprint of the magmatic fluids in the metasomatic process (BAKER and HELLINGWERF, 1988; VANDER AUWERA and ANDRE, 1991).

A sketch of the relationships between time of skarn formation and deformation events is shown in figure 4.

This skarn, as many others, shows a very complex mineral evolution both in time (with a succession of, in order, metamorphic, prograde and retrograde stages) and in space (with a mineral zonation). The detailed mineral evolution of this skarn is given in CHIARADIA (1993a) and CHIARADIA (1993b). For the needs of this paper it can be summarized in this way: after an initial metamorphic stage with limited diffusion phenomena which produced a thin pyroxene zone at the contact marble-paragneiss, fluids exsolving from the granite started the skarn-building process. During the initial phase of the prograde stage does the first precipitation of abundant scheelite occur in association with allanite and hedenbergitic pyroxene. In a second phase of the prograde stage the skarn formation process continues with the precipitation of arsenopyrite, loellingite, pyrrhotite, tetrahedrite and gold of first generation. The sulphide minerals result both from reactions between fluid and silicate minerals and, mostly, from intergranular precipitation directly from the fluid. In the retrograde stage does a hydration of the pyroxene (transformed to chlorite and epidote) occur, accompanied by the precipitation of a second generation of scheelite and gold.

Metal geochemistry of the units

The problem of establishing the source of metals in ore deposits is particularly ambiguous in the case where (like at Salanfe) the mineralization is strictly bound to intrusive bodies. The most controversal point is establishing whether the magma was the source of the metals or whether it only caused the mobilization of metal concentrations already existing in the host rocks (see also KWAK, 1987). This study represents a first step in the attempt to solve this question for the Salanfe skarn. For this purpose the very simple approach of geochemical analyses on tungsten contents of all the lithologies outcropping in the Salanfe area has been chosen. Results are summarized hereafter for each considered class of rocks. If these results were carrier of suitable informations, the

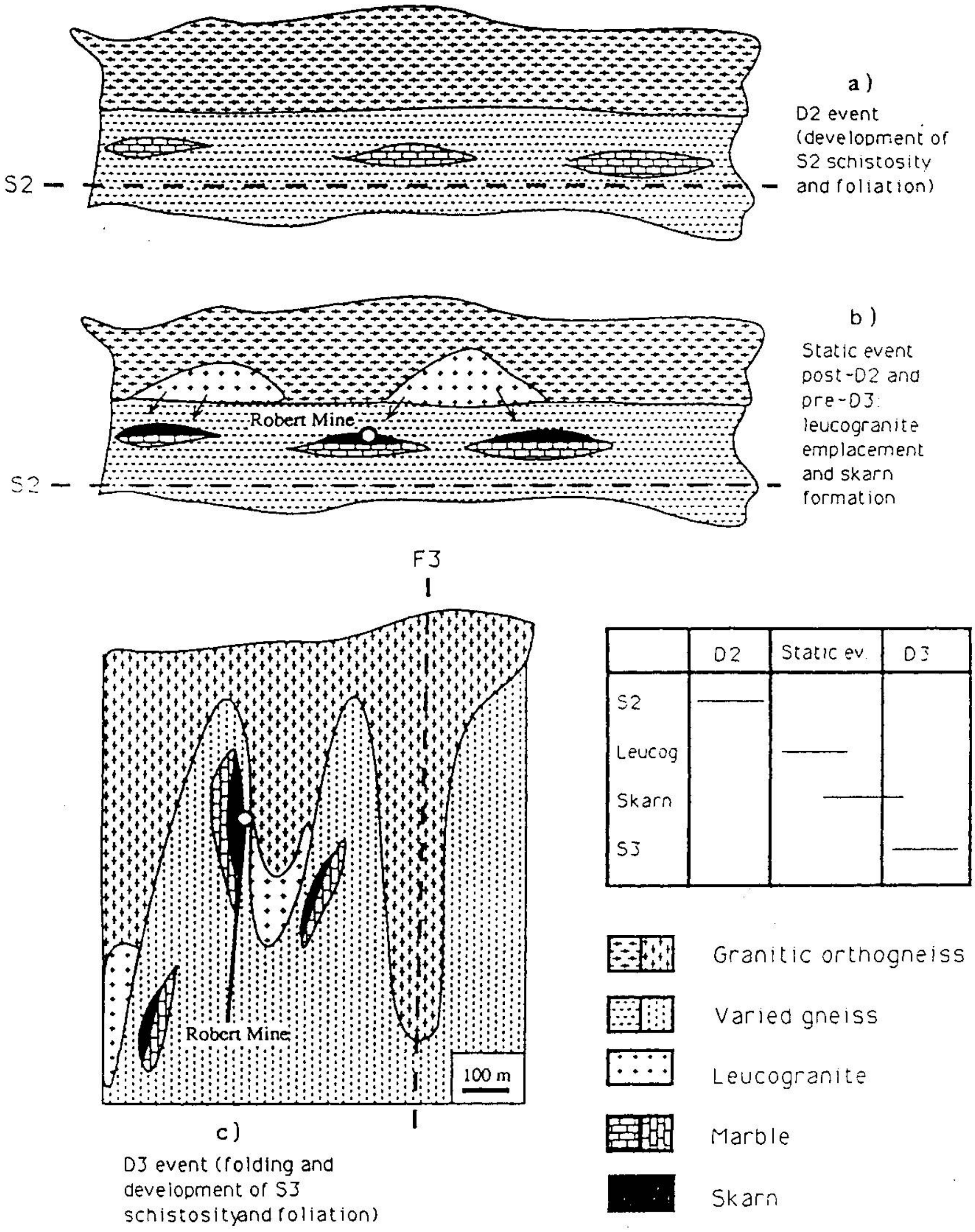

Fig. 4 Simplified horizontal cross-section of the Salanfe area showing the relationships between skarn formation and the deformational events D2 and D3: a) S2 schistosity is developed on the paragneiss and on the granitic gneiss; b) formation of the leucogranite from the in situ melting of the granitic gneiss during the high temperature static event; skarn formation (arrows indicate the path of the fluid exsolving from the leucogranite); c) F3 folding phase and development of S3 schistosity; present-day geometry of the skarn-leucogranite relationships (refer to Fig. 1 for a comparison with the actual geologic situation).

problem of the source of metals will be addressed to more sophisticated techniques (like lead isotopes, see later).

LEUCOGRANITE

The leucogranite might be a quite reasonable source of tungsten for this skarn because, as already reported, geochemical and structural arguments indicate that skarn was formed by the fluids released by the cooling leucogranite. Nevertheless the tungsten content of the leucogranite is very low (W = 3.4 ppm; Mo = 1 ppm; Sn = 6 ppm). This is not a conclusive argument for ruling out the leucogranite as a tungsten source. Indeed this low tungsten content can signify either that the

Tab. 1 Trace element geochemistry of the paragneisses of the Salanfe area. # = elements analyzed by ICP at the Assayers Ontario Laboratories, Toronto, Ontario, Canada; * = elements analyzed by ICP at the "Laboratoire de Spectrochimie et de Geostandards" of the Analytical Services, Vandœuvre, France; all the other elements analyzed by XRF at the Institute of Mineralogy and Petrography, University of Fribourg, Switzerland.

samp.	Ba	Cr	Cu	Ga	Nb	Ni	Pb	Rb	Sr	Th	V	Y	Zn	Zr	W#	Au#
SP1	880	65	8	17	9	29	1	170	115	6	110	12	33	185	34	24
SP2	370	81	8	21	11	157	1	138	224	14	961	52	53	148	56	48
SP3	809	87	15	21	13	50	35	234	150	9	116	30	245	152	36	15
SP4	668	83	1	21	14	54	10	130	402	10	91	32	112	150	32	10
SP5	741	113	22	24	11	61	1	208	57	9	142	23	60	161	21	17
SP6	619	105	49	21	11	76	23	197	129	8	155	29	307	144	32	25
SP7	389	84	8	19	14	68	20	208	85	8	109	29	219	145	33	9
SP8	789	67	5	14	9	41	1	183	113	10	93	9	59	200	12	51
SP9	740	79	70	19	13	39	7	203	202	10	103	31	114	268	16	24
SP10	602	106	24	16	14	54	4	232	183	6	118	38	116	170	17	27
SP11	708	108	21	21	15	56	1	207	189	8	147	30	109	165	20	31
SP12	603	103	59	24	12	58	1	214	154	1	171	27	132	139	21	19
SP13	691	68	11	17	12	35	9	210	249	8	89	26	83	191	28	33
SP14	407	43	5	11	9	23	1	121	219	6	51	26	51	196	30	24
SP15	621	93	2	22	10	52	1	231	38	1	115	13	134	153	19	18
SP16	382	45	8	11	9	19	1	132	9	1	54	18	38	274	31	20
SP17	645	103	20	23	14	59	29	187	100	2	132	23	261	149	26	26
SP18	462	50	8	11	9	21	6	117	212	2	54	27	51	229	21	28
SP19	832	100	43	21	15	49	4	267	288	7	128	25	107	178	35	16
SP20	1010	123	4	26	19	62	12	219	185	1	137	21	106	221	31	18
SP21	725	82	31	20	13	54	1	139	310	6	113	34	98	148	27	17
SP22	792	138	14	32	10	61	1	352	27	1	149	18	179	125	23	12
SP23	645	68	22	13	13	24	4	125	140	14	84	17	28	330	16	23
SP24	489	81	45	26	13	37	1	136	441	3	85	29	159	136	16	34
SP25	1045	100	3	27	12	40	1	323	24	1	146	31	98	135	24	30
SP26	468	96	11	20	11	56	1	214	90	4	108	22	118	147	34	28

samp.	Ba	Cr	Cu	Ga	Nb	Ni	Pb	Rb	Sr	Th	V	Y	Zn	Zr	Sn*	Mo*	W*
SQ1	506	76	52	14	10	72	71	156	53	29	544	17	467	112	1.5	29	6.6
SQ2	693	36	11	10	9	12	5	65	68	37	32	21	16	299	< 1	1.7	2.3
SQ3	250	19	8	9	8	10	4	25	115	40	25	17	23	209	3	1.6	2.1
SQ4	1283	102	45	27	14	44	1	290	34	22	114	26	367	136	4.5	1.0	2.0
SQ5	397	21	20	8	14	10	1	70	108	41	28	33	27	617	< 1	2.0	2.2
SQ6	619	37	6	12	11	18	4	89	89	33	47	19	33	282	< 1	1.5	1.6
SQ7	478	18	7	7	3	10	1	32	115	22	29	11	15	148	1.5	1.8	1.6
SQ8	310	23	9	12	12	12	9	30	162	32	26	26	16	288	13.5	1.0	2.3
SQ9	348	21	7	8	6	9	1	50	33	33	19	14	14	269	6	1.9	2.6
SQ10	477	38	21	16	14	10	5	190	49	41	51	44	25	303	16	1.0	36.6
SQ11	1307	16	10	7	8	11	5	69	69	24	13	20	10	411	4	1.9	2.2
SQ12	490	23	6	9	10	14	1	93	61	34	32	17	18	326	1	1.5	1.5
SQ13	654	30	16	8	5	10	1	59	75	21	39	17	13	274	< 1	1.8	2.7
SQ14	407	50	2	12	7	24	1	137	58	23	57	12	45	134	4.5	1.4	2.9
SQ15	375	27	10	7	6	12	1	55	53	31	28	18	14	276	2.5	1.8	1.8
SQ16	498	25	13	9	9	10	10	52	127	33	15	20	13	443	3.5	1.7	2.3
SQ17	456	33	7	7	6	8	3	75	40	31	24	11	14	243	3	2.3	2.8
SQ19	344	25	6	9	16	15	1	93	49	37	34	35	28	627	5	1.7	3.0
SQ19	665	72	60	13	10	150	10	170	126	25	976	38	138	120	3	76	2.1
SQ20	756	69	51	14	9	56	19	193	79	2	506	23	74	130	–	–	–

granite was not of a special composition or that it has released all its tungsten charge before solidifying. In fact, in presence of chloride and phosphate solutions, tungsten partitions into the aqueous phase give rise to a rock with low W content, whereas in presence of fluoride, carbonate and borate solutions, and water alone, tungsten partitions into the melt and a rock with high W content will form (MANNING and HENDERSON, 1984). As the fluid phase of the mineralization has not

Tab. 2 Comparison of some trace element contents in the Salanfe paragneisses with those in similar lithologies (data from WEDEPOHL, 1978).

Element	count	minimum	maximum	mean	world average
Ba	24	370	1045	673.958	110 → 2580
Cr	24	43	138	87.25	16 → 169
Cu	24	1	70	19.208	15
Ga	24	11	32	19.667	16 → 25
Ni	24	19	157	51.75	60
Pb	24	1	35	7.292	1 → 29.6
Th	24	1	14	6.208	6.4 → 16
V	24	41	961	148.667	60 → 100
Zn	24	28	307	116.375	13 → 83
Au (ppb)	24	9	51	23.542	3.9
W	24	12	56	26.708	3.7 → 22.8

been compositionally defined nothing can be concluded about this point.

ORTHOGNEISSES

It has been said previously that intrusive bodies of granitic/granodioritic and of tonalitic composition were emplaced into the metasedimentary sequence after D1 and before D2. Structural observations show that no skarn formation occurred as a consequence of these intrusions, skarns being clearly post-D2. Tungsten contents of these bodies (now orthogneisses) are anyway rather low, ranging between 1.7 and 4.2 ppm (Mo ranges between 2.1 and 11 ppm and Sn between 4 and 7 ppm).

THE PARAGNEISS SERIES

The following trace elements have been analyzed in samples of the metasedimentary sequence (Tab. 1): Au, Ba, Cr, Cu, Ga, Mo, Ni, Pb, Sn, Th, V, W, Zn. Among these elements Au, Ba, V, W and Zn show average concentrations slightly higher than those present in similar lithologies worldwide (WEDEPOHL, 1978; see Tab. 2). These anomalies are not limited to the rock volume comprised between the skarn and the leucogranite (in which case an epigenetic enrichement through magmatic fluid circulation could be proposed), but they are present also outside the metasomatized rocks. The positive correlation of Ba, V and Zn with H_2O (Fig. 5) indicates that these elements are hosted in the micas (micas being the only hydrated minerals present in this lithology). This can be interpreted as a positive correlation between metals and clay content in the original sediments (HAACK et al., 1984). Au and W display some major discordances with an H_2O-dependent trend (Fig. 6). However tungsten is concentrated in biotites of the paragneisses (see below) up to 500 ppm indicating that it also was probably adsorbed in the sedimentary sequence by clay minerals. The lack of a positive tungsten correlation with the total H_2O-content of the rock could indicate a process of partial leaching of this element from the micas by the metasomatic fluids and is, indirectly, an argument supporting a "sedimentary origin" for the tungsten present in the Salanfe skarn.

Besides the above reported anomalous background in the metasedimentary sequence, there are some particular lithologies, within this same unit, which present noticeable concentrations of W, Au, V, Mo and Sn (Tab. 1): graphite-bearing quartzitic schists have appreciable enrichments in V (500–1000 ppm), Mo (30–76 ppm) and sometimes W (30 ppm) while white quartzites show important enrichments in W (60 ppm), Au (80 ppb) and Sn (16 ppm). The tungsten enrichment in the metasediments is sometimes brought to a mineral expression, as scheelite, in apatite-rich horizons within the graphite-bearing schists and in garnet-rich horizons within the paragneisses.

BIOTITE ANALYSES

As reported above microprobe analyses have been carried out on biotites belonging to the graphite-bearing quartzitic schists and to the paragneisses l.s. (Tab. 3). Analyses were done at the Institute of Mineralogy and Petrography of Bern (Switzerland) using a CAMECA-SX 50 microprobe. Two different sets of analytical conditions have been used for the analyses of W and of the other elements: for W the regulated beam current was 50 nA and time analysis was 100 sec both on peak and background in order to detect

Tab. 3 Microprobe analyses on biotites of the paragneisses. SP27 = metagreywacke; SP20 = metagreywacke with garnet-rich layers; SQ18 = graphite-bearing quartz-schist with few grains of scheelite in an apatite-rich horizon.

sample	SP27	SP27	SP27	SP20	SP20	SP20	SQ19	SQ19	SQ19
SiO_2	29.50	34.09	31.07	35.56	35.44	35.54	32.98	33.52	33.91
TiO_2	0.46	1.39	1.68	1.99	2.60	1.40	3.36	3.39	3.20
Al_2O_3	17.15	16.34	15.69	17.09	16.69	17.25	16.25	17.08	17.03
FeO	27.68	22.54	23.34	17.82	19.67	19.09	15.97	15.48	16.51
MnO	0.36	0.25	0.26	0.23	0.27	0.26	0.18	0.18	0.19
MgO	11.73	9.60	10.05	12.56	11.16	12.03	11.37	11.39	11.62
CaO	0.09	0.00	0.01	0.00	0.00	0.00	0.01	0.02	0.00
Na_2O	0.01	0.06	0.07	0.11	0.13	0.07	0.08	0.08	0.07
K_2O	3.72	8.96	8.07	9.59	9.51	9.47	9.75	9.86	9.89
V_2O_5	0.00	0.00	0.00	0.01	0.00	0.20	2.85	2.89	2.88
WO_3	0.125	0.060	0.00	0.00	0.00	0.00	0.145	0.060	0.080
Total	90.70	93.24	90.25	94.96	95.48	95.26	92.30	93.39	94.80
Ox. Equiv.	22	22	22	22	22	22	22	22	22
Si	4.864	5.423	5.165	5.419	5.422	5.426	5.207	5.205	5.208
Al	3.332	3.063	3.073	3.069	3.009	3.104	3.024	3.126	3.082
Fe_2	3.816	2.998	3.245	2.271	2.517	2.437	2.109	2.011	2.121
Mg	2.883	2.277	2.491	2.853	2.545	2.737	2.676	2.636	2.659
Ca	0.016	0.000	0.002	0.000	0.000	0.000	0.002	0.004	0.000
Na	0.004	0.017	0.023	0.034	0.039	0.022	0.024	0.024	0.022
K	0.783	1.818	1.712	1.864	1.857	1.844	1.965	1.954	1.938
Ti	0.057	0.166	0.209	0.228	0.299	0.160	0.399	0.396	0.369
Mn	0.051	0.034	0.037	0.029	0.034	0.034	0.024	0.024	0.024
V	0.000	0.000	0.000	0.002	0.000	0.020	0.298	0.296	0.292
Tot. Cat	15.806	15.797	15.957	15.767	15.723	15.785	15.727	15.677	15.716

sample	SQ19	SQ19	SQ19	SQ19	SQ19	SQ19	SQ19	SQ19
SiO_2	36.20	36.07	36.74	36.01	34.23	34.04	36.01	35.81
TiO_2	3.22	2.73	2.76	3.12	3.29	3.24	3.62	3.33
Al_2O_3	16.90	16.93	17.90	17.06	16.63	17.01	17.22	17.28
FeO	15.53	17.49	16.11	16.69	15.54	16.49	16.13	16.28
MnO	0.14	0.22	0.22	0.20	0.20	0.19	0.21	0.23
MgO	12.06	12.22	11.58	12.02	12.14	11.69	11.48	11.68
CaO	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00
Na_2O	0.00	0.00	0.00	0.00	0.06	0.07	0.00	0.00
K_2O	9.51	9.30	9.28	9.75	9.71	9.69	10.05	9.89
V_2O_5	2.06	1.93	2.11	1.97	2.61	2.53	2.43	2.45
WO_3	0.065	0.025	0.045	0.015	0.00	0.00	0.00	0.00
Total	95.25	96.54	96.33	96.48	93.94	94.50	96.71	96.52
Ox. Equiv.	22	22	22	22	22	22	22	22
Si	5.444	5.397	5.453	5.386	5.269	5.231	5.371	5.355
Al	2.995	2.985	3.131	3.008	3.018	3.080	3.027	3.044
Fe_2	1.953	2.188	2.000	2.087	2.000	2.120	2.012	2.036
Mg	2.703	2.726	2.562	2.680	2.786	2.678	2.553	2.603
Ca	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.000
Na	0.000	0.000	0.000	0.000	0.017	0.021	0.000	0.000
K	1.824	1.775	1.757	1.859	1.907	1.900	1.912	1.886
Ti	0.364	0.307	0.309	0.351	0.381	0.374	0.406	0.375
Mn	0.017	0.027	0.027	0.026	0.026	0.025	0.026	0.029
V	0.204	0.190	0.207	0.194	0.265	0.257	0.239	0.242
Tot. Cat	15.505	15.595	15.447	15.592	15.670	15.687	15.546	15.570

concentrations of the metal down to 50 ppm (RAMSDEN and FRENCH, 1990). For the other elements (Si, Ti, Al, Fe, V, Mn, Mg, Ca, Na, K) the analytical conditions were: magnification 200,000, regulated current 20 nA, time analysis 15 sec on the peak and 7.5 sec on the background. Considering the tungsten and the vanadium content four different groups of biotites have been

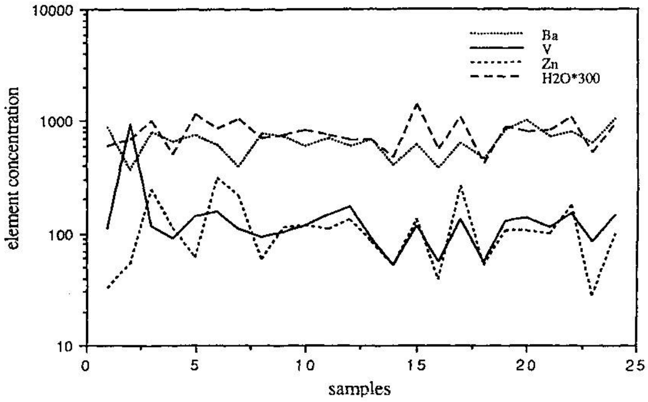

Fig. 5 Variation in the concentration of some elements (Ba, V, Zn) in comparison to that of H_2O, in samples from the paragneiss unit. A positive correlation between the concentration of these elements and that of water is evident.

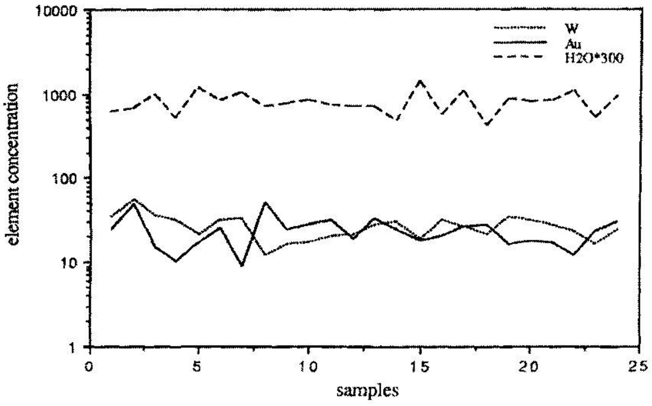

Fig. 6 Variation in the concentration of Au and W in comparison to that of H_2O, in samples from the paragneiss unit. Au and W do not display a good correlation with water content of the rock.

distinguished (Fig. 7): 1) V-bearing biotites with W contents around 500 ppm; 2) V-bearing biotites without detectable W; 3) "normal" biotites with W contents around 500 ppm; 4) "normal" biotites without detectable W.

Biotites of the groups 1 and 2 belong to samples of the graphite-bearing quartzitic schists, while those of the groups 3 and 4 belong to samples of the paragneisses l.s. The V content in biotites of the groups 1 and 2 is remarkable (ranging between 2.5 and 2.7% V_2O_5, Tab. 3). This is in agreement with the high V contents in the corresponding total rock analyses (Tab. 1). The structural formula of biotite calculated on the basis of 22 oxygens (Tab. 3) suggests that V occupies the crystallographic site of Fe^{3+}. W-bearing biotites, in both groups (vanadiferous and "normal"), are always slightly enriched in Fe with respect to the corresponding W-barren terms (Fig. 10) but the reason of such W affinity for the Fe-rich biotites, at the moment, is not understood. Vanadiferous biotites are also strongly enriched in TiO_2 with respect to normal biotites (Fig. 7).

The high W concentrations in biotites of the graphitic schists is chemically reasonable, because W (like V) displays very high average contents in sediments characterized by the presence of abundant carbonaceous matter (WEDEPOHL, 1978; KRIBEK, 1991). On the other side the presence of the same high W contents in "normal" biotites of the paragneisses l.s. seems to indicate the existence of a more or less continuous supply from an "independent source" which provided the tungsten even under changing conditions of sedimentation (whether associated or not with carbonaceous matter) in the depositional basin of the metasedimentary sequence.

Interpretation of data

The data above indicate that slight anomalies of W, Au, V, Zn and Ba are present in the metasedimentary unit. This makes reasonable the supposition that these rocks were the suppliers of metals for the Salanfe skarn. The correlation of V, Ba and Zn with H_2O content of the rock as well as the W-bearing biotites indicate that these elements were concentrated in the metasedimentary sequence by adsorption on clay minerals (now biotite). The lack of a good correlation of tungsten and gold with the total H_2O-content of the rock as well as the highly variable W-content of the biotites within single samples of paragneisses might indicate that these metals were selectively leached from their host rocks (and then eventually transported by the metasomatic fluids and finally deposited in skarn ores). This leaching must have occurred during the high temperature static event (between D2 and D3) when the breakdown of the D2-biotites (then recrystallized as static biotites) could have delivered the tungsten content of the micas to the fluid coming from the leucogranite. This argument is also supported (at least for the tungsten) by the observation that the W content in the rock volume comprised between the leucogranite and the main skarn horizon is, in some samples, quite lower (about 2–3 ppm) than the content in the same rock portions situated away from the leucogranite body (25–60 ppm; see Tab. 1).

The validity of the assessment that the paragneiss series is the source rock of the tungsten, can be furtherly tested by verifying numerically the assumption made in this model, i.e., that the rock volume of the metasedimentary sequence

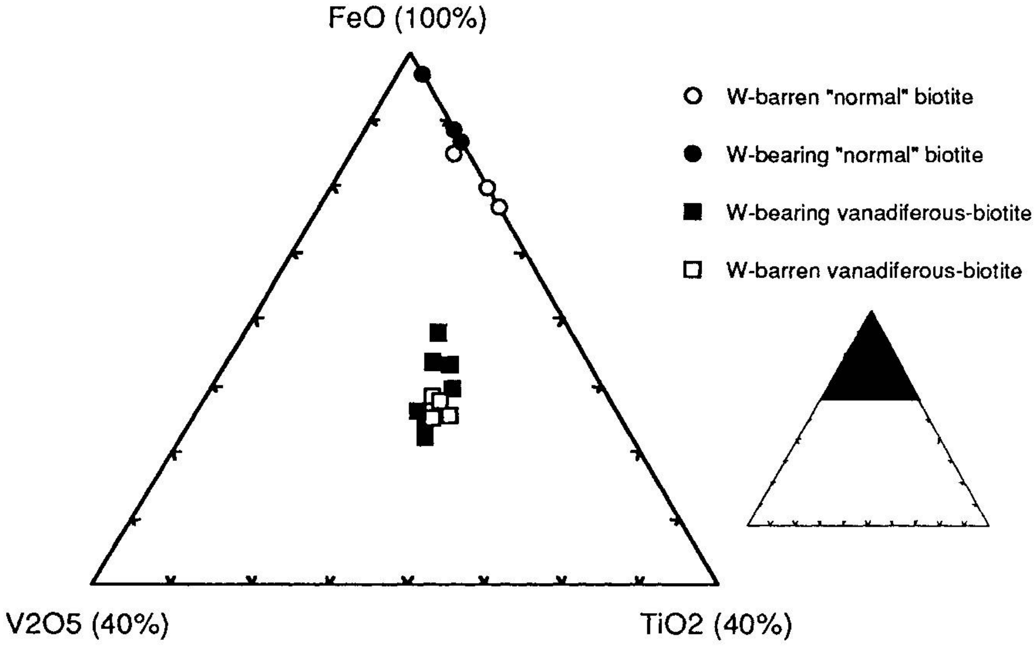

Fig. 7 FeO–V_2O_5–TiO_2 ternary diagram for W-bearing and W-barren biotites in samples of the paragneiss series. W-bearing biotites are Fe-richer than W-barren ones both in the graphitic schists (vanadiferous-biotites) and in the metagreywackes ("normal" biotites).

comprised between the leucogranite and the skarn was large enough, given an initial tungsten content in it compatible with the nowaday anomaly, to provide the W amount present in the skarn. The mineralized body at the Robert mine can be approximated to a tabular body with a length of 30 m, a depth of 50 m, a width of 0.2 m (Fig. 8) and with an average WO_3 content of 0.2% (= 0.158% W) (Woodtli et al., 1987). The mass of tungsten present in the mineralized body is given by $M_W = \%W \cdot M_{skarn} = \%W \cdot V_{skarn} \cdot \rho_{skarn}$ where %W = weight % of W = 0.158% and ρ_{skarn} = 4.5 g/cm^3. Hence $M_W = 2.133 \cdot 10^6$ g. Let us see which is the volume of the paragneiss that is necessary to furnish this W amount under the following assumptions:

– amount of W delivered = 30 ppm (then initial average amount of W in the series = 60 ppm because 30 ppm are still left). This is an arbitrary bur reasonable assumption based on the observation that the existence, in the same sample, of W-rich biotites and W-barren biotites indicates a process of selective leaching of this metal and that the nowaday measured W anomaly in these rocks has not to have the same value as that in the original sedimentary series. Then we have taken as top value of the original concentration of tungsten in the series the highest value of tungsten measured in a sample of paragneiss (Tab. 1);

– length of the tabular volume of the paragneisses = 30 m, depth = 50 m, width (y) to be determined (see Fig. 8).

Hence $M_W = \%Wpar \cdot Mpar = \%Wpar \cdot Vpar \cdot \rho_{par}$ where %Wpar = 30 ppm W = 0.003% W and ρ_{par} = 2.7 g/cm^3 (where the suffix 'par' relates to paragneiss). It follows $M_W = 2.133 \cdot 10^6$ g = $0.00003 \cdot (5000 \cdot 3000 \cdot y) \cdot 2.7$ and y = 1755 cm = 17.55 m. From this we can see that a thickness of only 17.55 m of the metasedimentary sequence is required to furnish the amount of tungsten necessary to form the mineralization. Indeed the thickness of the paragneiss squeezed between leucogranite and skarn does not attain this value (see Fig. 1) but this can largely be accounted for by the rock bulk shortening caused, during and after the skarn formation, by the D3 phase which strongly folded isoclinally all the sequence (see Fig. 4; in the granodioritic orthogneisses melanocratic inclusions are stretched with z/x ratio of 1/30).

Possible primary source of the metals

Even if the presence of metal concentrations in the original sedimentary series seems very probable on the basis of the above data, the primary source of the metals remains undefined. In other words how and why did the metals concentrate in the metasedimentary series at these anomalous values? Two extreme cases can be envisaged: a) tungsten came with the sediments in which it is now enriched and b) tungsten was derived by a different source with respect to these sediments.

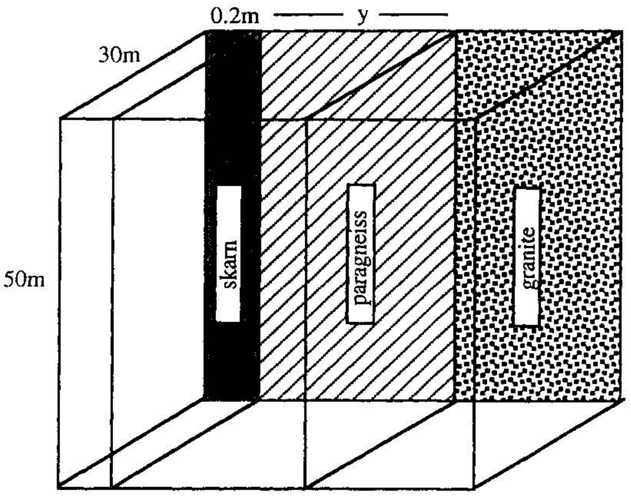

Fig. 8 Simplified sketch of the geometric relationships between ore body, paragneisses and leucogranite at Salanfe.

In the first case the metals could have been concentrated up to the slightly anomalous values in the metasedimentary sequence through a process of erosion and redeposition of crystalline rocks particularly enriched in W, As, Au, V; by this way the metal content would have been transferred from the source to the new depositional basin. A present day example of such a process is represented by the Searles Lake region (Ririe, 1989), where an evaporitic series strongly enriched in W has been depositing: W is leached by the meteoric waters from the many scheelite skarns present in the region. It is then transported in solution and deposited under evaporitic conditions. The high salinity of the solutions favours the solubility of W and appears to be an essential prerequisite for the formation of such anomalous concentrations (Ririe, 1989). In the case of the Salanfe sequence there are no mineralogical indications about the existence of such an evaporitic environment (for instance presence of scapolite, tourmaline, high Mg/Ca ratios; see Moine et al., 1981). On the other side a process of transfer of the metals from an enriched source rock to the product of its erosion maintaining such an anomaly is not feasible unless very high and homogeneous initial concentrations were present in the source lithology: this is a rather exceptional condition and is not matched by any known geological situation in the Aiguilles Rouges Massif.

In the second case the metals could have been "produced" at high rates by an independent source (inside or outside the sedimentary basin) coeval to the deposition process and could have mixed with detrital material. Exhalative activity could account for such a source. This possibility is indirectly supported for this mineralization by some observations:

- the diluted metal anomaly is more easily explained through a process of mixing of a more or less regular output of metals from an independent source and the detrital sediments supplying a basin. By this model we can justify the presence of tungsten anomalies in biotites belonging to different lithologies (paragneiss l.s. and graphitic schists). On the other side we can also explain the higher concentrations of metals in some particular horizons as the result of a lower sedimentation rate or the onset of peculiar conditions of sedimentation (carbon-rich for instance);
- the typical association with exhalative activity of all the elements anomalously enriched in the paragneiss series (see Bostrom and Fischer, 1971 for V, Hannington et al., 1990 for Au, Ag, Zn and Ba; Hedenquist and Henley, 1985; Henley and Roberts, 1983 for W, As and Au);
- the existence of a present day example (the Waiotapu geothermal field, New Zealand: Hedenquist and Henley, 1985; Henley and Roberts, 1983) in which the elemental association W-Au-V-P strongly enriched in silica gels is the same as that found with anomalous concentrations in the Salanfe paragneisses (see above);
- the existence of known W-mineralizations associated with exhalative activity in a l.s. volcanic arc environment (Mittersill, Tahlhammer, 1989; Waiotapu, Hedenquist and Henley, 1985; Henley and Roberts, 1983; Cheilletz, 1986; Plimer, 1980) which is possibly the deposition environment of the paragneiss series in the Salanfe area as indicated by the sedimentary association of the paragneiss series (back-arc basin).

On the other side true indicators of an exhalative activity are not present in the Salanfe area: neither exhalites nor volcanics have been found within the metasedimentary sequence. However, the outcropping surface of the metasedimentary series is too limited (Fig. 1) to exclude the possible existence of such lithologies (indeed basic volcanics have been found in a similar sequence few kilometres to the north, in the Lake Emosson region as already reported). Alternatively the sedimentation of this sequence could have occurred in a more or less distal position with respect to the exhalative centers as it is typical for W-mineralizations in back-arc basins (see also Cheilletz, 1987). In such a case the anomalous concentrations of W and of the other metals in the paragneiss could be the result of transport in a basin without exhalative activity.

Evolution of the metallogenic process

Finally the following speculative scenario can be proposed for the evolution of the metallogenic process in the Salanfe area:

1) existence of an exhalative activity in a more or less distal position with respect to the depositional basin of the metasedimentary series (?). This activity pours out metal solutions enriched in W, Au, V, Zn, Ba, P, (As?). The environment of deposition of the metasedimentary series could have been a l.s. volcanic arc environment as shown previously. More precisely we may suggest a back-arc basin;

2) transport (?) of the metals from the exhalative centers to the depositional basin of the paragneiss unit. The maintenance of the presumed originary exhalative association (W–As–V–P–As) also in the paragneiss series after the metal transport, could indicate that either the exhalative centers were not so far or that the exhalative activity was strongly developed;

3) deposition of these elements within the paragneiss unit by adsorption on clay minerals. This process is well documented by the correlation between V, Zn, Ba with H_2O content in the total rock and by W concentrations in biotites. The process of precipitation of these elements in the series is continuous throughout the sedimentation and leads to slightly anomalous concentrations of some metals in the sequence. Stronger concentrations of metals within particular lithologies intercalated in the paragneiss are bound to local and momentaneous peculiar conditions of sedimentation which "accelerated" the process of metal deposition. This seems to be the case for the graphite-bearing quartzites: here the establishment of anoxic conditions of sedimentation have concentrated elements such as V and Mo (see also JIA et al., 1990 and McKEAG et al., 1985) and, to a lesser extent, W (see also WEDEPOHL, 1978; KRIBEK, 1991).

4) during Late-Hercynian, mobilization of tungsten (and possibly of other metals) occurred as a consequence of the breakdown of the W-bearing biotites during a high temperature event and of a strong fluid circulation bound to the leucogranite cooling. The metals were then precipitated by such a fluid into the skarn to form the present day mineralization.

Conclusions

Even if the model of sedimentary tungsten protoconcentrations presented here for this mineralization seems to be quite probable on the basis of the data above, the author is aware that further analyses are needed in order to support in a more definitive way the model. Indeed Pb isotope analyses on total rock and on some sulphides belonging to the mineralization are intended.

Anyway the preliminar conclusion about a synsedimentary origin of the tungsten present in the Salanfe skarn would place this mineralization among the l.s. strata-bound W-deposits of the Variscan chain (CHEILLETZ, 1988). These deposits are generally hosted in Early Paleozoic or Upper Proterozoic volcano-sedimentary series which have been deformed and metamorphosed during the Variscan orogeny (VON RAUMER and CHIARADIA, 1992). Tungsten (and possibly other metals) has been concentrated up to economic grades during this stage but its ultimate origin remains strictly bound to the deposition of the volcano-sedimentary series (VON RAUMER and CHIARADIA, 1992). Under this point of view the example of Salanfe would represent, along with other better known W-deposits of the Variscan chain (BERAN et al., 1985; HOLL, 1977; BRIGO and OMENETTO, 1983; BOYER and ROUTHIER, 1974; SONNET et al., 1985; AYORA et al., 1986; GIMENO TORRENTE, 1986; OMENETTO et al., 1988), another hint that the Upper Proterozoic to Early Paleozoic time was, in the sense of PLIMER (1980) and BRIMHALL (1987), a fertile period for the tungsten transfer from mantle to crust.

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