W-SKARNS FROM RUBELITA, NORTHERN MINAS GERAIS STATE, BRAZIL: FLUIDS RELATED TO LITHOLOGICAL EVOLUTION

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ABSTRACT In the southern Rubelita area, mid-Jequitinhonha Valley, scheelite mineralizations associated to calc-silicate rocks (with quartz, pyroxene, amphibole and grossular) and apatite bearing quartz veins occur. These rocks were intruded by pegmatitic granitoids and muscovite-biotite granites now cropping out in the area. Microthermometry and micro-Raman analyses of early (primary?) fluid inclusions in quartz, titanite and grossular from calc-silicate matrix and quartz veins indicate the presence of nitro-carbonic phases. They consist of variable proportions of CH_4 and N_2 (X_{CH4} = 0.35 - 1.0; X_{N2} = 0.0 - 0.65). At a later stage, percolation of aquo-carbonic fluid in microfractures originated secondary fluid inclusions. This low salinity fluid is CO_2 dominated (X_{CO2} =0.95 - 1.0) with N_2 and CH_4 in trace amounts. These solutions have been studied in quartz veins of the calc-silicate rocks and presented fO_2 between 10^{-36} and 10^{-37} bars, formed under 1500 bar pressure and temperatures between 200 and 300°C. It is assumed that the O_2 increase in the fluids is a consequence of muscovite-biotite-granitoid intrusion. Although direct fluid inclusions study on scheelite crystals have not been feasible, the tungstate precipitation from these late aquo-carbonic solutions was estimated, based on paragenetic relations. These fluids may have originated from granitoids bodies and may probably have reacted with the host schists leaching Ca and Fe from them.

Keywords: w-skarn, fluid inclusions, scheelite, Rubelita-Araçuaí, Minas Gerais-Brazil

INTRODUCTION This paper presents a comparative study of fluid systems related to W-skarns associated to scheelite-bearing quartz veins and to host granitoids, both outcropping in the southern Rubelita area, located in the Araçuaí area, mid-Jequitinhonha Valley, Minas Gerais, Brazil (Fig.l).

Geology Regionally the oldest rocks are of Archaean age (kinzigitic-gneiss, and migmatite complexes) in which homophanous or locally oriented granitoids of Brasiliano age are intruded (Pedrosa-Soares 1984). During the Proterozoic, Salinas Formation (micaschists and quartzites) and Macaubas Group were generated (Pedrosa-Soares 1984, Monteiro 1986). Later, in the Upper Proterozoic, the rocks of the Salinas Formation were intruded by sin-, tardi-, and post-tectonic granitoids (Rb/Sr age = 525 ± 30 Ma) which were divided into biotite-muscovite granite, muscovite-biotite granite, and pegmatoid granite (Monteiro *et al* 1990, Pedrosa-Soares *et al.* 1997). They all fall in the granite-granodiorite domain with alkaline trend. Granitoids cutting the Salinas Formation in the western border of the area have post-tectonic character presenting a biotite-granite core and two mica granites or muscovite-garnet leucogranites at the boundaries (Correia-Neves *et al.*

1982, Pedrosa-Soares 1984, Correia-Neves *et al.* 1986, Monteiro 1986, Pedrosa-Soares *et al.* 1997). These granites originated the pegmatites of mid-Jequitinhonha Valley. They are hosted by these granitoids themselves or by the Salinas Formation schists and quartzites (Correia-Neves *et al.* 1986, 1987). During the Tertiary and Quaternary Sao Domingos Formation lacustrine siltstones were deposited (Pedrosa-Soares *et al.* 1987). Quartz schists with associated quartz veins and granitoid rocks of the muscovite-biotite granite type and pegmatoid granite are the lithologies outcropping in the southern Rubelita area.

SOUTHERN RUBELITA AREA **Metamorphic rocks**
Quartz, oligoclase (sericitized and epidotized), titanite, grossular, calcite, epidote and black and white mica are the main constituents of the schists (Salinas Formation). Layers dominated by gray-greenish garnet with boudinage were called "calc-silicates" by Pedrosa-Soares (1984) and Monteiro (1986). They consist of quartz and anorthite rich plagioclase (granoblastic matrix) followed by green amphibole, pyroxene, titanite, garnet, carbonates, pyrite, scheelite, and zircon (Monteiro 1990) and represent impure calcareous rocks. The
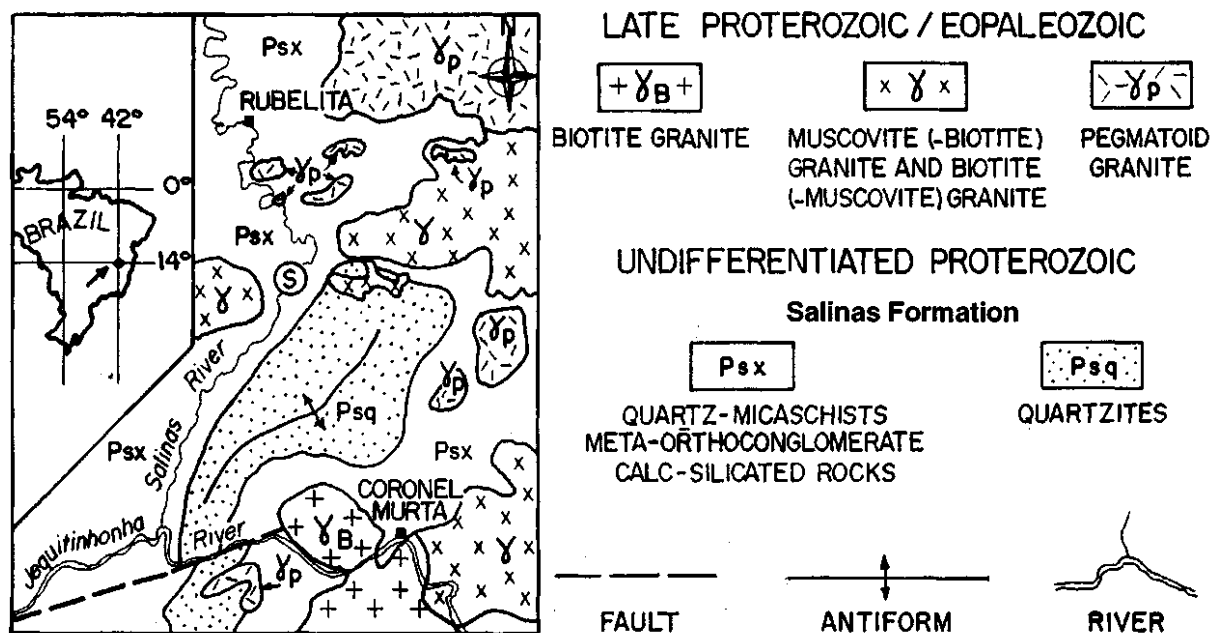

Figure 1 - Geologic map of the Rubelita Area, mid-Jequitinhonha Valley, Minas Gerais, Brazil (from Monteiro et al. 1990). (s): main scheelite studied mineralization.

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amphibole is Fe-actinolite, whereas the pyroxene, which appears to be later than the amphibole, has a diopsidic composition with up to 22.5% CaO and 11.5% MgO content (salite, up to ferrosalite). The grossular generally enclosing quartz, amphibole, pyroxene, and titanite, has average composition of 20% CaO, 21% Al_2O_3 , and 15% FeO. The scheelite and the carbonates are interstitial ana represent the latest crystallized phases. Grossular, muscovite, iron oxides, apatite, and rarely scheelite form the veins subordinate minerals. Near the granitoids, the scheelite frequently occurs at the central part of zoned boudins of quartz veins, as small grains intergrowth in the quartz-feldspathic matrix (Monteiro *et al.* 1990).

Granitoids They are of two main types: the pegmatoid granites and the muscovite-biotite bearing granites. The former ones are isotropic with quartz, K-feldspar, oligoclase, muscovite, and tourmaline. The muscovite-biotite bearing granites are quartz rich with subordinate biotite, muscovite, zircon, epidote, garnet, hematite, and magnetite composition (Monteiro 1986). Biotite encloses quartz, zircon, and iron oxides and is probably earlier than muscovite as it shows alteration to the latter. They are usually more altered than the pegmatoid granites.

FLUID INCLUSIONS STUDIES FI in quartz, garnet and apatite from calc-silicate rocks, in quartz veins, and in muscovite-biotite granites were studied. The results are summarized in Table 1.

Analytical methods Microthermometry was conducted on a Chaixmeca and a Fluid Inc cooling-heating stages at the Fluid Inclusion Laboratory in the "Centro de Desenvolvimento da Tecnologia Nuclear (CDTN)". Micro-Raman spectroscopy was performed at the Laboratory of Optics of the Department of Physics in the "Universidade Federal de Minas Gerais (UFMG)". Both laboratories are in the UFMG's Campus in Belo Horizonte, Minas Gerais.

Fluid Inclusion (FI) Types *TYPE 1A* They are early formed monophase carbonic or two phase aqueo-carbonic inclusions, with kidney to rounded shapes and 4-10 (am size, commonly confined to matrix quartz of the calc-silicate rocks. The carbonic phase of the aqueo-carbonic FI is 50% of inclusion volume and consists of N_2 and CH_4. Th $_B$ occurred between -110°C and -99°C invariably to the gas state. The high Tm_{CLAT} (17 to 21 °C) is probably due to the high CH content in the carbonic phase, which is formed by CH. (X = 0.35 to 1.0) and N_2 (X_{N2} = 0.0 to 0.65). CO_2, H_2S, and HS" have not been detected. Tht of two phase FI took place between 350 to 450°C (more frequently 375°C) with the expansion of the carbonic phase.

TYPE 1B They are early (L+V) FI in grossular and titanite from calc-silicate rock matrix. They are 8-10 urn in size and the gas phase (carbonic) reaches 10 to 30% of the inclusion volume. Mineral dark color prevented observations during cryometry. Only in a few inclusions, bubble recovery between -1.5 to -1.0°C was noticed, which might be credited to the final ice melting (Tm) or the clathrate dissociation. The vapor phase is formed by variable amounts of CH_4 (X 0.8 to 1.0) and N (X_{N2} 0.0 to 0.2). Tht occurred between 240 and 340°C, usually to the liquid phase, with concentration of values around 300°C.

TYPE 1C These FI were studied in quartz of veins cross cutting the calc-silicate rocks. They are early, two-phase (bubble <50% inclusion volume) or three-phase (L+V+S(amorphous, isotropic)) inclusions. The V

phase also consist of CH_4 (X_{CH4} = 0.7 to 1.0) and N_2 (X_{N2} = 0.0 to 0.3). Preliminary measurements on the aqueous phase suggested the presence of Ca^{++} (eutectic temperature [Te] =-*49°C*) and showed low Tm_{ICE} (-4.5 to -1.5°C). Although the clathrate formation had not been observed, the presence of CH_4 and N_2 indicate that the formation of their hydrates were highly possible. The actual salinity must, therefore, be higher than the 7 wt%NaCl equivalent determined from the Tm (Fuzikawa 1982). The Tht occurred always to the aqueous phase between 200 and 270°C.

TYPE 2 They are present in vein quartz apatites. They are primary, two-phase (bubble always <10% inclusion volume) FI, with tubular and rounded edges (4-20 urn long). Te of-48°C suggests the presence of Ca^{++} in the fluid. Tm_{ICE} between -3.5 and -1.5°C indicate salinity of 3.4 to 6.6 wt% NaCl equivalent. During micro-Raman analyses dark semi-circular solid phases were formed in the inclusions, probably due to the presence of carbonic phases. Heating caused homogenization to the liquid phase in a narrow range of 280 to 290°C.

TYPE 3A They are aqueo-carbonic inclusions of secondary nature, generally found in vein quartz. The carbonic phase occupies 50 to 100% of the inclusion volume and shows Tm_{CO2} between -61.5 to -57.5°C, revealing to be mainly composed of CO (X = 0.65 to 0.95) mixed with CH_4 (X_{CH4} = 0.05 to 0.3). In somerl stable solid phases were present after the micro-Raman analyses. It might be a product of reaction of any undetected hydrocarbon present in inclusions. Th_{CO2} occurred between -5.0 and 14.5°C, to the liquid state, indicating a density of 0.83 to 0.95 g/cm^3 CO_2 equivalent. Tm_{CLAT} occurred between 8.5 and 9.0°C suggesting a salinity of ~1 wt% NaCl equivalent (Diamond 1992). Final Tht occurred between 250 and 290°C to the carbonic phase.

TYPE 3B They are secondary, one and two phase, elongated and kidney shaped FI in quartz from granitoids outcropping near the skarns. The aqueous phase is <20% of the inclusion volume and one phase carbonic inclusions are common. Tm_{CO2} between -58.2 and -58.0°C, and micro-Raman analyses indicated X_{CO2}=0.95, X_{N2}=0.05, and absence of methane Tm_{CO2} to the liquid state, occurred between +18.5 and +22,5°C indicating a density of 0.83g/cc CO equivalent. Tm_{CLAT} near +8.0°C indicate salinity <2wt% NaCl equivalent. In addition to the methane absence in the carbonic phase, the lower CO_2 density differentiates the 3b (granite) from 3a (vein) inclusions.

DISCUSSIONS AND CONCLUDING REMARKS Fluid evolution The earliest fluids studied (Type la) involved in the precipitation or recrystallization of matrix quartz in the calc-silicate rocks had variable, but significant, concentrations of CH_4 and N,, (as well as the absence of CO_2 , suggesting strongly reducing conditions, Fig. 2) and a very subordinate aqueous phase. Sterner and Bodnar (1989) observed that changes in fluid composition during metamorphic processes are common. In this way, one can observe that fluids in grossular and titanite from the matrix present much lower N_2 content. It is suggested, therefore, that the Type 1 a FI with high N_2 content may represent remainder fluids surviving quartz recrystallization process. The solutions precipitating the minerals of the matrix are (probably) of metamorphic origin because the large amounts of CH found are unusual in fluids of magmatic origin (Roedder 1984, Kamili *et al* 1993, O'Reily *et al.* 1997). The presence of hydrocarbons may be related to graphite concentrations already identified in the Jequitinhonha area (Correia-Neves, person, comm.).

Table 1 - FI types and composition from Rubelita area (MG). Fill: degree of filling; Tmco2: CO_2 melting temperature; Th$_{CARB(PHASE)}$:homogenization temperature of the carbonic phase; Tm$_{CLATH}$ clathrate melting temperature; X: molar fraction; Tht: final homogenization temperature; (CC): Calc-silicate rocks; (1): nucleation of solid phases (see text);(G): homogenization into the gas phase

| FI Type	Mineral	Fill	Tm_{CO2} ("C)	Th$_{CARB}$ PHASE ("C)	Tm CLATH ("C)	X_{CH4}	X_{N2}	X_{CO2}	Salinity (wt% NaCl equiv.)	Tht ("C)
1a	Quartz (CC)	0.5			-110/-99 (G)	17/21	0.35/1.0	0.0/0.65	0.0		350/450
1b	Garnet, Titanite (CC)	0.7/0.9					0.8/1.0	0.0/0.2	0.0		240/340
1c	Quartz (veins)	>0.5					0.7/1.0	0.0/0.3	0.0	>7	200/270
2	Apatite (veins)	>0.9					(1)			3.4 to 6.6	280/290
3a	Quartz (veins)	0.0/0.5	-57.5/-61.5	5.0/14.5	8.5/9.0	0.05/0.3	0.0	0.65/0.95	1	250/290
3b	Quartz (veins/granite)	>0.8	-58.0/-58.2	18.5/22.5	8.0	0.0	0.05	0.95	<2	
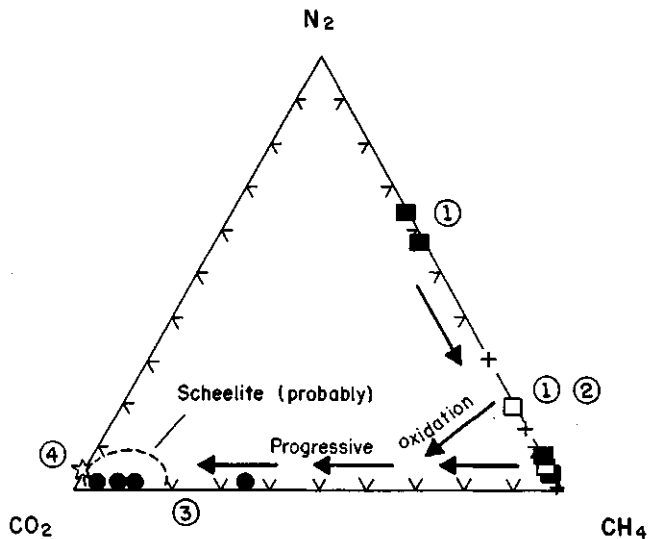
Figure 2 - N2-CH4-CO2 compositional diagram with fluid evolution path suggested for the Rubelita area. (1): calc-silicate matrix early fluids; (2): calc-silicate matrix and vein quartz early fluids; (3): quartz vein late fluids; (4): granitoid late fluids; (n): type la FI; (y): type Ib FI; (+): type Ic FI; (•): type 3a FI; (ft) type 3b FI.
N.B.: Roman spectroscopy of Type 2 FI produced high luminescence dificulting the obtention of valuable data.

A silicification event that followed the fracturing episode of calc-silicate rocks originated an extensive web of millimetric and centimetric quartz veins. Solutions present during this process kept compositions similar to those described above with the predominance of CH (Fig. 2). Later change in the physico-chemical conditions led to a slight increase in salinity and addition of CaCl during apatite precipitation. Textural relationships indicate that scheelite was formed by substitution of calc-silicate minerals as a result of late alteration processes related to the granitoid emplacements (Monteiro 1986). Subsequently, the circulation of late low salinity FLO-CO fluids probably caused the precipitation of muscovite. These fluids present in inclusions along micro-fractures contain high CO_2 proportions (>65%), which increase progressively (in relation to earlier fluids) while the CH_4 decreases until complete disappearance (Type 3b, Fig.2). This late stage aqueo-carbonic fluid circulated following the emplacement of granitoids. The density of the carbonic phases during type 3 fluid circulation indicated a minimum pressure of -1500 bars. After granitoid emplacement, nevertheless, the pressure decreased to 1000/1200 bars.

Reducing and oxidizing stages   Following quartz
precipitation in the veins, physico-chemical conditions started changing in such a way that the oxygen concentration became relatively high, leading to a progressive transformation of methane into carbon dioxide and of a very reducing environment into a less reducing (or oxidizing) one due possibly to the granitoid intrusions. A possible methane oxidation reaction could have been such as $CH_4 + 2O_2 \Leftrightarrow CO_2 + 2H_2O$ (1), which would have resulted in an increase of CO_2 and H_2O proportions.

The highly reducing early fluids from veins (Type Ic) did not contain CO_2. The oxidation process started, therefore, during the circulation of fluid 3a, although the possibility of it having started during apatite precipitation cannot be ruled out. The oxidizing conditions were established during the circulation of fluid 3b, after granitoid intrusion, as which coincides with the disappearance of methane.

Oxygen fugacity equilibrium conditions, for average temperatures of 300 C using reaction (1) and based on the Ohmoto & Kerrich (1977) equation of state:

logK = 41997/T + 0.7191/logT - 2.404,

where K is the equilibrium constant, and T is the temperature in °K, were calculated. The equilibrium constant is given by the ratio between the fugacity (f) of products and reactants, or:

$K = f_{CO2} f_{H2O} / f_{CH4} f_{O2};$

or in its logarithmic form:

$logK = logf_{CO2} + 2logf_{H2O} - logf_{CH4} - 2logf_{O2},$

or in terms of molar fractions (X) and fugacity coefficient (g):

$logK = log(X_{co2g CO2}) + 2log(X_{H2Og H2O}) - log(X_{CH4g CH4}) - 2log f_{O2}$

Using type 3 fluid molar fraction data and the gi data taken from Ryzhenko & Volkov (1971), for pressures of 1.5 to 2.0 kbar, f_{O2} values between 10^{-36} and 10^{-37} bar were calculated, which is very close to the CO_2-CH_4 (Ikbar) and WO_3/WO_2 buffer curves. This indicates that despite the dominance of CO_2 in the carbonic phase of type 3 a fluids the oxygen fugacity stood relatively low, consistent with reducing conditions. The obtained f_{O2} values are roughly coincident with the ones published in other W deposits (Fig. 3). The f_{O2} values for Rubelita la, Ib, and Ic fluids must, certainly, have been much lower considering the higher CH_4 content and the absence of CO_2.

Mineralizing fluid Which fluid system (or regime) would have been responsible for the W carriage and the scheelite precipitation in the Rubelita area? The absence of FI in scheelite prevented direct determination of these fluids. The FI study in minerals from rocks associated to the mineralization allowed a general constraint of the characteristics of this fluid. It must have percolated the rocks after the precipitation of vein quartz and grossular and have been coeval with apatite, which, in turn, is contemporaneous with scheelite. So, this fluid could be similar to those trapped as secondary FI in vein quartz (and probably in the apatite) consisting of a low salinity (with $CaCl_2$) aqueous solution with CO_2 as the main component and CH_4 in trace amounts in the carbonic phase. The temperature would be in the 250 - 300°C range with slightly reducing character as shown by fO_2 value around 10^{-36} bar. These physico-chemical characteristics are coincident with the ones postulated in other scheelite deposits (Roedder 1984, Ramboz et al. 1985, Durisova et al 1992, Salim 1996, Kilias & Konnei
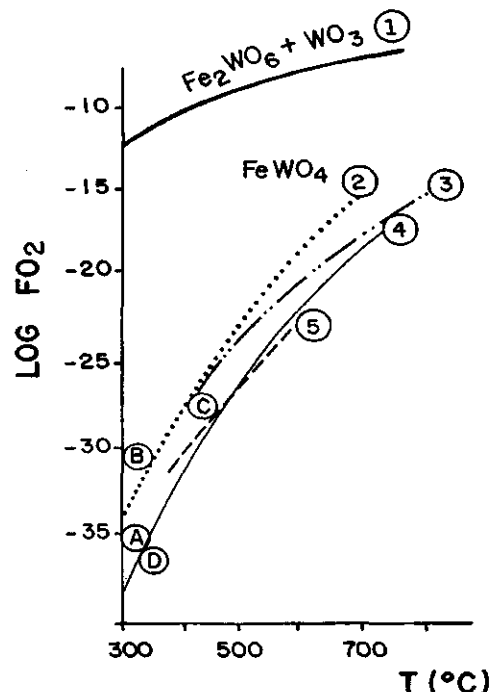

Figure 3 - Oxygen fugacity (logfo2) versus temperature diagram. Symbols: (A) = Type 3a aqueo-carbonic fluid from Rubelita; (B) - Mineralizing aqueo-carbonic fluid from Panasqueira W deposit, Portugal (Noronha et al. 1992); (C) - Aqueo-carbonic W mineralizing fluid of the Borne Granite-French Massif (Ramboz et al. 1985); (D) = Aqueo-carbonic mineralizing fluid from Pedra Preta W deposit, PA, Brazil (Rios 1995). Curves: (1) and (4) = Fe_2WO_6 + WO_3 and WO_3/WO_2, respectively, (Hsu 1976); (2) Buffer NNO for 2 kbar (Ohmoto & Kerrich 1977); (3) Representing the CH_4 + $2O_2$ Ú $2H_2O$ + CO_2 reaction for 2 kbar (Smith et al 1984); (5) Represents X_{CH4}= 0.1 for 2kbar (Schwartz & Surjono 1990).
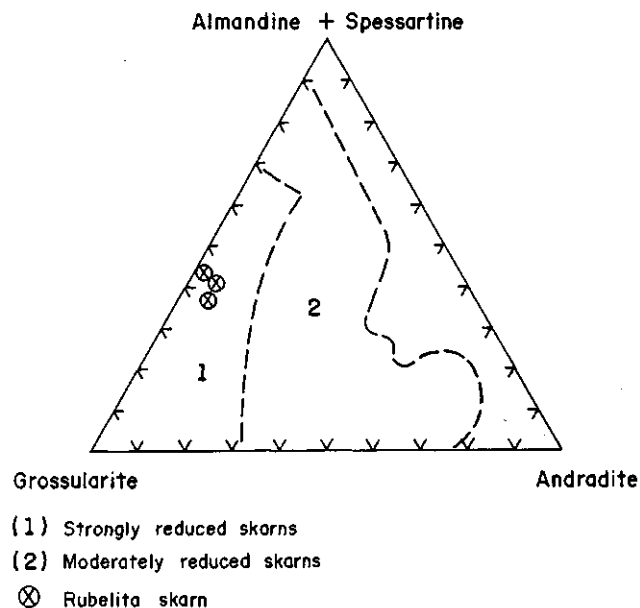
Figure 4 - Garnet ofRubelita skarn plotted in the subcalcic garnet diagram ofNewberry (1983).

Rubelita (this paper)	Oxidized W-Skarns (Newberry & Einaudi 1981), (Meinert 1992)	Reduced W-Skarns (Newberry & Einaudi 1981), (Newberry 1983), (Meinert 1992)
Small bodies	Small ore bodies	Large ore bodies
Grossular (dominant)	Andradite	Spessartine-Almandine
Diopside (Salite)	Diopside (Hd$_{0-40}$)	Hedenbergite
Mo poor Scheelite (Monteiro et al 1990)	Mo poor Scheelite	Mo rich Scheelite
Pyrite	Pyrite	Pyrrhotite, Chalcopyrite, Sphalerite, Arsenopyrite
Reducing stage: CH_4, N_2 (no CO_2) Oxidizing stage: CO_2 >>CH_4	CO_2 dominates over CH_4	CH_4 dominates over CO_2
Grossular (Type 1b FI) Tht (Max) = 340°C	Garnet (Prograde Mineral Assemb.) Tht = 600-800° C Salinities >52wt%NaCl	
Quartz (Type 1a FI) Tht = 350-450°C Salinity: ? Quartz (Type 3a FI) Tht = 250-290°C Salinity = 1wt%NaCl	Quartz (FI) Th 250-380° C Salinity = 2.5 to 28wt%NaCl equiv.	

Table 2 - Comparison between characteristics of Rubelita skarns and the reduced and oxidized W-skarn types.

Thus, it is assumed that the Rubelita W minerals were precipitated from solutions having an important magmatic character or that they may have been derived directly from granitoids. This statement is based on: 1) W mineralizations hosted in metamorphic thermal aureole promoted by the granitoid bodies; 2) the average W content of metamorphic rocks in the Rubelita area is <3 ppm, while in the nearby granitoids it may reach up to 8.2 ppm; geochemically, they have been considered slightly specialized and considered as the W source (Monteiro 1986, Monteiro *et al.* 1990); 3) scheelite and apatite are probably related to the aqueo-carbonic fluids compositionally identical to the late fluids investigated in quartz from the granites. Monteiro *et al.* (1990) argue that the W would have a magmatic source and the crustal granites, would have formed by melting of metamorphic rocks with anomalous W content. Aqueous fluids (with W) from the magma could have remobilized, by thermal convection, elements from the host rocks, forming the aqueo-carbonic fluids that transported W to the site of deposition. As the formation of scheelite needs high Ca^{++} activity, it is probable that the tungstic acid (H_2WO_4) reacted with calcic minerals from calc-silicate rocks leading to the scheelite precipitation. In addition, according to Marignac & Cuney (1991) the presence of N_2 could have had some importance in scheelite formation as solutions with X =0.1 would diminish the mineral solubility favoring its precipitation.

Considering the high K-alkalic signature, the met aluminous up to peraluminous character, and the high Sr^{87}/Sr^{86} initial ratio (0.713) of granites associated to the Salinas Formation schists Pedrosa-Soares *et al.* (1997) concluded that they could be included in the Ishihara's (1981) ilmenite series S type granites, which would suggest a reducing character to the magma. This would be in agreement with the data from late FI in granite quartz, which are slightly reducing. It should be noted that W presents a strong affinity to S-type granite (Ishihara 1981).

Finally, the Rubelita skarns do not fit well in the oxidized and reduced W-skarns types postulated by Newberry & Einaudi (1981) and Meinert (1992) (Table 2). The Rubelita skarns actually display characteristics from both types. The fluids of the garnet would represent reducing conditions (Fig.4). Nevertheless, the presence of pyroxene (salite) and low Mo bearing-scheelite (<6ppm, Monteiro 1986) is coincident with Meinert's (1992) oxidizing W-skarns (Table 2). Additionally, grossular and pyroxene at Rubelita are late in the calc-silicate mineral paragenesis, and may show intergrowths of both. In the Newberry & Einaudi (1981) proposal, this pyroxene would be an indication of the beginning of less reducing stage, during which scheelite must have precipitated. Supporting this hypothesis, pyrite is absent in scheelite-bearing calc-silicate rocks (Monteiro 1986).

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