

FLUID INCLUSION STUDY FROM XIHUASHAN TUNGSTEN DEPOSIT IN THE SOUTH-JIANGXI PROVINCE (CHINA)

Gaston Giuliani

ORSTOM – Caixa Postal 4021, alameda da Barra
Salvador – Bahia – Brazil

INTRODUCTION

The Xihuashan mine belongs to the Dayu mining district in the southern part of the Jiangxi province. This tungsten deposit represents the typical wolframite-bearing quartz vein type of the Nanling metallogenic province (Yan *et al.*, 1980), which is related to Jurassic biotite granites (Yenshan granites). The fluid phases associated with the wolframite-bearing quartz veins at different exploration levels from the Xihuashan mine were investigated using microthermometric and Raman spectrometric analyses. Knowledge of the bulk composition and density of the different fluid phases encountered in quartz permits the P-V-T-X evolution of the complex aqueous hydrothermal solutions, responsible for tungsten mineralization in the Xihuashan, to be followed.

GEOLOGY

The Xihuashan tungsten deposit is located at the border of a granitic stock composed of four intrusives, called chronologically $\gamma_{5^{2a}}$, $\gamma_{5^{2b}}$, $\gamma_{5^{2c}}$, $\gamma_{5^{2e}}$ which intrude arenaceous and argillaceous anchizonal Cambrian formations. The quartz-bearing veins developed mainly in $\gamma_{5^{2b}}$; this deposit has 615 economically valuable veins (medium grade: 1.08% in WO_3) characterized by four stages of mineralization.

SAMPLE AND ANALYTICAL TECHNIQUES

Samples

For this fluid inclusion study, the representative samples of quartz were collected from several locations of the Xihuashan mine. Samples were mainly taken in the veins n° 2.99 (the biggest vein at the mine) and n° 62, at the levels 632,594,538 and 431; the last level corresponds to the bottom part of the vein 2.99. The quartz vein is massive, grey coloured, sometimes milky and idiomorphic. Transparent to cloudy crystals of quartz can be seen in vugs.

Analytical techniques

Microthermometry: fluid inclusions have been studied using the Chaix-Meca stage (Poty *et al.*, 1976) that allows the temperature of phase transitions occurring in fluid inclusions to be determined during heating and cooling.

Raman spectrometry: the analyses of the non-aqueous part of the inclusions were undertaken with a Jobin-Yvon Raman microprobe type M.O.L.E. (Delhaye and Dhamelincourt, 1975). Three gases were identified by their Raman lines: CH_4 (2914 cm^{-1}), N_2 (2330 cm^{-1}) and CO_2 (1388 cm^{-1}). The area of each Raman line was measured with a planimeter with a precision of 1%. The mole fraction of each gas was calculated from the formulae listed in Dhamelincourt *et al.*, (1979); the relative cross sections of Raman scattering used were those listed by Schröter and Klöckner (1979): $CO_2 = 1.21$; $CH_4 = 9$; $N_2 = 1$. The prin-

principle of the calculation of the composition for carbonic fluids (H_2O-CO_2-NaCl) have been presented by Ypma (1963); Poty et al., (1974), Touret (1976) and were modified for the system H_2O-CO_2-NaCl -volatile by Ramboz (1980) and Ramboz *et al.*, (1985). The calculation is based on the knowledge, at temperature < 31°C, of the compositions and densities of the aqueous fluid and of carbonic vapour (Raman probe and microthermometric data interpreted according to the method of Heyen et al., (1982). The bulk composition has been calculated considering the $H_2O-CO_2-NaCl-CH_4$ systems; the molar fraction of N_2 has been added to the molar fraction of CH_4 for several reasons: - insufficient knowledge of the theoretical systems $CO_2-N_2-(CH_4)$ and specially $H_2O-CO_2-NaCl-CH_4-N_2$; $-CH_4$ and N_2 have almost the same volatility and the systems $CO_2-CH_4-N_2$ and CO_2-CH_4 are comparable (see Ramboz et al., (1985). Salinities were determined by clathrate melting and by depression of freezing points due to the effect of dissolved CO_2 in the aqueous phase.

ANALYTICAL DATA

Microthermometry: Inclusion types: Five main types of inclusions were identified based on microscopic, microthermometric and Raman spectrometric characteristics: CO_2 Type (Type I), CO_2-H_2O Type (Types IIA, IIB, IIC), H_2O Type (Type IIIA, IIIB), multiphase solid inclusions (Type IV) and H_2O-CO_2 (Type V). The microthermometric characteristics of these different types of inclusions are listed in Table 1.

Raman spectrometry: analyses of the gaseous part of the inclusion Types I, IIA, IIB and V, revealed that the main constituent is CO_2 with minor amounts of N_2 and CH_4 . Unmeasurable traces of CO_2 were detected in type IIIB. The bulk composition of these fluids is reported in Table 2.

RESULTS AND DISCUSSION

Qualitative and quantitative variations of the bulk composition of the fluids.

+ $H_2O-CO_2-CH_4-N_2$ inclusions

The diagram Th-Tm (Fig. 1) shows that the domain of Type V inclusions is quite different from that of Type IIA inclusions. Type V inclusions in idiomorphic drusy quartz have similar morphologies and microthermometric features (Tm CO_2 , TmC, TH CO_2) to Type IIA but they differ by their scattered degree of infilling (20% < DF < 70% volume of the inclusion), their higher salinity and their homogenization to the liquid; they apparently characterize the circulation of a different CO_2 -bearing aqueous solutions and are not considered as contemporaneous with Type IIA inclusions.

The determination of the pressure and the PVTX evolution for these carbonic fluids ($CO_2-CH_4-N_2-H_2O-NaCl$) is difficult. Considering the inclusion Type IIA as containing 25% moles CO_2 , the equilibrium $L + V \rightleftharpoons V$ is reached for 300°C at 550 bars (Takenouchy and Kennedy, 1964); this value fixes the thermometric conditions of the equilibrium $L + V \rightleftharpoons V$ and so, the minimum P.T conditions of trapping for Type IIA inclusions. This value should be considered as approximate because the amounts of salts calculated are over-estimated and the effects of CH_4 and N_2 were not taken in account.

+ $H_2O-NaCl$ inclusions

- homogenization temperatures: the Th-Tm diagram (Fig. 1) shows the complex evolution of Xihuashan fluid inclusions.

• TH < 270°C: this range of temperature is mainly found for Types IIIB and IV which are late aqueous inclusions. The scattered values for Type IIIB illustrate clearly the complexity of the hydrothermal evolution, affected by successive fracturing and associated fluid circulation. The diagram Th-Tm (Fig. 1) shows a negative correlation for Type IV: this fluctuation of salinity related to a small temperature interval is typical of a dilution process.

INCLUSION TYPES	type I			type II			type III		type IV	type V
	IIA	IIB	IIC	IIIA	IIIB	S				
SUB TYPES										
SIZE μm	12 to 15	10 to 50	10 to 20	20 to 30	10 to 55	5 to 60	25 to 75	25 to 180		
DEGREE OF INCLUSION FILLING AT 25 °C %	50 to 100	50 to 70	40 to 70	50 to 70	40 to 70	<30	10 to 30	20 to 70		
Tm CO_2 °C	-56.6 to -58.0	-56.7 to -51.5	-56.9 to -58.5	---	---	---	---	-56.6 to -57.1		
Tm C °C	---	+ 60 to + 80	+ 9.5 to +10.0	+ 7.8 to +3.0	---	---	---	+ 3 to +.85		
TH CO_2 °C	Liq: +16.8 Vap: +28 to +30	+ 214 to +290 in Vapor phase	---	---	---	---	---	+155 to +272 in vapor phase		
Tm _i °C	---	-14 to +4.0	-10 to +2.5	-13 to +.50	-0.5 to +.65	-0.1 to +.70	-0.5 to +.65	-1 to +.89		
TH °C	---	+ 300 to +370	+ 260 to +323	+ 220 to +420	+ 270 to +400	+ 100 to +280	+ 150 to +210	+ 180 to +340		
HOMOGENIZATION PHASE	---	VAPOR AND LIQUID	LIQUID VAPOR CRITICAL	LIQUID SOMETIMES VAPOR	LIQUID SOMETIMES VAPOR	LIQUID	LIQUID	LIQUID		

Table 1

Microthermometric characteristics of the different types of inclusions. S: multiphase solid inclusions; Tm: temperature of final melting (°C) of: $CO_2=$

CO_2 solid; C = clathrate; i = ice; Th: temperature of homogenization (°C) of: $CO_2=$ CO_2 liquid (Liq) or vapor (Vap).

Type of inclusion and sample	Salinities X NaCl (moles %)	X eq. CH ₄ x 10 ⁻²	v	ds	X H ₂ O	X CO ₂	X CH ₄	X N ₂	X NaCl
					moles %				
I	X594-12 BI-11				0.8	96.9	0.3	2.8	
	X594-12 BI-15				0.3	98.9	0.1	1.0	
II A	X632-3B AI-1	0.75	2.18	130	0.53	73.3	26.2	-	0.5
	X632-3B A5-2	1.72	0.47	120	0.55	71.7	27.8	-	0.5
	X594-12 BI-7	1.60	0.18	110	0.64	77.8	21.7	-	0.5
	X594-12 BI-21	1.33	0.00	90	0.59	54.2	45.6	-	0.2
	X431-6 CI	0.64	6.36	240	0.42	83.2	15.9	0.6	0.3
II B	X431-6 C2	1.12	6.24	220	0.52	86.7	12.3	0.3	0.4
	X594-12 HI	2.81	3.68	195	0.54	84.9	13.3	0.1	0.3
V	X594-12 GI	2.53	4.0	225	0.53	86.2	11.9	0.6	0.3
	X594-12 FI	2.62	2.42	225	0.69	91.6	6.8	-	0.6

Table 2

Bulk composition for types I, IIA, IIB, V inclusions from Xihuashan quartz veins. Xeq.CH₄ = XCH₄ + XN₂; v = molar volume (cm³ mole⁻¹); ds = bulk

density of the inclusion (g cm⁻³); XH₂O, XCO₂, XCH₄, XN₂, XNaCl = bulk composition (mole %).

- TH > 270°C: Type IIIA homogenize to liquid or to vapor between 270° and 420°C; Raman spectrometry has detected no traces of CO₂ or other volatile phases. The fluids are typically aqueous and of low density (2 to 3 wt % eq. NaCl); these observations indicate the presence of an early fluid that probably corresponds to a specific hydrothermal event. The inclusions which homogenize in the vapor phase are contemporaneous with those that homogenize into liquid (homogenization between 310° and 380°C). These observations can indicate unmixing of the fluid. Furthermore, the respective salinities of these inclusions are close to each other and so, the unmixing phenomena must have been quite limited. Unmixing of the fluid appears evident at 380°C (100 to 200 bar) and it is characterized by the existence of an aqueous solution richer in salts and a vapor of lower salinity (Fig. 1).

+ Fluid compositions.

- During the whole hydrothermal process, the chemical composition and the amounts of CO₂, CH₄, N₂ do not change significantly except in the case of the Type V inclusions which have higher salinity and lower carbonic content.

- Presence of nitrogen: the Raman microprobe demonstrates the presence of small amounts of nitrogen in Xihuashan fluid inclusions. Roedder (1972) summarized data on nitrogen in fluid inclusions, but the recent use of Raman technique shows very often the presence of this gas in inclusions from various environments: metamorphic rocks (Dhamelincoeur *et al.*, 1979; Kreulen and Schuiling, 1981), olivine crystals (Massare *et al.*, 1980), dolomite and quartz from Tunisia (Guilhaumou *et al.*, 1981) and also hydrothermal tungsten-bearing quartz veins from Central Morocco (Cheilletz, 1984; Giuliani, 1984). In these latter tungsten deposits, the amount of nitrogen can reach 5 mole % (Giuliani, 1984) and its source is not well explained. Kreulen and Schuiling (1981) considered three possibilities:

- breakdown of organic matters.
- breakdown of a K-silicate mineral (biotite, K-feldspar) in which NH₄⁺ substitutes K⁺.
- deep origin by concentration of N₂ in the gaseous phase. Bastoul (1983) described N₂-rich inclusions in three cases of black schists, from France and Morocco, affected by contact metamorphism. The amount of N₂ was related either directly to or-

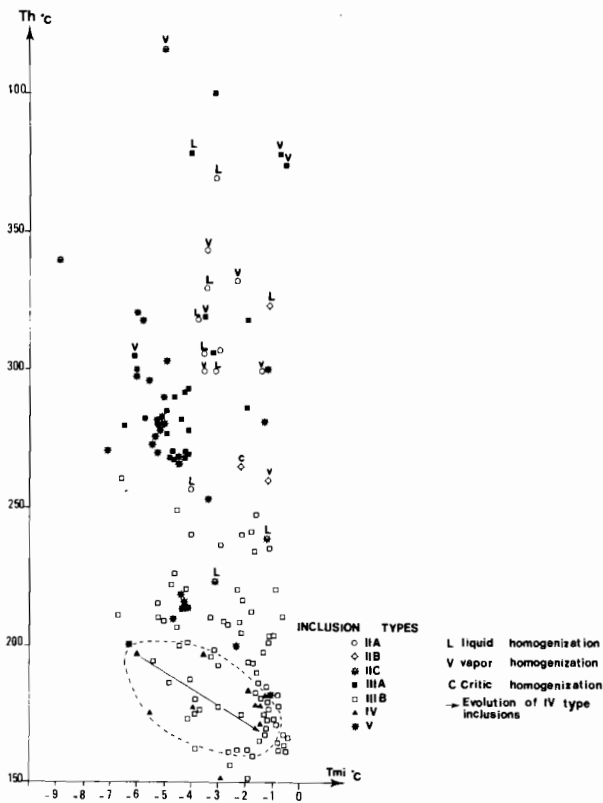


Figure 1
Th-Tmi diagram of fluid inclusion from Xihuashan quartz veins. Th(°C): temperature of homogenization; Tmi (°C): melting temperature of ice.

ganic matter from the black schists or to the breakdown of micas that acquired N₂ during the increase of the thermal gradient. The geological environment of Xihuashan is comparable and such possible sources for nitrogen can be considered.

CONCLUSIONS

The fluid inclusion study from the Xihuashan tungsten deposit shows that the hydrothermal quartz veins contain aqueous and CO₂ - bearing inclusions which homogenize in the liquid or

vapor phase between +150°C and 420°C with salinities of 1 to 10 wt%, equivalent NaCl. These results agree with the work of Lu et al., (1982) who have found the same microthermometric features in 10 hydrothermal veins from tungsten ore deposits in southern China.

The hydrothermal evolution results from an active fluid circulation corresponding to the succession of specific events such as opening and heating of fractures. The different peaks of temperature and ice melting record a number of discontinuous events during a continuous hydrothermal evolution of the system during cooling. The changes in the thermodynamic properties of the fluid phase are marked by a continuous evolution from the earlier to the late fluids. The earlier fluids are of two kinds: - low density and salinity, CO₂-bearing aqueous solutions circulating at temperatures up to 420°C, - low salinity (2 to 3 wt% eq.NaCl) aqueous solutions, lacking of CO₂, circulating at high temperatures (280°C up to 400°C) that correspond to a specific hydrothermal fracturing event; limited unmixing occurs at 380°C, 200 to 100 bar, probably in response to a sudden pressure drop.

The fluids related to the idiomorphic drusy quartz are typical CO₂-bearing aqueous solutions with low salinity (2.5 wt% eq.NaCl) homogenizing at low to moderate temperatures (180°C to 340°C).

The Xihuashan hydrothermal evolution ends with cooler fluids characterized by variable salinities and homogenizing in the liquid phase between 100°C to 175°C.

Many fluid inclusion studies from vein tungsten deposits show that complex carbonic fluids might play an important role in the transport and deposition of tungsten in hydrothermal systems (Naumov and Ivanova, 1971; Higgins, 1980; Ramboz, 1980; Ramboz et al., 1985). The precipitation of the tungsten is favoured by different mechanisms such unmixing of an homogeneous solution into two different fluids (Higgins, 1980, Ramboz et al., 1982) or by mixing of two fluids with different compositions (Giuliani, 1984; Ramboz et al., 1985). In other tungsten deposits, fluid inclusion studies indicate only the presence of aqueous fluids enriched in chloride (Jackson et al., 1979; Charoy, 1979).

So, the fluid inclusions present in quartz vein tungsten deposits vary in complexity and for Xihuashan many questions remain: - complexity of the hydrothermal evolution and the consequent difficulty in correlating the various types of fluid inclusions each other; - the supposed importance of the carbonic aqueous fluid inclusions in other deposits which form the least important type found here in the quartz, and importance of the role played by these CO₂-rich fluids in the transport of tungsten. In the case of Xihuashan, there is no evidence available to decide whether tungsten was transported by the early carbonic aqueous fluid or by the aqueous fluid circulating at high temperatures.

BIBLIOGRAPHY

- BASTOUL, A. – 1983 – Etude des fluides carbo-azotés associés au métamorphisme de contact des schistes noirs sur l'exemple des Jebilet centrales (Maroc). Comparaison avec la région des Bondons et de Penaran (France). Thèse 3^e Cycle Institut National Polytechnique de Nancy, 189 p.
- CHAROY, B. – 1979 – Définition et importance des phénomènes deutériques et des phases fluides associées dans les granites; conséquences métallogéniques. *Mém. Sci. de la Terre, France*, 37, 364 p.
- CHELLETZ, A. – 1984 – Caractéristiques géochimiques et thermobarométriques des fluides associés à la scheelite et au quartz des minéralisations tungstifères de Djebel Aouam (Maroc Central). *Bull. Minéral.*, 107: 255-272.
- DELHAYE, M.; DHAMELINCOURT, P. – 1975 – Raman microprobe and microscope with laser excitation. *Jour. Raman Spectrosc.*, 3: 33-43.
- DHAMELINCOURT, P.; BENY, J. M.; DUBESSY, J.; POTY, B. – 1979 – Analyse d'inclusions fluides à la microsonde Mole à effet Raman. *Bull. Minéral.*, 102: 600-610.
- GIULIANI, G. – 1984 – Les concentrations filoniennes à tungstène -étain du massif granitique des Zaër (Maroc Central): Minéralisations et phases fluides associées. *Mineral. Deposita*, 19: 193-201.
- GIULHAUMOU, N.; DHAMELINCOURT, P.; TOURAY, J. Cl.; TOURET, J. – 1981 – Etude des inclusions fluides du système N₂-CO₂ de dolomites et de quartz de Tunisie septentrionale. Données de la microcryoscopie et de l'analyse à la microsonde à effet Raman. *Geochim. Cosmochim. Acta*, 45: 657-673.
- HEYEN, G.; RAMBOZ, Cl.; DUBESSY, J. – 1982 – Simulation des équilibres de phases dans le système CO₂-CH₄ en dessous de 50°C et de 100 bars. Application aux inclusions fluides. *C. R. Acad. Sci. Paris*, 294: 203-206.
- HIGGINS, N.C. – 1980 – Fluid inclusion evidence for the transport of tungsten by carbonate complexes in hydrothermal solutions. *Can. Jour. Earth Sci.*, 17: 823-830.
- JACKSON, N.J.; MOORE, J. McM.; RANKIN, A.H. – 1977 – Fluid inclusions and mineralization at Cligga Head, Cornwall, England. *Jour. Soc. London*, 134: 343-349.
- KREULEN, R.; SCHUILING, R.D. – 1981 – N₂-CH₄-CO₂ fluids during formation of the Dôme de l'Agout, France. *Geochim. Cosmochim. Acta*, 46, 193-203.
- LU, H.; SHI, J.; YU, C.; XU, S. – 1982 – Geologic and fluid inclusion studies of ten types of tungsten ore deposits in South-China. *Geochemistry*, 1, 2: 200-217.
- NAUMOV, V.B.; IVANOVA, G.F. – 1971 – The pressure and temperature conditions for formation of wolframite deposits. *Geochim. Inter.*, 8: 381-394.
- MASSARE, B.; CHLOCCHIATTI, R.; TOURET, J. – 1980 – Fluides résiduels et minéraux réactionnels dans les olivines gemmes de l'île de Zebargard (Mer Rouge), signification pétrogénétique et tectonique. In: 8^e RAST, p. 244.
- POTY, B.; STALDER, T.; WEISBROD, A. – 1976 – Fluid inclusions studies in quartz from fissures of western and central alps. *Schweiz. Mineral. Petrogr. Mitt.*, 54,2/3: 717-752.
- POTY, B.; LEROY, J.; JACHIMOWICZ, L. 1976 – Un nouvel appareil pour la mesure des températures sous le microscope: l'installation de microthermométrie Chaixméca. *Bull. Soc. Fr. Min. Cristall.*, 99: 182-186.
- RAMBOZ, Cl. – 1980 – Géochimie et étude des phases fluides des gisements d'étain-tungstène du sud du Massif Central (France). Thèse 3^e Cycle Institut National Polytechnique de Lorraine Nancy, 278p.
- RAMBOZ, Cl.; PICHAVANT, M.; WEISBROD, A. – 1982 – Fluid immiscibility in natural processes: use and misuse of fluid inclusion data. II. In: *Chem. Geol.*, 37: 29-48.
- RAMBOZ, Cl.; SCHNAPPER, D.; DUBESSY, J. – 1985 – The PVTXFO₂ evolution of H₂O-CO₂-CH₄- bearing fluid in a wolframite vein: Reconstruction from fluid inclusion studies. *Geochim. Cosmochim. acta*, 49: 205-219.
- ROEDDER, E. – 1972 – Compositions of fluid inclusions. In: *Data of geochemistry*. Editor Fleischer M. U.S. Geol. Surv. Professional Paper, 440-JJ, 164p.
- SCHRÖTTER, H.W.; KLOCKNER, H.W. – 1979 – Raman scattering cross section in gases and liquids. In: *Raman Spectroscopy of gases and liquids*. Ed. Weber 4: 123-166 Springer Verlag.
- TAKENOUCHEY, S.; KENNEDY, G.C. – 1964 – The binary system H₂O-CO₂ at high temperatures and pressures. *Amer. Jour. Sci.*, 262: 1055-1074.
- TOURET, J. – 1976 – The significance of fluid inclusions in metamorphic rocks in thermodynamics in geology. *Nato advanced study institutes series, Series C, Donall G., Fraser Editors: 203-227*.
- YAN, M.Z.; WU, Y.L.; LI, C.Y. – 1980 – Metallogenic systems of tungsten in South-East China and their mineralization characteristics. *Granitic magmatism and related mineralization. Mineral. Geol. Spec. Issue*, 8, Japan, 215-221.
- YPMA, P. – 1963 – Rejuvenation of ore deposits as exemplified by the Belledone metalliferous province. Ph.D. Thesis, University Leiden. Holland.