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Mineral Deposits: From Their Origin to Their Environmental Impacts

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Fluid inclusion and stable isotope studies in Sn-W deposits of western Spain

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ABSTRACT: Most of the Spanish Sn-W mineralizations are related to the syn- to late-tectonic Hercynian granites. Fluid inclusion and stable isotope studies have been carried out in quartz, cassiterite, scheelite and wolframite from different types of deposits: Sn disseminations in apogranites (Golpejas and Penouta), Sn pegmatites (Feli) and Sn, Sn-W, W quartz veins (Teba, San Finx, La Parrilla and Virgen de la Encina). The fluids probably responsible for the Sn-W mineralizations belong to H₂O-NaCl-CO₂-CH₄-N₂-H₂S system with salinities below 15 wt. % eq. NaCl and homogenization temperatures ranging between 240 and 430°C. $\delta^{18}\text{O}_{(\text{SMOW})}\text{‰}$ values show small variations: from 9.4 to 15.6 in quartz, -3.8 to 7.3 in cassiterite, 5.8 to 6.9 in scheelite, 4.9 in wolframite, and -2.9 to 8.2 in water of the metalliferous fluids. These fluids are mainly magmatic or with incorporation of other isotopically lighter waters.

1 MINERALIZATIONS

The Sn-W metallogenic province of the Iberian Peninsula is one of the most important in the Hercynian orogenic belt of Europe. There are 150 Sn-W occurrences which extend from Galicia through the north of Portugal to the southwest of Spain. This study concerns seven Spanish Sn-W mineralizations that showed important economic interest during the '70 and '80, and belong to different types:

1. Tin disseminations in apogranites: Golpejas (Salamanca) and Penouta (Orense). Tin ore occurs as disseminations of cassiterite in the granites (G conc Q-Cs and P34 Q samples) and as greisenized zones (P115 Q-Cs) and quartz veins (G1 Q and G10 Q) which traverse both the alkaline granites and the surrounding metamorphic country rocks.

2. Tin pegmatites: Feli (Salamanca). At Feli deposit, a large pegmatite dyke (F13 Q sample) with Li-muscovite is associated with a stockwork of quartz and pegmatite dykes (F15 Q-Cs) cutting Cambrian schist, quartzites and amphibolites.

3. Quartz veins and stockworks with: cassiterite, Teba (Cáceres) --T1 Q-Cs and T2 Q-Cs samples--; cassiterite and wolframite, San Finx (La Coruña) --SF 3 Q-Wol, SF 67 Q-Cs and SF72 Q-Cs--; scheelite and cassiterite, La Parrilla (Cáceres) --Pa2 Q-Cs-Sch and Pa3 Q-Sch--; and wolframite-scheelite, Virgen de la Encina (León) --VE1 Q and

VE34 Q--. In these deposits, quartz veins and stockworks cut surrounding metamorphic rocks, in the exocontact of, or proximity to, Hercynian leucogranites and/or two-mica granites.

2 FLUID INCLUSION STUDY

The study of the fluid inclusions by microthermometry and Raman microprobe analyses was carried out on different samples of quartz, cassiterite and scheelite belonging to hydrothermal veins and greisenized rocks.

Taking into account their chemical composition, four types of inclusion have been defined:

-Type 1: Complex, CO₂ aqueous inclusions (H₂O-NaCl-CO₂-CH₄-N₂-H₂S system).

-Type 2: Complex, CO₂ inclusions (CO₂-CH₄-N₂-H₂S system).

-Type 3: Low salinity, aqueous inclusions (H₂O-NaCl system).

-Type 4: Mixed salt, aqueous inclusions (H₂O-NaCl and other salts system).

The microthermometric data are summarized in Table 1 and interpreted in Mangas and Arribas (1987).

The microthermometric results suggest that the fluid inclusions are evidence of continuous hydrothermal evolution. Assuming that the evolution of the deposits developed in response to decreasing

Table 1. Extreme microthermometric results obtained in quartz (Q), cassiterite (Cs) and scheelite (Sch) of studied Sn-W deposits.

SAMPLES	TYPE I.F.	Tm CO ₂ (°C)	Tm ice (°C)	Th hyd (°C)	Th CO ₂ (°C)	Tm NaCl (°C)	Th (°C)
G1 Q	1	-57/-58	0/-4	7/12	26/29 L		270/430 L,G (345)
	2	-56.6/-59.5			26/31 L,G		
	3		0/-4				180/400 L (295)
G10 Q	1	-56.6/-58	-2/-4.5	8/12	27/31 G		270/360 L,G (325)
	2	-56.6/-58.5			27/31 G,C		
	3		0/-4.5				70/400 L (270)
	4		-9/-12				90/110 L (105)
P34 Q	1	-55.6/-58.5	-2/-6	8.5/15	17/27 L,G		260/420 L,G (310)
	2	-57/-59			17/26 L,G		
	3		-0.5/-4.5				110/300 L (170)
	4		-15.5/-16.5				110/130 L (125)
P115 Q	1	-57.5/-59	-2.5/-5	9.5/11.5	16/21 L		250/320 L (285)
	3		0/-4				110/280 L (185)
	4		-9.5/-11.5				100/120 L (105)
F13 Q	1	-57/-58.5	-3/-7	6.5/10.5	17/25 L,G		250/390 L,G,C (325)
	2	-57/-58.5			16/25 L,G		
	3		0/-5.5				130/310 L (290)
	4		0/-30				70/130 L (95)
F15 Q	1	-56.6/-58.5	-1.5/-9	8/15	16/28 L,G		250/400 L,G,C (335)
	3		0/-4.5				100/290 L (255)
	4		-8/-24				70/110 L (95)
	T1 Q	1	-57.5/-63	-2/-5.5	9.5/12.5	3 G	
3		0/-4.5				150/320 L (255)	
T2 Q	1		-1/-5	8/13			240/320 L (265)
	3		0/-3.5				160/300 L (240)
	4		-23/-45			97	80/100 L (90)
Pa2 Q	1		0/-4	3.5/7.5			230/310 L (240)
	3		0/-4.5				210/350 L (235)
	4		-1/-5.5			110/190	80/160 L (85)
Pa2 Sch	3		0/-3.5				240/300 L (285)
Pa3 Q	1		-2.5/-4	8/11			210/260 L (220)
	3		0/-4.5				230/270 L (225)
	4		-7.5/-25				70/150 L (85)
SF3 Q	1		0/-3	8.5/14.5			220/290 L (245)
	3		-0.5/-2.5				130/290 L (235)
	4		-6.5/-17.5				130/170 L (135)
SF68 Q	3		0/-3.5				150/230 L (205)
	4		5/-31.5			98	90/170 L (105)
SF68 Cs	1		-1.5/-3	15.5/16.5	-85/-90 G *		250/300 L (265)
	3		0/-2				235/305 L (270)
SF72 Q	1		-1/-2.5	16.5/17.5			250/310 L (275)
	3		0.5/-3.5				140/360 L (245)
	4		-4.5/-11.5				130/170 L (145)
VE34 Q	1	-56.6/-59	-3/-5.5	7.5/11.5	14/22 G		240/380 L,G (310)
	3		0/-4				120/300 L (215)
	4		-13/-37				50/180 L (95)

* In SF68 Cs sample indicate Th CH₄ data.

Data between brackets in the Th column are the Th histogram mode and have been used for isotopic stu

Table 2. Oxygen-isotope data for quartz, cassiterite, wolframite and scheelite from Spanish Sn-W deposits and calculated parameters for mineralizing fluids.

SAMPLES	Th (°C)	$\delta^{18}\text{O}$ min ‰(SMOW) (range)	$\delta^{18}\text{O}$ min ‰(SMOW) (mean)	$\delta^{18}\text{O}$ fluid ‰(SMOW)	$\Delta(\text{A-B})$ ‰(SMOW)	T eq. (°C)
G1 Q	345	12.8/13.5	13.2	7.7		
G10 Q	325	13.8	13.8	7.8		
Geonc Q		14.5/15.1	14.8	(9.4)	9.8	
Geonc Cs		4.9/5	5	(8.1)		
P34 Q	310	12.9/13.7	13.4	6.9		
P115 Q	285	13/13.8	13.4	6	9.1	341
P115 Cs		4.3	4.3	(7.6)		
F13 Q	325	14.2	14.2	8.2		
F15 Q	335	13.8/14	13.9	8.2	7.6	459
F15Cs		6/6.6	6.3	(9.2)		
T1 Q	295	15/15.4	15.2	8.2	11.2	
T1 Cs		4	4	(6)		
T2 Q	265	15.5/15.6	15.6	7.4	8.3	408
T2 Cs		7.1/7.5	7.3	(8.2)		
Pa2 Q	240	14.3/14.5	14.4	5	8.9	359
Pa2 Cs		5.5	5.5	(5.3)		
Pa2 Sch	285	5.8	5.8	7.2		
Pa3 Q	220	13.8/13.9	13.9	3.5		
Pa3 Sch		6.9	6.9	(7.1)		
SF3 Q	245	11.3/11.9	11.6	2.5	6.7	443
SF3 Wol		4.9	4.9	(5.8)		
SF68 Q	205	9.4/9.7	9.6	-1.7	13.5	
SF68 Cs	265	-3.8	-3.8	-2.9		
SF72 Q	275	11.4/11.6	11.5	3.7	7.2	487
SF72 Cs		4.3	4.3	(5.6)		
VE1 Q		14.1/14.9	14.5	(8)		
VE34 Q	310	13.6	13.6	7.1		

Th: homogenization temperature mode of the type 1 inclusion from data Table 1.

T eq.: temperatures estimated by the oxygen-isotope geothermometer using co-existing Q-Cs and Q-Wol.

Data between brackets in the $\delta^{18}\text{O}$ fluid column are calculated with the quartz Th data, assuming co-existence quartz-mineral (Cs, Sch and Wol) in each studied sample and deposit.

temperatures and pressures, and taking into account the paragenesis and the microthermometric data, three main episodes can be distinguished:

1. The first episode is characterized by the entrapment of fluids belonging to H₂O-NaCl-CO₂-CH₄-N₂-H₂S system (type 1 and 2 inclusions) with salinities below 15 wt.%eq.NaCl and densities varying from 0.55 to 0.8 g/cc, trapped at minimum temperatures ranging between 200 and 430°C, and pressures below 3,250 bars. During this stage, the density of the aqueous solutions increases, the salinity and concentration of volatiles decrease as the temperature drops. These characteristics suggest a mixing and dilution of these early fluids with waters of low salinity. These early fluids are contemporaneous with deposition of Sn-W mineralization and related alteration.

2. The second episode is represented by low-salinity aqueous inclusions (type 3 inclusion) with salinities below 10 wt.%eq.NaCl and densities ranged between 0.7 and 0.95 g/cc, trapped at intermediate homogenization temperatures varying between 60 and 400°C, and pressures below 1,000 bars. This stage can be correlated with the precipitation of polymetallic sulphides.

3. The third episode is characterized by higher salinity aqueous inclusions (type 4 inclusion) containing NaCl and other chlorides, with salinities below 45 wt.%eq.NaCl and densities ranging between 0.9 and 1.3 g/cc, trapped at low homogenization temperature ranging between 50 and 170°C, and low homogenization pressures (below 100 bars). The different compositions and the contrast of salinities found between the second episode and the third is probably due to a mixing of magmatic-low salinity solutions with fluids of connate and/or metamorphic source.

3 STABLE ISOTOPIC ($\delta^{18}\text{O}$) STUDY

We have measured the oxygen isotope composition of quartz, cassiterite, wolframite and scheelite mineral separate and the oxygen extraction was done in the Stable Isotopes Laboratory of Salamanca University (Table 2).

The ^{18}O compositions of minerals are generally uniform though there are minor variations. The $\delta^{18}\text{O}$ values of quartz samples range from 9.4 to 15.6‰; San Finx show lighter values ranging between 9.4 and 11.9‰, and all remaining deposits show similar values of 13.4 to 15.2‰. The cassiterite, wolframite and scheelite data are also uniform and show values between 4 and 7.3‰, except for SI-68

Cs sample that show a result of -3.8‰.

Oxygen isotope compositions of the fluid were derived by relating the measured mineral isotope composition and mineral-water isotope fractionation factor at the temperature of crystallization. These $\delta^{18}\text{O}$ values of fluid data and the oxygen-isotope geothermometer were obtained using oxygen isotope fractionation equations between 250 and 500°C of Matsuhisa et al. (1979) for quartz, Zhang et al. (1994) for cassiterite and wolframite, and Wesolowski and Ohmoto (1986) for scheelite. Temperature of crystallization were based on fluid inclusion and these were Th histogram mode of type 1 inclusions in each sample. Thus, $\delta^{18}\text{O}$ values of fluid obtained range of 5 to 8.2‰, except for San Finx samples and one of La Parrilla that show data between -2.9 to 3.5‰. The first data are all within the range of magmatic water but the second suggest an incorporation of isotopically lighter (probably meteoric) fluid into the hydrothermal system. Involvement of surface water during mineralization has also been detected in data for quartz sample from other granite-related hydrothermal deposits in Hercynian orogenic belt.

The temperature calculated by the oxygen-isotope geothermometer are not in good agreement with data obtained by microthermometric studies (see Tables 1 and 2), indicating isotopic disequilibrium between Q-Cs and Q-Wol and different physico-chemical characteristics of formation for these minerals that apparently co-existing in the samples.

The hydrogen isotope data are not still available and they can not be combined to construct a δD versus $\delta^{18}\text{O}$ plot.

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