

A numerical approach for the formation of chlorite and sulphide-bearing greisen: a study based on the Navalcubilla system (Spanish Central System)

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Abstract

The formation of sulphide and cassiterite-bearing chlorite-rich greisens in the Navalcubilla granite has been modelled theoretically. Numerical simulation on the reaction of a hydrothermal fluid with a granitic rock predicts assemblages very similar to those found in nature, with progressive formation of muscovite, quartz, chlorite, microcline and plagioclase zones. The hydrothermal alteration of the rock produces a neutralization of the inflowing acid fluid, a drop in the f_{S_2} and, to a lesser degree, an increment in f_{O_2} . During hydrothermal alteration, f_{S_2} and f_{O_2} change abruptly between metasomatic zones, but chlorite seems to control their major changes. Scheelite and cassiterite are concentrated in the internal zones, while sulphides are related to the more external zones. Fluid–rock reactions seem to be very effective for precipitating cassiterite and scheelite, even from very Sn and W-poor fluids. Appreciable amounts of sulphides are only expected in systems with high concentrations of base metals. Boiling and simple cooling of the fluids acidifies and oxidizes them but chemical changes are not strong enough to induce significant precipitation of ore minerals, at least when the temperature changes are small. Continued circulation of fluids along fractures with previously precipitated quartz + wolframite produces replacement of wolframite by scheelite and sulphides.

KEYWORDS: greisen, fluid–rock reactions, scheelite, cassiterite, Spanish Central System.

Introduction

GRANITE-RELATED hydrothermal mineralization is one of the most studied ore forming processes. Its economic and geological significance has been the stimulus for much research (e.g. Eugster, 1985; Strong, 1988; Jackson *et al.*, 1989; Heinrich, 1990, and references therein). Many of the studies have pointed out the existence of a continuous evolution in space and time from early magmatic, spatially restricted, hydrothermal systems towards later, usually meteoric-dominated, huge convective cells. There is a paragenetic evolution from early wolframite \pm cassiterite (\pm molybdenite) to scheelite \pm arsenopyrite \pm cassiterite and late base metal sulphides with stannite. The progressive variation of the hydrothermal assemblage is accompanied by a drop in temperature, salinity and $\delta^{18}O$ of the fluids (e.g. Shepherd *et al.*, 1976, 1985; Kelly and Rye, 1979; Shelton *et al.*, 1987; Jackson *et al.*, 1989). The extent and mineralogy of the hydrothermal alteration

is related to the proportions of magmatic and meteoric fluids involved in the system. Fluid circulation is usually driven by the heat from the cooling granite and channelled along major discontinuities.

Greisens are the result of fluid–rock interaction in these hydrothermal systems. They are metasomatic rocks mainly composed of quartz and muscovite with minor amounts of topaz, fluorite, tourmaline and chlorite (e.g. Scherba, 1967; Burt, 1981). Ore minerals such as cassiterite, wolframite, scheelite and lesser amounts of sulphides (e.g. stannite, arsenopyrite, pyrrhotite, pyrite, sphalerite, chalcopyrite, bismuthinite) are also found. The formation of a greisen usually destroys the magmatic textures and mineralogy, and overprints earlier hydrothermal alterations, such as feldspathization (e.g. Pollard, 1983; Strong, 1988).

In the Variscan Belt of Iberia, different types of greisens are related to distinct magmatic and hydrothermal environments:

a) Sn-rich greisens, characterized by the pervasive replacement of small granitic cupolas by quartz, large muscovite crystals (usually Li-rich), topaz, fluorite and phosphates. Ore minerals are disseminated cassiterite and tantalite–columbite, with only trace amounts of sulphides and tungsten-bearing minerals (Mangas, 1987). They are usually related to volatile-rich peraluminous leucogranites of deep emplacement (>6 km) that intruded synchronously with the major Variscan deformation.

b) W and Sn-rich greisens occurring as massive replacements, usually of up to several metres in width, close to the quartz veins. They comprise quartz, muscovite, biotite, topaz, fluorite and/or tourmaline with wolframite, scheelite, cassiterite and sulphides (mainly arsenopyrite). Typical greisens of this type are located in the NW and W Iberian Peninsula (Leduc, 1978; Nesen, 1980; Kelly and Rye, 1979; Polyá, 1989) and are usually related to the formation of wolframite \pm cassiterite vein mineralization. They are similar to the greisens described in Cornwall by Charoy (1981), Shepherd *et al.* (1985) and Jackson *et al.* (1989). They have a close spatial association with epizonal peraluminous monzogranites to leucogranites that typically cut the major Variscan structures. These ore-bearing granites seem to be the more evolved bodies of a suite of aluminous to peraluminous granitoids that were intruded during the late collapse of the Variscan orogen. They have the characteristics of the Hercynotype granitoids of Pitcher (1982).

c) Chlorite-rich greisens, having significant amounts of base metal sulphides and minor proportions of cassiterite and/or scheelite. As for the previous examples, they are vein-controlled. The usual assemblage is quartz, chlorite (>20%) and muscovite and they are probably synchronous with the sulphide-rich stage of the nearby veins. Though not as common as earlier types, they can replace the type [b] greisens (Tornos *et al.*, 1993a). Similar rocks have been described in Cornwall (Charoy, 1981) and Canada (Lentz *et al.*, 1988).

Hydrothermal fluids related to the Sn and Sn-W veins and greisens (types [a] and [b]) are mainly CO₂-rich or hypersaline brines of high temperature and deep (magmatic or metamorphic) origin (e.g. Mangas, 1987; Tornos *et al.*, 1996). However, the late sulphide-rich stages of these mineralizations, as well as the chlorite-rich greisens, are usually associated with CO₂-poor and medium to low-salinity cooler fluids of probable meteoric origin (Mangas, 1987; Tornos *et al.*, 1993a).

Recent developments in theoretical geochemical modelling have been applied to the study of granite-related hydrothermal systems and to the mechanisms of ore leaching, transport and precipitation (e.g. Eugster, 1985; Heinrich, 1990). There have been

recent contributions to the understanding on the behaviour of tin, tungsten and arsenic in early, high-temperature, hydrothermal processes (Heinrich and Eadington, 1986; Heinrich, 1990). The general conclusions of these studies can be applied to the high-temperature greisens (types [a] and [b]), but cannot be used to evaluate the low-temperature processes and predict the formation of the chlorite-rich greisens, where fluids are cooler and geochemically different.

The present study attempts to build a general model for the formation of low-temperature, chlorite- and sulphide-bearing greisens, to complement the models developed at higher temperatures. The theoretical model is constrained by field, petrographic and geochemical studies of the hydrothermal system linked to the Navalucubilla granite, in the Spanish Central System (Tornos *et al.*, 1993a). General aspects and limitations of such a numerical approach have been described by Reed and Spycher (1985, 1988) and Heinrich (1990), and only special features will be discussed here. The application of simple titration models based on the assumption of local equilibrium can be justified in these high-temperature hydrothermal systems (e.g. Steefel and Lasaga, 1994; Heinrich *et al.*, 1995).

Recent thermochemical data for Sn (Patterson *et al.*, 1981; Jackson and Helgeson, 1985; Pabalan, 1986) and W (Wesolowski *et al.*, 1984; Heinrich, 1990 and pers.com. 1992) minerals and related aqueous species were merged in the SOLTHERM datafile (Reed and Spycher, 1988). These data provide information about equilibrium and dissociation constants below 350°C and pressures close to the water liquid-vapour curve. Activity coefficients for aqueous species were calculated using the algorithms and data in Helgeson *et al.* (1981) and Oelkers and Helgeson (1991) and incorporated into the SOLVEQ and CHILLER software (Reed and Spycher, 1988). The SOLVEQ code was also modified to calculate the compositions of fluids in equilibrium with minerals with solid solution. The muscovite is assumed to be the thermodynamic equivalent of all the white micas. Mineral activities were calculated assuming an ideal multi-site mixing behaviour (Helgeson *et al.*, 1978).

The Navalucubilla granite and related hydrothermal alterations

The theoretical approach of this study is based on the hydrothermal alteration of the Navalucubilla granitic stock (Spanish Central System), where greisens, although small, are well exposed. A full description of the geology of the granite is given in Tornos (1990) and Tornos *et al.* (1993a), but a summary of the main features will be given here.

The Navalcubilla granite outcrops in the northern part of the Spanish Central System as a small body intrusive into high-grade, pre-Variscan metamorphic rocks (mainly orthogneisses) and earlier Variscan monzogranites. The pluton has a composite structure with an (early) inner unit of porphyritic leucogranites and a more external leucogranite intrusion (Fig. 1).

The porphyritic unit is dominant and is characterized by the presence of quartz and oligoclase phenocrysts in a groundmass of fine-grained quartz, orthoclase, biotite and oligoclase. Accessory minerals are cordierite, andalusite, sillimanite, apatite, zircon, ilmenite and pyrrhotite. Muscovite is present as large plates and is probably post-magmatic in origin. Related to this granite are several porphyry dikes trending N110–120°E that cut the enclosing rocks. This unit is partially surrounded by later, fine-grained leucogranites with almost the same mineralogy (no sillimanite has been observed), but with equigranular texture. A characteristic feature of this rock is the presence of cm-sized miarolitic vugs containing wolframite + quartz + muscovite + topaz.

Geological evidence suggests that the pluton intruded at shallow depth ($P_1 \leq 1-1.5$ kbar), at temperatures greater than 700°C and along an extensional late-Variscan shear zone (Tornos *et al.*,

1993a). Geochemically, this granite is peraluminous and represents one of the most evolved batholiths of the Spanish Central System, dated between 345 ± 8 to 279 ± 10 Ma (Casquet *et al.*, 1988; Serrano Pinto *et al.*, 1988; Caballero, 1993). Typologically, this Navalcubilla granite is similar to the Hercynotype granites of Pitcher (1982), which are typically postcollisional.

Two main hydrothermal events are observed within the granite. The first is characterized by an irregular and minor feldspathization and the presence of abundant quartz veins with wolframite (\pm molybdenite) in the margins of the leucogranite. Locally, some type [b] greisens, with muscovite, biotite and quartz, are found in the wallrocks of the veins. The $\delta^{18}\text{O}$ whole-rock values of rocks affected by this event (ab. +12‰) are similar to those of the unaltered granite and indicate that the early hydrothermal fluids may be magmatic in origin (Tornos *et al.*, 1996). This hydrothermal alteration is minor, suggesting that the volume of these early fluids was low. K-Ar dating of micas of this stage give an age 291 ± 9 Ma, similar to the age of other wolframite-rich veins (302 ± 6 to 291 ± 7) and leucogranites (299 ± 3 to 287 ± 5 Ma; Serrano Pinto *et al.*, 1988; Tornos *et al.*, 1996) in the area. In the

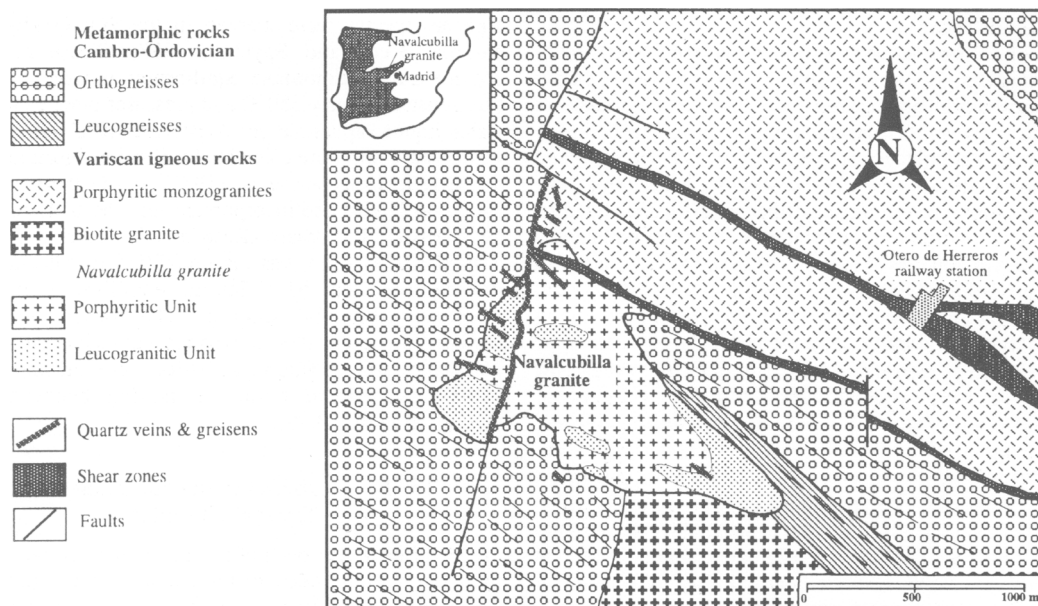


FIG. 1. Schematic geological map of the Navalcubilla granite showing the different granitic rocks and hydrothermal alterations. Modified from Tornos *et al.* (1993a)

quartz veins, no fluid inclusion record of this event has been found, since later deformation and recrystallization of the quartz has overprinted the original features. A similar situation was found by Charoy (1981) and Rankin and Alderton (1985) in Cornwall. However, comparison with similar systems of the Iberian Peninsula indicates that this early alteration was related to the circulation of CO₂ and NaCl-rich fluids at temperatures between 600 and 250°C (Mangas, 1987; Noronha *et al.*, 1992; Tornos *et al.*, 1993a).

Superimposed on hydrothermal rocks related with the early stage or unaltered granitoids there is a second hydrothermal event dated at 267 ± 7 Ma (K-Ar dating of sericites in the chlorite-rich greisen). Similar ages have been found in nearby hydrothermal rocks, such as episyenites and Fe-rich skarns (Caballero *et al.*, 1992; González Casado *et al.*, 1996). Comparison with the age of the early stage suggest a time span of more than 20 Ma between both hydrothermal events. In the quartz veins, this hydrothermal stage produced recrystallization and precipitation of quartz, replacement of the early wolframite by scheelite and precipitation of an accessory and complex sulphide assemblage (chalcopyrite, pyrite, arsenopyrite and minor amounts of pyrrhotite, sphalerite, galena, bismuthinite and native bismuth). This occurred in fissures and vugs, with some chlorite and phengitic mica also produced.

The most distinctive result of the alteration produced by the second hydrothermal event is the chlorite-rich greisen. This is found as a wall-rock alteration of the quartz veins or as irregular masses at the margins of the pluton, associated with small faults. These types are, respectively, the fissure- and diffuse-type greisens described by Charoy (1981). The fissure-type greisens have four distinct metasomatic zones (Fig. 2) that are not always recognizable in the diffuse greisens. The innermost zone is up to 5 cm thick and is composed of quartz and muscovite. This has a sharp contact with the wall of the quartz vein. Occasionally, a millimetric sized muscovite selvage with minute and dispersed grains of cassiterite is present. The central zone is up to 3 cm wide and composed by ripidolitic chlorite, quartz, sericite (fine-grained phengitic muscovite), minor sulphides (pyrite, sphalerite, chalcopyrite and occasional grains of galena and bismuthinite) plus traces of fluorite, anatase, monazite, apatite and cassiterite. The third and most external zone is 1–2 cm wide and contains the previous mineral assemblage together with microcline. The microcline is present either as neofomed hydrothermal masses intergrown with chlorite or as corroded former granite phenocrysts. Ore paragenesis is similar to that of the central zone, but the sphalerite and

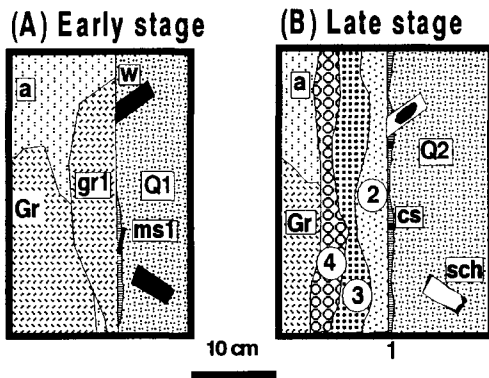


FIG. 2. Sketch of the relationship between the two main hydrothermal stages in the Navalcubilla granite. (A) Early hydrothermal stage. (B) Late hydrothermal stage. (Gr) Unaltered or slightly altered granite. Feldspathization (a), greisenization (gr1), formation of a local muscovite selvage (ms1) and wolframite (w) crystals in a quartz vein (Q1) are related to the early stage. The late stage is superimposed on the early alteration, with formation of late quartz (Q2) and replacement of wolframite by scheelite (sch). The chlorite-rich greisen replaces the early alteration with formation of a muscovite selvage (1) and quartz (2), chlorite (3) and microcline (4) zones. The plagioclase zone corresponds to the slightly altered granite.

chalcopyrite contents are somewhat higher. Scheelite has not been observed in this greisen. There is a sharp contact with the slightly hydrothermalized granite, with only chloritized biotites and feldspars partially replaced by fine grained sericites. This hydrothermal alteration is pervasive over a large area of the pluton, but mostly in the porphyritic unit.

Fluid inclusion studies in the veins and chloritic greisens indicate that they are related to the circulation of low to medium salinity (0–11.5 wt.% NaCl equiv.) aqueous fluids at temperatures between 253 and 383°C (Tornos *et al.*, 1993a). This range of temperatures is broader than that calculated by chlorite geothermometry (304–308°C) using the method of Walshe (1986) but is in agreement with the minimum temperatures estimated from the paragonite content of sericite (202–324°C) (Tornos *et al.*, 1993a). The presence of contemporaneous and likely primary liquid- and vapour-rich fluid inclusions with contrasting salinities homogenizing to liquid and vapour at temperatures, respectively, and roughly similar to those of independent geothermometers indicates that boiling has occurred in the system (Tornos *et al.*, 1993a). Boiling should take place at pressures between 40 and 217 bars, at depths

between about 400 and 3350 m, assuming that the fluid pressure was mainly hydrostatic. There is no significant correlation between the homogenization temperatures and salinity, indicating that fluid mixing has not occurred and boiling is the most likely reason for the variations in salinity.

Quartz samples from the veins that bear fluid inclusion, paragenetic and isotopic evidence of being related to the second stage, were crushed to approximately 1 mm and washed in hot hydrochloric acid and then twice in deionized water. A first fraction was decrepitated under vacuum and the bulk volatile content determined by mass spectrometry following the methodology of Shepherd *et al.* (1991). Another fraction was used for the estimation of the bulk electrolyte content by ICP analysis, after decrepitation in an argon flow (Thompson *et al.*, 1980). The results show that fluids were predominantly aqueous ($X_{\text{H}_2\text{O}} > 0.97$) with Na as the dominant cation; only small amounts of K, Ca, Mg and Fe were detected (Table 1).

The calculated $\delta^{18}\text{O}$ of the water in equilibrium with the hydrothermal minerals at 300°C varies between +2.1 and +4.3‰, while δD signatures in

fluid inclusions are mostly between -51 and -40‰ (Tornos *et al.*, 1996). These values suggest a major meteoric source, reflecting interaction with the enclosing igneous rocks at high fluid-granite ratios.

A geochemical model for the low-temperature hydrothermal processes

The formation of the chlorite-rich greisen and the replacement of earlier quartz plus wolframite by scheelite and sulphides has been theoretically modeled in a multicomponent (Cl-Na-K-Si-S-Al-Ca-Mg-Fe-Zn-Cu-Pb-Sn-W-F-O-H) chemical system. Calculations are based on simulating the evolution of a theoretical calculated hydrothermal fluid (see below) as it follows different geochemical paths. In the case of the greisen, fluid inclusion and geological evidence suggests that geologically reasonable mechanisms promoting mineral precipitation are: reaction with the enclosing granite, simple cooling and boiling. As quoted above, there are no indications of a major influence of fluid mixing. A pressure drop can be a likely mechanism of ore formation but its influence could not be tested. In any

TABLE 1. Compositions of the different fluids used for calculations

	[1]	[2]	[3]
pH	3.9	3.9	3.5
mΣCl	1.32	1.15	1.16
mΣSO ₄		-0.9821 × 10 ⁻⁴	-0.7465 × 10 ⁻⁵
mΣH ₂ S	0.00052	0.0088	0.00088
mCO ₂	0.00032	0.00023	0.00023
mΣSiO ₂	0.0063	0.0097	0.0097
mΣAl	0.0023	0.0026	0.0026
mΣCa	0.110	0.0135	0.0135
mΣMg	0.074	0.0082	0.0082
mΣFe	0.0092	0.0011	0.0011
mΣK	0.131	0.155	0.155
mΣNa	0.633	0.781	0.782
ppm ΣZn		5000	5000
ppm ΣCu		100	100
ppm ΣPb		10	10
ppm ΣF		100	100
ppm ΣSn		18	83
ppm ΣW		2	8
log f_{O_2}		-34.2	-34.1
log f_{S_2}		-11.6	-11.5

Fluid [1] determined from fluid inclusion analysis and the assumption of equilibrium with muscovite and quartz at 300°. Fluid [2] calculated from fluid A, but with about 10% of original Ca, Mg and Fe concentrations and saturated in cassiterite and scheelite. Total concentrations of Zn, Pb, Cu and F are arbitrarily imposed (see text). Oxygen and sulphur fugacities close to the Py-Po-Mt buffer. Fluid [3] is similar to fluid B, but at a pH of 3.5. Note that the negative SO_4^{2-} concentrations are a numerical artifact used for low oxygen fugacities (Reed and Spycher, 1988)

case, it should be minor since the ore forming process took place at shallow environments. In the veins, reaction of the fluid with the precursor quartz-wolframite assemblage has been also modelled.

Composition of the initial ore-forming fluid. Knowledge of the chemical composition of the original unmodified fluid is probably the most critical requirement for the development of numerical models in fossil hydrothermal systems. In this case, the fluid responsible for the alteration was probably external to the granite as based on age, oxygen isotope and fluid composition data. Therefore, no assumptions grounded on the composition of a magmatic water (e.g. Bottrell and Yardley, 1988; Heinrich, 1990) or from the magmatic paragenesis can be used to calculate its composition. Only fluid inclusion data and hydrothermal assemblages were used in the calculations. The first assumption in the development of the model is that fluids enclosed in the quartz veins, where fluid/rock ratios are extremely high, should represent the initial unreacted fluid. On this premise, previously cited fluid analyses obtained from quartz in the veins (Table 1) were used as an initial input for the calculations. These fluids are probably responsible for the slight, but pervasive, hydrothermal alteration of some zones of the pluton, indicating that they were in chemical disequilibrium with the granite.

The first numerical runs were performed with a fluid composition normalized to a $m\Sigma\text{Cl}$ close to 1.32, consistent with the mean liquid-rich fluid inclusion salinity, and the assumption of equilibrium with the vein minerals (quartz and muscovite; Table 1, fluid [1]) at 300°C and fluid pressures close to the saturation curve of water. The presence of quartz and muscovite in the veins indicates a pH between 2.2 and 5.1 for the calculated Na/K ratio (Henley *et al.*, 1984). Since kaolinite is not found in the greisens and feldspars are dissolved in the wall rock of the veins these values are extreme; a mean pH of 4 was chosen for further calculations. This pH is consistent with the circulation of fluids along fractures in cooling hydrothermal systems. Preliminary calculations show that fluids of this salinity that are in equilibrium with the KFMASH buffer (i.e. granitic: K-feldspar + muscovite + plagioclase + quartz + water) at 400°C reach a pH close to 4 by unbuffered cooling to 300°C due to acid dissociation. The Na/K ratios analysed in fluid inclusions are consistent with those described in granite-related hydrothermal systems (e.g. Charoy, 1981; Rankin and Alderton, 1985; Bottrell and Yardley, 1988; Polya, 1989; Heinrich *et al.*, 1992) and with the ratio resulting from the two feldspar equilibria. The Ca and Mg content of fluid inclusions, however, are well above the data obtained by the previous authors.

With these initial concentrations, the computer model predicts supersaturation of Ca- and Mg-bearing silicates and early precipitation of chlorite. These numerical results are in conflict with the petrographic data, since chlorite is absent in the inner zones of the greisen and tremolite-actinolite are not observed in these rocks and this suggests that the concentration of the divalent cations is overestimated. Their high concentration is probably due to the presence of microinclusions in the quartz, or to chemical problems due to the low concentration of the divalent cations in the fluid (D. Banks, pers. com.). To resolve this discrepancy, the concentration of Ca, Mg and Fe was modified by trial and error to a level where the results of the computer model match the actual mineralogy of the greisen. This occurred where Ca, Mg and Fe were approximately 10% of their analysed concentration (Table 1, fluid [2]). These amounts are close to the cation/Na ranges found by Polya (1989), Heinrich *et al.* (1992) and Noronha *et al.* (1992) in similar systems.

The $\text{H}_2\text{S}/\text{SO}_4^{2-}$ ratio was established for an initial log f_{O_2} of -34 at 300°C, close to the Pyrrhotite-Pyrite-Magnetite and NNO buffers ($f_{\text{O}_2} = 10^{-34.6}$ and $10^{-34.1}$ bars, respectively) and well above the QFM equilibrium ($10^{-35.6}$ bars); these conditions are consistent with granite-buffered hydrothermal systems. Since all these calculations were realized in the reduced and acid field, minor variations of the oxygen fugacity do not critically affect the general model; only solubilities of Sn minerals are influenced. The sulphur fugacity of the incoming fluid is established at $10^{-11.7}$ bars, close to the Pyrite-Pyrrhotite equilibrium ($10^{-11.6}$ bars). For a pH of 4, these sulphur and oxygen fugacities suggest a total sulphur content ($m\Sigma\text{S}$) close to 5×10^{-4} (Ohmoto, 1972). This value is well below the sulphur content of a fluid in equilibrium with pyrite ($m\Sigma\text{S} = 0.001$) or mean values in typical hydrothermal solutions (e.g. Barnes, 1979), but compatible with the low content of sulphides in the system.

Total molalities of Sn and W were estimated assuming saturation in cassiterite and scheelite. The contents of Cu, Zn and Pb were calculated after successive iterations of the fluid-rock reaction model, trying to reproduce undersaturation in the original fluid and precipitation of sphalerite and chalcopyrite but not of galena in the greisen. Assumed values were 100, 5000 and 10 ppm of Cu, Zn and Pb, respectively. However, the exact concentration of these metals, within reasonable values, do not affect the predictive model, and varies only in the amount of precipitated sulphides, with no appreciable changes in the metasomatic column nor thermodynamic evolution. In this solution, main complexes (>95% total metal) of Fe are FeCl_4^- and FeCl_2^+ , of Zn is ZnCl_4^- , of Pb, PbCl_3^-

and PbCl_2 and of Cu , CuCl_2^- , CuCl_3^- and CuCl^0 , respectively. Tin and tungsten have a different behaviour. The former is dominantly complexed as SnCl_3^- , $\text{Sn}(\text{OH})_4^0$ and $\text{Sn}(\text{OH})_2\text{Cl}_2^0$ whilst HWO_4^- and H_2WO_4^0 are the dominant aqueous species of tungsten. Fluor content was set to 100 ppm, a high value for fluorine content in geothermal systems (e.g. Henley and Hedenquist, 1986) and close to the concentration estimated for nearby fluorite-rich veins (200 ppm; Tornos *et al.*, 1993b). Despite this high concentration, fluor complexes of tin do not form any important aqueous species at these conditions as previously predicted by Jackson and Helgeson (1985).

In a fluid with the composition of fluid [2] (Table 1) at 300°C and with a pH close to 4, the ore-forming elements can reach concentrations of >10000 ppm Zn, 260 ppm Cu and 1000 ppm Pb. Tin and tungsten solubilities are much lower, 20 and 2 ppm, respectively. If the pH of the fluid is depressed half a unit then the solubility of the ore minerals increases dramatically and the fluid can transport more than 10^4 ppm Zn, Cu and Pb and 83 ppm Sn. The concentration of tungsten does not change. The calculated tin concentrations are similar to those predicted by Heinrich (1990) for the Na-K-Cl-Sn-H₂O system.

Concentrations of the initial fluid (Table 1) are within the ranges of hydrothermal waters (Barnes, 1979). As expected in non-magmatic and low-temperature granite-related hydrothermal fluids, the H₂S, CO₂, Fe, Sn and W contents are lower than those reported by Bottrell and Yardley (1988) in fluid inclusions of likely magmatic origin as well as the values used by Heinrich (1990) in his calculations on the hydrothermal chemistry of tin in magmatic fluids. However, they are higher than those calculated by Polya (1989) for Panasqueira rocks of similar origin. This is probably due to the fact that this author calculated the solubilities at pH estimated closer to the conditions of ore precipitation (pH5).

The more likely origin of the metals in the chlorite-rich greisens is the postmagmatic hydrothermal alteration of the granite, with pervasive replacement of magmatic minerals (such as biotite, ilmenite and feldspars) to chlorite, rutile, quartz and sericite. Chloritized micas and sericitized feldspars are widespread in the porphyritic unit of the Navalcubilla granite. Mass balance calculations show that this alteration is able to release more significant concentrations of metals into the hydrothermal fluid (Tornos, 1990).

Isolated simple cooling. The chemical evolution of fluid [2] during its cooling has been calculated for a wide range of temperatures, between 300 and 100°C, at fluid pressures above the liquid-vapour curve, without allowing gas separation nor reaction with

enclosing rocks. In a real system, this evolution would be equivalent to fluid flow at pressures high enough to prevent boiling along a fracture chemically isolated from the host rock. Progressive cooling would cause a significant and constant increase in aH^+ due to the dissociation of acids, mainly HCl (Fig. 3a). The pH would diminish from 4 at 300°C to 3.2 at 200°C and 2.9 at 100°C. This acidification seems to inhibit metal precipitation, due to the stabilization of H₂S at low pH and the fall of solubility constants of chloride and thiosulphide complexes. These features counteract the negative effect that temperature has on the solubility of ore minerals (e.g. Barnes, 1979). In our calculations, quartz is the main mineral precipitated (up to 0.4 g/kg fluid) throughout the process. Up to 0.07 g/kg solution (17 wt.%) of sphalerite can form, but only at lower temperatures (<260°C) than expected in the hydrothermal system described. Other minerals, such as muscovite, cassiterite and scheelite would precipitate in smaller proportions (Fig. 3a). Wolframite is unstable at the conditions discussed here. Higher Fe/Ca ratios and temperatures, and a lower pH, stabilize wolframite instead of scheelite. The precipitation of quartz is due to the decreasing solubility with decreasing temperature, while the formation of muscovite at temperatures higher than 250°C is related to the dissociation of Al-OH complexes at these low pH values. The f_{O_2} seems to be controlled only by the H₂-H₂O equilibrium and its trend is subparallel to the NNO buffer (Fig. 4). The precipitation of only minor amounts of sulphides with little change in the f_{O_2} or mH_2S also make the f_{S_2} trend fairly constant, with less than 2 log f_{S_2} units of absolute variation. No major differences are observed in rock-buffered simulations, where the cooling fluid is in continuous equilibrium with quartz, muscovite and chlorite. Only sphalerite is absent and traces of cassiterite and scheelite precipitate (<0.005 g/kg fluid).

If the initial pH is set to 3.5 (fluid [3]; Table 1) there are significant changes in the pH, f_{O_2} and f_{S_2} trends (Fig. 3b and 4). The higher solubility of tin in the fluid [3] leads to significant cassiterite precipitation (14 wt.%) and a tenfold increase in the amount of scheelite formed. Since the initial content of zinc in fluids [2] and [3] is the same, similar amounts of sphalerite precipitate. However, in more acid fluids, the precipitation of sphalerite will occur at lower temperatures.

These results show that quartz is the main mineral formed in cooling-only systems, but muscovite is also formed at high temperatures. In a system of these characteristics, cassiterite and sphalerite are the only ore minerals that can precipitate in noticeable amounts. However, cassiterite is restricted to Sn-saturated acid fluids while sphalerite can only form at

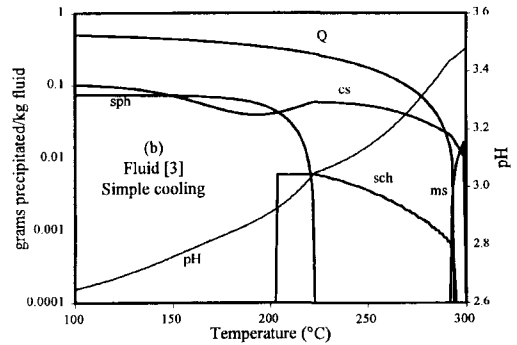
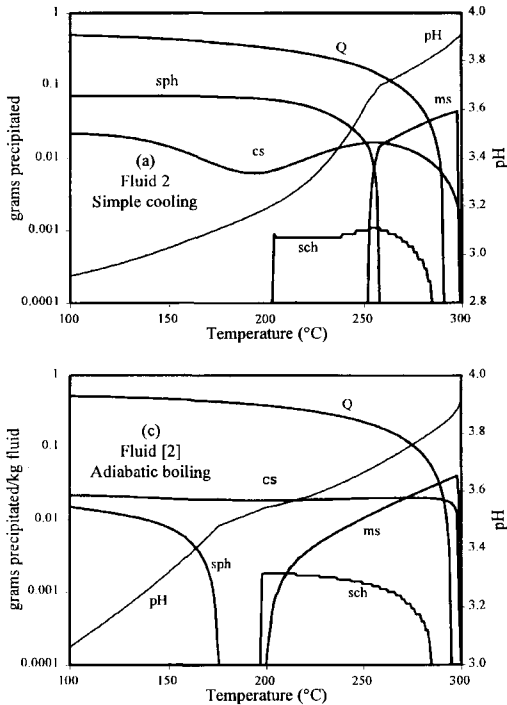


FIG. 3. Weight (g) of minerals precipitated by simple cooling of a kilogram of fluid [2] and [3] from 300 to 100°C (*a*, *b*) and by adiabatic boiling of a kilogram of fluid [2] from 300 to 100°C (*c*). ms: muscovite, Q: quartz, cl: chlorite s.s., mc: microcline, plag: plagioclase, sch: scheelite, cpy: chalcopyrite, sph: sphalerite, mt: magnetite, cs: cassiterite.

temperatures below those described (260°C). The fact that granite-hosted cooling-only hydrothermal systems do not show steep thermal gradients, at least below 300–250°C (Norton and Knight, 1977) suggest that no significant mineralization would be expected here. Such observations are consistent with the widespread presence in the Navalcubilla granite of abundant quartz veins with a muscovite selvage. The presence of this early muscovite selvage can be interpreted as critical for preventing fluid–rock interaction (Eugster, 1985).

Adiabatic boiling. Fluid inclusion data show that boiling has occurred, at least sporadically, in the Navalcubilla hydrothermal system. The process of isoenthalpic boiling can easily explain the presence of boiling fluids over a temperature range, as the heat used in vaporising the fluid cools the solution. Volatiles are quickly fractionated into the low-density phase, inducing changes in the chemical composition of the fluid. The main difference between boiling processes in CO₂-poor systems, such as that considered here, and those in CO₂-rich environments, is that in the former the gas loss is not always able to fully counteract the acidification due to cooling (Fig. 4) and only slightly less acid fluids than those obtained by simple cooling (pH of 3.1 instead of 2.9 at 100°C) are expected (Fig. 3c). In CO₂-rich systems the fluid becomes significantly

more alkaline, leading to the precipitation of significant amounts of silicates, sulphides and carbonates (e.g. Drummond and Ohmoto, 1985; Reed and Spycher, 1985). However, fractionation of H₂

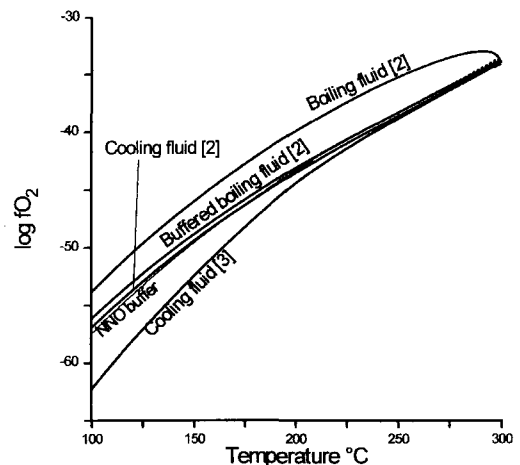


FIG. 4. Log f_{O_2} –temperature diagram showing the log f_{O_2} trend of cooling and boiling processes. The location of the NNO buffer is included for comparison.

and CO₂ to the gas phase slightly oxidizes the system, so these boiling systems evolve to moderately less acid and more oxidized fluids than those developed by simple cooling (Figs. 3c and 4). These minor chemical changes with respect to simple cooling do not significantly affect the mineral assemblages. Quartz is again the dominant phase, cassiterite is the more important ore mineral (up to 0.015 g/kg fluid 4.4 wt.%) and muscovite is stable over a wider range of temperatures than in cooling-only systems. The major difference with simple cooling is that sphalerite precipitates at lower temperatures, (<175°C) and in smaller quantities (2.9 wt.%). This behaviour is interpreted as related to the fractionation of H₂S into the gas phase, reducing the mSS of the fluid from 250 to less than 13 ppm. In spite of this, at 100°C *f*_{S₂} is slightly higher (<2 log units), owing to the fractionation of H₂ and lowering of H₂S_(aq) related to the acidification. No major mineralogical changes are expected during buffered boiling. Finally, isothermal boiling at 300°C produces a monotonous assemblage of muscovite and cassiterite.

These calculations show that boiling produces mineral assemblages hardly distinguishable from those produced by simple cooling. Cassiterite precipitates more efficiently and sphalerite forms at lower temperatures. However, such criteria are difficult to establish in real cases.

Isothermal reaction with the granites: The genesis of chlorite-rich greisens. The systematic presence of mineralized quartz veins and greisenization in their wall rock suggests that fluid-rock interaction has been a major hydrothermal process. The formation of greisens has been modeled by the reaction of fluid [2] with a leucogranite (Table 2). The progressive reaction of a fluid in disequilibrium with the granite produces different mineral zones in local equilibrium, as has been demonstrated by Korzhinskii (1970).

Progress in the reaction of a single amount of fluid [2] with the granite, assuming irreversible reaction, produces the mineral zonation from high to low fluid-rock ratios (Table 3).

Progress of the reaction (Fig. 5) produces an initial assemblage of muscovite (ms) plus minor quantities

TABLE 2. Selected compositions of rocks of Navalcubilla pluton

	1	2	3	4
SiO ₂	73.68	70.23	70.80	60.88
Al ₂ O ₃	13.53	15.88	14.06	17.19
Fe ₂ O ₃	1.16	2.40	2.19	6.59
MnO	0.04	0.05	0.05	0.13
MgO	0.82	0.72	1.09	0.53
CaO	0.31	1.36	1.07	1.07
Na ₂ O	4.25	3.82	3.98	3.55
K ₂ O	4.27	3.95	4.61	6.01
TiO ₂	0.06	0.31	0.24	0.42
L.O.I.	1.77	1.81	1.81	3.99
Total	99.93	99.99	99.98	100.87
Rb	260	250	230	760
Ba	<100	410	370	490
Sr	10	140	90	20
Zn	30	60	40	1310
Cu	30	30	10	2000
Pb	50	<10	40	50
Sn	30	<10	<10	490
W	10	<10	<10	<10

(1) Fine grained leucogranite (used for calculations).

(2 and 3) Slightly hydrothermally altered porphyritic granite.

(4) Greisen. Oxides in %, elements in ppm. Analyses by XRF (ITGE). Fe₂O₃ calculated as total Fe.

of cassiterite (cs, up to 2.5 wt.%). This zone probably represents the muscovite selvage or the mica-rich zone adjacent to the veins, that usually contains significant amounts of cassiterite (Fig. 2). In the next zone these minerals are stable along with quartz (Q) and minor amounts of scheelite (sch, <0.13 wt.%). In the muscovite zone, there are no significant changes in the pH and oxygen and sulphur fugacities (Figs. 5 and 6), while in the quartz zone the pH starts to increase gradually. Major chemical and mineralogical changes are related to the precipitation of the chlorite *s.s.* (chl), due to the destabilization of

TABLE 3. Mineral zonation

Muscovite zone	Quartz zone	Chlorite zone	Microcline zone	Plagioclase zone
Muscovite	Quartz + muscovite	Quartz + muscovite + chlorite	Quartz + muscovite + chlorite + microcline	Quartz + muscovite + chlorite + microcline + plagioclase

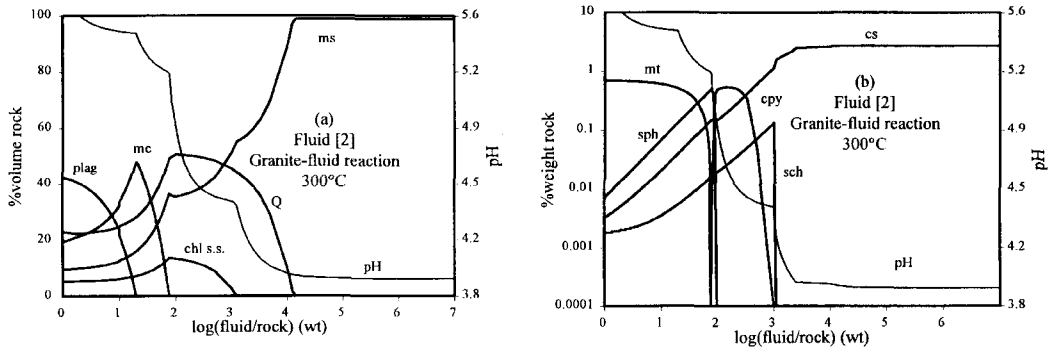


FIG. 5. Volume % of non-ore minerals (a) and weight % of ore minerals (b) against fluid-rock weight ratio for the reaction of a kilogram of the fluid [2] with an initial pH of 3.9 and the granite. Captions as in Fig. 3.

Al and Fe-bearing complexes in a progressively more alkaline fluid. The system becomes progressively more oxidized, while the sulphur fugacity drops gradually. Precipitation or dissolution of minerals controls the abrupt variations in the f_{O_2} - f_{S_2} space (Figs. 6 and 7). Chlorite seems to exert a critical control on the f_{O_2} and f_{S_2} of the system. Its stability field is close to that of magnetite (e.g. Barton *et al.*, 1977) and, thus, precipitation of chlorite *s.s.* drops the f_{S_2} of the system. In this chlorite zone the pH is high enough for sulphide precipitation, due to the destabilization of the chloride complexes. The Cu chloride aqueous species are more unstable than the Zn-Cl complexes, leading to an initial precipitation of chalcopyrite (cpy, 0.6 wt.%) that starts when the trend leaves the pyrrhotite-magnetite buffer (Fig. 7). Later destabilization of chalcopyrite produces an important increase of f_{O_2} and raises the amount of aqueous sulphur sufficiently to form sphalerite (sph, 0.7 wt.%). The appearance of magnetite (mt) and microcline (mc) defines the boundary of the microcline zone. Here, the oxygen fugacity is buffered at rather oxidizing conditions ($10^{-32.8}$ bars) by the chlorite + microcline + magnetite + quartz + muscovite assemblage. The sulphur fugacity is unbuffered and continues a gradual drop till a value of 10^{-15} bars, when the numerical run finished. The external metasomatic zone is characterized by stabilization of albite-rich plagioclase (plag) diminishing from Ab₁₀₀ to Ab₈₉ towards the granite at very low fluid/rock ratios. Since no mineralogical or chemical changes occur in the system until extremely low fluid/rock ratios are reached, this zone seems to depict the equilibrium of the fluid with the rock.

From the chlorite zone onwards, the chlorites become progressively more Fe rich, with Mg/(Mg+Fe) failing from 0.97 to 0.41. The fluid-rock reaction produces an increase in the pH, from 3.9 to 5.6, due to the neutralization of the acidic fluid

by the rock (Fig. 5). The pH increases sharply in the chlorite and microcline zones, while in the quartz and muscovite zones it is similar to that of the inflowing fluid (3.9–4), and in the plagioclase zone it is constrained to 5.6 by the quartz + muscovite + microcline + plagioclase assemblage. These mineralogical and thermodynamic trends suggest that the chemical composition of the plagioclase zone is controlled by the host rock, while characteristics of the muscovite and quartz zones are defined by the fluid. The chlorite and microcline zones define the transition between both of them, with abrupt changes in both the chemical composition and mineral assemblage.

The mineralogical evolution depicted above is broadly consistent with the petrographic observations of the greisen of Navalcubilla. However, the model predicts the formation of minor magnetite (<1 wt.%)

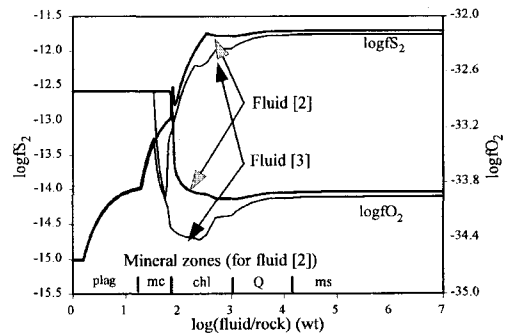


FIG. 6. Evolution of the oxygen and sulphur fugacity of the fluid during the reaction of the hydrothermal fluid with the granite. Solid line is for fluid [2] and dashed line for fluid [3]. For reference, mineral zones formed by the reaction of fluid [2] with the granite are shown.

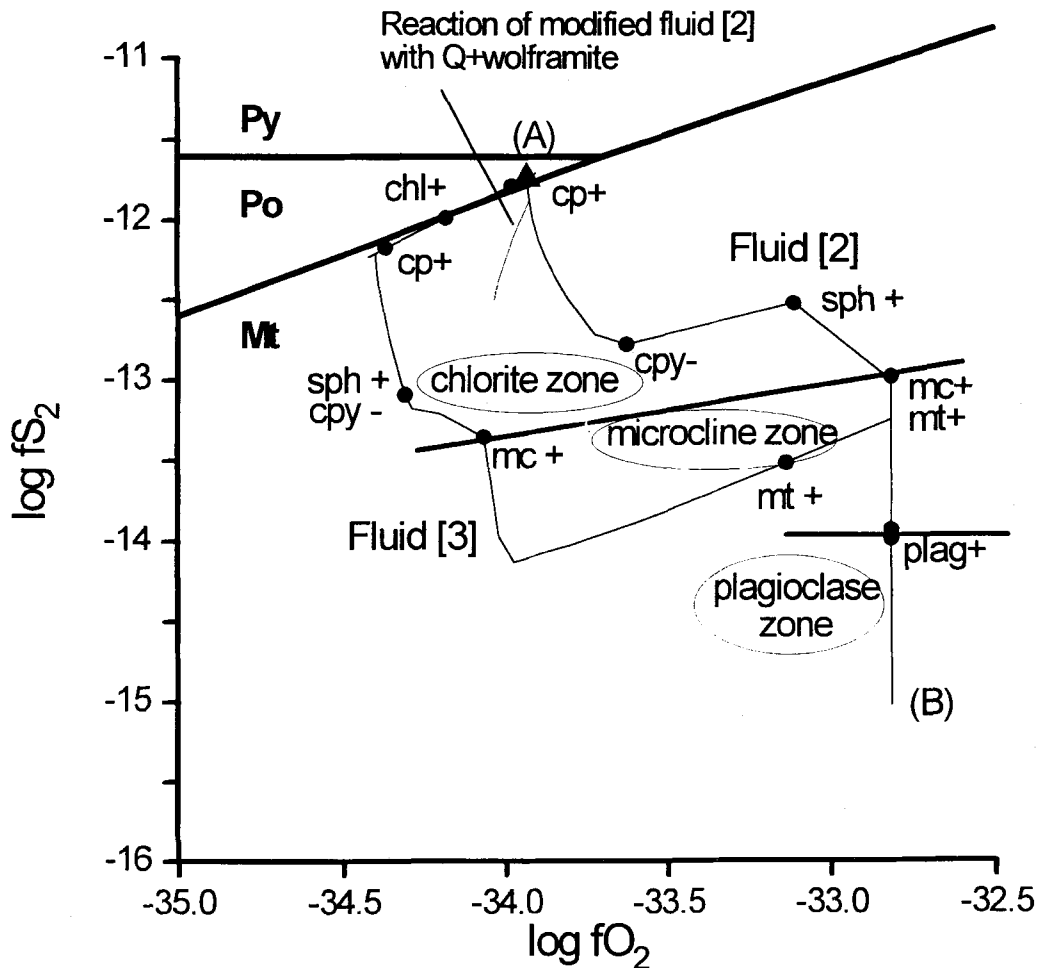


FIG. 7. Evolution of the fluid in the $\log f_{S_2}$ - $\log f_{O_2}$ space at 300°C and water saturation pressure during the reaction of the hydrothermal fluid with the granite. The pyrite-magnetite-pyrrhotite equilibrium is from Patterson *et al.* (1981). The formation of the chlorite, microcline and plagioclase metasomatic zones produce major variations in the f_{O_2} - f_{S_2} trends. The development of the muscovite and quartz zones does not produce noticeable f_{O_2} - f_{S_2} changes in the inflowing fluid. Dots show the points of precipitation (+) or dissolution (-) of key minerals. Heavy lines represent the limits between the mineralogical zones of the greisen. Triangle (A) represents the initial composition of the fluid and (B) its final composition, close to equilibrium with the host granite.

in the microcline and plagioclase zones, while magnetite has not been observed in the greisen. Its precipitation is independent of the composition of the inflowing fluid and, thus, it seems to be inherited from the original rock. Some of it represents the iron content of the sphalerite (with MFeS between 2.7 and 8%), but the location of most of it is unknown. Since the chlorite *s.s.* is the only significant iron-bearing mineral of the greisen, this iron is probably incorporated into its structure and numerical

discrepancies are due to the poor reliability of daphnite thermodynamic data. Another likely host for this iron is the ilmenite. It is not stable in the greisen, but is a widespread accessory of these granites.

The predicted mineral assemblages are produced by single-step irreversible reactions (Heinrich, 1990). In nature, the situation is more complex since the fluids in equilibrium with a mineral assemblage should react with the next zone producing new

assemblages. Extrapolation of results of Heinrich (*op. cit.*) suggests that in long-lived systems the quartz–muscovite zone should replace the others and the ore minerals reconcentrated to quite high ore grades.

The f_{O_2} – f_{S_2} evolution. Thermodynamic calculations based on fluid inclusion data, composition of chlorite and metallic minerals in the Navalcubilla greisen delimit a broad field of f_{O_2} – f_{S_2} (Tornos *et al.*, 1993). The gas (H_2O – H_2 – O_2 and CO_2 – CH_4 – H_2O – O_2) equilibria in fluid inclusions of the greisen (chlorite and microcline zones) give oxygen fugacities between $10^{-34.5}$ and $10^{-33.8}$ bars. Following the methodology of Walshe (1986), the chlorites of the chlorite zone are calculated to be stable in the f_{O_2} and f_{S_2} ranges of $10^{-35.9}$ to $10^{-30.9}$ and $10^{-13.5}$ to $10^{-11.1}$ bars, respectively. These ranges match the values predicted by the numerical model (Figs. 6 and 7). However, the range of f_{S_2} calculated from the composition of sphalerite (log f_{S_2} between –9 and –8) is too high. This may be due to the fact that estimation of the sulphur fugacity was performed assuming equilibrium between sphalerite and pyrite, while pyrite is not stable here.

The behaviour of metals. In spite of the high content of Zn and Cu in the fluid, the proportions of sphalerite and chalcopyrite in the greisen are always low (<0.7 wt.%). The major concentration of sulphides are within the chlorite and microcline zones. They are unstable at higher fluid–rock ratios, while their content drops gradually at lower fluid–rock ratios.

Reaction of the fluid [2] with a granite could extract metals from solutions with more than 80 ppm Cu, 4800 ppm Zn and 100 ppm Pb. Accordingly, copper and lead can be easily precipitated in these greisens, but detectable amounts of sphalerite would only be found if high concentrations of Zn exist in the source fluid. Since the most effective mechanism for precipitating base metal sulphides transported by chloride complexes is a pH increase of the fluid, the evolution of the greisen towards the reduced field partly inhibits the precipitation and ore grades are not expected to occur. The numerical model also predicts that base metal sulphides are more likely linked to the more alkaline environments of the greisen, the chlorite and feldspar zones. Maximum concentrations are achieved when there is a change in the mineralogy of the system (Fig. 5). Finally, galena should precipitate synchronously with the sphalerite, but the assumed initial low content of lead (10 ppm) in the fluid prevents its formation. Therefore, the low galena contents typical of these greisens can only be related to the low Pb concentration in the percolating fluid.

Cassiterite and scheelite show a different behaviour. Initial Sn and W contents in the fluid are

lower, but the formation of the greisen is highly effective in extracting almost all of the Sn and W from the fluid, even at high fluid/rock ratios (Fig. 5). The scheelite and cassiterite are stable all along the metasomatic column, but reach their major proportion in more internal, muscovite and quartz zones of the greisen.

Scheelite preferentially precipitates in the quartz and chlorite zones. Theoretically, tungsten concentrations above 0.01 ppm should cause precipitation of scheelite when the fluid reacts with the leucogranite (0.31% CaO; Table 2). Therefore, the absence of scheelite in the Navalcubilla greisen is probably due to the very low W content of the fluid. The formation of tungsten deposits is influenced by the capability of leaching and transport by the fluid which depends on its Ca and Fe contents. The influence of oxygen fugacity and pH seems to be minor. For example, with a pH of 4, if mΣCa is lowered to 1% of the original content, the fluid can transport up to 17 ppm W and scheelite can reach ore grades in the inner (quartz + muscovite) zone of the greisen. Some greisens such as Ponferrada (Leduc, 1978) and La Parrilla (Mangas, 1987) have subeconomic grades of scheelite (0.1 wt.% WO_3). They are developed at similar conditions to the Navalcubilla greisen, with temperatures below 350°C and in relationship with low-salinity fluids of probable meteoric origin. The presence of high quantities of scheelite in these greisens suggests that they are related to more Fe- and Ca-poor fluids than those discussed here.

Cassiterite is concentrated in the inner (muscovite and quartz) zones. Since the solubility of cassiterite is inversely related to the f_{O_2} and acidity of the system (Heinrich, 1990), the predicted trend during the formation of these greisens (Figs. 5 to 7) seems to be suitable for the precipitation of cassiterite for solutions with more than 2 ppm Sn.

The calculations do not include arsenic, since arsenopyrite is a trace phase of the Navalcubilla greisen. However, its presence is always indicative of reduced and desulphurized conditions, replacing pyrite as the main Fe-S phase. Arsenopyrite is common in tin-rich greisens related to granitic plutons that crosscut black shales, such as La Parrilla (Mangas, 1987) or Panasqueira (Polya, 1989). Also, Heinrich and Eadington (1986) have shown that arsenic and tin can be transported easily together in acid and reduced fluids. Thus, Sn-As rich greisens are probably formed at more reducing conditions than those estimated here. Black shales probably exert a fundamental control on the oxygen fugacity of the fluids in these systems, enhancing the solubility of both metals without significant variations in the pH.

Several calculations, with variations in the mΣS and oxygen and sulphur fugacities of the inflowing

fluid, were performed. Even at high values, with $m\Sigma S = 0.01$, f_{O_2} close to the magnetite-hematite buffer and/or f_{S_2} near the chalcopyrite-pyrite-bornite equilibrium, the results are very similar. They predict precipitation of the same silicates, with variations only in the proportions of formed ore minerals. The contents of sphalerite and chalcopyrite vary significantly, but these minerals always precipitate in the same zones. Pyrite can become a common phase in the inner chlorite zone; its stability field is enhanced by higher initial $m\Sigma S$ or f_{O_2} values. Further drop of the f_{S_2} destabilizes it. Major changes are observed in the behaviour of the cassiterite, since tin solubility depends dramatically on the f_{O_2} . Oxidized fluids transport and precipitate very low amounts of tin.

Variations in the pH. If the pH of the original fluid is reduced by 0.5 (fluid [3]; Table 1) the overall zonation and evolution of the greisen is more or less the same as in the previous example. Quartz is stable with muscovite in the internal zone and the other minerals precipitate at different fluid-rock ratios. This produces significant variations in the f_{O_2} - f_{S_2} path (Fig. 7), but the arrangement of the metasomatic zones and the initial and final compositions of the fluid do not change. As mentioned above, at this pH the solubility of ore minerals increases dramatically and the reaction with the granite can promote the precipitation of higher quantities of ore minerals. For example, cassiterite can form up to 12% by weight in the muscovite zone.

Replacement of wolframite by scheelite and sulphides. The presence of scheelite and sulphides as a late replacement of quartz + wolframite is a common feature in tungsten-rich veins and greisens (e.g. Leduc, 1978; Vindel, 1980).

As described above, wolframite is precipitated in quartz veins during early, high-temperature, hydro-

thermal alteration. It is usually replaced by scheelite and sulphides, suggesting that this late assemblage is formed by reaction of the wolframite with late-stage fluids (Fig. 2). The previous calculations show that neither boiling nor cooling of the hydrothermal fluids is able to precipitate significant amounts of scheelite and sulphides in the veins. Reaction of fluid [2] with the early assemblage (arbitrarily assumed to be 75 wt.% quartz and 25 wt.% wolframite in the vein) produces replacement of wolframite by scheelite. As is shown in Fig. 8a, at high fluid-rock ratios scheelite is the stable phase of tungstate. If the reaction occurs with a fluid that has previously reacted with the greisen (arbitrarily with a fluid-rock ratio of 170), then the predicted assemblage is quartz + muscovite + chlorite s.s. + scheelite + sulphides (chalcopyrite and sphalerite) (Fig. 8b). This association is similar to that found in the late stages of the veins, suggesting that some interaction with the enclosing rocks had taken place when the sulphides, white micas and chlorite formed as a replacement of the wolframite. All these reactions produce negligible variations in the pH and oxygen and sulphur fugacities of the fluid (Fig. 7).

Discussion and conclusions

The numerical model developed here shows that there is a correlation between the zonation and mineralogy of a chlorite-rich greisen in the Navalcubilla granite and the numerical prediction of the reaction of a hydrothermal fluid with the enclosing granite. Progressive fluid-rock reaction promotes an acid alteration of the rock and the formation of successive metasomatic zones. The first (outer) assemblage represents equilibrium between the fluid and the granite, and is composed of

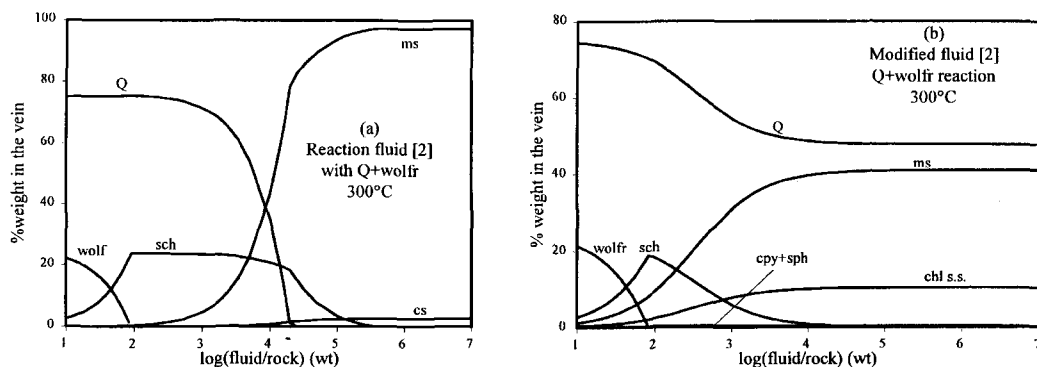


FIG. 8. (a) Weights of minerals precipitated by reaction of a kilogram of fluid [2] with an assemblage of 75% quartz and 25% wolframite. (b) Weight of minerals precipitated by reaction of a kilogram of modified fluid [2] (after the reaction with the granite) with an assemblage of 75% quartz and 25% wolframite. Captions as in Fig. 3.

plagioclase, microcline, chlorite *s.s.*, quartz and muscovite. Progressive removal of plagioclase, microcline, chlorite *s.s.* and quartz in the successive zones leads to the formation of a muscovite zone in the selvage of the quartz veins. Synchronously, there is a progressive and irregular change in the oxygen and sulphur fugacities, towards increasingly reduced and low f_{S_2} conditions. Oxygen and sulphur fugacities change dramatically between metasomatic zones, most notably in the chlorite and microcline zones. Thus, the values of f_{O_2} and f_{S_2} calculated from the mineral assemblage can be valid only for a very restricted volume of rock and cannot be extrapolated to the overall hydrothermal system.

The numerical model also predicts, with reasonable consistency, the behaviour of ore minerals. The ore mineralogy of the chlorite-rich greisens seems to be controlled by the redox state, pH and composition of the inflowing fluid. Fluid-granite reaction is a highly sensitive mechanism for precipitating almost all of the tin and tungsten in the fluid. While the concentration of tungsten depends on the Ca and Fe content of the fluid, the tin solubility is controlled by the pH and oxygen fugacity. Base metal solubility depends dramatically on the pH of the inflowing fluids. Cassiterite and scheelite can form in the more internal (quartz and muscovite-rich) zones while sphalerite and chalcopyrite precipitate in the outer zones of the greisen. The behaviour of base metals is very different than that of tin and tungsten and, except in the case of fluids carrying important quantities of Zn, Pb, Cu and/or sulphur, no significant mineralizations are predicted. Acid fluids have more capability of leaching metals from the rocks.

Fluid-rock reaction produces more variations in the pH, oxidation and sulphidization trends than the other mechanisms studied, cooling and boiling. Both boiling and cooling of low-salinity CO₂-poor hydrothermal fluids are ineffective as mechanisms of ore precipitation in these environments and no major ore mineral concentration can be expected to be due to these processes. Reaction of these fluids with previously precipitated wolframite causes replacement of wolframite by scheelite and sulphides.

The model is constructed for a specific greisen system and, thus, only roughly indicates what late stage (350–250°C) hydrothermal alteration of granites can produce. The variation of permeability along the metasomatic column, the kinetics of fluid-mineral reactions, the presence of mineral solid solutions and the numerical restrictions of the model make the conclusions only qualitative.

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