

Nucleation and Growth of Scheelite in a Diffusing-Reacting System

C. M. PINA, L. FERNÁNDEZ-DÍAZ*, J. M. ASTILLEROS*

Institut für Mineralogie, Universität Münster, Münster, Germany

* Dpto. Cristalografía y Mineralogía, Universidad Complutense de Madrid, Madrid, Spain

In this paper a study of the nucleation and growth behaviour of scheelite (CaWO_4) in a porous medium at 25 °C is presented. The experimental set-up involves the counter diffusion of calcium and tungsten through a silica gel column. This results in the continuous evolution of pH and Ca^{2+} and WO_4^{2-} concentrations and therefore in the generation of scheelite supersaturation profiles along the gel column. The limited ionic mobility of the system determines that nucleation occurs at high supersaturation. The characteristics of scheelite nucleation (waiting time, precipitate position and metastability levels) are explained by attending to both the way in which supersaturation is created and the $[\text{Ca}^{2+}]$ and $[\text{WO}_4^{2-}]$ distribution along the diffusion column. Crystal morphologies developed after nucleation are consistent with the high supersaturations observed. The results presented here are in agreement with the general crystallisation behaviour reported by PRIETO et al. (1989, 1991, 1997) for other sparingly soluble salts.

Keywords: scheelite, crystal growth, supersaturation, nucleation, gel method, crystal morphology

Introduction

Scheelite (CaWO_4) is one of the most common tungsten minerals. It occurs in nature in granite pegmatites, calc-silicate gneisses, and high temperature hydrothermal veins associated with granitic rocks. It can also form as a result of metasomatic reactions not directly related to granitic plutonism. (DE SMEDT & SONNET, 1988; GIBERT et al., 1989). Different geochemical and petrological studies indicate that tungsten is transported by fluid circulating through porous calc-silicate rocks (DERRÉ et al., 1982; GIBERT et al., 1992). Such fluids have been found to be saline solutions where the dominant tungsten species are WO_4^{2-} , HWO_4^- and H_2WO_4^0 . The precipitation of scheelite is controlled by the activities of the ions, $a(\text{Ca}^{2+})$ and $a(\text{WO}_4^{2-})$. The relative activity of the different tungsten species in solution is strongly dependent on pH values. Therefore, in order to understand the crystallisation of scheelite in nature, the influence of pH on the distribution of WO_4^{2-} , HWO_4^- and H_2WO_4^0 species and the characteristics of tungsten and calcium transport in solutions confined in a porous medium must be considered.

In this paper, an experimental study of the nucleation behaviour of scheelite in a diffusing-reacting system is presented. In the knowledge of the authors, no previous work dealing with the precipitation of a tungstenate in a porous medium has been carried out. The experimental set-up used allows the counter-diffusion of Ca and W through a silica gel column. The mass-transfer leads to the development of gradients of pH and ion concentration along the diffusion column. The profiles of pH, ionic concentration and, consequently, supersaturation change as function of diffusion time. Moreover, the transport properties of

the crystallisation medium determine that high supersaturation levels are reached before nucleation occurs.

The characteristics of scheelite nucleation and growth are discussed here in terms of the degree of supersaturation, distribution of tungsten aqueous species and superaturation rate at the nucleation time.

Experimental procedure and calculations

Scheelite has been crystallised at 25 °C and 1 atm in a counter-diffusion system. Fig. 1 shows the experimental set-up. The horizontal branch of the U-tube was filled with a silica gel prepared by acidifying a Na_2SiO_3 solution (Merck Sp. Gr.: 1.059 g/cm³, pH = 11.2) with HCl. The initial pH was adjusted to 5.5. The gelling process involves the formation of NaCl as a soluble by-product. The initial concentration of NaCl in the gel interstitial solutions was around 0.3 mol/l. The vertical branches, A and B, were filled with 8 ml of CaCl_2 and Na_2WO_4 solutions, respectively. A set of experiments, starting with mother solutions of different concentrations, was carried out. Table 1 shows the initial concentration of the solution used. In all experiments the precipitate location and the experimental waiting time (the time taken for the first crystallite to become visible under a magnification of x500) were determined. The growth evolution was monitored by optical microscopy. The experiments were stopped one month after nucleation. The crystals were extracted and confirmed to be scheelite by x-ray powder diffraction. The morphology of the crystals was studied by scanning electron microscopy (SEM).

Initial Concentration CaCl_2 - Na_2WO_4	Waiting time (hours)	Precipitate location (slices)	Supersaturation Threshold	Supersaturation Rate (hours ⁻¹)
1M-0.5M	168	9-11	12300	267
0.5M-0.5M	190	9-11	10000	133
0.3M-0.3M	240	9-11	8510	75

Table 1: Mother solution concentrations and nucleation parameters

Before each experiment starts, the gel column is homogeneous, with zero reagent concentration. The diffusion of CaCl_2 and Na_2WO_4 immediately leads to the development of gradients of pH, and Ca and W concentration along the diffusion column. To know the evolution of the composition of the interstitial aqueous solution as diffusion progresses it is necessary to carry out separate mass-transfer experiments for each reagent over specified periods of time. The protocol followed in such experiments is fully described in previous papers (PRIETO et al., 1989, 1994). It involves removing and slicing the gel column into 10 mm wide slices which were chemically analysed. The W analysis of the slices were carried out by means of ICP-AES spectrophotometry (JY-70 PLUS). The total Ca diffusion data were known from a previous work (PRIETO et al., 1988).

The pH evolution along time and location was determined from separate experiments where a pH universal liquid indicator was added to the Na_2SiO_3 solution during the gel preparation. The gel column initially shows a homogeneous colouring. As diffusion proceeds, it develops a colour banding from which the pH profile for a given diffusion time can be established.

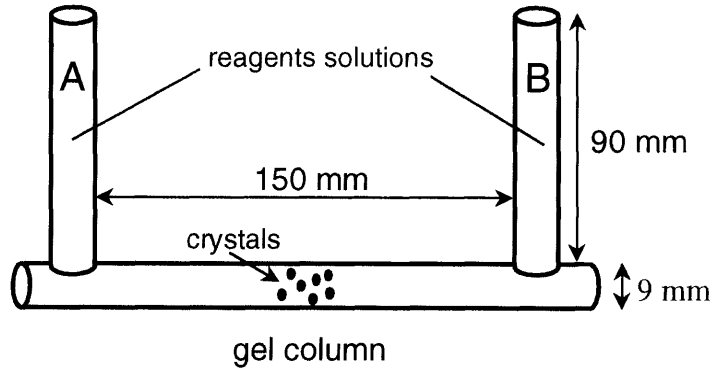


Fig. 1: Experimental set-up

The knowledge of the pH and the total W and Ca concentration profiles for different diffusion times allows to evaluate the change in the distribution of the different tungsten and calcium chemical species along the gel column. With this aim, a speciation program, WOLFRAM, has been especially designed. This program calculates the activity coefficients of the different chemical species by using the Debye-Hückel aqueous speciation model. The species considered were:

Charged species: H^+ , OH^- , HWO_4^- , WO_4^{2-} , $CaOH^+$, Ca^{2+} , HCO_3^- , CO_3^{2-} , Na^+ , $NaCO_3^-$ Uncharged species: $H_2WO_4^0$, $H_2CO_3^0$, $NaOH^0$, $NaHCO_3^0$.

Once Ca^{2+} and WO_4^{2-} activities profiles are known, the supersaturation profiles can be calculated as a function of diffusion time. The expression used to compute supersaturation with respect to scheelite was:

$$b = \frac{a(Ca^{2+}) \cdot a(WO_4^{2-})}{K_{Sch}}, \quad (1)$$

where $K_{Sch} = 10^{-8.67}$ is the scheelite thermodynamic solubility product.

The successive values of supersaturation at a certain location in the gel column define the function $\beta(t)$. The derivative $d\beta(t)/dt$ of $\beta(t)$ gives the supersaturation rate function ($R\beta$)(PRIETO et al., 1991), that describes the rate at which the system moves away from equilibrium.

Results

Nucleation behaviour

a)

The results of scheelite nucleation experiments for several concentrations of the parent solutions are shown in Table 1. The experimental waiting period, the location of the first precipitates and the supersaturation at nucleation time and location are reported. Higher initial concentration of the parent solutions results in shorter waiting periods and higher supersaturations at nucleation time. Figure 2 shows the profiles corresponding to pH, tungsten species distribution, supersaturation and supersaturation rate at the nucleation time when $CaCl_2 = 1$ mol/l and $Na_2WO_4 = 0.5$ mol/l mother solutions were used. The location of the first precipitate is outlined in the upper part of the graphic. As can be observed in figure 2a, the initial homogeneous pH changes and a pH gradient is produced.

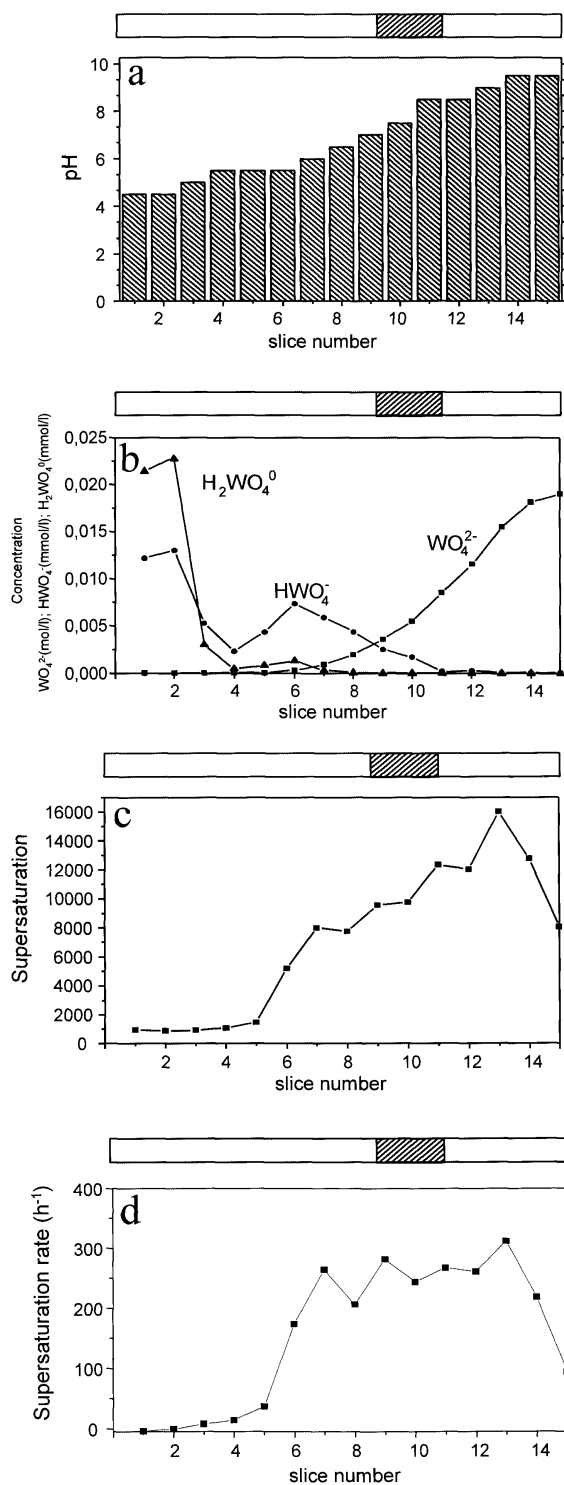


Fig. 2: (a) pH profile. (b) Profiles of the three tungsten species. Note the different concentration units: mol/l for WO_4^{2-} , mmol/l for HWO_4^- and $\mu\text{mol/l}$ for H_2WO_4^0 . (c) supersaturation profile (d) supersaturation rate profile. Mother solutions: CaCl_2 (1 mol/l) $-\text{Na}_2\text{WO}_4$ (0.5 mol/l). All these profiles correspond to the nucleation time. The nucleation zone is indicated on top of each plot.

The pH curve is sigmoidal and shows higher values in the slices closer to Na_2WO_4 reservoir. The pH determines the relative concentration of W species (WO_4^{2-} , HWO_4^- and H_2WO_4^0). At $\text{pH} > 9$, the contribution of HWO_4^- and H_2WO_4^0 to the total W concentration is negligible compared to that of WO_4^{2-} . On the contrary, at lower pH, HWO_4^- and H_2WO_4^0 are predominant (see Figure 2b)

The supersaturation curve (Figure 2c) shows higher values near the deposit of Na_2WO_4 (with a maximum in slice 13) and a decreasing for supersaturation toward the CaCl_2 deposit. The first scheelite precipitate location does not coincide with the location of the maximum

supersaturation value ($\beta \approx 16000$), but it occurs in the region where the pH gradient is maximum (between slices 9 and 11). In this region pH changes from 6.5 to 8 which results in a sharp increase of the WO_4^{2-} concentration. Moreover, the supersaturation rate profile

reaches several relative maxima and also a maximum ($R\beta \approx 265 \text{ h}^{-1}$) between slices 9 and 11 (figure 2d).

The supersaturation with respect to CaWO_4 at nucleation time and location was always very high and it strongly depends on the initial concentration of the mother solutions. When solutions with concentrations $\text{CaCl}_2 = 1 \text{ mol/l}$ and $\text{Na}_2\text{WO}_4 = 0.5 \text{ mol/l}$ were used,

supersaturation reached a value of $\beta \approx 12300$. Lower initial concentrations results in lower

supersaturation values ($\beta \approx 10000$ for $\text{CaCl}_2 = 0.5 \text{ mol/l}$ and $\text{Na}_2\text{WO}_4 = 0.5 \text{ mol/l}$ and $\beta \approx 8510$ for $\text{CaCl}_2 = 0.3 \text{ mol/l}$ and $\text{Na}_2\text{WO}_4 = 0.3 \text{ mol/l}$).

b) Growth morphologies

Scheelite crystallisation is characterised by the formation of a high number of spherulites within the nucleation region. Frequently spherulites form aggregates of numerous individuals and occasionally the formation of crust in the nucleation region occurs. In all experiments, a distribution of spherulite sizes can be observed within the precipitation region, with the higher sizes occupying the extreme closer to the Na_2WO_4 reservoir. The observation of the spherulites by SEM shows that they are built up by needle-shaped crystallites in a radial arrangement. Frequently, spherulites exhibit cracks generated during the metallisation of the samples under high vacuum. Figure 3a shows a scheelite spherulite with wavy surface grown from mother solutions with higher initial concentrations: $\text{Na}_2\text{WO}_4 = 0.5 \text{ mol/l}$ and $\text{CaCl}_2 = 1 \text{ mol/l}$. Figure 3b shows a section of a scheelite spherulite grown from mother solutions with initial concentrations of $\text{Na}_2\text{WO}_4 = 0.5 \text{ mol/l}$ and $\text{CaCl}_2 = 0.5 \text{ mol/l}$. In the image, the typical radial growth of small crystallites from the centre results evident. However, it is not possible to distinguish individual morphologies. When the concentration of the mother solutions is lower ($\text{Na}_2\text{WO}_4 = 0.3 \text{ mol/l}$ and $\text{CaCl}_2 = 0.3 \text{ mol/l}$), scheelite grows as spherulites and spheres. Frequently, two individuals grow together generating a typical dumbbell-like form (Figure 3c).

Discussion

The scheelite nucleation behaviour can be explained by considering two main factors: (i) the non-homogeneous evolutionary character of the diffusing-reacting crystallisation system used (PRIETO et al., 1997) and (ii) the low solubility of the scheelite.

The fact that in our crystallisation system mass-transport occurs exclusively by diffusion leads to the development of both time-dependent W and Ca and pH profiles within the gel column. As in the case of the carbonate anions, CO_3^{2-} , HCO_3^- and H_2CO_3 , tungsten chemical species in the interstitial solution of the gel depend strongly on pH. Thus, while for $\text{pH} < 3$, HWO_4^- and H_2WO_4^0 are dominant, for $\text{pHs} > 3$ the relative activity of WO_4^{2-} anion progressively increases, becoming the more important tungsten species for neutral and

alkaline conditions. Since WO_4^{2-} is the only relevant tungsten specie involved in the formation of scheelite, the evolving pH profiles as a consequence of the diffusion process play an essential role in the nucleation behaviour. Hence only in the regions of the gel column where the relative concentration of WO_4^{2-} is high (high pHs) the scheelite supersaturation is high and, therefore, nucleation can occur. However, the scheelite nucleation kinetics in the locations of relatively high WO_4^{2-} concentrations will be strongly conditioned by the low solubility product of scheelite ($K_{\text{sch}} = 10^{-8.67}$). For sparingly soluble salts the number of growth units in a supersaturated solution is very low in comparison to very soluble compounds and they are relatively distant from one to another. This results in a very low probability of nucleation, even for high supersaturation levels. Only for considerable departures from equilibrium the 'critical supersaturation' can be achieved and the metastability limit is overcome (WALTON, 1969).

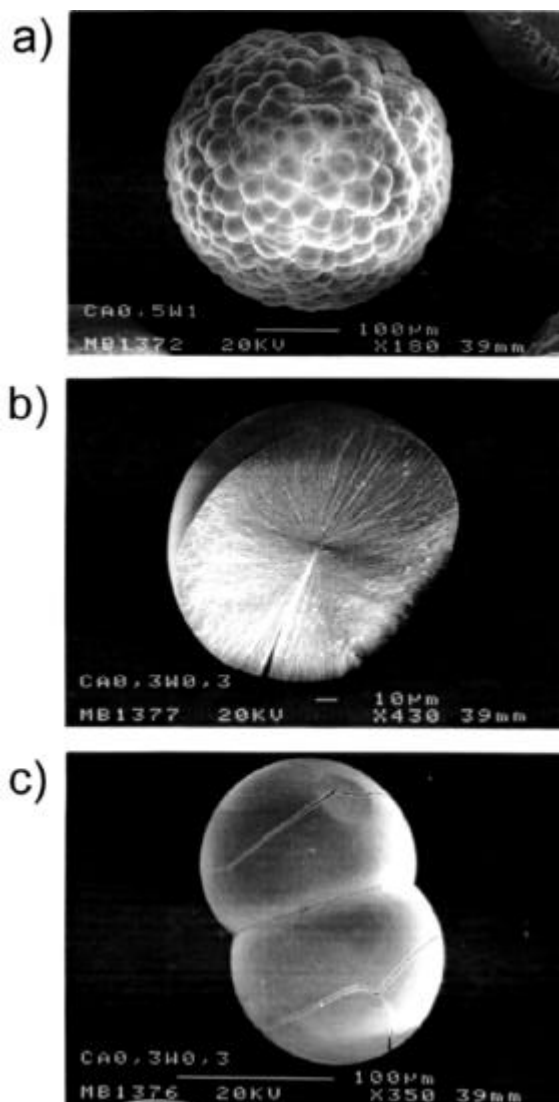


Fig. 3: (a) Scheelite spherulite (b) Section of a scheelite spherulite showing the radial arrangement of crystallites. (c) Dumbbell-like morphology

In the case of the crystallisation in diffusion reacting systems wider metastability zones than that for homogeneous aqueous solution are always observed, which is a direct consequence of the limited ionic mobility and, therefore, of the reduction of nucleation probability. In such systems the critical supersaturation concept becomes inadequate to interpret the nucleation behaviour and a kinetic description of departure from equilibrium, i.e., the

supersaturation threshold, β_{th} , is required (PRIETO et al. 1991, 1994). β_{th} is the supersaturation reached at the nucleation time for a system, which moves away from equilibrium, and its value depends, among other factors, on the supersaturation rate. The supersaturation

thresholds and supersaturation rates found for scheelite (Table 1) are similar to the β_{th} values shown by other compounds with solubility products in the range from 10^{-8} to 10^{-10} (e.g. $BaSO_4$, $SrSO_4$, $SrCO_3$, $BaCO_3$, $CaCO_3$) and under comparable experimental conditions (PRIETO et al., 1989, 1991, 1994).

Scheelite nucleation experiments show also that nucleation zone does not agree with the supersaturation maximum (close to the Na_2WO_4 reservoir), but it coincides with the column position where the supersaturation rate reaches several maxima. The rapid increase of supersaturation in this region of the diffusion column can be correlated to the drastic increase of the WO_4^{2-} species concentration. During this increase the concentration of WO_4^{2-} becomes similar to the concentration of Ca^{2+} and the equality range condition $[WO_4^{2-}]/[Ca^{2+}] = 1$ is fulfilled (HENISCH & GARCÍA RUIZ, 1986). Such a condition is not irrelevant for a stochastic controlled system of limited particle mobility, for which nucleation probability tends rapidly to zero when ionic ratio departs slightly from unity. Therefore, scheelite nucleation occurs in the region of the diffusion column where the kinetic parameters for nucleation are optimal.

Supersaturation and its evolution do not only control the scheelite nucleation behaviour, but affect also to the growth process. The high supersaturation at the nucleation time and initial stages of growth is reflected in the generation of spherulites with a radial internal distribution of crystallites. The rounded and rough surfaces of these spherulites indicate a continuous growth mechanisms, characteristic of interfaces of high kinetic roughness (SUNAGAWA, 1987). As a consequence of the maintenance of high supersaturation levels during the formation time of the spherulites, growth only occurs within the rough regime and no other growth mechanisms such as two-dimensional nucleation or spiral growth have been observed. The high growth rate of individual crystallites from the core of the spherulites implies the accumulation of defects during growth. This generates internal stress and it is common to find fractured spherulites.

The characteristic of the scheelite nucleation and growth described here confirm again the general nucleation behaviour reported for the crystallisation of other sparingly soluble substances ($BaSO_4$, $SrSO_4$, $SrCO_3$, $BaCO_3$, $CaCO_3$, $CdCO_3$) in a gel medium (PRIETO et al. 1989, 1991, 1994, 1997). Moreover, our experiments demonstrate the possibility of crystallising scheelite at ambient conditions in a diffusing reacting system.

Acknowledgements

The authors wish to thank Roberto Leal Ortega for computer assistance and Andrew Putnis for reading the manuscript. C.M. Pina acknowledges the receipt of a Marie Curie Fellowship from the European Commission. J.M. Astilleros thanks the Universidad Complutense de Madrid for a research grant. The W chemical analysis were carried out at the Atomic Spectrometry Laboratory of the Universidad Complutense de Madrid.

References

- DE SMEDT & SONNET, P.: In: Boissonas J., Omenetto, P. (eds) Mineral deposits within the European Community. Springer; Berlin Heidelberg New York (1988), 160

DERRÉ, C.; LECOLLE, M.; ROGER, G.: Miner. Deposita, 17 (1982) 363
 GIBERT, F.; CALEFFI, D., GIBERT, P.; MOINE, B. : Terra Abstract, 1,1 (1989) 121
 GIBERT, F.; MOINE, B.; SCHOTT, J.; DANDURAND, J.L.: Contrib. Mineral. Petrol., 112 (1992) 385. HENISCH, H.K., GARCÍA-RUIZ, J.M.: J. Crystal Growth, 75 (1986)195.
 PRIETO, M.; VIEDMA, C.; LÓPEZ-ACEVEDO, V.; MARTÍN-VIVALDI, J.; LÓPEZ-ANDRÉS, S.: J. Cryst. Growth, 98 (1988) 61
 PRIETO, M.; FERNÁNDEZ-DÍAZ, L.; LÓPEZ-ANDRÉS, S.: J. Cryst. Growth, 98(1989) 447
 PRIETO, M.; FERNÁNDEZ-DÍAZ, L.; LÓPEZ-ANDRÉS, S.: J. Cryst. Growth, 108 (1991) 770.
 PRIETO, M.; PUTNIS, A.; FERNÁNDEZ-DÍAZ, L.; LÓPEZ-ANDRÉS, S.: J. Cryst. Growth, 142 (1994) 225. PRIETO, M.; FERNÁNDEZ-GONZÁLEZ, A.; PUTNIS, A.; FERNÁNDEZ-DÍAZ, L.; Geochim. et Cosmochim. Acta, 16 (1997) 3383
 SUNAGAWA, I.: Morphology of crystals Vol.2, TERRAPUB Tokyo 1987
 WALTON, A.G.: Nucleation in liquids and solutions, in Zettlemoyer, A.C. Nucleation. New York 1969

Contact information:

C. M. PINA*
Institut für Mineralogie
Universität Münster
Corrensstraße 24 48149
Münster Germany

L. FERNÁNDEZ-DÍAZ, J. M. ASTILLEROS Dpto.
Cristalografía y Mineralogía Universidad
Complutense de Madrid 28040 Madrid
Spain

***corresponding author**

e-mail: pina@nwz.uni-muenster.de