Kinetics and Mechanism of Hübnerite ($MnWO_4$) and Ferberite ($FeWO_4$) Crystallization under Hydrothermal Conditions

J. Chr. Buhl and A. Willgallis
Institut für Mineralogie, Freie Universität Berlin

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The kinetics of the crystallization of hübnerite ($MnWO_4$) and ferberite ($FeWO_4$) was studied by hydrothermally reacting the metal (II)-chlorides and sodium tungstate in a special autoclave at two temperatures (300 °C, 400 °C) and a pressure of 1 kbar. The rates of crystallization were determined by continual removal of the reactants from the autoclave. At both temperatures, the decrease of tungstate concentration in solution followed at first order reaction. The rate constants of the reactions were calculated and the Jerofejev-equation was used to describe the kinetics.

The rate of hübnerite formation was larger and increased faster with temperature. This should affect the formation of mixed crystals by initiating a shift of the composition towards higher $MnWO_4/FeWO_4$ ratios and might well account for a zonation or inhomogeneity of natural wolframites.

Introduction

There are various opinions regarding the temperature dependence of the hübnerite/ferberite ratio (H/F ratio) of wolframites. According to some authors (Oelsner [1], [2]; Leutwein [3]; Hollister [4]; Amossé [5]) the H/F ratio increases with rising temperature of formation. Others (Churikov [6]; Ganeev, Sechina [7]) either deny it or even state the reverse.

So Oelsner's attempt to use the composition of wolframites as a geological thermometer is questionable. The heterogeneous composition of many wolframites, revealed by EPM-analysis (Willgallis [8]) is also a problem in this connection.

Numerous investigations involving parameters like alkalinity, redox potential and reactions with the wallrock were carried out (Chernyshev, Ivanova [9]; Hsu [10]; Horner [11]; Barabanov [12]), but the temperature dependence and inhomogeneity of the wolframite composition remained largely unexplained.

No work appears to have been done involving the mechanism of formation of manganese- and iron tungstates. So this study attempts to establish a relationship between temperature, wolframite-composition and differences in the reaction kinetics of hübnerite and ferberite.

In this paper the rates of the formation of hübnerite and ferberite under hydrothermal conditions between 300 °C and 400 °C and a pressure of 1 kbar are reported. According to investigations of fluid inclusions and isotope ratios, these values are believed to be the main conditions of formation of most wolframite deposits (Naumov, Ivanova [13]; Ivanova [14]; Kelly, Rye [15]).

Experimental

The tungstates were prepared by hydrothermally reacting reagent-grade metal(II)-chlorides and sodium tungstate.

The experiments were carried out in an autoclave of 27 cm^3 interior volume. A valve permitted continual sampling. Initially the dry mixture was kept in a small copper tube until the reaction temperature had been reached, then a pump operated by compressed air achieved the pressure of 1 kbar and simultaneously transferred the reactants into the liquid phase. Attainment of the required pressure was taken to be the start of the reaction. To determine the progress of the reaction the entire liquid phase was withdrawn from the reaction vessel at predetermined times and WO_3 determined after filtration by a wet chemical method: Precipitation with conc. HCl or HNO_3, subsequent ignition and weighing as yellow WO_3 (Classen [16]). The maximum reproducibility of the method is given by Willgallis [8] as ± 4% for duplicate determinations.

Reprint requests to Prof. Dr. A. Willgallis, Institut für Mineralogie, Freie Universität Berlin, Takustraße 6, 1000 Berlin.

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The decrease of the concentration of WO_3 in the hydrothermal solution with time constituted the basis of the kinetic measurements which can be correlated to the inclusion of tungsten in the crystalline solid phase and thus illustrates the kinetic mechanism. Subsequent X-ray analysis of the solids remaining in the autoclave confirmed the formation of Mn and Fe tungstates only; possible tungsten – containing intermediate products could not be identified. Comparative experiments in a teflon lined small autoclave (DAE 10)* made by Berghof/Tübingen at 200 °C and at 0.2 kbar (limit) showed that contamination by Fe from the autoclave material is within the tolerance of the wet chemical method of analysis. The more pronounced contamination under more severe conditions was disregarded in view of the short reaction times.

Results

In Fig. 1, the logarithm of the observed concentrations of WO_3 in solution is plotted vs. the time of reaction. From the linear time dependence it follows that first order reactions take place when $MnWO_4$ was well as $FeWO_4$ are formed, which can be expressed by the equation

$$\ln(a/x) = k\,t\,, \qquad (1)$$

where a is the initial concentration, x the concentration at time t and k the rate constant of the reaction. The average rate constants $\bar{k}$ and halfvalues $t\,(\frac{1}{2})$ were found to be:

	$FeWO_4$ (Ferberite)		$MnWO_4$ (Hübnerite)	
	300 °C	400 °C	300 °C	400 °C
$10^4\,\bar{k}\,(s^{-1})$	2.53	4.50	2.83	6.87
$t\,(\frac{1}{2})\,(s)$	2741	1542	2450	1010

Since both reactions are of first order, the process kinetics can be described by a general equation applicable to heterogeneous reactions and developed by Jerofejev [17]:

$$\alpha = 1 - \exp(-k\,t^n)\,, \qquad (2)$$

where α is the conversion and n an index (for $n = 2$ two dimensional seed, $n = 3$ three dimensional seed).

According to (2), using $n = 3$ and the $\bar{k}$-values obtained, the conversions for both reactions can be calculated. They are shown in Figure 2.

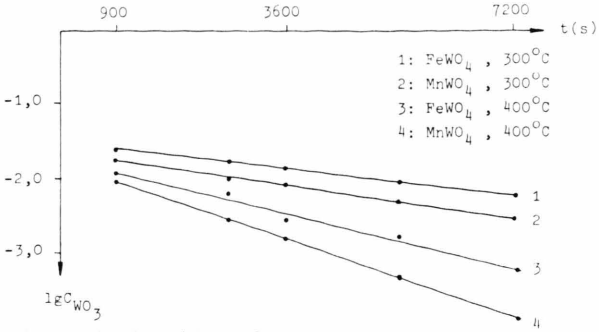

Fig. 1. The logarithm of the concentration of WO_3 in solution obtained at the corresponding times of reaction (temperature: 300 °C, 400 °C; pressure: 1 kbar).

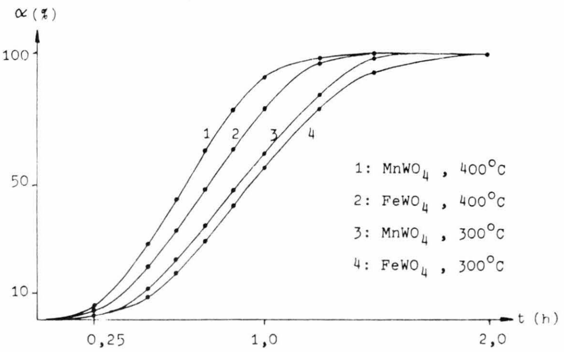

Fig. 2. The kinetic curves for hübnerite- and ferberite formation at 300 °C and 400 °C and a pressure of 1 kbar.

The increase in temperature from 300 °C to 400 °C led to an increase of the rate constant by 78% in the case of the formation of ferberite whilst the halfvalue decreased by a factor of 0.56. At the same time the rate constant for hübnerite increased by 143% and the halfvalue fell by a factor of 0.41. It is therefore evident that in the temperature interval considered here an accelerated formation of hübnerite compared with ferberite takes place. At the temperature of 300 °C the $\bar{k}$-value for the formation of hübnerite was 12% higher and the halfvalue 11% lower than for the ferberite crystallization. At 400 °C the $\bar{k}$-value for hübnerite formation was 53% higher and the halfvalue 35% lower than for the corresponding $FeWO_4$ crystallization.

Conclusions

The observed difference in the reaction kinetics of the pure components increases with a rise in

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* Made by Berghof, Tübingen.

temperature. This will affect correspondingly the formation of mixed crystals. The raised velocity of hübnerite formation will at first initiate a shift towards a higher $MnWO_4/FeWO_4$ ratio in the mixed crystal. This confirms Oelsners observation (Oelsner [1], [2]).

In a closed system, the different velocities with which atoms are accepted into the lattice and which increases with increasing temperature will bring about a shift in the distribution of Fe- and Mn-ions between the liquid and the solid phases. The solution would thus be impoverished in Mn^{2+}-ions, leading to an apparent enrichment in the Fe component. With a shortage of Mn being reached, iron will preferentially transfer from the solution to the crystal. In this case a ferberite rich wolframite would result.

Ideally, the differences in the course of the reaction should entail zoning in the mixed crystals. Ivanova et al. [18] has reported about such naturally zoned wolframites.

Possibly certain intergrowthstructures of various naturally occurring tungstates (Willgallis [8]) can be explained along these lines. In such heterogeneous wolframites spearlike forms invariably constitute the Mn-rich portions of the mixed crystal.

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