VAPOR-TRANSPORT OF TUNGSTEN AND ITS GEOLOGIC APPLICATION

SHIBUE, Y., Geoscience Institute, Hyogo University of Teacher Education, Yashiro-cho,
Kato-gun, Hyogo 673-14, Japan

INTRODUCTION

Crustal abundance of tungsten lies between 1 and 2 ppm (Krauskopf, 1970), which is obviously lower than those of copper, lead, and zinc (e.g., Turekian and Wedephol, 1961). Most of the analytical data on tungsten in granitic rocks show that the concentrations do not show any significant differences between those related to tungsten mineralization and those unrelated (e.g., Ivanova, 1963; Ivanova and Butsuzova, 1968; Shepherd et al., 1976). Newberry and Swanson (1986) stated that the bulk enrichment of tungsten does not appear to be prerequisite for the formation of scheelite skarn.

Einaudi et al. (1981) summarized and characterized the physico-chemical conditions for the formation of tungsten-, copper-, and lead and zinc skarn deposits in the world. The differences point to the formation of tungsten skarn at deeper environment (1 to 3 kilobars) and higher temperature (600° to 400°C) than that of the base-metal skarn. As the pressure and temperature of hydrothermal solution have a significant effect on mineral solubilities as well as the salt concentration, the difference can be considered as the cause for the enrichment of tungsten compared with the base metals in the deposits. Are there any other explanations for the localization and relative enrichment of tungsten compared with the other ore metals?

Exact evaluations of tungsten concentrations in the ore-forming solutions have not yet been carried out. There exists a possibility that the hydrothermal solutions for tungsten deposits are enriched in tungsten compared with the other ore metals. Judging from the previous analytical works on rock chemistry, the process for the enrichment of tungsten compared with the other ore metals in hydrothermal solutions should be considered if we stand on this point of view. "Volatility of tungsten" was discussed based on the facts that the boiling points of tungsten halides and tungsten oxyhalides are lower than those of base-metal chlorides (e.g., Lindgren, 1933). "Volatility of tungsten" is one of the possible causes for the enrichment of tungsten compared with base metals if we consider the concentrations in the vapor phase. As "volatility of tungsten" was discussed based on the behavior of tungsten in oxygen or halogen present anhydrous system at 1 bar, the validity should be examined in hydrous system at elevated pressures.

Shibue (1988a,b) showed some of the physico-chemical conditions for the formation of major tungsten deposits in Japan. Temperatures of the most intense mineralization range from 550° to 400°C, pressures are around 1 kilobar, and the salinities in the hydrothermal solutions are less than 10 NaCl eq. wt%. Considering the formation conditions of these deposits, experiments on the behavior of tungsten should be performed above and near the critical point (221 bar, 374°C) of H2O (Keenan et al., 1969). It is a convenient method that the weight of the product formed from the vaporized species is measured for purpose of the examination of the volatility. This method does not give the exact partition coefficient of the considered species between vapor and liquid phases. However, volatilities of various species can be compared by this convenient method, choosing appropriate captures for the vaporized species.

This paper aims to show the volatility of tungsten in hydrous system at elevated temperatures and pressures, and to present a tentative model for the enrichment of tungsten in hydrothermal solutions for the deposits related to granitic acitvities.

EXPERIMETNAL METHODS

All chemicals used in the present study are analytical reagent grade, and were ground in an agate mortar. In order to produce vapor-saturated solutions at 550° and 350°C, 17 or 15 ml of 20 wt% NaCl solutions are introduced into autoclaves whose internal volume is about 40 ml. Volume and concentration of NaCl solution are chosen based on the pressure-temperature-volume data for the system NaCl-H2O (Gehrig et al., 1983). Liquid and vapor phases fill the upper and lower parts within the autoclaves, respectively.

Shibue (1988a) showed that tungstate species is important for the transport of tungsten in the hydrothermal solutions for major tungsten deposits in Japan, and Helgeson (1964) discussed the importance of chloride-complexing of base metals in hydrothermal solutions. Powder of H2WO4, CuCl2·2H2O, PbCl2, or ZnCl2 is added to the initial solution. The amounts of H2WO4 and the base-metal chlorides range from 0.1 to 0.3 g and from 0.1 to 0.9 g, respectively. At room temperatures, H2WO4 and PbCl2 powders were not dissolved completely in the initial solutions.

Ca(OH)2 is chosen as the capture for vaporized tungsten species, and H2WO4 is chosen as the capture for the vaporized base-metal species. Tungstates will be produced from these captures because of the strong affinities of calcium ion for tungstate ion or the base-metal ions for tungstate ion (e.g., Urusov et al., 1967). These captures show very low solubilities in aqueous solutions even at supercritical conditions (e.g., Walther, 1986; Bryzgalin, 1976). It is assumed that these captures, which may be solids in the experiments, react with almost all the amounts of the vaporized species of the considered elements. The amounts of Ca(OH)2 range from 0.1 to 0.2 g, and those of H2WO4 range from 0.2 to 0.4 g. Moles of the captures exceed those of the H2WO4 or the base-metal chlorides which were initially added to the solutions. These conditions are intended to furnish excess amounts of the captures. A small gold dish, charged by the capture, is placed at the top of a gold rod introduced into the autoclave. The dish is placed without any contact with aqueous solution.

Experimental setting adopted in the present study is shown in Fig. 1. Free space within the autoclave is 37.4 ml. The errors of the experimental temperatures are within ±5 C, and the duration time is 24 hours. Small concentrations of H2WO4 or the base-metal chlorides are considered to have little effect on the phase relation in the system NaCl-H2O. Run products are identified by X-ray powder diffractometry.

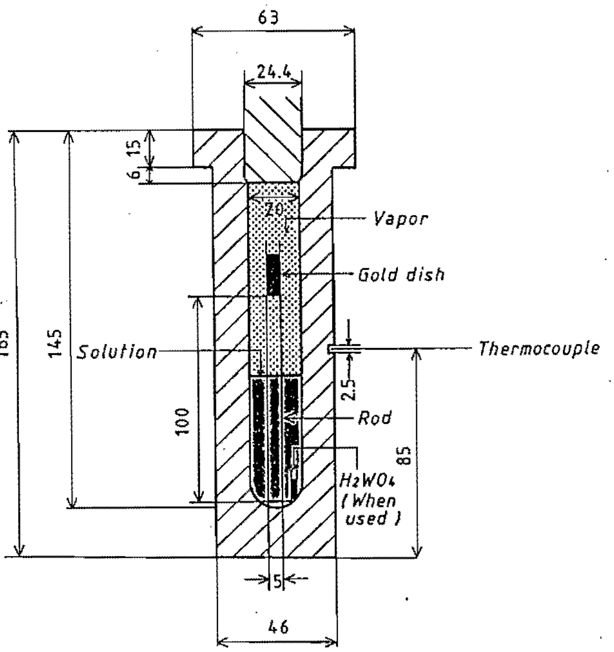
Analytical methods

Powders on the dish for the experiments on tungsten are fused with Na2CO3. The fused disk is dissolved in distilled water, and then the solution is filtered with use of Toyo membrane whose pore size is less than 1 μm. The filtered solution is mixed with concentrated HNO3+HCl solution, which produces H2WO4 as precipitate. After the filtration by the membrane, the precipitate is washed with distilled water and then dissolved with concentrated NaOH solution. Tungsten concentration in the solution is determined by the stannous-thiocyanate method (Charlot, 1964). Analytical results are expressed as the vaporized amounts of H2WO4.

Run product on the dish for the experiments on lead are decomposed by concentrated HNO3 solution, and those for copper and zinc are decomposed by concentrated HNO3+HCl solutions. Filtered solutions are analyzed by atomic absorption spectroscopy on lead, copper, or zinc. Analytical results are expressed as the vaporized amounts of the base-metal chlorides.

Analyses of the liquids are performed by the colorimetric method for tungsten, and by atomic absorption spectroscopy for the base metals.

Fig. 1. Experimental apparatus used in the present study. In order to produce vapor-saturated solution, 17 or 15 ml of 20 wt% NaCl solution is introduced into an autoclave. Vapor-captures are $Ca(OH)_2$ for tungsten and H_2WO_4 for base metals.



RESULTS AND DISCUSSIONS

Calcium tungstate and the base-metal tungstates are observed on the gold dishes after the heat treatments. Ratios of the vaporized amounts to the initial amounts are plotted in Fig. 2. Present results indicate that more than 1/3 of the initial amounts of H2WO4 is vaporized at 550° C, and more than 1/10 of the initial amounts are vaporized at 350°C. On the contratry, less than 1/10 of the initial amounts of the base-metal chlorides are vaporized at the experimental temperatures. The higher temperature favors the vaporization of the studied elements, which is conspicuous for tungsten.

Considering the same experimental conditions with regard to the temperature, volume and concentration of NaCl solution, and the duration time, the vaporized amounts reflect the concentrations of the metals in the vapor phase. Present results, therefore, suggest that the ratio of tungsten to the base metals is higher in the vapor phase than those in the liquid phase and also in the initial solution. It is also possible that the relative enrichment of tungsten compared with the base metals in the vapor phase occurs at higher temperatures and pressures if vapor and liquid phases coexist.

Variation in the ratios of the vaporized amounts to the initial amounts are recognized for the experiments on the studied elements, especially tungsten. It is possible that the ratios are influenced by the rates of the reactions between solids (captures) and vaporized species. The obvious differences in the ratios between those for tungsten and those for the base-metals under the same duration time, however, does not seem to be explained only by the unknown kinetic factors. It should also be emphasized that no opposite results against the relative volatility of tungsten compared with the base metals were obtained in the present study.

Before applying the present results to hydrothermal processes during the solifidication of the granitic magma, formation conditions of several tungsten deposits in Japan will be considered. There have been no evidences for the formation of breccia pipes, and no evidences for the large circulation of hydrothermal solutions around the deposits from the viewpoint of the extent of the hydrothermal alterations (e.g., Shibue, 1984, 1986). Burnham (1979) discussed that the large mechanial energy produced by the change in volume from melt to rock+fluid causes the fracturing at 0.5 kilobar pressure. He showed that the mechanical energy produced at 1 kilobar or the higher pressure is not so large. These lead to a hypothesis that the fluids evolved from the granitic magmas were stored within and around the granitic magmas and the suceeding rocks.

In "magmatic fluid reservoir", the hydrothermal fluids decrease in temperature owing to the decrease in temperature of the granitic magmas and the succeding rocks. When fracturing occurs in the the surrounding rocks or within the granitic rocks, the pressures of the hydrothermal fluids temporarily decrease. It is, then, possible that the fluids show an immiscibility into vapor and liquid phases. According to Sourirajan and Kennedy (1962), the coexistence of vapor and liquid phases occurs up to 650°C when NaCl concentration is 5.5 wt% (1 molal). Present experiments showed that the metal ratio of tungsten to the base metals

Fig. 2. Frequency diagrams on the ratios of the initial amounts to the vaporized amounts. Open areas show the data for tungsten, circles for copper, squares for lead, and crosses for zinc, respectively.

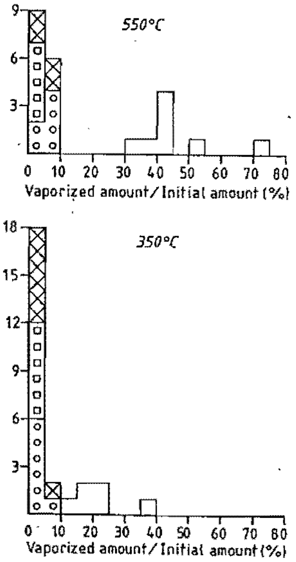
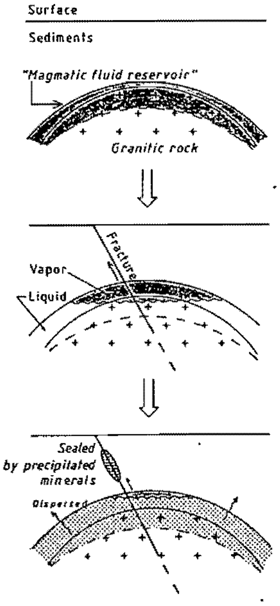


Fig. 3. Schematic model model for the generation of the hydrothermal solution enriched in tungsten compared with the base metals.



in the vapor phase is higher than that in the initial fluid. Vapor will ascent preferentially through the fractured zone owing to the buoyance force. Decrease in temperature of the vapor causes the precipitation of various minerals, including quartz and tungstates. A compressional stress arised from the difference between the lithostatic pressure and the hydrostatic one also narrows the channelways of the hydrothermal solutions. These can separate the channelways of vapor from those of liquid. The mineralized areas of tungsten are separated from those of the base metals in these processes. Present tentative model, emphasizing the vapor-transport of tungsten, can explain the presence of tungsten deposits without large minerlization of base metals. Fig. 3 schematically shows the processes mentioned above.

Finally present tentative model should be examined by future works, especially referring to the mechanical properties of rocks under high water vapor pressures.

References

Bryzgalin, O. V. (1976) On the solubility of tungstic acid in aqueous solutions at high temperatures. Geochem. Int., 155-159.

Burnham, C. W. (1979) Magmas and hydrothermal fluids. Geochemistry of Hydrothermal Ore Deposits. Edited by H. L. Barnes, John Wiley and Sons: New York.

Charlot, G. (1964) Colorimetric Determination of elements. Elsevier: Amsterdam.

Einaudi, M. T., Meinert, L. D., and Newberry, R. J. (1981) Skarn deposits. Econ. Geol., 75th Anniv. Vol., 317-391.

Gehrig, M., Lentz, H., and Franck, E. U. (1983) Concentrated aqueous sodium chloride solutions from 200° to 600°C and to 3000 bars-Phase equilibria and PVT-data. Ber. Bunsenges. Phys. Chem., 87, 597-600.

Helgeson, H. C. (1964) Complexing and Hydrothermal Ore Deposition. Pergamon Press: New York.

Ivanova, G. F. (1963) Content of tin, tungsten, and molybdenum in granites enclosing tin-tungsten deposits. Geochem. Int., 492-500.

Ivanova, G. F. and Butsuzova, Ye. G. (1968) Distribution of tungsten, tin, and molybdenum in the granites of Eastern Transbaykalia. Geochem. Int., 572-583.

Keenan, J. H., Keyes, F. G., and Moore, J. G. (1969) Steam Tables. John Wiley and Sons: New York.

Krauskopf, K. B. (1970) Tungsten. Handbook of Geochemistry. Edited by K. H. Wedephol, Springer: Berlin.

Lindgren, W. (1933) Mineral Deposits 4th ed. McGraw-Hill: New York.

Newberry, R. J. and Swanson, S. E. (1986) Scheelite skarn granitoids: A evaluation of the roles of magmatic sources and processes. Ore Geol. Rev., 1, 57-81.

Shepherd, T. J., Beckinsale, R. D., Rundle, C. C., and Durham, J. (1976) Genesis of Carrock Fell tungsten deposits, Cumbria: Fluid inclusion and isotope study. Trans. Min. Metall. Sec. B, 85, 298-303.

Shibue, Y. (1984) Chemical compositions of tourmaline in the vein-type tungsten deposits of the Kaneuchi mine, Japan. Mineralium Deposita, 19, 298-303.

Shibue, Y. (1986) Mineralization and transportation of tungsten in hydrothermal solutions: Some studies on several Japanese tungsten deposits. Unpublished PhD thesis, University of Tokyo.

Shibue, Y. (1988a) Importance of tungstate species for the transport of tungsten in hydrothermal solution: Case studies on major Japanese tungsten deposits. J. Min. Petrol. Econ. Geol., 83, 51-68.

Shibue, Y. (1988b) Importance of tungstate species for the transport of tungsten in hydrothermal solution: Case studies on major Japanese tungsten deposits. Goldschmidt Conf. Abstr. with Progs. p. 84.

Sourirajan, S. and Kennedy, G. C. (1962) The system NaCl-H20 at elevated temperatures and pressures. Am. J. Sci., 260, 115-141.

Turekian, K. K. and Wedephol, K. H. (1961) Distribution of the elements in some major units of the earth's crust. Geol. Soc. Am. Bull., 72, 175-192.

Urusov, V. S., Ivanova, G. F., and Khodakovskiy, I. L. (1967) Energetic and thermodynamic properties of molybdates and tungstates and some features of their geochemistry. Geochem. Int., 950-863.

Walther, J. V. (1986) Experimental determination of portlandite and brucite solubilities in supercritical H20. Geochim. Cosmochim. Acta, 50, 733-739.