Solubility of tin, tungsten and molybdenum oxides in felsic magmas

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Abstract. Saturation versus undersaturation of granitic melts in tin, tungsten and molybdenum oxides is discussed on the basis of experimental data. Results of dry and hydrothermal experiments are evaluated under the assumption of ideal solubility of Sn, W and Mo oxides in granitic melts. A conservative interpretation arrives at concentration levels of ≥ 1000 ppm SnO_2, WO_3 and MoO_3 respectively, considered as the maximum solubility of these components in granitic melts at $750\,°C$– $800\,°C$. Such values are never reached in natural granites unaffected by hydrothermal alteration and therefore even highly evolved granites are expected to be undersaturated in these metals. Consequently cassiterite and scheelite are neither common liquidus minerals of ore-bearing granites nor restite minerals from partial melting events.

Highly evolved granites of specialized composition (high SiO_2, low alkaline earth and iron oxide contents) are parental rocks of some tin, tungsten and molybdenum deposits of magmatic affiliation. Recent advances in the knowledge of their chemistry raised the question whether such specialized granites or rhyolites caused the concentration of metals into ore deposits. Among the principal questions which remain unanswered are whether ore-bearing granites became saturated or undersaturated in tin, tungsten and molybdenum, and if the data on Sn, W and Mo contents in granites are comparable with the results of experimental studies.

Recent experimental studies, however, indicate considerable problems in attaining equilibria in even long lasting runs at P-T conditions of the upper crust. The present study compares the results of runs carried out by different techniques to estimate the ranges of tin, tungsten and molybdenum oxides' saturation in granites under geologically realistic conditions.

Geochemistry of major-element oxides in ore-bearing granitoids

The granitoids with which tin, tungsten and molybdenum deposits are spatially and probably genetically associated are characterized by a relative excess of silica and the depletion of some major element oxides such as CaO, MgO, FeO and Fe_2O_3 (Štemprok and Škvor 1974). Such chemistry is even more distinct in albitic varieties of these granites called apogranites and considered to be of metasomatic origin. Albite keratophyres (ongonites) from the tungsten deposit of Ongon Khairkhan in Mongolia are examples of "quenched" dykes of "apogranitic" composition and are interpreted to be of magmatic origin (Kovalenko and Kovalenko 1976). The depletion/enrichment pattern of ongonites is shown in Fig. 1, normalized to the granite average according to Vinogradov (1962). Typical network-modifying cations of extrusive rocks according to Mysen (1987) are indicated. Highly evolved albite keratophyres which may model metallogenetically specialized magmas, are characterized by an enrichment in Li, Rb and Na, and a slight depletion in K but a major depletion in Ca, Fe and Mg. Thus Fig. 1 shows a maximum decrease in alkaline earth and ferrous and ferric iron which belong to the network-modifying cations in extrusive rock (Mysen 1987). The ratio of non-bridging oxygen to cations in tetrahedral coordination (NBO/T) is less or equal to 0.1 and hence the degree of polymerization of ongonites is higher than in normal felsic magmas. Depolymerizing cations are alkalies such as sodium and potassium, and in certain kinds of ongonites, lithium and rubidium. Anionic depolymerizers are hydroxyl ions and fluorine.

Tetravalent tin, and hexavalent tungsten or molybdenum are in felsic magmas in octahedral coordination with oxygen and their octahedra are probably copolymerized with aluminosilicate polyanionic components of granitic magma structure (Štemprok 1989). Divalent tin is in tetrahedral coordination with oxygens and it can probably replace silicon in silica tetrahedra.
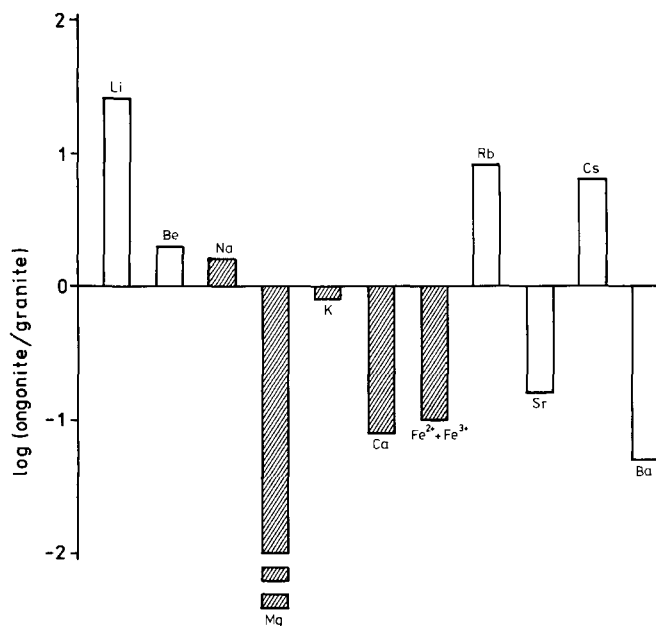
Fig. 1. The enrichment/depletion pattern of alkalies, alkaline earth and iron in albite keratophyres (ongonites) from the tungsten deposit of Ongon Khairkhan in Mongolia (unpubl. data). The most important network modifying cations in common extrusive rocks according to Mysen (1987) are dashed
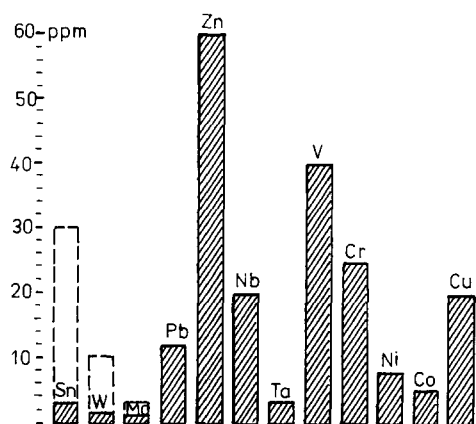

Fig. 2. The histogrammatic representation of average contents of Sn, W and Mo, and some other metals in granites according to Vinogradov (1962). Increased contents of average Sn, W and Mo in highly evolved granites are marked by a dashed contour

Abundances of tin, tungsten and molybdenum in felsic igneous rocks

The average amount of Sn in granites as estimated by Vinogradov (1962) is 3 ppm; of W, 1.5 ppm; and Mo, 1 ppm. Uzkut (1973) gave higher average Mo values: the average for granites is 2.4 ppm and for rhyolites 2.3 ppm Mo.

In highly evolved granites these amounts are increased to about 20–50 ppm Sn (average 30 ppm) (Tischendorf 1977; Lehmann et al. 1988); 5–12 ppm W (average 10 ppm) (Tischendorf 1977; Levashev 1978; Liu et al. 1982); and 3–4 ppm Mo (average 3 ppm) (Tischen-

dorfer 1977; Levashev 1978) (Fig. 2). Such values appear valid for granites unaffected by hydrothermal redistribution (Lehmann et al. 1988 for Sn). However, even such increased amounts do not reach the average contents of some other metals in granites not commonly accumulated by the activity of felsic magmas such as zinc, lead, chromium, or of metals which form minor mineral accumulations (Nb and Ta). This suggests that the process of Sn, W and Mo concentration must have been more efficient than that of other metals under the assumption that a granitic melt or solid granites were the source rocks for these deposits (Holland 1972).

Chemical equilibria in melts

Different solubility of various oxides in silicate melts has been explained by the concept of glass melt-structure (Dietzel 1941; Rawson 1967; and others). While some oxides are completely miscible with silica in any proportion, others are soluble only to a certain limit. Dietzel (1941) distinguished four categories of oxides in silicate melts from the most soluble to least soluble ones (e.g. from alkalies to sulphur species). The solubility of the three discussed metal oxides falls into the second or third category.

The solubility of a metal oxide in a silicate melt is the function of intensive variables such as T, P and of the composition C_x (molal proportion of network-forming cations and of network-modifying cations and oxygen fugacity of the system):

$$C_{Me_xO_y} = f(T, P, C_x) \qquad (1)$$

where $C_{Me_xO_y}$ is the solubility of a metal oxide in silicate melt.

In an ideal solution the ideal solubility of solids in liquids is expressed by:

$$\left(\frac{\partial \ln_{x_i}}{\partial T}\right)_{P,X} = \frac{L_i}{R T^2} \qquad (2)$$

where x_i = mol. fraction of the ith species in a condensed phase and L_i = heat absorbed (Denbigh 1963).

Hence the temperature dependence of the solubility of a metal oxide can be conveniently expressed by a log C versus l/T diagram which gives for an ideal solution a linear solubility dependence. In real solutions, especially at temperatures substantially lower than those of melting temperatures of solid phases dissolved, the linear dependence is changed to various curves shifted towards the l/T axis of the diagram (Kirillin and Shchedrin 1956). Thus the ideal solubility plot should be considered as the maximum solubility of a given oxide in silicate melt at constant pressure.

As the experiments discussed in the paper were carried out either in air or at a total pressure usually not exceeding 1.5 kb, the pressure interval is relatively narrow. The pressure dependence of the solubility of an oxide is expressed by the equation:

$$\left(\frac{\partial \ln C_{Me_xO_y}}{\partial P}\right)_{T,X} = \frac{\Delta V}{R T} \qquad (3)$$

Table 1. The review of literature data on the contents of SnO_2, WO_3 and MoO_3 in granitic melt in equilibrium with solid tin, tungsten or molybdenum-bearing phases or with hydrothermal solutions containing soluble salts of these metals

T °C	Type of exp.	Pressure	Buffer	Arit. mean. % mass.	n	Comp. range % mass.	Authors	Note
SnO₂								
750	H	1.5 kb	no	0.11	–	0.06–0.17	Ryabchikov et al (1978a)	Microliquation of Sn-enriched phase
750	H	1.5 kb	Ni/NiO Fe₂O₃/Fe₃O₄	0.19	–	0.13–0.26	Ryabchikov et al. (1978b)	
800	H	101 MPa	Ni/NiO	0.80	11	0.48–1.03	Nekrasov (1984)	Pure glasses
1000	H	101 MPa	Ni/NiO	0.86	1	–	Nekrasov (1984)	Pure glasses
1100	D	⩾1 bar	no	1.8	1	–	Štemprok (1982)	F containing syst.
1180 ± 10	D	–	–	0.9	1	–	⌠Barsukov et al. (1983)	Low silica globul.
		–	–	0.4	1	–	⌡Barsukov et al. (1983)	High silica matrix
1300	D	1 bar	air	3.5	–	–	Štemprok, Voldán (1978)	From phase diagram section
1300	D	1 bar	air	0.33	4	0.22–0.44	Nekrasov (1984)	
1600	D	1 bar	air	6.7	–	–	Štemprok, Voldán (1978)	From the diagram section
WO₃								
750	H	1.5 kb	Ni/NiO	0.41	2	0.41	Orlova et al. (1987)	
800	H	1.5 kb	Ni/NiO	0.32	1	–	Orlova et al. (1987)	
800	H	1.0 kb	no	0.44	14	0.12–0.71	⌠Manning (1984)	⌠Without WO₃ cryst.
800	H	1.0 kb	no	0.46	25	0.12–1.01	⌡Manning, Henderson (1984)	⌡Without WO₃ cryst.
850	H	1.5 kb	Ni/NiO	0.61	1	–	Orlova et al. (1987)	
850	H	–	Mo/MoO₂	3.30	1	–	Nekrasov (1984)	
1100	H	–	Mo/MoO₂	1.35	1	–	Nekrasov (1984)	
1200	D	1 bar	air	1.5	1	–	Štemprok, Voldán (1982)	
1600	D	1 bar	air	2.64	–	0.36–2.94	Štemprok, Voldán (1982)	Several methods
MoO₃								
750	H	1.5 kb	Ni/NiO	0.25	3	0.24–0.25	Ryabchikov et al. (1981)	
750	H	1.4 kb	Ni/NiO Qz/Mg/Fa	0.0062	8	0.0017–0.012	Candela, Holland (1984)	
750	H	1.4 kb	Ni/NiO Qz/Mg/Fa	0.0104	5	0.0066–0.018	Candela, Holland (1984)	
750	H	1.5 kb	Ni/NiO	0.23	6	0.1–0.3	Salova (1989)	
750	H	1.5 kb	Ni/NiO	0.20	7	0.07–0.33	Salova (1989)	
700–900	H	2.0 kb	no	0.45	18	0.30–0.53	Khitarov et al. (1982)	
850	H		W/WO₂	2.04	1	–	Nekrasov (1984)	
900	H	2.0 kb	no	3.9	8	3.30–4.20	Khitarov et al. (1982)	
1000	H		W/WO₂	2.16	1	–	Nekrasov (1984)	
1100	H	0.5 kb	–	0.76	–	not given	Tchekhmir per Salova (1989)	
1100	H		W/WO₂	3.25	1	–	Nekrasov (1984)	
1550–1600	D	1 bar	air	1.5	–	1.4–1.6	Štemprok, Voldán (1983)	Various methods

H – hydrothermal experiments in cold seal vessels
D – dry experiments

where ΔV is the change of the volume of the solution by dissolution of 1 mol. of the component. As ΔV is very small in the temperature interval examined, the results of experiments carried out in air and up to 1.5 kb are considered as isobaric in the present treatment.

Small differences in phase equilibria of felsic systems between the experiments at atmospheric pressure and those at 1 kb total pressure are also indicated by a similarity of phase diagrams of the Qz-Ab-Or system under these pressures (Schairer 1950; Tuttle and Bowen 1958).

Therefore, the log C versus l/T plot of data has been selected as the most useful graphical representation in discussing the solubility of metal oxides in granitic melts at geologically realistic conditions.

Starting materials

Granites associated with tin or tungsten deposits (El'-dzhurtin, Akchatau, Krásno, Přebuz) or artificial granites prepared by various methods have been used in experimental studies (Table 1). Low CaO, MgO, FeO and Fe₂O₃ in many ore-bearing granites make the use of the Qz-Ab-Or eutectic composition very convenient as a starting material. Synthetic granites were prepared from oxides by melting (Štemprok and Voldán 1978) or from gels using tetraethyl orthosilicate (Manning and Henderson 1984). In some runs also a more simple Qz-Ab composition was employed (Nekrasov 1984).

The oxides of the three elements were added to the starting materials as oxides with a variable oxygen ratio, e.g. SnO_2, SnO, MoO_2, MoO_3, WO_3, WO_2, or by using compounds including the oxides added. Metal-bearing compounds were also added as Na_2WO_4, Na_2MoO_4 or $CaWO_4$ mixed with granitic glass or gel or dissolved in aqueous fluids in equilibrium with granitic melts. Various solutions of water with chlorides, carbonates, borates, fluorides and phosphates were used to equilibrate with granitic melt in the studies of partitioning coefficients between the granite melt and a hydrothermal solution (Table 1). Repeated heating and grinding in some runs with a larger amount of starting materials and even the stirring of melts were used to obtain homogeneous glasses in dry experiments.

Experimental procedures and their limits

Two main experimental approaches have been used:

a) experiments in dry systems at high temperatures (1300 °C to 1600 °C)
b) hydrothermal experiments (commonly 750 °C to 850 °C) with controlled or uncontrolled oxygen atmosphere.

The experiments in dry systems are considerably hampered by the high viscosity of melts which is decreased at high temperatures. The viscosity is also lowered by the addition of alkalies or alkali silicates or alkaline compounds carrying the metal (e.g. Na_2WO_4 or Na_2MoO_4).

Equilibrium condition are estimated from the agreement of phase changes in phase diagrams and from the reversals of reactions fixing the phase transitions.

Hydrothermal experiments take advantage of the water effect which lowers the viscosity of granitic melts. The runs were carried out either as the transition of a metal from metal-enriched glass into metal-free solution (arrangement "from the glass") or vice versa (arrangement "from the solution") (Epel'baum 1988). Salova et al. (1989) suggest that the arrangement "from the solution" can give better results in the studies of Mo-containing granitic systems. A pioneer work on the solubility of zircon in granitic melts was done by Watson (1979) who used indirect methods to determine equilibria conditions when the reversal of zircon dissolution was found to be impossible.

In the lower temperature runs the analyses of quenched granitic glasses have been made either as bulk analyses or point analyses by electron or ion microprobe stating if the glass product was zoned or not. The large scatter of analytical results in some bulk composition and microprobe analyses has thrown doubts on the validity of conclusions about reaching equilibria in the runs (Manning and Henderson 1984; Epel'baum 1988). A compositional gradient was noted by Ryabchikov et al. (1981) who found the difference of 0.33 to 0.07% W in the distance of 10 to 50 μ in a granite glass at the contact with a scheelite grain. Candela and Holland (1984) reported

the lack of zoning in Mo contents in the glass-run products with a single exeption as studied by ion microprobe.

Epel'baum (1988) suggested using the metal concentration value in the surface layer of the glass product to eliminate the effect of zoning in measuring the partitioning coefficients in hydrothermal experiments. Liquid immiscibility in tungsten-bearing and molybdenum-bearing melt systems was observed in dry experiments (Štemprok and Voldán 1982, 1983) and in tin-bearing systems under hydrothermal conditions (Ryabchikov et al. 1978a). A significantly different tin content was found in immiscible silica-rich and silica-poor products of the system K_2O-Al_2O_3-SiO_2-FeO by Barsukov et al. (1983). All these data indicate considerable difficulties in reaching equilibrium mainly in the lower temperature runs and the need for a careful control of the homogeneity of the granitic glasses analyzed.

The valence state of metals

The valence state of metals in granitic melts has a certain effect on the solubility of metal oxides as demonstrated in tin-bearing systems by Nekrasov (1984) and in molybdenum-bearing systems by Tacker and Candela (1987). Sítek et al. (1981) reported some proportion of SnO component in granitic melts prepared in air, and Durasova et al. (1986) stated the equality of SnO and SnO_2 activities at the oxygen fugacities close to the quartz-faylite-magnetite buffer in the granitic systems examined. The effect of valency changes is little known for W and Mo cations. Therefore in the present work the data for W^{6+} and W^{4+} as well as for Mo^{6+} and Mo^{4+} are not differentiated. The difference between the solubility of Sn^{4+} and Sn^{4+} is, however, considerable and the present treatment considers only Sn^{4+} data in granitic systems.

Discussion of experimental data

Tin

The solubility data on tin dioxide measured in granitic melts at high temperatures (1300 °C–1600 °C) can be lineary extrapolated to the region of hydrothermal experiments. The actual data (Fig. 3) by Nekrasov (1984) and by Ryabchikov et al. (1978a, b) occur above and below the extrapolated line. This has the equation $\log C = 2.4 - 2.94 \times 1000/T$, and its intercept with the temperature axis *at 750 °C* has the solubility (C) value of *0.34* mass % SnO_2 and at 800 °C 0.46% SnO_2. This solubility line does not reach the values of tin dioxide solubility in the system $Na_2O - SiO_2$ (Štemprok and Voldán 1975), and it is higher than two values (0.9 and 0.4 mass % SnO_2) as found at 1180 ± 10 °C in immiscible melts of the system K_2O-Al_2O_3-SiO_2-FeO (Barsukov et al. 1983). None of these values approaches the amount of 30 ppm considered as an approximate average Sn content in tin-bearing granites in some metallogenic provinces and the measured values are about 100 × higher.
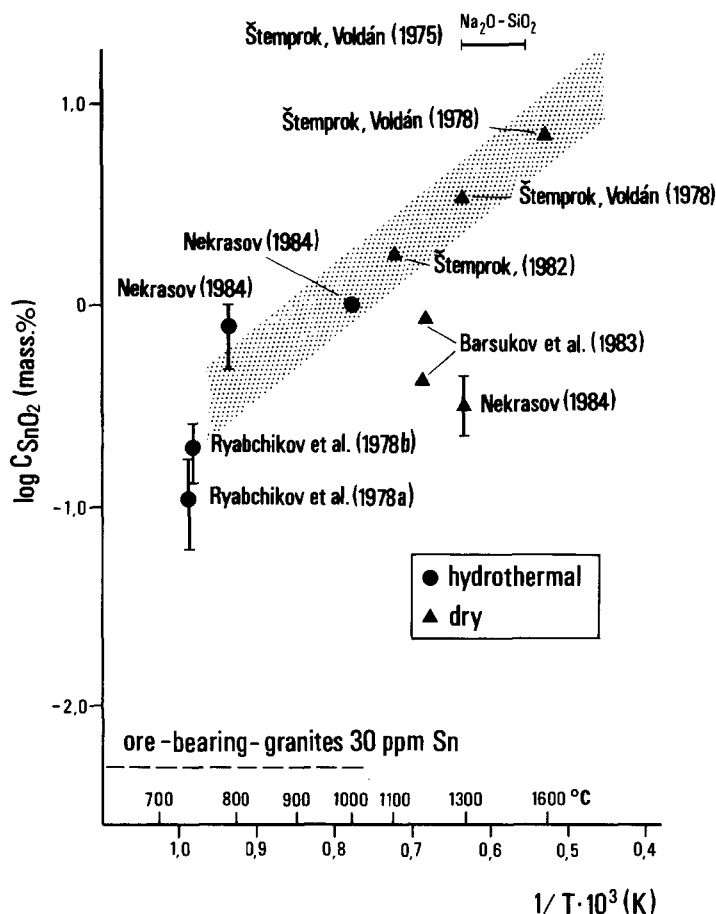
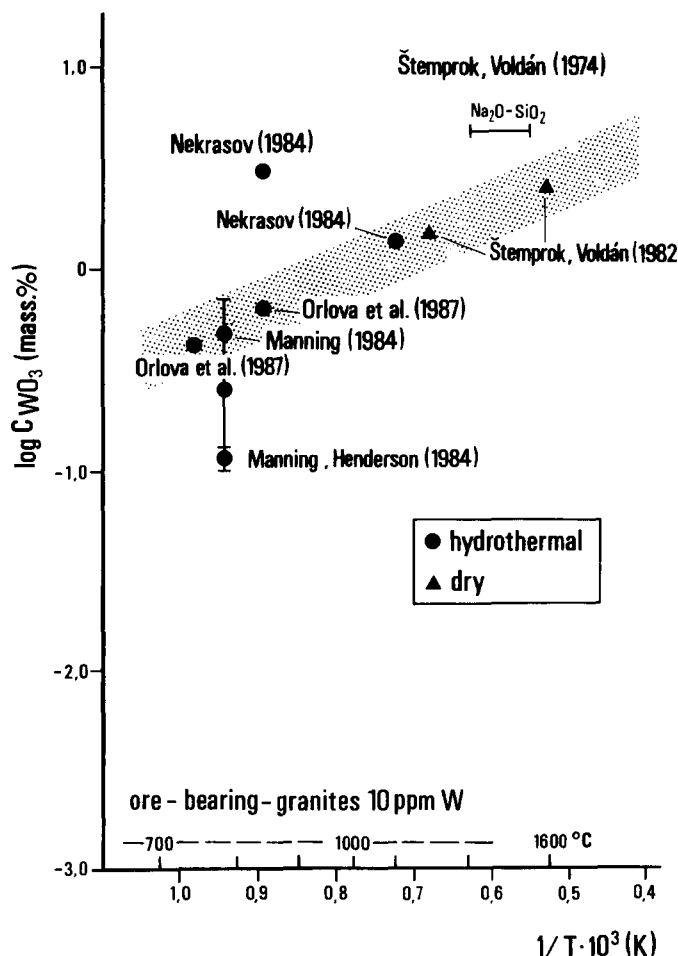**Fig. 3.** Solubility of SnO_2 in granitic melts: the comparison of the results of dry and hydrothermal experiments on SnO_2 solobility in granitic melts in log C vs. 1/T plot. The maximum solubility in the Na_2O-SiO_2 system is indicated. The source data are listed in Table 1. The line shows the extrapolation of dry experiments into the region of hydrothermal experiments. Arithmetic means of ranges of values are shown by points on the full lines

Fig. 4. Solubility of WO_3 in granitic melts. The comparison of dry and hydrothermal experimental data on WO_3 solubility in granitic melts in log C vs 1/T plot. The source data are in Table 1. The diagram shows the correlation of dry and hydrothermal experiments along a line obtained by extrapolation of dry experiments. Arithmetic means of ranges of values are shown by points on full lines. The maximum solubility of WO_3 in the Na_2O-SiO_2 system is shown for comparison

Tungsten

The data on tungsten solubility are in Fig. 4, which compares the results of dry and hydrothermal experiments. The binary system Na_2O-SiO_2 has a higher solubility of tungsten oxide than the granitic melt at the same temperature. The extrapolation of the data of dry experiments is consistent with the results of hydrothermal experiments as was pointed out by Manning and Henderson (1984) and Manning (1984). The intercept of the extrapolated line of the dry experiments gives at $750\,°C$ the solubility (C) value *0.48* mass % WO_3 and at 800° 0.57% WO_3. These values agree well with the experimental data of Orlova et al. (1987). The equation of the line is $\log C = 1.33 - 1.69 \times 1000/T$ and its slope is less steep than that of SnO_2.

Molybdenum

The data on molybdenum oxide solubility in granitic melts are compiled in Fig. 5. They exhibit a wide scatter in the low temperature region of the diagram which covers four concentration ranges. This scatter may be caused by the lack of equilibria in runs which is related to a low diffusivity of Mo in melts (Salova et al. 1989) or to undersaturation of Mo in granitic melts (Candela and Holland 1984). Highly Mo-enriched granitic glasses reported by Khitarov et al. (1982) are consistent with high molybdenum oxide solubilities in the system Na_2O-SiO_2 studied by Štemprok and Voldán (1974) and the values obtained in granitic glasses by Nekrasov (1984). The data by Candela and Holland (1984) appear reliable by the proof of the lack of zoning in the glass products of the runs. They are only about 10 times higher than are the contents of Mo in some ore-bearing granites.

However, the experiments by Candela and Holland (1984) were directed at the determination of the vapour-melt distribution coefficients in granitic systems and therefore they were performed at conditions well below Mo saturation.
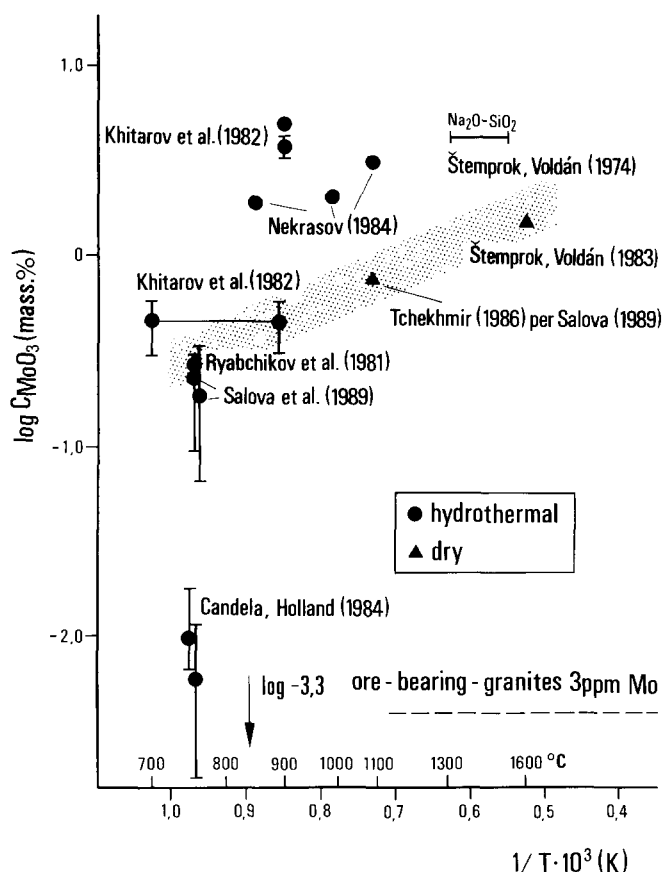
Fig. 5. Solubility of MoO_3 in granitic melts. The comparison of the results of dry and hydrothermal experimental data on MoO_3 solubility in granitic melts in log C vs. l/T plot. The source data are in Table 1. The diagram shows a wide scatter of experiments in the hydrothermal region and a considerable disagreement of dry hydrothermal experiments obtained by various authors. The points on full lines mark the arithmetic mean of ranges of results. The maximum solubility value of MoO_3 in the $Na_2O\text{-}SiO_2$ system is shown for comparison

association with Sn, W and Mo deposits are undersaturated with respect to Sn, W and Mo.

Cassiterite is the liquidus mineral of granites saturated with tin dioxide (Štemprok and Voldán 1978) and also of the binary $Na_2O\text{-}SiO_2$ system with SnO_2 added (Štemprok and Voldán 1975). Because of the much lower amount of Sn in the granites which are considered to be the products of magmatic crystallization (without a substantial effect of postmagmatic alterations) than is the saturation limit of SnO_2, primary crystallization of cassiterite appears very unlikely. Its existence should be expected only in highly evolved granitic residua.

The high tungsten trioxide solubility limits the probability for the primary crystallization of scheelite from granitic melts. This has been well demonstrated experimentally by Orlova et al. (1987). Liquid immiscibility of alkali tungstates from granitic melts appears to be improbable (Štemprok and Voldán 1983) and may exist only in highly specialized tungsten-rich granitic residua.

The considerable scatter of the solubility data of molybdenum trioxide indicates experimental conditions of undersaturation of granitic melts in molybdenum. However, the degree of undersaturation remains uncertain. The existence of molybdenite as a possible liquidus mineral in granitic systems is determined by the sulphur activity and Ryabchikov et al. (1981) calculated that the occurrence of primary molybdenite is theoretically justified at 750°C and 1.5 kb of total pressure with $XH_2S = 0.01$ mol.

The high solubility of cassiterite and scheelite in granitic melts eliminates these minerals from playing the role of restite minerals in the source regions of granitic melts. Cassiterite and scheelite, therefore, can be dissolved in fairly large amounts in anatectic melts produced from sediments which contained cassiterite and scheelite grains. These minerals might have played the role of restite minerals only at very high concentrations of SnO_2, WO_3 and MoO_3 in granitic melts which are comparable with the concentrations in economic mineral deposits (i.e. 0.3 and 0.5 mass % of the oxides.

The lack of a considerable difference between the results of hydrothermal experiments in the temperature range of 750°C to 800°C and 1.5 kb total pressure and the extrapolated data of dry experiments carried out in the range of 1300°C to 1600°C in air favour the explanation that OH groups are not important ligands of Sn^{4+}, W^{6+} and Mo^{6+} in granitic melts. These cations are surrounded by six oxygens (Štemprok 1989) and these octahedra units are probably copolymerized with silica-alumina structural units of the melt independently of OH groups. This is supported by the observation of Candela and Holland (1984) that in the molybdenum granitic system mononuclear complexes of Mo dominate in the melt.

Thus, the course of the ideal solubility line of molybdenum oxide in granitic melts in uncertain. The equation of the extrapolated line of dry experiments is $\log C = 0.98 - 1.52 \times 1000/T$ and its intercept with the temperature of *750°C* gives the solubility (C) value *0.32%* MoO_3 and at 800°C 0.37 mass % MoO_3 which is close to the solubilities found for SnO_2 and WO_3.

Geological application

The results of experiments on the solubility of tin dioxide and of tungsten and molybdenum trioxides in granitic melts indicate that they dissolve at maximum from 0.3 to 0.6 mass % of these oxides. This is 100 times to about 5000 times more than the average amounts of these elements in highly evolved ore-bearing granites. The values are also consistent with the data obtained by dry experiments and extrapolated to the lower, geologically realistic temperatures. Thus the granites even in a close spatial

Conclusions

The summary of the data on tin dioxide, tungsten trioxide and molybdenum trioxide saturation in granitic melts indicates that they can dissolve at maximum 0.34 mass %

SnO_2, 0.48 mass % WO_3 and 0.32 mass % MoO_3 at 750 °C and 1.5 kb total pressure. Granites even highly evolved do not reach these values and they are, therefore, undersaturated in these components. Cassiterite and scheelite are not the liquidus minerals of even highly evolved granitic compositions and consequently they are not the restite minerals of granitic residua of sedimentary origin. Such conditions could have been drastically changed in alkaline-rich residua from the crystallization of granites which may contain increased amounts of ore components (Štemprok 1984).

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Book review

Arno Mücke: Anleitung zur Erzmikroskopie, mit einer Einführung in die Erzpetrographie. Stuttgart: Enke, 1989, IX + 187 pp. ISBN 3-432-97861-8, DM 78,–, paperback

This book certainly fills a gap. It is a modern methodical introduction to ore microscopy, especially to *qualitative* methods of ore mineral identification, which seem to have been rather neglected in favour of quantitative optical methods and microprobe analysis during the last decades. The motto is well chosen: "Without a proper understanding and use of the microscope and microscopic methods, the most sophisticated investigation is for naught. Let us hope that this message will be noted and remembered!" (L. Cabri 1987). Apparently the last similar book was "Erzmikroskopisches Praktikum" by Hans Schneiderhöhn back in 1952.

According to the Preface, Mücke intends to teach the art of (qualitative) reflected-light microscopy including all the tricks, some of them developed by the author himself. Mücke stresses that besides reflectivity and microhardness, other neglected but reproducible properties can be helpful in the identification of ore minerals. In this respect, Chapters 5 to 8 are important: "Optical Effects of Reflected Light Using Polarizer Only" (23 pp.), the same "Using Crossed Polars" (23 pp.), "Additional Characteristic Properties" (12 pp.), and "Identification of Ore Minerals Using Qualitative Methods" (9 pp.).

Not only colour and reflectivity (= brightness) (Tables 1, 2 and 6) but also bireflection (= change of overall reflectivity during stage rotation) and reflection pleochroism (= change of colour with orientation; dispersion of the bireflection) are optical properties to be observed with the polarizer only (Tables 7 and 8), especially under oil immersion. The author strongly recommends that most ore microscopic studies be done under oil immersion, because the effects are generally much stronger than in air. The use of blue (p. 25) or green filters (p. 34) may be helpful.

Special emphasis is placed on the physical meaning of colours, i.e. on the combined effects of a white-gray-black component and "colour" s. str., which, for instance, leads to the effect that brown colours only occur at overall (white-light) reflectivities below about 27% (with "grey" as the "colourless" component of the reflected light – Table 1).

Provided the microscope is properly adjusted, optical effects under crossed polars can also be reproducible and thus be used for identification. Generally correctly crossed polars are necessary (Table 13), but also deviation from 90° between the polars (by, for example, 1° or 3° – Table 10) may be helpful if they cause special colour effects (Chapters 6.1.8, Table 14).

The tables mentioned may be used as identification tables for a number of important ore minerals; unfortunately there is no set of tables which would help in identifying *all* ore minerals by the methods discussed here. For identification by the quantitative properties, reflectivity and microhardness, the reader is referred to the various tables published since the first IMA-COM compilations, from Uytenbogaardt (1951) and Bowie and Taylor (1958) to Criddle and Stanley (1986). Mücke's book includes shorter chapters also on these quantitative methods as well as on the principal requirements and limits of qualitative and quantitative reflected-light microscopy. For further details on individual ore and gangue minerals, of course, Ramdohr's well-known textbook is the best reference.

In addition, the methods used for preparation of polished sections and in microscope photography are discussed briefly. Last but not least, Chapters 14 and 15 cover minerals intergrowths and their origin as well as the paragenesis of mineral which are important clues in "ore petrography". An appendix lists the minerals mentioned; 38 good colour photographs serve as illustrations to the various effects discussed in the text (unfortunately, there is no reference to them by minerals in the index), and an index of five pages by persons, subjects, and localities is provided.

The printing of this book is excellent and printing errors are very rare. The price is reasonable. The book is recommended to students and scientists active in reflected-light microscopy, especially to readers fluent in German. Translation into English should be considered, perhaps with the addition of identification tables.

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