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OXYGEN FUGACITY AND TIN BEHAVIOUR IN METALS AND FLUIDS

(Figs. 4, Tabs. 4)

Abstract: The paper presents experimental data on tin valence in magmatic phases and postmagmatic fluids at varied oxygen fugacities, as well as on tin behaviour during formation of immiscible liquids, fractional crystallization and magmatic distillation. Experimental data permit to describe tin behaviour throughout the development of magmatic and postmagmatic processes.

Tin occurring in typical magmatic settings is shows to be in two differing valence states, namely, Sn^{+2} and Sn^{+4}. Also described is the effect of redox conditions on the ratio of tin valence species in magmatic systems.

Oxygen potential buildup is identified as a factor accounting for an increase in the combined tin distribution coefficient in the course of crystallization differentiation and a drop in tin concentration observed in the resulting melt portions. When distillation is under way the increasing partial pressure of oxygen favours tin mobilization in the fluid phase in as much as the ratio Sn^{+4}/Sn^{+2} in melts is notably higher as compared to that in fluids of acidic composition given the conditions are similar with respect to f_{O_2}.

It is ascertained in the paper that under supercritical conditions it is the concentration of associated HCl, rather than free chloride ions, that controls tin concentration in the fluid, while the enhancing acid molality leads to generating Sn(II) chloride complexes at lower values of oxygen fugacity. It is thus concluded that the tin transfer by supercritical fluids at postmagmatic stage is largely due to neutral chlorine hydroxy and chlorine complexes of bivalent tin, with the contribution of fluorine complexes being rather limited.

Distribution pattern of tin valence species in magmatic phases and postmagmatic fluids is to a great extent responsible for migration paths and deposition of tin minerals.

Резюме: В работе представлены результаты экспериментальных исследований, направленных на выяснение валентного состояния олова в магматических фазах и постмагматических флюидах при различных летучестях кислорода, на изучение равновесий при ликвации, кристаллизационной дифференциации расплавов и дистилляции флюидов. Полученная физико-химическая информация позволила охарактеризовать поведение олова в ходе развития магматических и постмагматических процессов.

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Показана возможность присутствия олова в реальных магматических условиях в двух валентных состояниях Sn^{2+} и Sn^{4+}. Охарактеризовано влияние окислительно-восстановительных условий на соотношение валентных форм олова в магматических системах.
Установлено, что в ходе кристаллизационной дифференциации расплавов увеличение потенциала кислорода обусловливает рост комбинированного коэффициента распределения олова и снижение его концентраций в конечных порциях расплава. Повышение парциального давления кислорода способствует мобилизации олова во флюидную фазу при дистилляции в силу более высоких соотношений Sn^{4+}/Sn^{2+} в расплавах по отношению к флюидам кислого состава в близких по f_{O_2} условиям.
Показано, что именно концентрация ассоциированной HCl, а не свободного хлор-иона, определяет концентрацию олова во флюиде в надкритических условиях, и увеличение концентрации кислоты способствует образованию хлоркомплексов Sn (II) при меньших величинах летучести водорода. Сделан вывод о том, что перенос олова надкритическими флюидами на постмагматическом этапе осуществляется преимущественно нейтральными гидроксохлор- и хлоркомплексами двухвалентного олова при ограниченной роли фторкомплексов.
Особенности распределения разновалентного олова в магматических фазах и постмагматических флюидах во многом обуславливают пути миграции и отложения олова.

Forms of occurrence, mobilization and transport of ore elements varying in valence, tin included, in natural settings are mainly conditioned by the redox potential.

A series of runs has been carried out with the aim of evaluating the effect of oxygen fugacity on tin valence in melts and individual minerals, tin activity in melts, minerals and fluids as well as the effect of oxygen potential on mineral liquidus fields in basaltic and granitic systems. The experimental technique was described in published papers (Ryabchikov et al., 1978; Barsukov et al., 1983; Durasova et al., 1984 (1), 1984 (2)). It should be noted that the tests both in "dry" systems and in those with volatile components were run under appropriate redox conditions. In the course of experiments targetted at determination of tin valence by Mössbauer spectroscopy technique the tin compounds entered into initial charges were of 80 % enrichment with respect to ^{119}Sn isotope. Mössbauer spectra were gained on spectrometer of NZ type made in Hungary. Conditions of determination are given in the paper Barsukov — Durasova et al., 1983.

In this paper the results of experimental studies are considered with the attention focused on the data referring to the tin valence identification in the basaltic melt at different oxygen potentials. Plotted in Fig. 1 is the relation of Sn^{+2}/Sn(total) and oxygen fugacity defined by the MC technique for the range of study. The information obtained testifies to a possible contribution of stannous species along with stannic ones in magmatic systems.

Experimental data on Fe_3O_4—SnO_2 system are of particular interest from the geochemical point of view, owing it to the fact that magnetite crystallizing under a wide range of thermodynamic conditions is one of the most abundant accessory minerals in magmatic rocks and in many cases one of the minerals acting as tin concentrators. These studies provide ground for defining SnO_2 solubility in magnetite and the effect of oxygen potential and temperature on the attained equilibrium. Fig. 2 shows an increase in the solubility in

magnetite related to increasing temperature and decreasing oxygen potential. It has been determined by Mőssbauer spectroscopy technique that within the given range of f_{O_2} the tin admitted into magnetite structure is tetravalent and replaces iron in octahedral positions. The obtained data clarify that magnetites of magmatic provenance with a tin content hardly amounting to several hundredths of a percent (L y a c h o v i c h, 1973) are far from being tin saturated, it is most probable the state of tin existing in the mineral is isomorphous.

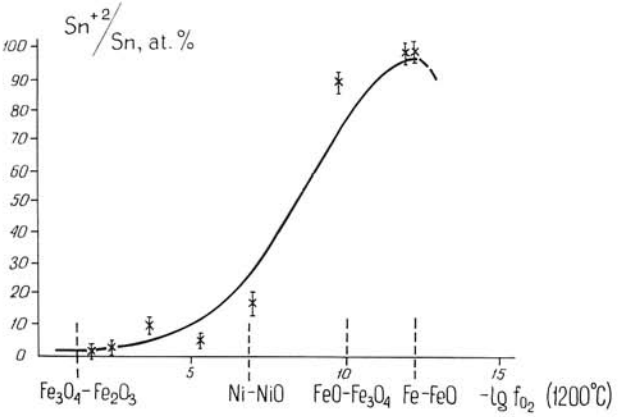

Fig. 1. Tin valence in hawaiite at different oxygen fugacities.
Note: Published oxygen fugacities for the given buffers correspond to 1227 °C, for details see D u r a s o v a et al., 1984.

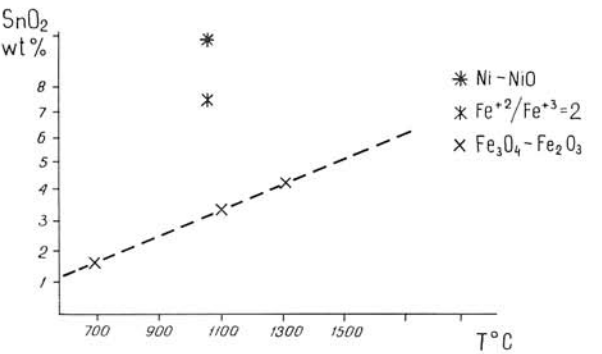

Fig. 2. Tin solubility in magmatite related to the oxygen potential and temperature.

While studying tin distribution in the course of basaltic melt crystallization at different values of oxygen fugacity we formulated a certain relationship which is largely due to alterations of phase composition following changes in redox conditions. Under reduction conditions, provided the f_{O_2} values are close to or under those of Ni-NiO buffer, plagioclase containing low concentrations of tin crystallizes thus enriching the melt with this element (Tab. 1). As

Table 1

Content and distribution coefficient of tin in different phases of hawaiite

phase	$-\lg f_{O_2} = 2.2 - 3.5$		$-\lg f_{O_2} = 6.0 - 11.8$	
	"SnO_2", wt. %	$K^{phase}/glass$*	"SnO_2", wt. %	$K^{phase}/glass$
glass	0.70 (0.55–0.80)		1.02 (0.92–1.13)	
plagioclase	0.04 (0.01–0.07)	0.05± 0.04	0.04– < 0.01	< 0.04
magnetite	0.72 (0.67–0.78)	1.00± 0.40		
titanic iron oxides	3.30 (2.10–4.50)	4.70± 3.30		

*) $K^{phase}/glass$ – coefficient of tin distribution in phases (plagioclase, magnetite and titanic iron oxides) and glass.

it has been said earlier, in this process tin is predominantly bivalent: Sn^{+2}. If the conditions are defined by elevated oxygen fugacities, along with plagioclase precipitated in the melt are magnetite and titanic iron oxides. The tin content in the minerals is rather high and the tin concentration in resulting melts lowers but insignificantly (Tab. 1). The cited data on Sn valence in the hawaiite melt and magnetite at given values of f_{O_2} provide a sound basis for concluding that the preferential species of tin is tetravalent one.

A series of runs on studying the effect of oxygen fugacity within the fields of tin and iron mineral's crystallization in the system granite-Sn-Fe-O-H has yielded information that allows to conclude that at relatively oxidation conditions which are close to or over f_{O_2} of Ni-NiO buffer, the tin solubility in silicate liquid drops two times as compared with the one typical of lower oxygen potentials (wustite-magnetite buffer) (Ryabchikov et al., 1978).

It is inferred from these data that at equal total tin concentrations in granitic magma an increase in oxygen fugacity facilitates the attainment of saturated conditions with respect to cassiterite.

We shall now consider the results gained in tin distribution studies for liquation in the system of K_2O-Al_2O_3-SiO_2-FeO at controlled oxygen potentials (Barsukov et al., 1983). Tab. 2 shows tin activity values in aluminosilicate melts contrasting with respect to FeO and SiO_2, distribution coefficient $K^{acid/base}$[1] is calculated equal to 0.4. Both tin and iron appear in the bivalent form (Sn^{+2} and Fe^{+2}).

[1] $K^{acid\ base}$ corresponds to $K^{matrix/globules}$.

[2] K^{C}_{Sn} — the combined coefficients for the partition of tin.

Table 2

Composition of phases under liquation

phases wt. %	SiO_2	FeO	K_2O	Al_2O_3	"SnO_2"**)	NBO*)/T
globules	46.1	44.2	2.9	5.9	0.9	1.33
matrix	70.0	13.5	4.0	6.9	0.4	0.54

*) Ratio of non-bridging oxygens and tetrahedron cations.
Error of determination: SiO_2 – 10 %, FeO – 10 %, K_2O – 30 %, Al_2O_3 – 15 %, SnO_2 – 30 %.
**) Tin concentrations are given in recalculation to "SnO_2" in wt. %. According to MS data, tin is present in the melt in form of Sn^{2+}.

Table 3

Coefficients of tin distribution between the fluid and melt

	K[1]	T°, C	P	f_{O_2}	composition of melt	composition of fluid
***	0.02	850	100 Mpa	10^{-13} (Ni–NiO)	granite (Na)	H_2O
***	0.005	–"–	–"–	10^{-17} (FeO–Fe_3O_4)	–"–	–"–
***	0.0004	1300	–"–	10^{-5} (Ni–NiO)	basalt	–"–
***	0.0001	–"–	–"–	$10^{-8.6}$ (FeO–Fe_3O_4)	–"–	–"–
**	0.2	750	150 Mpa	Ni–NiO	granite (eutectic)	1 normal by Cl pH – 3
*	0.02	1055	100 Mpa	Ni–NiO	basalt	was not determined

*** Data from (9), duration is not indicated; ** data obtained by the authors, test period is 12 days (Ryabchikov–Durasova–Barsukov, 1984); * data yielded by the analyses of the Eldfell eruption products (Durasova–Barsukov–Vakin et al., 1982).
[1] Coefficient K correspond to $K^{\text{fluid melt}}_{Sn}$.

Before passing to the consideration of oxygen potential effect on tin transfer from melt into fluid phase in the process of distillation and the analysis of experimental results (Nekrasov, 1984; Ryabchikov et al., 1984) it should be noted that the processes in question are rather complicated in kinetics. The values of tin distribution coefficients for fluid-melt systems cited in Tab. 3 are to be regarded as approximate and optimal. Nevertheless there are sufficient data to deduce that the oxygen potential build up is a factor intensifying tin release into magmatic fluid phase.

Earlier reports on tin distribution between magnetite and aluminosilicate melt of K_2O-Al_2O_3-SiO_2-FeO composition are rather convincing as regards the possibility of using the distribution coefficient values inferred from the experiments when analysing natural magmatic systems (D u r a s o v a et al., 1985).

Now we shall discuss tin behaviour in the evolution process of natural magmas making use of the data obtained in investigations and analyses of tin content in phenocrysts and the groundmass of effusives of varied compositions as applied to the range of typical oxidation-reduction conditions in natural magmas. The problem we are interested in is the effect of f_{O_2} on the value of bulk K distribution coefficient of tin when the basaltic magma crystallization is under way. It is confirmed experimentally that at relatively low f_{O_2} ($\leqslant f_{O_2}$ Ni-NiO) the tin concentration, with bivalent tin being predominant, increases but slightly in the melt and tends to drop at elevated f_{O_2} ($> f_{O_2}$ Ni-NiO). From the evaluation of K^{C}_{Sn}[2] which is equal to 0.6 for natural hawaiite lavas erupted by the Eldfell volcano and has been calculated on the basis of determined Sn contents in olivines, plagioclases, groundmass and quantitative mineral ratio (G e r a s i m o v s k y et al., 1978; J a k o b s s o n, 1975) at oxygen potentials corresponding to Ni-NiO, Fe_2SiO_4-Fe_3O_4-SiO_2 buffers (B a r s u k o v et al., 1986), it follows that residual melts of acid cmoposition should turn out somewhat enriched in tin. This is exactly what is observed in acid rocks of differentiated series in Iceland (G e r a s i m o v s k y et al., 1978).

In case of the formation of immiscible liquids in acid rocks at low f_{O_2} which is possible in nature and was actually observed during the study of Earth's and Moon's samples (R o e d d e r — W e i b l e n P. W., 1970; D e, 1974), the late stage of basic magma differentiation may involve generation of acid magma which is according to the experimental data about two times impoverished in tin as compared to coexisting more basic melts and distribution coefficient of Sn (fluid melt) must be higher in acid systems, which confirms to the above said.

The present paper does not touch upon chemical aspects of granitic melts' effect on Sn behaviour in the course of differentiation. These data have been reported earlier (R y a b c h i k o v et al., 1984). The only observation to be made is that from the point of view of intensive tin accumulation in melts undergoing the process of crystallization differentiation, most promising are low-calcium anatectic granites as well as low iron concentrations and low values of oxygen fugacity throughout the crystallization, which is supported by experimental data. Increasing oxygen fugacity extends crystallization fields of iron bearing minerals, magnetite, etc., which is rather significant in controlling tin behaviour in acid magmas. This latter fact is explained on the basis of the obtained and reported data (D u r a s o v a et al., 1984 (2); L y a c h o v i c h, 1973) indicating that these phases in most cases turn out to be main tin concentrators in granitoids. Thus, iron concentration in granites, crystallization time of iron bearig minerals and tin valence (primarily controlled by f_{O_2}) are to condition the final melt's enrichment or impoverishment in tin and the possibility of cassiterite formation at the magmatic stage.

The calculated from experimental data distribution coefficient of Sn between the fluid and melt indicates that the increase in oxygen potential is a factor favouring tin mobilization into fluid phace. Along witth f_{O_2} $K^{Fl/L}_{Sn}$ increaces both in granitic and basaltic systems, remaining lower for the latter ones.

Given in Tab. 3 is the value of $K_{Sn} = 0.02$ calculated from the data on metal bearing capacity of products erupted by the volcano Eldfell (gaseous and solid components) at f_{O_2} values corresponding to those of nickel-buneenite and quartz-fayalite-magnetite buffers (Barsukov et al., 1986; Durasova et al., 1982). This value is an order of magnitude lower than the experimentally defined one in the system fluid/melt of acid composition at f_{O_2} corresponding to the Ni-NiO buffer.

With the aim of describing particular features of tin behaviour in supercritical fluids under differing oxidation-reduction conditions, cassiterite has been studied through experiments as to its solubility in aqueous solutions of HCl and HF at T° = 500° and P = 100 MPa, with oxygen fugacity values being controlled (Ni/NiO and MnO_2/Mn_2O_3 buffer) (Kovalenko et al., 1986_1, Kovalenko et al., 1986_2). Tin content in aqueous solutions was determined by atomic absorption technique. Measurements of the ratio Sn(II) and Sn(IV) in the analysed solutions employed the elaborated technique of division and semi-quantitative determination of Sn(II) and Sn (IV) in a thin layer of sorbent (Kitayeva et al., 1985). The experiments have clarified that cassiterite solubility and tin valence in aqueous fluid are mainly conditioned by the medium's oxidation-reduction potential. Under reduction conditions with Ni-NiO as a buffer (lg $f_{H_2} = 0.24$) at a value of oxygen fugacity close to the one descriptive of most igneous rocks and hydrothermal deposits (after Ryabchikov (1975), it ranges from lg $f_{O_2} = -24$ ($f_{H_2} = 6.31$) to lg $f_{O_2} = -20$ ($f_{H_2} = 0.06$)), in fluids equilibrated with cassiterite tin is preferentially bivalent, while under oxidation conditions with MnO_2/Mn_2O_3 buffer it is mainly tetravalent.

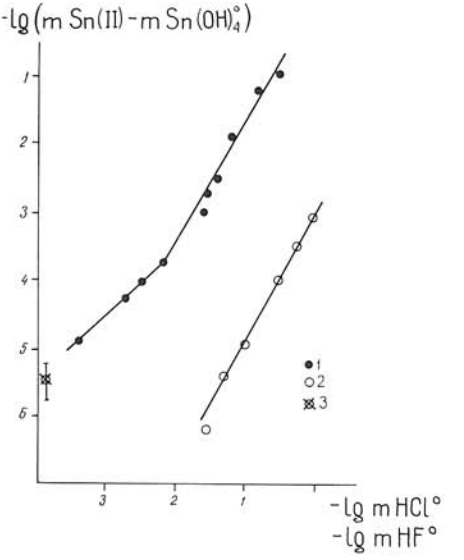

Fig. 3. Solubility of cassiterite vs. HCl° (1) and HF° (2) molality for the case of Ni-NiO buffer, (3) — cassiterite solubility in water.

Analysed thermodynamically the experimental data show (Fig. 3) that with Ni/NiO buffer and within a range of HCl molality of 0.001 m to 0.01 m the cassiterite solubility is defined by

(1)

$$SnO_2(cryst.) + H_2(gas) + HCl^\circ = SnOHCl^\circ + H_2O$$

whereas for HCl molality in the domain of 0.01 m to 0.5 m the predominant equilibrium is described as

(2)

$$SnO_2(cryst.) + H_2(gas) + 2HCl^\circ = SnCl_2^\circ + 2H_2O$$

In HF solutions ranging in molality from 0.05 m to 0.75 m, the fluid is dominated by SnF_2° complex:

(3)

$$SnO_2(cryst.) + H_2(gas) + 2HF^\circ = SnF_2^\circ + 2H_2O$$

HCl and HF molecules participate in SnO_2 solving reactions in acidic chloride and fluoride solutions which is consistent with the concept of predominating, under the given experiment parameters, non-dissociated HCl and HF molecules in conformity with dissociation constants of these acids.

With MnO_2 Mn_2O_3 buffer ($f_{H_2} = 8 \cdot 10^{-12}$) the prevailing equilibrium in the SnO_2-H_2O-HCl system is of the form

(4)

$$SnO_2(cryst.) + 3HCl^\circ = SnOHCl_3^\circ + H_2O$$

(5)

$$SnO_2(cryst.) + 4HCl^\circ = SnCl_4^\circ + 2H_2O$$

whereas in the SnO_2-H_2O-HF system within the range of considered HF molalities and at the given experiment parameters, Sn(IV) does not form any considerable amount of fluoride complexes and the cassiterite solubility does not exceed its solubility in pure water.

On the whole cassiterite solubility under reduction conditions (Sn II) is 1.5—2 orders higher than the one shown under oxidizing conditions (Sn IV) in acid solutions with equal pH, while the solving power of hydrochloric acid solutions with respect to tin is appreciably higher than that of fluorine bearing solutions (Tab. 4). Fig. 4 shows that HCl molality and oxygen fugacity initiating the formation of Sn complex Sn(II) are related in inverse proportion.

Now we shall proceed to analysing the supposed pattern of tin behaviour as an element of varying valence in natural postmagmatic processes making use of the data obtained. The analysis of bulk distribution coefficients of tin between the crystallizing minerals and coexisting melt in ongonites, as well as the equation from (Ryabchikov et al., 1978) and mean coefficients of tin distribution between the fluid and melt provided a basis for predicting (Antipin — Kovalenko, 1981) the tin possible transfer into the fluid in considerable amounts which may occur at the end of crystallization process of acidd tin-bearing melts. Tin concentration in such a fluid is estimated at 0.05 wt % (about 500 ppm) which conforms to the experimental evaluation given earlier. From the experimental data offered in Tab. 4 such a high tin concentration in fluids is attained through the effect of 0.05-m HCl solutions which is not the case with the studied range of HF molalities. Considering Fig. 4 it should be noted that the increasing acid molality favours the formation of fluoride complexes Sn(II) in fluids at lower values of oxygen fugacity. While at the level of oxygen fugacity created by Ni NiO buffer the Sn(II) complexes are predominant through the whole range of HCl molalities, the oxygen fugacity

Table 4

Experimental data on SnO_2 solubility in HF and HCl solutions at 500 °C, 1000 atm, Ni/NiO buffer

m HF, HCl	tin concentration, ppm	
	in HF solutions	in HCl solutions
H_2O	0.43	0.43
0.01	0.42	26
0.03	0.51	154
0.05	0.94	380
0.1	1.66	1780
0.3	1.42	7003
0.5	45.1	12345
0.75	102.08	—

The cited values are means from 2–4 tests.

close to magnetite/hematite buffer (lg f_{H_2} = —2.25) presupposes the existence of Sn(II) complexes only in 0.05-m solutions of HCl and the analysis by a thin-layer chromatography technique indicates that both Sn(II) and Sn(IV) species are present. Oxygen fugacity corresponding to the buffer association magnetite/hematite seems to be the boundary value which if exceeded means that the solution is abundant in tetravalent tin; consequently, SnO_2 solubility in the fluid drops in value and the emerging conditions lead to the formation of a separate cassiterite phase. It is not accidental that, for example, at Industrialny Deposit (N a u m o v — S o k o l o v, 1981) the earliest within the deposit ore-barren zones of tourmalinization with quartz, fluoride and magnetite are replaced by ore zones of chloride-sericite with cassiterite and hematite. On deposits of quartz-cassiterite (greisen) and silicate-cassiterite ore formations the relationship between ore mineralization and granitoid magmatism is well pronounced;

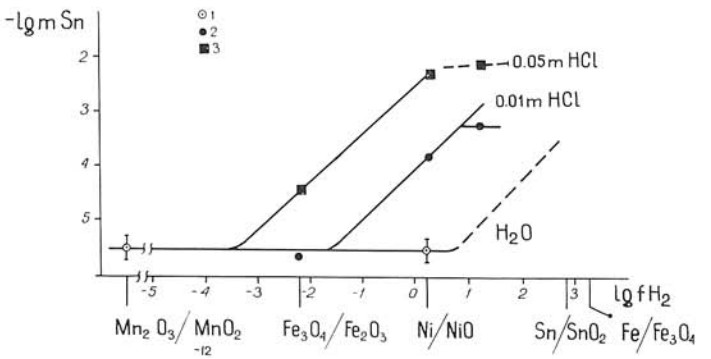

Fig. 4. Tin concentration vs. oxygen fugacity.
Explanations: tests with H_2O, 2 — tests with 0.01-m HCl, 3 — tests with 0.05-m HCl.

recognized as widely occurring are areal processes of metasomatic transformation of ore-bearing rocks subjected to the effect of acid fluids with a contributing action of chlorine, fluorine and boron, the ratio of these latter determining the type of ore mineralization. Emphasis should be made on the fact that tin concentration in a fluid is determined by HCl molality and not by free chloride ions. The HCl molality is controlled by entering basic metal chlorides into the system. The introduction of basic metal chlorides into the hydrochloric acid solution in quantities compatible with those determined in inclusions of mineral forming media (up to 4-m NaCl or KCl solutions) (Kovalenko et al., 1986_1) enhances pH of experimental solutions to approximately 4.5—5 which is rather close to the values measured in natural hydrothermal solutions (Barsukov, 1974).

I. D. Ryabchikov (1975) restricts the $pH^{25\,°C}$ value of solutions in the granite contact zone at T° = 720—770 °C and P = 100 MPa to a range of 0 — 1 and further points out that in case of a pressure drop (as is observed in volcanic gas, for example) chlorine is not transported by metal chlorides but preferably by HCl. We cannot rule out the possibility that at hypabyssal conditions typical of hydrothermal formation of most tin deposits, the fluids contain hydrochloric acid which seems to be difficult to identify in the inclusions of mineral-forming media because of its low molality. This explaines, to a certain extent, wide variations (from 8 to 60 mass % of equiv. NaCl) at chloride concentrations in fluids of ore deposits (Kovalenko — Naumov — Bogatikov, 1984) as they do not control the tin-ore load of fluids. Thus, in high temperature aqueous fluids under the conditions similar to those simulated in the experiment, tin is likely to be transported in the form of chlorine hydroxide and chloride complexes of bivalent tin, rather than in SnF_2° complexes.

The obtained data prompt the conclusion that under magmatic conditions tin may occur in the form of two species of different valences and describe thoroughly the effect of oxidation-reduction conditions on the ratio of tin species as well as the tin behaviour in the course of melt crystallization and fluid distillation. The increasing oxygen potential leads to an increase in the distribution coefficient of tin and a drop in its concentration in the final portions of the melt, but at the same time it contributes to tin mobilization into the fluid phase when distillation is in process. This regularity may be accounted for by the fact that the ratio Sn^{+4}/Sn^{+2} in melts is appreciably higher than in fluids of acid composition, f_{O_2} conditions being much the same. The form of tin occurrence and concentration in magmatic phases and postmagmatic fluids is largely responsible for further paths of its compounds' migration and deposition.

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