

THE MASS-BALANCE IN FLUID-MELT DISTRIBUTION OF CHLORINE AND SOME ORE-FORMING ELEMENTS (Zn, Pb) DURING GRANITIC MAGMAS DEGASSING

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The exsolution of magmatic fluids from granitic magmas at their rising to the surface and crystallization is one of the most important factors in lithospheric rocks alteration and generation of metalliferous hydrothermal systems genetically related to granitic magmas. The chlorine capability to form stable complexes with Zn, Pb, Cu, Sn and some other ore and trace elements in aqueous solutions determines its key role in the extraction of these elements from magmatic melt and their transportation by high temperature fluids. This publication presents numerical simulation results of Zn and Pb behavior during the degassing of H₂O- and Cl-bearing granitic magmas that permits to make quantitative estimations of Zn and Pb extraction scales from magmas depending on (1) the pressure of melt saturation with the volatiles, (2) the crystallization degree and (3) dynamics of fluid phase escape from magmatic system. The computer model based on experimental data generalization takes into consideration: a) the dependence of fluid-melt distribution coefficients for Cl, Zn and Pb from pressure and Cl concentration in the system; b) the possibility of fluid phase heterogeneity, i.e. its dividing into essentially aqueous (aq) and Cl-rich liquid (lq) phases in wide range of PTX conditions [1-3]. The calculations of Cl, H₂O, Zn, Pb distribution between fluid, crystals and melt in the process of degassing were conducted for the systems with varying degree of magmatic system openness.

The compositional variation of the fluid phase at nearly isothermal decompression-assisted degassing of magmatic melts is characterized by one general trend being independent of degassing depth and the degree of system openness. First deepest portions of fluid phase have the most high concentrations of chlorine and Zn and also Pb. For instance, Cl, Zn and Pb concentrations in the earliest fluid fraction generated by the rising melts that contain initially 0,2 wt.% of Cl, 5.5-5.7 wt.% of H₂O and 100 p.p.m. of both metals and start degassing at the depth corresponding to the pressure of 2-3 kbar may reach accordingly 4-6 m and 1200-1500 and 400-900 p.p.m. The drop of pressure causes the decrease of all these values. They decrease especially abruptly at open conditions when exsolving fluid can escape from magmatic system. Our balance calculations show, that a major part of ore-forming elements is extracted from magma at the earliest (i.e. deepest) stages of decompression-assisted degassing.

This can be illustrated by the case of decompression-assisted degassing, beginning at pressure of 3 kbar, shown on the fig.1. The Zn amount extracted from the melt by separating fluid at the earliest stages of degassing caused by the pressure drop from 3,0 to 2,5 kbar put together > 45% of its total quantity, that can be exsolved in the process of magma rising to the surface (pressure from 3,0 to 0,5 kbar). The amount of Pb, scavenged under the same conditions exceeds 70 wt.%. For the melts with equal H₂O content and ore-forming metals concentration, extraction degree of the metals is proportional to Cl concentration and accordingly to the Cl/H₂O ratio.

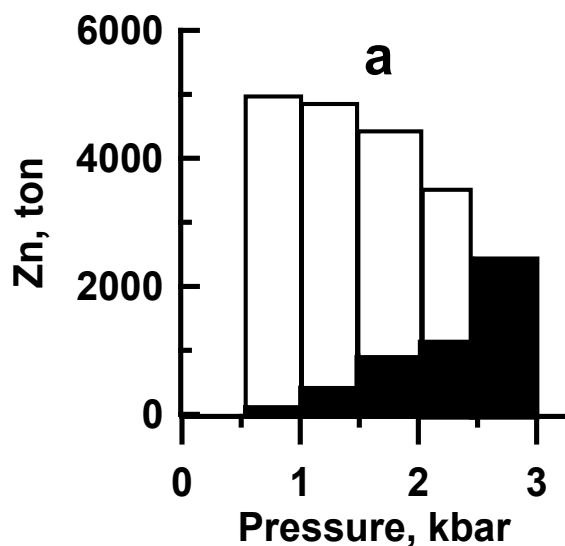
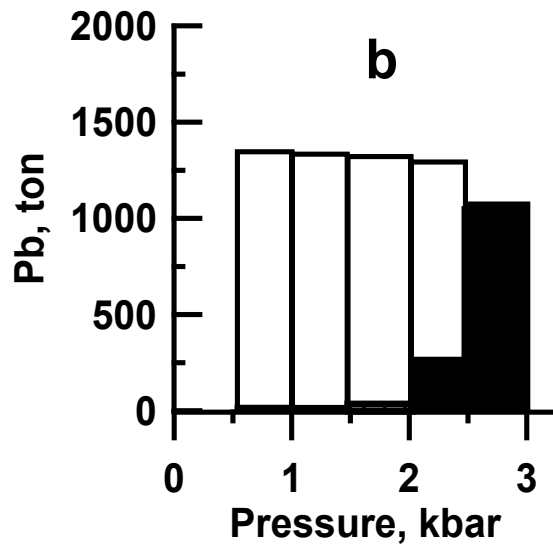


Fig.1. The amounts of Zn (a) and Pb (b) extracted by fluid phase in the process of decompression-assisted degassing of granitic melt at open conditions. Numerical simulation results for the melt with mass of 2.3×10^9 t (10^6 m³ by volume), containing 7.5 wt.% H₂O, 0,2 wt.% Cl and 100 p.p.m. Zn and Pb are shown. Solid rectangles represent the metal amount, exsolved together with the fluid by pressure drop of ~ 0,5 kbar. The light rectangles show the total amount of metal, extracted from the melt at corresponding stage of its rising to the surface.



In the case of isobaric *crystallization-assisted degassing* the changes of chlorine and metals concentrations are essentially determined by pressure (depth) during crystallization, by value of the bulk coefficient crystals-melt distribution of metals $D(\text{Me})_{s/m}$ and by the degree of system openness. The crystallization-assisted degassing of fluid saturated melt at high pressures ($> 1,5 - 2,0$ kbar) is characterized by decrease of the Cl, Pb and Zn concentrations in fluid. The concentrations are decreased especially abruptly in open conditions. The higher $D(\text{Me})_{s/m}$ value is the faster is the decrease of ore-metals concentrations in the fluid. The major part of ore-forming element is extracted at the earliest stages of degassing in both cases (crystallization - and decompression-assisted degassing). Fig.2

illustrates the case of crystallization-assisted degassing of the melt containing initially 0,2 wt.% of Cl, 5,8 wt.% of H_2O and 100 p.p.m of ore metal at pressure of 2 kbars. The fluid phase exsolved from magma after crystallization of 20% of the melt extracts $\sim 50\%$ of Zn and $> 75\%$ of Pb assuming the total amount of these metals is the amount that fluid is capable to scavenge from magma at its full ($> 90\%$) solidification.

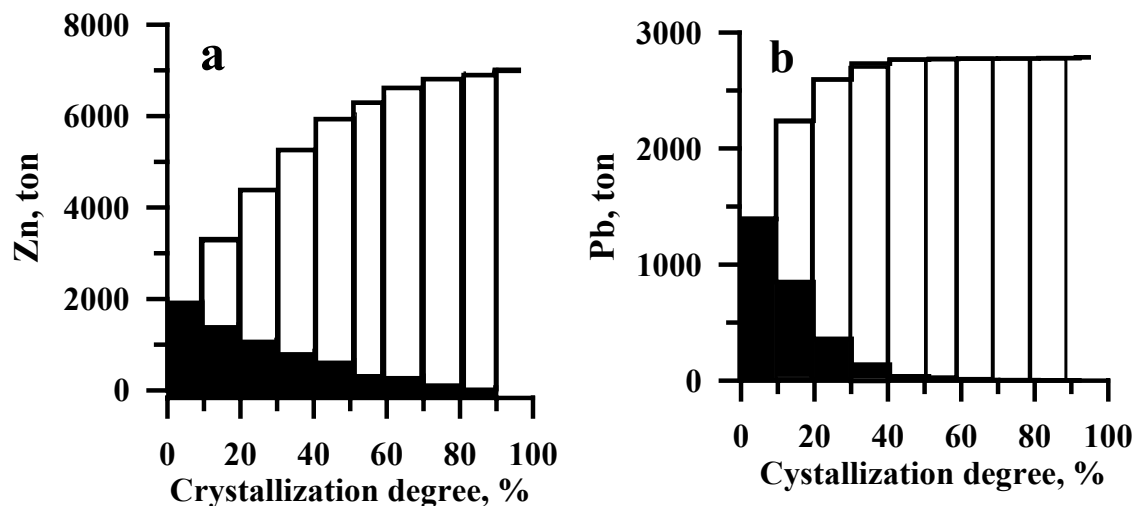


Fig.2. The amounts of Zn (a) and Pb (b) extracted from granitic melt in the process of its crystallization-assisted by degassing under open conditions at 2 kbar. The results of numerical modeling for the melt with mass of 2.3×10^9 t (10^6 m³ by volume) containing initially 0,2 wt.% of Cl, 5,8 wt.% of H_2O and 100 p.p.m. of each metal (Zn and Pb) are shown. Calculations were performed assuming that $D(\text{Zn})_{s/m} = 0,6$ and $D(\text{Pb})_{s/m} = 0,7$. The solid rectangles show amount of metal, exsolved by the fluid phase at 10% crystallization. The light rectangles show the total amount of the metal separated at this crystallization stage.

The character of ore-forming elements behavior at the shallow depth degassing ($P < 1$ kbar) is essentially changed as compared with that occurring at high pressure conditions. Cl and ore-forming elements concentrations in the fluid are increasing in the process of crystallization both at closed and open conditions. In this case each subsequent portion of separated fluid phase is characterized by higher capacity to scavenge the metals from magma. The progressive increase of Cl-content in fluid may lead to its heterogeneity (appearance of two coexisting phase $\text{aq} + \text{lq}$) at certain crystallization stage. The partition coefficients of Zn and Pb between chloride-rich liquid (lq) and acid silicic melt $D(\text{Me})_{\text{lq}/\text{m}}$ are roughly one order of magnitude higher than that of the same elements between aqueous vapor phase (aq) equilibrated with the lq and the same melt $D(\text{Me})_{\text{aq}/\text{m}}$. That is why with appearance of lq at open condition degassing we have abrupt increase in the concentration values of these elements

in fluid and accordingly in its ore-carrying potential. But with progressive increase of crystallization degree at open conditions ore-forming metals concentrations stop to grow and even turn to decrease. By this, the metal extraction degree on each subsequent crystallization stage remains nearly constant or even decreases. Fig 3. demonstrates the change of Zn amounts extracted at different stages of granitic melt crystallization at 0,6 kbar in open conditions, when all of exsolving fluid escapes from the system. At nearly 50% crystallization degree the heterogenization of the fluid phase takes place. The appearance of chloride rich brine leads to the abrupt increase of Zn extraction level although at each subsequent crystallization stage it remains roughly unchanged.

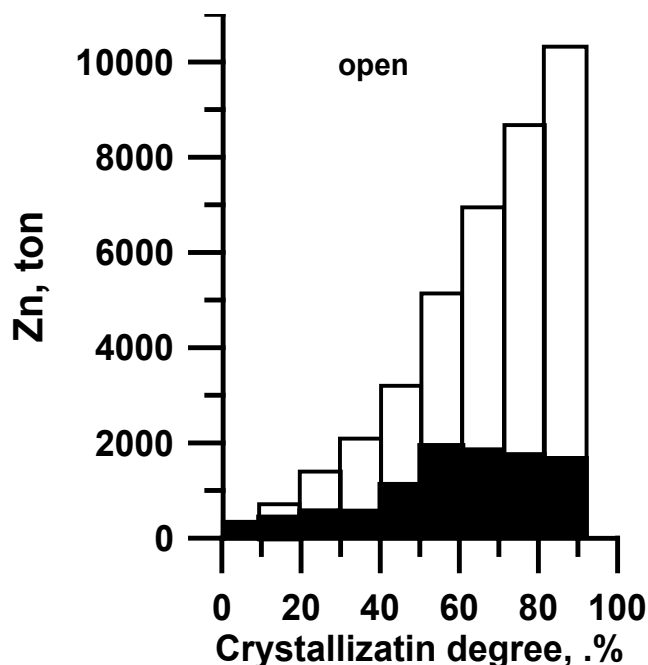


Fig. 3. The amount of Zn extracted by the fluid phase in the process of granitic melt crystallization-assisted by degassing at 0,6 kbar in open conditions. The initial melt with mass of 2.3×10^9 t contains 0,15 wt.% of Cl, 2,9 wt.% of H_2O and 100 p.p.m. of Zn. The values of $D(Zn)_{s/m}$ and $D(Zn)_{lq/aq}$ are equal, accordingly, to 0,6 and 10. The other symbols are the same as on the fig 2.

Analyzing the process of granitic magma degassing we can distinguish two the most favorable conditions for the formation of magmatic fluids with high chlorine and ore elements concentrations, that are able to extract significant amount of metals from granitic magmas. The first are the earliest stages of melt degassing caused by its rise to the surface and crystallization (at $P > 1,5-2,0$ kbar). The second one is magma crystallization at shallow depth ($< 1,0$ kbar) that may be accompanied with the formation of metalliferous hypersaline brines. The numerical simulation results determine the maximal amounts of ore-forming metals that may be extracted from magma during its degassing. They confirm statement that the quantities of ore-forming metals, extracted by magmatic fluids from granitic intrusions with initially Clarke concentrations of Zn and Pb may be quite sufficient for the formation of very large ore deposits [4 and others]. At the same time it should be noted that the total amount of extracted ore-forming elements is essentially dependent upon two factors: firstly, from volatile components concentrations (mainly from Cl concentration for such elements as Zn and Pb), secondly, from the concrete mechanism of fluid phase separation from magmas during its degassing. It is possible to draw general conclusion that so called "geochemical specialization of magmas" e.g. their capability to be the ore-forming components source for ore deposits is determined rather by initial content of volatiles and dynamics of fluid phase separation from magma in the process of degassing during its rising to the surface and crystallization than initial ore elements content in magma.

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