

The influence of Cl concentration and pH on solubility and species of Zn and Pb in water-chloride fluids at *T-P* parameters of granitoidic magmas degassing

O. A. Lukanin, N. A. Kurovskaya, B. N. Ryzhenko
 V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry RAS, Moscow
lukanin@geokhi.ru

Key words: zinc, lead, water-chloride fluid, granite magma degassing.

Citation: Lukanin O. A, N. A. Kurovskaya, B. N. Ryzhenko (2011), The influence of Cl concentration and pH on solubility and species of Zn and Pb in water-chloride fluids at *T-P* parameters of granitoidic magmas degassing, *Vestn. Otd. nauk Zemle*, 3, NZ6067, doi:10.2205/2011NZ000197.

The study of concentrations and species of ore elements in the aqueous fluid phases separating from magmatic melts during their uprising to the surface and crystallization is important for understanding of a role of magmatic fluids in ore-forming systems formation. The purpose of this investigation is determination of solubility and possible species of zinc and lead in water-chloride fluids at *T-P* parameters of granitic magmas degassing. In this report the results of thermodynamic modeling of equilibrium relations of Zn and Pb complexes in water-chloride solutions depending on temperature (600–900°C), pressure (0.7–5 kbar), composition and acidity of a fluid (NaCl, KCl, NaCl+HCl), and also initial concentration Zn and Pb in system in the form of ZnO_(c), PbO_(c) or ZnCl₂, PbCl₂ are presented. Modeling was conducted by means of program complex HCh [Shvarov, 1999] with use of thermodynamic information received by Shock model [Shock, 1997]. Values of free energy formations of solid phases are borrowed from bank of thermodynamic data of Holland and Powell [Holland, Powell, 1998].

In ZnO–NaCl–H₂O system within studied *T-P* range at low chlorine concentrations ($C_{Cl} < 0.1–0.5 m$) in a solution equilibrated with ZnO_(c), zinc OH-complexes prevail: Zn(OH)₂⁰, ZnOH⁺ (600–700°C) and Zn(OH)₃[–] (≥800°C). In PbO–NaCl–H₂O system the stability area of lead OH-complexes is much wider in comparison with that of Zn, especially at elevated temperatures. At $T > 700^\circ\text{C}$ Pb(OH)₃[–] is dominant complex within all investigated range of pressure and C_{Cl} .

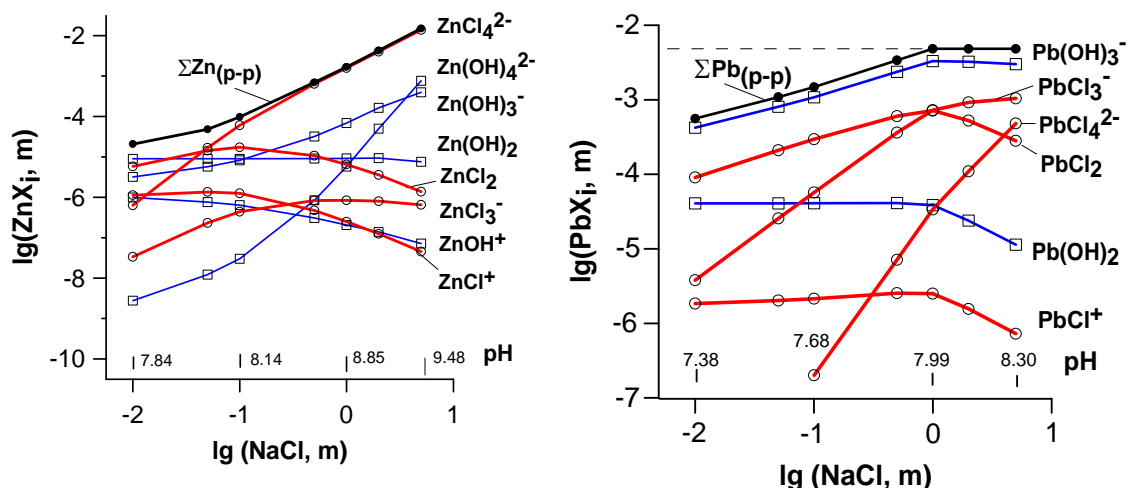


Fig. 1. The influence of NaCl concentration on species and total solubility of Zn (left) and Pb (right) in a fluid in ZnO–NaCl–H₂O and PbO–NaCl–H₂O systems at 800°C and 2 kbar. The content of each metals in the system is 1000 ppm

Cl-complexes fraction and general solubility of ore metals in solutions equilibrated with their solid oxides essentially increase with addition of chloride ion (in the form of NaCl, KCl, HCl) and decrease of pH. In ZnO–NaCl–H₂O system ZnCl₂⁰ and ZnCl⁺ complexes prevailing at low C_{Cl} with increase of C_{Cl} ($> 0.1–0.5 m$) are replaced by ZnCl₄^{2–} complex that becomes the basic form of zinc (fig. 1a and 2a). In the PbO–NaCl–H₂O system the increase of C_{Cl} also is accompanied by increase of stability of lead Cl-complexes.

Thus the general content of the dissolved metal raises in solutions equilibrated with $\text{PbO}_{(c)}$. Furthermore C_{Cl} influences on the kind of dominating Pb complex. For example, at $T \leq 700^\circ\text{C}$ and $P = 2$ kbar the basic type of Cl-complex changes with increase of C_{Cl} in following sequence: $\text{PbCl}_2^0 - \text{PbCl}_3^- - \text{PbCl}_4^{2-}$ (fig. 26).

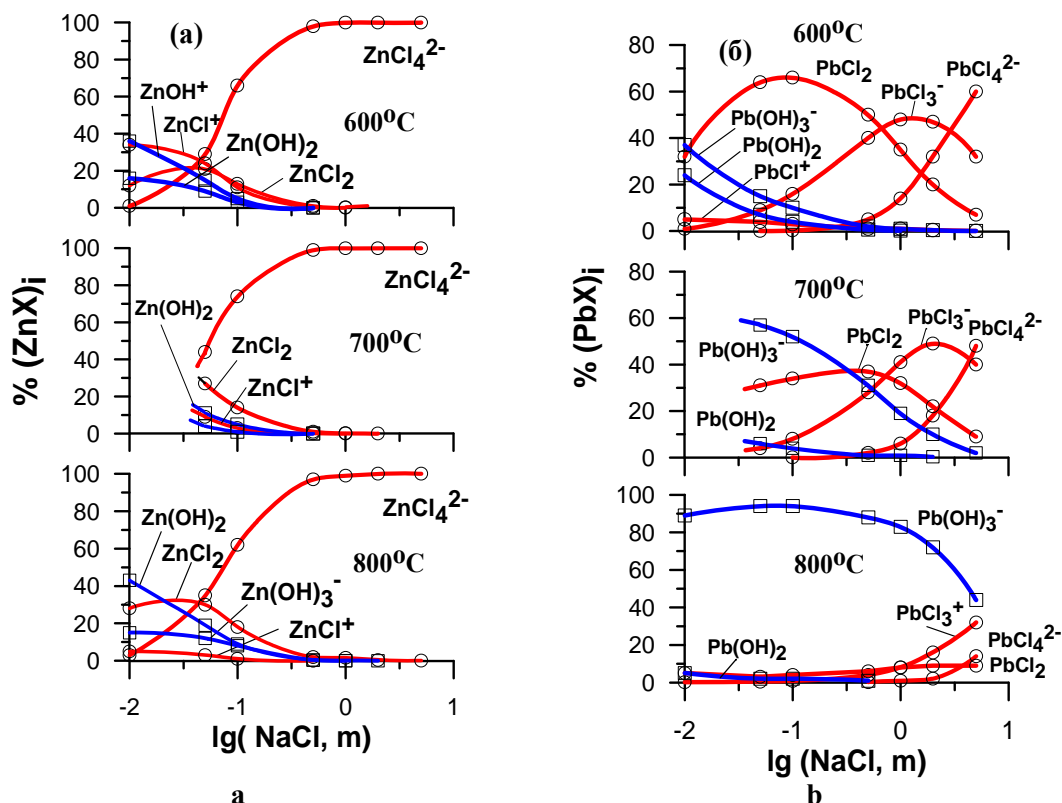


Fig. 2. The fraction (in %) various complexes of zinc (a) and lead (b) accordingly in ZnO–NaCl–H₂O and PbO–NaCl–H₂O systems depending on NaCl concentration and temperature ($P = 2$ kbar). The content of each metals in the system is 10 ppm

Increase of temperature ($P, C_{\text{Cl}} = \text{const}$) essentially reduces stability of chloride complexes of metals in a solution, it is especially essential to lead (fig. 2). Pressure causes (at T and $C_{\text{Cl}} = \text{const}$) an opposite effect. It promotes stability of Zn and Pb Cl-complexes and thereby increases the solubility of metals in a fluid. At $T = \text{const}$ the higher is the pressure, the lower is C_{Cl} at which Cl-complexes become the basic species of Zn and Pb in a water-chloride fluid. Addition of HCl to Na(K)Cl–H₂O solutions equilibrated with Zn and Pb oxides (at constancy of T, P and C_{Cl}) is accompanied by the reduction of pH and increase of metals Cl-complexes concentration, that in turn leads to essential increase of the total content of metals in a fluid phase (fig. 3a). In wide area of P – T – X parameters the Zn/Pb (at.) ratio in water-chloride solutions equilibrated with Zn and Pb oxides is more than 1. Zn/Pb ratio increases with the increase of C_{Cl} and acidity of the solution (fig. 3b).

Results of thermodynamic modeling confirm the assumption of predominant role of Cl-complexes at distribution of Zn and Pb between water-chloride fluids and granitoidic melts during their degassing. They agree well with experimental data at 800°C and 1–5 kbar [Urabe, 1987; etc.] that show: (1) the increase of Zn and Pb distribution coefficients between fluid and granitic melt ($D(\text{Zn})^{f/m}$, $D(\text{Pb})^{f/m}$) with increase of Na and K chlorides concentration in a water-chloride fluid; (2) the especially sharp increase of $D(\text{Zn})^{f/m}$ and $D(\text{Pb})^{f/m}$ with addition of HCl to fluid phase ($T, P, C_{\text{Cl}} = \text{const}$); (3) the higher values of $D(\text{Zn})^{f/m}$ in comparison with that of $D(\text{Pb})^{f/m}$ at given T – P – X conditions.

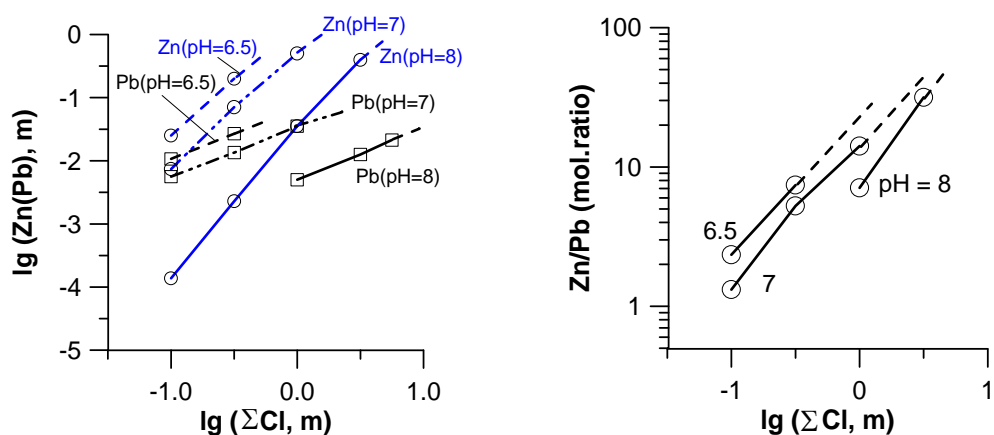


Fig. 3. Total solubility of Zn and Pb (left) and Zn/Pb atomic ratio (right) at various pH (T=800°C, P=2 kbar)

The work was supported by Russian Fund Basic Researches (08-05-00022) and Branch of Earth Sciences of the RAS (the program 2, 2011).

References

- Shvarov, Yu. V. (1999), Algorithmization of the numeric equilibrium modeling of dynamic geochemical processes, *Geochemistry International*, Vol. 37, No. 6, pp. 571–576.
- Shock, E. L., D. C. Sassani, M. Willis, D. A. Sverjensky (1997), Inorganic species in geological fluids: Correlations among standard molal thermodynamic properties of aqueous ions and hydroxide complexes, *Geochim. Cosmochim. Acta*, Vol. 61, pp. 907–950.
- Holland, T., R. Powell (1998), An internally consistent thermodynamic dataset for phases of petrological interest, *Journal of Metamorphic Petrology*, Vol. 16, No 3. pp. 309–343.
- Urabe, T. (1987), The effect of pressure on the partitioning ratios of lead and zinc between vapor and rhyolite melts, *Econ. Geology*, Vol. 82, pp. 1049–1052.