

# THERMODYNAMIC EVALUATION OF REE COMPLEXES IN CONCENTRATED SOLUTIONS (basing on the composition of fluid inclusions in the quartz of the rare-metal deposits)

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In spite of great interest to REE geochemistry there are only several results of chemical determination of REE concentrations in the mineral fluid inclusions, which are present in concentrated solutions, as a rule [1, 2]. Since the total fluid concentration in the inclusions can reach 9-10 mol/kg H<sub>2</sub>O, thermodynamic evaluations and treatments of similar analyses require to consider the ion activity coefficients in the solutions with great ion strength. This task has been solved as several variants using Cl<sup>-</sup> ion as an example within the temperature range of 100-350°C and at the pressure of saturated vapor (Fig.1). The  $\gamma_{Cl^-}$  coefficients are tested for NaCl solution with concentration about of 8.7 m for sample W3-3 [2] with the aid of a HCh computing package [3] according to equations of Helgeson [4] and Oelkers-Helgeson [5] for concentrated solutions (equations 1 and 2, respectively):

$$\log \gamma = -(A z^2 \sqrt{I}) / (1 + B a \sqrt{I}) - \log(1 + 0.0180153m) + C I \quad (1)$$

$$\log \gamma = -(A z^2 \sqrt{I}) / (1 + B a \sqrt{I}) - \log(1 + 0.0180153m) + b_\gamma I \quad (2)$$

Here A, B, C are coefficients of the Debye-Hukkel equation;  $b_\gamma$  – a coefficient, which takes into account the specific of strong electrolyte;  $m$  is the sum of molalities of all the components;  $a = r + r$  presents the sum of the ion effective electrostatic radii [6].

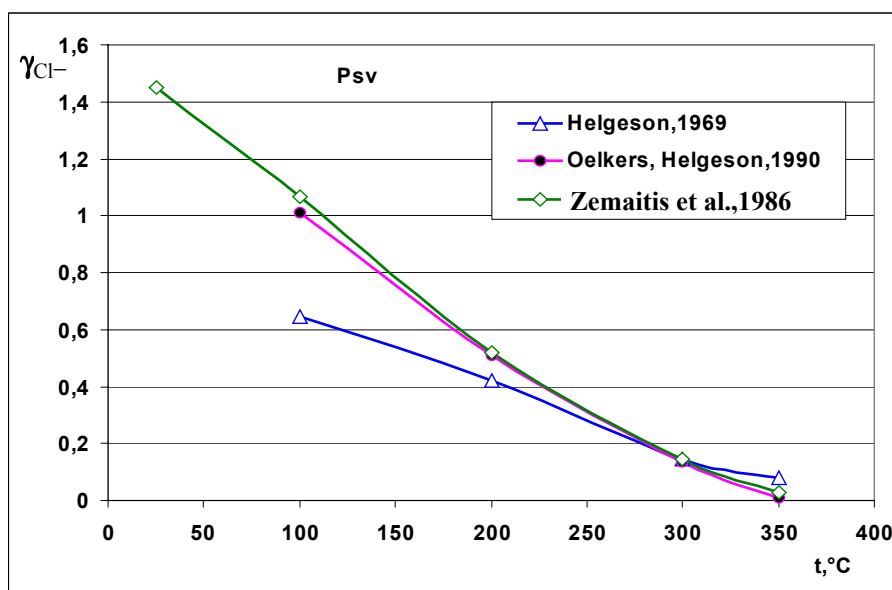


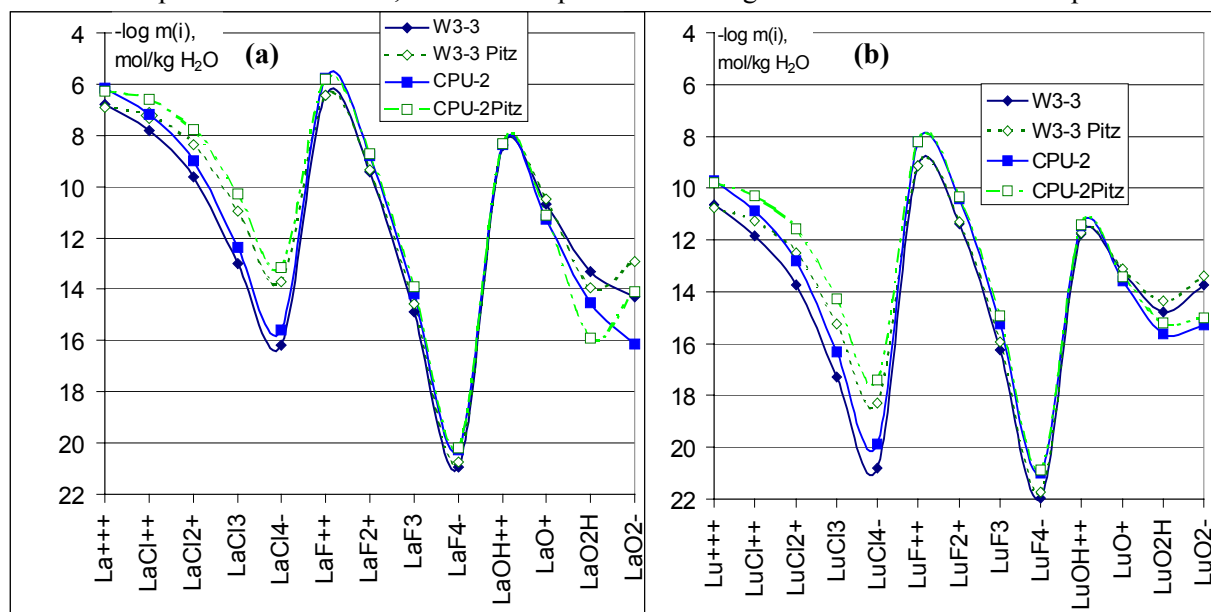
Fig.1.

The temperature influence on the activity coefficients of Cl<sup>-</sup> ion calculated according to equation 1, 2 and Pitzer method [7] up to 350°C at the saturated vapor pressure (Psv) for NaCl solution with concentration about of 8.7m (sample W3-3).

In Fig.1 rhombs represent the points, calculated by the Pitzer method in the variant given in [7], where the authors have used the empirical coefficients based on the abundant experimental data. The activity coefficients of Cl<sup>-</sup> ion, calculated by the Pitzer method and Oelkers-Helgeson equation are in the good agreement each other. This fact gives a chance to use equation 2 even at higher T-P parameters, when the Pitzer empiric coefficients are absent.

Fig. 2 demonstrates an example of the use of the discussed methods of calculation of activity coefficients of dominated electrolyte ions to evaluate possible complexes of La and Lu in the fluid phase of the inclusions in the quartz of quartz-fluorite veins with REE mineralization of the Capitan Pluton (USA). The total concentrations of La and Lu in the inclusions are taken from the chemical analyses of the two solutions in [2]. The total concentrations of Na and K chlorides in the fluids reach 10.5 mole for sample W3-3 (for veins from aplite), slightly decreasing for sample CPU-2 (for veins from granophyre) up to 9.5. High fluorine concentrations (0.28 – 0.09m) are distinguished in the inclusions. The calculated pH values at the temperature 350°C and the saturated vapor pressure for these samples are 4.5 and 4.0, correspondingly.

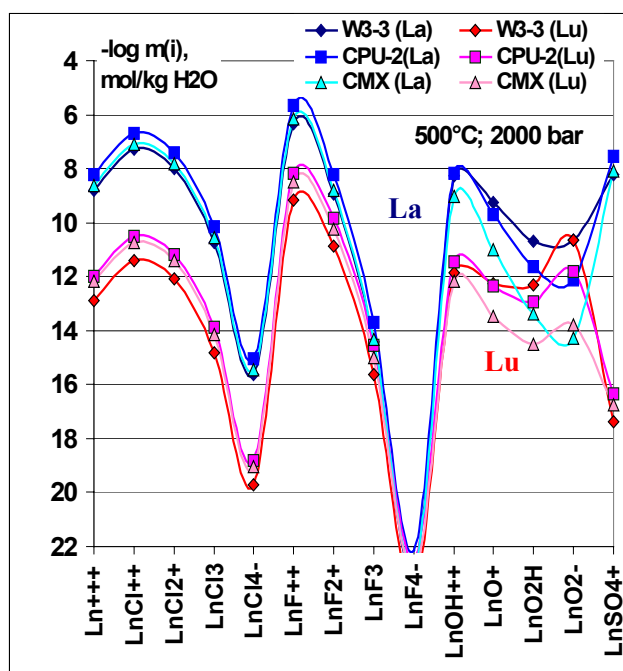
Fig. 3 represents the obtained relationships of concentrations of various fluorine-, hydroxide- and chlorine complexes of La and Lu, which are expected according to the calculations for temperature of



**Fig. 2.** The influence of the method of  $\gamma_{Cl^-}$ -calculation on the speciation of La (a) and Lu (b) at 350°C and the saturated vapor pressure (the solid lines – according to equation 2 and the dotted lines – according to Pitzer method).

500°C and pressure of 2000 bar in three fluids conserved in quartz. Because the fluid from aplites (sample W3-3) is mostly depleted in fluorine, the content of the hydroxide complexes of La, but especially of Lu, can compete with fluorine- and chlorine complexes. In this case, as in the previous calculation (Fig. 1, 2) the stability constants of REE complexes and the ions and species of solutions for other elements were used from the thermodynamic database SUPCRT98 [8,9].

The authors suppose that the accuracy of the calculations is enough restricted by the assumptions under the discussion, though the relative REE distribution according to the basic types of complexes in the fluid seems to be more correct.



**Fig. 3.** The distribution of La and Lu according to their forms in the fluids from the inclusions in quartz from aplite (sample W3-3) and granophyre (CPU-2, CMX) of the Capitan Pluton [2].

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## References

1. *Norman, D.I., Kyle, P.R., Baron, C.* (1989) *Econ. Geol.* 84, 162-166.
2. *Banks, D.A., Yardley, B.W.D., Campbel, A.R. & Jarvis, K.E.* (1994) *Chemical Geology* 113, 259-272.
3. *Shvarov, Yu.V.* (1999) *Geochemistry International* 37, 571-576.
4. *Helgeson, H.C.* (1969) *American Journal of Science* 267, 729-804.
5. *Oelkers, E.H., Helgeson, H.C.* (1990) *Geochim. Cosmochim. Acta* 54, 727-738.
6. *Shock, E. L. et al.* (1992) *J. Chem. Soc. Faraday Trans.* 88, 803-826.
7. *Zemaitis, J.F., Jr., Clark, D.M., Marshall Rafal, Scrivner, N.C.* (1986) *Handbook of aqueous electrolyte thermodynamics. Theory & Application.* New York: Am. Inst. Chem. Eng.
8. *Haas, J.R. et al.* (1995) *Geoch. Cosmochim. Acta.* 59: 4329-4350.
9. *Shock, E.L. et al.* (1997) *Geoch. Cosmochim. Acta.* 61: 907-950.

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