

3.6.P14**Ni(II)- and Co(II)-chloride complex equilibria in hydrothermal systems**A. SEELIGER AND T.M. SEWARD

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The aim of this on-going study is to obtain configurational and thermodynamic information pertaining to the formation of chloride complexes of Ni(II) and Co(II) in aqueous solutions over a range of temperatures and pressures from ambient to 400°C and 1500 bar. The emphasis of this current report is on quantum chemical computations using ab initio and density functional theory (DFT) but uv-vis-nir and x-ray absorption studies are also underway.

Geometry optimization of each complex with ab initio calculations have been carried out using the B3LYP-functionals of the density functional theory in combination with G6-311** functions as basis sets for ligands, while an effective core potential was used to approximate the metal center. TD-DFT calculations with these optimized structures provide information about electron excitations of the complex and are compared to the observed transitions in the experiments.

Uv-vis spectroscopic studies of the systems NiCl₂ – HCl – H₂O and CoCl₂ – HCl – H₂O in the temperature range from 25 to 90°C, indicate that tetrahedral complexes are present at high chloride concentrations. At $t > 100^{\circ}\text{C}$, species with T_d geometry become increasingly more important at lower chloride concentrations as noted by Susak and Crerar [1]. Equilibrium constants for the formation of Co(II)- and Ni(II)-chloride complexes have been calculated from the uv-vis spectra using the method of principal component analysis.

References

- [1] Susak N.J. and Crerar D.A. (1985) *GCA* **49**, 555-564

3.6.P15**Experimental study of palladium-hydrosulphide complexing in hydrothermal fluids**B. R. TAGIROV AND T. M. SEWARD

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Importance of hydrothermal activity in mobilization of platinum-group elements (*PGE*) have been recognized by field observations in a variety of environments, including high-temperature stratiform deposits in the Bushveld and Stillwater Complexes [1], and *PGE* mineralization associated with hydrothermal Cu ores formed at intermediate and low temperatures [2]. Experimental solubility measurements (e.g. [3, 4]) demonstrated that the main species controlling *PGE* hydrothermal transport are thio (*PGE*-HS) and chloride (*PGE*-Cl) complexes. However, available experimental data are scarce and inconsistent with respect to stoichiometry and stability of *PGE* aqueous complexes, especially those formed in sulphide bearing solutions at high temperatures. Therefore, the aim of the present study is to determine the stoichiometry of Pd-HS complexes and their stability at temperatures to 300°C.

Solubility of synthetic palladium sulphide (PdS, vysotskite, grain size 60-250 mkm) was measured in a flow-through Ti autoclave. The inlet solution was supplied with a Varian HPLC pump, and pressure was regulated using a Coretest back-pressure regulator. All parts in contact with experimental solution were made out of titanium, PEEK or TEFLON. NaOH and HCl were used to adjust pH. Samples for analyses of Pd, total S and pH measurements were taken at the low pressure end of the back-pressure regulator. The samples were evaporated to dryness, then the residue was dissolved in aqua regia, again evaporated nearly to dryness and diluted with 1.8% HNO₃. Pd analyses were performed using ICP-MS.

Pd concentration measured at 25°C was independent of experimental solution flow rate at 0.5-5 ml/min. This implies that the equilibrium solubility was attained. The PdS solubility of $6.6 \cdot 10^{-9}$ mol/kg was determined at 25°C, $m(\text{H}_2\text{S})=0.08$ and $\text{pH}=4.2$. This value is in good agreement with [4]. Further determinations of PdS solubility as a function of pH, $m(\text{H}_2\text{S})$ and temperature are in progress.

References

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 [3] Gammons C.H. and Bloom M.S. (1993) *GCA* **56**, 3881-3894.
 [4] Wood S.A., Pan P., Zhang Y. and Mucci A. (1994) *Miner. Deposita*, **29**, 309-317.