



	Experiment title: Unravelling the riddle of hydrothermal Pt and Ni deposit formation: the role of arsenic	Experiment number: ES-311
Beamline: BM30B	Date of experiment: from: 08.10.2015 to: 14.10.2015	Date of report: 04.12.2015
Shifts: 21	Local contact(s): Denis Testemale	<i>Received at ESRF:</i>
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Report:

The aim of experiment ES-311 was to obtain information on the effect of As on the solubility of Pt and Ni in aqueous HCl fluids at elevated temperature (T) and pressure (P). Arsenides are typical Ni minerals in hydrothermal nickel deposits, and some occurrences of sperrylite, PtAs₂, are thought to be in part related to remobilization by magmatic-hydrothermal fluids (Broken Hammer zone, Sudbury igneous complex, Canada; Tweefontein Hill, Bushveld igneous complex, South Africa). However, experimentally determined solubilities of Pt and, at near neutral pH, of Ni in chloridic aqueous fluids are too low to account for extensive hydrothermal mobilization of these elements [e.g. Pan1994, Liu2012]. Thus, we tested the hypothesis that complexation of Pt(II) and Ni(II) with As-O may be significant in addition to that with Cl⁻.

Dissolution experiments of PtAs₂ or Pt metal at 500 °C and 80 MPa and of NiAs or NiS at 400 °C and 80 MPa in H₂O+HCl fluids were carried out using a HP/HT He-pressurized autoclave with an internal glassy carbon cell as sample container [Testemale 2005]. The concentrations of dissolved Pt, Ni and As were monitored for several hours by in-situ XRF spectroscopy. The XRF signal was collected at an angle of 90° to the incident X-ray beam and was calibrated at room temperature by measurements of Pt, Ni and As standard solutions, which had the same or a similar matrix with respect to X-ray attenuation as the fluids in the experiments at 400 and 500 °C. In addition, transmission X-ray absorption spectra were recorded to obtain information about the complexation of Ni and the oxidation state of As. The carbon cell showed no sign of a reaction with water, i.e. the interior surface maintained its luster even after experiments at 500 °C for several hours. The Pt concentrations in 20% HCl at 500 °C, 80 MPa from dissolution of Pt metal were 6.5·10⁻⁴ to 9.6·10⁻⁴ molal or below the minimum detection limit (MDL) of 2.6·10⁻⁴ molal in the experiment with PtAs₂ (Fig. 1a). The lower Pt solubility in the As-bearing experiment indicates insignificant complexation of Pt(II) with As in high-temperature acidic chloridic aqueous fluids. More importantly, the very low hydrothermal Pt(II) solubility persists to very high HCl concentrations even at 500 °C. This excludes that sperrylite crystals in quartz-epidote veins in the Broken Hammer deposit precipitated from a hydrothermal fluid, and suggests that they represent insoluble relicts of the hydrothermal replacement of a preexisting sulfide matrix.

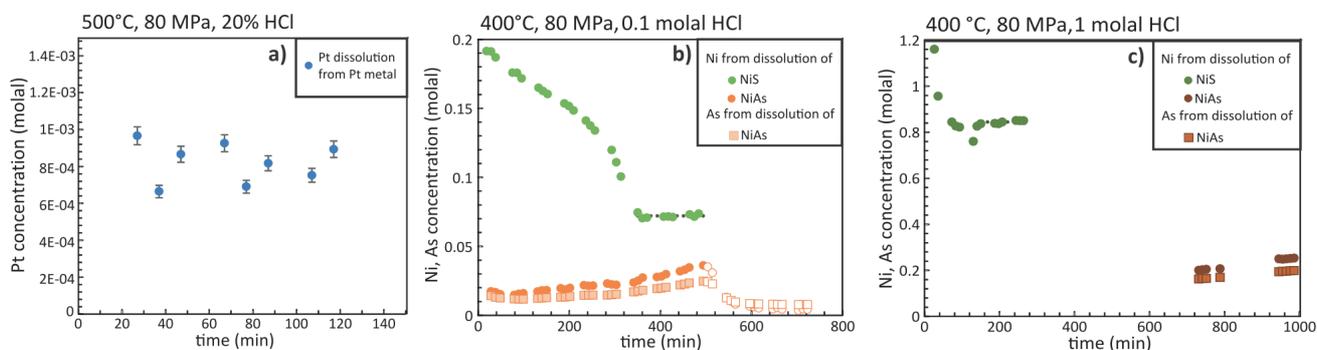
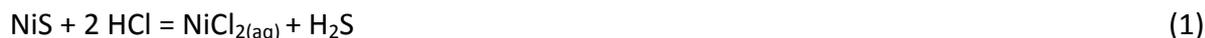


Fig.1: (a) Pt concentrations in the fluid from dissolution of Pt metal in 20% HCl at 500 °C and 80 MPa as function of elapsed time. (b, c) Ni and As concentrations in the fluid from dissolution of NiAs (orange symbols, circles – Ni, squares – As) and NiS (green symbols) in (b) 0.1 molal HCl or (c) 1 molal HCl at 400 °C and 80 MPa as function of elapsed time. Dashed lines – equilibrium Ni concentration. Open symbols indicate measurements during cell leakage.

Figures 1b and 1c show Ni and As concentrations in the fluid measured during dissolution of NiAs and NiS at 400 °C and 80 MPa in 0.1 molal and 1 molal HCl. The MDL were $3.4 \cdot 10^{-3}$ molal Ni and $1.38 \cdot 10^{-4}$ molal As, as determined from the NiAs + 1 molal HCl experiment. Addition of HCl results in a large increase in the Ni solubility. In comparison, Ni solubilities are quite low in 1 and 2 molal NaCl fluids (5 to 10 ppm at 300 to 600 °C, 100 and 200 MPa) [Scholten2014], which indicates that they strongly depend on Cl^- activity. Dissolution behavior of NiS and NiAs was very different. The Ni concentration in the NiS dissolution experiments decreased with time until equilibrium was attained. Equilibration was faster at 1 molal HCl, which is in agreement with reports of faster reaction kinetics with increasing HCl molality [Schmidt2007]. Subsequent SEM images of the solid reaction products indicated formation of millerite (trigonal NiS). This explains the initial decrease of the Ni concentration in the fluid, which is caused by the conversion of the loaded hexagonal NiS to the stable NiS phase, and also signifies congruent dissolution via



Dissolution of NiAs was incongruent, with Ni > As in the fluid (Figs. 1b, 1c) and, consequently, formation of a solid with Ni < As as confirmed by SEM-EDS analyses. The obtained Ni and As concentrations are internally consistent, i.e. they are about ten times higher with a tenfold increase in HCl concentration. Equilibrium was not attained even at the longest run duration of more than 16 hours, but comparison to the solubility of Ni from NiS suggests that there is no significant Ni(II)-As complexation. The XANES K-edge spectra obtained for Ni (Fig. 2a) are indistinguishable from that of aqueous $\text{NiCl}_2 + \text{HCl}$ solutions at high temperature [Tian2012]. Arsenic, however, was oxidized to As(V) (Fig. 2b). Because of the low pH, the predominant As(V) species was probably H_3AsO_4 . This indicates the following dissolution reaction:

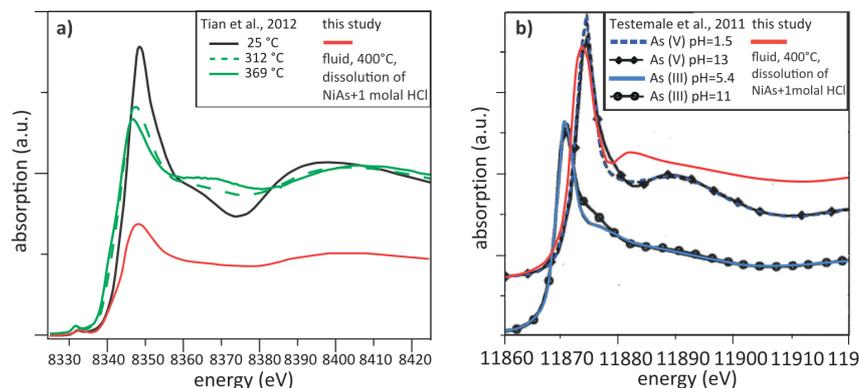


Fig.2: (a) Ni K-edge XANES spectrum of the fluid from the NiAs + 1 molal HCl dissolution experiment at 400 °C, 80 MPa compared to spectra of a $\text{NiCl}_2 + \text{HCl}$ solution at 25, 312, and 369 °C reported by Tian et al., 2012. (b) As K-edge XANES spectrum of the fluid from the NiAs + 1 molal HCl dissolution experiment at 400 °C, 80 MPa compared to literature data at ambient pressure and temperature from Testemale et al., 2011.

References:

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