

EXPERIMENTAL STUDY OF THE TRANSFORMATION OF PENTLANDITE/PYRRHOTITE TO VIOLARITE

Wai Yin Hui¹, Christophe Tenailleau¹, Allan Pring¹ & Joël Brugger^{1,2}

¹Department of Mineralogy, South Australian Museum, North Terrace, Adelaide, SA, 5000

²CRC LEME, School of Earth and Environmental Sciences, University of Adelaide, SA, 5005

BACKGROUND

Violarite, with an ideal formula of FeNi_2S_4 , is the most economically important member of the thiospinel group of minerals. In nature, violarite forms either by exsolution during the cooling of pentlandite ($(\text{Fe,Ni})_9\text{S}_8$; Figure 1a) or, more commonly, by the oxidation of pentlandite in the supergene zone (Figure 1b). Understanding the thermodynamics and kinetics of the formation of violarite in the weathering profile is important for the comprehension of weathering patterns in and around nickel deposits. The formation of violarite also has significant implications for ore processing. Supergene violarite does not float well, resulting in poor nickel recovery. However, a proportion of violarite in the nickel concentrate is required to kick-start the smelting process, as the burning of violarite is a highly exothermic reaction. Hence, the roasting of nickel sulphide ores would benefit from the ability to reproduce the natural transformation of pentlandite to violarite, while nickel recovery may be improved if it is possible to transform violarite back to pentlandite.

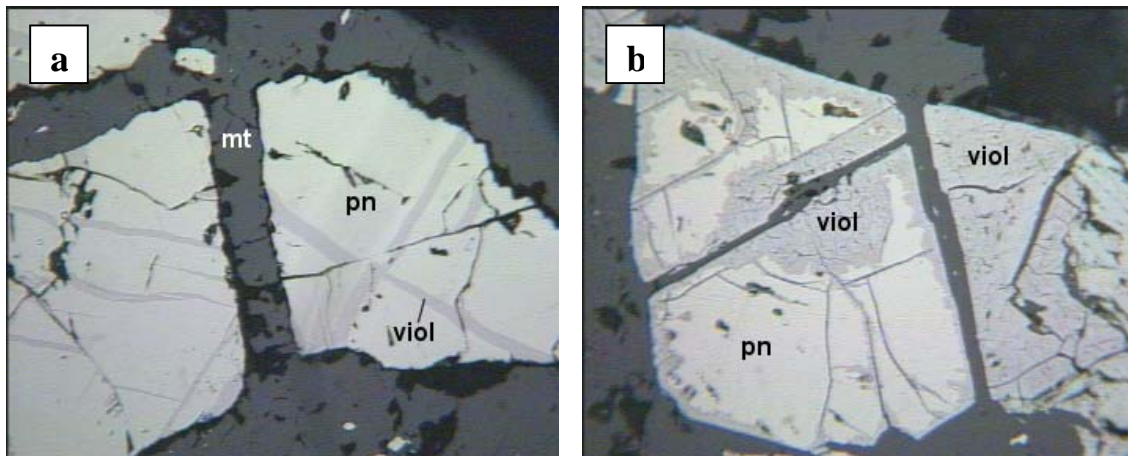


Figure 1: Occurrences of violarite in ore deposits. **(a)** Violarite forming as exsolution from pentlandite. Mt Keith Nickel Mine, WA. **(b)** Violarite forming during the weathering of pentlandite along rims and cracks of pentlandite crystals. Mt Keith Nickel Mine, WA. Field of view for both images is 250 μm .

Violarite adopts the spinel structure and contains metal cations in both octahedral and tetrahedral sites. In normal spinels (e.g., magnetite), the divalent cation occupies the octahedral site and the trivalent cation the tetrahedral site, but other ordering arrangements are possible. The inverse spinel represents an extreme case, in which half of the divalent cations enter the tetrahedral site, while the other half the octahedral site and the trivalent cation occupies the octahedral site (Figure 2). Transformation from one ordered arrangement to another, or to a disordered state, can change the magnetic properties significantly. In the thiospinels, the solid solution fields extend from violarite towards greigite (Fe_3S_4) and polydimite (Ni_3S_4). Since pentlandite and violarite both share a cubic close-packed S lattice, the mineral transformation can take place topotactically with a change in volume of around 16%. Above 610°C pentlandite, which is invariably associated with pyrrhotite (Fe_{1-x}S), forms the Monosulphide Solid Solution (MSS) which has the NiAs structure. The composition field of MSS includes the bulk composition of the sulphide phases of many Fe-Ni-Co sulphide deposits. Pentlandite exsolves from MSS upon cooling, concentrating the Ni and leaving pyrrhotite (Fe_{1-x}S) (Etschmann *et al.* 2004). Under the right compositional relationships, the pentlandite will, with further cooling, exsolve violarite. This process of violarite formation takes place in the primary (or hypogene) zone of the ore body.

Synthetic (near) stoichiometric violarite can be prepared by melting Fe, Ni, and S in 1:2:3 ratios at approximately 1000°C in a sealed tube, cooling, and crushing the product, and finally adding 33% additional sulphur and annealing again in a sealed tube at 300°C for a week (Townsend *et al.* 1977). Magnetic

susceptibility, thermoelectric power and Mössbauer spectroscopy measurements indicate that Fe(II) in FeNi_2S_4 could occupy the tetrahedral site with delocalised electrons or the octahedral site with an essentially localised low-spin configuration. A low-spin configuration should be adopted by Ni(III) and would imply an occupation of the octahedral site. With Fe(II) in the octahedral site, an inverted spinel structure results.

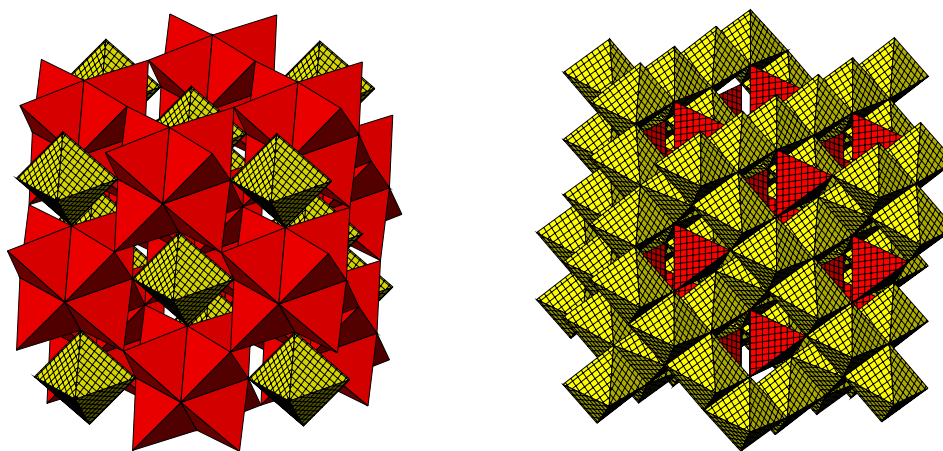


Figure 2: Comparison of the crystal structure of pentlandite (**left**) a cubic closed packed array of S atoms with metals in 1/2 of the tetrahedral (Fe) sites and in 1/8th of the octahedral (Ni) sites; and, violarite (**right**) a cubic closed packed array of S atoms in 1/8th of the tetrahedral (Fe) voids and 1/2 of the octahedral (Ni) voids.

Vaughan & Craig (1985) have suggested that violarite, which is a metallic and Pauli paramagnetic phase, contains Fe mainly in the octahedral site but also Fe comparable to that in the tetrahedral site in pentlandite. The Fe/Ni ratios of these supergene violarites depend upon the starting pentlandite (and pyrrhotite) compositions and on the nature of the oxidizing conditions. This could explain why the natural violarites often exhibit higher Fe/Ni stoichiometries than the synthetic ones and expected from crystal chemical considerations.

The transformation of pentlandite to violarite under supergene conditions could also proceed topotactically, by the interdiffusion of cations with the S lattice, however the porous texture of supergene violarite suggests that the reaction proceeds via dissolution and reprecipitation. In such reactions the dissolution step and the reprecipitation step must be closely coupled and there is no free space at the reaction interface (Putnis 2002). The fluid must catalyse the reaction, but this process is poorly understood.

Below are the results of preliminary experiments aimed at delineating conditions suitable for the study of the kinetics and mechanisms of the pentlandite-to-violarite reaction. The experiments were conducted both as solid-state reactions and as dissolution-reprecipitation reactions. These experiments serve as a basis for experiments that will be conducted with a new flow-through reactor developed at the University of Adelaide and the South Australian Museum for the *in situ* measurement of hydrothermal crystallisation and phase transition of minerals using neutron diffraction under both solid-state and hydrothermal conditions. Neutron diffraction is a very powerful tool for determining the amount and structure of a material at a specific temperature and pressure. The flow-through hydrothermal cell was designed for *in situ* neutron measurements at ANSTO, Sydney, over a wide range of temperatures (25-300°C) and pressures (1-85 bars) under controlled chemical conditions (ion concentrations, pH, redox).

RESULTS

Exsolution Reactions (solid state reaction)

The exsolution of violarite from pentlandite can be represented by the equation:



This reaction *in situ* will be studied using neutron diffraction on the high resolution diffractometer HRPD instrument available at ISIS, UK, in December. Preliminary results obtained from quenching experiments conducted at the South Australian Museum are reported here. Samples of synthetic exsolved pentlandite/pyrrhotite mixtures of various bulk compositions were placed in silica tubes (10 mm diameter and

around 150 mm length) and sealed under vacuum. The sample charges were buffered with natural pyrrhotite (separated from the sample by silica wool) to provide the extra sulphur necessary for the transformation to violarite (see Equation (1)). The samples were annealed at 300°C and 400°C for a range of periods. According to the Fe-Ni-S ternary phase diagrams, $(\text{Ni,Fe})_3\text{S}_4$ is formed from an appropriate starting composition, but the Fe/Ni ratio is variable at 400°C. A complete solid solution exists between FeNi_2S_4 and Ni_3S_4 below 356°C (Chamberlain *et al.* 1998, Vaughan *et al.* 1985). Since polydimite, the nickel end member of the solid solution, decomposes above this temperature, it is presumed that violarite with varying Fe:Ni ratios may behave similarly. Those two phenomena guided the choice of annealing temperatures for the experiments.

All samples were annealed under the conditions described above, at 300°C or 400°C, for periods of 1 day to 1 month and then quenched in cold water. The samples were ground in acetone and X-ray diffraction patterns were recorded in order to monitor the progress of the transformations with annealing time. So far, none of the annealed samples have shown any traces of violarite except for one sample annealed over a week at 300°C with the buffer, which had been exposed to a small amount of oxygen during annealing (Figure 3). When this sample was further annealed in an evacuated silica tube with a pyrrhotite buffer, the violarite transformed back to pentlandite/pyrrhotite (see Figure 3). Therefore, it seems that the mixture pentlandite/pyrrhotite needs an oxidising agent to transform to violarite.

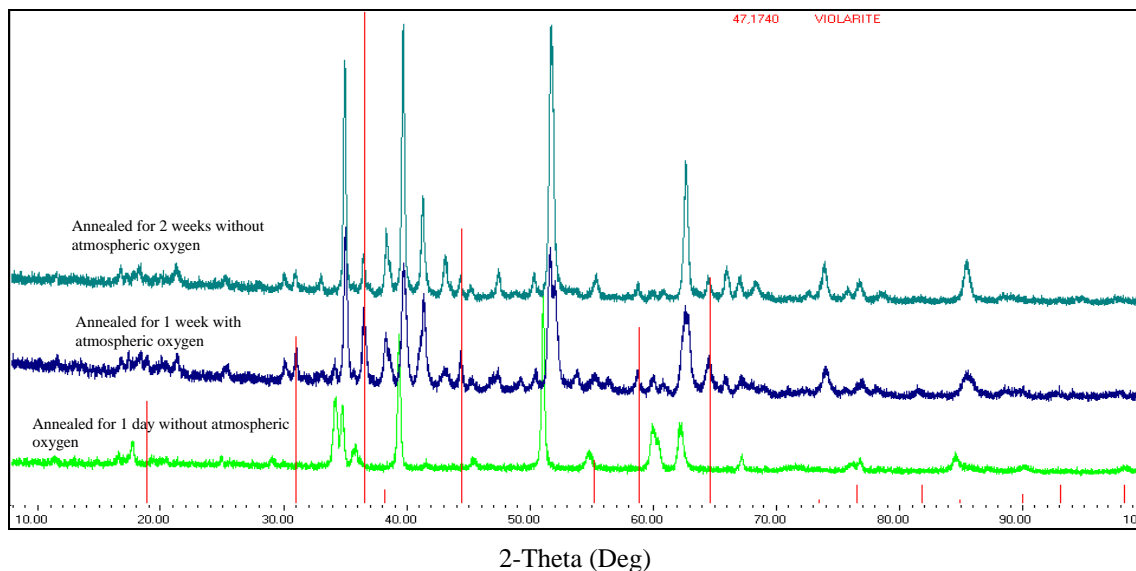
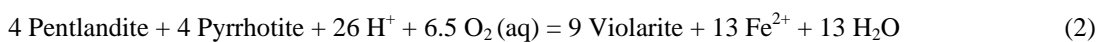


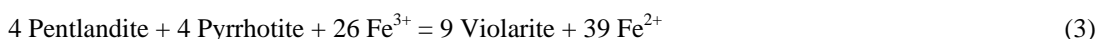
Figure 3: Stacked X-ray diffraction traces (Co $K\alpha$ radiation) of pentlandite samples annealed under different conditions. Violarite appears after annealing for 1 week with atmospheric oxygen and diminishes after annealing for 2 weeks without atmospheric oxygen.

Hydrothermal Experiments (dissolution-precipitation reaction)

A series of water bath experiment was undertaken to explore the stability of violarite under supergene conditions. The calculated solubility diagram is shown in Figure 4. The transformation of pentlandite and pyrrhotite to violarite under aqueous conditions can be written:



or, using Fe^{3+} as an oxidant,



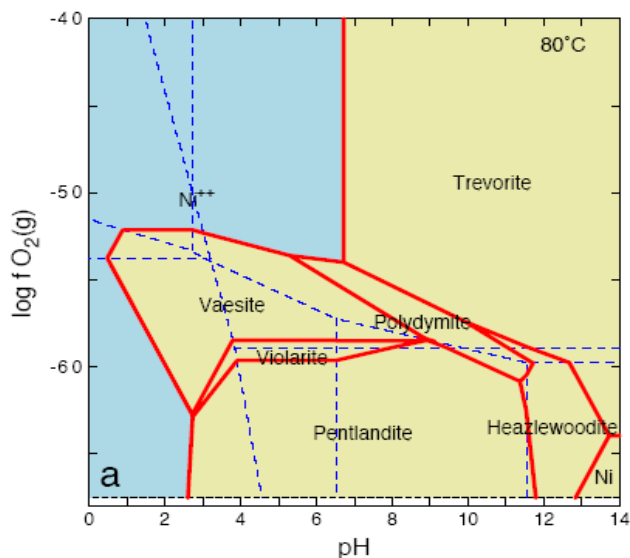


Figure 4: Diagram illustrating the mineral solubility and phase relationships in the H_2O -Fe-Ni-S-Cl system as a function of redox potential (expressed as $\log f \text{O}_2(\text{g})$) and pH at 80°C . Thermodynamic properties are from the Lawrence Livermore database (LLNL V8 R6), except for violarite and pentlandite [5]. The diagram is drawn assuming an activity of dissolved Fe species of 1, of Ni species of 10^{-6} , and of S species of 10^{-3} . The dashed lines show the positions of the boundaries in the Fe-O-H and S-O-H sub-diagrams.

Solutions with variable pH (from 3 to 5) were prepared using acetic acid and sodium acetate buffer. Samples of approximately 200 mg of exsolved pentlandite/pyrrhotite were inserted into a series of flasks containing 100 ml of a solution of known pH. Six samples were run simultaneously in the water bath. Early experiments run in contact with atmospheric oxygen produced poorly crystalline Ni- and Fe sulfates, so subsequent experiments were conducted under a controlled atmosphere. Nitrogen gas was bubbled through the first three flasks and $\text{H}_2\text{S}/\text{N}_2$ gas through the others. The water bath was maintained at specific temperatures varying from 60 to 80°C . After a week, the samples were filtered on sintered glass funnels and the X-ray diffraction patterns recorded on a Guinier camera with a $\text{Co K}\alpha$ radiation. The experiments were continued for successive weeks with fresh acid solutions which were changed every week. The pH remained fairly constant during the reactions.

Most samples exhibit no sign of violarite, except for the 50% natural pentlandite sample, which contains traces (<5 vol. %) of violarite. Violarite grew in samples run under N_2 and H_2S gas. After running the sample for 7 days at 80°C , pH 4, the amount of violarite increased to ca. 25% of the sample (Figure 5). It was concluded that the reaction might need an oxidising agent to set off the transformation from pentlandite/pyrrhotite to violarite. Thus, a series of similar water bath experiments has been initiated with Fe(III) acetate added to the solution, in order to test this hypothesis (Equation 3).

CONCLUSION AND PERSPECTIVES

These preliminary experiments show that violarite is a difficult mineral to synthesize. It can be prepared by exsolution from pentlandite but requires mildly oxidizing conditions. Finding the right redox buffer may be critical for the success of these experiments. Our experiments under supergene conditions suggested that nucleation of violarite is the critical step. If violarite is already present, the transformation can be easily driven to produce more, but initiating the reaction is difficult. Much additional work needs to be done on understanding this transformation under both hypogene and supergene conditions. This is only first step in understanding the kinetics and thermodynamics of these important reactions.

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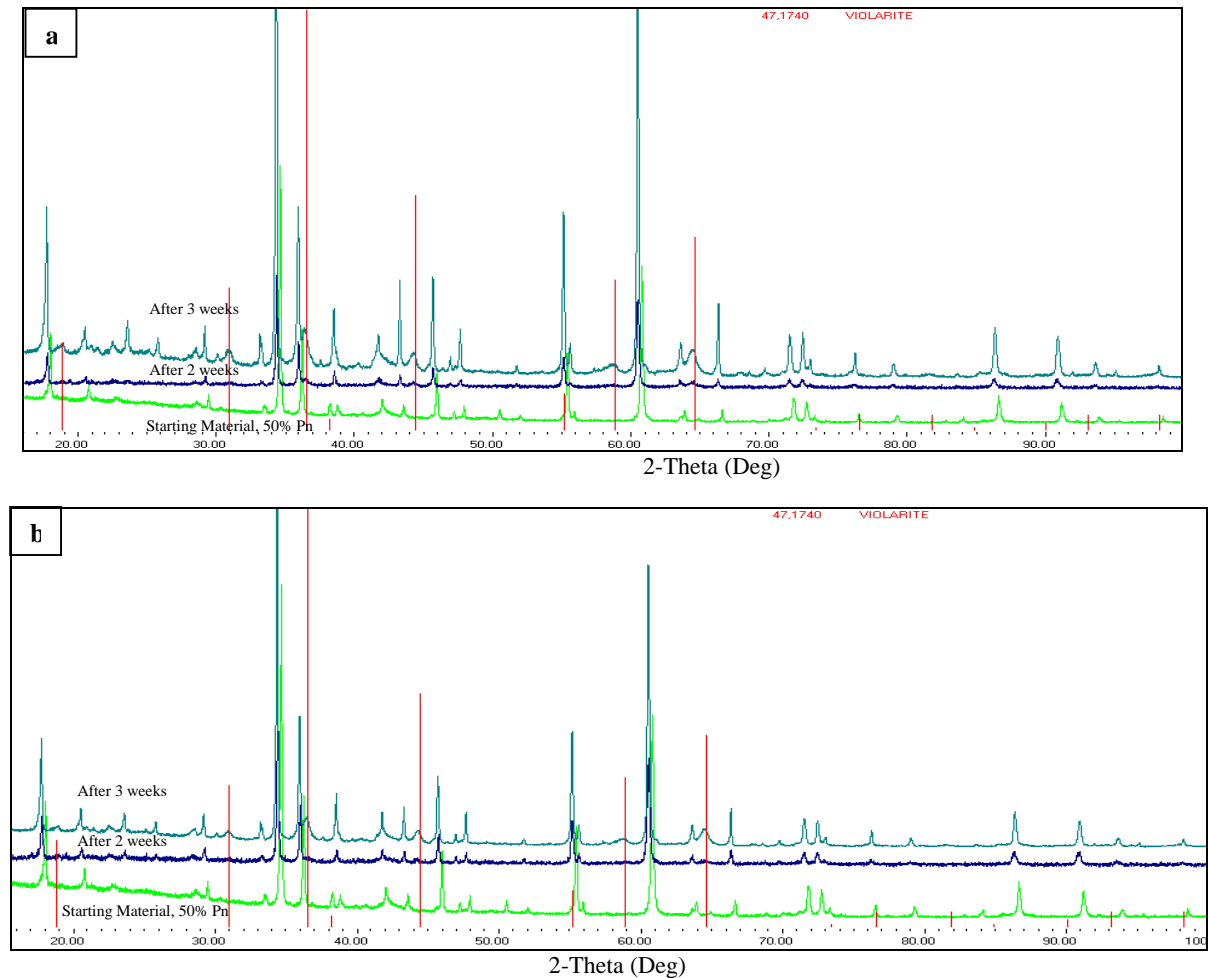


Figure 5: (a) 50% natural pentlandite in pH 4 solution bubbled with N₂ gas at 80°C for 2 and 3 weeks, showing an increase in the presence of violarite. (b) 50% natural pentlandite in pH 4 solution bubbled with H₂S(g) at 80°C for 2 and 3 weeks, showing an increase in the presence of violarite.