THE TRANSFORMATION OF PENTLANDITE TO VIOLARITE UNDER MILD HYDROTHERMAL CONDITIONS: A DISSOLUTION-REPRECIPITATION REACTION

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INTRODUCTION

Violarite, $FeNi_2S_4$, occurs abundantly in the supergene alteration zones of many massive and disseminated Ni sulfide deposits, where it replaces primary nickel sulfide minerals such as pentlandite (Nickel 1973, Misra & Fleet 1974). The nickel deposits of Western Australia's Yilgarn Craton have deep weathering profiles and supergene violarite constitutes a considerable proportion of the ore in some of these deposits. Thus, violarite is probably the most economically important member of the thiospinel mineral group. Violarite can also form as a primary phase by exsolution during the cooling of pentlandite ($(Fe,Ni)_9S_8$) (Grguric 2002). Understanding the thermodynamics and kinetics of the formation of violarite in the weathering profile is important for understanding alteration patterns in and around nickel deposits and has significant implications for ore processing. Supergene violarite is generally very fine-grained and relatively porous and it has a poor response in the floatation systems used to treat many massive sulfide ores. On the other hand, a proportion of violarite in the nickel concentrate facilitates smelting, as the burning of violarite is a highly exothermic reaction (Dunn & Howes 1996). Hence, the processing of nickel sulfide ores could benefit from an understanding of the conditions and mechanisms of the transformation of pentlandite to violarite.

Violarite adopts the spinel structure, which can be treated as a cubic closed packed array of S atoms with metal ions occupying 1/2 of the octahedral sites and 1/8 of the tetrahedral sites of the array (Vaughan & Craig 1985). The composition field of violarite extents towards both greigite (Fe_3S_4) and polydymite (Ni_3S_4) and in this paper we shall use the term violarite to designate any intermediate composition between greigite and polydymite rather than to just the composition Ni_2FeS_4.

The formation of violarite from pentlandite by supergene processes has long been recognized as a replacement reaction (Misra & Fleet 1974 and references therein). Misra & Fleet (1974) suggested that the reaction might be topotactic, as pentlandite also has a structure based on cubic close packing of S with Fe and Ni atoms occupy 1/2 the tetrahedral sites and 1/8 of the octahedral sites (Rajamani & Prewitt 1973). Thornber (1975) proposed that the formation of violarite from pentlandite was an anodic process with the orebody acting as a corrosion cell. He proposed that at depth the primary sulfides such as pentlandite lose iron to solution to become more S–rich and the electrons are conducted away through the ore towards the surface. The groundwater acts as an electrolyte to complete the cell. However, Putnis (2004) suggested that the porous and cracked texture exhibited by supergene violarite indicates a dissolution-reprecipitation reaction rather than a topotactic transformation. We have undertaken a detailed laboratory study of the replacement of pentlandite by violarite using a series of waterbath and hydrothermal cell experiments. We report here preliminary results of these studies into the conditions under which the transformation proceeds and on the kinetics and mechanism of the reaction.

EXPERIMENTAL

Both natural and synthetic pentlandite was used as the starting material for the transformation experiments. Pure pentlandite, in grains larger than 1 mm, is very difficult to obtain from nature or to prepare synthetically and one must use either natural or synthetic exsolved pentlandite in pyrrhotite or fine grained pentlandite concentrates.

A high-grade pentlandite concentrate from the Mount Keith deposit, Western Australia, that contains 90 wt. % pentlandite and 9 wt. % pyrite with minor amounts of hydrotalc minerals, serpentine minerals and magnetite, was used for many of the preliminary waterbath experiments, but proved to be too fine grained (< 0.1 mm) for easy use in hydrothermal cell experiments. For these experiments we used a range of synthetic pentlandites that had been prepared and annealed by Etschmann *et al.* (2004).

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A series of water bath experiments were undertaken to establish the approximate conditions for the transformation of pentlandite to violarite. Sets of experiments were performed at 80ºC and in the pH range 3 to 5 fixed with the acetic acid/sodium acetate (CH_3COONa) buffer (ca. 0.2 M total acetate concentration). In all experiments, approximately 1.0 g of pentlandite concentrate was added to a flask containing 100 ml of acid solution. Argon (Ar) gas was slowly bubbled through the solution to minimize the mixing with air. Duplicate experiments were performed for each pH value, with a small amount of H_2S (less than 0.05%) being mixed with the Ar stream in the second set of experiments. To some of the runs a mild oxidizing agent, 1 ml of 0.1 M $Fe(CH_3COO)_2(OH)$ solution, was added.

To study the transformation at temperatures above 100°C, a series of synthetic pentlandite-pyrrhotite samples were used in a flow through hydrothermal cell (O'Neill *et al.* 2005). The synthetic pentlandite ($Fe_{4.66}Ni_{4.29}S_8$) was exsolved from monosulfide solid solution at 150°C for 672 hrs and contained 39 wt. % pentlandite and 61 wt. % pyrrhotite ($Fe_{0.81}Ni_{0.16}S$) (see Etschmann *et al.* 2004). The sample was coarsely crushed to give an approximate grain size of 2 mm. Samples of between 1 and 5 grams of synthetic pentlandite were loaded into a fine mesh stainless steel sample tube in the hydrothermal cell and heated to 120°C and a pressure of 3.5 bars. An acetic acid–sodium acetate solution of pH 3.5 was pumped around the cell. The transformation reaction was interrupted every 24 hours and a small part of the sample removed for X-ray diffraction analysis. The experiments were typically run for 8 days and the acid solution was also changed each day.

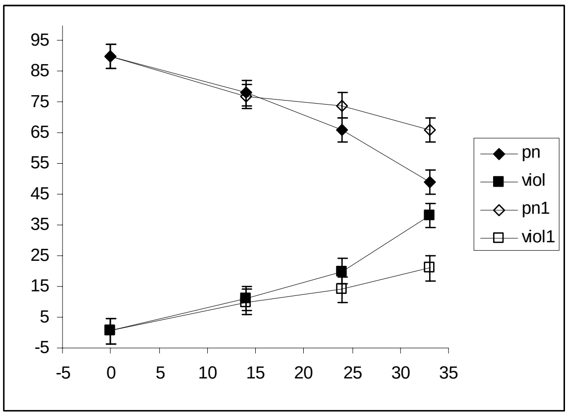

Figure 1: Transformation of pentlandite to violarite at 80˚C and pH 3.4. Both experiments were ran under Ar with Fe^{3+} acetate as an oxidant. $H_2S(g)$ was added to the run marked with solid symbols.

Progress of the transformation was followed by quantitative phase analysis using Rietveld refinement of the powder diffraction patterns. The "Rietica" program was used in all analyses. Powder x-ray diffraction patterns on the samples from the waterbath and the hydrothermal call were measured using a Huber Imaging Plate Guinier Camera with Co$K\alpha_1$ radiation. Polished mounts of some of the reaction products were examined using backscattered electron diffraction imaging and energy dispersive x-ray analysis on a PHILIPS XL30 Field Emission Gun Scanning Electron Microscope.

RESULTS

The waterbath experiments showed that the transformation of pentlandite to violarite occurs at 80°C over the pH range 3 to 5. Around 20(4)% of the pentlandite will transform to violarite is 35 days (Figure 1). The value of the pH within the range 3 to 5 did not seem to significantly influence the rate of the transformation. The transformation of pentlandite is promoted by the addition of small amount of $H_2S(g)$ to the Ar stream and 1 ml of a 0.1 M solution of $Fe(CH_3COO)_2(OH)$ to the acetic acid solution. Under these conditions 50(4)% of the pentlandite is transformed to violarite in 35 days. At 120°C and 3.5 bars the pentlandite to violarite transformation occurs over 3 days; after that time the pyrrhotite starts to transform to marcasite or pyrite indicating significant dissolution of the pentlandite and pyrrhotite releasing $H_2S(aq)$ into solution during the experiment (Figure 2).

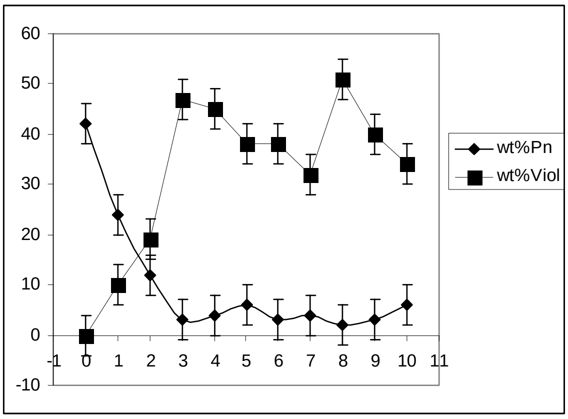

Figure 2: Transformation of pentlandite to violarite at 120˚C and 3.5 bars at pH 3.9.

The cell parameters of pentlandite, violarite and pyrrhotite do not change significantly over the course of the reactions indicating no compositional re-adjustment during the transformation. The cell variation observed by Rietveld refinement is less than 2 standard deviations. It should be noted that these experiments were performed in batch mode with a coarse grained sample and there was no independent phase standard so the results are only semi-quantitative. The variation in the weight fractions for violarite and pentlandite after the first 3 days of reaction provides an indication of the relative uncertainties in the phase quantities (Figure 2).

Backscattered electron images show that the pentlandite lamellae are progressively transformed to violarite (Figure 3a). Note that where pentlandite is transformed to violarite, the pyrrhotite host is cracked and fractured allowing fluid flow through the matrix. Figure 3 also shows a gap of between 200 and 400 nm between the end of the pentlandite lamellae and the violarite. Higher magnification images reveal the finely cracked and pitted texture of the secondary violarite (Figure 3b). This texture is very similar to that observed by Grguric (2002) for supergene violarite (figure 2e in that work). Backscattered electron diffraction showed the mineral to be very fine-grained and not a single crystal.

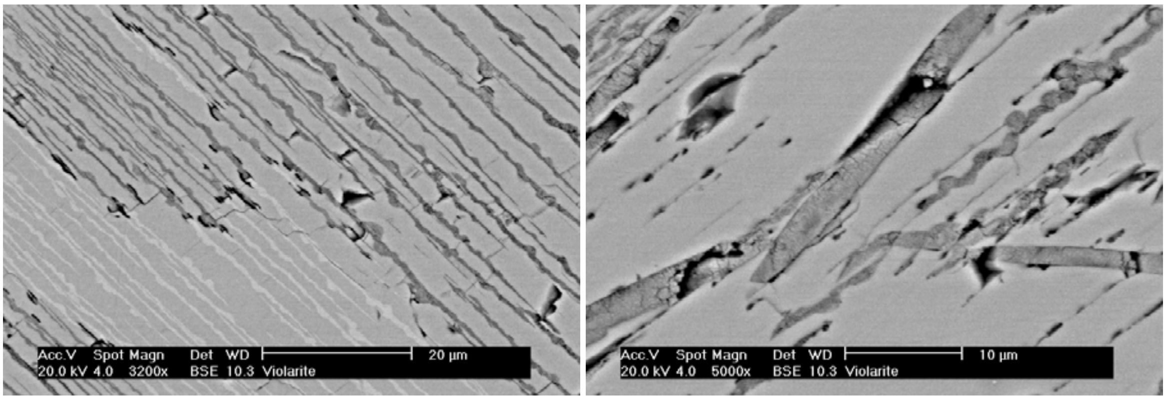

Figure 3: Backscattered electron image showing the partial transformation of the pentlandite/pyrrhotite to violarite/pyrrhotite. **a (left):** The light mineral is unaltered pentlandite, the matrix is pyrrhotite and the darker mineral is violarite. Note that where the pentlandite is transformed to violarite, the pyrrhotite matrix is cracked and pitted and that there is a gap of between 0.2 to 0.4 μm gap between the end of the pentlandite lamella and the violarite. **b (right):** High magnification view of the newly formed violarite, showing that the violarite is finely cracked and pitted giving it a porous texture.

DISCUSSION

This study is the first to reproduce experimentally, under mild hydrothermal conditions, the reaction of supergene oxidation of pentlandite into violarite. The SEM imaging indicates unambiguously that the transformation mechanism is dissolution-reprecipitation (e.g., Putnis 2004) and not a topotactical leaching of metal from pentlandite. The reaction front is occupies only a small volume ($<< 1\ \mu m^3$) of fluid.

The pentlandite to violarite reaction is complex, depending upon a large number of solution parameters, including pH, oxidation/reduction potential, and speciation and concentration of sulfur, iron and nickel in solution (Figure 4). Available thermodynamic properties (Warner *et al.* 1996) indicate that, under acidic conditions, the reaction happens under very reducing conditions ($fH_2(g)$ ca. 0.2 bars; Figure 4b). An overall reaction using a Fe-sulfide (e.g., the thermodynamically stable pyrite) as an Fe-sink, $H_2S(aq)$ as the aqueous sulfur species (Figure 4a) and oxygen as an oxidant (reaction (1) on Figure 4c) can be written as:

$$\textbf{Pentlandite} + 2.75\ O_2(g) + 5.5\ H_2S(aq) = 2.25\ \textbf{Violarite} + 2.25\ \textbf{Pyrite} + 5.5\ H_2O \quad (1)$$

According to this equation, the transformation of pentlandite to violarite is not pH dependant. However, SEM work does not show evidence for precipitation of an iron sulfide coupled with the violarite precipitation. Hence, we can assume that the excess iron was carried away in the solution:

$$\textbf{Pentlandite} + 1.625\ O_2(g) + H_2S(aq) + 4.5\ H^+ = 2.25\ \textbf{Violarite} + 2.25\ Fe^{2+} + 3.25\ H_2O \quad (2)$$

This reaction is promoted by more acidic pH and by high $H_2S(aq)$ concentrations. The equilibrium solubility of Fe and Ni at 80˚C for conditions under which pyrite, pentlandite and violarite co-exist in presence of 0.2 molal of the Na-Acetate-acetic acid buffer was calculated to vary from 58 ppm Fe and 1.14 ppm Ni at pH 3.62 to 48 ppb Fe and less than a ppb Ni at pH 5.18, and hence is high enough to explain the preferential leaching of Fe.

In the experiments where Fe^{3+} was added, we can assume that the oxidant was Fe^{3+}:

$$\textbf{Pentlandite} + 6.5\ Fe^{3+} + H_2S(aq) = 2\ H^+ + 2.25\ \textbf{Violarite} + 8.75\ Fe^{2+} \quad (3)$$

Equation (3) is promoted by higher Fe^{3+} and $H_2S(aq)$ concentrations; this explains why the reaction happens faster when $Fe^{3+}(CH_3COO)_2(OH)$ and $H_2S(g)$ are added to the solution.

A detailed investigation in the kinetics and mechanism of the transformation is currently under way and will be reported at a later date.

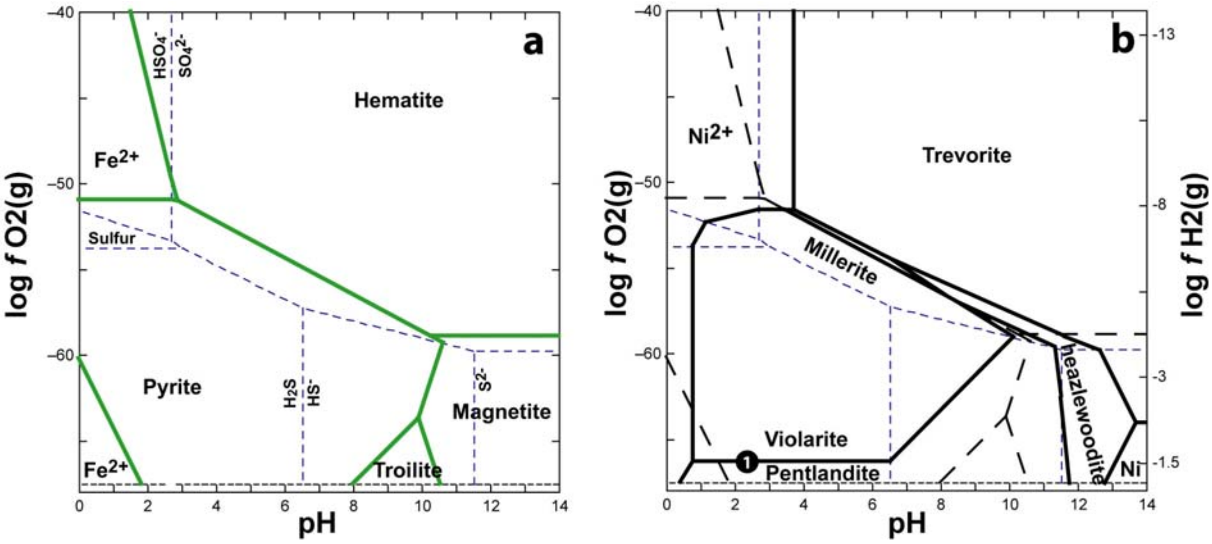

Figure 4: Log fO_2(g) versus pH diagram illustrating the solubility and phase relationships among Fe-sulphides (left) and Fe-Ni-sulphides (right) at 80˚C. Thin dashed lines on both diagrams show the sub-diagram for sulphur (activity of sulphur species = 10^{-3}). The diagram on the right was built assuming that the Fe involved in the reactions among Ni-bearing minerals is taken from the dominant species in the diagram on the left. Violarite is metastable relative to vaesite and polydymite, and these two minerals were not considered. Thermodynamic properties are from the Lawrence Livermore National Laboratory database (version 8, revision 6), except for the following species: first ionisation constant of H_2S(aq) from Suleimenov & Seward (1997), violarite and pentlandite from Warner *et al.* (1996).

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