

LETTER

Transformation of pentlandite to violarite under mild hydrothermal conditions

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ABSTRACT

The transformation of pentlandite, $(\text{Ni,Fe})_9\text{S}_8$, to violarite, $(\text{Ni,Fe})_3\text{S}_4$, has been investigated under mild hydrothermal conditions, at constant values of pH (range 3 to 5) controlled by the acetic acid/sodium acetate buffer. At 80 °C, 20(4) wt% of the pentlandite transforms to violarite in 33 days; with the addition of small amounts of $\text{Fe}^{3+}(\text{CH}_3\text{COO})_2(\text{OH})$ and H_2S the reaction reaches 40(4) wt% completion in this time. At 120 °C and a pressure of 3.5 bars the reaction is complete in 3 days at pH 3.9. Electron backscatter diffraction and backscattered electron imaging reveal that the reaction textures are typical of a coupled dissolution-precipitation reaction, rather than a solid state electrolytic process as has been previously reported. The gap between the dissolution front and the precipitation front of violarite is less than 400 nm. The violarite produced by these hydrothermal transformations is texturally similar to supergene violarite, being fine grained, porous and finely cracked.

Keywords: Transformation, replacement reactions, pentlandite, sulfides, violarite

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 and can be a significant part of the ore (Nickel et al. 1974; Misra and Fleet 1974). Violarite can also form as a primary phase by exsolution from pentlandite (Grguric 2002). Michener and Yates (1944) reported that the transformation of pentlandite to violarite occurs in drill cores containing primary pentlandite over a 25 year period when left exposed to the weather in Sudbury, Canada, indicating that the reaction can occur rapidly on a geological time scale. 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 fine-grained and relatively porous and it has a poor response in the floatation systems used to beneficiate 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 and 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 close-packed array of S atoms with metal atoms occupying

$\frac{1}{2}$ of the octahedral sites and $\frac{1}{8}$ of the tetrahedral sites of the array (Vaughan and Craig 1985). The composition field of violarite extends toward 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 just the composition Ni_2FeS_4 .

The formation of violarite from pentlandite by supergene process has long been recognized as a replacement reaction (Misra and Fleet 1974, and references therein). Misra and Fleet (1974) show that supergene violarite inherits the crystallographic orientation from the pentlandite it replaces. Pentlandite, $(\text{Fe,Ni})_9\text{S}_8$, also has a structure based on ccp S with Fe and Ni atoms occupying $\frac{1}{2}$ of the tetrahedral sites and $\frac{1}{8}$ of the octahedral sites (Rajamani and Prewitt 1973). Thornber (1975) proposed that the formation of violarite from pentlandite took place in the solid state and that electrochemical processes drove metal diffusion, with the ore body acting as a corrosion cell. Warner et al. (1992) attempted to transform pentlandite to violarite electrochemically using anodes of massive pentlandite-pyrrhotite in an electrochemical cell with a strongly acidic solution and an oxidizing potential of 0.8 V. Over several minutes they transformed the ends of their electrodes to amorphous elemental S with no evidence of violarite. Putnis (2002) suggested that the porous and cracked texture exhibited by supergene violarite indicates a dissolution-precipitation reaction rather than a topotactic transformation. Recent studies have shown that crystallographic orientations can be inherited in couple dissolution-precipitation reactions (Putnis et al. 2005; Labotka et al. 2004). We have undertaken a detailed laboratory study of this transformation using a series of free drift water bath and flow-through hydrothermal cell experiments. We report here preliminary results of these studies into

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the conditions under which the transformation occurs and on mechanism of the reaction.

EXPERIMENTAL METHODS

Both natural and synthetic pentlandite were used as the starting material for the transformation experiments. Pure pentlandite, in grains larger than 1 mm, is difficult to obtain naturally or to prepare synthetically and one must use either natural or synthetically 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 hydrotalcite minerals, serpentine minerals, and magnetite, was used for many of the preliminary water bath experiments, but proved to be too fine grained (<0.1 mm) for easy use in the hydrothermal cell experiments. For these latter experiments we used a range of synthetic pentlandites that had been prepared and annealed by Etschmann et al. (2004).

A series of water bath experiments was undertaken to establish the approximate conditions for the transformation of pentlandite to violarite. Sets of experiments were performed at 80 °C and in the pH range 3 to 5 fixed with the acetic acid/sodium acetate (CH_3COONa) buffer (~0.2 M total acetate concentration). In all experiments, 1.0 g of pentlandite concentrate was added to a flask containing 100 mL of acid solution. Duplicate experiments were performed for each pH value, one set of experiments had Ar gas slowly bubbled through the solution to minimize the mixing with air. In the second set a small amount of H_2S (less than 0.05%) was mixed with the Ar stream. To some of the reactions a mild oxidizing agent, 1 mL of 0.1 M $\text{Fe}(\text{CH}_3\text{COO})_2(\text{OH})$ 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 ($\text{Fe}_{4.66}\text{Ni}_{4.29}\text{S}_8$), was exsolved from monosulfide solid solution at 150 °C for 672 h and buffered by an equal mass of natural monoclinic pyrrhotite. The samples contained 39 wt% pentlandite and 61 wt% pyrrhotite $\text{Fe}_{0.81}\text{Ni}_{0.16}\text{S}$ and had a texture of massive pyrrhotite host with parallel 1 μm lamella of pentlandite. The sample was coarsely crushed to give an approximate grain size of between 1 and 2 mm. Samples of between 1 and 5 grams of synthetic pentlandite-pyrrhotite were loaded into a fine mesh stainless steel sample tube in the hydrothermal cell and heated to 120 °C with a pressure of 3.5 bars. An acetic acid-sodium acetate solution of pH 4.0 was pumped round the cell. The transformation reaction was interrupted every 24 h, 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 changed each day. Samples removed from the cell were allowed to dry on blotting paper at room temperature for 2 to 3 days before they were analyzed.

Progress of the transformation was followed by quantitative phase analysis using Rietveld refinement of the powder diffraction patterns. The program Rietica was used in all analyses (Hunter 1997). Powder X-ray diffraction pattern on the samples from the water bath and the hydrothermal cell were measured using a Huber Imaging Plate Guinier Camera G670 with $\text{CoK}\alpha_1$ radiation. Polished mounts of the reaction products were examined by EBSD, BSE imaging and EDS analysis on a PHILIPS XL30.

RESULTS

The water bath experiments showed that the transformation of pentlandite to violarite occurs at 80 °C over the pH range 3 to 5. Around 20(4) wt% of the pentlandite will transform to violarite in 33 days (Fig. 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 amounts of $\text{H}_2\text{S}(\text{g})$ to the Ar stream and 1 mL of a 0.1 M solution of $\text{Fe}(\text{CH}_3\text{COO})_2(\text{OH})$ to the acetic acid solution. Under these conditions 40(4) wt% of the pentlandite is transformed to violarite in 33 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 into marcasite or pyrite, indicating significant dissolution of the pentlandite and pyrrhotite, releasing $\text{H}_2\text{S}(\text{aq})$ into solution during the experiment (Fig. 2). These experiments were performed in batch mode with

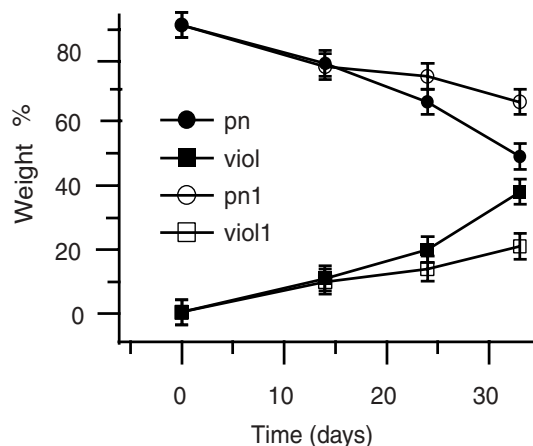


FIGURE 1. The wt% phase variation with time during transformation of pentlandite (Pn) to violarite (VI) at 80 °C and pH 3.4. Open symbols (reaction 1) with Ar gas and Fe acetate in solution; solid symbols (reaction 2) with Ar + H_2S gas and Fe acetate.

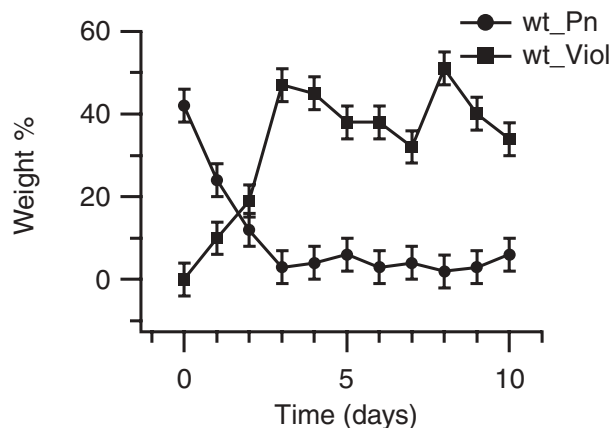


FIGURE 2. Transformation of pentlandite to violarite at 120 °C and 3.5 bars (pH ~3.9).

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 (Fig. 2). Monitoring of the cell parameters of pentlandite and violarite showed that they 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 ± 3 standard deviations.

Backscattered electron images show that the pentlandite lamellae are progressively transformed to violarite (Figs. 3a and 3b). Where pentlandite is transformed to violarite, the pyrrhotite host is cracked and fractured allowing fluid flow through the matrix, the boundaries between the transformed and untransformed regions are clearly indicated in Figure 3a by cracking in the pyrrhotite. Figure 3b also shows a gap of approximately 200 and 400 nm between the end of the pentlandite lamellae and

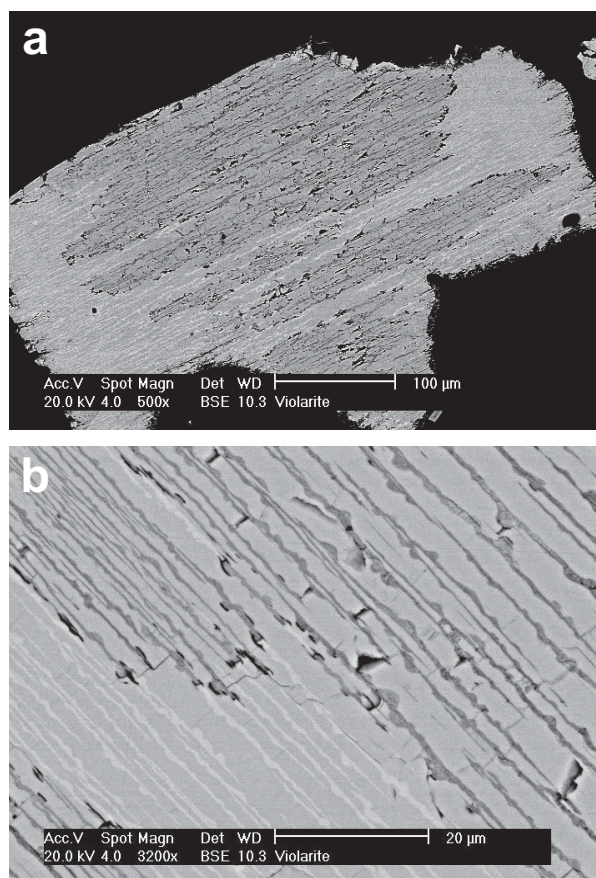


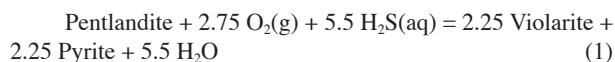
FIGURE 3. Backscattered electron image showing the partial transformation of the pentlandite/pyrrhotite to violarite/pyrrhotite. (a) The light mineral is unaltered pentlandite, the matrix is pyrrhotite, and the darker mineral is violarite. Note where the pentlandite is transformed to violarite, the pyrrhotite matrix is cracked. (b) A closer view reaction front between pentlandite-pyrrhotite and violarite-pyrrhotite and pitted and that there is a gap of approximately 0.2 to 0.4 μm between the end of the pentlandite lamella and the violarite. Note finely cracked and pitted porous texture of the violarite.

the violarite, and shows the finely cracked and pitted texture of the secondary violarite. This texture is similar to that observed by Grguric (2002) for supergene violarite (Fig. 2e in that work). The volume change associated with the transformation is 11.4% when calculated from the volumes of the pentlandite and violarite unit cells both of which contain 32 S atom *ccp* arrays. The shrinkage reflects the loss of 12 cations from the cell; in this case mainly Fe.

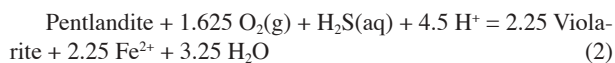
DISCUSSION

This study is the first to reproduce experimentally, under mild hydrothermal conditions, the reaction of supergene oxidation of pentlandite into violarite. The SEM images indicate that the transformation mechanism is dissolution-reprecipitation and not a solid state diffusion of metal from pentlandite. The gap at the reaction front and the porous microcrystalline texture are strong indicators of a coupled dissolution-reprecipitation reaction (Putnis 2002; Putnis et al. 2005; Labotka et al. 2004),

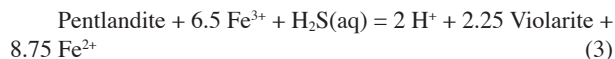
i.e., the pentlandite is completely dissolved into the solution layer at the interface, and violarite crystallizes from metal and sulfide ions in the solution layer. The gap at the reaction front may have expanded during drying as it is often contiguous with “cracking” of the pyrrhoite—although this cracking is probably a recrystallization front in pyrrhoite. However, it is clear that the volume occupied by the fluid is small ($\ll 1 \mu\text{m}^3$) and the local composition of the fluid may be quite distinct from that of the bulk. Attempts to use EBSD to establish crystallographic relations between the unaltered pentlandite-pyrrhotite and transformed violarite-pyrrhotite were not successful because violarite and the surrounding pyrrhotite would not give EBSD patterns, probably due to their small crystallite size. The pentlandite to violarite reaction appears to be 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. Available thermodynamic properties (Warner et al. 1996) indicate that under acidic conditions, the reaction takes place under very reducing conditions [$f_{\text{H}_2}(\text{g}) \sim 0.2$ bars; Fig. 4c]. An overall reaction using a Fe-sulfide (e.g., the thermodynamically stable pyrite) as an Fe-sink, $\text{H}_2\text{S}(\text{aq})$ as the aqueous sulfur species (Fig. 4a), and oxygen as an oxidant (reaction 1 in Fig. 4c) can be written as:



According to this equation, the transformation of pentlandite to violarite is not pH dependent. 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:



This reaction is promoted by more acidic pH and by high $\text{H}_2\text{S}(\text{aq})$ 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 m of the Na-Acetate-acetic acid buffer was calculated using the Lawrence Livermore National Laboratory database (version 8; revision 6), except for the following species: first ionization constant of $\text{H}_2\text{S}(\text{aq})$ from Suleimenov and Seward (1997); violarite and pentlandite from Warner et al. (1996). This solubility varies from 58 ppm Fe and 1.14 ppm Ni at pH 3.62 to 48 ppm Fe and less than 1 ppm Ni at pH 5.18, and hence is high enough to explain the preferential dissolution of Fe. In the experiments where Fe^{3+} was added, we can assume that the oxidant was Fe^{3+} :



Equation 3 is promoted by higher Fe^{3+} and $\text{H}_2\text{S}(\text{aq})$ concentrations; this explains why the reaction happens faster when $\text{Fe}^{3+}(\text{CH}_3\text{COO})_2(\text{OH})$ and $\text{H}_2\text{S}(\text{g})$ are added to the solution. This correlation between solution chemistry and reaction rate supports the textural evidence for a coupled dissolution-reprecipitation

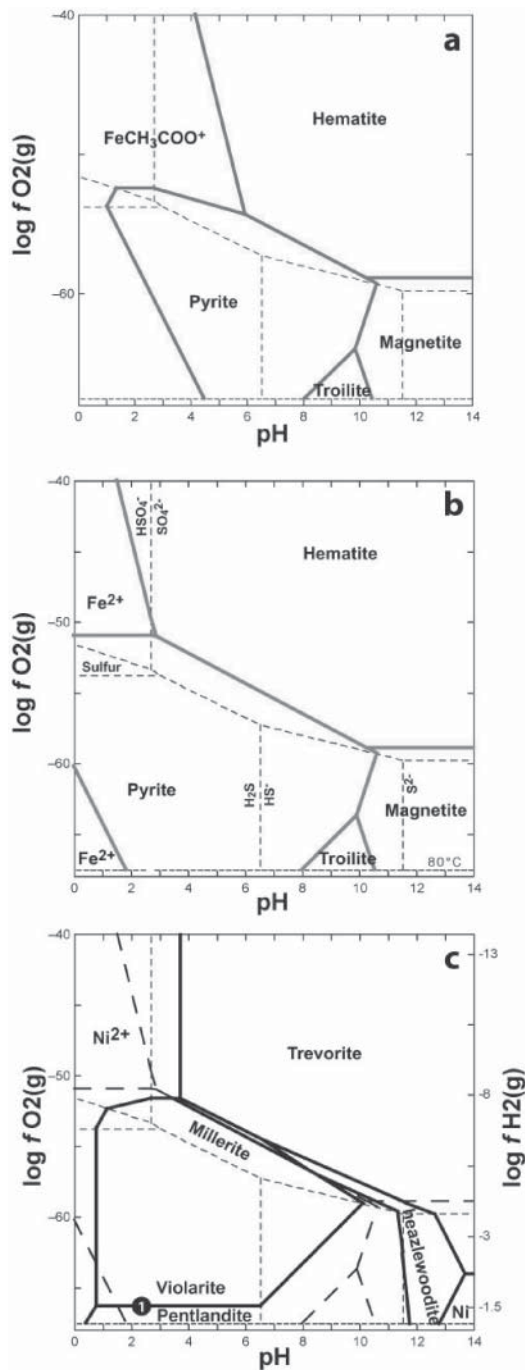


FIGURE 4. $\log f_{\text{O}_2}(\text{g})$ vs. pH diagram illustrating the solubility and phase relationships among Fe-sulfides (left) and Fe-Ni-sulfides (right) at 80 °C. Thin dashed lines on both diagrams show the sub-diagram for sulfur (activity of sulfur species = 10^{-3}). The diagram on the right 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. (See text for details.)

mechanism rather than the idea of an electrolytic solid state process.

Extrapolation of the reaction rates obtained in these preliminary experiments to 20 °C suggests that that transformation can take place in Nature over a period of 5 to 10 years, a figure in keeping with the finding of Michener and Yates (1944). Detailed investigation in the kinetics and mechanism of the transformation is currently under-way and will be reported at a later date.

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REFERENCES CITED

- Dunn, J.G. and Howes, V.L. (1996) The oxidation of violarite. *Thermochimica Acta*, 282/283, 305–316.
- Etschmann, B., Pring, A., Putnis, A., Grguric, B.A., and Studer, A. (2004) A kinetic study of the exsolution of pentlandite (Ni,Fe)₉S₈ from the monosulfide solid solution (Fe,Ni)S. *American Mineralogist*, 89, 39–50.
- Grguric, B.A. (2002) Hypogene violarite of exsolution origin from Mount Keith, Western Australia: field evidence for a stable pentlandite-violarite tie line. *Mineralogical Magazine*, 66, 313–326.
- Hunter, B.A. (1997) IUCr Powder Diffraction 21, 22—Rietica 1.7.7
- Labotka, T.C., Cole, D.R., Fayek, M., Riciputi, L.R., and Stadermann, F.J. (2004) Coupled cation and oxygen-isotope exchange between alkali feldspar and aqueous chloride solution. *American Mineralogist*, 89, 1822–1825.
- Michener, C.E. and Yates, A.B. (1944) Oxidation of primary nickel sulphide. *Economic Geology*, 39, 506–514.
- Misra, K.C. and Fleet, M.E. (1974) Chemical composition and stability of violarite. *Economic Geology*, 69, 391–403.
- Nickel, E.H., Ross, J.R., and Thornber, M.R. (1974) The supergene alteration of pyrrhotite-pentlandite ore at Kambalda, Western Australia. *Economic Geology*, 69, 93–107.
- O'Neill, B., Tenailleau, C., Ngothai, Y., Struder, A., Brugger, J., and Pring, A. (2005) A flow-through hydrothermal cell for in-situ neutron diffraction studies of phase transformation. *Physica B*, in press.
- Putnis, A. (2002) Mineral replacement reactions: from microscopic observations to microscopic mechanisms. *Mineralogical Magazine*, 66, 689–708.
- Putnis, C.V., Tsukamoto K., and Nishimura, Y. (2005) Direct observations of pseudomorphism: compositional and textural evolution at a fluid-solid interface. *American Mineralogist*, 90, 1909–1912.
- Rajamani, V. and Prewitt, C.T. (1973) Crystal chemistry of natural pentlandites. *Canadian Mineralogist*, 12, 178–187.
- Suleimenov, O.M. and Seward, T.M. (1997) A spectrophotometric study of hydrogen sulphide ionisation in aqueous solutions to 350 °C. *Geochimica et Cosmochimica Acta*, 61, 5187–5198.
- Thornber, M.R. (1975) Supergene alteration of sulphides, I. A chemical model based on massive nickel sulphide deposits at Kambalda, Western Australia. *Chemical Geology*, 15, 1–14.
- Vaughan, D.J. and Craig, J.R. (1985) The crystal chemistry of iron-nickel thiospinels. *American Mineralogist*, 70, 1036–1043.
- Warner, T.E., Rice, N.M., and Taylor, N. (1992) An electrochemical study of the oxidative dissolution of synthetic pentlandite in aqueous media. *Hydrometallurgy*, 31, 55–90.
- Warner, T.E., Rice, N.M., and Taylor, N. (1996) Thermodynamic stability of pentlandite and violarite and new Eh-pH diagrams from the iron-nickel-sulphur aqueous system. *Hydrometallurgy*, 41, 107–118.

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