

The Use of *in situ* Neutron Diffraction Methods to Determine the Kinetics of Mineral Reactions in Iron Nickel Sulfides.

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The penetrating power of a beam of neutrons together with its scattering interactions with minerals offers a number of advantages over alternative techniques such as synchrotron and conventional laboratory sources for the study of the kinetics and mechanisms of mineral reactions.

Pentlandite is a primary mineral that forms as an exsolution product from the breakdown of the monosulfide solid solution (*mss*), an immiscible sulfide melt, from mafic and ultramafic magmas. Violarite, is an abundant supergene alteration product in massive and disseminated Ni sulfide deposits, where it replaces pentlandite and can be a significant part of the ore. To measure the kinetics of the exsolution of pentlandite from *mss* we undertook a series of *in situ* cooling neutron diffraction experiments and anneal/quench experiments. These showed that the temperature at which exsolution commences, upon cooling, decreases from 873 K for $\text{Fe}_{0.7}\text{Ni}_{0.3}\text{S}$ to 823 K for $\text{Fe}_{0.9}\text{Ni}_{0.1}\text{S}$ and that exsolution effectively between 598 and 548 K. Both high Ni content and high M:S ratio served to facilitate nucleation rate, indicating that nucleation occurs at S vacancies within *mss* crystals rather than at grain boundaries.

Having a low M:S ratio ($\text{M}_{0.97}\text{S}$) in the starting *mss* revealed makes the kinetics of the system is more complex and a refined Avrami model kinetic model had to be employed. (Wang et al., 2005). The lowest rates of reaction are observed for the more S rich compositions. The activation energy (E_a) varies from 49.6 to 20.7 $\text{kJ}\cdot\text{mol}^{-1}$ with reaction extent (y). The decrease in E_a with y is related to the increasing vacancy concentration in the host phase during the course of exsolution.

The kinetics and mechanism of the transformation of pentlandite, $(\text{Ni,Fe})_9\text{S}_8$, to violarite, Ni_2FeS_4 , have been studied using a specially built flow through cell for *in situ* neutron diffraction under hydrothermal conditions.

The reaction was studied at constant values of pH (range 3 to 5) controlled by an acetic acid/sodium acetate buffer. At 353 K 20(4) wt% of the pentlandite transforms to violarite in 33 days; with the addition of small amounts of $\text{Fe}^{\text{III}}(\text{CH}_3\text{COO})_2(\text{OH})$ and H_2S the reaction reaches 40(4) wt% completion in this time. At 393 K 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-reprecipitation reaction, rather than a solid-state electrolytic process as has been previously reported. (Tenailleau et al 2006)

References

- Tenailleau, C., Pring, A., Etschmann, B., Brugger, J., Grguric, B. and Putnis, A. (2006) *Am. Mineral.*, 91,706-709.
Wang, H., Pring, A., Ngothai, Y., O'Neill, B. (2005) *GCA*, 69, 415-125,