The synthesis of metavivianite and the oxidation sequence of vivianite

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A mixture of metavivianite, vivianite, and spheniscidite was obtained from an aqueous solution of FeSO₄·7H₂O and (NH₄)₂HPO₄ at temperatures between 50 and 60 °C. The oxidation sequence of partially oxidized vivianite toward santabarbaraite or a solid solution between β-Fe₂(PO₄)O and Fe₄(PO₄)₃(OH)₃, without passing through metavivianite, was also demonstrated.

Keywords: Vivianite, Metavivianite, XRD, XAFS

INTRODUCTION

Vivianite [Fe⁺⁺³(PO₄)₂·8H₂O], named after an English mineralogist John Henry Vivian, is a hydrous phosphate of ferrous iron. Its structure was first determined by Mori and Ito (1950) and further discussed by Bartl (1989) and Capitelli et al. (2012). Vivianite typically occurs as a secondary mineral in the oxidized zone of metallic ore deposits or in the weathering products of phosphorus-rich granitic pegmatites. Vivianite is also found as a mineral replacing organic material in fossilized bones and leaves and as a scale buildup of valves and flowmeters due to the chemical precipitation reaction of Fe²⁺ with the orthophosphate anion. Unaltered vivianite is generally colorless, but usual vivianite can be green to indigo blue in the most of occurrences. The reduction of the mineral form into the powder form by grinding leads to a rapid change in color (from colorless to deep blue). This change in color of the parent vivianite is associated with the oxidation of ferrous iron to ferric iron (Watson, 1918; McCammon and Burns, 1980; Hanzel et al., 1990). On the other hand, metavivianite was first described as a triclinic Fe⁺⁺³⁺Fe⁺⁺⁺(PO₄)₂·8H₂O isostructural with symplectite Fe⁺⁺³⁺(AsO₄)₂·8H₂O (Ritz et al., 1974). Based on subsequent studies on ferric ions in vivianite and metavivianite (Dormann and Poullen, 1980; Dormann et al., 1982; Rouzies and Millet, 1993), the chemical formula of metavivianite was proposed as Fe⁺⁺³⁺Fe⁺⁺⁺(PO₄)₂(OH)₂·6H₂O (Chukanov et al., 2012). In this context, metavivianite was considered as an oxidized form of vivianite, and the colorization of vivianite was frequently discussed along with the formation of metavivianite. Nevertheless, the extent of oxidation in natural vivianite does not necessarily imply the formation of metavivianite (Dormann and Poullen, 1980; Dormann et al., 1982), and several studies have indicated that crystalline vivianite oxidizes into an X-ray amorphous state without passing through the metavivianite state (Miot et al., 2009; Rothe et al., 2014; Bae et al., 2018). It should be noted that the direct production of metavivianite has not been reported to the best of our knowledge, although the synthesis of vivianite through the reaction of ferrous cations in orthophosphoric solutions has been reported in many studies (Roldán et al., 2002; Rouzies and Millet, 1993; Bae et al., 2018).

In this technical note, a new synthetic method for the production of metavivianite was demonstrated for the first time, together with the oxidation process of the synthesized vivianite.

EXPERIMENTAL PROCEDURE

Vivianite was synthesized according to the method described by Roldán et al., (2002). An aqueous solution of 0.60 g (NH₄)₂HPO₄ (Wako Pure Chemical Industries, LTD., 99.0%) and 18 mL distilled water was prepared, and 1.80 g of FeSO₄·7H₂O (FUJIFILM Wako Pure Chemical Corp., 99.0%) was added while stirring the pa-
rent solution at 300 rpm using a hot stirrer (DLAB MS-H280-Pro). White precipitates were obtained just after the dissolution of FeSO₄·7H₂O. However, the color of the precipitates gradually changed from white to blue. This change in color indicated partial oxidation of the vivianite (Watson, 1918; McCammon and Burns, 1980). The obtained precipitates were filtered after stirring for 1 h and subsequently dried for 24 h at the various temperatures of 24 (room temperature), 50, 65, 70, and 90 °C using a constant temperature dryer (ETTAS EO-300B). The color of the sample dried at 24 °C was blue, and it was subsequently used as a synthesized parent vivianite (viv-SY) in this study. The samples heated at 50, 65, 70, and 90 °C are hereafter abbreviated as viv-H50, viv-H65, viv-H70, and viv-H90, respectively. In order to investigate the structural change in viv-SY due to water immersion, a series of samples were prepared by aging the parent viv-SY in high-temperature distilled water for 24 h. The samples obtained in distilled water maintained at 50, 60, 70, and 90 °C are hereafter abbreviated as viv-W50, viv-W60, viv-W70, and viv-W90, respectively. We also conducted an experiment by controlling the reaction temperatures of the parent solutions at 50, 60, 70, and 90 °C. The obtained precipitates were filtered after stirring for 24 h and subsequently dried at 24 °C. The samples prepared from the solutions at 50, 65, 70, and 90 °C are hereafter abbreviated as viv-S50, viv-S65, viv-S70, and viv-S90, respectively.

The constituent phases of the samples were identified by means of X-ray diffraction (XRD, Rigaku Ultima III) with Co Kα radiation. The lattice constants for the vivianite phases in viv-SY, viv-H50, viv-W50, viv-W60, and viv-W70 were refined, and the results are listed in Table 1. The X-ray absorption fine structure (XAFS) spectra of Fe K-absorption edges were measured at Institute of Material Structure Science (IMSS), High Energy Accelerator Research Organization (KEK), Tsukuba, Japan. The X-rays were monochromatized with a Si (111) double-crystal monochromator. The appropriately weighted samples were mixed with BN powders to adjust the samples to a thickness suitable for XAFS measurements. The obtained mixtures were pressed into pellets with a diameter of 10 mm, and measured in transmission mode. We also measured the spectra of olivine (Mg,Fe²⁺)₂SiO₄ and vivianite (Fe³⁺(PO₄)₂·8H₂O) from San Carlos, Arizona, U.S.A., and the Tomokoni mine Potosi Department, Bolivia, respectively. Natural specimens were crushed into powder forms, and the powders were used to prepare sample pellets with BN powders. The corresponding X-ray absorption near edge structure (XANES) spectra were extracted from the measured spectra using the Athena and Artemis software package (Ravel and Newville, 2005).

**RESULT AND DISCUSSION**

Figure 1 shows the XRD patterns of the viv-SY, viv-H50, viv-H65, viv-H70, and viv-H90 together with the calculated patterns of vivianite (Mori and Ito, 1950) and metavivianite (Chukanov et al., 2012). The XRD pattern of viv-SY indicates relatively sharp Bragg peaks of vivianite with unit cell constants of \(a = 10.159(4)\,\text{Å}, \ b = 13.443(8)\,\text{Å}, \ c = 4.688(2)\,\text{Å}, \ \beta = 104.75(2)^\circ\) and \(V = 619.1\,\text{Å}^3\) (s.g. \(C2/m\)). On the other hand, the peaks of viv-H50 were broader than those of viv-SY and were

| Table 1. Calculated lattice constants for the vivianite phase |
| --- |
| **Space group** | \(a\) (Å) | \(b\) (Å) | \(c\) (Å) | \(\beta\) (°) | \(V\) (Å³) |
| Viv-SY | \(C2/m\) | 10.159(4) | 13.688(8) | 4.688(2) | 104.75(2) | 619.1 |
| Viv-H50 | \(C2/m\) | 10.116(10) | 13.349(5) | 4.673(1) | 104.71(4) | 604.0 |
| Viv-W50 | \(C2/m\) | 10.150(2) | 13.477(4) | 4.685(1) | 104.75(1) | 619.8 |
| Viv-W60 | \(C2/m\) | 10.142(3) | 13.458(6) | 4.689(1) | 104.73(2) | 619.0 |
| Viv-W70 | \(C2/m\) | 10.143(2) | 13.485(5) | 4.689(1) | 104.73(1) | 618.6 |
shifted towards the higher angle region. The lattice dimensions and the corresponding volume of viv-H50 [C2/m; \(a = 10.116(10)\) Å, \(b = 13.349(5)\) Å, \(c = 4.673(1)\) Å, \(\beta = 104.71(4)°\), \(V = 610.4\) Å³] were smaller than those of viv-SY. These observations correspond to structural collapse due to development of oxidation (McCammon and Burns, 1980) together with formation of structural disorder (Rouzies and Millet, 1993). The XRD patterns were significantly different for viv-H65 and viv-H70, and showed the appearance of a hollow pattern underneath the weak and broad Bragg peaks. Together with the weak spike peaks of vivianite, two peaks were observed at \(2\theta = 11.0°\) and 16.4°. The weak peak at 11.0° was found in the parent viv-SY and viv-H50. Therefore, an impurity phase appears to have been included in our syntheses of viv-SY. The mixed valence iron phosphates of the ferric or ferrous analogue of strunzite (Peacor et al., 1983; Peacor et al., 1987) are possible candidates for the peak at 11.0°. However, a lack of information did not allow us to identify the responsible structures. The peak at 16.4° was identified as 020 reflection of lepidocrocite FeOOH, which was also suggested as an oxidized product of vivianite (Roldán et al., 2002). The XRD pattern of viv-H90 showed no clear Bragg peaks, indicating the disappearance of the long-range ordering structure. Recently, a new mineral of santabarbaraite, \(\text{Fe}^{3+3} \left(\text{PO}_4\right)_2\left(\text{OH}\right)\cdot 5\text{H}_2\text{O}\) of an amorphous ferric iron hydroxyl phosphate hydrate was reported as a pseudomorph obtained by in situ oxidation of vivianite (Pratesi et al., 2003). In these contexts, the structure of vivianite was decomposed at high temperatures over 65 °C and the annealing at 90 °C for 24 h (viv-H90) was enough to produce amorphous santabarbaraite. The colors of samples viv-H50, viv-H65, viv-H70, and viv-H90 were blue, green, yellow, and brown, respectively.

Figure 2 shows the XRD patterns of the samples aged in distilled water at high temperatures. The XRD patterns of viv-W50, viv-W60, and viv-W70 indicate that the parent vivianite structure was almost intact and their lattice constants showed no significant differences. However, the XRD pattern of viv-W90 indicates a breakdown of vivianite, and the peaks were identified as those of \(\beta\)-\(\text{Fe}_2\left(\text{PO}_4\right)\text{O}\) and \(\text{Fe}_4\left(\text{PO}_4\right)\left(\text{OH}\right)_3\cdot 2\text{H}_2\text{O}\) solid solution series (Schmid-Beurmann, 2000), which are closely related to the synthetic lipscombite \([\text{Fe}^{2+}\text{Fe}^{3+}\left(\text{PO}_4\right)\left(\text{OH}\right)\left(\text{H}_2\text{O}\right)\_x]\) (Vochten and De Grave, 1981). The color of samples viv-W50, viv-W60 and viv-W70 was blue green, and that of viv-W90 was black blue.

Figure 3 shows the XRD patterns of the samples precipitated in high-temperature solutions. The most of the diffraction peaks from viv-S50 were attributed to vivianite and metavivianite. However, several peaks could not be assigned to vivianite and metavivianite. These peaks suggest the co-precipitation of a small amount of spheniscidite, \(\text{NH}_4\text{Fe}^{3+2} \left(\text{PO}_4\right)\left(\text{OH}\right)\cdot 2\text{H}_2\text{O}\) (Cavellec et al., 1994). The XRD pattern of viv-S60 indicates the appearance of vivianite, metavivianite, and spheniscidite, and the metavivianite/vivianite ratio was higher than that of viv-S50. These results suggest that metavivianite with good crystalline quality could be produced from the solutions maintained at approximately 60 °C. The XRD patterns of viv-
S70 and viv-S90 were different from those prepared from the solutions at lower temperatures, and the main constituent phase was spheniscidite. In the case of viv-S70, some additional peaks indicate the possible co-precipitation of green rust II (Simon et al., 2003), ferric or ferrous analogues of strunzite, and barbosalite $[\text{Fe}^{2+}\text{Fe}^{3+}2(\text{PO}_4)2(\text{OH})_2]$ (Redhammer et al., 2000). The XRD pattern of viv-S90 indicates that a single phase of spheniscidite was obtained, and this sample was subsequently used as a standard for Fe$^{3+}$ for the XANES measurements. The colors of samples viv-S50, viv-S60, viv-S70, and viv-S90 were blue green, green, yellow green, and pale green, respectively.

The oxidation states of Fe contained in the samples were studied by evaluating the energy of the Fe K-absorption edge of the XANES profiles. The position of each absorption edge was determined according to the position of $\mu t = 0.5$ in the normalized absorption coefficient profile, and the obtained values are summarized in Table 2.

**Table 2. The observed Fe K-absorption edge positions**

|          | Olivine | Vivianite | Viv-SY | Viv-S60 | Viv-H70 | Viv-S90 |
|----------|---------|-----------|--------|---------|---------|---------|
| Energy (eV)$^*$ | 7117.1  | 7117.7    | 7119.4 | 7120.0  | 7122.4  | 7122.7  |
| Shift (eV)   | +0.0    | +0.6      | +2.3   | +2.9    | +5.3    | +5.6    |

$^*$ Energy shift was calculated based on the position of olivine.

Figure 4 shows the XANES spectra for olivine, vivianite, viv-SY, viv-S60, viv-H70, and viv-S90. The oscillation behavior of the XANES spectrum for vivianite from Bolivia was identical to that observed in a previous study (Pratesi et al., 2003). Its Fe K-absorption edge was slightly higher but almost consistent with that of olivine, suggesting that the powdered sample prepared by crushing natural crystalline vivianite showed no significant oxidation in this case. On the other hand, the absorption edge for viv-SY was located at a higher energy value, and its XANES profile showed features similar to those observed for oxidized vivianite (Taylor et al., 2008). It could be interesting to estimate the fraction of Fe$^{3+}$ in viv-SY using the absorption edge energy positions listed in Table 2. The estimated fraction of Fe$^{3+}$ in viv-SY was approximately 0.40 when the edge positions of olivine and viv-S90 (spheniscidite) were utilized as the standard for pure Fe$^{2+}$ and Fe$^{3+}$, respectively. This value is still smaller than that calculated from the ideal chemical composition of metavivianite, as proposed by Chukanov et al. (2012). The edge positions shifted toward the higher energy side in the order viv-SY, viv-S60, viv-H70, and viv-S90. This shift suggests an increase in the Fe$^{3+}$ fraction enhanced by the formation of metavivianite, spheniscidite, and santabarbarite. The spectrum for viv-H70 was similar to that of santabarbarite (Pratesi et al., 2003).

**CONCLUSION**

This study demonstrated the formation of metavivianite from an aqueous solution of FeSO$_4$·7H$_2$O and (NH$_4$)$_2$HPO$_4$ at temperatures from 50 to 60 °C. Although the obtained sediment was a mixture of oxidized vivianite, metavivianite, and spheniscidite, this is the first report of the direct formation of metavivianite. The oxidation sequence of the partially oxidized vivianite toward santabarbarite or a solid solution between $\beta$-Fe$_2$(PO$_4$)O and Fe$_4$(PO$_4$)$_3$(OH)$_3$ without passing through metavivianite was experimentally confirmed.

**ACKNOWLEDGMENTS**

This study was conducted under the Inter-university Cooperative Research Program of the Institute for Materials Research, Tohoku University (Proposal 19K0051).
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Manuscript received April 17, 2020

Manuscript accepted August 7, 2020

Manuscript handled by Hiroki Okudera