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Rodolicoite and grattarolaite, intermediates in the thermal transformation of synthetic P-doped ferrihydrite

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Rodolicoite $FePO_4$ and grattarolaite Fe_3PO_7, naturally occurring anhydrous iron(III) phosphates have been identified in coal samples derived from Santa Barbara lignite mine, as final products of the progressive thermal conversion and oxidation of vivianite $Fe_3^{2+}(PO_4)_2$•$8H_2O$ to amorphous phase [1]. In natural environment however, the conversion steps of amorphous phase into these nanominerals are extremely difficult to identify. We propose to fill this gap by utilizing the nanoparticles of synthetic P-doped ferrihydrite Fe_5HO_8•$4H_2O$ as a source of amorphous hydrated iron(III) phosphate. This phase, at certain conditions, undergoes thermal conversion to rodolicoite and grattarolaite.

Synthetic anhydrous iron(III) phosphate analogs of berlinite $AlPO_4$ and α- quartz, particularly rodolicoite, receive a lot of attention in mineral sciences partly because of their geologic importance and partly because of their prospective applications as raw material for lithium iron phosphate batteries $LiFePO_4$[2]. In this case, potential presence of impurities and intermediates during thermal synthesis or oxidation steps of rodolicoite is inexpedient. Thus, the main goal of this research was to characterize the products of thermal transformation of P-doped ferrihydrite. Ferrihydrite synthesized in the presence of phosphate PO_4^{3-} was used. P-ferrihydrites were synthesized by precipitation from aqueous solutions of $Fe_2(SO_4)_3$ and K_2HPO_4 at pH 8.2. The thermal transformation experiments were carried out using ferrihydrites with various P/Fe ratios (0.00, 0.20, 0.50 and 1.00) at various heating temperatures. All samples were characterized by XRD, FTIR, SEM and differential thermal analysis prior and after the experiments.

The results indicate that the presence of phosphate not only stabilizes the structure of ferrihydrite but also controls its thermal transformation to hematite α-Fe_2O_3 in more complex manner. Pure ferrihydrite transforms immediately to hematite at the temperature below 500˚C. When ferrihydrite with P/Fe=0.20 and P/Fe=0.50 was annealed, the presence of tetragonal maghemite γ-Fe_2O_3 was detected between 650 and 700˚C, followed by formation of hematite α-Fe_2O_3 at higher temperatures. Hematite is accompanied with small amounts of trigonal rodolicoite $FePO_4$ which forms between 800 and 900˚C. This intermediate phase is not very stable and completely vanishes in the sample of P/Fe=0.20 at temperatures above 900˚C (transforms into hematite). In contrast, a further increase in temperature of the sample of P/Fe=0.50 causes formation of hematite associated with grattarolaite Fe_3PO_7. Thermal transformation of ferrihydrite containing the highest-P ratio (P/Fe=1.00) results in the formation of rodolicoite and hematite at 700˚C, grattarolaite at 800˚C, and a mixture of two anhydrous phosphates with hematite around 1000˚C.

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