Dehydration processes in the meta-autunite group minerals meta-autunite, meta-\( \text{saléeite} \), and metatorbernite

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ABSTRACT

We investigated dehydration processes in uranyl phosphate minerals of the meta-autunite group that consist of uranyl phosphate sheets and interlayer cations, and water molecules. Meta-autunite \( [\text{Ca(UO}_2\text{PO}_4\text{)}_2, 6\text{H}_2\text{O}] \), meta-\( \text{saléeite} \) \( [\text{Mg(UO}_2\text{PO}_4\text{)}_2, 8\text{H}_2\text{O}] \), and metatorbernite \( [\text{Cu(UO}_2\text{PO}_4\text{)}_2, 8\text{H}_2\text{O}] \) were selected for our study. The change in basal spacing between two adjacent uranyl phosphate sheets with temperature was examined by temperature-controlled X-ray diffraction (XRD) analysis from room temperature (RT) to 300 °C to determine structurally distinct, dehydrated phases. Thermogravimetric and differential thermal analyses (TG/DTA) were also performed under conditions similar to those used for the XRD analysis to clarify the hydration states of the dehydrated phases. Retention of the structure of the uranyl phosphate sheets under a high vacuum, equivalent to 300 °C, was confirmed by transmission electron microscopy. Meta-autunite, meta-\( \text{saléeite} \), and metatorbernite decreased their basal spacings by losing water molecules. Comparison of the TG/DTA and XRD results indicates that the changes in basal spacings of the dehydrated phases with temperature are as follows: 8.32 Å (6 H\(_2\)O per unit formula) at RT, 7.31 Å (? H\(_2\)O) and 6.68 Å (? H\(_2\)O) at 75 °C, 6.34 Å (2 H\(_2\)O) at 120 °C, and 5.81 Å (1 H\(_2\)O) at 300 °C for meta-autunite; 8.29 (8 H\(_2\)O) and 7.73 Å (? H\(_2\)O) at RT, 6.62 Å (probably, 2 H\(_2\)O) at 40 °C, 6.54 Å (2 H\(_2\)O) at 160 °C, and 5.52 Å (1 H\(_2\)O) at 300 °C for meta-\( \text{saléeite} \); and 8.61 Å (8 H\(_2\)O) at RT, 8.07 Å (4 H\(_2\)O) at 100 °C, 6.58 Å (2 H\(_2\)O) at 200 °C, and 5.60 Å (1 H\(_2\)O) at 300 °C for metatorbernite. The dehydration processes revealed by XRD and TG/DTA under similar experimental conditions are slightly different from those obtained by previous studies. Our results clearly demonstrate the presence of previously unknown dehydrated phases of the meta-autunite group minerals with basal spacings less than 6 Å that may have distinct thermodynamic properties.

INTRODUCTION

Uranium mobility in near-surface settings is mainly controlled by redox transformations between soluble hexavalent uranium [U(VI)] and insoluble tetravalent uranium [U(IV)] (Langmuir 1978; Klinkhammer and Palmer 1991; Suzuki et al. 2002, 2003, 2004a, 2004b). Reduction of U(VI) to U(IV) that occurs under reducing conditions leads to precipitation of U(IV)-bearing minerals such as uraninite, UO\(_2^{3+}\). Under oxidizing conditions, oxidative dissolution of U(IV)-bearing minerals results in mobilization of uranium due to formation of uranyl carbonate complexes (Langmuir 1978). In a wide range of uranium deposits, uranyl ions released from U(IV)-bearing minerals in primary orebodies are immobilized in insoluble uranyl phosphate minerals that persist for geological periods (Leo 1960; Snelling 1980). Nanocrystalline uranyl phosphate minerals that form during crystallization of iron oxides have been suggested to be ubiquitous (Murakami et al. 1997; Sato et al. 1997). Thus, uranyl phosphate minerals play important roles in long-term immobilization of uranium. To remediate contaminated groundwaters, sediments, and soils, technologies that enhance formation of uranyl phosphate minerals have recently drawn attention. For example, reactive barriers that use apatite [\( \text{Ca}_3(\text{PO}_4)_2(\text{F},\text{OH}) \)] to promote uranyl phosphate precipitation have been studied to suppress uranium transport in groundwaters (Fuller et al. 2002). In addition, micro-organisms capable of precipitating uranyl phosphate minerals (Maccaskie et al. 2000; Suzuki and Banfield 1999, 2004) have potential to be used for immobilization of uranium.

Uranyl phosphate minerals are diverse and occur in five major structural divisions, of which the autunite, meta-autunite, and the phosphuranylite groups are the most important (Finch and Murakami 1999). The autunite and meta-autunite group minerals are more important than the phosphuranylite group minerals in terms of natural abundances because of their low solubilities (Grenthe et al. 1992). The autunite and meta-autunite group minerals possess uranyl phosphate or arsenate sheets that are connected by interlayer cations and water molecules. Minerals in the autunite and meta-autunite groups are easily dehydrated by heating, desiccation, and evaporation. Thermal analysis of these minerals has been extensively conducted (Vochten et al. 1979; Vochten and Deliens 1980; Vochten and Van Doorselaer 1984; Weigel and Hoffman 1976). In contrast, few studies on structural changes associated with dehydration have...