CONTRIBUTION TO THE MINERALOGY OF ACID DRAINAGE OF URANIUM MINERALS: MARECOTITE AND THE ZIPPEITE-GROUP

J. BRUGGER,1,2,* PETER C. BURNS,3 AND N. MEISSER4

1Department of Geology and Geophysics, The University of Adelaide, North Terrace, 5005 Adelaide, South Australia
2Division of Mineralogy, South Australian Museum, North Terrace, 5000 Adelaide, South Australia
3Department of Civil Engineering and Geological Sciences, 156 Fitzpatrick Hall, University of Notre Dame, Notre Dame, Indiana 46556-0767, U.S.A.
4Musée Géologique Cantonal & Laboratoire des Rayons-X, Institut de Minéralogie, UNIL-BFSH2, CH-1015 Lausanne-Dorigny, Switzerland

ABSTRACT

Sulfate-rich acid waters produced by oxidation of sulfide minerals enhance U mobility around U ores and U-bearing radioactive waste. Upon evaporation, several secondary uranyl minerals, including many uranyl sulfates, precipitate from these waters. The zippeite-group of minerals is one of the most common and diverse in such settings. To decipher the nature and crystal chemistry of the zippeite-group, the crystal structure of a new natural hydrated Mg uranyl sulfate related to Mg-zippeite was determined. The mineral is named marecottite after the type locality, the La Creusaz U prospect near Les Marécottes, Western Swiss Alps.

Marecottite is triclinic, P1, with a = 10.815(4), b = 11.249(4), c = 13.851(6) Å, α = 66.224(7), β = 72.412(7), and γ = 69.95(2)°. The ideal structural formula is Mg,(H2O)18[(UO2)4O3(OH)(SO4)2]2(H2O)10. The crystal structure of marecottite contains uranyl sulfate sheets composed of chains of edge-sharing uranyl pentagonal bipyramids that are linked by vertex-sharing with sulfate tetrahedra. The uranyl sulfate sheets are topologically identical to those in zippeite, K(UO2)2(SO4)O2·H2O. The zippeite-type sheets alternate with layers containing isolated Mg(H2O)6 octahedra and uncoordinated H2O groups. The uranyl sulfate and Mg layers are linked by hydrogen bonding only.

Magnesium-zippeite is redefined as Mg(H2O)3.5(UO2)2(SO4)O2, based on comparison of the powder X-ray diffraction pattern of micro-crystalline co-type material with the pattern of a synthetic phase. Magnesium-zippeite contains zippeite-type uranyl sulfate sheets with Mg located between the layers, where it is in octahedral coordination. In Mg-zippeite, distorted Mg octahedra are linked by sharing vertices, resulting in dimers. The apices of the Mg octahedra correspond to two O atoms of uranyl ions, and four H2O groups.

Magnesium-zippeite and marecottite co-exist, sometimes in the same sample, at Lucky Strike no. 2 mine, Emery County, Utah (type locality of Mg-zippeite), at Jáchymov, Czech Republic, and at La Creusaz. This study provides insight into the complexity of the zippeite-group minerals containing divalent cations, where different arrangements in the interlayers result in different unit cells and space groups.

INTRODUCTION

U SULFATES AND ACID LEACHING OF U MINERALS

The oxidation of sulfides by oxygen-bearing waters produces sulfate-rich (>1000 ppm SO42−) acid (pH < 5) waters that can leach and transport large quantities of heavy metals (e.g., Edwards et al. 2000; Evangelou and Zhang 1995). Such waters are responsible for large-scale mobility of U and other actinides around U-bearing mine sites and tailing dumps, even long after mining has ceased (e.g., Fernandes et al. 1995). Acid sulfate waters also may be present in and around high-level radioactive waste deposits, in particular those located in sulfide-bearing host-rocks such as shales (e.g., the proposed Swiss repository in Mesozoic shales; Thury and Bossart 1999; Vinard et al. 1993). Available thermodynamic data (Cox et al. 1989; Grenthe et al. 1992; Shock et al. 1997) indicate that U6+ sulfate complexes, mainly UO2(SO4)2−, are the principal aqueous species responsible for the high U solubility under those conditions (Fig. 1). In contrast, U6+ carbonate complexes become dominant under neutral and alkaline conditions (Fig. 1).

Uranium sulfate minerals commonly are widespread around U-bearing mine sites, where they usually form during the evaporation of acid sulfate-rich mine drainage waters (Finch and Murakami 1999). Uranopilite, (UO2)6(SO4)(OH)10·12H2O (Burns 2001); johannite, Cu(UO2)2(SO4)2(OH)·8H2O (Cejka et al. 1988); schröckingerite, Na2Ca3(UO2)SO4)(CO3)3F·10H2O; coconinoite Fe2Al2(UO2)2(PO4)4(SO4)(OH)2·20H2O; and zippeite-group minerals are the most common uranyl sulfates. In addition, several new uranyl sulfates have been described recently: deliensite, Fe(UO2)2(SO4)2(OH)·3H2O (Vochten et al. 1997); jáchymovinite, (UO2)3(SO4)(OH)·13H2O (Cejka et al. 1996); and rabejacite, Ca(UO2)4(SO4)2(OH)6·6H2O (Deliens and Piret 1993). The latter phases may be more widespread than...