

CRYSTAL CHEMISTRY OF URANYL PHOSPHATES, ARSENATES AND
OXYSALTS OF CHROMIUM(V): IMPLICATIONS FOR REMEDIATION

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by

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Abstract

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The chain of events involved in the production and use of uranium for power generation and defensive purposes has serious environmental consequences. Study of the crystal chemistry of uranium minerals and compounds can help to lead to effective approaches to remedy uranium contamination in the environment, and aid in the development of reliable strategies for the long-term disposal of spent nuclear fuel nuclear waste.

The research presented herein focuses on the structures and crystal chemistry of hexavalent uranium (uranyl) phosphate, arsenate and chromium(V) compounds as revealed mainly by single-crystal X-ray diffraction. The uranyl phosphates and uranyl arsenates are of particularly low solubility under environmental conditions, and thus may control the mobility of uranium in groundwater and at some contaminated sites.

A total of fifty-six single-crystal structures were studied using diffraction data (collected with a three-circle X-ray diffractometer, Mo radiation, and a charge-coupled-

device area detector), in conjunction with the results of other instrumental techniques. Only three of these compounds are from mineral specimens; the rest are synthetic in origin (although many are synthetic equivalents of mineral species), and were grown either by gel-diffusion or by hydrothermal methods. Of the refined structures, twenty-five are uranyl phosphates, twenty-seven are uranyl arsenates, and four are uranyl chromium(V) oxysalts. Four principal structural themes are observed in the uranyl phosphates and uranyl arsenates: 1) structures based on infinite chains of uranyl polyhedra and either phosphate or arsenate tetrahedra; 2) structures based on the sheet found in phosphuranylite; 3) structures based on the sheet found in autunite; and 4) layered and framework structures containing uranyl phosphate or uranyl arsenate sheets whose sheet-anion topology is identical to that found in uranophane. The four uranyl chromium(V) oxysalts are structurally analogous to the uranyl vanadate carnotite.

Uranyl phosphates and their chemically corresponding uranyl arsenates are generally, but not always, isostructural. Similarly, hybrid organic-inorganic compounds, which contain protonated amines rather than simple cations, exhibit structural themes that are analogous with their inorganic counterparts.

DEDICATION

For Josette.