

Cation replacement mechanisms in uranyl phosphates and development of weathering profiles

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Uranyl phosphate minerals are important phases in weathered U ore deposits. The Nisa deposit is one example showing different stages of replacement reactions among the uranyl phosphates of the autunite group. The cations in these minerals can be indicators of the local geochemical environment. In zones of U mineralization hosted in granite, the main mineral is torbernite (Cu) [1], and in metamorphic contact schists, saleeite (Mg) and in lesser amounts autunite (Ca) prevail [2]. However, later replacement reactions favour the partial/total substitution of the first stage uranyl phosphates by uranocircite (Ba) followed by an increased acid-leaching and formation of cation-depleted phases - phosphuranylite [1, 2]. Not all domains of the weathered mineralized zones show these features. Some show pristine torbernite crystals with little or no sign of alteration.

Mineral replacement reactions are usually considered as the result of dissolution/precipitation mechanisms [3], but the substitution in uranyl phosphates is rather akin of a cation-exchange mechanism. Laboratory experiments with natural torbernite/autunite samples have shown to react with Ba solutions at ambient temperatures displaying similar substitution features as in natural environments. However, in spite the Ba phase being thermodynamically favoured as shown it hardly crystallizes jointly with torbernite although affecting torbernite crystal growth [4]. These results while lending support to field observations are ambiguous in establishing the phase relations between uranyl phosphates. Nevertheless, they may provide an invaluable geochemical indicator of a weathering profile development important both to mineral exploration and the environmental behavior of U.

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