

Alunite supergroup dissolution rates and products: comparing mechanisms

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Alunite supergroup minerals ($AB_3(XO_4)_2(OH)_6$) are commonly found in acidic rock drainage assemblages, acid lakes, fumaroles, and acidic soils on Earth and have also been observed in sedimentary rocks and possible hydrothermal deposits on Mars. In addition, alunite supergroup phases are commonly produced during ore processing to sequester unwanted metals for later disposal. Dissolution studies provide critical data for modeling mineral lifetimes and metal/acid release rates, as well as reaction products. In addition, kinetic data can be used to interpret mineral dissolution mechanisms, allowing geochemists to predict mineral behavior beyond conditions measured in the laboratory.

Alunite ($KAl_3(SO_4)_2(OH)_6$) and jarosite ($KFe_3(SO_4)_2(OH)_6$) dissolution experiments were conducted under similar conditions, allowing for direct comparison of dissolution rates and reaction products. Alunite dissolution rates in dilute solutions are 2-3 orders of magnitude slower than jarosite dissolution rates under comparable conditions. Both minerals dissolve faster at very acidic and very alkaline conditions, suggesting H^+ and OH^- mediated reaction mechanisms respectively. The inflection point for jarosite dissolution lies at pH 3.5-4, while in alunite the minimum rate is observed at pH 5-6. However, dissolution rates for both phases converge in high salinity $CaCl_2$ and $NaCl$ brines. This suggests that Cl-Fe and Cl-Al surface complexation likely drives dissolution in brines, while hydration and hydrolysis of Fe and Al likely control dissolution rates in dilute solutions. Water exchange rates with Fe are 2-3 orders of magnitude faster than water-Al exchange rates, resulting in faster jarosite dissolution rates in dilute systems.

While crystalline iron oxide nanominerals dominate jarosite reaction products at pH >4, only amorphous reaction products were observed in alunite reaction products, despite highly incongruent K/Al ratios. Therefore, jarosite dissolution produces abundant iron oxide nanoparticles which may transport heavy metals downstream in sulfide oxidation environments. On the other hand, metals associated with the amorphous reaction products of alunite dissolution might be released to solution or incorporated during the formation of more crystalline phases over time.