American Mineralogist, Volume 99, pages 44–56, 2014

Weathering of cobalt arsenides: Natural assemblages and calculated stability relations among secondary Ca-Mg-Co arsenates and carbonates

Gregor Markl[1,*], Michael A.W. Marks[1], Insa Derrey[1,2] and Jan-Erik Gühring[1]

[1]Fachbereich Geowissenschaften, Universität Tübingen, Wilhelmstr. 56, D-72074 Tübingen, Germany
[2]Institut für Mineralogie, Leibniz Universität Hannover, Callinstr. 3, D-30167 Hannover, Germany

Abstract

The supergene alteration of cobalt arsenides produces various characteristic mineral assemblages including erythrite, pharmacolite, and other Ca±Mg±Co-bearing arsenates, which upon precipitation remove Co and As from natural waters. Their paragenetic relationships and stability conditions have not been investigated in detail. We present a detailed study on these assemblages, their successions and coexisting fluid compositions from the mining area of Wittichen, southwest Germany, where primary skutterudite and safflorite in granite-hosted barite-calcite veins are undergoing oxidation. Water analyses from the old mines, a semi-quantitative stability diagram and quantitative reaction path modeling are used to constrain their conditions of formation.

Cobalt- and arsenate-bearing solutions invariably precipitate erythrite first and hence buffer Co concentrations to very low values. Both during skutterudite or safflorite dissolution and erythrite precipitation, the fluid's Co/As ratio decreases rapidly. Therefore, spherocobaltite (Co carbonate) is unstable in the presence of arsenate ions under most conditions.

The formation of various mineral assemblages precipitating after or simultaneously with erythrite strongly depends on Ca^{2+} and Mg^{2+} activities and pH. Small changes in one of these parameters lead to different mineral assemblages. These small changes are partly governed by fluid-host rock or fluid-vein mineral reactions and partly by the precipitation of the secondary arsenate minerals themselves. This complex interdependence produces the rich variety of mineral assemblages observed, which effectively serves as a very sensitive monitor of fluid compositions. Furthermore, the assemblages themselves are able to buffer the Ca-Mg-Co-As concentrations in the fluid to some extent and effectively immobilize both As and Co in close proximity to the ore deposit.

Keywords: Cobalt, arsenate, weathering, erythrite, pharmacolite, spherocobaltite, phase stabilities, reaction path modeling