

Gypsum-Jarosite incrustation on limestone: an unusual occurrence

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Abstract

The joint planes of massive limestone at Sahasradhara, Dehra Dun have a thin crust containing jarosite with gypsum blades. This occurrence is different from the usual chemical weathering in a ferruginous environment. An evaluation of the chemistry of local river and groundwater suggests that these minerals form by evaporation in dry seasons.

Introduction

Massive limestones of the Krol Series occur in a river gorge at Sahasradhara (30°23'N, 78°08'E) near Dehra Dun, U.P. During recent geochemical work in this area, it was noticed that the joint planes of the limestone on river banks have a peculiar rust coloured coating. On further examination under a microscope, this incrustation was found to contain thin white blades of gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and a fine grained yellowish brown material. X-ray diffraction (Fig. 1) revealed the presence of gypsum and jarosite, $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$.

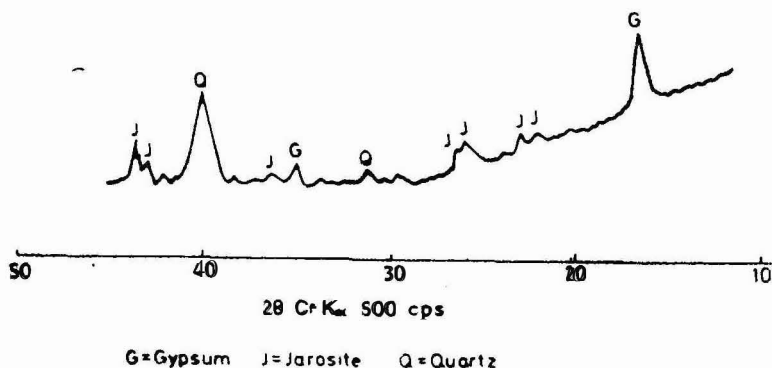


Figure 1. X-ray diffractogram of incrustation on limestone.

Although jarosite is frequently reported from limonite crusts on ferruginous ores and rocks (Palache *et al*, 1961) this occurrence in association with gypsum, a common evaporite mineral, is unusual. As the incrustation is found on joint planes of fresh limestone, it does not appear to be a product of weathering. The iron content of local surface and ground waters is extremely low (less than 0.1 ppm). The limestone does not contain any x-ray detectable iron mineral. The reported Fe_2O_3 content is 0.32% (Mehta *et al*, 1959). In order to understand the mechanism of formation of the gypsum-jarosite assemblage, the solubility of these minerals with reference to the water chemistry in this region has been evaluated.

Water Chemistry

The local river and groundwaters were found to contain 250 to 990 ppm, of dissolved sulphate. Figure 2 shows our calculation of the ion activity product (IAP)

for gypsum in the river and a local waterfall which originates from groundwater seepage. The sampling periods of December, May and October cover the prevailing seasons of winter, summer and monsoon. It is clear that during the period of our observation, the waters remained undersaturated with respect to gypsum, although the solubility product was approached in summer. We have also observed that the water percolating into the limestone caves in this area remain grossly undersaturated through all seasons. These calculations indicate that gypsum has not spontaneously precipitated under equilibrium conditions. It must have formed by non-equilibrium evaporation of river and groundwater in dry periods. Smith and Drever (1976) have reported the formation of authigenic gypsum from undersaturated groundwaters by a similar process.

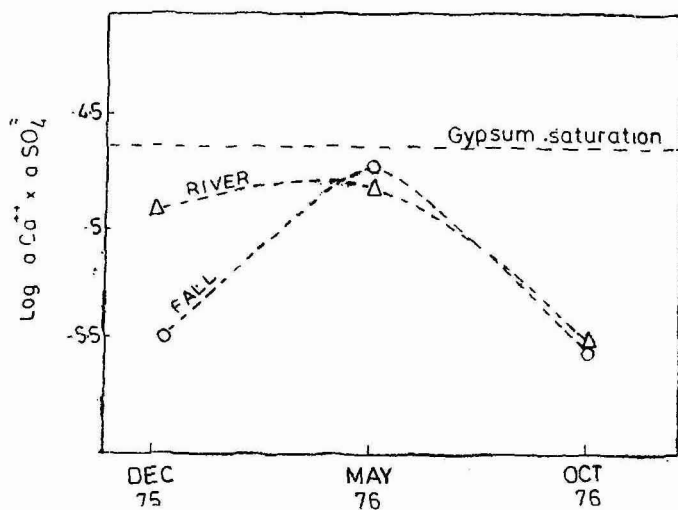


Figure 2. Seasonal variation of $\text{Ca}^{++} \times \text{SO}_4 =$ ion activity product.

We are suggesting that jarosite, because of its close association with gypsum here, is also a product of evaporation. The solubility product value of such natural jarosites is not known. We have used free energy data on synthetic end members (Kashkay *et al.*, 1975) to estimate the Fe-level for saturation at the prevailing water composition. A sample calculation is given below.

ΔG°_f of $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6 = -788.64$ Kcal/mole. For ionisation, $\Delta G^\circ_r = +133.56$ Kcal. $\log K = -97.7$ at 25°C , where $K =$ solubility product. In May, 1976, river water $\text{pH} = 6.4$ at 22°C , $\text{K}^+ = 0.5$ mg/l, $\text{SO}_4 = 863$ mg/l, ionic strength = 0.01. Substituting $\log a\text{K}^+ = -4.95$, $\log a\text{SO}_4 = -2.26$, $\log a\text{OH}^- = -7.6$, $a\text{Fe}^{3+} = 10^{-4}$ moles/l which is equivalent to about 10^{-4} ppm total iron.

Such calculations show that the waters would be supersaturated with respect to jarosite at very low iron levels. We conclude, therefore, that the gypsum and jarosite bearing incrustation on limestone at Sahasradhara results when sulphate rich river or groundwater, trapped in joint planes, undergoes evaporation and becomes supersaturated with respect to these minerals.

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