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DECOMPOSITION OF PYRITIZED CARBONACEOUS SHALE TO  
HALOTRICHITE AND MELANTERITECHARLES B. SCLAR, *Battelle Memorial Institute, Columbus, Ohio*

In April, 1959, the writer examined several polished sections of gold- and silver-bearing pyritic zinc ore from a locality in the Dominican Republic. Three sections, two composed dominantly of pyrite disseminated through carbonaceous illitic shale and the third composed dominantly of sphalerite with minor pyrite, were stored in a desk drawer. In August, 1959, the desk was moved into a centrally air conditioned area where the temperature is controlled during the summer months between 21° and 24° C. except for infrequent interruptions of short duration (<48 hours). The local dehumidification equipment is somewhat inefficient so that the relative humidity in the room is high and not unlike that in mines and caves. In August, 1960, the writer noticed a white efflorescence of acicular crystals on both the polished and the rough surfaces of the pyritized shale specimens; the sphalerite-rich specimen was unaffected.

The white efflorescence is water soluble and is composed dominantly of radial-fibrous aggregates of halotrichite  $[\text{Fe}^{+2}(\text{Fe}^{+3}, \text{Al})_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}]$  and subordinately of lath-shaped to tabular-vermiform crystals of melanterite  $[\text{FeSO}_4 \cdot 7\text{H}_2\text{O}]$  (Fig. 1). These minerals are intimately associated and appear to be in equilibrium. X-ray powder diffraction data agree with those reported for halotrichite by Bauer and Sand (1957) and for melanterite on ASTM card 1-0255. A spectrographic analysis showed that the major cations are Fe and Al; trace amounts (<0.5%) of Ca, Mg, Zn and Cu are also present. The presence of  $\text{SO}_4$  was confirmed by the  $\text{BaSO}_4$  test.

The acicular crystals of halotrichite have  $\gamma = 1.490 \pm 0.002$ ,  $Z \wedge c = 38^\circ$ , and weak birefringence. The individual crystals have a maximum length of 1.5 mm. and range in thickness from about 1.5 to 5 microns. An aqueous solution of the efflorescence gave a positive reaction for iron with both potassium ferro- and ferricyanide and with ammonium hydroxide which suggests that this halotrichite contains some ferric iron proxying for aluminum and represents an intermediate composition in the halotrichite-bilinite  $[\text{Fe}^{+2}\text{Al}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}] - [\text{Fe}^{+2}\text{Fe}^{+3}(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}]$  series.

Abundant shale and unaltered brass-yellow pyrite fragments ranging in size from a few microns to 0.2 mm. in diameter are enclosed in the halotrichite aggregates. Many fragments have a specular facet which

shows that they were once part of the now disrupted and pitted polished surface.

In immersion mounts the tabular melanterite crystals appear as straight, hook-shaped, semicircular to almost annular and S-shaped forms. They have  $\beta = 1.478 \pm 0.002$  and (+)2V large ( $\sim 75^\circ$ ). Most of these crystals are oriented in immersion mounts and show slightly to moderately off center  $Bx_a$  and  $Bx_o$  interference figures. Such crystals have the optic plane transverse to the elongation, small extinction

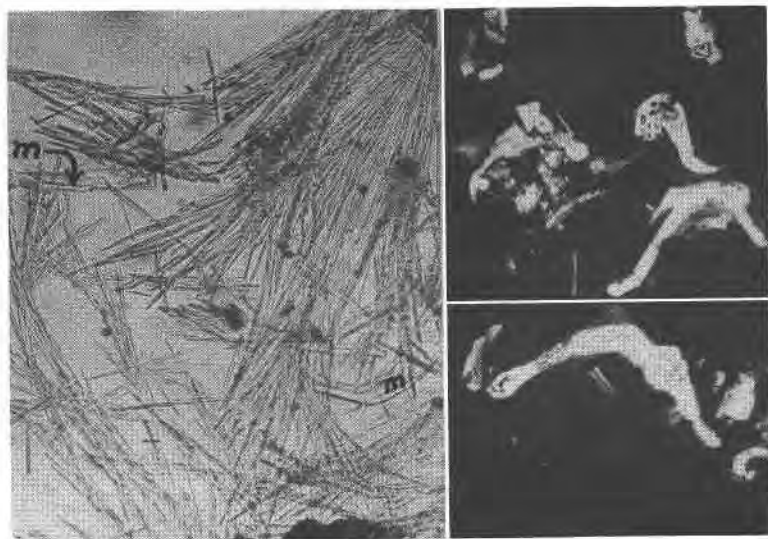


FIG. 1. (Left) Photomicrograph of halotrichite crystals. Two melanterite crystals are labeled (m). Plane polarized light.  $\times 80$ . (Right) Curved tabular crystals of melanterite. Crossed nicols.  $\times 80$ .

angles ( $0^\circ$ – $12^\circ$ ), and positive and negative elongation for  $Bx_a$  and  $Bx_o$  sections, respectively.

Halotrichite and melanterite are fairly common weathering products of pyritic aluminous rocks and accumulate in protected cracks and reentrants. They also coexist in efflorescences which form on the walls and timbers of underground workings, particularly those in pyritic coal seams and pyritic ore deposits. In a recent paper, Brant and Foster (1959) briefly described discrete occurrences of halotrichite and melanterite on the surface of a basement-stored pyritic coal core, and concluded that both minerals formed under similar conditions. This paper supports their viewpoint.

Where the relative humidity is high, pyrite decomposes rapidly, and

weakly acid sulfate solutions are released which attack aluminous minerals and bring aluminum into solution. Evaporation of films of these aqueous solutions results in crystallization of halotrichite and/or melanterite. The halotrichite/melanterite ratio at any point is probably determined by the local concentration of clay minerals or other soluble aluminous minerals in the pyritic rock.

Occelshaw (1925; see Mellor, 1935, and Campbell and Smith, 1951) has shown that halotrichite is a congruently saturating compound which is in equilibrium at 25° C. with aqueous solutions containing between 4 and 10% of FeSO<sub>4</sub> and between 25 and 20% of Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, respectively, and that melanterite is in equilibrium at 25° C. with aqueous solutions containing higher concentrations of FeSO<sub>4</sub> and correspondingly lower concentrations of Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>. His equilibrium diagram also shows that when alunogen [Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·16H<sub>2</sub>O] is not present in the crystallized product, the corresponding aqueous solutions contained at least 10% FeSO<sub>4</sub> and less than 20% Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> during crystallization or a minimum Fe/Al weight ratio of about 1.15. To obtain a solution with this minimum ratio would require the dissolution of about 3 grams of iron-free illite containing 25% Al<sub>2</sub>O<sub>3</sub> for each gram of pyrite. These data support the hypothesis proposed above that local shifts in the Al<sup>+3</sup> and Fe<sup>+2</sup> concentration levels of the aqueous solutions are responsible for the variable halotrichite/melanterite ratio of the efflorescence and that the two minerals crystallize under the same physical conditions. The reduced state of the iron in these minerals is probably due to the combined effect of the low acidity of the parent solutions and the carbonaceous matter in the shale.

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