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Tamarugite from Anglesea, Victoria, Australia

THE water soluble double sulphate tamarugite, $\text{NaAl}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, has been described from only a few localities, most of which appear to have been from a dry or arid environment (e.g. see Keller, 1935; Bandy, 1938). Hutton (1970), however, reported this mineral as forming on altered volcanic rocks some 50 m above sea level on the island of Nevis in the West Indies, an area with a wet winter climate. Tamarugite has only been described once before from an Australian locality, an arid area in Western Australia (Simpson, 1923). Recently, however, it was found on rocks on the sea shore in southern Victoria, Australia, an area with a temperate climate and an annual rainfall of about 600 mm distributed throughout the year with a small maximum in winter.

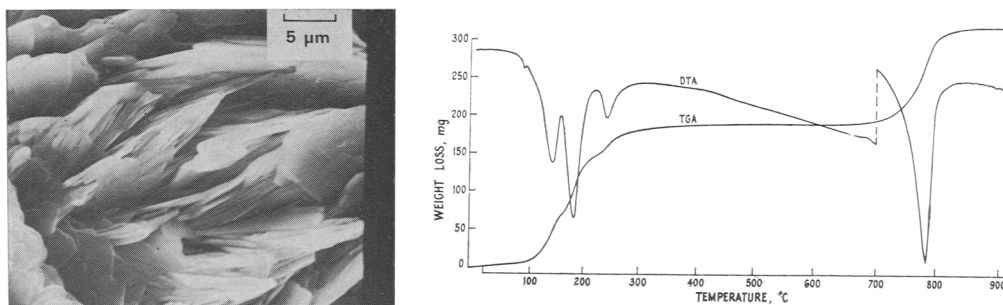
The tamarugite occurred as yellow efflorescences and crusts about 1 cm thick coating black pyritic carbonaceous shales of Eocene age (Raggatt and Crespin, 1955). These shales form cliffs some 50 m high at the back of a sandy beach, and blocks of the shale up to a metre or more in size litter the beach at the base of the cliffs. The mineral formed the yellow (occasionally white) coating mainly on the fallen blocks. The coating was built up of small yellow rosettes, generally about 2 mm in diameter, of very fine apparently fibrous crystals of the mineral, often mixed with fine quartz, clay, and some alunogen. The scanning electron micrograph of fig. 1, however, shows that the crystal morphology is that of very thin platelets.

The X-ray diffraction pattern showed broadening of the diffractometer peaks, so that very close spacings were not resolved. Otherwise, the pattern agreed very closely with that of Robinson *et al.* (1966). The mineral was too finely crystalline for accurate measurement of optical properties; the refractive index, however, was near 1.48.

A chemical analysis (Na, K, Al, Fe by atomic absorption) gave the following result: 6.5% Na_2O , 0.01% K_2O , 11.7% Al_2O_3 , 0.5% Fe_2O_3 , 35.6% SO_3 , 9.1% H_2O (at 100°C), 32.9% H_2O (100-250°C), 1.4% Cl. The excess alumina and sulphur trioxide over that required for tamarugite are present in the proportions required to form alunogen, which is present to a small extent in the sample. The small amount of iron may be

substituting for aluminium in the tamarugite structure, or could be present as an iron sulphate mineral. In either case it accounts for the yellow colour of the material. The high water content is due to hygroscopic water absorbed by the very finely crystalline material, and the presence of alunogen.

Differential thermal and thermogravimetric analysis curves of the Victorian tamarugite are shown in fig. 2. The DTA curves show three strong endotherms at low temperatures: 140°, 180°, and 240° when run at a heating rate of 2°/min, and 165°, 195°, and



FIGS. 1 and 2: FIG. 1 (left). Scanning electron micrograph showing aggregation of platy crystals of tamarugite. FIG. 2 (right). DTA and TGA curves of tamarugite. Heating rate 2 °C/min. Sample weight 500 mg.

270° when run at 10°/min. The associated weight loss curve indicated that the three peaks were associated with the loss of 2, 3, and 1 mole of water respectively. The total loss of water was slightly higher than the theoretical for $\text{NaAl}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$; again, this was due to some alunogen in the sample, and some physically adsorbed water. The significance of the very small endotherm at 80° is uncertain. A further strong endotherm at 785° (2°/min) or 820° (10°/min) is to be attributed to the loss of SO_3 resulting from the decomposition of the sulphate.

Residues from DTA runs were examined to determine the nature of the breakdown products. The residue from a run stopped at 420°, after loss of water of crystallization, but before decomposition of sulphates, consisted mainly of the compound $\text{NaAl}(\text{SO}_4)_2$. The residue from a run stopped at 920° after loss of SO_3 contained the compound $3\text{Na}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3$, together with another unidentified phase.

The black shales on which the tamarugite occurs are very fine-grained rocks containing finely disseminated iron sulphide. When the surface of the shale is exposed to the atmosphere, oxidation rapidly occurs, resulting in the formation of sulphuric acid. This attacks the clay minerals of the shale, and together with the sodium derived from sea spray causes the formation of the double sulphate. The surprising fact is that the mineral is found at all, as the material occurs only 2 or 3 m above high tide level on an exposed windy coast, combined with appreciable rainfall throughout the year. The locality has recently been revisited, and the mineral is still quite abundant; one can only assume, therefore, that the process of formation is quite rapid, and the mineral is continuously forming as fast as it is washed away.

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New data on woodwardite

WOODWARDITE was originally reported from Cornwall, and has subsequently also been identified in material from Klausen in Italy (Meixner, 1940). The formula is given as 'probably $\text{Cu}_4\text{Al}_2(\text{SO}_4)(\text{OH})_{12} \cdot 2-4\text{H}_2\text{O}$ ' by Palache *et al.* (1951). The X-ray powder-diffraction data for alleged woodwardite from Carnarvonshire, Wales, is given in the JCPDS file under the number 17-132, but there are major discrepancies between these powder data and those published by Meixner.

Four samples labelled 'Woodwardite, Cornwall' were obtained from the British Museum through the kindness of Mr. P. G. Embrey; sample numbers were BM 40035, BM 40077, BM 40079, and BM 40083. All four samples produced similar X-ray powder-diffraction patterns, which consist of only a few broad, diffuse lines. Measurements made on one of the Debye-Scherrer patterns are tabulated in Table I; X-ray diffractometer tracings gave equivalent results.

Comparison of these X-ray diffraction data with those given by Meixner (also included in Table I) shows several apparent discrepancies. The chief one is the absence of the 9.1 Å line in the latter's data. Since Meixner did not report his camera size it is possible that he employed a small-diameter camera in which the beam stop blocked the imprint of this line. The single 4.43 Å line observed in this study is very broad and diffuse; it is quite possibly made up of the two lines at 5.30 Å and 3.91 Å reported by Meixner, and presumably better resolved in his pattern. Finally, Meixner's weak 1.297 Å line is matched approximately by a very faint shadow on the writer's patterns,