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TAMARUGITE FROM VULCANO, AEOLIAN ISLANDS, ITALY

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ABSTRACT

At Vulcano, Italy, tamarugite $NaAl[SO_4]_2 \cdot 6H_2O$ occurs as incrustations in cavities of a recent crater. Chemical analyses of impure tamarugite samples gave Al_2O_3 13.30, Na_2O 8.44, SO_3 43.81, Cl 1.75, H_2O 31.20 wt. %. Optical and SEM studies show that the mineral consists of very thin euhedral crystals with maximum dimensions less than 500 µm. The DTA curve shows two well-developed endothermic peaks at 185°C (loss of water) and at 755°C (desulfurization) and two minor ones below 100°C. From the TG curve, 32 wt. % is lost below 400°C and 24% is related to the desulfurization process. Field evidence suggests that this tamarugite is of supergene origin.

Keywords: sodium aluminum hydrated sulfate, XRD, thermal analysis, SEM, chemistry, Vulcano, Sicily, Italy.

SOMMAIRE

La tamarugite $NaAl[SO_4]_2 \cdot 6H_2O$ se présente sous forme d'incrustations dans une cavité d'un cratère récent, à Vulcano (Sicile, Italie). Les échantillons non-purifiés contiennent, en moyenne, Al_2O_3 13.30, Na_2O 8.44, SO_3 43.81, Cl 1.75, H_2O 31.20% (en poids). En microscopie (optique et électronique à balayage), la tamarugite se présente en cristaux idiomorphes très minces, de moins de 500 µm de longueur. La courbe ATD montre deux pics endothermes bien nets, dus à la perte d'eau (185°C) et à la désulfuration (755°C), ainsi que deux faibles maxima sous 100°C. A l'analyse thermogravimétrique, la tamarugite perd de son poids 32% sous 400°C et 24% dans la réaction principale de désulfuration. Les observations faites sur le terrain font penser à une origine supergène.

(Traduit par la Rédaction)

Mots-clés: sulfate hydraté de sodium et d'aluminium, diffraction X, analyse thermique, microscopie électronique à balayage, composition, Vulcano, Sicile, Italie.

INTRODUCTION

On the island of Vulcano, Aeolian Archipelago, north of Sicily, there are common occurrences of many species of secondary minerals derived from the action of fumaroles and supergene processes on Quaternary heterogeneous volcanic products (Cossa 1878, 1883, De Fiore 1922, Dessau 1934, Lacroix 1907, Panichi 1914, Zambonini *et al.* 1925, Wolfe 1938). On the island, at Vulcanello, the authors discovered abundant incrustations of tamarugite, a hydrated sulfate (ideally, $NaAl[SO_4]_2 \cdot 6H_2O$) of the krausite–tamarugite group known from several localities (Palache *et al.* 1951, Hutton 1970, Segnit 1976, Zodrow *et al.* 1979). X-ray powder-diffraction data for Chilean samples are given in Robinson *et al.* (1966); the structure was determined by Robinson & Fang (1969) on the same sample. Optical, XRD, SEM and thermal data are presented for a sample from Vulcano in order to provide further characterization of this uncommon species.

OCCURRENCE AND SAMPLE DESCRIPTION

The tamarugite was found on the eastern internal wall of the crater of Vulcanello, situated at the northern end of the island of Vulcano. The mineral forms incrustations on the walls and ceilings of cavities in basanitic pyroclastic rocks. These rocks are heavily altered, with marked bleaching and loss of competence, in an area characterized by the relative enrichment in silica. The cavities are due to erosion as well as to human activities.

Tamarugite occurs as white, porous aggregates of very thin, fragile, lamellar crystals with maximum dimensions of less than 500 µm. A sample of several grams, with a tamarugite content of more than 85%, was collected. Enrichment caused problems, owing to the fine grainsize of the material, the very thin lamellar habit of tamarugite and its solubility in water. Therefore, analyses were done on a fraction hand-

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TABLE 1. CHEMICAL DATA FOR TAMARUGITE FROM VULCANO*

	Vulcano	Theoretical		Vulcano	Theoretical
Al_2O_3	13.30	14.56	Mn	tr	
MgO	0.79		Zn	tr	
CaO	0.17		Cu	tr	
Na_2O	8.44	8.85	Pb	tr	
K_2O	0.19		H_2O	31.20	30.87
SO_3	43.81	45.72	Insol. Residue	0.72	
Cl	1.75				
Rb	tr		Total	100.37	

* Obtained on a 91% pure sample.

picked under the binocular microscope from what appeared to be the most uniform part of the sample.

CHEMICAL COMPOSITION

Results of several analyses on the same sample of tamarugite from Vulcano are given in Table 1. Na, K, Ca, Mg, Rb and Cl were determined spectrophotometrically; Al was determined both spectrophotometrically and gravimetrically, S only gravimetrically. Energy-dispersion analyses on a SEM specimen show traces of Mn, Cu, Zn and Pb. The H_2O content was determined by thermogravimetry. Heating at 110°C induces a very slow weight-loss, with steady values of 19.39 g after 42 hours.

XRD data show that the water-insoluble residue consists of a mixture of a member of the alunite series and cristobalite. Judging from its chemistry, the analyzed sample seems to have consisted of 91% tamarugite, with the remainder in part water-soluble components, among which NaCl was identified in XRD traces. On such patterns, several small peaks occur that are not related to tamarugite or NaCl. Their pattern is similar to that of some evaporite sulfates and chlorides. These may contain minor quantities of K, Ca and Mg and some H_2O and SO_3 that are not part of tamarugite, though no specific species could be identified.

X-RAY POWDER DATA

Values of d and I/I_0 were obtained with Cu $K\alpha$ radiation at $\frac{1}{4}$ ° min^{-1} scanning speed, with silicon as internal standard, on a random sample prepared with the device described by Byström-Asklund (1966). The d values and intensities are close to those of Robinson *et al.* (1966), although intensities of some peaks are influenced by the presence of associated phases, such as NaCl and a member of the alunite series.

Segnit (1976), working on a tamarugite sample from Australia, found that "the X-ray diffraction pattern showed broadening of the diffractometer peaks, so that very close spacings were not resolved." This may be due to preferred orientation of the very well-developed platy habit of the crystals. Our material, X-rayed using semirandom samples, did not reveal the doubled peaks at 4.20 and 3.15 Å. In truly random samples, the doubling is evident at a scanning speed of 1° min^{-1}.

OPTICAL AND MORPHOLOGICAL CHARACTERISTICS

Under the optical microscope, tamarugite appears as euhedral, tabular (010) lamellae, without alteration or inclusions, and with maximum dimensions of 500 μm. The measured indices of refraction are γ 1.4964, β 1.4869, α 1.4842 (± 0.0002); $2V_\gamma = 57\text{–}60°$, $X\Lambda c = 3°$.

Fracture surfaces of several tamarugite aggregates were studied by SEM, using an attached energy-dispersion-analysis system for chemical control. Single crystals are usually euhedral (Fig. 1) and commonly form "books" when joined along (010) faces. Some squat prismatic crystals also are present. The degree of idiomorphism is unrelated to crystal dimensions. All analyzed crystals are fairly homogeneous in composition.

Energy-dispersion analyses show that a few crystals found scattered in a matrix of tamarugite constitute a different mineral containing Al, S, Ca, Na and traces of Cu, Zn, Pb. Minute quantity and poorly developed habit made better definition of this impurity impossible.

THERMAL ANALYSES

Figure 2 shows DTA and TG curves of tamarugite obtained by means of a Mettler Thermoanalyzer under the following experimental conditions: sample weight 11.3 mg, Pt crucibles, Pt–Pt_{90}/Rh_{10} annular thermocouples; analyses in static air, heating rate 10°C min^{-1}.

The stepwise loss of the six H_2O molecules of tamarugite occurs as follows. Between 75 and 120°C, two small DTA peaks correspond to a total weight-loss of about 1.8%. Variations in sample compaction and crucible type contribute to different shapes and height ratios of these two peaks, as shown in Figure 2. The main dehydration peak occurs at 180°C and corresponds to a weight loss of about 23%. Above this temperature, the H_2O evolution is continuous up to 320°C; an increase in rate of weight loss at about 260°C, evident on the DTG curve (not

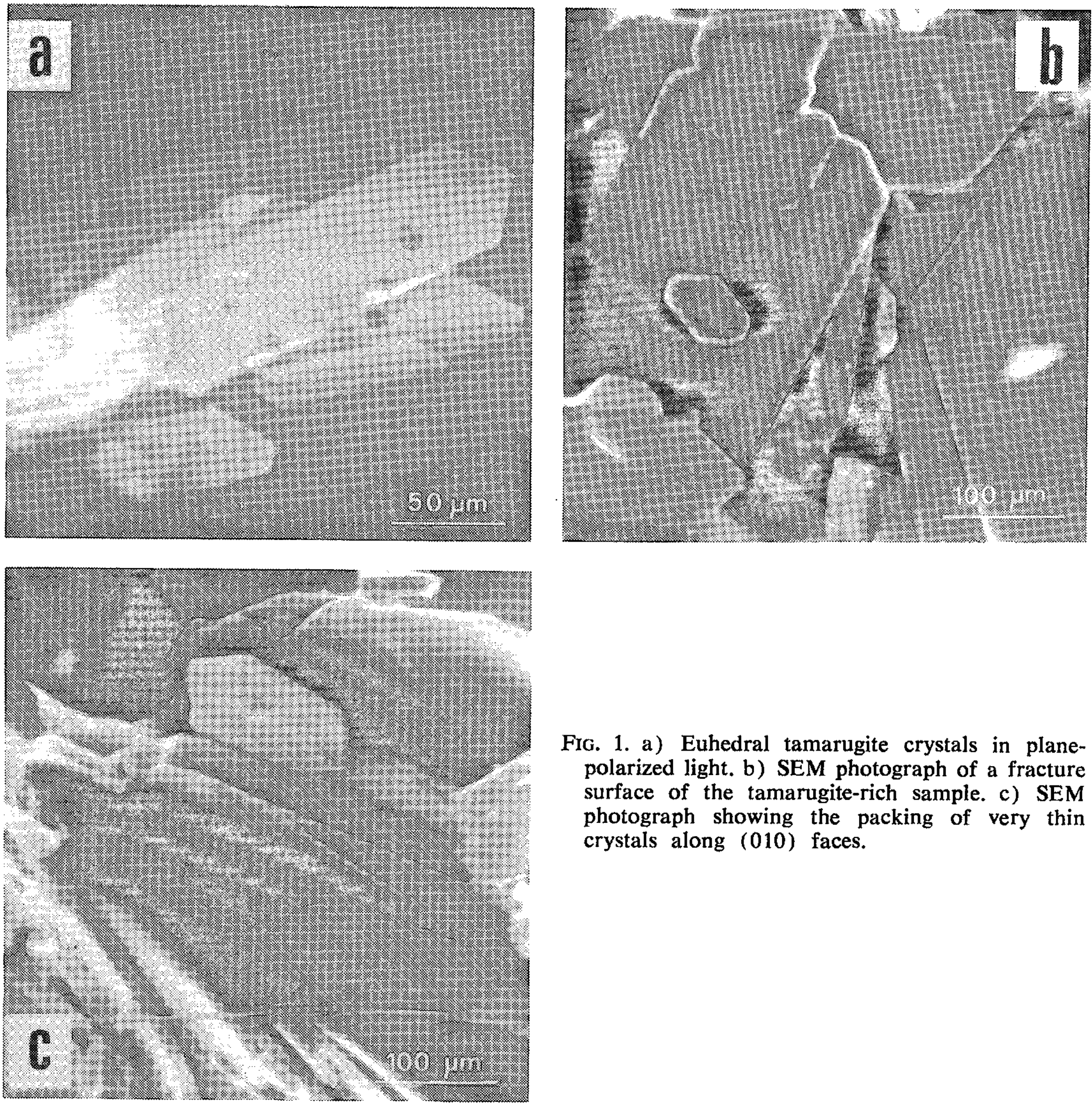

FIG. 1. a) Euhedral tamarugite crystals in plane-polarized light. b) SEM photograph of a fracture surface of the tamarugite-rich sample. c) SEM photograph showing the packing of very thin crystals along (010) faces.

shown in Fig. 2), causes an endothermic effect on the DTA.

At about 500°C, the desulfurization process begins. Its main DTA peak occurs at 755°C and corresponds to a 30% weight loss (about two-thirds of the total tamarugite SO_3 content). Our pattern shows a distinct doubling of the peak, which could be attributed to the presence of associated NaCl. Upwards, the weight loss proceeds continuously to 1600°C with an increase in rate above 1200°C. This increase might be due to the decomposition of sulfates that form after the collapse of the tamarugite structure, as observed in other sulfate minerals such as the members of the alunite series, as well as to the volatilization of the NaCl impurities.

Even after six hours at 1600°C and a total loss of over 75 wt. %, the tamarugite decomposition products still lost weight.

The DTA peak temperature depends on the amount of the reactant material. A curve showing the dependence on sample amount [the "Proben-Abhangigheit" curve of Smykatz-Kloss (1974)] was constructed for tamarugite, on the basis of three DTA curves obtained with different sample weights under identical conditions. From this curve (Fig. 3), one can see that the main dehydration peak at low temperature is

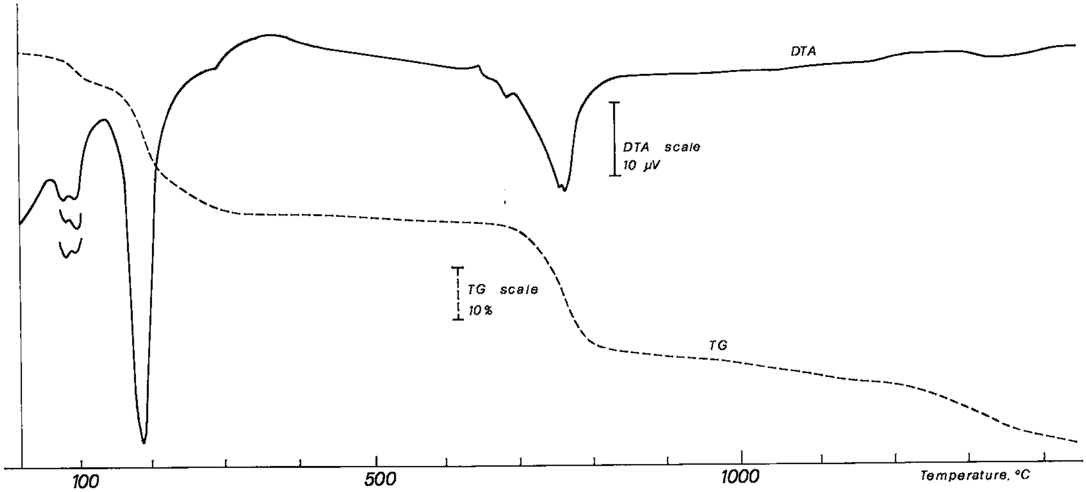

FIG. 2. DTA and TG curves for tamarugite from Vulcano.

not strongly affected by the sample amount. However, in the main desulfurization process, the DTA peak temperature ranges from an extrapolated 718°C for samples of 1 mg to 782°C for 35-mg samples.

CONCLUSIONS

Tamarugite from Vulçano has properties similar to those listed in the literature for this species. Formation of the mineral may have been due to low-temperature gaseous emanations reacting with the host rocks. Na and Al would have been supplied by the surrounding volcanic rocks, and S-rich compounds are common products of the late activity of the Vulcanello crater (which was formed in the late nineteenth century). However, the high solubility of the mineral and its presence on ceilings and walls of cavities suggest a very recent origin from water percolating through the heavily altered volcanic rocks. No evidence has been found of a possible derivation by dehydration from a previous phase, such as mendozite Na$[AlSO_4]_2 \cdot 11H_2O$.

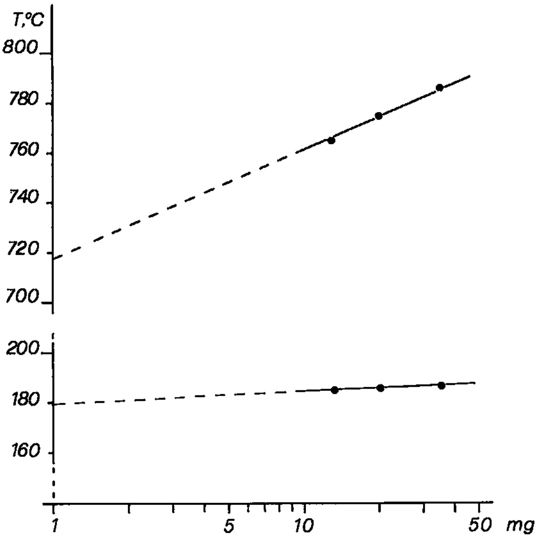

FIG. 3. Dependence of peak temperature on sample weight for the main thermal effects of tamarugite.

Tamarugite seems to be relatively stable. A part of the original sample left open to an ambient atmosphere subjected to seasonal variations of temperature and humidity for fifteen months showed no modification of its XRD and DTA–TG traces.

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