

Iron oxide mineralogy of a hydrothermal assemblage on Santorini Island, Aegean Sea

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ABSTRACT. Basement rocks of Santorini have been locally impregnated by iron oxides and other minerals. The hydrothermal fluids which caused the mineralization have extensively altered the impregnated rocks, but left granditic garnets in these unaffected.

Mössbauer spectroscopy and differential X-ray diffraction show that the iron oxides present are goethite and hematite in a ratio of about 2:1. The presence of hematite indicates that these minerals formed, directly from a hydrothermal phase, at higher temperatures than the recent submarine iron oxide deposits of Santorini, which contain no hematite.

SANTORINI is the only active volcano in the eastern Mediterranean. The volcanic activity manifests itself in sporadic lava eruptions and less spectacular but continuous fumarolic exhalations. The latter have locally altered the originally erupted calc-alkaline volcanics (Schorin, 1980), and are responsible for the current production of submarine iron oxide deposits (Behrend, 1936; Puchelt *et al.*, 1973).

A hydrothermal assemblage, characterized by euhedral granditic garnets up to 1 cm across, is exposed at the base of the caldera wall near Thermia (Murad, 1976). This garnetite and neighbouring phyllitic schists have been locally impregnated by iron oxides, chrysocolla, and other minerals in bands up to several cm thick (fig. 1). Where concentrated, the iron oxides impart a conspicuous red to reddish-brown colour (Munsell 10R 4/8 to 2.5YR 4/8) to the affected rocks. The iron oxides are very fine grained and cannot be identified in thin section. Because of the mineralogical complexity of the garnetite, standard X-ray diffraction procedures give diagrams in which identification of the iron oxides is often complicated by interference from peaks of other minerals.

The purpose of the present study was to obtain evidence bearing on the genesis of these iron oxide bands, and to uncover possible similarities or differences to the previously described recent submarine deposits.

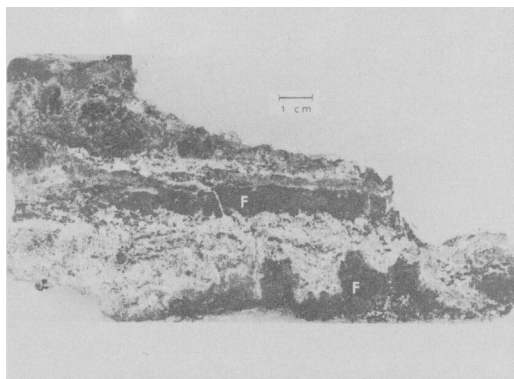


FIG. 1. Polished section of garnetite from Thermia, Santorini. Bands impregnated with iron oxides are marked 'F'.

Experimental. For the preparation of thin sections the often brittle garnetite first had to be impregnated with a synthetic resin (Ciba-Geigy 'Araldit'). From this mechanically stabilized material it was possible to prepare sections up to 100 cm² in size, which allowed the observation of textural relations over a relatively large area.

For chemical analysis the samples were hand-picked and manually ground in a mortar. Total iron oxides (Fe_d) of a reddish-brown sample (791B; Munsell 2.5YR 4/8) were determined in a dithionite-citrate-bicarbonate extract (Mehra and Jackson, 1960), and oxalate-soluble iron (Fe_o) was measured in an acid ammonium oxalate extract (Schwertmann, 1964) using a Perkin Elmer 420 atomic absorption spectrometer. The dithionite treatment resulted in the dissolution of secondary copper minerals ('chrysocolla' *s.l.*) and subsequent precipitation of elemental Cu, which was removed by treatment with 1N HNO₃ at about 50°C for 30 min. Another sample was ultrasonically dispersed in distilled water and the fraction < 2 μm (sample 791C, colour as 791B) obtained, following sedimentation, by centrifuging and freeze drying.

Mössbauer spectra were taken using a $^{57}\text{Co}/\text{Rh}$ source mounted on a loudspeaker-type drive system providing a sinusoidal motion. Spectra were run at room temperature and after cooling both source and absorber to about 120 and 4 K in a cryostat. Absorbers consisted of *c.* 35 mg of sample, spread uniformly over an area of 2 cm² in a plexiglas holder. The transmitted radiation was registered with a proportional counter and fed into a 1024 channel analyzer. Counting proceeded until sufficiently good statistics, visually monitored with an oscilloscope, had been attained. The mirror halves of the spectra were folded and plotted, and Lorentzian curve fits were carried out by a computer procedure. Pure metallic iron served as standard for velocity calibration and as reference material for isomer shifts.

X-ray diffraction was carried out using Co-K α radiation and a Philips PW1040 vertical goniometer equipped with a graphite monochromator. Clay minerals were determined on an oriented specimen of the clay fraction sedimented on a glass slide. Differential X-ray diffraction (DXRD) patterns were obtained by subtracting step-scanned powder diffraction data for untreated samples from data obtained after selective dissolution of the iron oxide minerals. Procedural details and instrumental settings are given by Schulze (1981).

Infra-red absorption spectra were recorded from 1:300 KBr discs with a Beckman 4250 spectrometer.

Results. The most prominent features visible in thin section are the large, zoned, alternately isotropic and birefringent garnets. Calcite (occasionally in well-crystallized grains several mm in size), chalcedony (often associated with fine-grained masses of a chrysocolla-like mineral), and the iron oxides fill spaces between the individual garnet crystals and seal fractures in them. The garnets are partly surrounded by fibrous aggregates of a colourless to yellow-green pleochroic mineral, identified by X-ray diffraction as a calcic amphibole. These uralitic masses, the iron oxides, and the chrysocolla often form distinct layers which, however, appear to leave the garnet crystals undisturbed.

Chemical analyses show the bulk sample (791B) to have an Fe_a value of 23.1% Fe, corresponding to 33–7% iron oxides. A low Fe₀ value of 0.8% indicates that ferrihydrite is virtually absent.

The room temperature Mössbauer spectrum of the untreated bulk sample (fig. 2a) consists of a rather broad superparamagnetic doublet and a weak magnetically split sextet. The hyperfine field of 491 kOe and broad lines of the sextet are indicative of rather poorly crystallized and/or

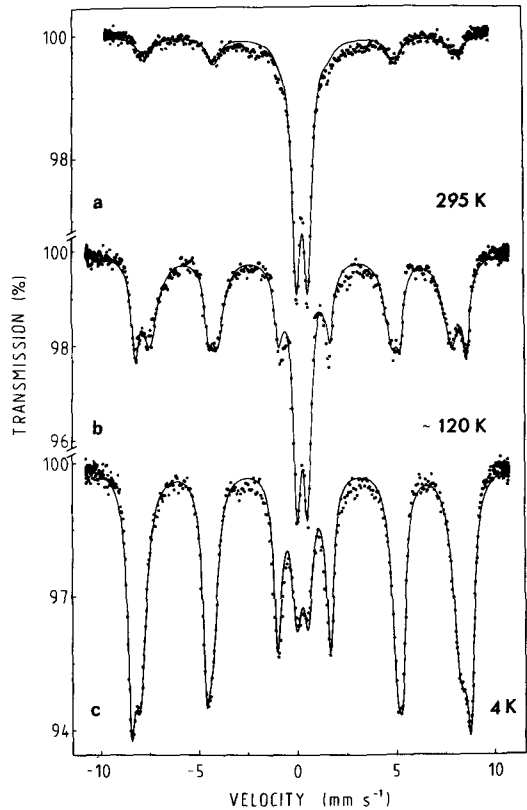


FIG. 2. Mössbauer spectra of iron-oxide-rich bulk garnetite 791B at (a) room temperature, (b) *c.* 120 K, and (c) 4 K.

Al-substituted hematite. At about 120 K the lines of the doublet are somewhat narrower than at room temperature and there are two magnetically split components (fig. 2b). Hyperfine fields of 522 and 476 kOe indicate that these sextets result from hematite and goethite, respectively. At 4 K only a weak doublet remains (fig. 2c). Because the sample contains hematite, goethite and granditic garnets, all of which have magnetically split Mössbauer spectra at this temperature, three sextets were fitted to the spectrum. With the exception of the quadrupole splitting for the garnets (which was determined on a pure, hand-picked specimen from this sample, and then held fixed in the fitting procedure) the parameters obtained correspond to those of the named minerals. The relative intensities of the constituent sextets suggest a hematite:goethite ratio of about 0.4:0.6 (Table I). The quadrupole splitting of +0.17 mm s⁻¹ shows that the hematite has not passed through a Morin spin flip transition. A significant proportion of this mineral furthermore is not magnetically ordered down to 120 K. The

doublet remaining at 4 K results from paramagnetic Fe^{3+} -bearing silicates.

At room temperature the Mössbauer spectrum of the clay fraction (sample 791C) consists essentially of an Fe^{3+} doublet (fig. 3a). A subordinate, strongly relaxed magnetic component with a maximum hyperfine field of *c.*470 kOe can be ascribed to hematite. At 120 K the Mössbauer spectrum of this sample is made up of a strong Fe^{3+} doublet and two sextets with hyperfine fields of 519 and 475 kOe (fig. 3b and Table I). At 4K (fig. 3c) the spectrum comprises—in contrast to the bulk sample—only two sextets. The hyperfine fields of 531 and 500 kOe are indicative of hematite and goethite, respectively. The central doublet is weaker than at 120 K, but makes up a higher proportion of the total spectrum than in the bulk sample. Visual inspection indicates that this doublet is composite, probably containing contributions from nontronite, which XRD and IR show to be present in the sample, and other Fe^{3+} -bearing silicates. Noticeable deviations between the spectrum and the model used for fitting (two sextets plus one doublet) at about -2.5 and $+3 \text{ mm s}^{-1}$ are the result of incipient magnetic hyperfine splitting, probably also of nontronite. The relative areas under the respective sextets indicate that the clay fraction has a lower proportion of hematite to goethite than the bulk sample.

Conventional X-ray diffractograms of various

samples show lines of garnet, hematite, quartz, calcite and a smectitic clay mineral (fig. 4a). The diffraction pattern of the dithionite treated sample (fig. 4b) shows lines of two relatively similar garnets (an almost pure andradite and a phase containing about 33% of the grossular molecule), quartz, and a calcic amphibole with $b = 18.2 \text{ \AA}$. The DXRD diagram (fig. 4c) shows complete patterns of hematite and goethite. Broad lines indicate that these minerals are not well crystallized. The goethite d_{111} spacing of 2.449 \AA suggests an Al substitution of about 4% (Thiel, 1963; Jónás and Solymár, 1970).

An oriented sample of the clay fraction shows a strong smectite peak at 15.1 \AA , relatively well-developed goethite, and weaker hematite lines. The observation of a higher goethite to hematite ratio than in the bulk sample is in agreement with the Mössbauer spectra.

The IR spectrum of the clay fraction (791C) shows an OH stretching band at 3550 and an OH bending band at 830 cm^{-1} ; which are typical for nontronite (Farmer and Russell, 1967). OH stretching bands at 3200 and OH bending bands at 890 cm^{-1} can be assigned to goethite.

Discussion. Fumarolic solutions rich in iron are being presently extruded at numerous localities in the Santorini caldera. Precipitation of metals transported by these solutions and local accumulation of the precipitates result in submarine deposition of iron oxides, siderite, opal and vivianite

TABLE I. Mössbauer parameters of the bulk sample 791B and the clay fraction 791C

Sample	T (K)	δ (Fe)	ΔE_Q	W	H_i	I_{rel}	Minerals	
791B	295	0.36(2)	0.21(4)	0.94(9)	491(2)	0.25(1)	Hm	
		0.38(1)	0.58(1)	0.52(2)	—	0.75(1)	Hm, Gt, S	
	~ 120	0.36(1)	0.17(1)	0.42(2)	522(1)	0.19(1)	Hm	
		0.36(1)	0.20(1)	1.02(3)	476(1)	0.50(2)	Gt	
	4	0.35(1)	0.53(1)	0.50(1)	—	0.31(1)	Hm, Gt, S	
		0.36(1)	0.17(1)	0.44(2)	535(1)	0.29(2)	Hm	
		0.33(2)	0.02 *	0.6 (2)	513(4)	0.13(3)	Ga	
		0.36(1)	0.26(2)	0.80(3)	502(1)	0.44(3)	Gt	
	791C	292	0.35(1)	0.58(2)	0.6 *	—	0.13(1)	S
			0.31(6)	0.1 (1)	1.5 *	470(5)	0.15(2)	Hm
~ 120		0.35(1)	0.52(1)	0.52(2)	—	0.85(1)	Hm, Gt, S	
		0.37(1)	0.17(2)	0.35(3)	519(1)	0.10(1)	Hm	
4		0.35(1)	0.22(1)	1.00(3)	475(1)	0.52(1)	Gt	
		0.36(1)	0.48(1)	0.51(1)	—	0.38(1)	Hm, Gt, S	
		0.36(1)	0.18(1)	0.35(1)	531(1)	0.22(1)	Hm	
		0.35(1)	0.24(1)	0.72(2)	500(1)	0.58(1)	Gt	
			0.33(1)	0.59(1)	0.6 *	—	0.19(1)	S

* Parameter fixed.

Isomer shifts (δ), quadrupole splittings (ΔE_Q) and widths (W) given in mm s^{-1} , magnetic hyperfine fields (H_i) in kOe. Minerals: Ga = garnet, Gt = goethite, Hm = hematite, S = silicates.

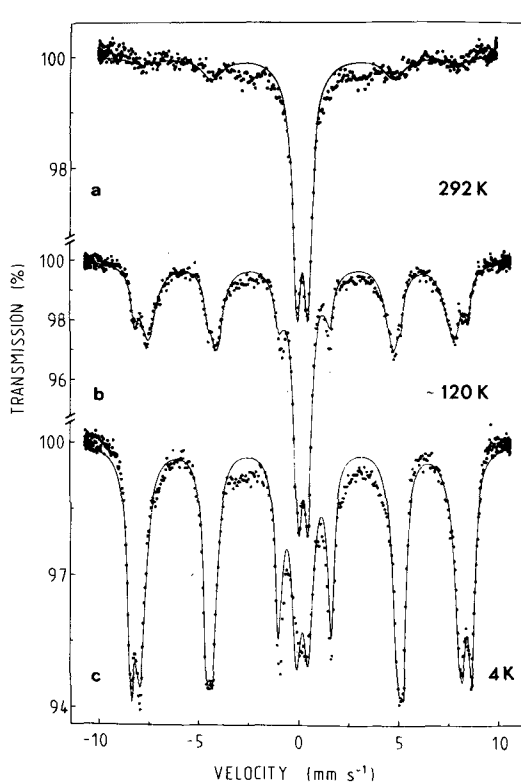


FIG. 3. Mössbauer spectra of clay fraction 791C from iron oxide band in garnetite at (a) room temperature, (b) c.120 K, and (c) 4 K.

(Puchelt *et al.*, 1973). The iron oxides comprise protoferrihydrite, ferrihydrite, and poorly crystallized goethite (Chukhrov, 1973). The solutions also contain notable amounts of other heavy metals, e.g. manganese, zinc, and copper, which are deposited at varying distances from the fumarolic outlets (Smith and Cronan, 1975).

The iron oxide mineralogy of the described hydrothermal assemblage differs significantly from that of the recent submarine deposits. Mössbauer spectroscopy and differential X-ray diffraction show the fossil samples to contain only hematite and goethite. The absence of magnetic hyperfine splitting of goethite at room temperature and of a Morin transition in hematite down to 4 K indicate that these minerals have particle sizes below 200 Å (van der Kraan and van Loef, 1966; Niningger and Schroerer, 1978) and/or noticeable substitution of other elements for Fe (magnetic dilution). The large temperature range (from above room temperature to below 120 K), over which hematite orders magnetically, is an indication of a wide distribution of small particle sizes. The low hyperfine fields (e.g. 501 and 533 kOe at 4 K, as compared to 507 and

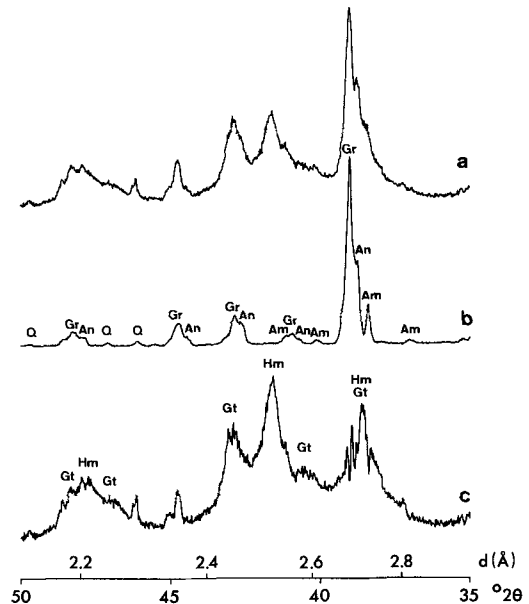


FIG. 4. X-ray diffractograms of (a) untreated bulk iron oxide band in garnetite 791B, (b) same sample following dithionite dissolution of iron oxides, and (c) differential X-ray diagram showing pattern which disappears upon dithionite treatment. Characteristic peaks are marked Hm (hematite), Gt (goethite), Am (amphibole), An (amphibole), Gr (granditic garnet, c.A₆₅Gr₃₄Sp₁), and Q (quartz).

543 kOe for pure, bulk goethite and hematite, respectively) support these observations. Broad and somewhat displaced X-ray diffraction lines suggest that the deviations from ideal behaviour are the outcome of both small particle size and isomorphous substitution.

Two alternative explanations can be put forward to account for the differing iron oxide mineralogy of the fossil and recent systems: (1) the fossil assemblage was formed at higher temperatures than the recent submarine exhalative deposits and the iron oxides crystallized directly in their present form, or (2) the assemblage was initially similar to the recent deposits but subsequently subjected to a mild metamorphism.

The recent iron-rich sediments were precipitated in a submarine environment. Hot, acid hydrothermal Fe²⁺-bearing fluids will be quenched upon discharge into this temperature, pH and Eh buffer. These sudden changes will favour the formation of ferrihydrite and other iron oxides of extremely poor crystallinity (Carlson and Schwertmann, 1981). Such minerals are, in fact, found in these deposits (Chukhrov, 1973).

In the fossil deposits described here, on the other hand, hydrothermal fluids were injected into pre-

existing basement rocks. These fluids, which transported the constituents of the epigenetic minerals hematite, goethite, chrysocolla, chalcocopyrite, and calcite altered minerals less resistant than garnet, thereby forming the uralitic amphiboles and nontronite found in the assemblage. Cracks in the garnets were also filled with these minerals.

This mineralization probably took place at higher temperatures than those encountered by the recent deposits and (because, in contrast to the submarine deposits, the solutions were not quenched) under conditions more closely approaching equilibrium. It is therefore not unlikely that the iron oxides impregnating the Santorini basement rocks crystallized directly in their present form.

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REFERENCES

- Behrend, F. (1936) *In* Reck, H. Santorin. *Der Werdegang eines Inselvulkans und sein Ausbruch 1925-1928*, vol. II. Reimer/Andrews & Steiner, Berlin.
- Carlson, L., and Schwertmann, U. (1981) *Geochim. Cosmochim. Acta*, **45**, 421-9.
- Chukhrov, F. V. (1973) *Mineral. Deposita*, **8**, 138-47.
- Farmer, V. C., and Russell, J. D. (1967) *Clays Clay Minerals*, **15**, 121-42.
- Jónás, K., and Solymár, K. (1970) *Acta Chim. Acad. Sci. Hungar.* **66**, 383-94.
- Mehra, O. P., and Jackson, M. L. (1960) *Clays Clay Minerals*, **7**, 317-27.
- Murad, E. (1976) *Mineral. Mag.* **40**, 715-19.
- Nininger, R. C., and Schroeder, D. (1978) *J. Phys. Chem. Solids*, **39**, 137-44.
- Puchelt, H., Schock, H. H., Schroll, E., and Hanert, H. (1973) *Geol. Rundschau*, **62**, 786-812.
- Schorin, H. (1980) *Ibid.* **69**, 226-44.
- Schulze, D. G. (1981) *Soil Sci. Soc. Amer. J.* **45**, 437-40.
- Schwertmann, U. (1964) *Z. Pflanzenernährung, Düngung, Bodenkunde*, **105**, 194-202.
- Smith, P. A., and Cronan, D. S. (1975) *Oceanology Internat.* **75**, 111-14.
- Thiel, R. (1963) *Z. anorg. allg. Chem.* **326**, 70-8.
- van der Kraan, A. M., and van Loef, J. J. (1966) *Phys. Lett.* **20**, 614-16.

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