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Zoned, birefringent garnets from Thera Island, Santorini Group (Aegean Sea)

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SUMMARY. A garnetite that occurs locally in phyllitic schists exposed by the Santorini caldera consists mainly of euhedral garnet crystals showing alternating isotropic and birefringent lamellae. X-ray diffraction revealed two garnets with unit cell dimensions a of $12{\cdot}052 \pm 0{\cdot}002$ and $11{\cdot}984 \pm 0{\cdot}005$ Å, corresponding respectively to almost pure andradite and a granditic phase. Mean compositions determined by microprobe analysis are $An_{97}Sp_1Alm_2$ for the isotropic and about $An_{63}Gr_{33}Sp_1Alm_3$ for the birefringent layers.

The garnets are deduced to have been produced mainly by thermal metamorphism of the schists. Although cyclic variations in the composition of circulating fluids could have brought about the zoning, this may just as well be the result of temperature fluctuations, individual garnet compositions being indicative of the respective formation temperature.

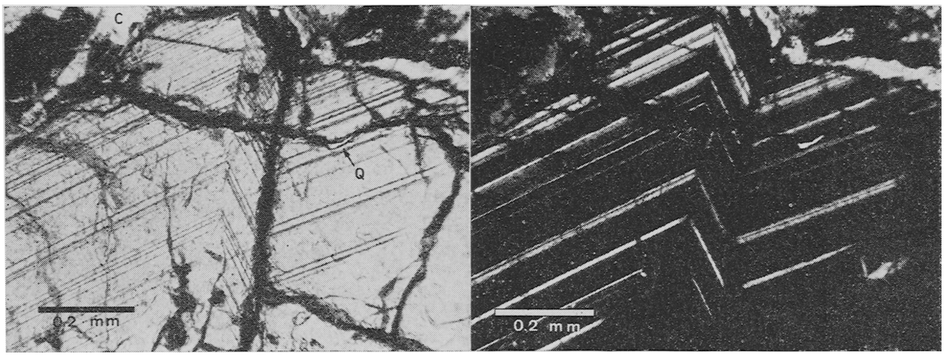
THE Santorini Group, located in the southern Aegean Sea, consists of five essentially volcanic islands. Three of these constitute the remains of a stratovolcano the centre of which collapsed in the wake of violent pumice eruptions some 3500 years ago, leaving an area of about 83 sq. km to be flooded by the sea. These islands are, for the most part, made up of intermediate volcanics of the calc-alkaline association, as are two younger isles that have since emerged within the caldera.

Prominent outcrops of country rock on the main island, Thera, include the 566 m high Profitis Elias mountain, which consists mainly of Triassic limestone (Papastamatiou, 1958). Eocene phyllitic schists (Tataris, 1964) are well exposed by the eastern part of the caldera wall near the port of Athinios. These schists have, at numerous localities, been hydrothermally altered and impregnated by ore-bearing solutions (Murad and Hubberten, 1975). At Thermia, roughly 2 km south-west of Athinios, mineralization has resulted in conspicuous bands of chrysocolla associated with hematite, calcite, and chalcedony. The country rock here locally consists of a garnetite constituted, beside the named minerals, almost exclusively of up to 10 mm large, brown dodecahedral crystals of garnet.

Mineralogical description. Thin sections show the garnets to be made up of alternating isotropic and birefringent zones (the latter having a double refraction of about 0·004) with sharp boundaries between the two varieties (figs. 1 and 2). The figures produced by such crystals in thin section have been described by Schaacke (1949). In plane-polarized light the anisotropic lamellae are colourless, whereas the isotropic layers are of a pale-yellow colour. Practically all of the sectioned garnets show dodecahedral twinning, tallying with descriptions of andradite-rich garnets by Goldschmidt (1911), Holser (1950), Kennedy (1953), and Lessing and Standish (1973).

Occasional undulatory extinction, kinks, and cracks in the garnets indicate post-crystalline deformation. Red stains are developed in patches and along such cracks. Quartz inclusions form an- to euhedral grains. Younger calcite veins, associated with the copper mineralization, fill fissures in and between the garnet crystals.

X-ray powder data from a diffractometer tracing yielded two superposed garnet patterns, one strong and the other—with the exception of the 400 reflex—relatively faint. The main pattern gave a unit cell dimension a of $12{\cdot}052 \pm 0{\cdot}002$ Å and differs only negligibly from that of andradite (powder diffraction file card 10–288); the other garnet has $a = 11{\cdot}984 \pm 0{\cdot}005$ Å.



FIGS. 1 and 2: FIG. 1 (left). Zoned garnet from Thermia showing sharp boundaries between individual zones. Plane-polarized light, Q: quartz inclusion, C: calcite. FIG. 2 (right). As fig. 1, crossed polarizers.

A chemical analysis of the crystal shown in fig. 3 was effected at twelve points along the indicated traverse using an ARL EMX-SM electron microprobe. Instrumental settings included a beam diameter of 3 μm, an accelerating potential of 15 kV and a mean sample current of 20 nA. Minerals of known composition and pure element standards served for calibration; raw data were corrected using a modified version of a computer program by Goldstein and Cornelia (1969). Results of the analyses and molecular data calculated from these are given in Table I.

The most conspicuous feature revealed by the analyses is an unequivocal inverse relationship between Al and Fe, birefringent zones having high Al concentrations and vice versa. Other, positive, though not so pronounced correlations exist between Al and Mn, Ca and Si. To achieve structural balance, part (on an average about 6 %) of the total iron content is considered to be in the divalent state, resulting in noticeable proportions of almandine. Extreme depletion of Al in some of the isotropic zones causes Mn and excess Fe in these to form calderite and skiagite components, which, however, for reasons of simplicity are given here as spessartine and almandine, respectively. The garnet compositions fall into two distinct groups: almost pure andradite ($An_{97}Sp_1Alm_2$) and andradite–grossular mixed crystals (averaging about $An_{63}Gr_{33}Sp_1Alm_3$). Unit cell dimensions calculated from end-member data for such garnets ($a = 12{\cdot}044$ and $11{\cdot}970$ Å, respectively) resemble those actually determined for the Santorini garnets.

Genesis of the garnets. Occurrence of the garnets in close neighbourhood with the copper mineralization might suggest a genetic relation between these. A microscopic investigation, however, revealed the garnets to have been formed prior to the mineralization. The mineralogical composition of the latter, moreover, indicates this to have been intruded at a relatively low temperature. Submarine discharge of hot springs at Thermia demonstrates the current continuation of such processes.

TABLE I. *Chemical composition of garnet crystal from Thermia (fig. 3)*

	1	2	3	4	5	6	7	8	9	10	11	12
Optics*	B	I	I	B	I	B	I	B	B	I	B	B
SiO_2	35·6	34·8	34·7	36·4	34·5	36·2	35·7	36·7	36·9	35·2	37·4	37·4
Al_2O_3	7·44	0·84	1·13	8·12	1·57	6·34	0·76	8·25	8·51	0·23	8·32	9·80
TiO_2	0·13	0·12	0·03	0·23	0·07	—	0·04	0·04	—	0·01	0·02	0·08
Fe_2O_3†	22·5	33·0	31·2	22·1	30·7	24·6	31·9	22·1	22·4	33·5	22·5	20·6
MnO	0·44	1·71	0·31	0·43	0·34	0·40	0·30	0·48	0·37	0·30	0·43	0·47
CaO	33·2	29·8	32·2	33·2	32·1	32·9	31·8	33·4	33·2	31·8	33·3	33·0
Sum	99·3	100·3	99·6	100·5	99·3	100·4	100·5	101·0	101·4	101·0	102·0	101·3
Number of cations on a basis of 24 oxygens												
Si	5·857	5·889	5·887	5·892	5·865	5·914	5·992	5·904	5·901	5·908	5·948	5·939
Al	0·143	0·111	0·113	0·108	0·135	0·086	0·008	0·096	0·099	0·046	0·052	0·061
Al	1·300	0·056	0·113	1·439	0·180	1·135	0·142	1·469	1·506	—	1·506	1·770
Ti	0·016	0·015	0·004	0·028	0·009	—	0·005	0·005	—	0·001	0·002	0·010
Fe	2·688	3·895	3·885	2·519	3·813	2·854	3·823	2·517	2·473	3·997	2·462	2·184
Fe	0·093	0·301	0·101	0·170	0·113	0·165	0·195	0·160	0·221	0·241	0·230	0·276
Mn	0·061	0·245	0·045	0·059	0·048	0·055	0·043	0·065	0·050	0·043	0·058	0·063
Ca	5·856	5·402	5·857	5·748	5·843	5·757	5·711	5·755	5·698	5·713	5·666	5·604
End-member molecules per cent												
An %	67·5	90·8	97·2	63·9	95·5	71·6	95·6	63·3	62·2	95·3	62·1	55·4
Gr %	30·0	—	0·4	32·2	1·8	24·7	0·5	33·0	33·3	—	33·1	38·9
Sp %	1·0	4·1‡	0·7	1·0	0·8	0·9	0·7	1·1	0·8	0·7‡	1·0	1·1
Al %	1·5	5·1‡	1·7	2·8	1·9	2·8	3·2	2·7	3·7	4·0‡	3·9	4·6

* B = birefringent, I = isotropic.
† Total iron as Fe_2O_3.
‡ Spessartine molecule including calderite; almandine including skiagite.
—: Below limit of detection (0·01 % TiO_2). Cr_2O_3 and MgO were below the limit of detection (0·01 and 0·03 %, respectively) throughout.

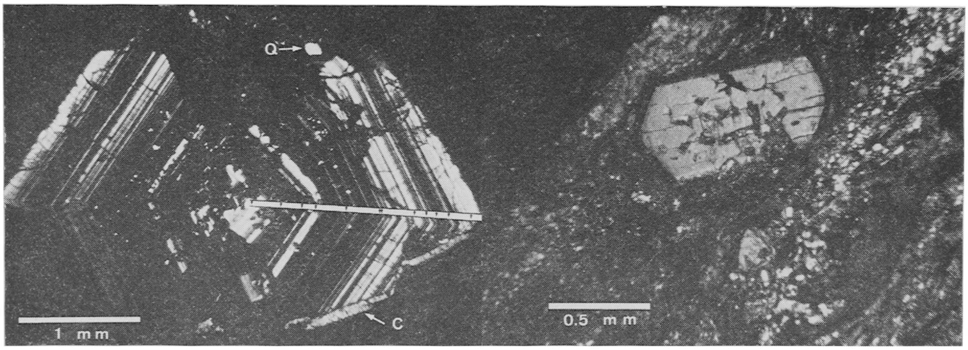
Two fundamentally different processes that might have led to the garnet formation are *metasomatism of limestone* intercalations in the phyllitic schists and essentially *isochemical metamorphism* of the schists proper.

Limestone intercalations, frequent in the schists, are probably derived from the Triassic mass that constitutes several morphological elevations on Thera. An analysis by Puchelt and Hoefs (1969) of a limestone from the Profitis Elias showed this to be extremely pure, consisting of 99·1 % $CaCO_3$. Fumarolic action, entailing addition of iron and silica to such samples, might have produced the garnets as a result of the reaction:

$$\underset{\text{calcite}}{3CaCO_3}+Fe_2O_3+3SiO_2 \rightarrow \underset{\text{andradite}}{Ca_3Fe_2[SiO_4]_3}+3CO_2 \qquad (1)$$

Though thermally metamorphosed and metasomatized fragments of marbles and schists bearing typical tactite minerals (calcic pyroxene–anhydrite/wollastonite–plagioclase with titaniferous andradite garnet and sphene as accessories) occur as inclusions in the Santorini lavas (Nicholls, 1971), the notable absence of such minerals at Thermia tends to advocate the latter process for this locality.

Chemical analyses of schists from Athinios—heterogeneous as these may be (Murad and Hubberten, 1975)—indicate that the garnets could well have been formed without major transfer of material, physico-chemical conditions permitting. Huckenholz and Yoder (1971) pointed to the preferential occurrence of granditic garnets in mineral assemblages formed at high temperatures and low pressures, conditions that may doubtlessly have prevailed at Thermia for some time.



FIGS. 3 and 4: FIG. 3 (left). Garnet crystal analysed by microprobe. Individual analysed points along the white traverse are indicated by arrows; enumeration in Table 1 is consecutive from the centre outwards. Q and C as for fig. 1. FIG. 4 (right). Augite porphyroblast in phyllitic schist from between Thermia and Athinios.

Varet (1970) suggested the following reaction to have led to the formation of andradite in a fumarolic environment at Menoyre (France):

$$\underset{\text{hedenbergite}}{6CaFe[Si_2O_6]} + 1{\cdot}5O_2 \rightarrow \underset{\text{andradite}}{2Ca_3Fe_2[SiO_4]_3} + \underset{\text{hematite}}{Fe_2O_3} + 6SiO_2 \qquad (2)$$

Although no pyroxenes were encountered in the immediate vicinity of the garnetite, schists exposed between Athinios and Thermia are, indeed, locally rich in up to 10 mm large augite porphyroblasts (fig. 4). While alternative reactions leading to the garnet formation would also be conceivable, the possibility of reaction (2) is supported by the presence of the other products as inclusions in the Thermia garnets. Substantial quantities of magnesium, which would have been set free if the garnets were derived from the hedenbergite component of augites in the described manner, could have—at least in part—been incorporated into a montmorillonite mineral identified in the garnetite by X-ray diffraction.

Fluctuations in the composition of circulating fumarolic fluids, involving in particular their aluminium content or the iron/aluminium ratio, could have given rise to the zoning. Lessing and Standish (1973) consider such cyclic variations in the composition of hydrothermal solutions to have caused similar oscillatory zoning in granditic garnets from Crested Butte, Colorado. In these garnets, however (contrary to those from Santorini) dark zone (i.e. more or less isotropic) lamellae correspond to high aluminium concentrations.

An alternative explanation for the development of the zoning is provided by the results of experimental work by Huckenholz *et al.* (1974) who found that, at constant pressure and bulk chemical composition, the grossular content of granditic garnets synthesized from fassaite-bearing assemblages tends to increase with falling temperatures. Applied to the garnetite from Thermia, this would indicate higher formation temperatures for the isotropic, andradite-rich zones than for the birefringent ones, the oscillatory zoning thus suggesting cyclic variations of temperature. The fact that the outer fringe of the garnets usually consists of a wide, birefringent zone (the point—No. 12—with the highest grossular/andradite ratio on the traverse along the garnet shown in fig. 3 incidentally lies on just this zone) indicates, quite credibly, the formation of these to have come to a gradual end with decreasing temperature.

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