Low-Temperature Metasomatic Garnets in Marine Sediments [and Discussion]

A. J. Easton, D. Hamilton, D. R. C. Kempe, S. M. F. Sheppard and S. O. Agrell

Phil. Trans. R. Soc. Lond. A 1977 **286**, 253-271
doi: 10.1098/rsta.1977.0116

Phil. Trans. R. Soc. Lond. A. **286**, 253–271 (1977) [253]
Printed in Great Britain

Low-temperature metasomatic garnets in marine sediments

By A. J. Easton
Department of Mineralogy, British Museum (Natural History), London SW7
D. Hamilton
Department of Geology, University of Bristol
D. R. C. Kempe
Department of Mineralogy, British Museum (Natural History), London SW7
and S. M. F. Sheppard†
Scottish Universities Research and Reactor Centre, East Kilbride, Glasgow

[Plate 1]

The paragenesis of low-temperature metasomatic calcium-iron garnets or hydrogarnets in marine sediments is discussed. Oxygen isotope data indicate that the garnetiferous (micarb) chalk from DSDP site 251, southwest branch, Indian Ocean Ridge ($gros_{52}and_{40}py_6alm_{1.5}sp_{0.5}$), formed at about 170 °C from circulating seawater hydrothermal solutions passing through the underlying altered basalts. Other possible examples of the hydrothermal metasomatic formation of garnets are found on bleached coprolites in the basal Bone Bed at the junction of the Rhaetic and the underlying Triassic Tea Green Marls at Larne, Antrim, in association with montmorillonite, analcime, magnetite, fluorite, and calcite, near to Tertiary basalts ($and_{89.4}gros_{6.1}sp_{3.1}alm_{1.0}py_{0.4}$); in recrystallized chalk and glauconitic sandstones, associated with zeolites and other minerals, near a dolerite dyke, at Portmuck, Antrim (andraditic); and in a calcareous sedimentary lens in bedded trachytic tuffs, cut by dolerite dykes, at Fuerteventura, Canary Islands ($gros_{94.5}and_{5.0}py_{0.5}$). An extensive search through DSDP basal sediments has revealed no further examples.

Introduction

Metasomatic garnets (figures 1 and 2, plate 1) have been described from Deep Sea Drilling Project site 251, southwest branch of the Indian Ocean Ridge, by Kempe & Easton (1974) and Cook, Zemmels & Matti (1974). The garnets occur in recrystallized calcite (micarb) chalk overlying the basement basalt and forming the lowest 18 m of a 450 m thick sequence of nannoplankton ooze and chalk. Kempe & Easton reported an analysis (table 1) of the garnet but shortage of material and technical difficulties associated with the possible water content of adsorbed residual colloidal silica prevented determination of the H_2O^+ content. The molecular composition was given as $gros_{52}and_{40}py_6alm_{1.5}sp_{0.5}$, with $a = 1.19265$ nm (not: 11.92658 Å, as printed in the abstract of Kempe & Easton (1974)) and $n = 1.764$. The garnet is considered to be a nearly anhydrous member of the hydrogarnet series although, as already stated, a water determination is impracticable.

The garnet occurrence was considered by Kempe & Easton to be unique within present knowledge. Possible analogues were mentioned briefly and the paragenesis discussed; although several alternatives were put forward the most likely origin was thought to be the metasomatic introduction by hydrothermal activity of Si, Al, and Fe^{3+} into an essentially wet $CaCO_3$

---

† Present address: C.R.P.G., C.O. no. 1, Vandoeuvre-les-Nancy, 54500, France.

Table 1. Chemical analyses of low-temperature metasomatic garnets

	1	2	3
SiO_2	38.18	34.82	41.31
TiO_2	0.42	0.10	n.d.
Al_2O_3	11.89	2.24	21.49
Cr_2O_3	0.01	n.d.	n.d.
Fe_2O_3	11.69	27.68†	2.30*
FeO	0.64	0.54†	—
MnO	0.26	1.29	n.d.
MgO	1.47	0.12	0.11
CaO	34.87	31.00	26.66
Na_2O	0.10	0.28	n.d.
K_2O	0.02	0.21	n.d.
H_2O^+	n.d.	—	n.d.
H_2O^-	n.d.	n.d.	n.d.
P_2O_5	n.d.	0.01	n.d.
total	99.55	98.29†	91.87
almandine	1.5	1.0	—
andradite	39.4	89.4	5.0
grossular	52.2	6.1	94.5
pyrope	6.3	0.4	0.5
spessartine	0.6	3.1	—
uvarovite	—	—	—

n.d., not determined; *, total iron as Fe_2O_3.

1, Andraditic hydrogrossular, DSDP site 251, southwest branch, Indian Ocean Ridge (sample 26-251A-29-1, 137) (Kempe & Easton 1974). Anal: A. J. Easton.

2, Grossular-bearing andradite, Rhaetic Bone Bed, Waterloo foreshore, Larne, Co. Antrim, Northern Ireland. Anal: A. J. Kemp (†, Fe_2O_3, FeO, and total are adjusted for an estimated 2 % of included disseminated magnetite).

3, Andradite-bearing grossular, calcareous carbonate sediment lens in trachytic tuffs, Barranco de Ajui, western Fuerteventura, Canary Islands (no. 2771). Anal: R. F. Symes & J. C. Bevan (semi-quantitative analysis by electron microprobe).

Description of plate 1

Figure 1. Andraditic hydrogrossular garnet, DSDP site 251, southwest branch, Indian Ocean Ridge (sample 26-251A-29-1, 137). Photomicrograph of smear slide showing garnet in calcite (micarb) chalk. Length of bar 10 µm. From Kempe & Easton (1974), reproduced by courtesy of the National Science Foundation of America and the Deep Sea Drilling Project.

Figure 2. Andraditic hydrogrossular garnet, DSDP site 251, southwest branch, Indian Ocean Ridge. Scanning electron microscope photograph by H. A. Buckley. Length of bar 10 µm. From Kempe & Easton (1974), reproduced by courtesy of the National Science Foundation of America and the Deep Sea Drilling Project.

Figure 3. Andradite-bearing grossular garnet in calcareous carbonate sediment (lens) in trachytic tuffs, Barranco de Ajui, western Fuerteventura, Canary Islands. Photomicrograph; length of bar 100 µm. Material collected by M. J. Le Bas (no. 2771).

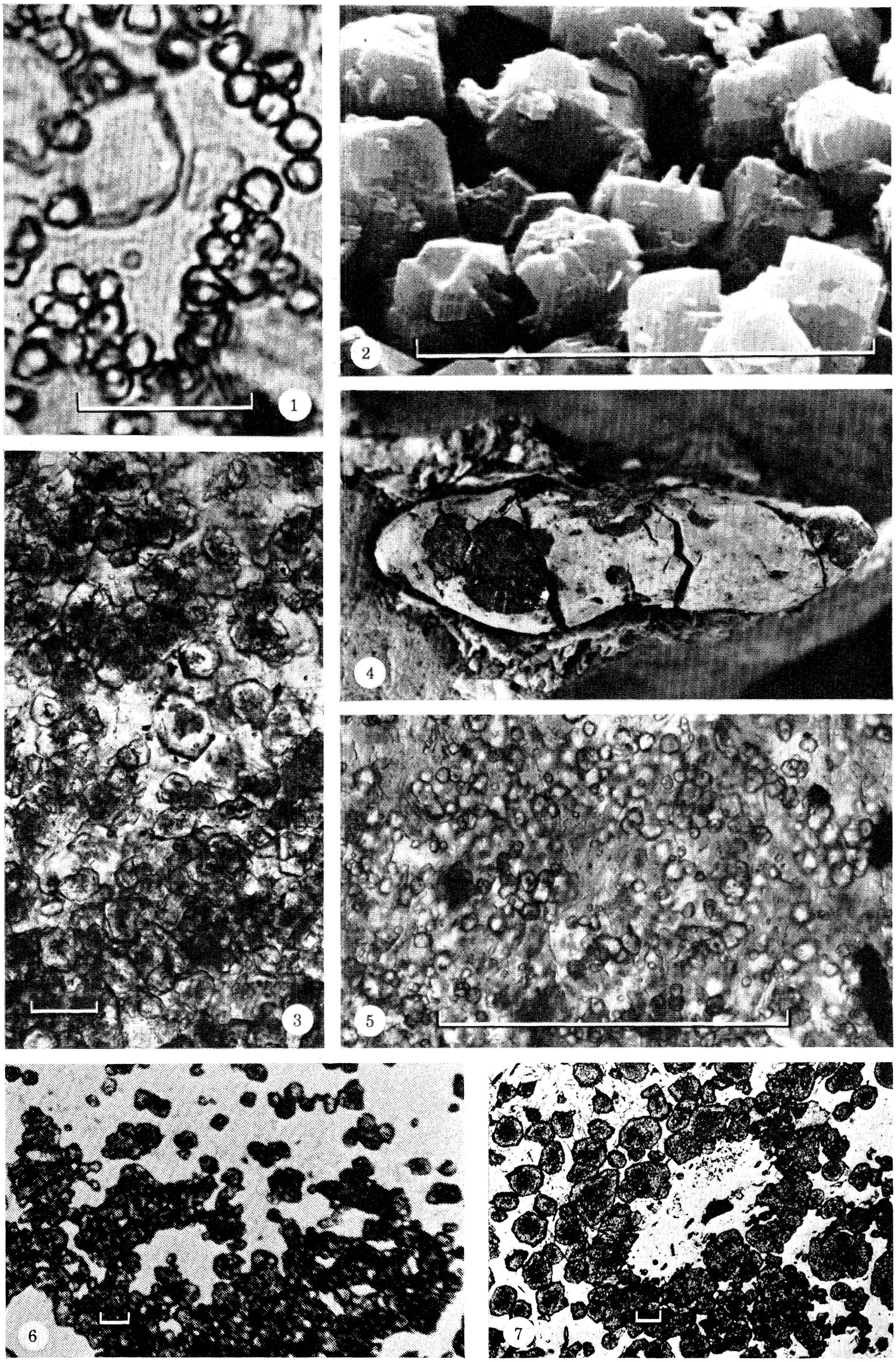
Figure 4. Grossular-bearing andradite garnet partially encrusting coprolite from the Rhaetic Bone Bed, Waterloo, Larne, Northern Ireland. Length of coprolite 1.8 cm.

Figure 5. Spessartine garnet, with chlorite and muscovite, in the Manganese Shale Group, Harlech Dome, Merioneth. Photomicrograph of material supplied by R. K. Harrison, Institute of Geological Sciences. Length of bar 100 µm.

Figure 6. Spessartine garnet, with quartz, chlorite, and muscovite, in coticule forming part of the aureole of the Leinster Granite, Republic of Ireland. Photomicrograph; length of bar 100 µm. From Kennan (1972), reproduced by courtesy of the *Geological Magazine*.

Figure 7. Spessartine garnet, with quartz, forming coticules at Sandford, Nova Scotia. Photomicrograph; length of bar 100 µm. From Schiller & Taylor (1965), reproduced by courtesy of the *American Mineralogist*.

MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES
THE ROYAL SOCIETY A
PHILOSOPHICAL TRANSACTIONS OF



FIGURES 1–7. For description see opposite.

mud. The only occurrences comparable in terms of T and P of formation were thought to be synthetic: no natural garnet was known to have formed at the low temperatures (< 300 °C) which must have prevailed in the Indian Ocean example.

In this paper a more extensive review of possible similar occurrences is given, of which two are thought possibly to be closely analogous, and the paragenesis is reconsidered. Finally, evidence is derived from oxygen isotope data which support the hydrothermal nature of the occurrence and suggest temperatures of formation of the order of 170 °C, requiring a revision of the stability relations of at least the hydrogarnet sub-group of the garnet family.

Other examples of garnets in sediments

A thorough search of the literature by Kempe & Easton (1974) failed to find any strictly comparable occurrences of hydrogarnets in sediments. The two or three examples previously quoted are mentioned again below, but are now regarded as highly dubious.

Dubious examples

Caribbean Sea

Donnelly & Nalli (1973) described two garnet occurrences in sediments drilled on leg 15 of the DSDP. The first, considered to be authigenic, consists of rectangular plates, 20 μm or more across, of a golden brown garnet, apparently spessartine, from site 146. The second occurrence, from site 153, consists of brownish, dodecahedrally modified octahedral grains, generally less than 10 μm across, in a single smear slide. Unfortunately, further crystals of this rare-habit garnet could not be located for X-ray confirmation, although an X-ray photograph of the smear slide garnets was consistent with such an identification. Donnelly & Nalli considered that this example might be volcanic.

Green River Formation

Although not known to have been reported by C. Milton and his co-workers, the possibility of the presence of authigenic garnet in the Green River Formation of Wyoming, Utah, and Colorado was suggested by M. N. Bass (personal communication to D.R.C.K., 1973).

Millstone Grit of the Midlands and Trias of the Cheshire Basin, northern England

Our attention was drawn to the presence of stepped (etched) garnet grains in these sediments by G. P. L. Walker (personal communication 1975), who has regarded them as of authigenic origin.

North Germany

An occurrence is known in sands, again of unknown origin but interpreted as being authigenic (Walker, personal communication 1975).

Spessartines of metamorphic origin

The spessartine molecule is present in many garnets of mainly almandine composition formed by low grade regional metamorphism (Deer, Howie & Zussman 1962). However, predominantly spessartinic garnets are common in low grade regionally metamorphosed manganese-rich sediments, as well as in skarns. In these sediments, some of which are of greywacke and chert type, the possibility of metamorphosed palaeo-manganese nodule beds, or metal-enriched sediments, might form an explanation for the Mn-rich layers (see Kennan 1972). Three typical examples of spessartine, in which the garnets occur in clusters or bands of minute crystals, resembling those from site 251 (although larger by a factor of ten), are shown in figures 5, 6 and 7, plate 1. The garnets in the Manganese Shale Group from the Harlech Dome, Merioneth, occur with, mainly, chlorite and muscovite. There seems little doubt that the garnet derives from low grade greenschist regional metamorphism (Woodland 1939; personal communication 1975). Similarly, the spessartine–quartz 'coticules' from Sandford, Nova Scotia, derive from similar low grade regional metamorphism (Schiller & Taylor 1965). The ellipsoidal clusters of spessartine which occur, with chlorite and muscovite, in the garnet–quartz coticules forming the Leinster Garnetiferous Beds are part of the thermal aureole of the Leinster Granite and are again of low grade metamorphic origin (Brindley 1954; Kennan 1972); they are thought to derive from the reconstitution of original sedimentary concretions.

Garnetiferous sediments in Co. Antrim, Northern Ireland

Garnets, which have grown in altered sedimentary rocks, have been recorded from near Portmuck, Islandmagee, by Walker (1948, 1959, 1960). A new occurrence is reported here from Waterloo, north of Larne, also on the northeast coast of Co. Antrim.

Numerous dykes are associated with the Antrim basic igneous complex. Commonly these dykes cut both the underlying sedimentary successions and the overlying basaltic lavas but generally the dykes have very little metamorphic effect on the adjacent sediments. Exceptions are the comparatively intense metamorphism of Triassic sandstones produced by the Waterford dyke in Co. Antrim (Reynolds 1940) and the extensive alteration of both lavas and sediments by dolerite dykes at Portmuck. Garnets have been recorded only from the Portmuck locality and the following brief description is based on Walker's work.

The garnets occur most abundantly where dolerite dykes cut the Chalk, as on the coast of Islandmagee, 1.5 km north of Portmuck, and again, adjacent to the bar, 0.8 km southeast of Portmuck. These are brown andradite garnets, the largest crystals being more than 6 mm in diameter. Where found in place, the garnets are most common close to the basic dykes so that the andradite–diopside rocks, together with the occurrence of magnetite, ilmenite, and apatite, are related to the contact metamorphic effects of the dykes.

The second occurrence of garnets occurs at Waterloo, about 2 km north of Larne Lough. Along the coast, an extensive wave-cut platform, backed by cliffs, occurs from the entrance to Larne Harbour to beyond Waterloo. In this platform, the sedimentary succession (from south to north) of Triassic Keuper and Tea Green Marls, Rhaetic, and Liassic sediments, is clearly exposed as the beds dip northwest at between 8° and 20°. The succession is cut by two small dolerite dykes, one about 500 m south of the Tea Green Marl–Rhaetic contact and the other in Liassic sediments about 40 m north of the same contact. Adjacent to both these dykes, the sediments are bleached by contact metamorphic effects for only 2 to 5 cm. No major changes in texture or mineralogy occur.

Basaltic lavas form a prominent erosional escarpment adjacent to the coastal road north of Waterloo, where the lavas overlie Chalk. The escarpment is some 150 m away from the wave-cut platform at Waterloo; originally, the lavas could have spread over the sediments forming the coastal cliffs at Waterloo. Since the cliffs rise about 30 m, it is considered that the lavas could not at any previous time have been closer than this to the sediments now exposed in the wave-cut platform. However, there is evidence of igneous activity nearby in the Chalk escarpment by the coastal road to the north of Larne. Hancock (1961) reports reddening of the Chalk, and large blocks of basalt occur in the disturbed Chalk (P. I. Manning, personal communication 1968). These two Waterloo occurrences lie on a northwesterly line, which is a direction of faulting in the area.

The sedimentary succession along the coast is easily recognizable by the distinctive colour sequence: red Keuper Marl, pale blue-green Tea Green Marl, dark grey cyclic Rhaetic sediments (Hamilton 1962), and dark Liassic mudstones and limestones. However, several atypical features occur, including:

(1) An unusually thick development of the Tea Green Marls. Towards the top of this succession the texture becomes mottled and then abundantly nodular. These small nodules are really pseudo-ooliths, shown by X-ray diffraction to consist of analcime.

(2) Montmorillonite occurs with the analcime pseudo-ooliths in the Tea Green Marl, and also in the lower part of the Rhaetic succession, wherever the original sediments were clayey.

(3) Magnetite occurs in joints and in the sediments close to the Tea Green Marl–Rhaetic contact.

(4) The Rhaetic Bone Bed at the base of the Rhaetic succession is white, instead of the usual black colour of the phosphatic coprolites, bones, and fish teeth, and these are locally encrusted with garnet.

The garnets (figure 4, plate 1) occur as cloudy, pale straw to clear medium-brown, scale-like crystals encrusting the white phosphatic masses and also penetrating, as scales and plates, the joints within them. The garnets may form an almost continuous coating, about 1 mm thick, over the phosphate, with a rough inner surface and an outer surface often consisting of a single crystal face, sometimes strongly striated, with only rare adjacent (110) faces; there are thus no euhedral forms of the garnet. The garnets have a = 1.2040 nm and contain minute inclusions of magnetite (estimated at about 2 %), especially in the darker forms. Chemically (table 1) the darker garnets are andradites, with a molecular composition $\mathrm{and}_{89.4}\mathrm{gros}_{6.1}\mathrm{sp}_{3.1}\mathrm{alm}_{1.0}\mathrm{py}_{0.4}$.

The coprolites, teeth and bones at Larne almost certainly consisted originally of carbonate fluoro-phosphate, similar to unaltered examples taken from this horizon in southwest England, and thus represented a concentrated source of calcium ions; the Tea Green Marls below and the basal Rhaetic above are usually only slightly calcareous. Thus the favoured site of garnet nucleation was obviously on the phosphate. Isotypy between phosphates and garnets has been shown to occur by Thilo (1941). Mason & Berggren (1941) and Mason (1957) have reported that PO_4 may replace some of the SiO_4 groups of spessartine garnets but there is only 0.01 % of P_2O_5 in the Waterloo garnets (table 1). Thus there is virtually no incorporation of phosphorus in the andradite structure, despite its ready availability, although it may have acted as a catalyst. Exclusion may be due to the low temperature of formation of the garnets, but it is notable that no concentration of phosphorus has been detected in the site 251 or Canary Island calcareous sediments forming the matrix to the garnets at these localities.

The original sediment enclosing the phosphatic Bone Bed material was a siltstone. The sediment has been altered extensively to analcime, albite, and rare diopside, whilst in adjacent sediments there is extensive corrosion of quartz by sericite. Magnetite and other iron oxides are disseminated through these sediments, but garnets are restricted to the Bone Bed. The alteration is thought to be related to the very extensive zeolitization of the Antrim basalts (Walker 1959, 1960), which is linked to the period of main movement along faults.

Chemical analyses of the underlying Tea Green Marl and the overlying Rhaetic sediments reflect changes in the composition of the original sediments (table 2 and figure 8) rather than a local enrichment in the immediate vicinity of the garnetiferous Bone Bed. In particular, the content of K_2O, Na_2O, MgO, and Al_2O_3 of the Tea Green Marl is remarkably constant in samples taken up to 250 m (horizontally) south of the Bone Bed. There is a distinctive change in the levels of concentration of these oxides in the overlying Rhaetic sediments, which to the north of the Bone Bed show rapid variations (figure 8) owing to the presence of small scale fining-upwards sand/clay cycles in the Rhaetic (Hamilton 1962). The CaO content tends to be variable through the whole succession.

Table 2. Chemical analyses of sediments

	Tea Green Marl					Rhaetic					
	584	550	573	585	A	586	450	531	533	526	677
SiO_2	50.14	51.63	50.76	41.14	50.72	68.17	57.68	58.74	63.83	58.21	54.39
TiO_2	0.94	0.77	0.64	0.57	1.50	0.73	0.63	0.93	0.71	0.86	0.77
Al_2O_3	14.38	13.06	14.53	11.31	11.21	13.04	16.42	18.49	12.01	16.72	19.92
Fe_2O_3	5.35	2.86	3.19	3.60	4.46	2.22	2.83	6.20	2.54	3.57	—
FeO	3.67	3.53	3.26	3.64	—	2.13	2.11	1.26	2.19	3.79	6.78†
MnO	0.08	0.11	0.11	0.30	—	0.06	0.01	0.07	0.08	0.08	0.07
MgO	12.60	12.42	10.07	14.92	12.40	3.27	4.26	3.73	3.47	3.96	2.21
CaO	1.29	1.94	3.31	7.88	3.65	0.26	0.44	0.46	4.08	1.91	0.48
Na_2O	2.88	2.69	3.27	2.22	0.40	1.18	1.15	1.75	0.60	1.81	0.20
K_2O	3.58	4.16	5.21	2.20	3.87	6.53	10.63	4.57	5.39	6.12	5.64
H_2O^+	3.36	4.86	4.01	6.58	—	1.85	2.58	3.53	2.34	2.17	—
P_2O_5	0.22	0.15	0.20	0.56	—	0.10	0.08	0.15	0.10	0.05	0.05
CO_2	1.30	1.48	2.17	5.63	—	0.22	0.48	0.25	2.55	0.75	—
total	99.79	99.66	100.73	100.55		99.76	99.30	100.13	99.89	100.00	

584, 550, 573, 585, 586, 450, 531, 533, and 526. See figure 8 for distance north or south of the garnetiferous Bone Bed. Anal: R. Lewis. A, Grey and reddish-brown Keuper Marl, M5 Motorway, East Lodge, Hereford & Worcester (Sherwood & Hollis 1966). 677, Rhaetic shale, Aust Cliff, Gloucestershire (Hamilton 1966). Anal: A. J. Kemp (†total iron as FeO; Fe_2O_3/FeO ratio not determinable because of high organic content).

Comparison of the Larne analyses with those of a mottled green and red Keuper Marl from the Midlands and a Rhaetic sample from Aust Cliff (samples A and 677 in table 2) suggests that there has been considerable enrichment in Na_2O at Larne. The source of the Na_2O, present in both analcime and smectite, is unlikely to be basalt; a probable source lies in the abundant salt horizons present at depth in the Keuper Marl of the area, recorded in the Larne borehole (Manning *et al.* 1975). The rise of basalt through such saliferous horizons could have resulted in spilitization of the basalt; alternatively, intrusion of the basalt or strong fluid activity may have mobilized sodium. Reaction of this sodium with the sediments could have given rise to analcime pseudo-ooliths and combination with MgO, possibly from both clays and dolomite, could have produced the widespread smectites. Iron, on the other hand, may well have been derived from the basalt. In a low-calcium environment, coupled with silica deficiency, an excess of iron has resulted in the widespread dissemination of magnetite; this suggestion is perhaps supported by a consistent Fe_2O_3/FeO ratio through Tea Green Marl and Rhaetic sediments from 250 m south to 30 m north of the Bone Bed. Limited

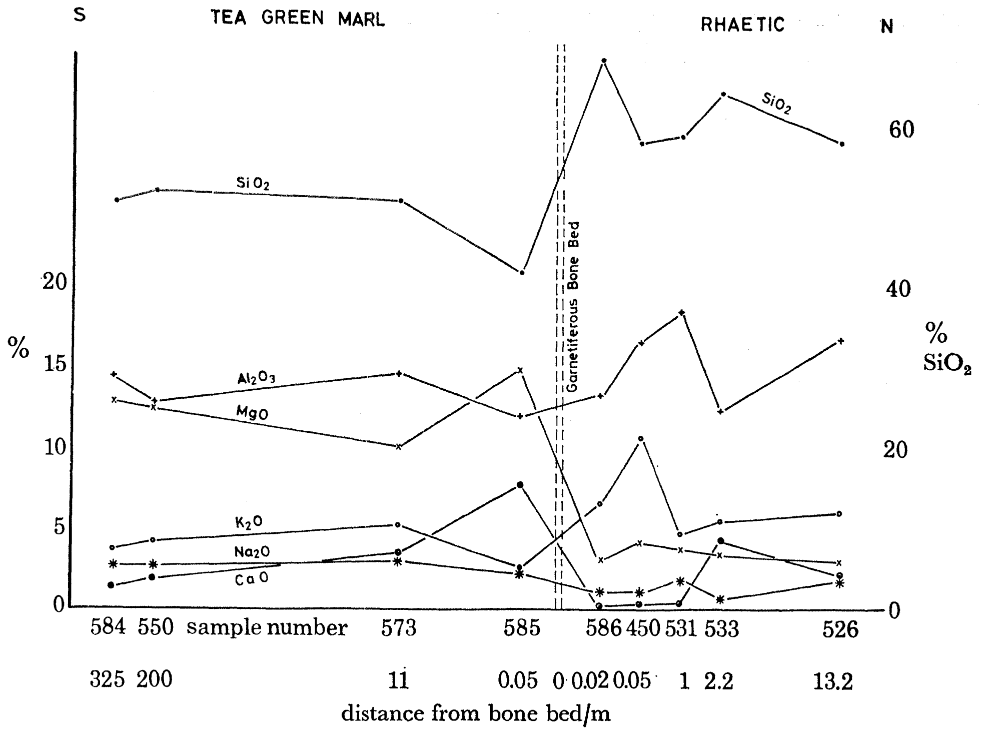


Figure 8. Oxide variation diagram, plotted against distance (*m*) from the garnetiferous Bone Bed, Waterloo, Larne, Northern Ireland, from the Upper Triassic Tea Green Marl to the Rhaetic.

andradite formation, on the other hand, was controlled by the silica level and occurred in the locally lime-rich environment of the Bone Bed.

Canary Islands

Possibly the closest known resemblance to the DSDP site 251 garnet is found in the grossular or hydrogrossular garnet (figure 3, plate 1) which occurs in calcareous carbonate sediment forming a lenticular band in steeply-dipping bedded trachytic tuffs, cut by numerous dolerite dykes, in the Barranco de Ajui, western Fuerteventura, Canary Islands (M. J. Le Bas, personal communication, 1974). A semi-quantitative microprobe analysis (by R. F. Symes & J. C. Bevan) of these garnets (table 1) shows them to be grossular (or hydrogrossular), relatively low in iron; a suggested approximate formula is gros$_{94.5}$and$_{5.0}$py$_{0.5}$. Although low in structural iron, the garnets are full of iron-rich inclusions which, taken together with their small size, make the garnets very difficult to analyse. Metasomatism from the basic intrusions could have supplied Si, Al and Fe^{3+} in the same manner postulated for the DSDP garnets (Kempe & Easton 1974; this paper). A possible alternative – that the garnets result from contact metamorphism by the dykes – is possible but unlikely in view of the localized occurrence of the garnet.

DSDP SEDIMENTS

No other garnet occurrence (apart from those from the Caribbean, leg 15) have been reported from DSDP cores. Samples of those recrystallized or generally reconstituted calcite sediments which overlie basement basalt on legs 1 to 26 were therefore requested and examined optically, and by X-ray powder photography, for the presence of garnet but none was found in the 21 examples examined. Sediments variously termed indurated metamorphosed ooze, chalk, limestone, micrite, micarb, and marble were studied, and their X-ray mineralogy, with notes on the optical examination, are given in table 3.

Table 3. Mineralogy of acid residues for DSDP carbonate sediments, overlying basement basalt, examined for the (negative) presence of garnet

sample								
leg	site	core	sec-tion	interval cm	ocean	type of sediment	X-ray minerals	comments (optical observations)
2	10	19	1	104–106	N. Atlantic	indurated, marble-like carbonate	montmorillonite	
3	14	10	1	80	S. Atlantic	marble	talc	volcanic glass
3	20A	4	1	70	S. Atlantic	marble	quartz + feldspar	
9	79	17	1	0–3	E. Pacific	chalk	amorphous	microspicules
9	81	7	1	82–84	E. Pacific	clay–chalk	amorphous + baryte	siliceous microfossils
19	192A	5	1	84–86	N. Pacific	nannofossil chalk	quartz + feldspar	
22	211	13	1	95–97	Indian	micarb-rich nanno ooze	quartz + feldspar	
22	212	39	1	45–47	Indian	limestone	feldspar + quartz	clay material
22	212	39	3	138–140	Indian	limestone	feldspar + montmorillonite	
22	215	17	CC		Indian	limestone	nearly amorphous	
22	216	36	3	97–99	Indian	micrite clay limestone	?glauconite + tr. quartz	clay material
23	220	18	3	145–147	Indian	micarb-rich nanno chalk	quartz + feldspar	clay material
23	221	18	6	143–146	Indian	micarb nanno chalk	amorphous + ?glauconite	siliceous microfossils
23	224	11	1	136–138	Indian	nanno micarb-rich claystone	palygorskite	clay minerals
24	231	62	1	124–126	Indian	nanno chalk	quartz + 1 nm clay	
24	233A	7	5	108–110	Indian	micarb nanno ooze	quartz + cristobalite	clay material
24	236	33	3	102–104	Indian	nanno chalk	clay minerals + cristobalite	clay minerals
25	245	16	CC		Indian	clayey nanno chalk	saponite	clay minerals
26	257	12	1	53–55	S. Indian	micarb limestone	feldspars	
26	257	15	1	29–31	S. Indian	detrital clay	feldspar + quartz	clay material
26	257	16	1	43–51	S. Indian	micarb limestone	feldspars	
37	335	7	3	29–31	N. Atlantic	foram limestone	amorphous	volcanic glass
37	335	8	1	15–23	N. Atlantic	foram limestone	amorphous	volcanic glass
37	335	9	3	117–124	N. Atlantic	foram limestone	amorphous	microspicules
37	335	10	1	63–65	N. Atlantic	foram limestone	amorphous	microspicules
37	335	12	1	36–38	N. Atlantic	foram limestone	amorphous	microspicules
37	335	14	1	84–86	N. Atlantic	foram limestone	amorphous	volcanic glass and micro-spicules
45	396	15	3	105–108				
				(*a*)	N. Atlantic	altered volcanic glass	feldspar + 0.7 nm clay + tr. mica	
				(*b*)		carbonate-rich altered volcanic glass	mica + 0.7 nm clay + tr. feldspar	

X-ray analysis by Miss E. E. Fejer & J. G. Francis. tr., trace; CC, core-catcher sample.

The final seven samples in table 3 are from leg 37, intercalated with basement basalt at site 335, and from leg 45 (site 396). The absence of garnet at site 335 has been reported by Kempe, Easton & Fejer (1977). The three site 257 (leg 26) samples are also intercalations within the sequence of basalt flows.

Synthesis of garnets

Examples of synthetic garnets considered remotely comparable with those from DSDP site 251 were reviewed by Kempe & Easton (1974). To these examples may be added the data of Mill' & Kalinin (1966) who, investigating garnet formation in skarns, found that andradite could be synthesized at 255 °C upwards in lime-rich chloride ($CaCl_2$) or alkaline ($Na_2B_4O_7$) solutions, the controlling factor being not pH but excess of lime. Grossular, on the other hand, forms at temperatures of 500 °C upwards and in chloride solutions only. Amthauer, Kurtz, Rost & Schloemer (1974) compared andradites in serpentinites with those synthesized at 370 °C and between 0.5 and 1.5 kbar (50 and 150 MPa). However, by far the most relevant example seems still to be the synthesis of hydrogarnet in highly alkaline solution (pH 13.5), at 1 bar (10^5 Pa) and a temperature between 85 and 105 °C, by Ito & Frondel (1967).

Oxygen and carbon isotope ratios at DSDP site 251

Seven samples were selected for stable isotope analysis from the 500 m long core collected at DSDP site 251. Two samples consisting of about 90 % calcite are representative of the nannoplankton ooze and chalk overlying the garnetiferous calcite (micarb) chalk. Two samples, approximately 10 m apart, come from the 18 m thick yellowish-brown, semilithified garnet–calcite chalk that immediately overlies the basalts. The three underlying basalt samples appear to come from pillow lavas that are altered and fractured to varying degrees (Kempe 1974). Their water contents of up to 1.5 % are considerably higher than typical fresh unaltered oceanic basalt ($H_2O^+ < 0.5$ wt %).

Table 4. Oxygen and carbon isotope analyses of carbonates, garnets, and basalts from Deep Sea Drilling Project site 251, southern Indian Ocean

sample number	description	depth† m	mineral‡	$\delta^{18}O$§ ‰ s.m.o.w.	$\delta^{13}C$§ ‰ p.d.b.
26-251A-9-6, 142–144	Nannoplankton ooze, Upper Pliocene	80	Ct	31.86	1.75
26-251A-27-2, 8–10	Nannoplankton chalk, Lower Miocene	460	Ct	31.27	2.08
26-251A-28-1, 140–142	Garnet–calcite (micarb) chalk	470	Ct	11.45	0.61
	(~ 20 % garnet), Lower Miocene		Gt	−0.94	
26-251A-29-2, 130–132	Garnet–calcite (micarb) chalk	480	Ct	9.82	−0.03
	(~ 25 % garnet), Lower Miocene		Gt	−1.38	
26-251A-30-1, 140–145	Basalt, vesicular and very highly altered	485	WR	9.47	—
	(H_2O^+ = 1.47 %)				
26-251A-31-1, 39–41	Basalt, vesicular and highly altered				
	(H_2O^+ = 1.16 %)	490	WR	7.17	—
26-251A-31-4, 29–31	Basalt, altered and fractured				
	(H_2O^+ = 0.90 %)	495	WR	7.09	—

† Depth in metres below sea-floor.
‡ Abbreviations: Ct, calcite; Gt, garnet; WR, whole rock.
§ Analytical precision on duplicate analyses: calcite = ± 0.05‰; whole rock = ± 0.1‰; garnet = ± 0.2‰.

Analytical methods and results

Carbon and oxygen isotope ratios of the calcite samples were determined on CO_2 liberated by the reaction with 100 % phosphoric acid (McCrea 1950; Sharma & Clayton 1965). Oxygen was liberated from the garnet mineral separates, prepared by removing all coexisting calcite using dilute HCl, and from whole-rock basalts using BrF_5, and converted quantitatively to CO_2 (Clayton & Mayeda 1963). The CO_2 gases were analysed on a double-collecting McKinney–Nier type mass spectrometer. The corrected carbon and oxygen isotope data are reported as δ-values where:

$$\delta = ((R_{\text{sample}}/R_{\text{standard}})-1)\ 1000 \quad \text{in per mille (‰)}$$

and $R = {}^{13}C/{}^{12}C$ or ${}^{18}O/{}^{16}O$ ratio relative to the p.d.b. standard for carbon and standard mean ocean water (s.m.o.w.) for oxygen. Reproducibility on duplicate preparations was routinely ±0.05‰ for the carbonates, ±0.1‰ for whole rocks, and ±0.2‰ for garnet. The preferred value for NBS-28 is $\delta^{18}O = 9.60$‰.

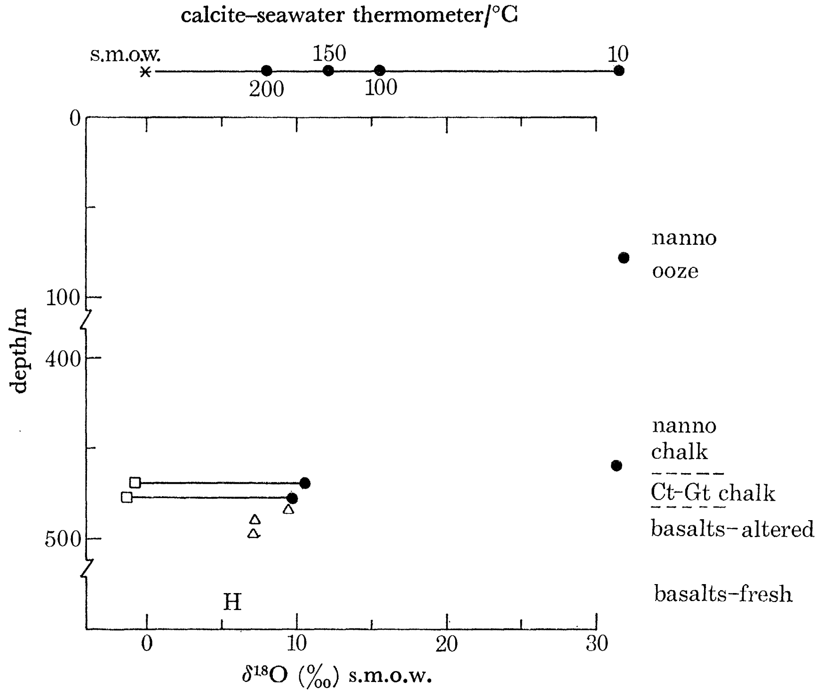


FIGURE 9. Plot of $\delta^{18}O$ values of (●) calcites, (□) garnets, and (△) whole rock basalt samples as a function of their depth below the present sea-floor. Tie lines connect coexisting calcite and garnet. The δ-range for fresh oceanic basalts and the isotopic composition of calcite in equilibrium with seawater (s.m.o.w.) at selected temperatures are given for reference.

The analytical results and brief sample descriptions are given in table 4. Differences or fractionations in ^{18}O among coexisting minerals and waters are of interest, and the fractionation factor, α_{A-B}, between two phases A and B is related to the δ-values in the following way:

$$\alpha_{A-B} = \left(1+\frac{\delta A}{1000}\right) \Big/ \left(1+\frac{\delta B}{1000}\right).$$

Isotopic relationships

The nannoplankton ooze and chalk have oxygen and carbon isotope ratios typical of marine carbonates (e.g. Garlick 1969). Calcites from the two garnet–calcite chalk samples are dramatically depleted in ^{18}O relative to 'normal' marine carbonates. Their $\delta^{13}C$ values are within the 'normal' marine carbonate range but are depleted by up to 2‰ relative to the calcite ooze and chalk. In so far as calcite sample 26-251A-27-2, 8-10, is only 10 m above the garnet–calcite sample 26-251A-28-1, 140–142 (table 4), it is inferred that the change in the isotopic composition of the calcite coincides with the garnet–calcite chalk–nannoplankton chalk boundary (figure 9). Although there are no other directly comparable data on garnets, calcite would be expected to concentrate ^{18}O relative to cogenetic garnet over a wide range of temperatures, as observed here (Garlick 1969). A single calcite–grossularite fractionation of 3.6‰ was observed in a marble skarn at the contact with a granite (Shieh & Taylor 1969).

The three basalts have $\delta^{18}O$ values of 7.1 to 9.5‰ with the $\delta^{18}O$ content increasing with increase in water content. Fresh unaltered oceanic tholeiitic basalts have a very narrow range of $^{18}O/^{16}O$ ratios, +5.5 to 6.5‰ (Taylor 1968; Muehlenbachs & Clayton 1972; Pineau, Javoy, Hawkins & Craig 1976), and hence all of the site 251 basalts are enriched in ^{18}O. These values are characteristic of altered basalts from oceanic dredge samples (Muehlenbachs & Clayton 1972; Pineau, Javoy, Hawkins & Craig 1976; Sheppard 1977; Sheppard & Jehl, in preparation) and from ophiolite complexes (Javoy 1970; Spooner, Beckinsale, Fyfe & Smewing 1974; Heaton & Sheppard 1977). Although the alteration of oceanic basalts is due in part to submarine weathering (halmyrolysis), more detailed studies usually indicate the importance of zeolite or greenschist facies metamorphic assemblages (see, for example, Miyashiro, Shido & Ewing 1971; Jehl 1975), and hydrogen and oxygen isotope data have demonstrated that major seawater convective circulation occurred in the upper layers of the oceanic crust during sub-sea-floor metamorphism (Heaton & Sheppard 1977; Sheppard 1977).

Oxygen isotope geothermometry

Mean seawater today has an oxygen isotope composition very close to 0‰. Departures of larger than 0.5 to 1.0‰ from this value are considered unlikely during the past few tens of millions of years (Knauth & Epstein 1973, 1976). If it is assumed that the calcites formed in isotopic equilibrium with seawater ($\delta^{18}O = 0.0$‰), then the isotopic temperatures given in table 5 can be calculated from the calcite–water oxygen isotope fractionation factors determined experimentally over the temperature range 0–500 °C (O'Neil, Clayton & Mayeda 1969). Taking the analytical uncertainties into account, temperatures can be determined to ±0.5 °C at 10 °C and ±2° C at 200 °C. The calcite ooze and chalk give geologically plausible temperatures of about 10 °C. (The detailed interpretation of these temperatures is not of concern here.) In marked contrast, the two garnet–calcite chalk samples give temperatures of 160 °C and 185 °C – again assuming that $\delta^{18}O$ water = 0.0‰ (figure 9). Present day deep Indian Ocean water has $\delta^{18}O = -0.2$‰ (Craig & Gordon 1965). Such departures from mean ocean water values are not considered here because their effects on our calculated temperatures are extremely small.

Recently Shackleton & Kennett (1975) have proposed that the oxygen isotope composition of the Cainozoic Ocean was −1.0‰ (s.m.o.w.) before the accumulation of the Antarctic ice sheet during the Miocene. Taking $\delta^{18}O$ water = −1.0, application of the calcite–seawater oxygen isotope thermometer to the two Lower Miocene garnet–calcite chalk samples gives temperatures of 147 and 171 °C, about 14 °C lower than those using $\delta^{18}O$ water = 0.0‰, which is used in this paper.

Garnet–water or calcite–garnet fractionation factors have not been calibrated experimentally as a function of temperature. However, a qualitative expression is derived here partially to test our assumptions concerning the attainment of isotopic equilibrium and the isotopic composition of the water. At metamorphic temperatures (T > 500 °C) Bottinga & Javoy

(1975) have derived a garnet–mineral fractionation expression by combining observed garnet–mineral fractionation data from assemblages that are consistent with their being in isotopic equilibrium with experimentally calibrated mineral–H_2O fractionation factors. Three calcite–garnet fractionation expressions are derived here by combining the calcite–H_2O (O'Neil, Clayton & Mayeda 1969) and garnet–feldspar or quartz fractionation expressions (Bottinga & Javoy 1975) with (1) the feldspar–H_2O fractionation expression (O'Neil & Taylor 1967), or the quartz–H_2O fractionation expressions of (2) Clayton, O'Neil & Mayeda (1972) or (3) Knauth & Epstein (1976). This multiple approach is used here to emphasize the problems associated with the experimental calibrations at temperatures below 400 °C and with extrapolating the garnet and other data to temperatures several hundred degrees below those for which the data apply. Although the calcite–garnet temperatures given in table 5 are very approximate, relative temperatures are probably more precise.

Table 5. Oxygen isotope temperatures (°C)

isotopic thermometer	sample number 26-251A-9-6, 142–144	26-251A-27-2, 8–10	26-251A-28-1, 140–142	26-251A-29-2, 130–132	remarks
calcite–seawater†	9	12	160	185	$\delta^{18}O_{\text{seawater}} = 0.0‰$
calcite–garnet‡			90	105	(1) $10^6 \ln \alpha_{\text{Ct–Gt}} = 1.56(10^6 T^{-2}) + 0.3$
			155	180	(2) $10^6 \ln \alpha_{\text{Ct–Gt}} = 2.28(10^6 T^{-2})$
			180	200	(3) $10^6 \ln \alpha_{\text{Ct–Gt}} = 2.57(10^6 T^{-2}) - 0.2$

† Temperature calculated using $1000 \ln \alpha_{\text{calcite–H}_2\text{O}} = 2.78(10^6 T^{-2}) - 3.39$ (O'Neil, Clayton & Mayeda 1969).
‡ See text for origin of expressions (1), (2), and (3).

The 100–200 °C temperatures given by the calcite–garnet thermometers are considered to be in very good agreement with the calcite–seawater thermometer. The calcite–water thermometer gives *minimum* values for the temperature because, in an oceanic environment, waters more ^{18}O depleted than seawater are isotopically unattainable. Waters as ^{18}O-rich as about 6‰ are possible if either seawater has exchanged oxygen with very hot basalts at low water/rock ratios or if there is a dominant magmatic water component in the hydrothermal solutions. This places a maximum temperature limit of about 350 °C ($\delta^{18}O$ water = 6.0‰). Therefore, the temperature of 100 °C given by expression (1) in table 5 of the calcite–garnet thermometer is rejected and it is suggested that the 150–200 °C calcite–garnet temperatures strongly support the calcite–water temperatures of about 170 °C. This implies that the initial assumptions made here are satisfactory.

These data support a metasomatic origin for the garnets and imply that the garnet–calcite chalk was involved in a seawater–hydrothermal convection system. In so far as there is no evidence for the water having a $\delta^{18}O$ value greater than 0‰, the amount of oxygen in the circulating hot seawater must have been large relative to the amount of exchangeable oxygen within the hydrothermal system. At 170 °C, the seawater controlled the oxygen isotope composition of the 18 m thick garnet–calcite chalk unit, and may have modified the carbon isotope ratio also.

It is noted that the two isotopic thermometers give a similar temperature difference between samples 26-251A-28-1, 140–142, and 26-251A-29-2, 130–132 (table 5), indicating a temperature gradient of about 2 °C/m. Such seawater–hydrothermal fluids would be well below their boiling point at pressures equivalent to a few hundred metres of water.

The relatively high ^{18}O character of the underlying altered basalts (zeolite facies?) is also consistent with the proposed seawater–hydrothermal convection model. A simple interpretation of the whole rock $\delta^{18}O$ data is difficult because the samples represent a mixture of inherited igneous minerals and recrystallized minerals produced by metamorphism. However, altered oceanic basalts with $\delta^{18}O$ values similar to those of the site 251 basalts have been interpreted as having formed through the interaction of seawater at temperatures of 100 to 450 °C (Heaton & Sheppard 1977; Sheppard & Jehl, in preparation).

The proposed metasomatic genesis of the garnets has assumed that the calcite (micarb) chalk was originally a nannoplankton ooze. No relict trace of nannofossils has been found to confirm this fact. The first sediments to overlie new oceanic basalts are commonly heavy-metal enriched sediments interpreted as a product of chemical precipitation around submarine hot springs which are discharging from the basalts into the sea near active spreading ridges (cf. Boström & Peterson 1966; Boström, Farquarson & Eyl 1972; Cronan *et al.* 1972). Such an origin for the micarb chalk can be ruled out here because the temperature of formation, ~ 170 °C, is far too high for such a process to occur in an oceanic environment.

Implications of the isotope data

During the past few years hydrogen and oxygen isotope studies of high level epizonal intrusions and their surrounding country rocks and of oceanic igneous rocks have demonstrated that large scale interaction of heated meteoric ground waters or seawater with hot igneous rocks is a widespread phenomenon (cf. Taylor & Forester 1971; Taylor 1974; Heaton & Sheppard 1977). Whenever there is a thermal anomaly – emplacement of a pluton or dyke, etc. – in the upper oceanic or continental crust, in country rocks which are permeable to fluid flow, then convective circulation of that fluid, usually seawater or meteoric water, is to be expected. The permeability of the rocks, especially fracture permeability, may be increased during the processes associated with magma emplacement or during tectonic processes, including fracturing, that accompany sea-floor spreading.

On being heated, the water undergoes ion and isotope exchange with the host rocks because initially they are out of equilibrium with each other. Transfer of both mass and heat results. However, the nature of the processes when considered in detail is related to many variables: initial composition of the water, nature and mineralogy of the host rocks, temperature, rate of fluid flow, water/rock ratio, etc.

At DSDP site 251 the thermal anomaly which drove the convection system is inferred to lie within the basalts below the sediments. This is consistent with the fractured and altered character of the basalts which are probably best regarded as belonging to the zeolite facies of metamorphism, for which temperatures in the range 100–300 °C are generally accepted. The lack of evidence for any '^{18}O-shift' in the thermal waters away from the seawater composition implies that there was overwhelmingly more oxygen, originating in seawater, in the thermal solutions than was present in the exchangeable minerals in the rocks undergoing alteration. If there was a magmatic water component present it was probably immeasurably small (Heaton & Sheppard 1977; Sheppard & Jehl, in preparation). The lack of an '^{18}O-shift' does not imply that the chemistry of the initial seawater has not been modified through exchange processes.

Convective circulation of seawater through the oceanic crust probably starts shortly after the formation of new oceanic crust. The occurrence of fresh unaltered basalts is restricted to the ridge crest region and interpretation of the heat flow data on the ridge flanks is consistent with the importance of convective heat transfer (Lister 1972). Site 251 is the first known example where the convection system also operated within the overlying sediments; a search through other DSDP basal sediment samples and through the literature has not revealed further examples. This suggests that the phenomenon of convective circulation in the first sediments to overlie the basement basalts must be rare. However, this could be a sampling problem in so far as no active submarine hot spring has yet been recognized in the ridge areas, sites of proposed geothermal activity (Aumento, Ade-Hall & Keen 1975). These data indicate that the convective circulation usually had ceased before the first sedimentary debris accumulated. Elder (1965) has shown that the life of a geothermal system is typically less than 10^4–10^5 years, a short time in which to accumulate any great thickness of sediment.

PARAGENESIS

The few occurrences comparable with that at DSDP site 251 all have compositions in the grossular (or hydrogrossular)–andradite range. The spessartinic occurrences, superficially resembling the others in texture, all appear to be the product of regional continental greenschist facies or higher grade metamorphism as originally stated by the workers who studied them. There is the possibility, however, that the manganese-rich sediments which were metamorphosed into spessartine-bearing rocks were metal-enriched oceanic sediments or manganese nodule-bearing sediments. Virtually all known occurrences of grossular are the product of contact (thermal) metamorphism of calcareous sediments. The authors are indebted to S. O. Agrell for drawing their attention to papers describing the unusual contact metamorphic effects produced by a wide (41 m) olivine dolerite dyke intruding rocks of the Carboniferous Limestone series just south of Plas Newydd, Angelsey (Henslow 1822; Harker 1887; Greenly 1919). A calcareous shale is converted into 'a kind of lydianite, containing calcite and clusters of garnet and analcime crystals'. The latter mineral is apparently seen developing from whitish concretionary spots in the shale to perfectly developed crystals, sometimes studding or penetrating *Productus* valves, and also altering to prehnite, a mineral often associated with contact metamorphism. The greenish-yellowish-brown garnets reach 1.8 cm in diameter and contain many inclusions. The occurrence is notable, as remarked by Harker, for the presence of analcime in a thermal metamorphic aureole.

The garnet–calcite chalk at site 251 developed during hydrothermal alteration of the basalts and metasomatism of the overlying ooze. By analogy, the other examples from Ireland and the Canary Islands are considered to have developed within hydrothermal convective systems. The origin of the water was most probably meteoric ground water unless these regions were in a submarine environment at the time of formation. Interaction between meteoric waters and hot epizonal igneous intrusions is particularly well documented for the Tertiary Brito–Arctic igneous province which includes Ireland (cf. Taylor & Forester 1971).

The proposed metasomatic genesis of the garnets which, in one of the examples studied, formed in an environment with a high thermal gradient at temperatures down to 160 °C or a little lower discounts either an authigenic or diagenetic origin in the usual meaning of these terms. Two types of metasomatism show some resemblances to the garnet occurrences. Rodingites, in which hydrogrossular garnet characteristically develops, are formed by migrating Ca-rich solutions; it is worth mentioning that hydrogarnet-bearing rodingites have been reported from serpentinites from the equatorial Mid-Atlantic Ridge (Ploshko, Bogdanov & Knyazova 1970; Honnorez & Kirst 1975). Possibly a closer analogy is provided by skarns, in which andradite is the characteristic garnet. The American Geological Institute's Glossary of geology and related sciences definition of 'skarn' states 'the term generally reserved for rocks composed nearly entirely of lime-bearing silicates and derived from nearly pure limestones and dolomites into which large amounts of Si, Al, Fe and Mg have been introduced'. It seems that the stability field of natural hydrogarnet may need to be extended down to the level previously reached only by synthetic hydrogrossular in order to accommodate the site 251 occurrence. An origin by baking or low grade contact metamorphism, as erroneously reported by Christensen *et al.* (1973), is not considered possible; the basalt is basement and not an intrusive sill. Further, if the growth of such garnets was caused by thermal metamorphism, their occurrence would be widespread. A similar argument and the results of this study preclude an origin by primary (hydrogenous) precipitation from seawater, as tentatively proposed by A. J. Horowitz (in Kempe & Easton 1974); the calcite (micarb) chalk is regarded as nearly certainly recrystallized nannoplankton ooze or chalk; in fact, traces of coccoliths and possibly foraminifera have recently been found in scanning electron micrographs (J. M. Hancock, personal communication).

Apart from the major mass transfer of Si, Al, and Fe that is necessary to produce the chalk with some 20 mass % of garnet, few limits can be set on the composition of the metasomatizing fluid. Study of the rare earth element content of site 251 material (Fleet, in preparation) shows that the garnets have a similar r.e.e. chondrite-normalized abundance pattern to that of the calcite (micarb) chalk in which they occur and also to the nannoplankton chalk above, and to other marine calcareous sediments. A slight negative Ce anomaly is present relative to the other light r.e.e., which are otherwise all enriched relative to the heavy r.e.e. The pattern in the garnets from the micarb chalk is quite different from those generally recorded for garnets from meta-igneous and metasedimentary rocks and shows a smaller negative Ce anomaly than seawater and seawater-derived metalliferous sediments from, for example, the Troodos Massif, Cyprus (Robertson & Fleet 1975). The relative enrichment of the light r.e.e. in the normalized abundance pattern suggests that the metasomatizing fluid was markedly enriched in these elements relative to the heavy r.e.e. A similar enrichment has been noted for garnets in metasomatized meta-anorthosite from South Harris, Scotland, in contrast to the light r.e.e. depletion in garnets from anorthosite unaffected by metasomatism (P. Henderson, personal communication 1976). The abundance of differential fractionation of the r.e.e. between chalk and garnet suggests that, if the phases are coexisting at equilibrium, the crystal chemical controls on the r.e.e. distribution are similar in the two phases.

Summary and conclusions

Further examples are postulated of garnet in the andradite–grossular (or hydrogrossular) range which, in keeping with the DSDP site 251 garnets, may have formed at relatively low temperatures and pressures by the action of metasomatic hydrothermal addition of elements into a wider range of environment than the previously known calcite (micarb) chalk. One characteristic common to all examples is the presence of excess calcareous material in the environment, although in the case of the Rhaetic basal Bone Bed the calcium was present as phosphate. That phosphorus is not a procurer for the formation of garnet is shown by the absence of high concentrations of this element at site 251 and the Canary Islands. Isotope study has enabled a temperature range to be given for the formation of at least one of the examples (DSDP site 251), where it provides another example of the importance of seawater as a source of hydrothermal fluids.

We are grateful to D. S. Cronan and A. J. Fleet for critically reading the manuscript; also, in addition to analysts and others mentioned in the text, we should like to thank the following for helpful suggestions, discussion, and assistance in many ways: J. Borthwick, R. Bradshaw, G. Day, R. Godwin, F. Hodson, R. A. Howie, B. E. Leake, and D. Robinson. The Isotope Geology Unit of the Scottish Universities at the Scottish Universities Research and Reactor Centre is supported by a N.E.R.C. research grant. Finally, we thank the National Science Foundation of America and the Deep Sea Drilling Project for making available the material from site 251, drilled on leg 26 in which one of us (D.R.C.K.) was fortunate to participate, as well as the samples listed in table 3 which were examined for the (negative) presence of garnets.

Note added in proof, 7 April 1977. Ten samples from leg 49 (Mid-Atlantic Ridge) have also been examined and, again, found to contain no garnets: Kempe, Easton & Francis (in the press).

REFERENCES (Easton *et al.*)

Amthauer, G., Kurtz, W., Rost, F. & Schloemer, H. 1974 Chemismus und Genese des Andradits aus dem Serpentinit des Val Malenco. *Schweiz. Min. Petr. Mitt.* **54**, 691–706.
Aumento, F., Ade-Hall, J. M. & Keen, M. J. 1975 1974 – the year of the Mid-Atlantic Ridge. *Rev. Geophys. Space Phys.* **13**, 53–65.
Boström, K. & Peterson, M. N. A. 1966 Precipitates from hydrothermal exhalations on the East Pacific Rise. *Econ. Geol.* **61**, 1258–1265.
Boström, K., Farquarson, B. & Eyl, W. 1972 Submarine hot springs as a source of active ridge sediments. *Chem. Geol.* **10**, 189–203.
Bottinga, Y. & Javoy, M. 1975 Oxygen isotope partitioning among the minerals in igneous and metamorphic rocks. *Rev. Geophys. Space. Phys.* **13**, 401–418.
Brindley, J. C. 1954 The Garnetiferous Beds of the Leinster Granite aureole and their small-scale structures. *Scient. Proc. R. Dubl. Soc.* **26**, 245–262.
Christensen, N. I., Frey, F. A., MacDougall, D., Melson, W. G., Peterson, M. N. A., Thompson, G. & Watkins, N. 1973 Deep Sea Drilling Project: properties of igneous and metamorphic rocks of the oceanic crust. *Eos, Wash.* **54**, 972–982.
Clayton, R. N. & Mayeda, T. K. 1963 The use of bromine pentafluoride in the extraction of oxygen from oxides and silicates for isotopic analysis. *Geochim. cosmochim. Acta* **27**, 43–52.
Clayton, R. N., O'Neil, J. R. & Mayeda, T. K. 1972 Oxygen isotope exchange between quartz and water. *J. geophys. Res.* **77**, 3057–3067.
Cook, H. E., Zemmels, I. & Matti, J. C. 1974 X-ray mineralogy data, southern Indian Ocean – Leg 26 Deep Sea Drilling Project. In *Initial reports of the Deep Sea Drilling Project* (eds T. A. Davies, B. P. Luyendyk *et al.*), vol. 26, pp. 573–592. Washington: U.S. Government Printing Office.
Craig, H. & Gordon, L. I. 1965 Deuterium and oxygen – 18 variations in the ocean and marine atmosphere. *Symp. Marine Geochim., Narragansett Marine Lab., Univ. R.I. Publ.* **3**, 277.
Cronan, D. S., van Andel, T. H., Ross Heath, G., Dinkelman, M. G., Bennett, R. H., Bukry, D., Charleston, S., Kaneps, A., Rodolfo, K. S. & Yeats, R. S. 1972 Iron-rich basal sediments from the eastern equatorial Pacific: Leg 16, Deep Sea Drilling Project. *Science, N.Y.* **175**, 61–63.
Deer, W. A., Howie, R. A. & Zussman, J. 1962 *Rock-forming minerals*, vol. 1. London: Longmans.
Donnelly, T. W. & Nalli, G. 1973 Mineralogy and chemistry of Caribbean sediments. In *Initial reports of the Deep Sea Drilling Project* (eds N. T. Edgar, J. B. Saunders *et al.*), vol. 15, pp. 929–961. Washington: U.S. Government Printing Office.
Elder, J. W. 1965 Physical process in geothermal areas. In Terrestrial heat flow. *Geophys. Mon.* **8** NAS-NRC No. 1288. Amer. Geophys. Union, 211–239.
Garlick, G. D. 1969 The stable isotopes of oxygen. In *Handbook of geochemistry* (ed K. H. Wedepohl), vol. II/1 B. Berlin, Heidelberg and New York: Springer.
Greenly, E. 1919 The geology of Anglesey. *Mem. geol. Surv. U.K.* vol. 2, 980 pp.

Hamilton, D. 1962 Some notes on the Rhaetic sediments of the Filton by-pass substitute, near Bristol. *Proc. Bristol Nat. Soc.* **30**, 279–285.

Hamilton, D. 1966 Disseminated galena in Rhaetic shales at Almondsbury, near Bristol. *Proc. Bristol Nat. Soc.* **31**, 221–224.

Hancock, J. M. 1961 The Cretaceous system in Northern Ireland. *Q. Jl geol. Soc. Lond.* **117**, 11–37.

Harker, A. 1887 Woodwardian Museum notes: on some Anglesey dykes. I. *Geol. Mag.* **4**, 409–416.

Heaton, T. H. E. & Sheppard, S. M. F. 1977 Hydrogen and oxygen isotope evidence for sea-water-hydrothermal alteration and ore deposition, Troodos Complex, Cyprus. In *Volcanic processes in ore genisis* (ed. M. J. Jones), pp. 42–57. London: Instn Mining Metall. and Geol. Soc.

Henslow, J. S. 1822 Geological description of Anglesea. *Trans. Camb. phil. Soc.* **1**, 359–452.

Honnorez, J. & Kirst, P. 1975 Petrology of rodingites from the equatorial Mid-Atlantic fracture zones and their geotectonic significance. *Contr. Miner. Petrol.* **49**, 233–257.

Ito, J. & Frondel, C. 1967 New synthetic hydrogarnets. *Am. Miner.* **52**, 1105–1109.

Javoy, M. 1970 Utilisation des isotopes de l'oxygène en magmatologie. Unpublished D.Sc. Thesis, University of Paris, 196 pp.

Jehl, V. 1975 Le métamorphisme et les fluides associés des roches océaniques de l'Atlantique nord. Unpublished D.Ing. Thesis, University of Nancy, France, 242 pp.

Kempe, D. R. C. 1974 The petrology of the basalts, Leg 26. In *Initial reports of the Deep Sea Drilling Project* (eds T. A. Davies, B. P. Luyendyk *et al.*), vol. 26, pp. 465–503. Washington: U.S. Government Printing Office.

Kempe, D. R. C. & Easton, A. J. 1974 Metasomatic garnets in calcite (micarb) chalk at Site 251, southwest Indian Ocean. In *Initial reports of the Deep Sea Drilling Project* (eds T. A. Davies, B. P. Luyendyk *et al.*), vol. 26, pp. 593–601. Washington: U.S. Government Printing Office.

Kempe, D. R. C., Easton, A. J. & Fejer, E. E. 1977 On the absence of metasomatic garnets at Site 335, Leg 37, DSDP. In *Initial reports of the Deep Sea Drilling Project* (eds F. Aumento, W. G. Melson *et al.*), vol. 37. Washington: U.S. Government Printing Office.

Kempe, D. R. C., Easton, A. J. & Francis, J. G. (in the press). Further observations on the absence of metasomatic garnets: from MAR sediments drilled on DSDP/IPOD Leg 49, with notes on their mineralogy. In *Initial reports of the Deep Sea Drilling Project* (eds J. R. Cann, B. P. Luyendyk *et al.*), vol. 49. Washington: U.S. Government Printing Office.

Kennan, P. S. 1972 Some curious garnet clusters from the Garnetiferous Beds of the Leinster Granite aureole. *Geol. Mag.* **109**, 165–170.

Knauth, L. P. & Epstein, S. 1973 Implications of the isotopic composition of cherts for the climatic temperature history of the earth. *Geol. Soc. Amer. Ann. Mtg.*, Abstracts with programs, p. 695.

Knauth, L. P. & Epstein, S. 1976 Hydrogen and oxygen isotope ratios in nodular and bedded cherts. *Geochem. cosmochim. Acta* **40**, 1095–1108.

Lister, C. R. B. 1972 On the thermal balance of a mid-ocean ridge. *Geophys. J. R. astr. Soc.* **26**, 515–535.

Manning, P. I., Wilson, H. E., Warrington, G., Harland, R., Miller, J. M. & Fenning, P. J. 1975 The stratigraphy of the Larne borehole, County Antrim. *Bull. geol. Surv. Gt. Br.* **50**, 1–50.

Mason, B. 1957 Larnite, scawtite and hydrogrossular from Tokatoka, New Zealand. *Am. Miner.* **42**, 379–392.

Mason, B. & Berggren, T. 1941 A phosphate-bearing spessartite garnet from Wodgina, Western Australia. *Geol. För. Stockh. Förh.* **63**, 413–418.

McCrea, J. M. 1950 The isotopic chemistry of carbonates and a paleotemperature scale. *J. Chem. Phys.* **18**, 849–857.

Mill', V. B. & Kalinin, D. V. 1966 Lower temperature limit of garnet formation in the skarn process (experimental data). *Dokl. Acad. Sci. USSR, Earth Sci. Sect.* **167**, 84–86.

Miyashiro, A., Shido, F. & Ewing, M. 1971 Metamorphism in the Mid-Atlantic Ridge near 24° and 30° N. *Phil. Trans. R. Soc. Lond.* A **268**, 589–603.

Muehlenbachs, K. & Clayton, R. N. 1972 Oxygen isotope studies of fresh and weathered submarine basalts. *Can. J. Earth Sci.* **9**, 172–184.

O'Neil, J. R., Clayton, R. N. & Mayeda, T. K. 1969 Oxygen isotope fractionation in divalent metal carbonates. *J. Chem. Phys.* **51**, 5547–5558.

O'Neil, J. R. & Taylor, H. P., Jr. 1967 The oxygen isotope and cation exchange chemistry of feldspars. *Am. Miner.* **52**, 1414–1437.

Pineau, F., Javoy, M., Hawkins, J. W. & Craig, H. 1976 Oxygen isotope variations in marginal basin and ocean-ridge basalts. *Earth Planet. Sci. Lett.* **28**, 299–307.

Ploshko, V. V., Bogdanov, Yu. A. & Knyazeva, D. N. 1970 Gabbro-amphibolite from the abyssal Romanche trench, Atlantic region. *Dokl. Acad. Sci. USSR, Earth Sci. Sect.* **192**, 40–43.

Reynolds, D. L. 1940 Contact metamorphism of a Tertiary dyke at Waterfoot, Co. Antrim. *Geol. Mag.* **77**, 463–469.

Robertson, A. H. F. & Fleet, A. J. 1975 The origins of rare earths in metalliferous sediments of the Troodos massif, Cyprus. *Earth planet. Sci. Lett.* **28**, 385–394.

Schiller, E. A. & Taylor, F. C. 1965 Spessartite-quartz rocks (coticules) from Nova Scotia. *Am. Miner.* **50**, 1477–1481.

Shackleton, N. J. & Kennett, J. P. 1975 Paleotemperature history of the Cenozoic and the initiation of Antarctic glaciation: oxygen and carbon isotope analyses in DSDP sites 277, 279, and 281. In *Initial reports of the Deep Sea Drilling Project* (eds J. P. Kennett, R. E. Houtz *et al.*), vol. 29, pp. 743–755. Washington: U.S. Government Printing Office.

Sharma, T. & Clayton, R. N. 1965 Measurement of $^{18}O/^{16}O$ ratios of total oxygen of carbonates. *Geochim. cosmochim. Acta* **29**, 1347–1353.

Sheppard, S. M. F. 1977 The identification of the origin of ore-forming solutions by the use of stable isotopes. In *Volcanic processes in ore genesis* (ed. M. J. Jones), pp. 25–41. London: Instn Mining Metall. and Geol. Soc.

Sherwood, P. T. & Hollis, B. G. 1966 Studies of the Keuper Marl: chemical properties and classification tests. *Rept. Road Res. Lab.* no. 41, 18 pp.

Shieh, Y. N. & Taylor, H. P., Jr. 1969 Oxygen and carbon isotope studies of contact metamorphism of carbonate rocks. *J. Petrol.* **10**, 307–331.

Spooner, E. T. C., Beckinsale, R. D., Fyfe, W. S. & Smewing, J. D. 1974 O^{18} enriched ophiolitic metabasic rocks from E. Liguria (Italy), Pindos (Greece), and Troodos (Cyprus). *Contr. Miner. Petrol.* **47**, 41–62.

Taylor, H. P., Jr. 1968 The oxygen isotope geochemistry of igneous rocks. *Contr. Miner. Petrol.* **19**, 1–71.

Taylor, H. P., Jr. 1974 The application of oxygen and hydrogen isotope studies to problems of hydrothermal alteration and ore deposition. *Econ. Geol.* **69**, 843–883.

Taylor, H. P., Jr. & Forester, R. W. 1971 Low-^{18}O igneous rocks from the intrusive complexes of Skye, Mull and Ardnamurchan, Western Scotland. *J. Petrol.* **12**, 465–497.

Thilo, E. 1941 Über die Isotypie zwischen Phosphaten der allgemeinen Zusammensetzung $(Me_1)_3\,(Me_2)_2\,[PO_4]_3$ und den Silikaten der Granatgruppe. *Naturwissenschaften* **29**, 239.

Walker, G. P. L. 1948 A preliminary note on the metamorphic rocks of the Portmuck area, Islandmagee, County Antrim. *Ir. Nat. J.* **9**, 165–168.

Walker, G. P. L. 1959 The amygdale minerals in the Tertiary lavas of Ireland. II. The distribution of gmelinite. *Mineralog. Mag.* **32**, 202–217.

Walker, G. P. L. 1960 The amygdale minerals in the Tertiary lavas of Ireland. III. Regional distribution. *Mineralog. Mag.* **32**, 503–527.

Woodland, A. W. 1939 The petrography and petrology of the Lower Cambrian manganese ore of West Merionethshire. *Q. Jl geol. Soc. Lond.* **95**, 1–35.

Discussion

S. O. AGRELL (*Department of Mineralogy and Petrology, University of Cambridge*). In view of the low temperature occurrence and the association with analcime of some of the garnets described, have the authors found any evidence for the presence in them of the hydrogarnet component?

I draw the authors' attention to another locality described by Henslow (1822) and later by Harker (1887). This is the contact of the Plas Newydd dyke exposed on the Anglesey shore of the Menai Staits. Here a Tertiary olivine dolerite cuts interbanded argillaceous limestones and calcareous shales of Carboniferous (D2) age with the development of grossular garnet and analcime.

References

Harker, A. 1887 Woodwardian Museum notes: on some Anglesey dykes. I. *Geol. Mag.* **4**, 409–416.

Henslow, J. S. 1822 Geological description of Anglesea. *Trans. Camb. phil. Soc.* **1**, 359–452.

A. J. EASTON. We strongly suspect the Site 251 garnets, at least, to belong to the hydrogarnet series, but for the reasons given in Kempe & Easton (1974, p. 594), it cannot be proved.

D. R. C. KEMPE. We are extremely grateful to Dr Agrell for drawing our attention to the Plas Newydd occurrence, and for providing some of Henslow's original specimens for examination. Certainly the occurrence of garnet and analcime invites comparison with the example described from Antrim, but the development of the minerals is rather different.

Of the twelve rocks we have seen, two contain analcime and three garnet. The analcime occurs in very fine-grained metacalcareous rocks, in association with feldspar only (as determined by X-ray powder photograph). The garnets, on the other hand, reach some 1 cm in diameter and form coarse-grained veins in porcelanous hornfels. They contain many dark impurities but also show very narrow, pale yellow concentric zones, especially near the peripheries of the crystals. The garnets are mainly anisotropic, with a birefringence of some 0.004, while the narrow zones appear totally isotropic. In thin section, the garnets have a hexagonal outline resulting from dodecahedral twinning, showing six of the triangular sections of the pyramidal sectors, with their apices meeting at the centre of the crystals. Opposite pairs of sectors pass into extinction under crossed polars when the bases of the pyramids, forming two of the six sides, are parallel to the vibration direction of polarizer or analyser.

Henslow (1822, pp. 407–410) and, later, Harker (1887, pp. 413–414), in describing in detail the growth of these two minerals, refer to Henslow's specimen numbers 511 to 523. It would seem that nos. 511 to 516 refer to analcime-bearing rocks which, in the specimens we have examined, cannot be resolved by the microscope, while nos. 517 to 523 contain only garnet. Unfortunately, therefore, we have not seen the trapezohedral analcime, also having a 'concentric zonary structure', described by Henslow and Harker.

The Plas Newydd garnets are very similar to, but not quite identical with, others described by Holser (1950), Kennedy (1953), Lessing & Standish (1973) and, more recently, Murad (1976). In these the zonal lamellae are generally much broader and are anisotropic, whilst the bulk of the crystals are isotropic. The Anglesey garnets have a cell edge of 1.1882 ± 0.0002 nm, suggesting a bulk composition near to pure grossular, whilst those of Murad and, largely, the earlier workers, are mainly andraditic (isotropic), with some grossular (anisotropic and birefringent). Murad's microprobe analyses show a correlation between high Al and birefringence, and between high Fe and isotropy, which supports this relationship. As in Anglesey, most of the examples cited above result from contact (thermal) metamorphism, but hydrothermal metasomatism is also sometimes invoked.

J. G. Francis carried out the X-ray determinations and cell edge measurement, and joins us in adding this note to the discussion.

References

Harker, A. 1887 Woodwardian Museum notes: on some Anglesey dykes. I. *Geol. Mag.* **4**, 409–416.

Henslow, J. S. 1822 Geological description of Anglesea. *Trans. Camb. phil. Soc.* **1**, 359–452.

Holser, W. T. 1950 Metamorphism and associated mineralization in the Philipsburg region, Montana. *Bull. geol. Soc. Am.* **61**, 1053–1090.

Kempe, D. R. C. & Easton, A. J. 1974 Metasomatic garnets in calcite (micarb) chalk at Site 251, southwest Indian Ocean. In *Initial reports of the Deep Sea Drilling Project* (eds T. A. Davies, B. P. Luyendyk, K. S. Rodolfo, D. R. C. Kempe, B. C. McKelvey, R. D. Leidy, G. J. Horvath, R. D. Hyndman, H. R. Thierstein, R. C. Herb, E. Boltovskoy & P. Doyle.), vol. 26, pp. 593–601. Washington: U.S. Government Printing Office.

Kennedy, G. C. 1953 Geology and mineral deposits of Jumbo Basin, southeastern Alaska. *Prof. Pap. U.S. geol. Surv.* **251**, 46 pp.

Lessing, P. & Standish, R. P. 1973 Zoned garnet from Crested Butte, Colorado. *Am. Miner.* **58**, 840–842.

Murad, E. 1976 Zoned, birefringent garnets from Thera Island, Santorini Group (Aegean Sea). *Mineral. Mag.* **40**, 715–719.

Figures 1–7. For description see opposite.