Textures of diffusion-controlled reaction in contact-metamorphosed Mg-rich granulite, Kokchetav area, Kazakhstan

	in Mineralogical Magazine · April 1998 0/002646198547585
CITATION	
17	75
6 autho	rs, including:
	Reverdatto Vladimir
	Sobolev Institute of Geology and Mineralogy
	238 PUBLICATIONS 1,965 CITATIONS
	SEE PROFILE
Some o	f the authors of this publication are also working on these related projects:
Project	Metamorphic and geodynamic evolution of orogenic belts along the continental margins of ancient cratons (on example of Yenisey Ridge, Urals, and Dzhugdzhur–Stanovoi fold belt) View project
Project	Метаморфизм сверхвысоких давлений (UHP метаморфизм) View project

Textures of diffusion-controlled reaction in contactmetamorphosed Mg-rich granulite, Kokchetav area, Kazakhstan

J. R. ASHWORTH

School of Earth Sciences, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK

V. V. REVERDATTO, V. YU. KOLOBOV, V. V. LEPETYUKHA, V. S. SHEPLEV,

AND

N. A. BRYXINA

United Institute of Geology, Geophysics and Mineralogy, Siberian Branch of Russian Academy of Science, Universitetsky pr. 3, Novosibirsk 90, 630090 Russia

ABSTRACT

In a granulite from the Kokchetav massif, a complex mineral assemblage and intricate textures have resulted from a combination of unusual rock composition and two-stage metamorphic history. The second, contact metamorphism produced mainly cordierite and anthophyllite, reflecting a bulk composition attributed to pre-metamorphic alteration of basic igneous rock. From the first, highpressure metamorphism, garnet relics persist while another mineral has been completely pseudomorphed. The garnet is partly replaced by a symplectite of three minerals: orthopyroxene vermicules in a coarser intergrowth of cordierite and calcic plagioclase. Despite variable proportions of cordierite and plagioclase, the Al:Si ratio of the symplectite is almost constant, because the proportion of orthopyroxene is smaller where the dominant aluminous mineral is cordierite (Al:Si ≈ 0.8) than where the even more aluminous plagioclase (Al:Si ≈ 0.89) is prominent. The bulk Al:Si ratio of this symplectite, approximately 0.69, is very close to that of reactant garnet (0.66), indicating that Al and Si have been retained almost completely during the local reaction, while other elements were more mobile. In the pseudomorphs, aluminous cores (with Al:Si ratios 1.61-1.93) indicate that the mineral which has been completely replaced was probably kyanite. These cores comprise plagioclase, zoisite, corundum and spinel, and are surrounded by layers of plagioclase and cordierite. Fe, Mg, and Ca have diffused to the core, through layers with low bulk concentrations of these elements, probably by grainboundary diffusion in the solid state.

KEYWORDS: symplectite, pseudomorph, diffusion, cordierite-orthoamphibole rocks, Kokchetav massif.

Introduction

METAMORPHIC textures contain clues about reaction mechanisms. Diffusion, if it is the rate-controlling step in reaction, tends to produce spatially organised textures (Fisher, 1978). One kind of spatial organisation is a symplectite, in which two or more minerals are intergrown as roughly periodically spaced, elongate grains, with the elongation parallel to the growth direction. A likely explanation is that at least two chemical species diffused slowly, relative to the growth rate

of the minerals, so that the spacing of the elongate grains is controlled by the diffusive segregation of these species (Mongkoltip and Ashworth, 1983). A variety of symplectites replacing plagioclase have Al:Si ratios approximately the same as in the reactant feldspar. This is surely not a chance coincidence: it indicates that Al and Si are both retained almost entirely during the reaction and are thus the slow-diffusing elements responsible for the symplectite texture (Ashworth and Birdi, 1990). Another kind of spatial organisation (often containing a symplectite within it) consists of

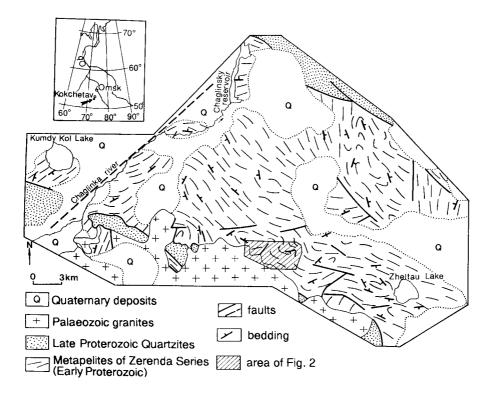
layered coronas or reaction rims between two reactant minerals. Several examples have been interpreted in terms of diffusion-controlled reaction with local equilibrium (e.g. Ashworth and Birdi, 1990; Ashworth *et al.*, 1998).

Many granulite-facies rocks contain interesting textures of retrograde reaction. These include the effects of decompression after high-pressure metamorphism. They have been studied mainly for the purpose of constraining the pressuretemperature-time histories of the rocks (e.g. Harley, 1989). In this paper we concentrate on reaction mechanism, in a high-pressure granulite which has subsequently reacted at lower pressure in the contact aureole of a granitic intrusion. The textures imply diffusion processes which can be compared with those previously inferred in a prograde granulite reaction (Ashworth et al., 1998) and in retrograde reactions at lower temperatures (e.g. Ashworth and Birdi, 1990). The textures include a symplectite which differs from those reviewed by Ashworth and Birdi (1990), by containing three minerals instead of

two, and replacing garnet instead of plagioclase. The other feature of interest comprises pseudomorphs with a layer structure. These are not amenable to detailed modelling, because one reactant mineral has been completely consumed and the other reactant was the matrix of the rock rather than a single mineral of well-defined composition. However, they do offer some indications of diffusion mechanism.

Geological setting

The Kokchetav massif, north Kazakhstan, is noted for high-pressure metamorphism (Shatsky *et al.*, 1995). Microdiamond-bearing rocks occur near Kumdy Kol Lake, west of the Chaglinka river in Fig. 1. The present area, east of the river, probably experienced less extreme conditions. Indications of granulite-facies peak pressure and temperature are heterogeneous, in the range 10–21 kbar and 625–950°C at an estimated date of 530 Ma, with subsequent more homogeneous conditions of 7 kbar, 500–550°C at approximately 517 Ma



IG. 1. Geological sketch map of the north-eastern part of the Kokchetav massif (located by arrow on the inset).

DIFFUSION-CONTROLLED REACTION TEXTURES

(Lepetyukha et al., 1995). The main unit affected, the Zerenda Series, is predominantly pelitic. In the study area (Fig. 2), it contains boudins and disrupted sheets of metabasic rocks (Reverdatto et al., 1993). The granulite-facies metamorphism predated intrusion of the large Zerenda granitoid, which is probably Ordovician in age (Reverdatto et al., 1993). The rock studied in detail is from its contact aureole, which is ~ 1 km wide as indicated by skarns and by the reactions in metabasic rocks. Reverdatto et al. (1993) estimate the general conditions of contact metamorphism as $500-700^{\circ}$ C at a pressure which is poorly constrained but probably in the range 2-8 kbar.

Rock composition

The specimen studied here, numbered 9-L-8-1 by Reverdatto *et al.* (1993), is from the lithological unit mapped as pyroxenite (Fig. 2). Relative to typical metabasites, represented by analyses in Table 2 from the same Zerenda Series, these pyroxenites have high MgO. In AFM and Si–Al–Mg diagrams (Fig. 3), they plot in the Mg-rich part of the field of selected ultramafic and mafic granulites from other parts of the world. They are similar in composition to some metapelites

(Fig. 3), but are generally less aluminous and more magnesian than the plotted metapelites with sapphirine or gedrite. Relative to other Kokchetav metabasites (Table 2), they also have low alkalis and, with one exception, low CaO (Table 1). These features are reflected in the mineral assemblage of 9-L-8-1, which lacks clinopyroxene but contains orthopyroxene; in the rock matrix this is subordinate in amount to anthophyllite, accompanied by cordierite and minor biotite. Representative mineral analyses are given in Table 3. The bulk composition and mineral assemblage ally these rocks with cordierite-orthoamphibole rocks from other regions. Likely origins of these rocks are reviewed by Robinson et al. (1982, pp. 160-163) and by Moore and Waters (1990). The rock compositions suggest a low-temperature pre-metamorphic mineral assemblage of mainly chlorite plus quartz. One possible origin is hydrothermal alteration of basic volcanic rocks, well documented in modern oceanic crust (e.g. Humphris and Thompson, 1978), which can produce chlorite-quartz rocks (Mottl, 1983). An alternative alteration process is weathering (Moore and Waters, 1990). Another possible protolith is a chemical sediment, either of

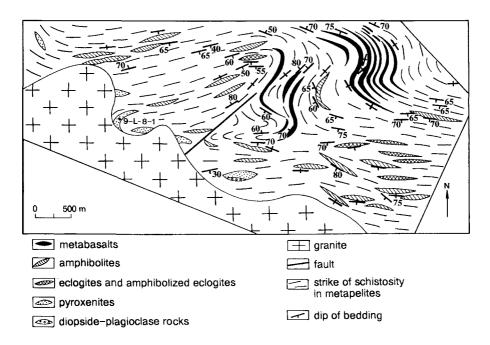


Fig. 2. Detailed geological map of the setting of the specimen studied.

TABLE 1. X-ray fluorescence analyses of pyroxenites from the study area

	4	4-1	9-L-8-1	AC-35	95c	95b	95h	118b
SiO ₂	32.42	48.61	47.20	47.58	47.88	48.93	48.40	33.70
TiO ₂	2.43	0.58	2.11	1.01	0.99	0.94	1.89	2.04
Al_2O_3	20.20	10.31	12.97	16.43	16.20	15.70	15.22	20.96
Fe_2O_3	14.52	5.98	10.12	14.98	13.76	14.14	11.89	17.55
MnO	0.28	0.09	0.12	0.15	0.11	0.14	0.08	0.24
MgO	23.68	10.61	21.96	16.18	17.49	15.61	18.09	24.15
CaO	1.97	22.58	3.62	1.42	1.64	1.54	1.13	2.02
Na ₂ O	0.32	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30
K_2O	0.07	0.04	0.35	0.12	0.08	0.14	0.05	0.03
P_2O_5	0.13	0.15	0.16	0.03	0.03	0.03	0.08	0.18
L.O.I.	4.06	1.06	1.22	2.32	1.88	3.08	2.82	-0.72
Total	100.08	100.01	99.83	100.21	100.03	100.22	99.65	100.16
$\frac{100 \text{Mg}}{\text{Mg+Fe}}$	76.4	77.9	81.1	68.2	71.6	68.6	75.1	73.2

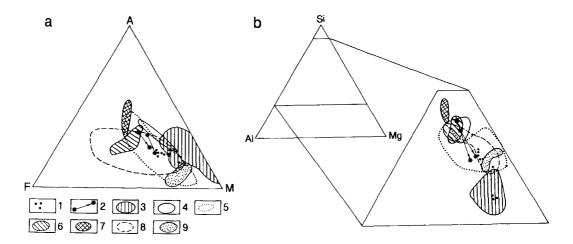


Fig. 3. Comparison of Kokchetav pyroxenites with other rocks in (a) AFM and (b) Al-Si-Mg diagram. 1 – pyroxenites of the studied locality (Table 1 and Reverdatto et al., 1993, Table 2). 2 – hydrothermally altered basalts, Mid-Atlantic Ridge (Humphris and Thompson, 1978, samples 1-97 and 2-142: arrows show change from less altered to more altered part of sample). 3 – sapphirine-bearing mafic granulites from Antarctica (Segnit, 1957; Sheraton 1980; Sheraton et al., 1982) and Western Australia (Wilson, 1971). 4 – sapphirine-bearing metapelites (Sheraton, 1980). 5 – pyroxenites, peridotites and mafic granulites from Beni Bouchera, Morocco (Kornprobst, 1969) and xenoliths in volcanics, Hungary (Embey-Isztin et al., 1990). 6 – metabasalts and amphibolites from the Zerenda Series (Table 2). 7 – gedrite-bearing metapelites, Yellowknife area, Canada (Kamineni, 1979). 8 – anthophyllite-bearing metapelites and metabasites, Ontario (Tilley, 1957), Cornwall (Floyd, 1965), New South Wales (Vallance, 1967), Antarctica (Sheraton, 1980), NE Scotland (Hudson and Harte, 1985), and Queensland (Reinhardt, 1987). 9 – micaceous pyroxenites with or without sapphirine, Western Australia (Wilson, 1971) and Antarctica (Ravich and Kamenev, 1975).

Table 2. X-ray fluorescence analyses of metabasalts and amphibolites from the Zerenda Series of the Kokchetav region

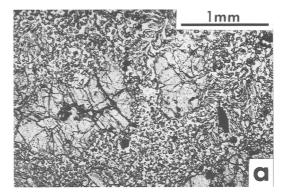
									erect ministers of inconcession and uniprocesses from the following series of the regression region						AUVANOS	uy ivgi	. T	
	5a	5b	7	8	9a	13g2	19	20	23	29	34	37	19	62	71	74	79b	80
SiO_2	49.98	47.84	47.54	50.21	47.98	49.04	48.57	49.88	48.02	44.79	48.18	48.50	49.41	47.44	48.88	49.19	49.90	47.12
TiO_2	1.18	1.31	2.48	1.28	0.99	1.55	1.02	1.25	1.00	1.68	1.62	1.12	1.41	1.13	1.03	1.42	1.34	0.97
Al_2O_3	13.51	16.03	12.51	13.12	16.37	13.36	14.71	13.88	14.99	14.59	14.22	14.25	12.85	17.56	14.53	13.62	14.14	18.41
$\mathrm{Fe}_2\mathrm{O}_3$	15.31	12.90	17.86	16.23	13.78	15.60	13.06	14.42	12.13	18.73	14.27	13.02	14.69	11.11	13.72	14.01	14.44	10.06
MnO	0.20	0.18	0.19	0.21	0.18	0.22	0.18	0.19	0.18	0.22	0.18	0.19	0.18	0.17	0.19	0.19	0.20	0.16
$_{ m MgO}$	6.52	69.9	5.92	6.20	98.9	6.48	7.14	6.28	7.72	6.24	6.42	7.37	6.04	6.71	7.06	7.01	6.87	7.04
CaO	10.48	12.16	6.78	10.24	10.88	10.69	12.55	10.60	11.97	11.07	12.07	10.75	10.20	12.17	11.48	11.42	10.10	12.73
Na_2O	1.98	1.66	2.55	1.75	1.75	1.60	1.63	1.85	1.78	1.74	1.95	1.44	1.80	1.68	1.93	1.89	1.46	1.53
K_2O	0.43	0.19	0.34	0.33	0.43	0.49	0.14	0.26	0.61	0.33	0.13	0.52	0.22	0.45	0.39	0.36	0.49	0.30
P_2O_5	0.23	0.27	0.34	0.25	0.24	0.28	0.28	0.26	0.27	0.26	0.34	0.25	0.25	0.26	0.23	0.28	0.24	0.25
L.O.I.	0.17	0.49	3.47	0.18	0.55	0.73	0.74	1.18	1.35	0.37	0.62	2.60	2.93	1.39	09.0	0.63	0.84	1.43
Total	66.66	99.72	86.66	100.00	100.01	100.04	100.02	100.05	100.02	100.02	100.00	100.01	86.66	100.07	100.04	100.02	100.02	100.00
$\frac{100 { m Mg}}{{ m Mg+Fe}}$	45.8	50.7	39.6	43.1	49.7	45.1	52.0	46.3	55.8	39.8	47.1	52.9	44.9	54.5	50.5	49.8	48.5	58.1

exhalative association or evaporitic, also possible precursors of cordierite-orthoamphibole rocks (Beeson, 1988). Evaporitic mudstones have been suggested as the precursors of sapphirine-bearing granulites (Harley, 1993). In the Kokchetav massif, the association with normal metabasic rocks suggests derivation from them by some alteration process.

Symplectite replacing garnet

Relict garnet grains are surrounded by extensive patches of symplectite (Fig. 4a). Orthopyroxene forms vermicules set in material of low optical relief. The latter consists of two minerals, cordierite and plagioclase, which are fully resolved only in backscattered-electron (BSE) images (Fig. 4b). The vermicular or rodsymplectite structure thus comprises rods of a low-Al mineral (orthopyroxene) scattered through high-Al matrix, the latter made up of a coarser intergrowth of the two high-Al minerals. Table 3 contains analyses from the symplectite patch studied in detail. Plagioclase varies from An₈₂ to An₉₅ (34 analyses), with a mean An content $(\pm 2 \times \text{standard error}) \text{ of } 88.30 \pm 1.37. \text{ As in a}$ cordierite-plagioclase-sapphirine symplectite described by Harley et al. (1990), the plagioclase has a very similar Al:Si ratio to the cordierite, though in this example the plagioclase is slightly more aluminous (4.4-4.5 Al atoms per 5 Si, in comparison with a ratio almost exactly 4:5 in cordierite).

Garnet is zoned (Table 3). Its composition has probably changed by internal diffusion during the symplectite-forming reaction. It seems likely that the garnet edge may have been close to equilibrium with adjacent symplectite minerals. The analyses in Table 3, from garnet edge and closely adjacent grains, can therefore be used for approximate thermobarometry. Assuming a pressure in the range 2-8 kbar, the Fe-Mg exchange geothermometers for garnet-cordierite and garnetorthopyroxene give temperatures in the range 642-693°C according to the calibration of Berman and Aranovich (1996) and 645-717°C in calculations from the dataset of Holland and Powell (1990), using the activity models of Berman and Aranovich (1996) for garnet and cordierite, and the model preferred by Guiraud and Powell (1996) for orthopyroxene. In summary, the best temperature estimate is 680 $\pm 40^{\circ}$ C, though this may be a closure temperature for Fe-Mg diffusion (cf. Harley, 1989), and thus



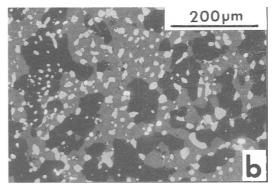


Fig. 4. Symplectite replacing garnet in specimen 9-L-8-1. (a) Garnet relics surrounded by symplectite in thinsection. (b) Backscattered electron image of the symplectite, showing cordierite (black), plagioclase (grey) and orthopyroxene (lighter grey). A few very bright gains are ilmenite.

may post-date the peak temperature of the symplectite-forming event.

Geobarometric calculations (giving a maximum pressure, in the absence of quartz) were carried out for the assemblage garnet-orthopyroxene-plagioclase from the dataset of Holland and Powell (1990), using activity model 3 of Holland and Powell (1992) for plagioclase. The end—member reactions concerned are almandine + grossular + SiO_2 = ferrosilite + anorthite, and pyrope + grossular + SiO_2 = enstatite + anorthite. These give maximum pressure limits, assuming local equilibrium among the minerals, of 5.8 to 7.2 kbar at $650-750^{\circ}C$.

Modal (volume) proportions of minerals in the symplectite were estimated from their areas in BSE images, measured using a digitising table attached to a microcomputer. Six photomicrographs were analysed, each representing an area

DIFFUSION-CONTROLLED REACTION TEXTURES

TABLE 3. Representative electron-probe microanalyses of minerals in specimen 9-L-8-1

							J 1	ctite rep	lacing		
		Ma	trix		Gar	rnet		Garnet			omorph
	Crd	Ath	Opx	Bt	interior	edge	Crd	P1	Opx —	Zo	Spl
SiO ₂	49.46	55.53	51.65	38.87	37.68	37.98	48.91	46.02	49.45	39.49	n.d.
TiO_2	n.d.	0.20	0.10	2.11	0.03	0.18	n.d.	0.10	0.30	n.d.	0.17
$Cr_2\tilde{O}_3$	n.d.	0.11	0.09	0.21	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.15
Al_2O_3	33.28	1.60	2.43	15.41	21.02	21.13	32.92	34.81	2.96	32.47	62.68
FeO*	4.88	17.25	22.62	10.00	32.57	28.88	7.21	0.32	29.61	1.91	23.98
MnO	n.d.	n.d.	n.d.	n.d.	2.01	1.21	n.d.	n.d.	0.26	n.d.	n.d.
MgO	10.87	22.61	22.42	18.73	4.66	4.37	9.40	n.d.	16.23	0.18	12.06
CaO	n.d.	0.40	0.10	0.09	2.27	6.60	0.10	18.49	0.42	24.44	_
Na ₂ O	0.12	0.56		0.30	n.d.	n.d.	0.35	1.15	_	0.09	****
K_2O	n.d.	n.d.	-	8.09	n.d.	n.d.	n.d.	n.d.	_	n.d.	_
Total	98.60	98.26	99.42	93.81	100.23	100.34	98.89	100.88	99.23	98.57	99.03
Recalcula	ation:										
Oxygen	18	23	24	22	24	24	18	8	24	25	24
Si	4.997	7.841	7.733	5.692	5.993	5.982	4.987	2.105	7.696	5.980	_
$\mathrm{Al}^{\mathrm{iv}}$		0.159	0.267	2.308				1.876	0.304	0.020	_
		8.000	8.000	8.000				3.981	8.000	6.000	
Al ^{vi} Fe ³⁺	3.964	0.079	0.162	0.352	3.941	3.923	3.957	_	0.240	5.776 0.218	11.887
Ti	~	0.021	0.011	0.232	0.004	0.021		0.003	0.035		0.020
Cr	_	0.013	0.011	0.025		_	_	_	armer .	-	0.019
					3.945	3.944				5.994	11.926
Fe ²⁺	0.412	2.030	2.833	1.225	4.321	3.804	0.615	0.012	3.853	_	3.228
Mn	_	_	_	_	0.271	0.161	_	_	0.034	-	_
Mg	1.636	4.743	5.002	4.088	1.105	1.027	1.429	_	3.766	0.040	2.891
Ü	2.048			5.922			2.044				6.119
Ca	_	0.061	0.017	0.015	0.387	1.114	0.011	0.906	0.071	3.966	
Na	0.023		0.017	0.086	_	_	0.068	0.102		0.028	
K	-	_		1.512	_			_		-	
		7.100	8.036	1.613	6.084	6.106		1.023	7.999	4.034	

Mineral abbreviations: Ath = anthophyllite; Bt = biotite; Crd = cordierite; Opx = Orthopyroxene; Pl = plagioclase; Spl = spinel; Zo = zoisite

of approximately 0.2 mm². One homogeneous-looking area was subdivided into four to assess the random statistical variation in the measurements, with the result that mineral proportions can be regarded as precise to within ± 0.5 volume percent. The proportions of cordierite and plagio-clase are highly variable from one analysed area

to another, some areas being plagioclase-free. The proportions of cordierite, plagioclase and orthopyroxene are plotted in Fig. 5. This neglects ilmenite (0.7 to 1.7 vol. percent) which, however, does not affect the Al:Si ratio, because its contents of both Al and Si are negligible. Contours of atomic Al:Si ratio are shown in

Geoscan-Link energy-dispersive electron microprobe, Manchester University. Analyst J.R.A.

n.d. not detected; - not analysed

^{*}total Fe as Fe₂O₃ in zoisite; FeO in other minerals

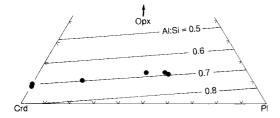


Fig. 5. Measured modal proportions of cordierite, plagioclase and orthopyroxene in symplectite. Also shown are contours of calculated atomic ratio Al:Si.

Fig. 5, calculated for the average plagioclase composition of $An_{88.3}$. The proportion of orthopyroxene increases with increasing ratio of plagioclase (which has Al:Si ≈ 0.89) relative to cordierite (Al:Si ≈ 0.8), so that the Al:Si ratio of the bulk symplectite is consistently close to 0.7. The main uncertainties are those mentioned above: the variation of plagioclase composition and the sampling error in modal analysis. Taking both into account, the Al:Si ratio of the symplectite is estimated as 0.69 + 0.02.

The digitising procedure is tedious. An alternative is to analyse an area $\sim 0.1~\text{mm}^2$ in the electron probe, by rastering the beam during analysis. This is expected to be less accurate than the combination of modal analysis and point electron-probe analyses, mainly because the ZAF corrections to the analysis are uncertain where the material analysed is not homogeneous. Nevertheless, the method was used on two areas of the same symplectite patch modally analysed, for comparison with the above results. Indicated Al:Si ratios were 0.677 and 0.689, in excellent agreement with the other method.

The Al:Si ratio in the symplectite is very similar to that in garnet (ideally 0.667 in the absence of substituents for Al and Si; 0.65-0.66 in the analyses in Table 3). In contrast, proportions of Fe, Mg and Ca in this symplectite vary greatly as the proportions of cordierite and plagioclase vary. It seems clear that Al and Si have been inherited from reactant garnet with very little gain or loss, while the other elements were much more mobile. Restricted diffusion of Al and Si explains the fine scale of the intergrowth between Al-poor orthopyroxene and Al-rich, Si-poorer minerals. The latter (cordierite and plagioclase) are intergrown on a relatively coarse scale, because relatively little Al and Si movement is required, the major differentiation being Fe,Mg (in cordierite) versus Ca (in plagioclase), these being mobile elements. The symplectite is evidently closely analogous to those previously studied, replacing plagioclase (Ashworth and Birdi, 1990).

Aluminous pseudomorphs

The specimen contains distinctive patches, up to a few mm in size, of finely intergrown minerals (Fig. 6). In section, some are ovoid in shape (Fig. 6a), others have more nearly straight edges and are roughly rhomb-shaped. The core intergrowth is generally surrounded by a layer of plagioclase, then a layer of cordierite adjacent to the rock matrix (Fig. 6a), though some examples lack one or other of these layers. The core consists mainly of plagioclase, zoisite, corundum and spinel (Fig. 6b). These objects are evidently pseudomorphs, after a mineral of the granulite-facies assemblage which they have completely replaced.

Analyses of zoisite and spinel are given in Table 3. Identification of zoisite rather than clinozoisite is based on a non-anomalous firstorder grey interference colour, and lower Fe contents than would be expected in clinozoisite formed at the relevant temperatures (Franz and Selverstone, 1992). The presence of zoisite suggests a pressure greater than approximately 5 kbar at 700°C (Chatterjee et al., 1984, Fig. 4), though the effect of impurity of the zoisite cannot be quantified. Plagioclase in the core and in the plagioclase layer is anorthite (An_{94-97}). Corundum gives low analysis totals, indicating alteration to diaspore. Other, minor minerals detected by electron probe are margarite and muscovite. These too may be alteration products. The cordierite layer around pseudomorphs is commonly altered to very fine-grained alkalibearing material (pinite).

To infer what mineral has been replaced, we make use of the Al:Si ratio, following the finding that symplectite replacing garnet in the same rock has nearly preserved the Al:Si ratio of that mineral. In the pseudomorph cores, Al:Si was measured by the quick method described above (raster analysis). Results for seven areas are in the range 1.61 to 1.93. The most likely precursor mineral is an Al₂SiO₅ polymorph (possibly with inclusions of less aluminous minerals, to account for the low part of the measured Al:Si range). The most likely polymorph to have formed in the high-pressure granulite-facies event is kyanite.

DIFFUSION-CONTROLLED REACTION TEXTURES

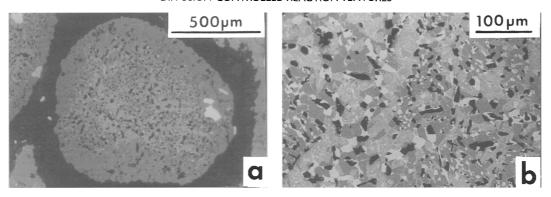


Fig. 6. Backscattered electron images of pseudomorphs. (a) layer structure: the mineral intergrowth in the core passes into a plagioclase layer (mid grey), which is separated by a cordierite layer, now pinitised (black) from the rock matrix (right and lower left) or the next pseudomorph (upper left). Bright grains are ilmenite. (b) detail of the core of a pseudomorph, consisting of four intergrown minerals: corundum (black), plagioclase (grey), zoisite (lighter grey) and spinel (lightest).

Another aluminous mineral that might be considered is sapphirine, but this would have much higher Al:Si (generally in the range 4-7, Deer et al., 1978, pp. 617-24). Thus the major minerals in the granulite-facies assemblage of this unusual metabasic rock were probably garnet, kyanite and anthophyllite and/or orthopyroxene, probably with some clinopyroxene and possibly quartz. We have calculated the stable mineral assemblage at various pressures and temperatures for a model rock with a composition approximating that of 9-L-8-1, but simplified by neglecting components other than CaO-FeO-MgO-Al₂O₃-SiO₂. The calculations use the database of Holland and Powell (1990) with the simplifying assumptions of ideal solid solution and linear changes of free energies of minerals over a limited range of pressure and temperature. The results indicate orthopyroxene-clinopyroxene-garnet-kyanite-quartz as the stable assemblage in a pressure range approximately 8−12 kbar at $T \approx 700$ °C. The stable assemblage at higher pressures lacks kyanite; at lower pressures, both kyanite and garnet are absent while plagioclase becomes stable in this model.

The pseudomorphs are similar to the aluminous enclaves in cordierite-gedrite metavolcanics studied by Schumacher and Robinson (1987), which also have cores of aluminous minerals surrounded by layers of plagioclase and cordierite. There, combinations of cordierite, sapphirine, corundum, staurolite and plagioclase have been formed by reactions, between sillima-

nite and amphibole, caused by pressure decrease. Relics of sillimanite remain in the cores of the enclaves to show that it was the aluminous mineral replaced. In granulite-facies metapelites, there are several instances of sillimanite incompletely replaced, during decompression of the regions, by symplectites of cordierite + spinel (e.g. Clarke and Powell, 1991) or cordierite + sapphirine + plagioclase (e.g. Harley et al., 1990; Bertrand et al., 1992). Harley et al. (1990) describe a monomineralic cordierite layer surrounding the symplectite, and note that the mineral proportions in the symplectite are such as to preserve approximately the same Al:Si ratio as the precursor sillimanite. These symplectites in metapelites are more magnesian, in comparison with the relatively calcic nature of the assemblage found here in more calcic rocks interpreted as metabasites; rock analyses by Harley et al. (1990, Table 1) show very low Ca contents.

An occurrence with a comparable mineral assemblage to ours, in charnockitic Moldanubian granulites (Petrakakis and Jawecki, 1995), comprises 'aggregates' of spinel, corundum, zoisite and white mica. These are attributed to reaction at approximately 6 kbar following peak metamorphism at about 11 kbar. The textures are not easy to interpret. The mineral distribution is less regular than in the Kokchetav rock, and three minerals appear to be partially replaced: corundum, plagioclase and garnet (Petrakakis and Jawecki, 1995). In a Moldanubian mafic granulite, 'mosaics' of anorthite + spinel have

completely replaced a mineral that was probably kyanite (Owen and Dostal, 1996).

Conclusions

Textures in the contact-metamorphosed Kokchetav granulite are closely analogous to symplectites and coronas previously interpreted in terms of diffusion control in regional metamorphic contexts (e.g. Ashworth and Birdi, 1990; Ashworth *et al.*, 1998). As in those examples, Al and Si diffused relatively little, in distance and amount, in comparison with Fe, Mg and Ca. Diffusion of Al and Si undoubtedly controlled the scale of spacing of orthopyroxene vermicules in the symplectite replacing garnet, and probably also the scale of intergrowth in the pseudomorphs. It has been shown that the Al:Si ratio is an aid to inference of the identity of the mineral that has been pseudomorphed.

It is unlikely that a fluid phase pervaded the grain boundaries sufficiently to provide an interconnected network through which diffusion could occur from source to sink of components. As in the examples studied by e.g. Ashworth and Birdi (1990), the small scale of the structures and the regularity of the spatial patterns, unrelated to any possible fluid channels such as cracks, indicates diffusion in the solid state. The main diffusion medium was probably the grain boundaries, which are crystallographically disordered relative to grain interiors, thus providing easier paths for diffusion and the possibility of deviation from the composition of the bulk crystal.

It is interesting that the pseudomorph core assemblage (Fig. 6) containing both a ferromagnesian mineral (spinel) and calcic ones (plagioclase and zoisite), is surrounded by a layer almost free of Fe and Mg (plagioclase) then a layer almost free of Ca (cordierite). If all parts of this structure grew simultaneously, then Fe, Mg and Ca must all have diffused through layers where their bulk concentrations are very small. This seems much more likely than that the layers developed sequentially, first by addition of Ca without Mg and Fe to form the plagioclase layer, then by addition of Mg and Fe without Ca to form the cordierite. Simultaneous growth of the layers is possible provided that the diffusion medium (grain boundaries) contained all the elements involved. Thus the observations strongly suggest that the grain boundaries had compositions different from those of the bulk mineral grains.

Acknowledgements

This work forms part of a Royal Society Joint Project with the Former Soviet Union. The electron-probe and BSE work was supported by NERC, and carried out by JRA at the Department of Earth Sciences, University of Manchester, with the essential help of Tim Hopkins and David Plant.

References

Ashworth, J.R. and Birdi, J.J. (1990) Diffusion modelling of coronas around olivine in an open system. *Geochim. Cosmochim. Acta*, 54, 2389–401.

Ashworth, J.R., Sheplev, V.S., Bryxina, N.A., Kolobov, V.Yu. and Reverdatto, V.V. (1998) Diffusioncontrolled corona reaction and overstepping of equilibrium in a garnet granulite, Yenisey Ridge, Siberia. J. Metam. Geol. (in press).

Beeson, R. (1988) Identification of cordierite-anthophyllite rock types associated with sulphide deposits of copper, lead and zinc. *Trans. Inst. Mining Metall.*, **97**, B108–15.

Berman, R.G. and Aranovich, L.Ya. (1996) Optimized standard state and solution properties of minerals I. Model calibration for olivine, orthopyroxene, cordierite, garnet, and ilmenite in the system FeO-MgO-CaO-Al₂O₃-TiO₂-SiO₂. *Contrib. Mineral. Petrol.*, **126.** 1–24.

Bertrand, P., Ouzegane, Kh. and Kienast, J.R. (1992) *P-T-X* relationships in the Precambrian Al-Mg-rich granulites from In Ouzzal, Hoggar, Algeria. *J. Metam. Geol.*, **10**, 17–31.

Chatterjee, N.D., Johannes, W. and Leistner, H. (1984)
The system CaO-Al₂O₃-SiO₂-H₂O: new phase equilibria data, some calculated phase relations, and their petrological implications. *Contrib. Mineral. Petrol.*, **88**, 1–13.

Clarke, G.L. and Powell, R. (1991) Decompressional coronas and symplectites in granulites of the Musgrave Complex, central Australia. J. Metam. Geol., 9, 441–50.

Deer, W.A., Howie, R.A. and Zussman, J. (1978) Rockforming Minerals, vol. 2A: Single-chain Silicates. Longman, London.

Embey-Isztin, A., Scharbert, H.G., Dietrich, H. and Poultidis, H. (1990) Mafic granulites and clinopyroxenite xenoliths from the Transdanubian Volcanic Region (Hungary): implications for the deep structure of the Pannonian Basin. *Mineral. Mag.*, **54**, 463–83.

Fisher, G.W. (1978) Rate laws in metamorphism. Geochim. Cosmochim. Acta, 42, 1035-50.

Floyd, P.A. (1965) Metasomatic hornfelses of the

- Land's End aureole at Tater-du, Cornwall. *J. Petrol.*, **6**, 223–45.
- Franz, G. and Selverstone, J. (1992) An empirical phase diagram for the clinozoisite-zoisite transformation in the system Ca₂Al₃Si₃O₁₂(OH) Ca₂Al₂Fe³⁺Si₃O₁₂(OH). *Amer. Mineral.*, 77, 631–42.
- Guiraud, M. and Powell, R. (1996) How well known are the thermodynamics of Fe-Mg-Ca garnet? Evidence from experimentally determined exchange equilibria. *J. Metam. Geol.*, 14, 75–84.
- Harley, S.L. (1989) The origins of granulites: a metamorphic perspective. Geol. Mag., 126, 215–47.
- Harley, S.L. (1993) Sapphirine granulites from the Vestfold Hills, East Antarctica: geochemical and metamorphic evolution. Antarctic Science, 5, 389-402.
- Harley, S.L., Hensen, B.J. and Sheraton, J.W. (1990) Two-stage decompression in orthopyroxene-sillimanite granulites from Forefinger Point, Enderby Land, Antarctica: implications for the evolution of the Archaean Napier Complex. J. Metam. Geol., 8, 591–613.
- Holland, T.J.B. and Powell, R. (1990) An enlarged and updated internally consistent thermodynamic dataset with uncertainties and correlations: the system K₂O-Na₂O-CaO-MgO-MnO-FeO-Fe₂O₃-Al₂O₃-TiO₂-SiO₂-C-H₂-O₂. *J. Metam. Geol.*, **8**, 89–124.
- Holland, T. and Powell, R. (1992) Plagioclase feldspars: Activity-composition relations based upon Darken's quadratic formalism and Landau theory. *Amer. Mineral.*, 77, 53-61.
- Hudson, N.F.C. and Harte, B. (1985) K₂O-poor, aluminous assemblages from the Buchan Dalradian, and the variety of orthoamphibole assemblages in aluminous bulk compositions in the amphibolite facies. Amer. J. Sci., 285, 224–66.
- Humphris, S.E. and Thompson, G. (1978) Hydrothermal alteration of oceanic basalts by seawater. *Geochim. Cosmochim. Acta*, 42, 107–25.
- Kamineni, D.C. (1979) Metasedimentary cordieritegedrite rocks of Archean age near Yellowknife, Canada. Precambr. Res., 9, 289-301.
- Kornprobst, J. (1969) Le massif ultrabasique des Beni Bouchera (Rif Interne, Maroc): Etude des péridotites de haute température et de haute pression, et des pyroxénolites, à grenat ou sans grenat, qui leur sont associées. Contrib. Mineral. Petrol., 23, 283–322.
- Lepetyukha, V.V., Reverdatto, V.V., Ten, A.A. and Khlestov, V.V. (1995) Polymetamorphism in northeastern part of the Kokchetav massif (northern Kazakhstan). *Dokl. Akad. Nauk*, **340** (5), 653–8 [in Russian].
- Mongkoltip, P. and Ashworth, J.R. (1983) Quantitative estimation of an open-system symplectite-forming reaction: restricted diffusion of Al and Si in coronas

- around olivine. J. Petrol., 24, 635-61.
- Moore, J.M. and Waters, D.J. (1990) Geochemistry and origin of cordierite-orthoamphibole/orthopyroxene-phlogopite rocks from Namaqualand, South Africa. *Chem. Geol.*, **85**, 77–100.
- Mottl, M.J. (1983) Metabasalts, axial hot springs, and the structure of hydrothermal systems at mid-ocean ridges. Geol. Soc. Amer. Bull., 94, 161–80.
- Owen, J.V. and Dostal, J. (1996) Contrasting corona structures in mafic granulite from the Blansky Les complex, Bohemian Massif, Czech Republic. *Canad. Mineral.*, 34, 959–66.
- Petrakakis, K. and Jawecki, C. (1995) High-grade metamorphism and retrogression of Moldanubian granulites, Austria. Eur. J. Mineral., 7, 1183–203.
- Ravich, M.G. and Kamenev, E.N. (1975) Crystalline Basement of the Antarctic Platform. Wiley, New York
- Reinhardt, J. (1987) Cordierite-anthophyllite rocks from north-west Queensland, Australia: metamorphosed magnesian pelites. J. Metam. Geol., 5, 451–72.
- Reverdatto, V.V., Lepetyukha, V.V. and Kolobov, V.Yu. (1993) Contact effect of the Zerenda granites on the Berlyk Suite rocks in the Kokchetav anticlinorium. Russian Geology and Geophysics, 34(12), 117-24.
- Robinson, P., Spear, F.S., Schumacher, J.C., Laird, J., Klein, C., Evans, B.W. and Doolan, B.L. (1982) Phase relations of metamorphic amphiboles: natural occurrence and theory. In *Amphiboles: petrology and experimental phase relations* (D.R. Veblen and P.H. Ribbe, eds.), *Reviews in Mineralogy*, **9B**, 1–227.
- Schumacher, J.C. and Robinson, P. (1987) Mineral chemistry and metasomatic growth of aluminous enclaves in gedrite-cordierite gneiss from southwestern New Hampshire, USA. *J. Petrol.*, **28**, 1033–73.
- Segnit, E.R. (1957) Sapphirine-bearing rocks from MacRobertson Land, Antarctica. *Mineral. Mag.*, **31**, 690–7.
- Shatsky, V.S., Sobolev, N.V. and Vavilov, M.A. (1995) Diamond-bearing metamorphic rocks of the Kokchetav massif (northern Kazakhstan). In Ultrahigh Pressure Metamorphism (R.G. Coleman and X. Wang, eds.), Cambridge University Press, Cambridge, 427-55.
- Sheraton, J.W. (1980) Geochemistry of Precambrian metapelites from East Antarctica: secular and metamorphic variations. BMR Journal of Australian Geology and Geophysics, 5, 279-88.
- Sheraton, J.W., England, R.N. and Ellis, D.J. (1982) Metasomatic zoning in sapphirine-bearing granulites from Antarctica. BMR Journal of Australian Geology and Geophysics, 7, 269-73.
- Tilley, C.E. (1957) Paragenesis of anthophyllite and hornblende from the Bancroft area, Ontario. *Amer.*

J. R. ASHWORTH ETAL.

- Mineral., 42, 412-6.
- Vallance, T.G. (1967) Mafic rock alteration and isochemical development of some cordierite-anthophyllite rocks. J. Petrol., 8, 84–96.
- Wilson, A.F. (1971) Some geochemical aspects of the sapphirine-bearing pyroxenites and related highly metamorphosed rocks from the Archaean ultramafic

belt of South Quairading, Western Australia. In Symposium on Archaean Rocks (J.E. Glover, ed.), Spec. Publ., Geol. Soc. Austral., 3, 401–11.

[Manuscript received 10 November 1996: revised 20 August 1997]