Variations in mineral chemistry across a shear zone in phlogopite peridotite

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Abstract—Variations in mineral chemistry with increasing shear strain have been observed in a shear zone developed in a phlogopite peridotite. These variations are attributed to re-equilibration of the system towards changing rock composition and the physical conditions (*P–T*) prevailing during the formation of the shear zone. The re-equilibration is enhanced by the deformation which raises the internal strain energy of the crystals, thereby increasing intracrystalline diffusion and promoting recrystallization.

INTRODUCTION

LOCALIZED ZONES of shearing provide examples of the effects of deformation on a mineral assemblage because the original mineral assemblage is present adjacent to the assemblage produced by shearing. Ductile shear zones are generally zones of grain size reduction produced by recrystallization during plastic deformation (dominated by dislocation motion) in response to the applied shear stress. Generally they are open systems, as shown by the increase in volatile content often observed, together with the formation of hydrated mineral phases in a retrograde metamorphic assemblage (Boyle 1961, Beach 1976). In an open system, reactions are likely to proceed more readily due to the availability of volatile or mobile constituents which may act as catalysts or react with the recrystallizing assemblage.

Following Harker's (1932) observation that shearing stress in a rock will enhance the rate of reaction, the effect of the localized deformation occurring within shear zones in producing the observed mineralogical and chemical changes found in natural examples has been considered by several authors (Boyle 1961, Beach 1973, 1976, Kerrich *et al.* 1977). In order to interrelate chemical and deformational changes, variations in rock and mineral chemistry across a shear zone developed in a course grained Alpine phlogopite peridotite have been investigated, together with optical, textural and modal variation and the detailed dislocation microstructure of the main mineral phases. This paper summarizes the mineral chemistry aspects of this study, concentrating on compositional variation and its relation to the increasing shear strain towards the centre of the shear zone. The detailed chemical and microstructural variations (Brodie 1979) will be published in a subsequent paper.

FINERO SHEAR ZONES

The phlogopite peridotite studied is from the Finero ultramafic massif in the Ivrea Zone of Northern Italy. This body is thought to be an upthrust slice of upper mantle material (Berckhemer 1969, Lensch 1969) which has undergone three main metamorphic and deformational events, under granulite facies, amphibolite facies and later greenschist facies conditions respectively (Vogt 1962, Steck & Tièche 1976). The shear zone investigated is thought to have been initiated during the amphibolite facies metamorphism. It is subparallel to the foliation produced during the amphibolite facies metamorphism and the zone of deformation and is approximately one metre in width.

Petrology

The phlogopite peridotite, in general, is coarse grained, equigranular and composed predominantly of olivine (Fo_{91-92}) with lesser orthopyroxene (En_{92}), phlogopite, pargasitic hornblende, chrome spinel and clinopyroxene. The olivine, enstatite and hornblende are euhedral to subhedral and form an interlocking network; orthopyroxene also appears as an interstitial phase. Euhedral chrome spinel is included within olivine and orthopyroxene grains as well as occurring along grain boundaries. Recrystallization is minor and the rock is completely fresh. Locally a foliation is defined by aligned phlogopite and amphibole grains. Widely spaced, diffuse kink-band boundaries are occasionally observed in the olivine along with rare kink-bands in the orthopyroxene. The hornblende appears to be a primary phase, with large well formed crystals showing no evidence of replacement.

Little indication is seen of mineral disequilibrium, but a reaction of the form olivine → spinel + orthopyroxene is suggested by the presence of subhedral orthopyroxene and spinel grains recrystallizing along kink-band boundaries in olivine. In addition, very fine grained worm-like intergrowths of amphibole and brown spinel are present along some amphibole–orthopyroxene or olivine boundaries.

The main changes which occur within the peridotite progressively into the shear zone are summarized in Table 1 and textural changes illustrated diagrammatically in Fig. 1. From these it can be seen that the degree

Table 1. Variation of grain size, kink-band spacing and percentage of recrystallization with increasing shear strain progressively into the shear zone, together with modal variations (determined both optically, in the coarser grained samples, and approximately by XRD)

	031I/019	026M	026A	026B	026C/K	026E	026F/G
OLIVINE GRAIN SIZE (mm) relict	2.25	2.1	2.1	1.5	1.2	0.9	1.0
recryt.	none	0.22	0.13	0.08	0.04-0.01	below resolution	
% RECRYSTALLIZATION (approx.)	0	5	12	50-60	85-90	95	99
KINK-BAND SPACING (mm)	1-0.35	0.3-0.15	0.13	0.08		0.02	
LENGTH/WIDTH RATIO PORPHYROCLASTS	1:1	2:1	2:1	3:1	4:1	2:1	

MODE %	optical	XRD	optical	XRD	optical	XRD	optical	XRD	optical	XRD	optical	XRD	optical	XRD
olivine	83	83.5	69	74	70.5	64	53		68.4	68	65		64	
enstatite	11	9	4.5	11	4.5	12	8.5		1.2	5	3.5		2	
phlogopite	0.5	0.5	7	1	11.8	7.5	14		21.4	11	13		6	
hornblende	3	3	10	3	0.4	1	1.5		1.2	2	3		3	
diopside	1.5	2.5	2	-	0.2	-	-		0.8	-	-		-	
spinel	1	-	1.5	-	0.4	-	-		0.2	-	-		-	
antigorite	-	-	-	2	12	11	12		7	8	7		20	

of recrystallization of the peridotite increases progressively with the increasing shear strain into the shear zone, recrystallization at first being restricted to grain boundaries and kink-band boundaries in the olivine. With further deformation elongate phlogopite crystals lying along grain boundaries define a distinct fabric, and merge to form an anastomising network surrounding lenses of relict and recrystallized olivine. Amphibole shows alteration to phlogopite. Once recrystallization becomes pervasive there is a relatively rapid reduction in grain size and in the centre of the shear zone a fine grained mylonite is produced with rare, elongate porphyroclasts of olivine and orthopyroxene set in a matrix of recrystallized olivine and phlogopite with minor orthopyroxene. Alteration to antigorite is more widespread in the centre of the zone. Pronounced changes in modal abundances of minerals occur as phlogopite increases progressively within the shear zone, and amphibole, olivine and orthopyroxene decrease. The marked increase in hydrated minerals in the shear zone indicates a flux of fluid into or through the zone.

Bulk chemistry

Rock compositional changes into the shear zone (Brodie 1979) were determined by X-ray fluorescence analysis, the results of which will be published in a later paper. An increase in H_2O, K_2O, TiO_2, Al_2O_3, Rb and Ba and a decrease in MgO, Ni, Cr, total Fe and SiO_2 relative to the surrounding coarse grained peridotite, is observed progressively into the shear zone, with minor redistribution of other elements. Fe^{2+} is oxidised to Fe^{3+}, some of which enters secondary magnetite. These

changes reflect the observed modal variations of increasing phlogopite and decreasing olivine, orthopyroxene and amphibole. Across the area of rapid grain size reduction the variations in chemistry show the same trends but these become more marked.

Mineral chemistry

The composition of the coexisting phases present in the sequence of rock samples taken across the shear zone, and in representative undeformed peridotite, were determined by electron probe analysis using a Cambridge Instruments Mark 5 probe fitted with a Link Systems energy dispersive analyser. Fe is taken as divalent in all minerals except spinel where Fe^{3+} was estimated assuming a stoichiometric composition (Finger 1972). A representative set of averaged analyses from an unsheared (026M) and a sheared (026F) sample are given in Table 2. It must be emphasized that although the variations observed are small, repeated analyses show them to be systematic into the shear zone.

Olivine. Olivine compositions were found to be very consistent, Fo_{91-92}, with no noticeable difference being observed between samples or between relict and recrystallized grains. Minor Ni and Mn were present as expected in Mg-rich olivines.

Orthopyroxenes. No significant variation from orthopyroxene compositions of En_{92} was observed but the minor oxide concentrations, Al_2O_3 and Cr_2O_3 appear to decrease progressively in samples into the shear zone. This decrease is more pronounced in the recrystallized grains. Similar changes are observed within crystallized orthopyroxene which forms along the
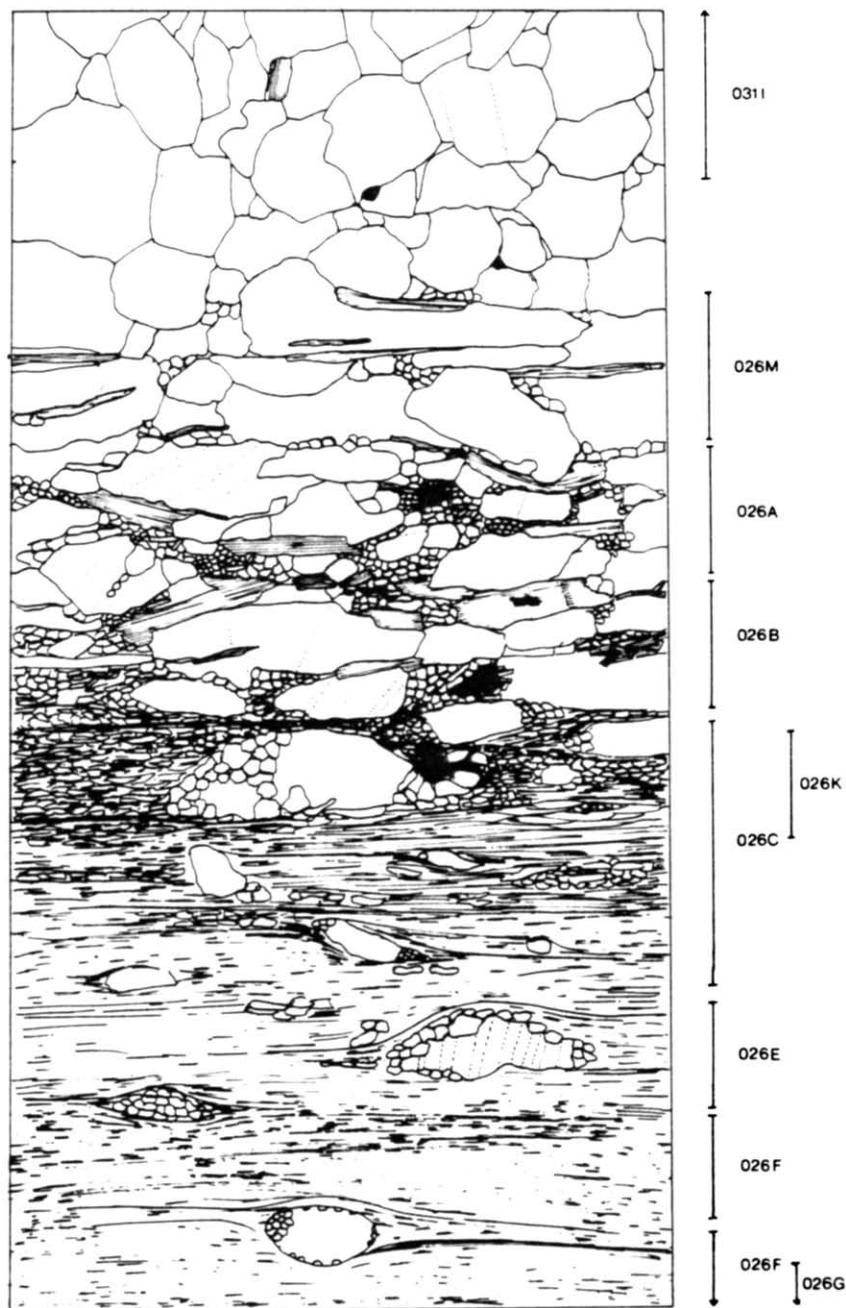
Fig. 1. Diagrammatic sketch from thin sections of the textural changes occurring into the shear zone. Phlogopite: parallel lines, spinel: black, olivine (& lesser orthopyroxene): white, kink-bands: dotted lines. Location of the samples referred to in Table 1 indicated (distance 1m).

highly deformed peripheries of olivine porphyroclasts. Analyses for Al_2O_3 made across orthopyroxene porphyroclasts, perpendicular to the mylonitic foliation, show a gradient of decreasing Al_2O_3 from centre to both edges of the grains (large orthopyroxenes outside the shear zone show no such heterogeneity). This is in agreement with the observed decrease in Al_2O_3 on recrystallization. Similar changes in recrystallized orthopyroxenes from peridotites have been documented by other authors (Green 1963, Wilshire & Jackson 1975). Traverses across some kink-bands present in orthopyroxene prophyroclasts within the mylonites show regular increases in Al and Cr and decreases in Si, Mg and Fe across the kink-band boundary. These anal-

yses are complicated by the presence of clinopyroxene lamellae perpendicular to the kink-bands.

Al is the most abundant minor element to substitute into the pyroxene crystal lattice and is also the most important: by displacing Si^{4+} it maintains the charge balance necessary for Al^{3+}, Cr^{3+}, Ti^{3+} etc. to substitute into the octahedral sites. The problem of the effect of pressure and temperature on the solubility of Al in orthopyroxene is a subject of some confusion (Wilshire & Jackson 1975, Presnall 1976, Obata 1976), and it will only be noted here that although P–T conditions exert an influence, bulk chemical composition must exert a strong control, particularly in an Al-poor rock. In these samples there is a negative correlation between Al_2O_3

Table 2. Representative examples of mineral analyses from relatively unsheared (026M) and sheared (026F) samples determined by electron microprobe (dashes indicate elements not detected). Olivines: average of 8–10 analyses, others: average of 5–7 analyses. In the case of the mylonitized sample (026F) analyses of both relict and recrystallized grains are presented, and variation of composition with grain size indicated for the spinels (small = 0.12–0. 2mm, large = 0.25–0. 4mm). 014 represents a mylonite from an adjacent locality. Some examples of standard deviations calculated for the analyses are indicated on the graphs in Fig. 2. Standard deviations calculated for spinel/orthopyroxene analyses are in the order of SiO_2: 0.07/0.21, TiO_2: 0.06/0, Al_2O_3: 0.31/0.05, Cr_2O_3: 0.55/0.05, FeO: 0.37/0.17, MnO: 0.10/0, MgO: 0.15/0.24, CaO: 0/0.05 respectively

	OLIVINE			SPINEL						
	026M relict	026F relict	026F recryst.	026M relict	026A centre	026A edge	026A small	026F large	026F medium	026F small
SiO_2	40.98	41.19	41.75	-	-	0.21	0.25	0.27	0.14	0.15
TiO_2	-	-	-	-	0.30	0.25	0.19	0.16	0.14	0.20
Al_2O_3	-	-	-	25.27	11.87	10.85	11.14	12.26	10.92	9.76
Cr_2O_3	-	-	-	40.59	49.96	51.41	48.76	50.25	50.65	50.54
FeO	8.52	8.70	8.63	24.25	30.03	29.80	32.66	28.70	30.70	32.62
MnO	0.11	-	-	0.28	0.81	1.22	1.12	1.11	1.18	0.52
MgO	50.07	49.92	50.03	10.54	6.71	6.26	5.18	6.98	5.90	5.25
NiO	0.38	0.35	0.29	-	-	-	-	-	-	-
Total	100.06	100.16	100.70	100.93	99.68	100.00	99.30	99.73	99.63	99.04
Formulae										
O	(4)	(4)	(4)	(32)	(32)	(32)	(32)	(32)	(32)	(32)
Si	0.999	1.003	1.009	-	-	0.057	0.068	0.07	0.04	0.04
Al	-	-	-	7.292	3.755	3.448	3.582	3.86	3.49	3.16
Ti	-	-	-	-	0.061	0.051	0.039	0.03	0.03	0.04
Cr	-	-	-	7.840	10.579	10.935	10.496	10.60	10.84	10.97
Fe^{2+}	0.174	0.177	0.174	4.097	5.193	5.314	5.743	5.08	5.41	5.81
Fe^{3+}	-	-	-	0.867	1.545	1.403	1.708	1.33	1.54	1.69
M,O	0.002	-	-	0.058	0.184	0.279	0.259	0.25	0.27	0.12
Mg	1.819	1.811	1.802	3.845	2.683	2.514	2.106	2.78	2.38	2.15
Ni	0.007	0.007	0.006	-	-	-	-	-	-	-
$\frac{Fe}{Fe+Mg}$	0.087	0.089	0.088	0.516	0.659	0.679	0.732	0.646	0.694	0.730

	ORTHOPYROXENE				CLINOPX	AMPHIBOLE		PHLOGOPITE		
	026M relict	026F relict	026F recryst.	014 edge ol.	026C relict	026M relict	026C relict	026M relict	026F relict	026F recryst.
SiO_2	56.91	58.04	57.98	57.62	54.90	44.49	46.45	38.37	39.38	38.86
TiO_2	-	-	-	-	-	0.50	0.85	1.03	1.64	1.31
Al_2O_3	1.13	0.51	0.26	0.41	0.53	11.40	8.96	15.61	14.27	13.92
Cr_2O_3	0.25	0.21	0.14	-	0.42	1.89	1.72	1.10	1.11	1.12
FeO	6.13	5.86	6.18	6.05	1.86	3.37	3.23	2.66	2.47	2.93
MnO	0.20	-	-	0.20	-	-	-	-	-	-
MgO	34.95	34.79	35.04	34.68	17.24	18.27	18.95	23.90	24.21	24.90
NiO	-	-	-	-	-	-	-	0.13	0.23	0.20
CaO	0.21	0.28	0.26	0.22	24.44	12.40	12.45	-	-	-
Na_2O	-	-	-	-	-	1.78	2.21	0.43	0.35	-
K_2O	-	-	-	-	-	0.88	0.58	9.15	9.51	9.38
Total	99.78	99.69	99.86	99.18	99.39	94.98	95.40	92.38	93.17	92.62
Formulae										
O	(6)	(6)	(6)	(6)	(6)	(23)	(23)	(22)	(22)	(22)
Si	1.967	1.998	1.996	1.997	2.000	6.487	6.725	5.575	5.680	5.649
Al	0.046	0.021	0.011	0.017	0.023	1.958	1.529	2.673	2.426	2.384
Ti	-	-	-	-	-	0.055	0.093	0.113	0.178	0.143
Cr	0.004	0.006	0.004	-	0.012	0.218	0.197	0.126	0.127	0.129
Fe	0.177	0.169	0.178	0.175	0.057	0.411	0.391	0.323	0.298	0.356
Mn	0.006	-	-	0.006	-	-	-	-	-	-
Mg	1.800	1.785	1.798	1.792	0.936	3.970	4.089	5.176	5.205	5.395
Ni	-	-	-	-	-	-	-	0.015	0.027	0.023
Ca	0.008	0.010	0.010	0.008	0.954	1.937	1.931	-	-	-
Na	-	-	-	-	-	0.503	0.620	0.121	0.098	-
K	-	-	-	-	-	0.164	0.107	1.696	1.750	1.739
$\frac{Fe}{Fe+Mg}$	0.09	0.086	0.090	0.092	0.057	0.094	0.087	0.059	0.054	0.062

content of the orthopyroxene and whole rock Al_2O_3 into the shear zone. Hence the observed variation in the orthopyroxene is not due to bulk chemical change. Under the influence of deformation the rate of equilibration of the orthopyroxene to the lower P–T conditions prevailing during the shearing is enhanced, producing the observed variations; Al appears to be stable in the orthopyroxene lattice only under high P–T conditions.

The dependence of Cr^{3+} substitution on charge balance being maintained by Al^{4+} substitution is reflected by the decrease in Cr with decreasing Al.

Clinopyroxene. The low modal abundance of clinopyroxene within these rocks makes any systematic study of chemical variation within this mineral difficult.

The analyses indicate that the clinopyroxene is diopside.

Amphibole. Analyses indicate that the amphibole lies between pargasite and hornblende in composition with a generalized formula of $Na_{0.5}Ca_2Mg_4Al_{0.5}(Cr, Ti, Ni)_{0.5}Si_{6.5}Al_{1.5}O_{23}$. The Na, Mg and Ti contents of the amphiboles increase and Al and K decrease progressively into the shear zone. There is a positive correlation between TiO_2 and Na_2O and whole rock TiO_2 (Fig. 2) and Na_2O respectively. Conversely whole rock MgO decreases while MgO in amphibole increases (Fig. 2); the decrease in whole rock MgO is due to the progressive breakdown of olivine into the shear zone and presumably the Mg^{2+} becomes available to enter the amphibole structure. Whole rock Al increases while Al in amphibole decreases (Fig. 2c): the Mg^{2+} if available
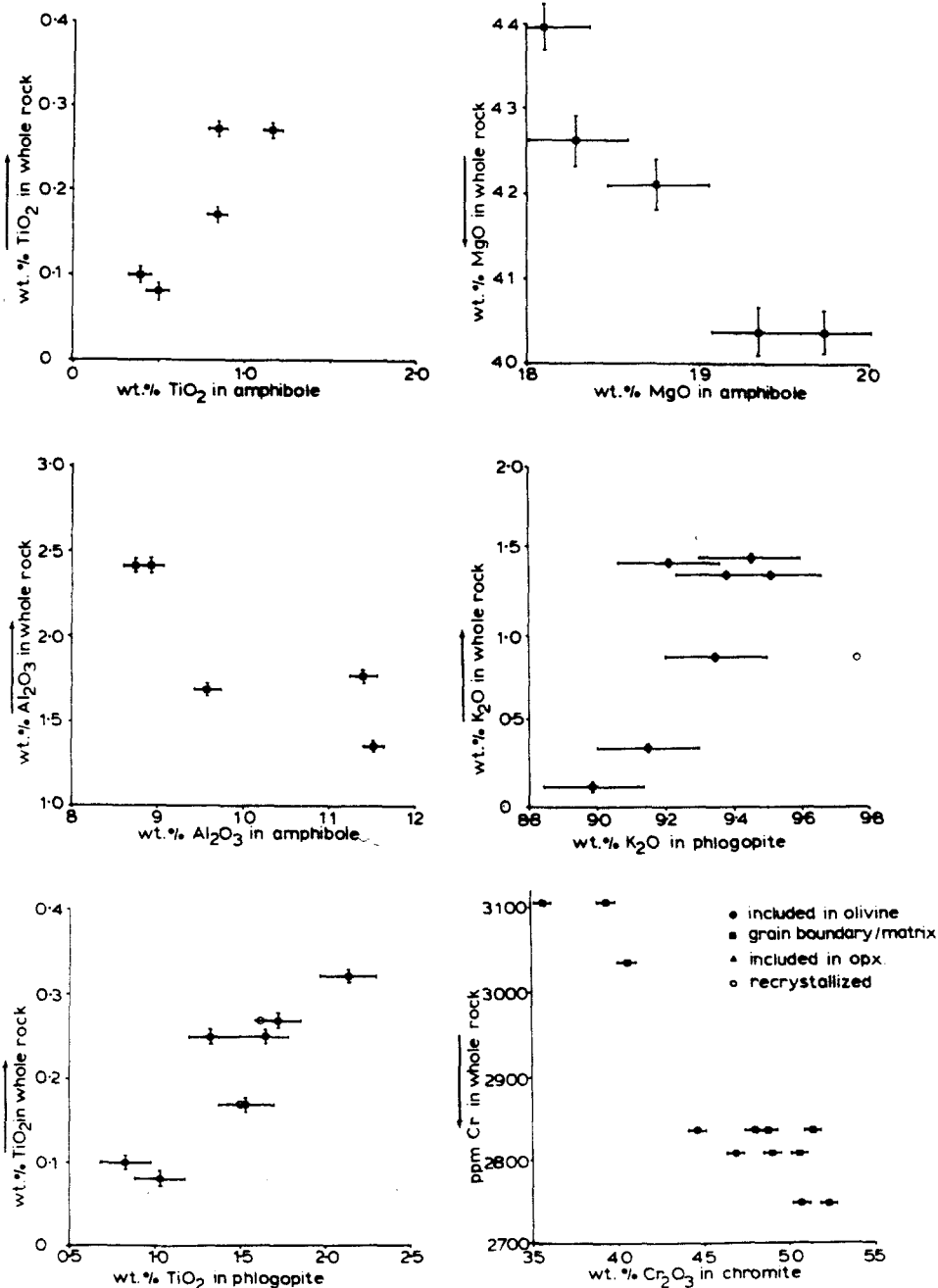

Fig. 2. Variations in element oxide concentrations in minerals with the equivalent rock composition. Arrows indicate variation with increasing shear strain.

enters the Y site in preference to Al^{3+} due to its lower charge.

Phlogopite. MgO, K$_2$O and TiO$_2$ contents of the phlogopite increase into the shear zone while Al$_2$O$_3$ decreases. As in the amphiboles, variation in K$_2$O and TiO$_2$ (Figs. 2d and e) can be positively correlated with whole rock changes while the inverse correlation with rock MgO may be explained in a similar way.

Spinel. The spinels analysed are of the form (Fe^{2+}, Mg) Cr$_2$O$_4$ and lie at the chromite end of the chromite–magnesiochromite solid solution series. In general Mg and Al decrease and Fe and Cr increase progressively in the chromites with increasing shear strain. Figure 3 shows an approximate correlation between Cr/Al and Fe^{2+}/Mg ratios although there is a lot of scatter.

Of all the minerals present in these samples, the chromites show the most variation and heterogeneity into
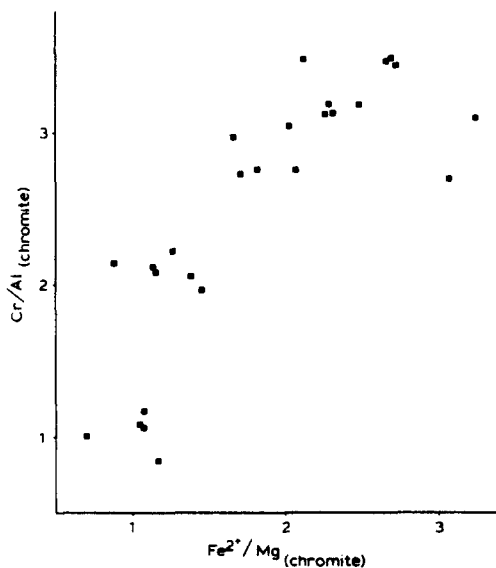
Fig. 3. Variation in Cr/Al with Fe^{2+}/Mg in the chrome spinels.

and within the shear zone. Within the mylonitized area the composition of the chromites varies with size or from centre to edge of a given grain (size may simply be a function of sectioning but it is still likely that a small spinel grain represents the equivalent of an edge region in a larger spinel). It appears that the small grains or edges of larger grains are re-equilibrating towards the new conditions prevailing in the sheared zone. No such variation is observed in the undeformed peridotite. Chromites included within olivine porphyroclasts in the ultramylonites tend to preserve the original chemistry. The same trend of compositional changes is seen progressively into the shear zone as is seen between chromites of differing sizes within one sample.

Geothermometry

The overall homogeneity of mineral composition, both within and between grains, in the undeformed peridotite samples is consistent with a close approach to

equilibrium conditions. Various published geothermometers utilizing different mineral equilibria were used to determine the temperature of equilibrium of the assemblage. These included the geothermometers of: Wood & Banno (1973) and Wells (1977) based on the diopside–enstatite miscibility gap; Herzberg & Chapman (1976) based on Ca–Mg–Al partitioning between clinopyroxene–spinel–olivine; Mercier & Carter (1975) based on Ca content of clinopyroxene or orthopyroxene; Irvine (1965) and Jackson (1969) based on Fe–Mg in olivine and spinel; MacGregor (1974), Obata (1976) based on Mg–Al in spinel–olivine–orthopyroxene; and Mysen & Boettcher (1975) based on Al^{4+}–Cr in orthopyroxene and clinopyroxene. A spread of temperature values was obtained, probably reflecting the different closure temperatures of the various minerals as well as the uncertainty in many of the calibrations of the geothermometers. In general temperatures between 613° and 1000°C were obtained, the majority being around 900°C.

Temperatures based on clinopyroxene–orthopyroxene equilibria (Wood & Banno 1973, Wells 1977, Mercier & Carter 1975) tend to show no consistent trend into the shear zone, while those based on spinel equilibria (Irvine 1965, Jackson 1969) show a trend of decreasing temperature into the shear zone. Although the absolute temperatures obtained are different, the same relative changes are indicated by the various spinel based on Al^{4+}–Cr partitioning between orthopyroxene and clinopyroxene (Mysen & Boettcher 1975). In addition, the chemical variation noted with size and from centre to edge in the spinels from the mylonitized samples indicate that the spinels are re-equilibrating to the lower temperature conditions associated with the mylonitization: the degree of re-equilibration is greater near the edges and in the smaller spinels. A drop in temperature of around 200°C is indicated in the most deformed samples. Although the errors associated with such temperature estimates are high, the qualitative trends in temperature variation are consistent.

The variations in temperature calculated from the mineral equilibria are consistent with field and petrological observations which support the view that the massif equilibrated under granulite facies temperatures and that the shear zones formed during lower temperature amphibolite facies metamorphism (Steck & Tièche 1976).

CHEMICAL VARIATION WITH INCREASING SHEAR STRAIN

Variations in chemical composition in relation to purely hydrostatic pressure and temperature changes, both experimentally and from natural rocks, are well documented. These variations form the basis for the calculations of pressure and temperature conditions prevailing during equilibration of mineral phases (see earlier).

It has been demonstrated theoretically, by the use of thermodynamics (Gresens 1966), that structural features in rocks imply mean stress gradients which produce gradients in chemical potential. These can produce concentration increases in preferred structural positions, which, in turn, can lead to nucleation of a new phase or replacement of a preexisting mineral phase.

Several investigations of chemical variations occurring in rocks associated with the differential stress gradients produced by structures such as folds, shear zones and boudins, have been reported in the literature (Boyle 1961, Carpenter 1968, Beach 1973, 1976, Berglund & Ekström 1974, Parker 1974, Stephansson 1974, Kerrich et al. 1977). Intragranular variations have also been noted (Green 1963, Basu & MacGregor 1975, Goode 1978) in response to stress gradients existing within grains during deformation. The enhancement of reactions by deformation (Dachille & Roy 1964) has similarly been recorded. For example, in these mylonites the formation of orthopyroxene along highly deformed peripheries of olivine porphyroclasts has been observed (Brodie & White 1978); development of orthopyroxene is observed in undeformed samples but it more copious where deformation has occurred.

Deformation increases the internal strain energy within a crystal which:

(i) Introduces vacancies and dislocations which enhance intra-crystalline diffusion (Cohen 1970), and hence reaction rate, by: (a) pipe diffusion along dislocation cores, or along dislocation arrays; (b) picking up impurities; (c) moving through the lattice, disrupting it, and increasing the probability of atoms coming into contact with the dislocation;

(ii) Promotes recrystallization leading to grain size reduction. Recrystallization involves movement of grain boundaries which are highly disordered regions within the lattice (containing a high concentration of voids and impurities) and hence provide high diffusivity paths (Shewmon 1963). As grain boundaries move they break the lattice, releasing ions and impurities. In addition it has recently been shown that diffusion in metals is even faster along a moving grain boundary than along a stationary one (Smidoda et al. 1979).

DISCUSSION

Mineral compositional variations occurring in response to increasing shear strain have been observed in this study, the deformation enhancing intracrystalline diffusion, increasing internal strain energy, and promoting recrystallization. This has enabled re-equilibration to the changing chemical environment (produced as a result of the mean stress gradients), and the differing physical conditions (P-T) prevailing during the deformation.

Compositional changes in mineral phases within the shear zone tend to reflect partly bulk chemical changes. For example, TiO_2 and Na_2O concentrations increase in the amphiboles, and similarly TiO_2 and K_2O increase in the phlogopites, as bulk TiO_2, Na_2O and K_2O increase progressively into the shear zone. Recrystallization has allowed the easier influx of a fluid phase which has modified the bulk chemical composition and catalyzed mineral reactions. As solid phases recrystallize, their constituents are effectively removed from the system and the existing chemical potential gradients, producing the influx of material, will be maintained.

Recrystallization has enabled some minerals to alter their composition more effectively and to reject impurities form their lattices. In the case of the orthopyroxenes, Cr_2O_3 and Al_2O_3 are lowered on recrystallization and concentrate along low mean stress regions, associated with kink-band boundaries in the relict grains.

The observed changes in chemical composition are not simply the result of elemental rearrangement into denser, more compact mineral structures in response to an increase in mean stress as has been suggested (Stephansson 1974). Within a given crystal, the larger oxygen ions would be expected to exert the main control on the degree of compression of the lattice in response to differential stress, rather than the smaller cations, although the influence of cations of Si-O bonding is marked (Donnay et al. 1959). The distribution of smaller cations will be controlled by the interplay of various factors including:

(a) Availability, i.e. initial concentration, since this is likely to influence chemical potential gradients;

(b) Relative mobility, in turn dependent on such factors as ionic size, chemical potential, compressibility, activation energy for diffusion;

(c) Mineral phases stable under prevailing P-T, σ and compositional conditions: the availability of lattice sites for the incorporation of elements into a solid phase will influence the element distribution (particularly in the case of trace elements: for instance concentrations of Ba, Rb, Ti in the rock increase as phlogopite abundance increases and Ni decreases as modal olivine decreases).

The composition of spinels in granulite facies peridotites, particularly the Cr/Al ratio, is likely to be a function of many factors including rock composition, the modal proportion of spinel and pyroxene, as well as pressure and temperatures (Medaris 1975). The observed variations within the chromites analysed here can be interpreted in terms of the interaction of all these factors. For example, an inverse correlation is observed between the variation of Cr and Al in the chromites with whole rock Cr_2O_3 (Fig. 2f) and Al_2O_3 contrary to the normally reported correlation between Cr/Al ratios. Fewer, more Cr-rich spinels are forming within the sheared zone. Chromite is the only phase present which will contain Cr to any marked extent, and any Cr present will be preferentially partitioned into the chromite; only traces are present within the pyroxene, amphibole and phlogopite phases, and the amount decreases in grains from sheared samples. Balanced with this, the spinels may be re-equilibrating to the new, lower temperature conditions prevailing during shearing. The kinetics of the re-equilibration, usually too slow for changes to

occur to the extent necessary for detection, may be enhanced by the deformation. Little variation is observed in the chromites from the undeformed peridotites, whilst those from the sheared samples show evidence of re-equilibration to lower pressure and temperature conditions. Since inverse correlations are obtained between variations in mineral and rock compositions, the observed changes are unlikely to be due to the differing bulk chemistry within the sheared region. This relatively rapid re-equilibration is presumably due to the fast cation diffusion rates reported for spinels (Grimes 1972, Lindner & Akerstrom 1958).

CONCLUSIONS

Compositional changes in mineral phases within the shear zone tend to reflect partly the bulk compositional changes. The deformation has increased the internal strain energy within the minerals, promoting grain size reduction by recrystallization. Recrystallization has facilitated the influx of a fluid phase, modifying the bulk chemical composition and catalyzing mineral reactions. In addition it has enabled some minerals to re-equilibrate their composition towards the changing chemical environment and reject impurities from their lattices.

Changes in Cr spinel composition seem to indicate re-equilibration towards the lower temperature conditions prevailing during the deformation that produced the shear zones. In general, mineralogy reflects the highest grade of metamorphism which the assemblage has undergone (in this case granulite facies) unless the rate of diffusion, and hence of re-equilibration to later, lower grade conditions (amphibolite facies) is enhanced by deformation as seen within the shear zone.

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