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MINERAL CHEMISTRY OF THE CHILAS MAFIC–ULTRAMAFIC COMPLEX, KOHISTAN ISLAND ARC, N. PAKISTAN: OXIDE PHASES

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ABSTRACT

The Chilas Complex contains a great variety of Fe^{3+}, Al, Cr, and Ti oxide phases. The principal gabbronorite association (PGA), which forms much of the complex, and the amphibolite dykes which represent a younger magmatic event in the Chilas Complex, contain magnetite-ilmenite pair exsolved from an initially single phase; no Cr-Al spinel occurs in these rocks. The ultramafic-mafic-anorthosite association (UMAA) of rocks, which appears to be emplaced in the PGA, contains oxides covering the entire range from pleonaste through Al-Cr-Fe^{3+} spinel (with a maximum of 39 wt. % Cr_2O_3) to magnetite. These display complete ranges for $Cr/(Cr+Al)$ and Fe^{3+}/R^{3+} ratios which decrease with increase in $Mg/(Mg+Fe^{2+})$ ratio (0.7 to 0.0). The composition of the UMAA spinel varies from one to another sample and in some cases from grain to grain within a single specimen. The variations are attributed to subsolidus re-equilibration with adjacent silicate grains and to exsolution. The exsolved pairs define a complete solvus similar in shape to those reported elsewhere. The UMAA also contains pleonaste formed in reaction coronas between calcic plagioclase and olivine, and in few cases, ilmenite formed during exsolution of Cr-Al-Fe^{3+} spinel. Exsolved oxide phases in both the associations of rocks have re-equilibrated under low oxygen fugacity during cooling of the complex at temperatures ranging from >800 to <500°C. The detailed microprobe analytical data for the oxide phases discussed in this paper support our earlier view that the Chilas Complex is related to the Kohistan arc and probably formed during intra-arc rifting in initial stages of development of a back-arc basin.

INTRODUCTION

The 1000 km long Kohistan–Ladakh island arc in western Himalaya developed in response to north-directed subduction of the neo-Tethyan ocean lithosphere. The available data have so far established the following sequence of magmatic and tectonic events in Kohistan:

1) Formation of a late Jurassic-Cretaceous island arc, the deepest levels of which are represented by the Jijal, Chilas and Tora Tigga mafic-ultramafic complexes, 2) Intra-arc basin

sediments with Aptian-Albian fossils, overlaying the early Kohistan volcanics, 3) 110–95 Ma diorite and tonalite plutons, 4) Closure of the back-arc basin, and deformation and tilting of the arc between 102–85 Ma, after which it became an Andean-type margin attached to the Karakoram plate, 5) Further northward subduction gave rise to an Andean-type (Kohistan) batholith with a volcanic cover, 6) Final closure of the neo-Tethys (50–40 Ma), resulting in the suturing of the arc with the Indian plate, and 7) Splitting of the arc into Kohistan and Ladakh sectors by northward indentation and Quaternary uplift of the Nanga Parbat massif (Khan et al., 1989; Treloar et al., 1989). The Chilas Complex extends for 300 km between Nanga Parbat and western Dir. It was described in considerable detail by Jan and Mian (1971), Chaudhry and Chaudhry (1974), Chaudhry et al. (1974), Shams (1975), Jan (1979), Jan et al. (1984a), Khan et al. (1985) and Khan (1988). Jan et al. (1984a) and Khan et al. (1989) suggested that its origin is related to the development of the Kohistan-Ladakh arc.

The complex is predominantly composed of gabbronorites (with minor pyroxenite and anorthosite layers) and subordinate hypersthene-quartz diorites, collectively referred to as the principal gabbronorite association (PGA). These rocks are characterized by a lack of olivine and presence of plagioclase of andesine to labradorite composition. Seemingly intrusive into these rocks are veins, dykes and lensoid bodies (< 1 m to 5 km²) of ultramafic rocks, gabbronorites, gabbros, anorthosites, and mafic pegmatites collectively named as UMA association. These rocks occur mainly around Chilas and are characterized by the presence of a more calcic plagioclase (calcic bytownite to anorthite) and olivine. Although layering is locally developed in the PGA, the UMA association displays excellent sedimentary depositional features (e.g., size and/or mineral graded-, rhythmic- and phase layering; wedge layering and truncation of earlier by later layers; cross-bedding; slump folding; syndepositional faults, dykes and breccias). Both the associations of rocks are intruded by a set of basic dykes with an assemblage comprising plagioclase and amphibole, and are referred to as amphibolite dykes.

Preliminary accounts of the mineral chemistry of the Chilas Complex have been presented by Jan and Howie (1980, 1982, 1987), Jan et al. (1984a), Bard (1983) and Khan et al. (1989). Detailed mineral chemistry is planned to be presented by us in a series of papers, beginning with the present one which deals with the oxide phases. Although the present data were collected on samples mostly from the east-central part, they are applicable to the entire complex because the western part is an uninterrupted extension of the PGA over the entire length.

CHEMISTRY OF THE OXIDE PHASES

Oxide phases occur in accessory amounts in most rocks of the Chilas Complex. These commonly make up 1 to 3 volume per cent of the rocks, but rarely exceed 5%. In the UMA association there are streaks and thin layers, mostly less than 3 cm thick, of Cr spinel that may be cut off, disrupted, pinched and swelled (Fig. 1). There also are local lenses and nests less than half a meter across. These are referred to as segregated spinel or chromitite although the Cr_2O_3 content of all the analyzed spots is below 40 wt. %. The disseminated oxides in UMAA occur in the form of tiny, discrete grains in the interstices and as inclusions in the silicate phases. No chromite segregations of commercial interest have so far been found in the complex.

This paper is based on microprobe analyses of the oxide phases in several dozen samples. The analyses were performed mostly at the University of Leicester, but many sections were

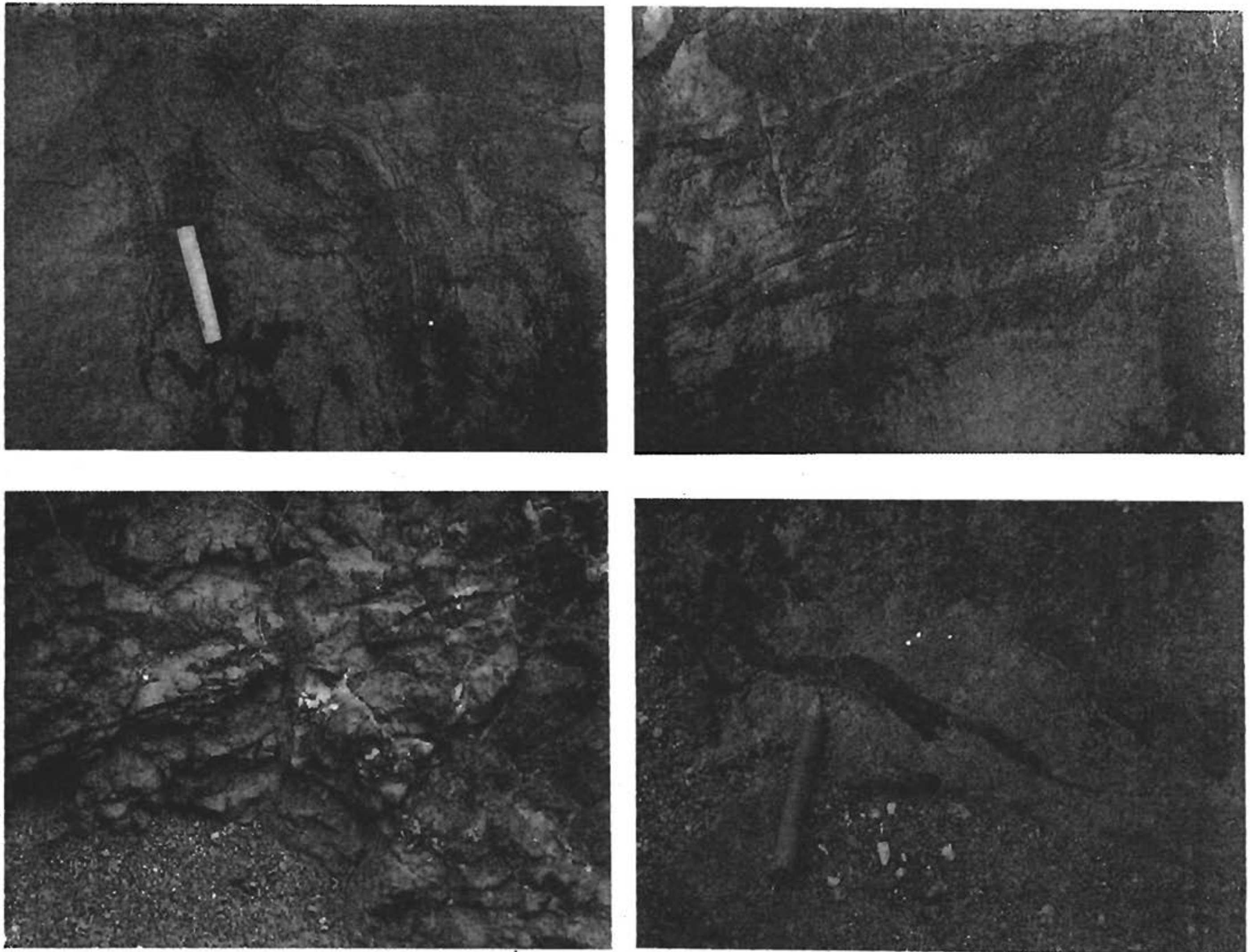

Fig. 1. Chromitite layers (black) in olivine-rich ultramafic rocks around Chilas. Slump folding in top two and bottom right, and wedge-shape layering in the bottom left are sedimentary structures commonly found in the UMAA. The maximum thickness of chromitite layers in the field photograph at the bottom left is 2 cm.

also studied at the University of Peshawar and Imperial College. Analytical procedure has been summarized in Khan et al. (1989) and Jan and Windley (1990).

An unusual feature of the Chilas oxide phases, as in Granada (Arculus, 1978), is the great diversity of their chemical composition. The PGA commonly contains magnetite-ilmenite pairs but no Cr-Al spinel. In the UMA association, ilmenite occurs only rarely. The oxide phases in the rocks of this association display a complete range from pleonaste through Al-Cr-Fe^{3+} compositions to magnetite. There is also another generation of pleonaste in reaction coronas between olivine and calcic plagioclase. In the following, we present details of the various oxide phases in the PG and UMA associations.

The Principal Gabbronorite Association (PGA)

The mineral assemblage in the PGA is characterized by an ubiquitous presence of magnetite–ilmenite oxide mineral pairs. These minerals occur in minor to accessory amounts (generally less than 5 volume %). Textures suggest that they crystallized either simultaneously with or subsequent to the major constituent minerals (plagioclase, clinopyroxene, orthopyroxene) of the gabbronorites in the PGA. In most rocks, typical igneous mosaics comprising tabular to prismatic silicate phases contain oxide-mineral grains, either as discrete constituents of the mosaic, or as inclusions in silicate phases and vice versa. This textural relation is suggestive of a near-cotectic crystallization of the oxides with the silicates. In some rocks there is a tendency of the oxide grains to be interstitial to the silicate phases suggesting a relatively later crystallization than the accompanying silicate phases. The oxide phases in the amphibolite dykes are virtually similar to those in the PGA in terms of texture and composition and are thus not dealt with separately in the following discussion. Representative analyses of iron-titanium oxides from the gabbronorites of the PGA are shown in Table 1.

The phase chemistry of the oxide phases in the rocks of the PGA is presented in Fig. 2. Both the ilmenite and the magnetite display a wide range of composition, owing to subsolidus exsolution. There is a common exsolution of ilmenites into lamellae rich in ilmenite and hematite components, whereas magnetites are exsolved into lamellae of magnetite-rich and ulvospinel-rich components. Exsolved magnetite and ilmenite may together be present in a single grain. In any one sample a wide variety of compositions appears to be present, including phases rich in magnetite, ulvospinel, ilmenite and hematite with various mole proportions of these end members.

Coexisting iron-titanium oxides are commonly used for the determination of temperatures of equilibration and oxygen fugacity ($f\,O_2$) (Buddington and Lindsley, 1964; Spencer and Lindsley, 1981; Stormer, 1983). The mineral pairs from the PGA of the Chilas Complex yield a wide range of temperature (1000–450 °C) and $f\,O_2$ (–10 to –26). On a temperature vs. $f\,O_2$ plot (Fig. 3), the PGA data are scattered in a broad band between the FQM and MH buffers. Such a variation is clearly a manifestation of subsolidus re-equilibration in the form of exsolution under slowly decreasing temperatures. Haggerty (1976) compiled T and $f\,O_2$ variations in a number of rock suites of diverse compositions. Although the Chilas Complex has all the features of a major layered body, the $f\,O_2$ is distinctly higher than the type layered complexes such as Kiglapait, Skaergaard, Somerset Dam, and Kape Edward Holm, particularly at higher temperatures. Oxygen fugacity in these tholeiitic intra-continental layered bodies is generally close to the FQM buffer, whereas in the Chilas Complex it reaches the magnetite-hematite (MH) buffer. Amongst the suites listed by Haggerty (1976), $f\,O_2$ comparable to that of

TABLE 1. REPRESENTATIVE MICROPROBE ANALYSES OF COEXISTING IRON-TITANIUM OXIDES IN THE PG ASSOCIATION, CHILAS COMPLEX.

Sample	K36		CH221		K71	K71	K71	K71	K71
	S	R	S	R	S	S	S	S	R
SiO_2	0.00	0.34	0.53	0.37	0.30	0.00	0.00	0.00	0.00
TiO_2	0.28	43.49	16.91	47.82	0.28	14.09	16.74	20.62	46.53
Al_2O_3	0.40	1.25	0.28	0.13	0.48	0.45	0.29	0.26	0.08
Cr_2O_3	0.20	0.06	0.66	0.12	1.58	0.85	0.63	0.69	0.16
Fe_2O_3	67.26	17.07	32.47	10.06	65.33	39.92	34.91	26.14	10.43
FeO	30.78	38.13	45.99	41.33	31.52	42.99	45.85	48.19	38.98
MnO	0.12	0.59	0.12	0.54	0.00	0.27	0.26	0.22	0.88
MgO	0.12	0.44	0.38	0.88	0.10	0.41	0.37	0.50	1.06
NiO	0.02	0.00	0.01	0.00	0.00	0.03	0.04	0.05	0.08
Total	99.18	101.37	97.35	101.25	99.59	99.01	98.59	96.68	98.21
Si	0.000	0.004	0.021	0.009	0.012	0.000	0.000	0.000	0.000
Ti	0.008	0.813	0.491	0.894	0.008	0.404	0.482	0.602	0.897
Al	0.018	0.037	0.013	0.004	0.022	0.020	0.013	0.012	0.002
Cr	0.006	0.001	0.020	0.002	0.048	0.026	0.019	0.021	0.003
Fe^{3+}	1.959	0.319	0.944	0.188	1.891	1.146	1.005	0.763	0.201
Fe^{2+}	0.997	0.792	1.486	0.859	1.014	1.371	1.451	1.564	0.835
Mn	0.004	0.012	0.004	0.011	0.000	0.009	0.008	0.007	0.019
Mg	0.007	0.016	0.022	0.033	0.006	0.023	0.021	0.029	0.041
Ni	0.001	0.000	0.000	0.000	0.000	0.001	0.001	0.002	0.002
X_{usp}	0.008	—	0.514	—	0.009	0.417	0.492	0.616	—
X_{ilm}	—	0.834	—	0.903	—	—	—	—	0.896
T°C	602		913		574	867	917	1010	
$\log f O_2$	−15.20		−12.16		−17.17	−12.63	−11.95	−10.73	

S = Spinel phase; R = Rhombohedral Fe-Ti oxide (ilmenite). Formula is based on four oxygens in the spinel phases, and three oxygens in the case of ilmenites. Formula and the mole fractions of ulvospinel (X_{usp}) and ilmenite (X_{ilm}) are calculated from the analyses of Fe-Ti oxides using recalculation scheme of Stormer (1983), and T°C and $-\log f O_2$ have been determined using the model of Spencer and Lindsley (1981). All the calculations have been done using a microcomputer programme written and supplied by J.C. Stormer.

the Chilas Complex (but at relatively higher temperatures) is found in intermediate extrusive suites. The calc-alkaline nature and an island arc-related origin of the PGA in the Chilas Complex is in agreement with this comparison. The oblique trend of the Chilas Complex relative to the FQM buffer on the temperature-$f O_2$ plot (Fig. 3) suggests that re-equilibration and exsolution started under high $f O_2$ at high temperatures, and continued under reducing conditions at subsolidus temperatures.

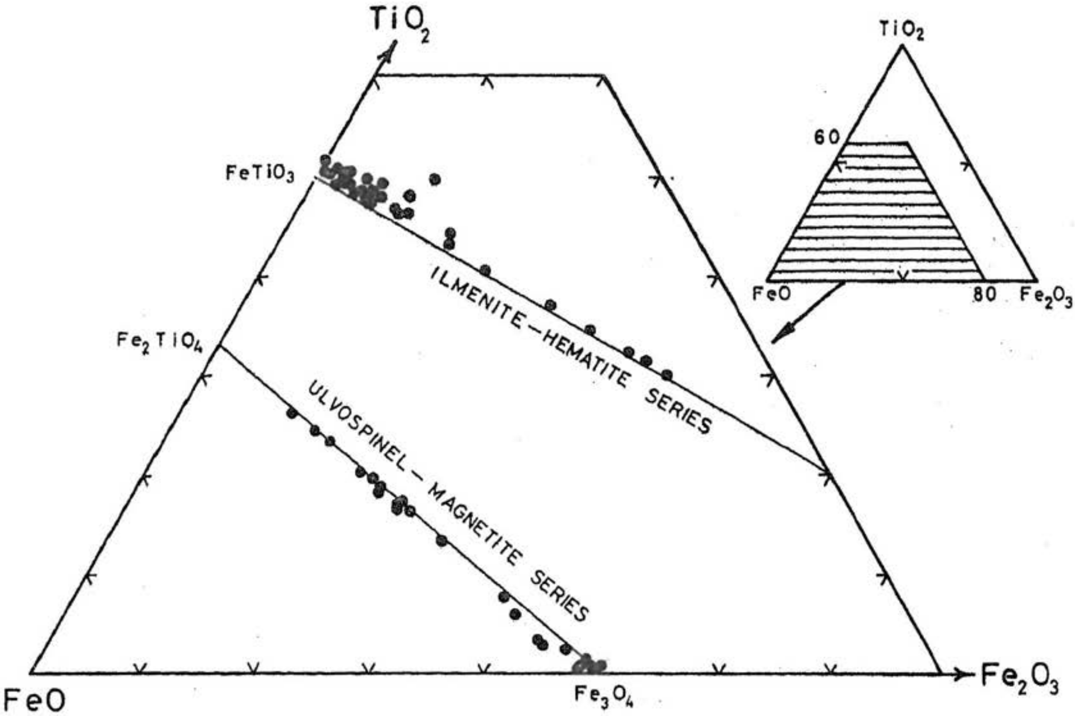

Fig. 2. Phase chemistry of oxide minerals in the PG association of the Chilas Complex. The broad compositional variations forming magnetite-ulvospinel and ilmenite-hematite series are due to extensive exsolution at subsolidus temperatures.

The Ultramafic-Mafic-Anorthosite Association (UMAA)

Al-Cr-Fe³⁺ Spinels

Spinels in the UMA association are characterized by a great variation in composition (Table 2). In this respect, they resemble those of the xenoliths and plutonic blocks in the Aleutian (Conrad and Kay, 1984; DeBari et al. 1987) and lesser Antilles island arcs, especially those of Granada (Arculus, 1978; Arculus and Wills, 1980). The variation is not restricted to different samples and model mineralogy; within a single thin section there may be substantial variations in the tiny grains of accessory spinel. There are three types of variations.

1. Exsolution. Cr-Al spinel with intimately associated lamellae, blebs and margins of Fe^{3+}-rich compositions (henceforth referred to as magnetite). In one chromitite, brown-green chromite grains contain trails of magnetite blebs which are identical in composition to the magnetite matrix of the chromite grains (Fig. 4c). Magnetite-spinel association of this type is a typical product of exsolution of homogeneous grains during subsolidus re-equilibration and cooling. The exsolved magnetite, like the host spinel, varies in composition from sample to sample (but rarely from grain to grain within a thin section) in terms of its Fe^{3+}, Al and, especially, Cr contents. The exsolved spinels can broadly be grouped into two types, one of which is much finer grained than the other. The exsolved phase forms blebs, lamellae and rods, in some cases concentrated along the margins of the host grains. Fig. 4 shows some features of the exsolved oxide grains.

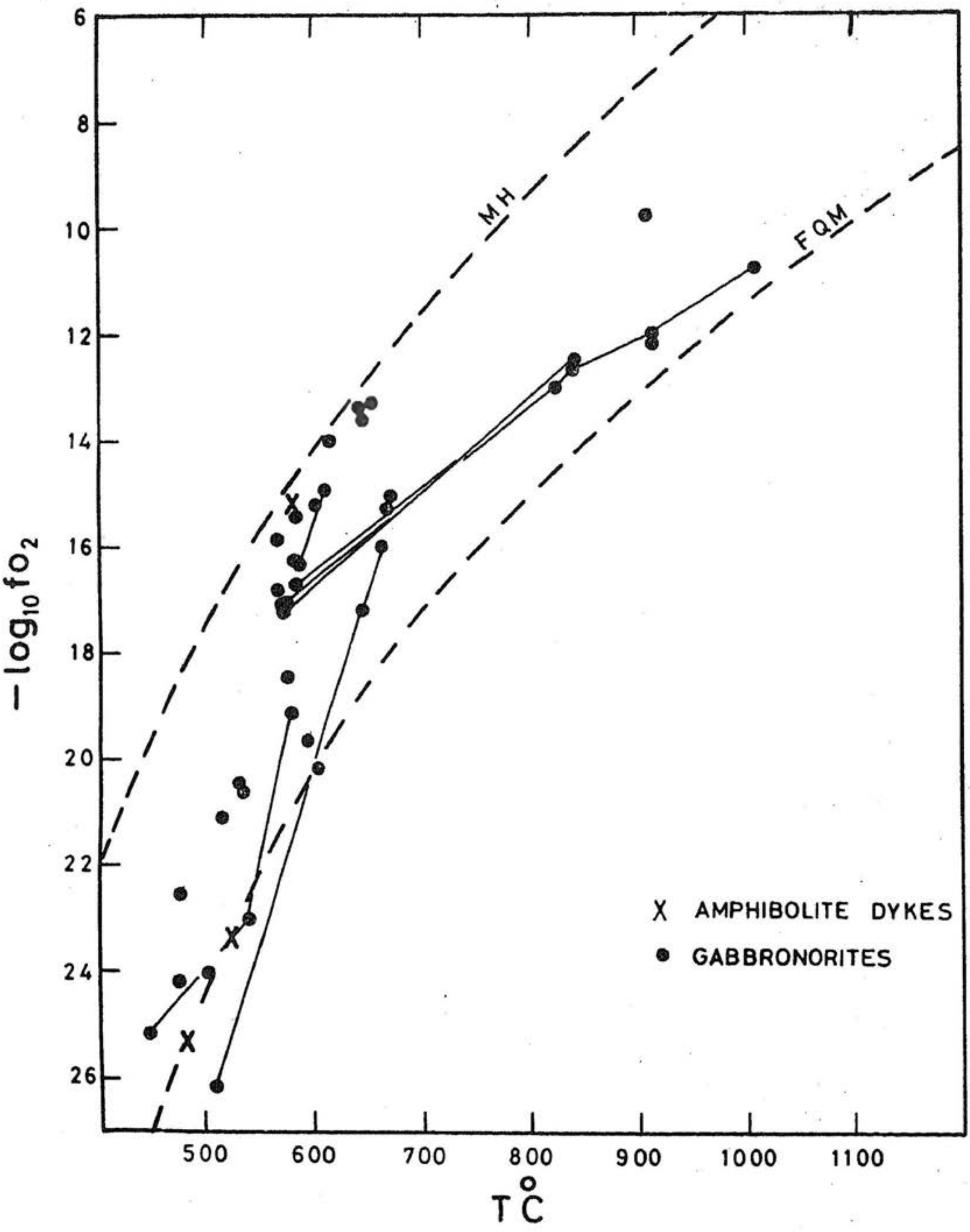

Fig. 3. T °C- log fO_2 relationship between co-existing Fe-Ti oxides from the gabbronorites of the PG association and the amphibolite dykes. Note that some samples contain several generations of exsolved Fe-Ti oxides with different compositions so that these samples show a broad range of temperatures-log fO_2.

TABLE 2. REPRESENTATIVE MICROPROBE ANALYSES OF SPINELS FROM THE UMA ASSOCIATION, CHILAS COMPLEX.

Sample	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
	CH889	CH889	CH889	CH889	CH889	IK981	6143	K62	K62	K62	K62	K74	K32	K64	K79
	E	H (4)		H	E	(2)		H	E	(3)	(3)	(4)	C (2)	C (2)	C (2)
SiO_2	0.32	0.11	0.42	0.19	0.37	0.27	0.22	0.21	0.00	0.26	0.21	0.37	0.00	0.00	0.20
TiO_2	2.11	0.14	7.58	1.33	4.24	0.95	1.65	0.00	0.05	0.21	0.04	1.38	0.07	0.00	0.02
Al_2O_3	4.05	41.45	10.83	20.53	6.13	16.94	11.07	51.33	0.71	34.59	60.11	1.74	57.82	60.09	64.73
Cr_2O_3	14.49	17.44	22.93	28.60	21.62	36.99	31.09	10.07	8.12	21.27	3.79	23.83	1.65	0.10	0.09
FeO*	70.64	29.80	51.00	40.48	59.87	33.78	48.72	21.94	79.26	32.99	18.85	67.81	24.50	21.58	17.32
MnO	0.35	0.33	0.60	0.14	0.62	0.57	0.17	0.28	0.00	0.23	0.16	0.39	0.31	0.21	0.26
MgO	1.14	9.57	3.06	6.05	3.09	8.39	5.16	14.49	2.04	8.62	16.28	1.41	13.44	14.78	18.07
NiO	0.43	0.28	0.06	0.00	0.03	0.17	0.28	0.35	0.00	0.16	0.20	0.13	0.00	0.13	0.19
Total	93.53	98.89	96.48	97.33	95.97	98.06	98.36	98.67	90.18	98.33	99.64	97.06	97.79	96.89	100.88
FORMULA PROPORTIONS ON THE BASIS OF 4 OXYGENS															
Si	0.01	0.00	0.01	0.01	0.01	0.01	0.01	0.01	0.00	0.01	0.01	0.01	0.00	0.00	0.01
Ti	0.06	0.00	0.20	0.03	0.12	0.02	0.04	0.00	0.00	0.01	0.00	0.04	0.00	0.00	0.00
Al	0.18	1.43	0.45	0.80	0.26	0.65	0.45	1.67	0.03	1.24	1.86	0.08	1.86	1.91	1.94
Cr	0.43	0.40	0.64	0.75	0.62	0.96	0.84	0.22	0.25	0.51	0.08	0.69	0.04	0.00	0.00
Fe^{3+}	1.28	0.16	0.47	0.38	0.86	0.35	0.65	0.10	1.71	0.23	0.04	1.17	0.11	0.08	0.05
Fe^{2+}	0.93	0.57	1.04	0.74	0.94	0.57	0.75	0.41	0.89	0.61	0.37	0.90	0.45	0.41	0.32
Mn	0.01	0.01	0.02	0.00	0.02	0.02	0.01	0.00	0.00	0.01	0.00	0.01	0.01	0.01	0.01
Mg	0.06	0.42	0.16	0.30	0.17	0.41	0.26	0.59	0.12	0.39	0.64	0.08	0.55	0.60	0.68
Ni	0.01	0.01	0.00	0.00	0.00	0.01	0.01	0.01	0.00	0.01	0.00	0.00	0.00	0.00	0.00
Cr no	70.6	21.9	58.7	48.4	70.5	59.4	65.3	11.6	88.5	29.2	4.1	90.2	1.88	0.13	0.06
Mg no	6.4	42.1	13.3	28.8	13.3	71.7	26.1	59.4	11.8	39.0	63.2	7.8	54.83	59.20	67.95
Cr	22.7	20.3	41.0	38.9	35.6	48.9	43.5	11.0	12.6	25.9	4.0	35.5	1.78	0.13	0.06
Al	9.5	71.9	28.8	41.5	14.9	33.3	23.1	84.0	1.6	62.7	93.8	3.9	92.8	96.04	97.67
Fe^{3+}	67.9	7.8	30.1	19.7	49.4	17.9	33.4	4.9	85.8	11.4	2.2	60.6	5.41	3.83	2.27

FeO* = Total iron as FeO; H = Host; E = Exsolved. C = Corona spinels. Average analyses are indicated by numbers in parentheses.
CH889 = Chromite layered peridotite;. 1, 2, 3 from the peridotite layer, 4 and 5 from the chromitite streak. IK981 and 6143 = chromitites. K62 = peridotite. K74 = dunite. K32 = olivine gabbro. K64 = banded gabbronorite-anorthosite. K79 = plagioclase-bearing peridotite.

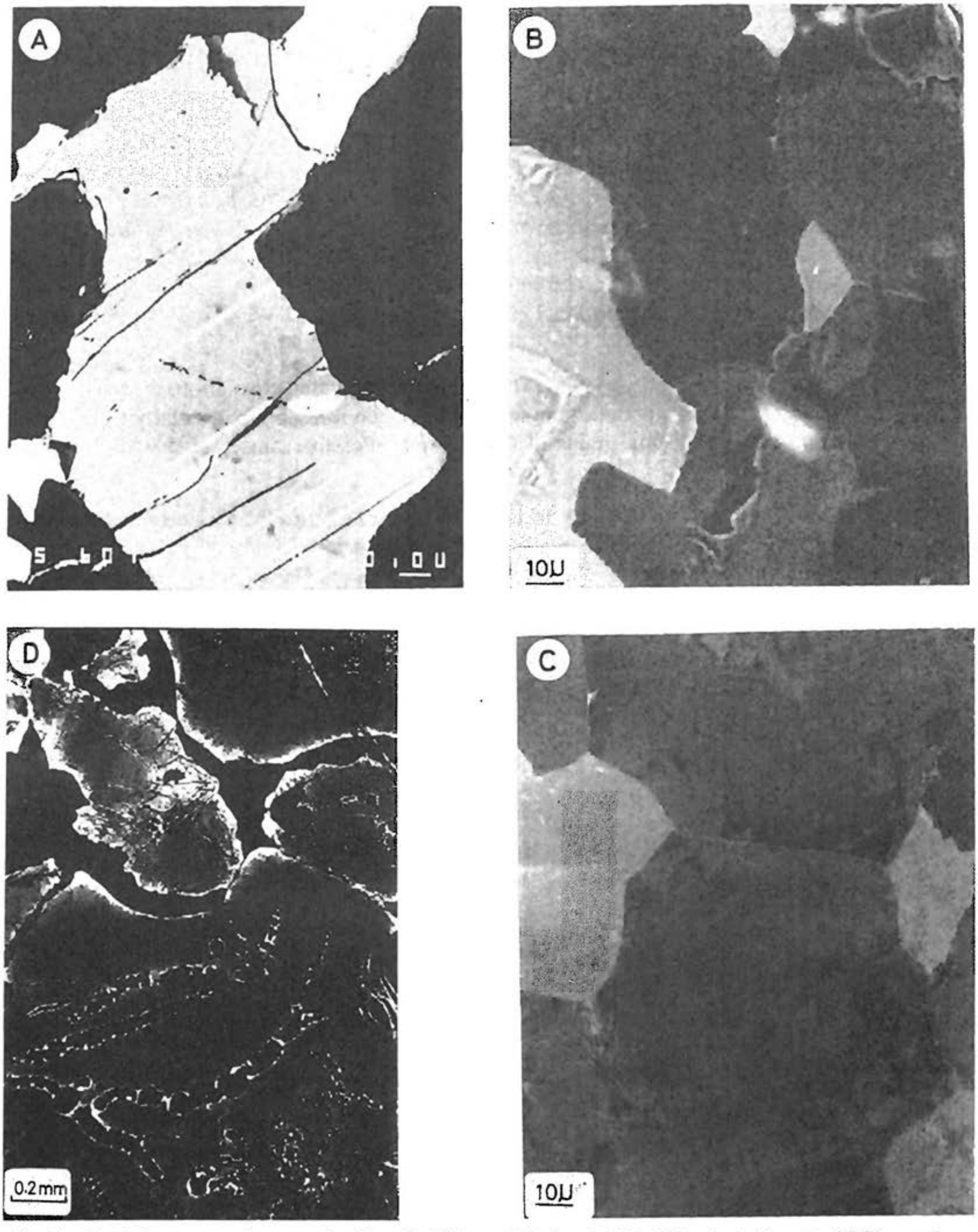

Fig. 4. Exsolution textures in magnetite (from the PG association) and Al-Cr-Fe^{3+} spinels (from the UMA association), Chilas Complex. A) Co-existing magnetite (gray) and ilmenite (white) oxide-mineral phases, with magnetite showing exsolved lamellae and relatively coarser blebs of ilmenite. B) Exsolution of spinels into Fe^{3+}-rich (gray) and Al-rich (dark gray) compositions (both contain 100 $Cr/R^{3+} \sim 32$). Each of the two exsolved phases shows considerable variation in Al/Fe^{3+} ratio, reflected in various shades of gray and dark gray in the atomic image. The exsolution is typically in the form of coarse blebs and lamellae. Whitish areas are silicate phases. C) Exsolution of spinel into coarse as well as finally exsolved components. D) Chromite grains containing trails of exsolved magnetite blebs. These blebs are compositionally identical to the magnetite interstitial to the chromite grains. A, B, and C are back-scattered electron images, while D is a photomicrograph taken under plain-polarized light.

2. Zoning. Some zoned grains have cores that contain generally higher Cr and margins that have higher Al and, in few cases, a little Fe^{3+}; reverse relations are noted rarely. Some of these might be the product of reaction between magma and early formed crystals but most appear to be due to re-equilibration with the associated silicates: diffusion of Cr from the margins of spinel grains into the silicate neighbours or, less likely, alumina in the reverse direction. Small amounts of chlorite (with up to 2% Cr_2O_3) and serpentine occur in some samples and secondary hornblende in many. The growth of these minerals may have variably influenced the composition of the adjacent spinel grains. The outer zones, however, are quite differnt from ferritchromite (±magnetite) produced during chromite alteration (Weiser, 1967; Beeson and Jackson, 1969; Onyeagocha, 1974; Bliss and MacLean, 1975; Hoffman and Walker, 1978; Ahmed and Hall, 1981; Jan et al., 1985).

3. Grain-to-grain chemical variation. This variation, excluding exsolution, is seen in many samples. It is generally less pronounced in most of the chromitites, but particularly extensive in some peridotites containing tiny grains of Cr-Al spinel. Possible causes of this variation are discussed later.

The spinel analyses are plotted in terms of Cr-Al-Fe^{3+} in Fig. 5. Tie-lines have been drawn between the exsolved Cr-Al spinel and magnetite pairs. These define nicely a solvus (Fig. 6) which is similar to those of the pairs from Fiskenaesset, Greenland (Steele et al. 1977), Red Lodge, Montana (coarsely exsolved type of Loferski and Lipin, 1983), Tugela Rand, S. Africa (Eales et al., 1988), and Miyamori, Japan (Ozawa, 1988). The solvi for the finely exsolved spinels from the Red Lodge (Loferski and Lipin, 1983) are somewhat, and those of Kusa, Sweden (Zakrzewski, 1989), considerably different from these. The plots of the Chilas

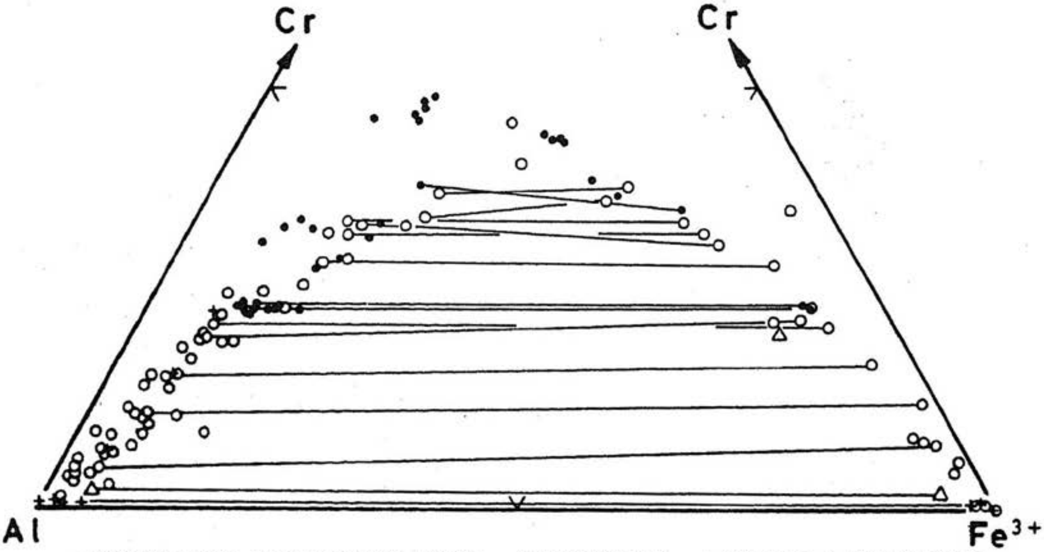

Fig. 5. Cr-Al-Fe^{3+} plots of the spinels from the UMA association, Chilas Complex. In four analyses of the exsolved spinel, Ti was added to Fe^{3+}. Tie-lines have been drawn between exsolved pairs only; others have been omitted for the sake of clarity. In several cases, analyses of similar composition within a thin section were averaged to avoid overcrowding. Segregated chromites with high Cr content are unexsolved and plot above the solvus shown in Fig. 6.

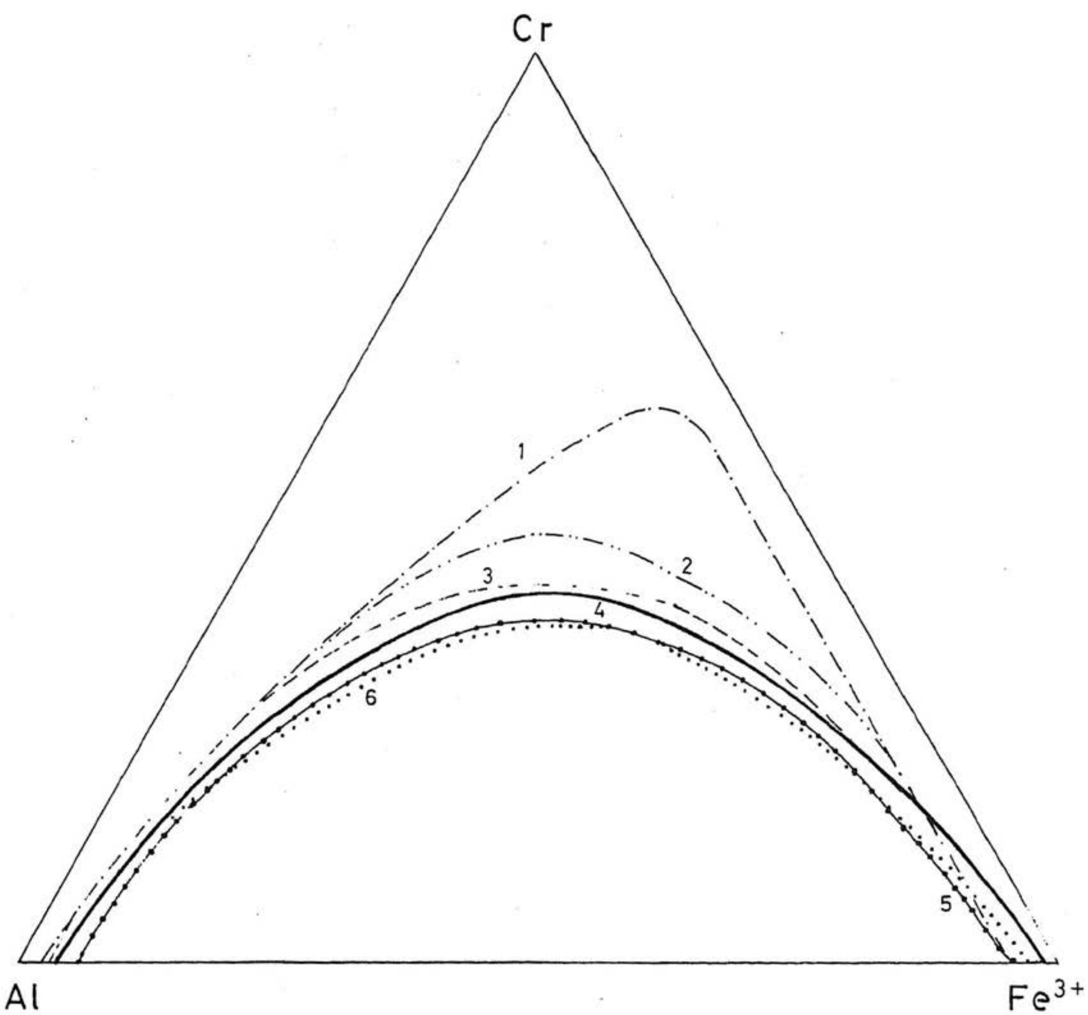

Fig. 6. The system (Mg-Fe^{2+})Fe$^{3+}_2$O$_4$–(Mg-Fe^{2+})Cr$_2$O$_4$–(Mg-Fe^{2+})Al$_2$O$_4$ with the positions of solvi for spinel pairs from different areas. 1: finely unmixed, 2: coarsely unmixed spinels from Red Lodge, Montana (Loferski and Lipin, 1983); 3: Fiskenaesset, Greenland (Steele et al., 1977); 4: Chilas (this study); 5: Miyamori, Japan (Ozawa, 1988); 6: Tugela Rand, S. Africa (Eales et al., 1988). Fe^3 for No. 6 = Fe^3+2Ti. Coexisting spinels reported by Muir and Naldrett (1967), Purvis et al. (1972) and Springer (1974) plot in the region occupied by solvi 3 to 6.

spinels along the solvus in Fig. 5 suggest that they may have steadily cooled from high (>800°C) to low (<500°C) temperature (cf. Turnock and Eugster, 1962).

The grain-to-grain variation within some samples is displayed in Fig. 7. When present, this variation is best seen in Cr-Al spinels although magnetite is also variable in some specimens. Fig. 7A shows the plots of three thin sections with segregated and seven thin sections with accessory spinel. Two of the former display some variation in Al and Fe^{3+} but less so in Cr contents, whereas the third sample shows a considerable variation in all three components in the five spots analyzed. This sample was collected from a highly disrupted, 2 cm thick band of

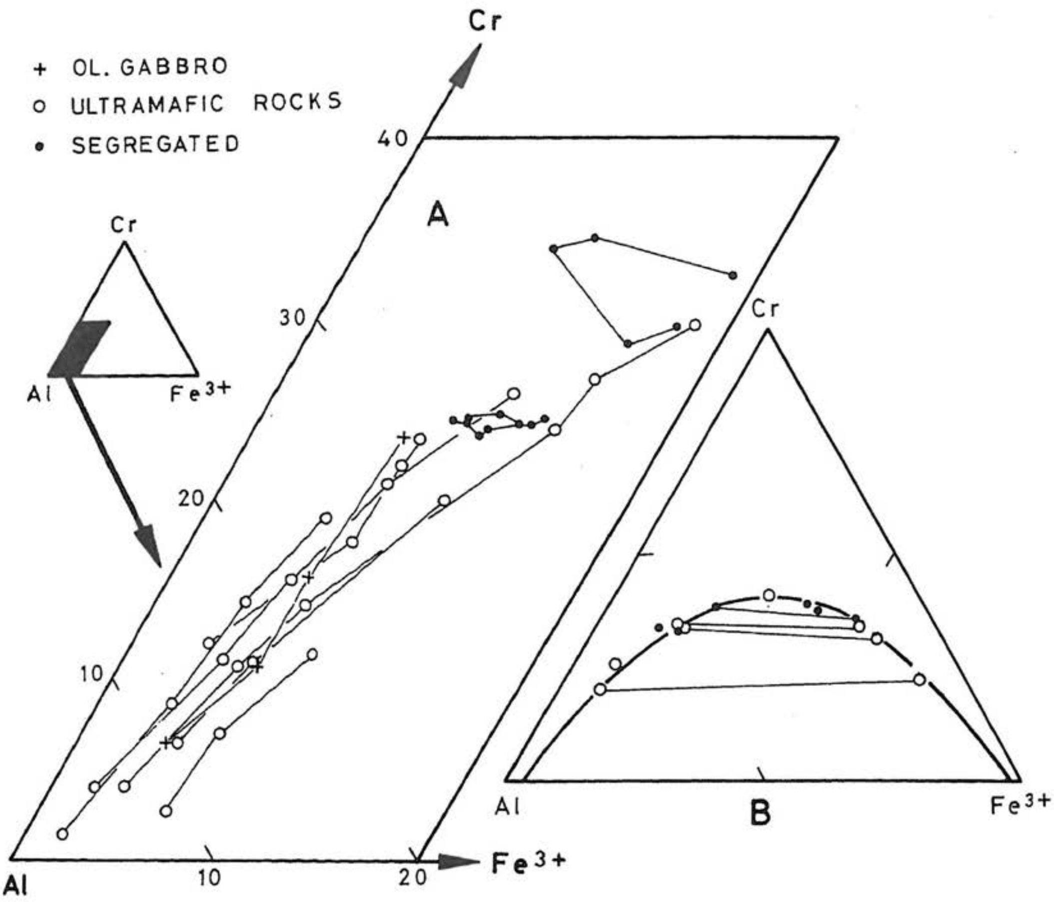

Fig. 7. A. Extent of variation in the composition of the Chilas spinels in nine ten sections. Tie-lines connect analyses within a thin section. Exsolved Fe^{3+}-rich compositions are not shown. B. Variation in spinel composition within a thin section of a layered peridotite (CH889) containing streaky bands of chromite (< 2 mm thick). Note the location of the analyses along the solvus. Tie-lines connect exsolved pairs.

"chromite" intermixed with olivine-rich silicate matrix. Both re-equilibration with the silicates and alteration may have contributed to the compositional variability. The variation in the accessory spinel is noteworthy. In one thin section the extreme compositions in seven grains are $Cr_{29.7}Al_{52.2}Fe^{3+}_{18.1}$ and $Cr_{4.0}\,Al_{92.3}Fe^{3+}_{3.7}$.

An important aspect of the accessory spinel is that despite the variation, the analyses plot along or close to the solvus. This is particularly true of a layered peridotite with streaky bands (< 2 mm thick) of chromite in which 14 analyzed points fall along the Cr-rich portion of the solvus (Fig. 7B). This leads to conclude that the spinels have chemically adjusted themselves to falling temperatures by reacting with the neighbouring silicates.

Some discrete spinel grains, probably lying initially along the plagioclase-olivine interfaces, are incorporated in orthopyroxene-hornblende-pleonaste coronas. These have variably lower Cr/Al ratios than those grains away from coronas. These became impoverished in Cr in favour of hornblende, leading to a second generation of Al spinel (pleonaste).

Variation in the composition of spinel can also be explained by invoking disequilibrium crystallization or continuously changing magma composition (magma mixing, fresh supply of magma, assimilation, thermal diffusion, turbulence). But these processes do not appear to be plausible mechanisms for the Chilas spinels because (1) they cannot explain variations in those grains that are included in the silicates, (2) the chromitite spinels are fairly homogeneous, and (3) the spinel-associated primary silicates are chemically uniform throughout a thin section. We close this discussion with the assertion that compositional variations in the Chilas spinels within the domain of a thin section have been caused by reaction with adjacent silicates during cooling, and by exsolution. Diffusion profiles in the adjacent silicates support the hypothesis of re-equilibration.

The projection of the analyses onto the Pc-Ch-He-Sp face of the spinel prism is shown in Fig. 8A. Interestingly, the spinels cover the entire range of Cr numbers (100 Cr/(Cr + Al)); however, if the magnetite analyses (100 Fe^{3+}/R^{3+} or Fe^{3+} no > 50, 100 $Mg/(Mg+Fe^{2+})$ or Mg no < 20) are excluded, their range for Cr nos is reduced to a maximum of 65. Of these the segregated spinels range from 25 to 65, whereas the corona spinels have very low Cr numbers. The magnetite analyses cover the entire range of Cr numbers and the gaps may be due to insufficient analyses. Ignoring irrelevent magnetite analyses with low Cr numbers, the Chilas spinels diaplay a well-defined linear trend where Cr number increases as Mg number decreases. Such a relation is also displayed by spinels from SE Alaskan-type complexes, abyssal and alpine-type (residual) peridotites (compare Dick and Bullen, 1984; Jan and Windley, 1990). But the Chilas spinels have a significant difference with abyssal and alpine-type peridotites: their Mg nos for their respective Cr nos are much lower and their Cr nos vs. Mg nos trend has a less steep slope than those of the latter (Fig. 9A). The Mg nos of the Chilas spinels are also lower than those of the spinels in xenoliths and plutonic rocks in Lesser Antilles and Aleutian island arcs (see Fig. 8A).

The segregated spinel in Chilas can be distinguished from the accessory spinel in two ways: 1) they have higher Mg nos for their respective Cr nos (or higher Cr nos for their Mg nos) than the accessory spinel, and 2) they display a limited range for these numbers. Indeed the most Cr–rich spinels occur in chromitite seams, lenses and stringers. Enrichment in Cr and Mg nos in segregated relative to accessory chrome-spinels have been reported in the Sakhakot-Qila (Ahmed, 1984), Jijal (Jan and Windley, 1990), Waziristan (Jan et al., 1985), Shangla and Bela (Arif, 1990) areas of Pakistan and many other areas of the world. The various mechanisms suggested for this difference have been summarised by Jan and Windley (1990). The corona spinels, shown for comparison in Fig. 8A, have typically low Cr nos.

In order to project the analyses onto the Mf-Mt-Ch-Pc face of the spinel prism, their Fe^{3+} nos are plotted against Mg nos in Fig. 8B. Again there is a negative correlation between the two variables. The analyses fall within as well as outside the field of island arc rocks. The Chilas spinels have a more expanded and complete range of Fe^{3+} nos than even the island arc spinels. The Fe^{3+} nos of the magnetite, expectedly, are the highest, whilst the Cr-Al spinels have Fe^{3+} nos below 35. Broadly speaking, for a particular Mg no, the segregated spinels display higher Fe^{3+} nos than those of the peridotites which in turn are higher than those of the mafic rocks and coronas. This observation is in harmony with that of Dick (1977).

Several workers have shown that the composition and stability of spinel is dependent not only on bulk composition, pressure, and temperature, but also on oxygen fugacity (fO_2)

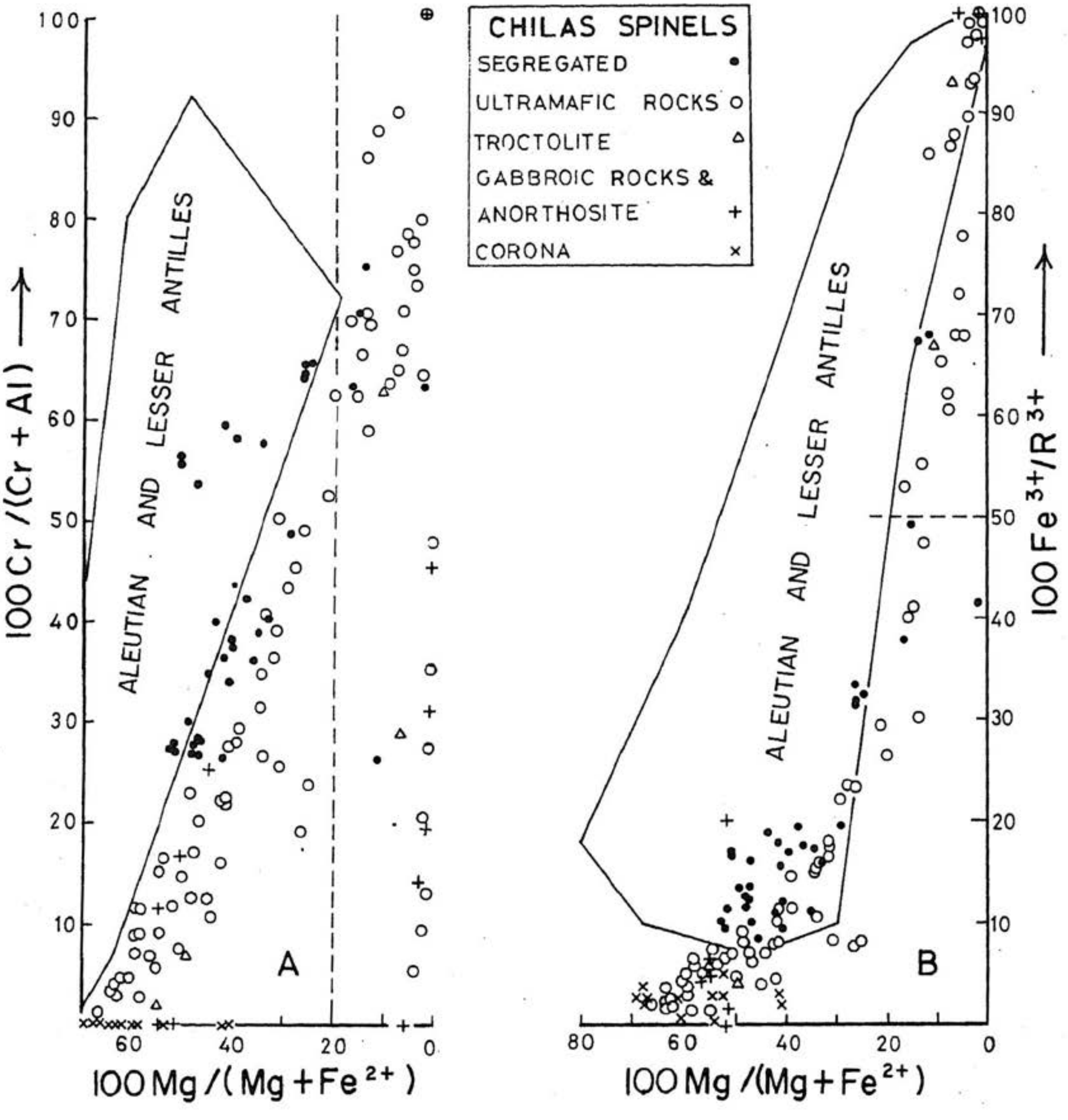

Fig. 8. Plots of Cr nos (100 Cr/(Cr+Al)) and Fe^{3+} nos (100 Fe^{3+}/R^{3+}) against Mg nos (100 Mg/(Mg+Fe^{2+})) in the Chilas spinels. Fields for spinels from the Lesser Antiles and Aleutian island arcs are based on the data of Arculus (1978), Arculus and Wills (1980), Conrad and Kay (1984), and DeBari et al. (1986). Dashed line with Mg no 20 separates magnetitic compositions (except five spots) on the right from Cr-Al spinel (left) in Fig. 8A. Dashed line in Fig. 8B also demarcates magnetite (above) from Cr-Al spinel analyses (below).

(cf. Rivalenti et al., 1981). Hill and Roeder (1974) and Fisk and Bence (1980) found that with increasing $f\ O_2$, Cr spinel becomes enriched in Fe^{3+} and impoverished in Mg. Therefore $f\ O_2$ may be determined from spinel composition alone if olivine and pyroxene are associated with it. Thus Irvine (1965) contoured the spinel prism with a set of surfaces representing the possible compositions for different $f\ O_2$ at constant P and T. The intersections of these surfaces

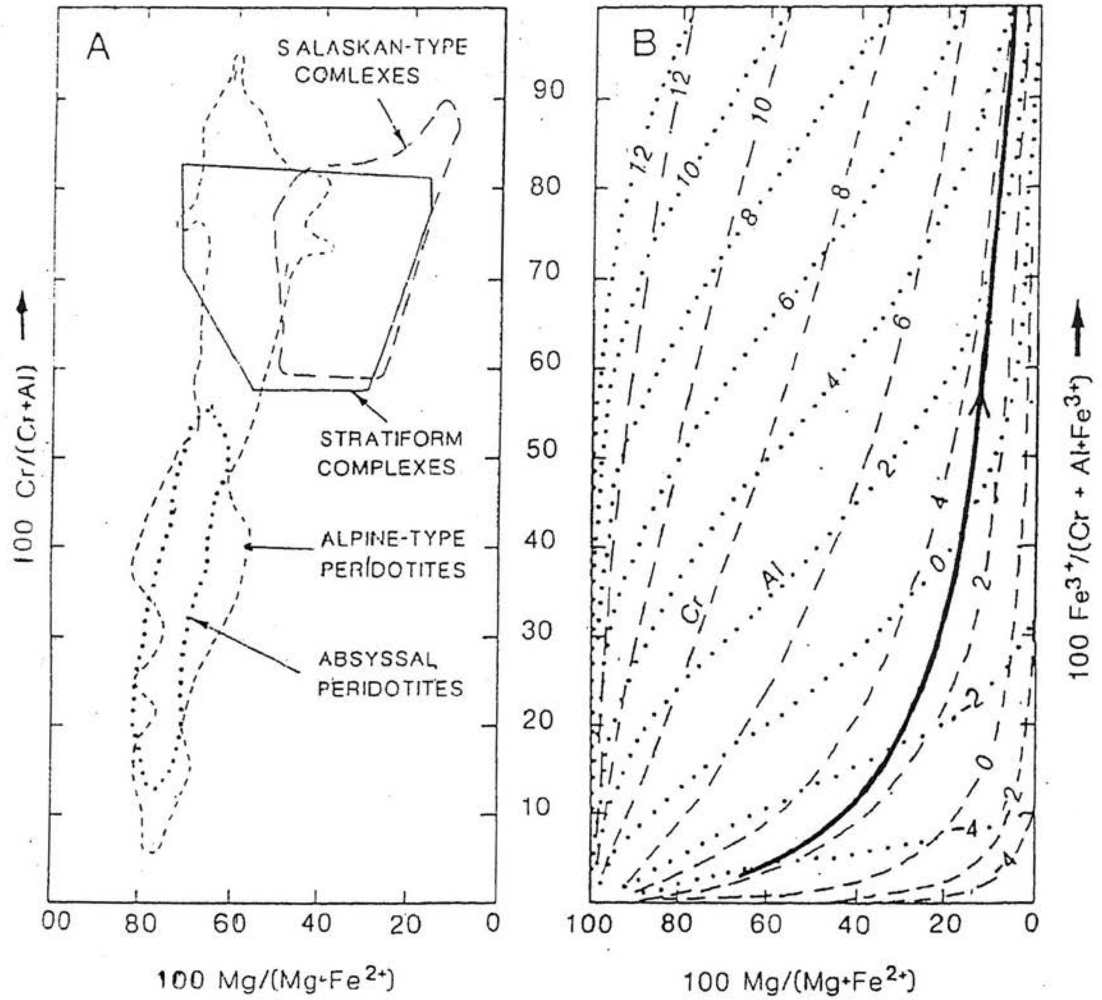

Fig. 9. Plots of Cr and Fe^{3+} nos against Mg nos.

A. Fields of Cr-Al spinels from various types of complexes for comparison with Chilas (Fig. 8A) are based on the data of Irvine (1967), Bird and Clarke (1976), Dick and Bullen (1984), and Jan and Windley (1990).

B. Contours of theoretical oxygen fugacity isobars (Irvine, 1965). Dashed lines are projections of isobars for Al-free system and dotted lines for Cr-free system. Arrowed curve shows the trend of the UMAA spinels and is based on Fig. 8B.

(fO_2 isobars) with Cr- and Al-free faces of the spinel composition prism are shown in Fig. 9B, together with the trend for the Chilas spinels. The trend resembles closely the low fO_2 isobars for Cr spinel. Thus the spinel compositions may have been at least partly driven in the direction of the arrowed trend during subsolidus re-equilibration with the neighbouring silicates or exsolution. The relative constancy of composition in most of the segregated spinel samples, coupled with the small amounts of associated silicates (mostly olivine), suggests that subsolidus re-equilibration would not have much affected their composition. Therefore, their plots along the trend of the accessory spinel suggest that the Cr-Al-Fe^{3+} oxides in the Chilas UMAA have formed under low fO_2, broadly similar to those in layered complexes.

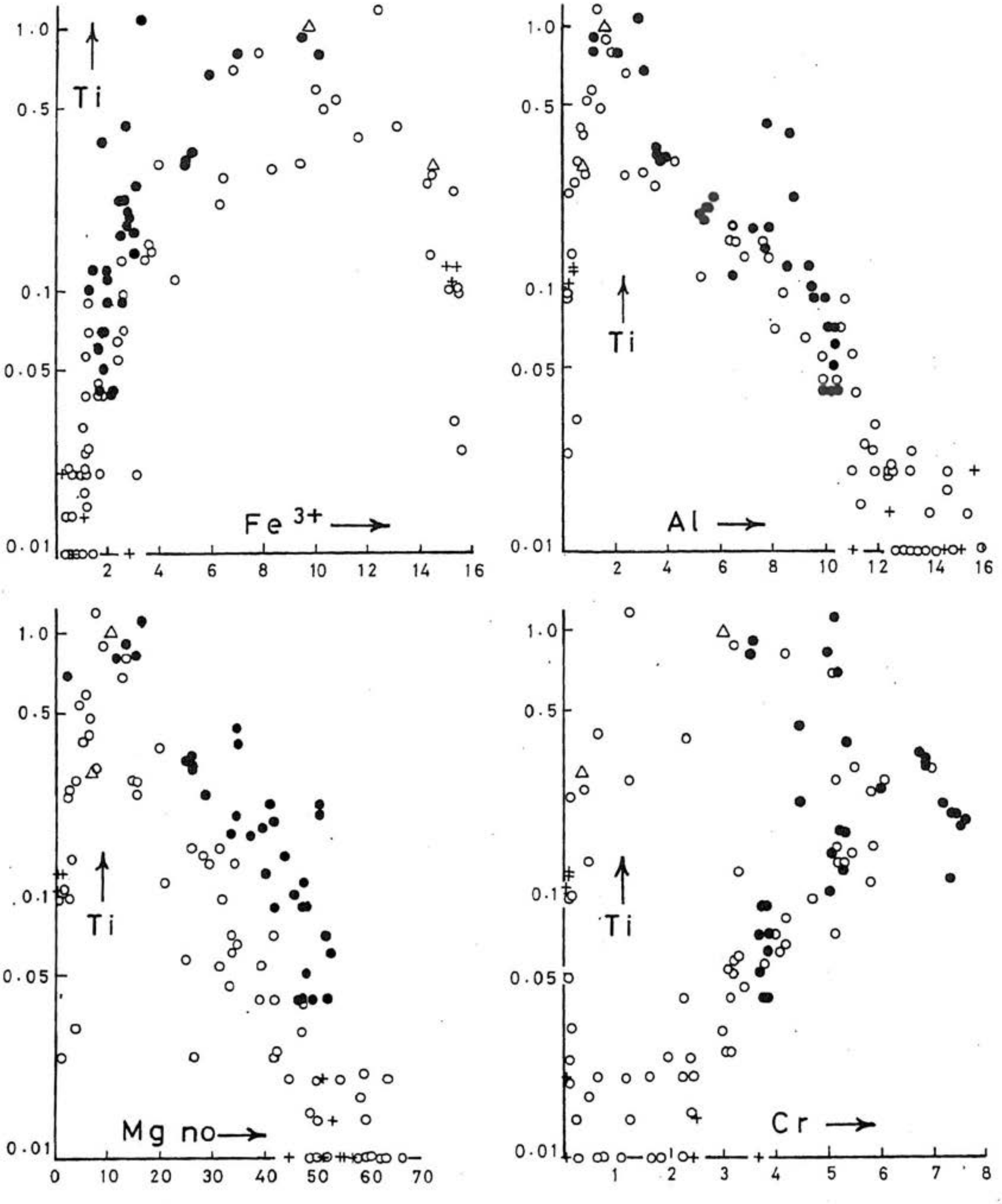

Fig. 10. Plots of Ti against Fe^{3+}, Al, Cr (per 32 oxygens) and Mg no in the UMAA spinels occurring in segregations (dots), and accessory amounts in ultramafic rocks (circles), troctolite (triangles), and gabbronorites and anorthosites (crosses).

The TiO_2 content of the spinels is very variable and ranges from 0.01 to 4.0 wt. %, but mostly from 0.1 to 2.0 %. With one exception, the TiO_2 against Cr_2O_3 plots of the analyses fall outside the fields of oceanic cumulates and tectonites investigated by Herbert (1982). This is because of their lower Cr_2O_3 (and consequently higher TiO_2/Cr_2O_3 ratios) than the oceanic

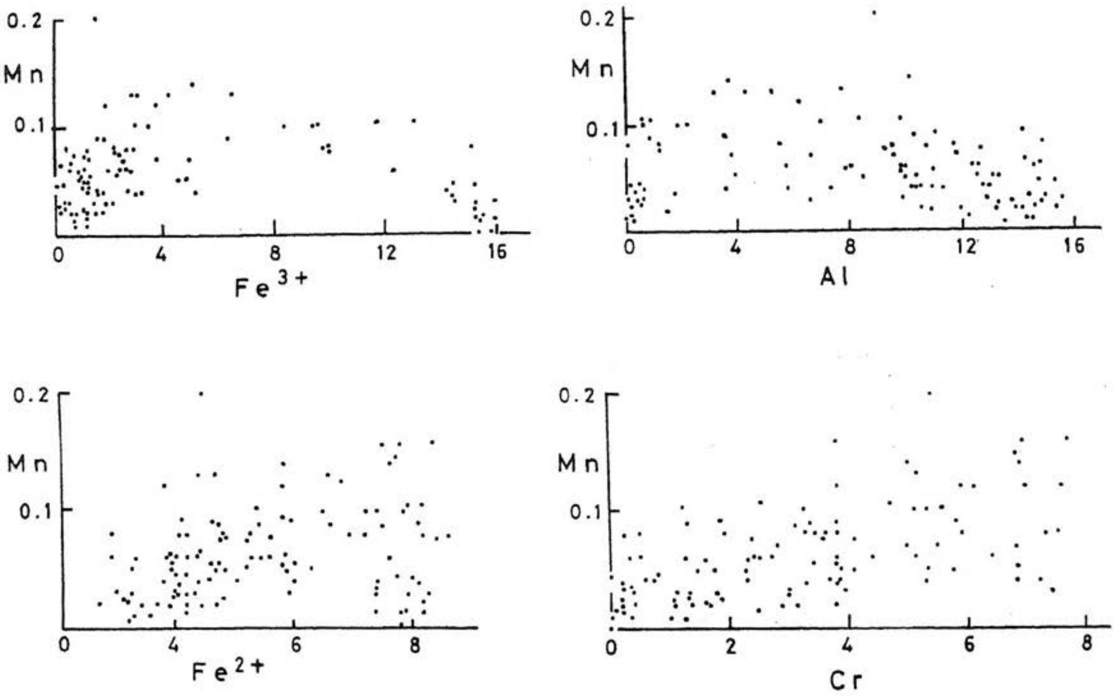

Fig. 11. Plots of Mn against Fe^{2+}, Fe^{3+}, Al, Cr (per 32 oxygens) in the spinels of UMAA.

rocks. In terms of TiO_2 content alone, the UMAA spinels are comparable to those produced in a variety of tectonic environments, however, residual peridotites typically contain lower levels of TiO_2, generally below 0.3 wt. % (Dickey, 1975; Herbert, 1982; Dick and Bullen, 1984).

The Ti against Fe^{3+}, Al, Cr (per 32 oxygens) and Mg no plots are shown in Fig. 10. Ignoring some magnetite analyses, Ti shows a positive correlation with Fe^{3+} and Cr, and a negative correlation with Al and Mg nos. In the Jijal complex, Jan and Windley (1990) report a positive correlation in Ti and Fe^{3+}, a negative correlation in Ti and Cr, and no significant correlation between Ti and Al. In fact the negative correlation between Ti and Cr in Jijal is similar to that in SE Alaskan-type complexes (see Fig. 5 of Jan and Windley, 1990), and the opposite relation in the Chilas spinels is surprising. The Jijal ultramafic rocks are also regarded to be deep-seated island arc cumulates but their olivine and pyroxenes are more magnesian than those of Chilas and they contain high-Cr chromite.

The Mn content of the Chilas spinels is plotted against Fe^{2+}, Fe^{3+}, Cr, and Al in Fig. 11. Ignoring the magnetite plots, Mn shows an increase with Fe^{2+}, Fe^{3+}, and Cr, and a decrease with Al. The Mn against Fe plots clearly show that Mn decreases as magnetite component increases in the spinels beyond 50 mole percent. In other words, the positive correlation between Mn-Cr and Mn-Fe^{3+} are the artifacts of Mn-Fe^{2+} substitution in spinels not enriched in the magnetite component, rather than an assumed Mn^{3+} substitution for Cr and Fe^{3+}.

The NiO content of the analyses is below 0.2 wt. % in most cases, but reaches up to 0.5%. The accuracy of determination for such low levels can be suspected, as also suggested by the discrepancy arising in the samples analyzed in different laboratories (values determined in Peshawar are characteristically lower than those at Leicester). For this reason, the relaionships between Ni and other elements were not explored.

Ilmenite

Only nine of the several hundred spot analyses in the oxide phases of UMAA turned out to be ilmenite. These were found in two dunites, a chromitite and a layered gabbronorite–anorthosite. The ilmenite is intimately associated with either magnetite or Fe^{3+}-Cr-Al spinel and appears to be a product of subsolidus exsolution. Compositionally it is broadly similar to the ilmenite from the PGA and contains 43.9 to 53.2% TiO_2, 43.8 to 50.5% FeO, 0.3 to 1.0% (but two higher values) MnO, and 0.8 to 5.4% MgO. Compared to average ilmenite from PGA, the UMAA average contains much higher amounts of Al_2O_3 (0.16 and 0.28%, respectively), Cr_2O_3 (0.11 and 0.29%), MgO (0.67 and 2.48%), and lower MnO (1.14 and 0.94%). These differences reflect those of their host rocks (Khan et al., 1989) despite that the ilmenites under discussion are not magmatic.

The ilmenite in the layered gabbronorite-anorthosite sample is intimately associated with magnetite which also contains tiny spots of green pleonaste. The latter is depleted in Cr and Fe^{3+} and the magnetite in Cr and Al (all < 0.3 atoms per 32 oxygens). The pleonaste in the norite layer and magnetite in the anorthosite layer are also impoverished in Ti (< 0.1 atoms), but the pleonaste in the anorthosite layer contains 3.6% TiO_2 (0.59 atoms).

Corona Spinel

Excellent coronas, developed due to olivine-calcic plagioclase reaction, have been described from the Chilas Complex (Shams, 1975; Jan et al., 1984b). These are considered to have formed during either metamorphism or, more likely, cooling and uplift. The most common coronas consist of shells with the following disposition: olivine—>orthopyroxene-hornblende–hornblende+spinel symplectite <— calcic plagioclase. Clinopyroxene occurs in a few of them but garnet has not been noted, ignoring the Chilas-like rocks near Khwaza Khela, Swat. In some ultramafic rocks, small grains of accessory plagioclase have totally been consumed in the reaction. In a rare layered rock the reaction products occur in the form of thin bands/layers between the formerly adjecent anorthosite and perodotite layers.

The composition of the corona apinel is a clear reflection of the reactants olivine and plagioclase which are depleted in Mn, Cr and Fe^{3+}. That is why this spinel is invariably aluminous (Al_2O_3 57.3 to 65.2%) and contains only small amounts of Fe_2O_3, MnO (0.0 to 0.3%) and, especially Cr_2O_3 (0.0 to 0.4%). The 100 $Mg/(Mg+Fe^{2+})$ of the analyses ranges from 52.6 to 69.0, ignoring two with markedly low values of 41. They can therefore be classified as pleonaste (Deer et al., 1962). The 100 $Cr/(Cr+Al)$ and 100 Fe^{3+}/R^{3+} vs. 100 $Mg/(Mg+Fe^{2+})$ plots of the spinels are given in Fig. 8 and the Al-Fe^{3+}-Cr plots in Fig. 12. The low Fe^{3+} and, especially, Cr numbers of the corona spinels distinguish them clearly from the remaining analyses.

DISCUSSION AND CONCLUSIONS

The principal gabbronorite association in the Chilas Complex contains magnetite-ilmenite pairs exsolved from a single phase Fe-Ti oxide during metamorphism and/or cooling.

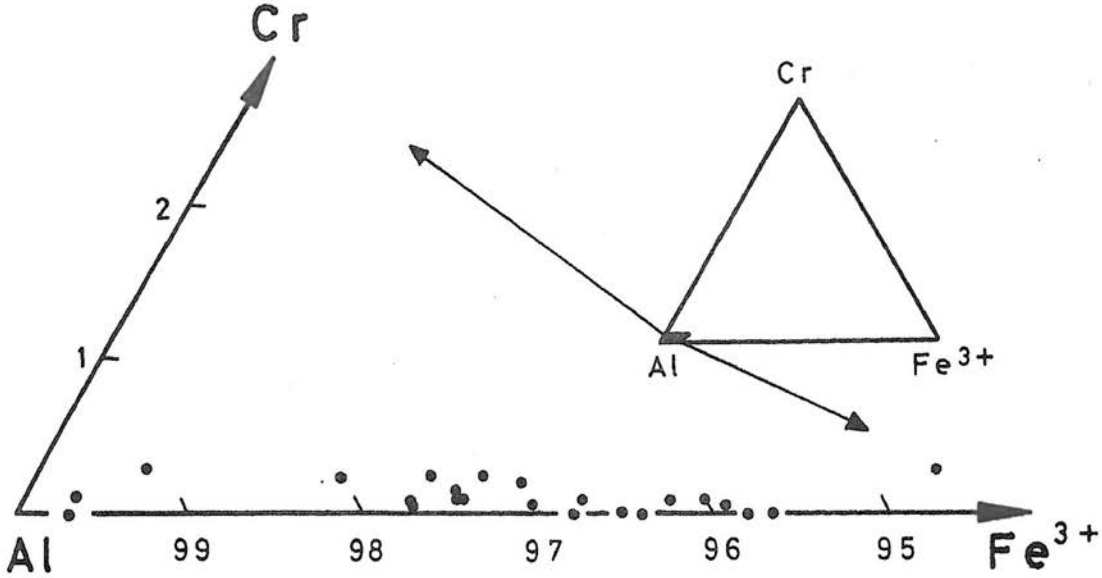

Fig. 12. Al-Cr-Fe^{3+} plots of the corona spinels in symplectitic intergrowths with hornblende.

No Cr-Al spinel occurs in this association. The ultramafic-mafic-anorthosite association of rocks, considered to be the product of a more primitive magma (Khan et al., 1989), is characterized by a great variation in the composition of the oxide phases:

1) Al-Cr-Fe^{3+} phases, ranging from Cr-poor pleonaste through chromite with a maximum Cr_2O_3 content of 39 wt. % to Cr-poor magnetite. These may be very variable in composition from one to another sample, in thin adjecent layers of different lithologies, and from grain to grain within a single thin section. It is worth mentioning that the accessory spinel in ultramafic rocks typically occurs in very tiny grains and displays more variation than the segregated Cr spinel. This variation is related to a) subsilidus re-equilibration with adjacent silicates, b) exsolution along a well defined and complete solvus similar in shape to the few solvi reported elsewhere in the world, and c) due possibily to marginal alteration in very rare cases. Exsolution, however, has not occurred in some chromitites containing chromitewith high Cr_2O_3.

2) Cr-free and Fe^{3+}-poor pleonaste in symplectitic intergrowths with hornblende and rarely clinopyroxene in reaction coronas between olivine and calcic plagioclase. The coronas also contain orthopyroxene but are devoid of garnet and probably formed during cooling (Jan et al., 1984b).

3) Rare ilmenite and titanomagnetite associated with Cr-Al-Fe^{3+} spinel. This possibly resulted from the exsolution of Ti-bearing spinel during cooling by oxidation process described by Buddington and Lindsley (1964; see also Irvine, 1974).

The magnetite-ilmenite pairs from the PGA and Cr-Al spinel–Cr-Fe^{3+} spinel pairs in the UMAA yield a wide range of temperature (from > 800 to < 500 °C) for the exsolution. At high temperatures the exsolution was characteristically under high oxygen fugacity (approaching MH buffer), comparable with that suggested for the extrusive intermediate suites (cf. Haggerty, 1976). Re-equilibration at decreasing temperatures was accompanied by considerable fall in the $f\,O_2$.

Several workers (e.g. Irvine, 1965, 1967; Thayer, 1970) have suggested that spinel composition can have petrogenetic significance. Dick and Bullen (1984) classified alpine peridotites and associated volcanic rocks into three types on the basis of spinel compostion: (I) those with Cr nos < 60; these are thought to be derived from oceanic lithosphere formed at mid-ocean ridges, although other environments (e.g. back-arc basins) are not precluded; (III) those containing spinel with Cr nos > 60, which are considered to have formed in island arc-related rocks, continental intrusions, and oceanic plateau basalts; and (II) those with spinel spanning the full range of composition between type I and Type III, which reflect a composite origin, such as formation of an island arc on oceanic crust.

It is debatable whether the UMAA spinels can be used for petrogenetic considerations because of the subsolidus changes in their chemistry. However, with the exclusion of the exsolved magnetite, an overwhelming majority of the UMAA spinel analyses have Cr nos below 60, and this groups them with type I complexes (ocean ridge or back-arc basin) of Dick and Bullen (1984). On several grounds the UMAA spinels cannot be considered to have a mid-ocean ridge origin: a) they have low Mg nos than in oceanic peridotites, b) they do not plot with oceanic rocks on TiO_2 vs. Cr_2O_3 basis, c) exsolved spinels have not been reported in oceanic rocks, and d) the whole-rock geochemistry and silicate compositions in the Chilas Complex suggest an island arc-related environment (Khan et al., 1989). Indeed the complete ranges (0 to 100) of Cr and Fe^{3+} nos in the UMAA spinels are similar to those of arc-related rocks in the Lesser Antilles and Aleutians (Arculus, 1978; Conrad and Kay, 1984; DeBari et al., 1987). High ranges of Cr nos have also been reported in Border Ranges mafic-ultramafic complex (Burns, 1985; DeBari and Coleman, 1989), Canyon Mountain ophiolite (Himmelberg and Loney, 1980), and Miyamori ultramafic complex (Ozawa, 1983), which are considered to have formed in island arc-related environments.

It is most likely that the Chilas Complex represents magma generated and emplaced at deep levels of the Kohistan arc, probably during an intra-arc rift event in the initial stages of back-arc basin evolution (Khan et al., 1989). The spinel compositions corroborate this view.

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