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REACTION ISOGRADS AND P–T ESTIMATES IN METASEDIMENTS ON THE EDGE OF THE KARAKORUM PLATE, HUNZA, N. PAKISTAN

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ABSTRACT

The Hunza area of N. Pakistan contains a metasedimentary sequence on the southern margin of the Karakorum Plate. The sequence is largely pelitic with carbonate layers, cut by amphibolite and granite sheets, and is bounded to the N.E. by the Karakorum Batholith, and to the S.W. by the Northern Suture at Chalt.

The grade of metamorphism increases from S.W. to N.E., and this is marked by variation in mineral chemistry, and changes in mineral assemblages at a series of reaction isograds, which separate zones in which stable mineral pairs are: garnet-chlorite, chloritoid-biotite, staurolite-biotite, kyanite-biotite and sillimanite-biotite from S.W. to N.E. respectively. A reaction isograd marked by the paragenesis forsterite-diopside-calcite-dolomite occurs in the siliceous dolomites, and the northeasterly dip of the isograds indicates that the zones are inverted.

At Hunza, maximum metamorphic conditions given by pelitic rocks are 669°C and 5.5 kb, with XCO_2*, Fl = 0.66. The inversion of the metamorphic zones was associated with major southward thrusting during collision of the Karakorum Plate with the Kohistan Arc.*

INTRODUCTION

The Hunza area extends from 74°20'E to 75°E at a latitude of 36°20'N within the Karakorum Range of the Himalayas of northern Pakistan. A section along the Hunza Valley has been made accessible by the recent construction of the Karakorum Highway. The section is bounded to the south-west by the Northern Suture near Chalt, which represents the junction between the Kohistan sequence to the south and the Karakorum plate to the north (Tahirkheli and Jan, 1979). In the suture at Chalt there is a tectonic melange, with blocks and lenses of limestone, conglomerate and basic to ultramafic rocks in a slate matrix

(Coward *et al.,* 1982 a, b). This is followed eastwards by a progressive increase in metamorphic grade from slates to phyllites, schists and gneisses with interlayered marbles, and occasional sheets of amphibolite and leucogranite. At the eastern end of the section, the metasediments have a contact with the Karakorum Batholith, which dips north-eastwards at about 45°, suggesting that the metamorphic zones are inverted, and probably developed in a southward facing overfold, with the batholith emplaced into the high grade axial zone. Desio (1974) distinguished three formations, and assigned ages of Permian to Cretaceous, based on laterally equivalent unmetamorphosed fossiliferous rocks. No isotopic data are available for the metasediments. Preliminary petrographic and microprobe studies (Broughton, 1981) indicated an increase in metamorphic grade towards the batholith, from lower greenschist to amphibolite facies.

Near Hunza, garnets with inclusions indicating 540° of rotation were reported in a garnet staurolite schist (Powell and Vernon, 1979), and a study of corundum-bearing marbles near Hunza yielded metamorphic conditions of 600–620°C and 6–7kb (Okrusch *et al.,* 1976).

A series of reaction-isograds has been established and although samples from the Hunza Valley only were studied, the isograds are assumed to be parallel to the regional strike which is WNW–ESE. The lowest grade zone for which we have adequate material is that in which garnet-chlorite is stable (Fig. 1). The first isograd is defined by the assemblage muscovite-chloritoid. This is followed by a zone in which chloritoid-biotite is stable, and then a staurolite-biotite isograd:

chloritoid + muscovite + quartz = staurolite + biotite + H_2O.

The zone in which staurolite is stable terminates at the kyanite-biotite isograd, represented by the bivariant reaction:

staurolite + muscovite + quartz = kyanite + biotite + H_2O

which will probably take place over a certain temperature range (Hoschek, 1969).

Coexisting kyanite and sillimanite have not been found, and the first appearance of sillimanite is probably due to the reaction:

muscovite + quartz = k-feldspar + sillimanite + H_2O.

The highest grade pelite isograd is a result of the reaction:

biotite + sillimanite + quartz = garnet + k-feldspar + H_2O.

Further east there is a change in lithology to dominantly carbonate rocks with occasional amphibolite and granite sheets. We have defined one isograd within the carbonate esquence, where we find the equilibrium paragenesis of reaction 14 of Winkler (1974, p. 112):

diopside + dolomite = forsterite + calcite + CO_2

which occurs over a narrow temperature range.

In a recent paper, Coward *et al.* (1982b) invoked tectonic telescoping of the sequence to explain the apparently rapid northward increase in metamorphic grade. The aim of this paper is to present data on the isograds and metamorphic

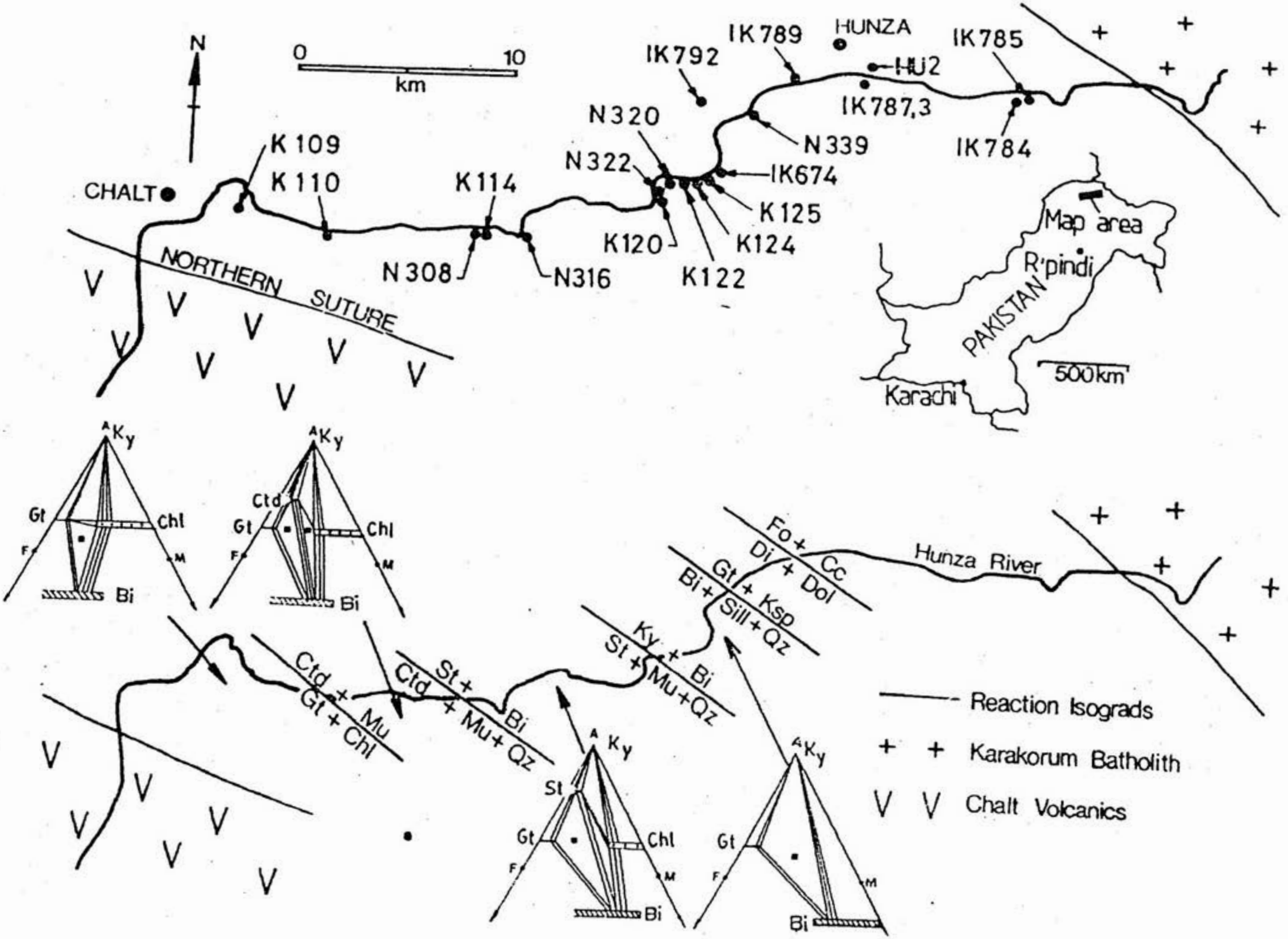

Fig. 1. Map of the Hunza Valley at Hunza, showing location of samples and reaction isograds. with AFM projections (all $+Mu+Qz+H_2O$) for pelite zones.

zones, determine the metamorphic conditions, and deduce the metamorphic history of this area of the Karakorum.

PETROGRAPHY

Pelites : Syn- and post-tectonic textures are shown by porphyroblasts in most rocks. At the low-grade end are post-tectonic porphyroblasts of chlorite and chloritoid in fine grained slaty groundmasses. There are spectacular sheaves of post-tectonic chloritoid normal to the foliation in K110 and N308 (Fig. 2a). Up-grade the groundmasses become more schistose, crenulated assemblages of mu-bi-qz-pl-ilm-ap-qz.

In the garnet zone, garnet porphyroblasts have helicitic trails, and reach sizes of around 4mm. Small prisms of staurolite pseudomorphing chloritoid occur in K114, and up-grade, staurolite is present as 2–6mm euhedral porphyroblasts containing dusty graphite and inclusion trails of quartz. In places the staurolite is enclosed by large euhedral, inclusion free garnets, up to 9mm (Fig. 2b).

Kyanite is found within and adjacent to staurolite in N320 (Fig. 2c). Sillimanite in the form of fibrolite is associated with muscovite, and euhedral prismatic sillimanite occurs with gt-bi-mu-qz-ksp in N339 (Fig. 2d).

Calc-silicate rocks: are mainly granular aggregate of calcite and sometimes dolomite, with silicate phases. Near Hunza sub- to euhedral grains of tremolite and diopside coexist with calcite, dolomite and aluminous phases chlorite and phlogopite. Further east the paragenesis forsterite-diopside-calcite-dolomite is found, with euhedral forsterite intimately related to diopside. Deformation of lamellae in calcite is observed in places, but no exsolution of dolomite from calcite was observed. The samples are largely unaltered, with the exception of the development of yellowish clinohumite from olivine in two sections.

Metabasic rocks: these are essentially assemblages of green hornblende, plagioclase and quartz, with minor amounts of sphene, biotite and clinozoisite. Some samples possess a foliation, with aligned hornblende and interstitial granular plagioclase and quartz. Mineralogical banding is developed in some samples, with alternating bands of mafic and felsic minerals.

ANALYTICAL PROCEDURE AND METHODOLOGY

Mineral analyses were obtained with a Cambridge Instruments Microscan 5 microprobe at the University of Leicester, by both wavelength and energy dispersive techniques. Operating conditions were 15kV and a specimen current of

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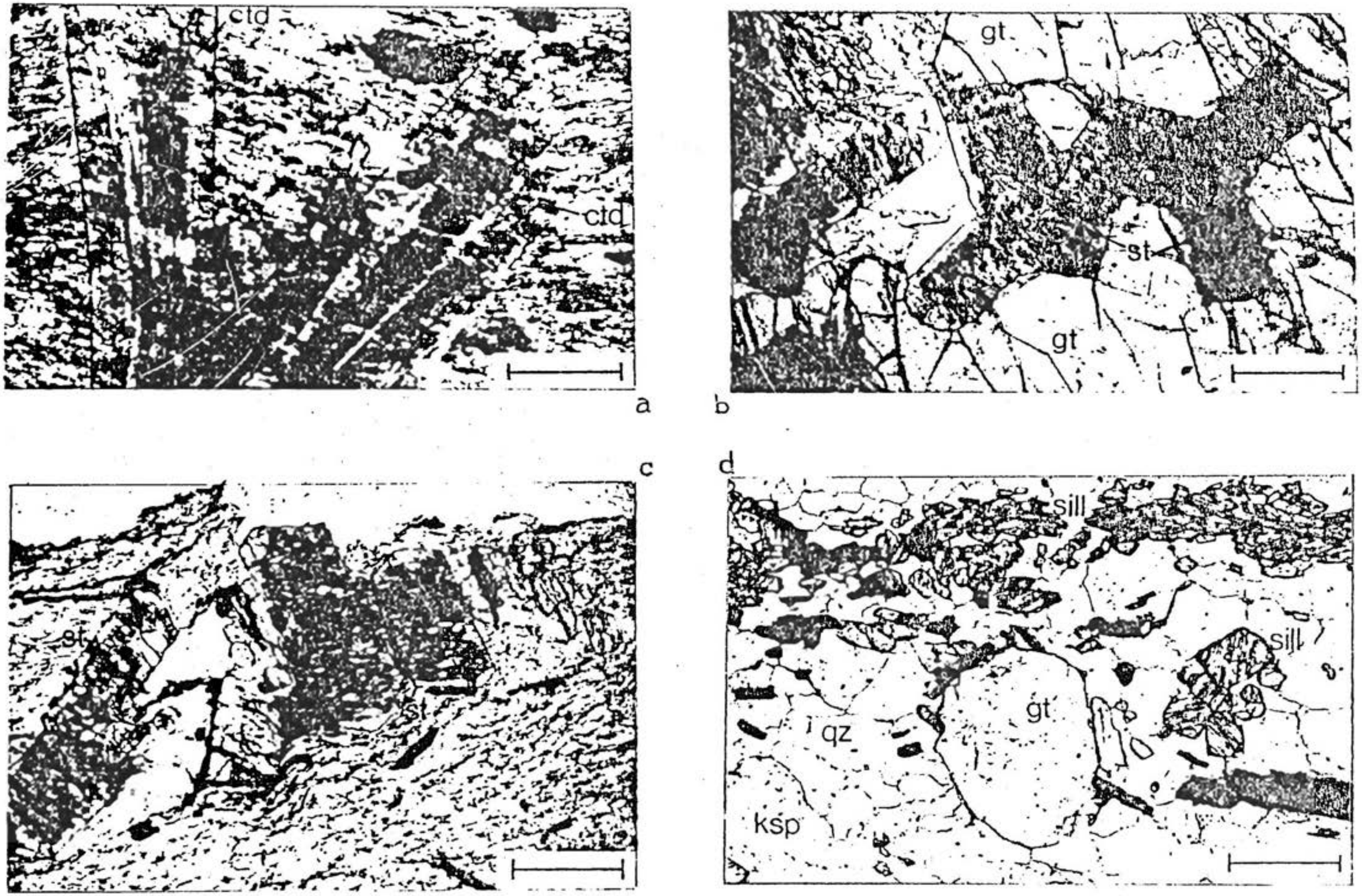
Fig. 2. Photomicrographs (scale bar = 0.5 mm).

(a) Sheaves of chloritoid (K110)

(b) Inclusion free garnet enclosing staurolite (K120)

(c) Staurolite-kyanite schist (N320)

(d) Garnet-sillimanite-biotite in quartzofeldspathic groundmass (N339).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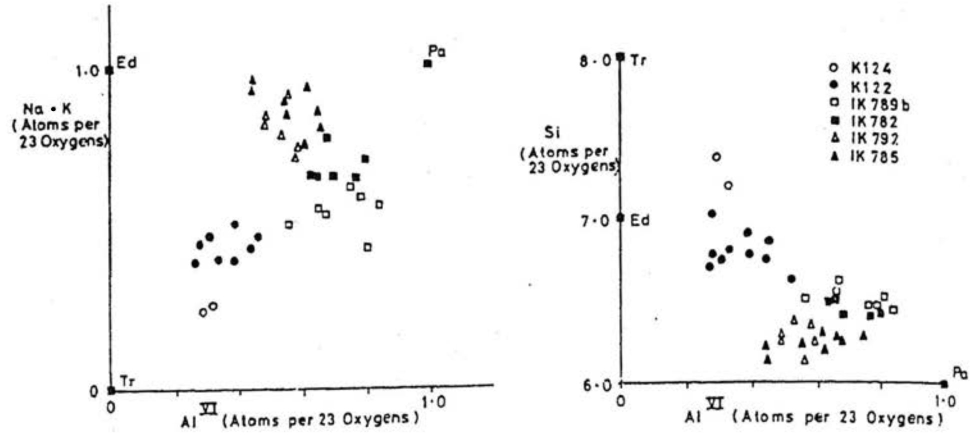

Fig. 3. Compositional variation in calcic amphiboles from meta-basic rocks. Al^{VI} = octahedrally co-ordinated Al.

3na on Co for energy dispersive analysis, and 15kV with a specimen current of 22na on Cu for wavelength dispersive analysis. A range of natural and synthetic mineral and pure element standards were employed, with dead time and full ZAF correction applied using the computer program FRAME (Yakowitz *et al.*, 1973). Microprobe traverses were made across all grains to detect intra- as well as inter-grain variation. Calcite analyses were obtained with a defocussed beam to try and include any exsolved dolomite.

Thermodynamic data were taken from the internally consistent data-set of Powell (1978, Appendix A), which utilizes molar volumes from Robie *et al.* (1967); entropies and enthalpies from Robie and Waldbaum (1968) and sundry enthalpies from phase equilibrium experiments. Activities of end-member components in analysed mineral phases were calculated assuming ideal mixing on sites, with the exception of anorthite in plagioclase, for which molecular mixing and an activity coefficient of 1.2 (Orville, 1972) was employed. Activities of H_2O and CO_2 in fluid phases were calculated using a regular solution model.

MINERAL CHEMISTRY

In pelitic rocks with coexisting ferromagnesian phases, the mole fraction of magnesium (XMg) in the various phases has the following order :

XMg chl > ctd > st > gt

which is commonly found in Fe-rich pelites (e.g. Yardley *et al.*, 1980). A similar sequence exists in analysed phases from the siliceous dolomites :

XMg dol > clhm > chl > ol > amph > sp

The consistent Mg-Fe partitioning between mineral phases in adjacent siliceous dolomites (Fig. 4) is indicative of the attainment of exchange equilibrium.

TABLE 1. MINERAL ASSEMBLAGES IN PELITIC, CALC-SILICATE AND METABASIC ROCKS.

PELITES	
K109	bi — chl — mu — qz — ilm — cc
K110	ctd — chl — mu — qz — ilm — cc — tour
N308	ctd — bi — mu — qz — ilm
K114	st — ctd — bi — mu — qz — ilm — tour — ap
N316	gt — pl — bi — mu — qz — ilm — tour
K120	st — gt — bi — mu — qz — ilm
N322	st — gt — bi — mu — qz — pl — ilm — tour
IK674	gt — bi — hb — mu — qz — pl — ilm
N320	ky — st — bi — mu — qz — ilm
N339	sill — gt — bi — mu — qz — pl — ksp
IK789a	sill — gt — bi — mu — qz — pl — czs — sph — ksp
CALC-SILICATE ROCKS	
IK783	amph — cpx — cc — dol — pl — qz
IK787	sp — ol — cpx — chl — cc — dol — ilm — bi
HU2	sp — ol — chl — cpx — cc — dol — clhm — ilm — bi
IK783a	sp — ol — chl — cc — dol — clhm
METABASIC ROCKS	
K122	hb — pl — cpx — bi — sph
K124	hb — pl — bi — sph — ilm — qz
IK792	hb — pl — cpx — sph — qz
IK789b	hb — pl — bi — qz — ilm
IK782	hb — pl — cpx — czs — bi — qz
IK785	hb — pl — sph — qz

Abbreviations : ap = apatite, bi = biotite, cc = calcite, chl = chlorite, ctd = chloritoid, gt = garnet, hb = hornblende, ilm = ilmenite, ksp = k-feldspar, ky = kyanite, mu = muscovite, pl = plagioclase, qz = quartz, sill = sillimanite, st = staurolite, tour = tourmaline, amph = amphibole, cpx = clinopyroxene, clhm = clinohumite, dol = dolomite, ol = olivine, sph = sphene, sp = spinel.

Pelitic rocks

Biotite composition is dependent on many factors; including P, T, aH_2O, composition of coexisting phases, rock composition, and is consequently highly variable. Certain compositional parameters such as the Ti content of biotite show a positive correlation with metamorphic grade (Broughton, 1981) and similar trends have been noted elsewhere, e.g. Schmidt and Wood (1976). The Ti content of biotite in the Hunza area ranges from 0.16 atoms (gt-chl zone) to 0.44 atoms (sillimanite zone) per 22 oxygens. XMg variation is not correlated with grade of metamorphism, and ranges from 0.21 to 0.82.

Chloritoid porphyroblasts show slight compositional zoning, with margins slightly richer in Mg (XMg = 0.14) than the cores (XMg = 0.10), see Table 3a.

TABLE 2. MINERAL REACTIONS IN PELITIC AND CALC-SILICATE ROCKS

PELITES

gt + chl + mu = ctd + bi + H_2O
3.1 ctd + mu + 0.2 qz = 1.6 st + bi + 4.6 H_2O
6 st + 4 mu + 7 qz = 31 ky + 4 bi + 6 H_2O
3 pl = gt + 2 sill + qz
qz + mu = ksp + sill + H_2O
bi + sill + 2 qz = gt + ksp + H_2O

CALC-SILICATES

tr + cc = 4 di + dol + CO_2 + H_2O
di + 3 dol = 2 fo + 4 cc + $2CO_2$

Abbreviations as per Table 1.

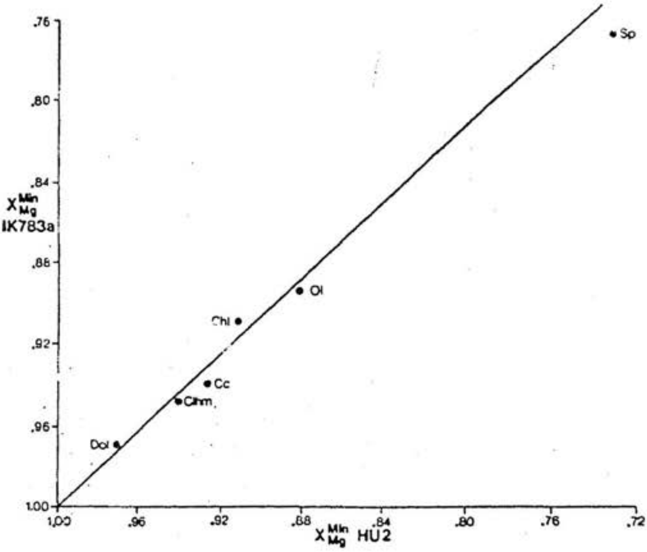

Fig. 4. Fe-Mg partitioning among analysed minerals from IK783 and HU2. XMg = molecular Mg/(Mg+Fe).

Garnet. In rocks up to staurolite grade, garnets with textures indicating syn-tectonic growth have 'normal' zoning, i.e. Ca-Mn rich cores, and Fe-Mg rich margins. Garnets at sillimanite grade show slight reverse zoning, with Ca-Mn rich margins and Fe-Mg rich cores. Garnets interpreted as being post-tectonic have no inclusions, and show no compositional zoning. All garnets are essentially almandine-pyrope binary solutions, with minor grossular and spessartine components, e.g. $\text{Alm}_{87}\text{Pyr}_{11}\text{Sp}_{1}\text{Gr}_{1}$. The composition of garnet in equilibrium with biotite has

TABLE 3a. REPRESENTATIVE MINERAL ANALYSES FROM PELITIC ROCKS.

	K109/1 bi	K114/1 ctd	K114/2 st	K120/1 gt	K120/2 bi	K120/3 st	IK784/1 gt	IK784/2 pl	IK784/3 bi	K125/1 gt	K125/2 bi	N339/1 gt	N339/1 bi
SiO_2	34.57	24.32	28.02	37.33	35.93	28.30	37.01	61.19	34.90	38.37	34.86	37.49	35.69
TiO_2	1.32	—	0.25	—	1.75	0.50	—	—	3.26	—	1.84	—	3.82
Al_2O_3	18.92	39.61	52.26	21.33	20.63	53.81	20.40	23.27	16.96	20.25	17.75	21.22	19.05
Fe_2O_3*	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.31	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
FeO	21.87	24.15	12.92	38.12	16.78	13.38	26.76	—	27.61	28.83	18.54	38.00	19.72
MnO	—	—	—	0.06	—	—	3.97	—	0.39	4.34	—	1.32	—
MgO	8.58	2.69	1.30	3.12	9.30	1.48	0.89	—	3.81	2.83	10.58	2.60	8.03
CaO	—	—	—	0.37	—	—	9.28	6.94	—	4.91	—	1.14	—
Na_2O	—	—	—	—	0.44	—	—	6.59	—	—	—	—	—
K_2O	8.87	—	—	—	8.55	—	—	0.17	9.70	—	9.50	—	9.56
ZnO	n.d.	n.d.	0.79	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Total	94.13	95.87	95.54	100.33	93.38	97.47	99.62	98.16	96.63	99.52	93.07	101.78	95.87

n.d. = not determined

Fe_2O_3* = determined by charge balance.

been used to estimate temperature of metamorphism (Table 4) and representative garnet analyses are given in Table 3a.

Staurolite. The composition of staurolite is constant, with XMg = 0.16. Porphyroblasts have slight compositional zoning, with Mg-rich cores and Fe-rich margins. In a staurolite chloritoid schist – K1114, staurolite prisms contain up to 0.8 wt. % ZnO (Table 3a).

Plagioclase compositions range from An_{28} to An_{54} in kyanite-biotite and sillimanite zones, but we have no analyses of plagioclase from lower amphibolite or greenschist facies. Plagioclase in equilibrium with garnet, sillimanite and quartz has been used to evaluate P-T conditions of metamorphism.

Siliceous Dolomites

Spinel analyses depart from ideal spinel composition, due to substitution of Cr + Fe^{+3} for Al on the B site, and Fe^{+2} + Zn for Mg on the A site. Analysed green spinel from IK787 has $Al/(Al + Fe^{+3} + Cr) = 0.98$, and $Mg/(Mg + Fe + Zn) = 0.73$. Compositional zoning was not detected.

Olivine tends to be unzoned, with XMg values ranging from 0.87 to 0.89, with minor Al_2O_3 and CaO contents of 0.15 and 0.23 wt. % respectively (Table 3b). Ni, Zn and Cr were below detection by wavelength analysis.

Clinopyroxene is diopsidic, with XMg = 0.90 and is unzoned. There is minor substitution of up to 0.25 wt. % Al_2O_3 for SiO_2 (Table 3b).

Compositional zoning was not detected in amphibole analyses, which indicate tremolite with minor tschermakite substitution. Recalculated analyses indicate 0.35 Al atoms per 23 oxygens on the Z site, and 0.25 on the Y site. The remainder of the Y sites are occupied by Mg and Fe, with XMg = 0.79. Sodium was not detected on the A site (Table 3b).

TABLE 3b. REPRESENTATIVE MINERAL ANALYSES FROM CALC-SILICATE ROCKS

	IK787/2 sp	IK787/3 ol	IK783/1 amph	IK783/2 cpx	IK787/1 cpx
SiO_2	—	40.21	53.95	54.98	55.01
TiO_2	—	—	—	—	—
Al_2O_3	65.02	0.15	3.49	0.25	0.21
Cr_2O_3	1.11	—	—	—	—
FeO	13.26	12.34	7.27	3.15	1.98
MnO	—	—	—	—	—
MgO	19.25	47.20	18.73	16.52	17.91
CaO	—	0.23	13.27	25.89	25.45
Na_2O	—	—	—	—	—
K_2O	—	—	—	—	—
ZnO	1.17	n.d.	n.d.	n.d.	n.d.
Total	99.81	100.13	96.70	100.78	100.56

n.d. = not determined

been used to estimate temperature of metamorphism (Table 4) and representative garnet analyses are given in Table 3a.

Staurolite. The composition of staurolite is constant, with XMg = 0.16. Porphyroblasts have slight compositional zoning, with Mg-rich cores and Fe-rich margins. In a staurolite chloritoid schist – K1114, staurolite prisms contain up to 0.8 wt. % ZnO (Table 3a).

Plagioclase compositions range from An_{28} to An_{54} in kyanite-biotite and sillimanite zones, but we have no analyses of plagioclase from lower amphibolite or greenschist facies. Plagioclase in equilibrium with garnet, sillimanite and quartz has been used to evaluate P-T conditions of metamorphism.

Siliceous Dolomites

Spinel analyses depart from ideal spinel composition, due to substitution of Cr + Fe^{+3} for Al on the B site, and Fe^{+2} + Zn for Mg on the A site. Analysed green spinel from IK787 has Al/(Al + Fe^{+3} + Cr) = 0.98, and Mg/(Mg + Fe + Zn) = 0.73. Compositional zoning was not detected.

Olivine tends to be unzoned, with XMg values ranging from 0.87 to 0.89, with minor Al_2O_3 and CaO contents of 0.15 and 0.23 wt. % respectively (Table 3b). Ni, Zn and Cr were below detection by wavelength analysis.

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	IK787/2 sp	IK787/3 ol	IK783/1 amph	IK783/2 cpx	IK787/1 cpx
SiO_2	—	40.21	53.95	54.98	55.01
TiO_2	—	—	—	—	—
Al_2O_3	65.02	0.15	3.49	0.25	0.21
Cr_2O_3	1.11	—	—	—	—
FeO	13.26	12.34	7.27	3.15	1.98
MnO	—	—	—	—	—
MgO	19.25	47.20	18.73	16.52	17.91
CaO	—	0.23	13.27	25.89	25.45
Na_2O	—	—	—	—	—
K_2O	—	—	—	—	—
ZnO	1.17	n.d.	n.d.	n.d.	n.d.
Total	99.81	100.13	96.70	100.78	100.56

n.d. = not determined

Calcite contains detectable amounts of $MgCO_3$, $FeCO_3$ and $MnCO_3$ (up to 8.3, 0.4 and 0.07 mole % respectively). The $MgCO_3$ content of calcite in equilibrium with dolomite is fixed by the calcite-domomite solvus, and has been used to estimate temperature of recrystallization (Table 4). Owing to the possibility of exsolution cf dolomite from the host calcite, the temperatures calculated must be minimum estimates. Dolomite shows minor substitution of $FeCO_3$ (up to 2.04 wt. %) but negligible $MnCO_3$. XMg = 0.97 in analysed grains from most sections.

Metabasic rocks

All analyzed amphiboles are paragasites, although there is some degree of chemical variation. There is a general correlation between metamorphic grade (as indicated by pelitic assemblages) and amphibole chemistry. With increasing content of octahedrally co-ordinated Al (Al^{VI}), there is a decrease in Si, and an increase in Na + K (Fig. 4, Table 3c).

There is no apparent correlation between metabasite plagioclase chemistry and metamorphic grade, or amphibole chemistry. Plagioclase compositions vary from An[illegible] to An[illegible].

Calcic pyroxenes with similar XMg (0.6) occur in three samples, with Al substituting for Si in the rock at the lower grade end of the section (Table 3c).

TABLE 3c. REPRESENTATIVE MINERAL ANALYSES FROM METABASIC ROCKS.

	K124/1 amph	K122/1 amph	IK785/1 amph	IK792/1 cpx	IK782/1 cpx
SiO_2	52.23	45.01	41.46	48.62	52.22
TiO_2	0.11	1.20	2.51	0.48	—
Al_2O_3	4.60	9.15	13.34	3.17	0.84
Fe_2O_3*	2.87	0.73	1.10	n.d.	n.d.
FeO	4.83	15.26	17.56	11.74	12.68
MnO	0.23	0.44	0.38	0.25	0.48
MgO	18.82	10.81	8.93	9.91	10.35
CaO	11.90	12.24	11.93	23.08	23.31
Na_2O	0.95	1.26	2.63	0.53	0.42
K_2O	0.07	0.74	1.10	—	—
Total	96.61	96.84	100.75	97.78	100.30

Fe_2O_3* = determined by charge balance n.d. = not determined

ESTIMATION OF PHYSICAL CONDITIONS

Pelitic rocks

Garnet-Biotite Thermometry. We have used four samples with garnet and biotite to estimate temperatures of metamorphism. The exchange reaction

$$\underset{\text{garnet}}{Fe_3Al_2Si_3O_{12}} + \underset{\text{biotite}}{KMg_3AlSi_3O_{10}(OH)_2} = \underset{\text{garnet}}{Mg_3Al_2Si_3O_{12}} + \underset{\text{biotite}}{KFe_3AlSi_3O_{10}(OH)_2}$$

was calibrated experimentally by Ferry and Spear (1978), and on empirical observations by Thompson (1976). The reaction is highly sensitive to temperature but virtually insensitive to pressure and water activity. The widespread existence of ilmenite instead of magnetite is indicative of low f_{O_2}, and hence temperatures should be fairly accurate. Although there are some data on mixing in garnet solid solutions (e.g. Newton, 1978), mixing in biotites is not well understood. We have assumed that non-ideal mixing in garnet and biotite is mutually cancelling, and although this is less plausible, it should provide better temperature estimates than accepting non-ideal mixing in garnet only.

Mineral analyses are given in Table 3a, and temperatures listed in Table 4. Errors on the Ferry and Spear (1978) temperatures are ± 50°C. At 5.5 kb the temperature estimate of 633°C for IK674 (sillimanite-biotite zone) and 571°C for K125 (kyanite-biotite zone) lie respectively within the sillimanite and kyanite stability fields of Holdaway (1971). Temperatures obtained for K120 and N316 are considerably lower, around 500–520°C. In these sections, the garnet appears to be post-tectonic, and the temperatures are interpreted as recording the crystallization of the garnet during a static cooling phase post-dating the metamorphic peak.

TABLE 4. CALCULATED CONDITIONS OF METAMORPHISM

Garnet-biotite		Temperature (°C)	
Sample	K_D	Ferry & Spear	Thompson
IK674	0.207	633	603
K120	0.148	520	519
K125	0.172	571	555
N316	0.139	506	505

Calcite-dolomite		Temperature (°C)
Sample	$XMgCO_3,Cc$	(Rice, 1977)
IK787a	0.083	608
HU1	0.070	594
HU2	0.073	602

Garnet-plagioclase-sillimanite-quartz equilibrium. Two samples contain the equilibrium assemblage garnet-plagioclase-sillimanite-quartz, for which :

$$\underset{\text{plagioclase}}{3CaAl_2Si_2O_8} = \underset{\text{garnet}}{Ca_3Al_2Si_3O_{12}} + \underset{\text{sillimanite}}{2Al_2SiO_5} + \underset{\text{quartz}}{SiO_2}$$

Using data from Powell (1978, Appendix A) the free energy change for the above reaction is :

$$\Delta G^\circ_{P,T} = -32.0 + 0.1268T - 5.47\ (P-1)\ kJ$$

Analogous expressions were derived by Schmidt and Wood (1976) from the experimental work of Hays (1966) and Hariya and Kennedy (1968), and by Ghent (1976):

$$\Delta G^\circ_{P,T} = -10{,}300 + 31.83 - 1.3045\ (P-1) \pm 1000\ cals$$

Schmidt and Wood (1976)

$$\Delta G^\circ_{P,T} = -11{,}673 + 32.81T - 1.30\ (P-1)$$

Ghent (1976)

Assuming ideal mixing on sites activity for grossular in garnet, and molecular mixing with an activity coefficient of 1.2 (Orville, 1972) for anorthite in plagioclase, the reaction was plotted in P–T space (Fig. 6).

Garnet-biotite-k-feldspar-plagioclase-sillimanite quartz-H_2O equilibrium. One sample containing the above assemblage was used to estimate maximum metamorphic conditions by assuming PH_2O = P total. The relationship is:

$$\underset{\text{biotite}}{KMg_3AlSi_3O_{10}(OH)_2} + \underset{\text{sillimanite}}{Al_2SiO_5} + \underset{\text{quartz}}{2SiO_2}$$

$$= \underset{\text{pyrope}}{Mg_3Al_2Si_3O_{12}} + \underset{\text{orthoclase}}{KA1Si_3O_8} + \underset{\text{fluid}}{H_2O}$$

There are no experimental data available for the breakdown of biotite in the above reaction. Thermodynamic data were estimated by Schmidt and Wood (1976) from experimental work by Hensen and Essene (1971) and Wones and Dodge (1966). The expression is:

$$1nK = \frac{-16975}{T} + 20.53 + \frac{(P-1)\ 0.2748}{T}$$

Using ideal mixing on sites activities for phlogopite in biotite, and pyrope in garnet, the reaction was plotted in P–T space (Fig. 6). It intersects the plagioclase-garnet-sillimanite-quartz reaction at 5.5 kb and 632°C. This estimate represents maximum metamorphic conditions, when $XH_2O = 1$.

Siliceous Dolomites

Calcite-dolomite thermometry. Analyses of calcite co-existing with dolomite in three rocks were used to determine the temperature of metamorphism. Temperatures (Table 4) were obtained using the equation of Rice (1977):

$$\log XMgCO_3, Cc = -1690/T + 0.795$$

Although exsolution of dolomite from calcite was not observed, the temperatures in Table 4 must be minima.

Two isobaric univariant reactions in the sub-system $CaO - MgO - SiO_2 - CO_2 - H_2O$ have been used to estimate temperature and fluid composition during metamorphism. The two reactions have been modelled assuming a pressure of 5.5 kb (derived from pelitic assemblages).

Tremolite-calcite-dolomite-diopside-H_2O-CO_2 equilibrium. The balanced reaction describing the above equilibrium is :

$$\underset{\text{amphibole}}{Ca_2Mg_5Si_8O_{22}(OH)_2} + \underset{\text{calcite}}{CaCO_3} = \underset{\text{clinopyroxene}}{4CaMgSi_2O_6} + \underset{\text{dolomite}}{CaMg(CO_3)_2} +$$

$$\underset{\text{fluid}}{CO_2} + \underset{\text{fluid}}{H_2O}$$

for which :

$$\Delta G^{\circ}_{P,T} = 160.2 - 0.3029T - 5.501\ (P-1)\ kJ$$

data from Powell (1978, Appendix A). This assemblage is present in IK783, and representative analyses are given in Table 3b. The reaction was plotted in $T - XCO_2$ (Fig. 5) space at a pressure of 5.5 kb, using analysed compositions, and the activity-composition relationships below :

$$a\ Trem, Amph = (XCa,X)^2 (XMg,Y)^5 (XSi,Z)^8$$

$$a\ CaCO_3, Cc = XCa,Cc$$

$$a\ CaMg(CO_3)_2, Dol = XMg, Dol$$

$$a\ Di,Cpx = XMg,Cpx$$

A regular solution model was used to estimate activity coefficients for H_2O and CO_2 in the fluid phase :

$$RT\ln\gamma n,Fl = (1 - Xn)^2\ W \qquad \text{where } W = 20.8 - 0.015T$$

Forsterite-calcite-dolomite-diopside-CO_2 equilibrium. The reaction for this equilibrium is :

$$\underset{\text{clinopyroxene}}{CaMgSi_2O_6} + \underset{\text{dolomite}}{3CaMg(CO_3)_2} = \underset{\text{olivine}}{2Mg_2SiO_4} + \underset{\text{calcite}}{4CaCO_3} + \underset{\text{fluid}}{2CO_2}$$

for which :

$$\Delta G^{\circ}_{P,T} = 220.6 - 0.3797T - 2.381\ (P - 1)\ kJ,$$

data from Powell (1978, Appendix A). This assemblage is present in IK787, and representative analyses are given in Table 3b. The reaction was plotted in

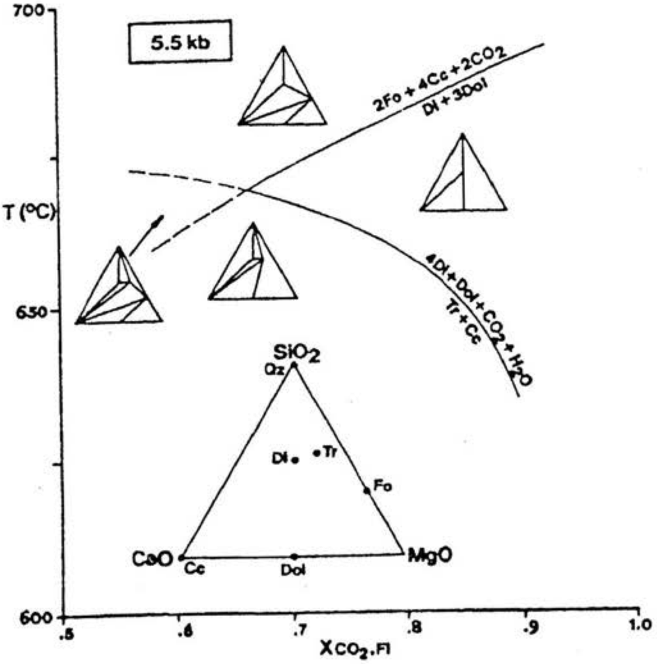

Fig. 5. T-XCO_2, Fl plot of reactions from calc-silicate rocks.

$T - XCO_2$ space (Fig. 5) as for the reaction above, using the activity-composition relationships above and, additionally :

$$a\ Mg_2SiO_4,O1 \quad = \quad (XMg,O1)^2$$

At the preferred pressure of 5.5 kb, the two isobaric univariant equilibria intersect at a temperature of 669°C, with the fluid containing 66% mole CO_2 (Fig. 5).

Discussion of P-T estimates

The temperature estimate for the siliceous dolomites at Hunza of 669°C at 5.5 kb is in good agreement with the 632°C and 5.5 kb derived for pelitic rocks. These temperatures exceed those indicated by calcite-dolomite solvus thermometry. Similarly, temperatures of around 500–520°C from metapelitic garnet-biotite pairs (K120 and N316) indicate, either a real decrease in temperature westwards, or they are due to equilibration below the metamorphic peak conditions during a static cooling phase. The estimates are also close to the conditions deduced by Okrusch *et al.* (1976), of 6–7 kb and 600–620°C for corundum-bearing marbles.

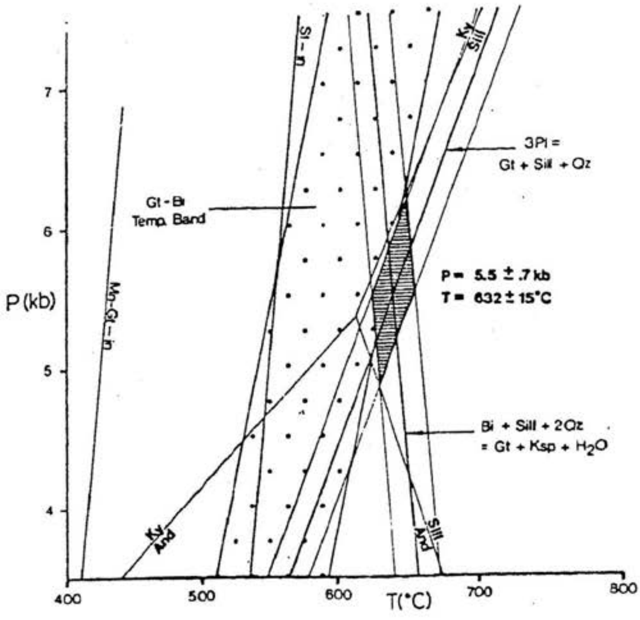

Fig. 6. P–T plot for pelitic rocks. Hatched area represents maximum metamorphic conditions, when PH_2O = P Total. Aluminium silicate triple point is after Richardson *et al.* (1969).

DISCUSSION

We have not been able to map out the reaction isograds in two dimensions. However, with the extreme relief in this area, it may be possible in the future. The Karakorum Betholith is at the high-grade end of the section in the sillimanite-biotite zone, and has a contact with the metasediments which dips to the NNE at about 45°. It seems likely, therefore, that the two dimensional isograd surfaces dip to the NNE conformably with the batholith contact, and regional foliation. If so, the zones are inverted, with higher grade rocks at upper structural levels.

Inverted metamorphic zones are a common feature of the Himalayan belt, but all published examples are on the south side of the Indus-Zangbo suture, and formed in connection with thrust stacking near the Main Central Thrust, e.g. Lal *et al.* (1981). The Hunza zones lie to the north of the northern suture, on the north side of the Kohistan-Ladakh island arc (Coward *et al.,* 1982a,b).

St-Onge (1981) described inverted isograds under the funnel-shaped Hepburn Batholith, but such large-scale contact metamorphism seems an unlikely cause of the Hunza zones, because the presence of kyanite-sillimanite, to the exclusion of andalusite, is indicative of moderately high pressure regional metamorphism.

The Hunza isograds formed in connection with major southward overthrusting of the metasediments during collision with the Kohistan arc, and this involved the Karakorum Batholith which is internally highly sheared. This overthrusting caused substantial crustal thickening which gave rise to moderately high pressures in the lower part of the thrust pile.

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