

Oxidized eclogites and garnet-blueschists from Oman: P – T path modelling in the NCFMASHO system

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ABSTRACT Eclogites and garnet-blueschists exposed at the deepest structural levels of the Oman Mountains in north-eastern Saih Hatat, Oman, indicate that the Arabian continental margin was subducted and subsequently exhumed. The peak metamorphic pressure has been a matter of debate for over a decade, with initial thermobarometric estimates, based on garnet–clinopyroxene–phengite barometry and the presence of radial cracks around quartz inclusions in garnet, yielding values in excess of 20 kbar; these estimates have been questioned by some researchers. The high-pressure minerals (glaucofane, omphacite and epidote) contain significant amounts of ferric iron, previously postulated to displace the stability fields of the eclogite and blueschist assemblages to less extreme conditions. In the present study, we have calculated phase diagrams and pseudosections in the model system NCFMASHO, using the program THERMOCALC and the thermodynamic database of Holland and Powell, which incorporates data for Fe^{3+} -bearing end-members. It is found that the phase compositions and modal abundances for typical bulk compositions are matched successfully at 520 ± 15 °C and 20 ± 1.6 kbar for the eclogites and 510 – 530 °C and 17 – 20 kbar for the garnet blueschists. These results support the original high-pressure estimates for the eclogites, and indicate that crossitic amphibole and aegirine-rich pyroxene do not necessarily reflect lower pressure conditions. The data set and activity models are applicable to other oxidized high (and ultra-high) pressure mineral assemblages.

Key words: eclogite; Oman; P – T paths; subduction; THERMOCALC.

INTRODUCTION

One of the world's largest and best preserved ophiolite sequences, the Semail Ophiolite, is exposed in northern Oman. Windows through the Semail Ophiolite expose continental margin sequences, onto which the ophiolite was emplaced. Structures associated with the obduction of the ophiolite are restricted to ~ 1 km beneath the ophiolite. The presence of mafic layers and boudins preserving garnet-blueschist and eclogite facies mineral assemblages in the deepest structural levels of the Oman mountains (near As Sifah village, NE Saih Hatat; Fig. 1) implies that the continental margin of Oman was subducted to depths > 45 km ($P > 16$ kbar) and subsequently exhumed. It is now generally agreed that the subduction occurred during the later stages of ophiolite emplacement, with the high-pressure (HP) rocks recording a peak metamorphic age of *c.* 80 Ma, i.e. 15 Myr after ophiolite formation (El-Shazly *et al.*, 2001; Warren *et al.*, 2003, 2005; Gray *et al.*, 2004a). Although the peak temperature reached by the eclogites and garnet-blueschists is fairly well constrained by conventional thermometry at 520 – 580 °C for the eclogites and

~ 500 °C for the blueschists (El-Shazly *et al.*, 1990; Searle *et al.*, 1994; El-Shazly, 2001), the peak pressures are still debated.

Accurate estimation of the highest pressures reached during HP metamorphic events has long been problematic because of the lack of tightly constrained equilibria. Until recently, pressure estimates for eclogites were commonly minima, based on the jadeite content of omphacite coexisting with quartz, in the absence of albite (e.g. Holland, 1980). The earliest pressure determinations of the Oman eclogites and blueschists were such minimum estimates, yielding poorly constrained pressures of 5 – 10 kbar for the garnet-blueschists and 10 – 12 kbar for the eclogites, based on the intersection of Grt-Cpx and Grt-Ph Fe-Mg exchange equilibria (Goffé *et al.*, 1988) and on the jadeite content of omphacite (El-Shazly *et al.*, 1990) respectively.

The garnet-clinopyroxene-phengite geobarometer (Wills *et al.*, 1991; Waters & Martin, 1993; Waters, 1996) yielded the first estimate of HP peak pressure of 23.1 ± 2.5 kbar (Searle *et al.*, 1994). This result supported calculations of entrapment pressures of > 20 kbar needed to create radial cracks around quartz (but not necessarily retrograded coesite) inclusions in almandine garnet (Wendt *et al.*, 1993). This barometer has been shown to successfully predict

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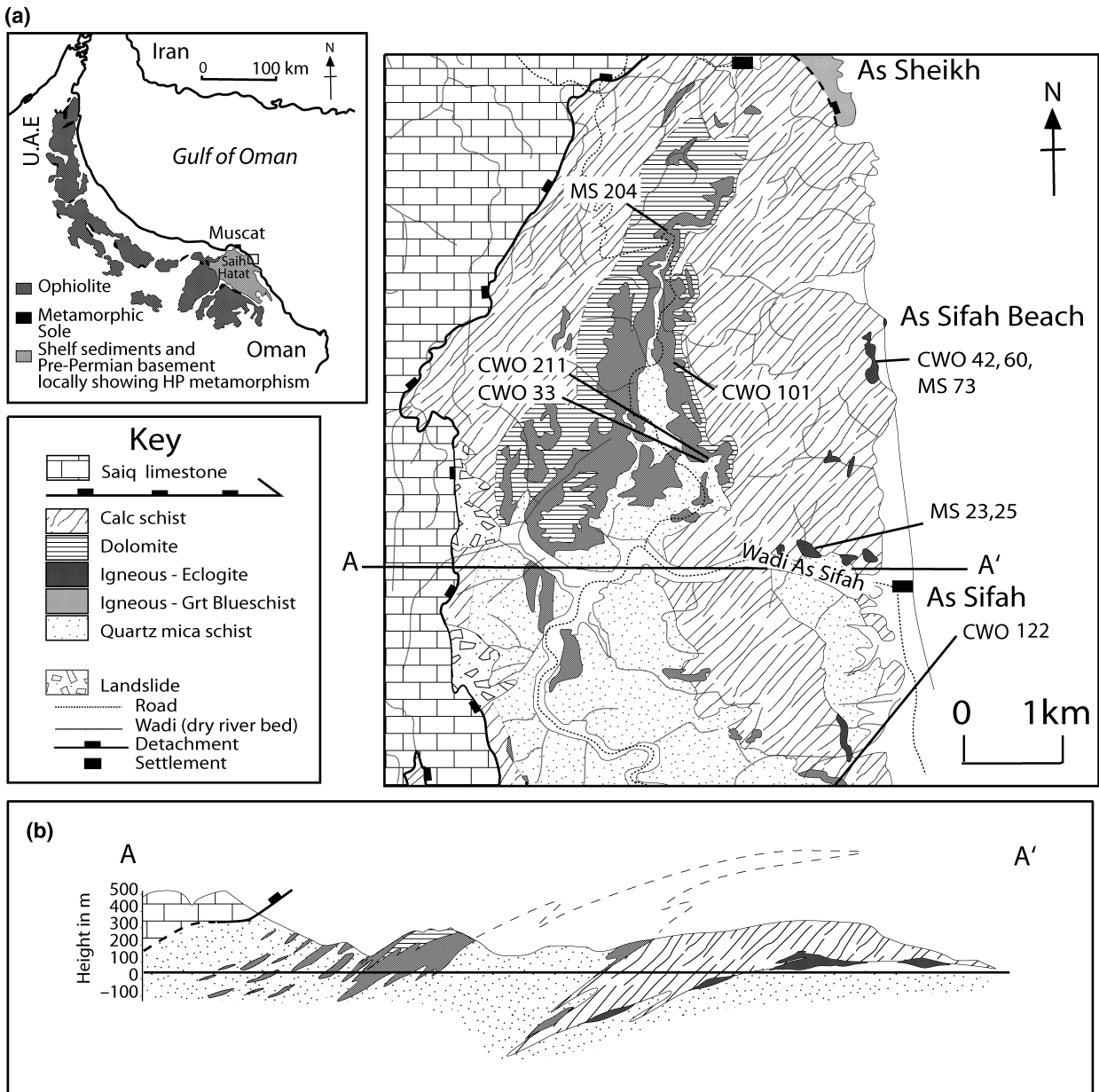


Fig. 1. (a) Geological sketch map of the As Sifah region of Saih Hatat, with insert showing the position Saih Hatat within Oman and the NE Arabian Peninsula. Based on the geological maps of Le Métour *et al.* (1986) and Warren (2004). Localities of samples mentioned in the text are marked. (b) Schematic cross-section across line marked on map.

the peak pressures of phengite-bearing HP and UHP eclogites from China (Carswell *et al.*, 1997; Schmid, 2001), Norway (Wain, 1998; Cuthbert *et al.*, 2000; Wain *et al.*, 2001) and the Alps (Nowlan *et al.*, 2000).

Petrogenetic grid calculations in the NCFMASH (Na₂O-CaO-FeO-MgO-Al₂O₃-SiO₂-H₂O) system indicate that garnet + jadeitic clinopyroxene + ‘crossite’ + epidote (peak granuloblastic eclogite assemblage, see below) occurs between 14 and 20 kbar, and 520 and 610 °C conditions (e.g. El-Shazly, 2001; Wei *et al.*, 2003). Note that the term ‘crossite’ is used throughout

this paper to indicate amphibole containing between 30% and 70% Fe³⁺/(Fe³⁺ + Al). Although this classification was abandoned by Leake *et al.* (1997), many of the Oman sodic amphiboles lie on the boundary between glaucophane and riebeckite in their classification. The NCFMASH grids predict the presence of paragonite, not generally found as a major phase in the HP rocks of Oman, and also that chloritoid is only stable in the presence of lawsonite, whereas it is found in equilibrium with epidote in Oman. On the basis of calculations in the NCFMASH system, El-Shazly (2001) argued that the peak pressure for the

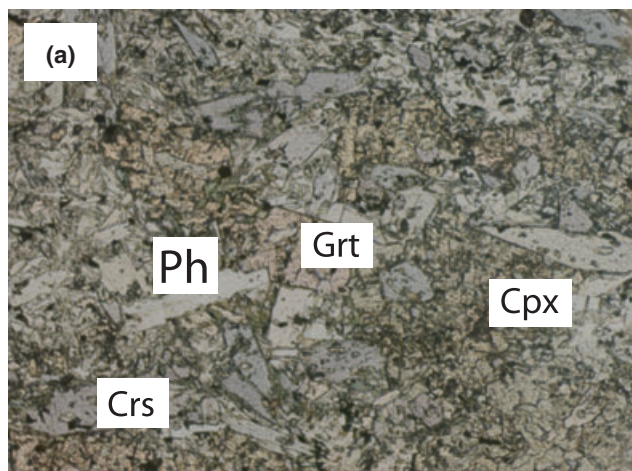
Oman eclogites was < 16 kbar, rather than the higher 22–23 kbar calculated by Searle *et al.* (1994).

In many eclogites, the contribution of Fe^{3+} to Fe_{total} is negligible. Other eclogites, such as those from Oman or the Ile de Grôix in France, are highly oxidized, and the assumption that all the iron is Fe^{2+} will inherently lead to increasingly large errors in thermobarometric calculations. The inclusion of Fe^{3+} into model systems has been predicted to widen the stability fields of the principal Fe^{3+} -bearing minerals, which in Oman are clinopyroxene, sodic amphibole and epidote.

The present study presents the results of pseudo-section modelling of the Oman eclogites and associated garnet-blueschists. The crucial advance of this study over previous studies is that an attempt has been made to model the ferric-iron end-members of important solid-solution minerals such as omphacite and sodic amphibole.

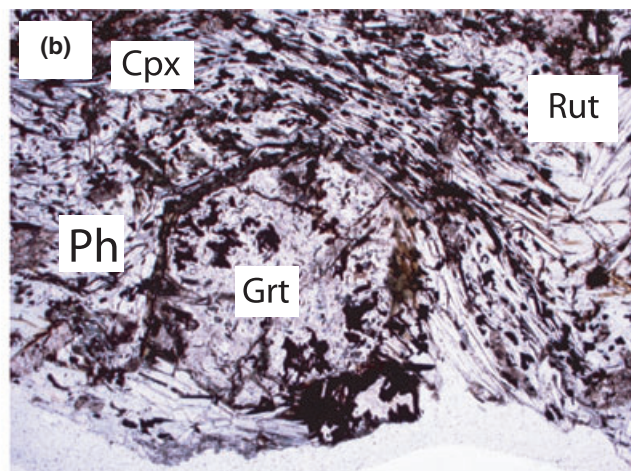
THE OMAN ECLOGITES AND BLUESCHISTS

The eclogites in Oman are exposed in kilometre-scale lenses along the coast and just inland of As Sifah village, NE Oman (Fig. 1). They are underlain by quartz-mica schists and overlain by calc-phengite schists and dolomite layers. Three main types of mafic eclogites have been recognized: granoblastic, foliated and chloritoid eclogites (see also El-Shazly *et al.*, 1997). The granoblastic eclogites (e.g. MS 73, Fig. 2a) contain almandine garnet and omphacitic clinopyroxene, with minor sodic amphibole, quartz, epidote and phengite. These eclogites have no preferred fabric orientation. The foliated eclogites (e.g. CWO 122; Fig. 2b) contain more sodic amphibole, phengite and quartz, and have a strong preferred fabric orientation formed by the alignment of phengite and blue amphibole. The chloritoid eclogites (e.g. MS 25; Table 1, Figs 2c & 4d)



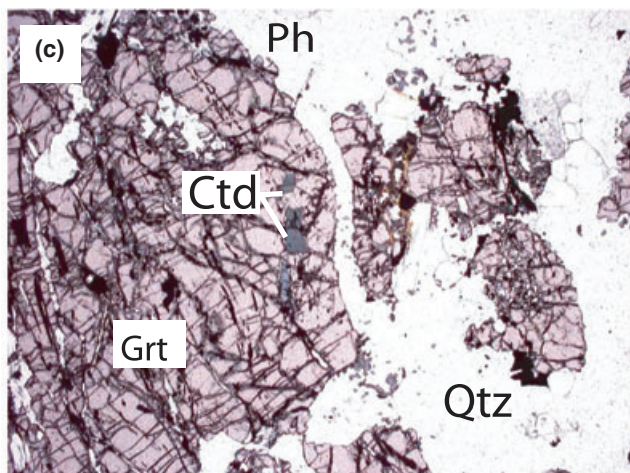
MS 73

2.25 mm



CWO 122

1.3 mm



MS 25

2.25 mm

Fig. 2. Thin-section photomicrographs of typical eclogites from As Sifah (see Fig. 1 for locations). (a) Granoblastic eclogite MS 73 with more clinopyroxene (omphacite/chloromelanite) than phengite. (b) Foliated eclogite CWO 122 with more phengite than clinopyroxene (omphacite/chloromelanite). (c) Chloritoid eclogite MS 25 contains chloritoid in garnet as well as in the matrix (see also Fig. 4d). The pseudo-section in Fig. 8 refers to this sample. Size underneath photomicrographs refers to width of picture.

Table 1. Mineral composition data for chloritoid-eclogite MS 25

Place:	Cpx	Grt	Grt Rim	Grt Mid	Gln Core	Ph	Ep	Ctd
No. of analyses:	15	5	5	5	8	10	3	3
SiO ₂	55.29	36.80	36.59	36.48	55.67	52.04	37.50	23.80
TiO ₂	0.06	0.05	0.06	0.05	0.04	0.31	0.05	0.01
Al ₂ O ₃	9.84	20.89	20.72	20.71	8.17	22.66	22.89	39.77
FeO	17.04	37.58	37.00	32.79	17.41	6.27	13.78	26.11
MnO	0.02	0.14	1.04	5.68	0.08	0.02	0.44	0.33
MgO	1.35	1.86	1.66	1.39	7.83	3.55	0.07	2.46
CaO	2.69	3.77	3.58	3.45	0.61	0.03	21.62	0.01
Na ₂ O	12.29	0.03	0.02	0.00	6.84	0.01	0.00	0.02
K ₂ O	0.01	0.00	0.00	0.00	0.02	11.07	0.02	0.01
Total	98.57	101.12	100.67	100.55	96.67	95.95	96.38	92.53
Calculated ions								
Si	2.01	2.95	2.95	2.95	7.90	7.03	3.01	1.97
Ti	0.00	0.00	0.00	0.00	0.00	0.03	0.00	0.00
Al	0.42	1.97	1.97	1.97	1.37	3.61	2.16	3.89
Fe ³⁺	0.42	0.13	0.12	0.12	0.76	0.19	0.81	0.17
Fe ²⁺	0.10	2.39	2.37	2.10	1.31	0.52	0.11	1.64
Mn	0.00	0.01	0.07	0.39	0.01	0.00	0.03	0.02
Mg	0.07	0.22	0.20	0.17	1.66	0.71	0.01	0.30
Ca	0.11	0.32	0.31	0.30	0.09	0.00	1.86	0.00
Na	0.87	0.00	0.00	0.00	1.88	0.00	0.00	0.00
K	0.00	0.00	0.00	0.00	0.00	1.91	0.00	0.00
Sum	4.00	8.00	8.00	8.00	14.98	14.00	8.00	8.00

Proportions of Fe³⁺ in clinopyroxene and sodic amphibole have been estimated from stoichiometric charge balance from electron microprobe analyses (Spear & Kimball, 1982; Droop, 1987).

are similar to the foliated eclogites but contain chloritoid in the matrix and as inclusions in garnet. The clinopyroxene is aegirine-jadeite rather than omphacite. Note that the sodic clinopyroxene classification scheme of Essene & Fyfe (1967) is used here in preference to the IMA-approved scheme (Marimoto, 1989), because many of the natural examples from Oman lie on the 50:50 Fe³⁺:Al boundary. The mineral assemblage and chemistry of the eclogites have been well documented in numerous publications (Lippard, 1983; El-Shazly *et al.*, 1990, 1997; Searle *et al.*, 1994).

About 500 m inland of the As Sifah coastline, a regional-scale recumbent anticline exposes a layer of mafic rocks metamorphosed to garnet-blueschist grade (Fig. 1). The blueschists are generally more foliated than the eclogites, with phengite and blue amphibole being the main fabric-forming minerals (Fig. 3a–c). They contain garnet, sodic amphibole, phengite, quartz, chloritoid, epidote and rutile. Rare samples also contain omphacite-chloromelanite clinopyroxene (Fig. 3b); these samples never contain chloritoid.

The eclogites and blueschists can be divided into two main compositional groups: those which do not contain chloritoid and those which do. The chloritoid-free eclogites contain ubiquitous omphacitic-chloromelanitic clinopyroxene, whereas the chloritoid-bearing eclogites contain clinopyroxene of more aegirine-jadeite composition. The chloritoid-free blueschists sometimes contain clinopyroxene, and when they do, it is omphacite-chloromelanite. Chloritoid-bearing blueschists containing clinopyroxene have yet to be reported.

One unanswered question about the evolution of the Oman blueschists and eclogites is whether the lack of clinopyroxene in the garnet-blueschists is due to a difference in *P–T* conditions or bulk composition. The eclogites are exposed in lenses (which may be tectonic boudins, or the result of initially non-layercake stratigraphy, or both) in the lower limb of a major regional recumbent fold (Fig. 1b). The overlying calc-phengite schists and the underlying quartz-mica schists contain abundant evidence of intense non-coaxial shear. The blueschists are exposed in a more coherent mafic layer on the upper limb of this fold, with the over- and underlying rocks also showing the effect of intense deformation. Recently, Gray *et al.* (2004b) and Searle *et al.* (2004) published maps showing a tectonic break separating the garnet blueschists from the eclogites, yet evidence for a major tectonic break on the ground is sparse. Pseudosection modelling of the *P–T* evolution for samples from both units may indicate whether a large enough difference in peak *P–T* estimates exists such that a tectonic break is required between these units.

Two representative chloritoid-bearing samples were selected from the Oman eclogites and garnet-blueschists for modelling purposes. At the metamorphic peak, garnet-blueschist sample CWO 211 (Fig. 3c) contained almandine garnet, crossitic sodic amphibole, chloritoid, epidote, phengite, rutile and quartz. The chloritoid-eclogite sample MS 25 (Figs 2c & 4d) additionally contained aegirine-jadeite clinopyroxene. Pseudomorphs of epidote and paragonite after lawsonite are common as inclusions in garnet in both rocks. Garnet, clinopyroxene and sodic amphibole are all extensively zoned; details of the mineral chemistry are presented below. The chemical zoning is consistent with growth from a constantly changing (fractionating) available bulk composition. A retrograde overprint in both rocks includes albite and green calcic/sodic amphibole.

Petrographical constraints on evolution

Three generalized mineral growth stages have been described in the eclogites and garnet-blueschists, culminating at the metamorphic peak (Martin, 1994; Searle *et al.*, 1994). The prograde part of the garnet-blueschist path is represented by garnet and sodic amphibole cores, and chloritoid, phengite and pseudomorphs after lawsonite in garnet. The peak metamorphic conditions are calculated from the inner rims of the garnet, the inner rims of the amphibole, chloritoid and epidote. The prograde part of the eclogite path is represented by the cores of garnet (with pseudomorphs after lawsonite), sodic amphibole, phengite, chloritoid and sodic clinopyroxene. The metamorphic peak is represented by the inner rims of the garnet, the rims of the matrix clinopyroxene, and the inner rims of the amphibole, chloritoid and epidote. A greenschist facies retrograde

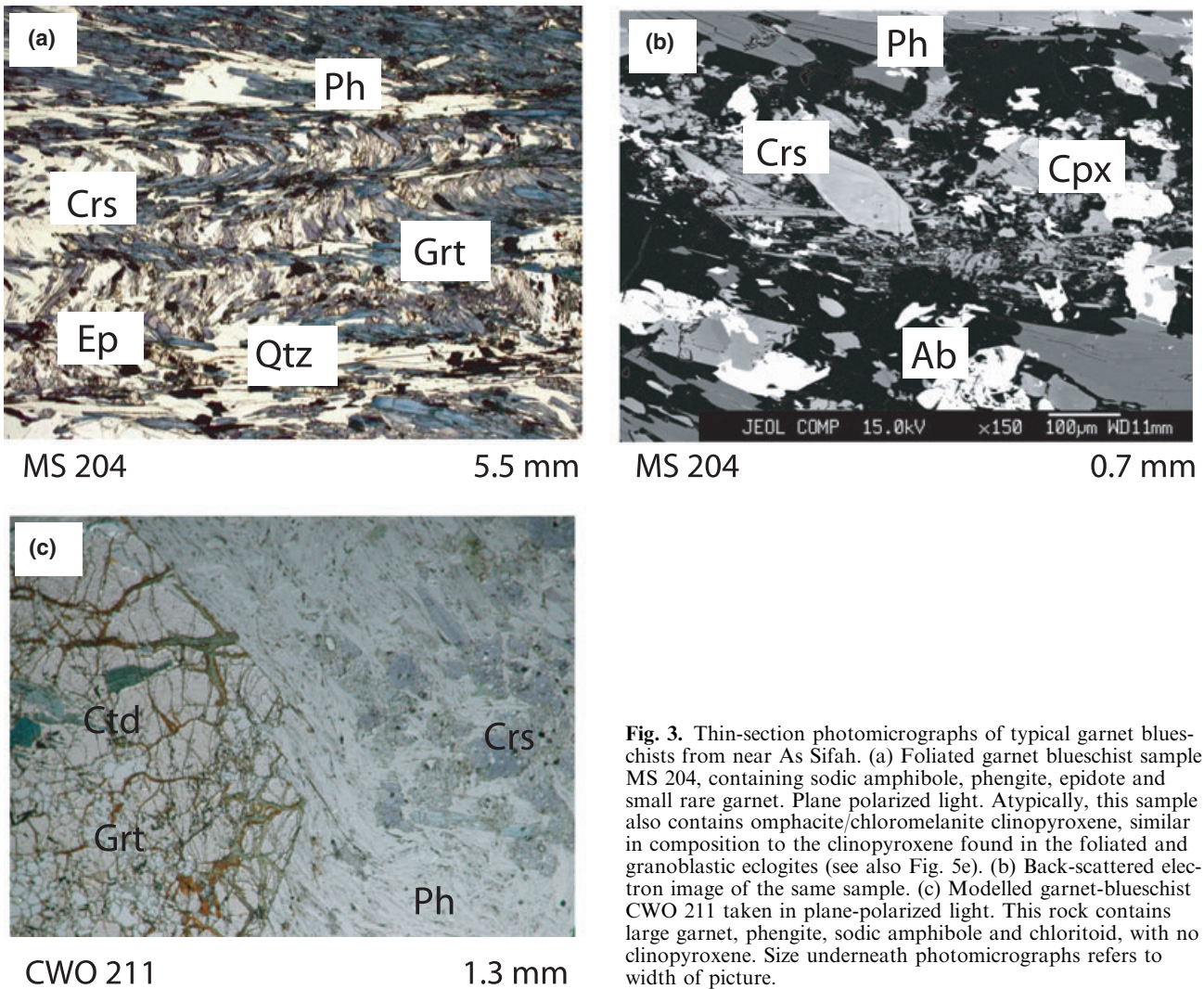


Fig. 3. Thin-section photomicrographs of typical garnet blueschists from near As Sifah. (a) Foliated garnet blueschist sample MS 204, containing sodic amphibole, phengite, epidote and small rare garnet. Plane polarized light. Atypically, this sample also contains omphacite/chloromelanite clinopyroxene, similar in composition to the clinopyroxene found in the foliated and granoblastic eclogites (see also Fig. 5e). (b) Back-scattered electron image of the same sample. (c) Modelled garnet-blueschist CWO 211 taken in plane-polarized light. This rock contains large garnet, phengite, sodic amphibole and chloritoid, with no clinopyroxene. Size underneath photomicrographs refers to width of picture.

overprint consisting of albite, green sodic-calcic amphibole and epidote affects all the HP rocks in Oman.

Although lawsonite has not been documented in the HP rocks from Oman, prismatic aggregates of paragonite and epidote in garnet in both the blueschists and eclogites have been interpreted as pseudomorphs after lawsonite (El-Shazly & Liou, 1991; Searle *et al.*, 1994; Fig. 4a). These imply that all the HP rocks must have passed through the stability field of lawsonite during garnet growth. Epidote is preserved as the peak assemblage Ca-Al-Fe³⁺ silicate.

A single sample containing talc as a major phase was collected during the present study from amongst the garnet-blueschists (Fig. 4b). El-Shazly *et al.* (1997) reported talc as a minor retrograde phase in one of their samples. During the present study, relatively iron-rich talc ($X_{Mg} = 0.85$) has been found coexisting with garnet, chloritoid, blue amphibole and quartz (mineral analyses in Table 3). Previous studies (e.g. Goffè *et al.*,

1988; Searle *et al.*, 1994) noted the lack of talc in the Oman HP assemblages, although it is a common phase in rocks of similar P - T history from other terranes. Garnet-talc-chloritoid is an assemblage which only occurs outside the stability field of chlorite, and indicates pressures > 20 kbar at 500–550 °C (Wei & Powell, 2004). This sample therefore suggests that the garnet-blueschists and the eclogites may have had similar P - T histories and that the difference in peak assemblages may largely reflect different bulk compositions.

El-Shazly (2001) suggested that pressures ≥ 16 kbar for the mafic eclogites are not supported by mineral assemblages in cofacial interlayered pelitic and quartzofeldspathic mica schists because 'none of the retrograde textures [in the quartz- and quartzofeldspathic mica schists] suggest the former presence of phases stable at ≥ 20 kbar'. Aggregates of albite and phengite rimmed with magnetite, found in quartzofeldspathic schists interlayered with the eclogites

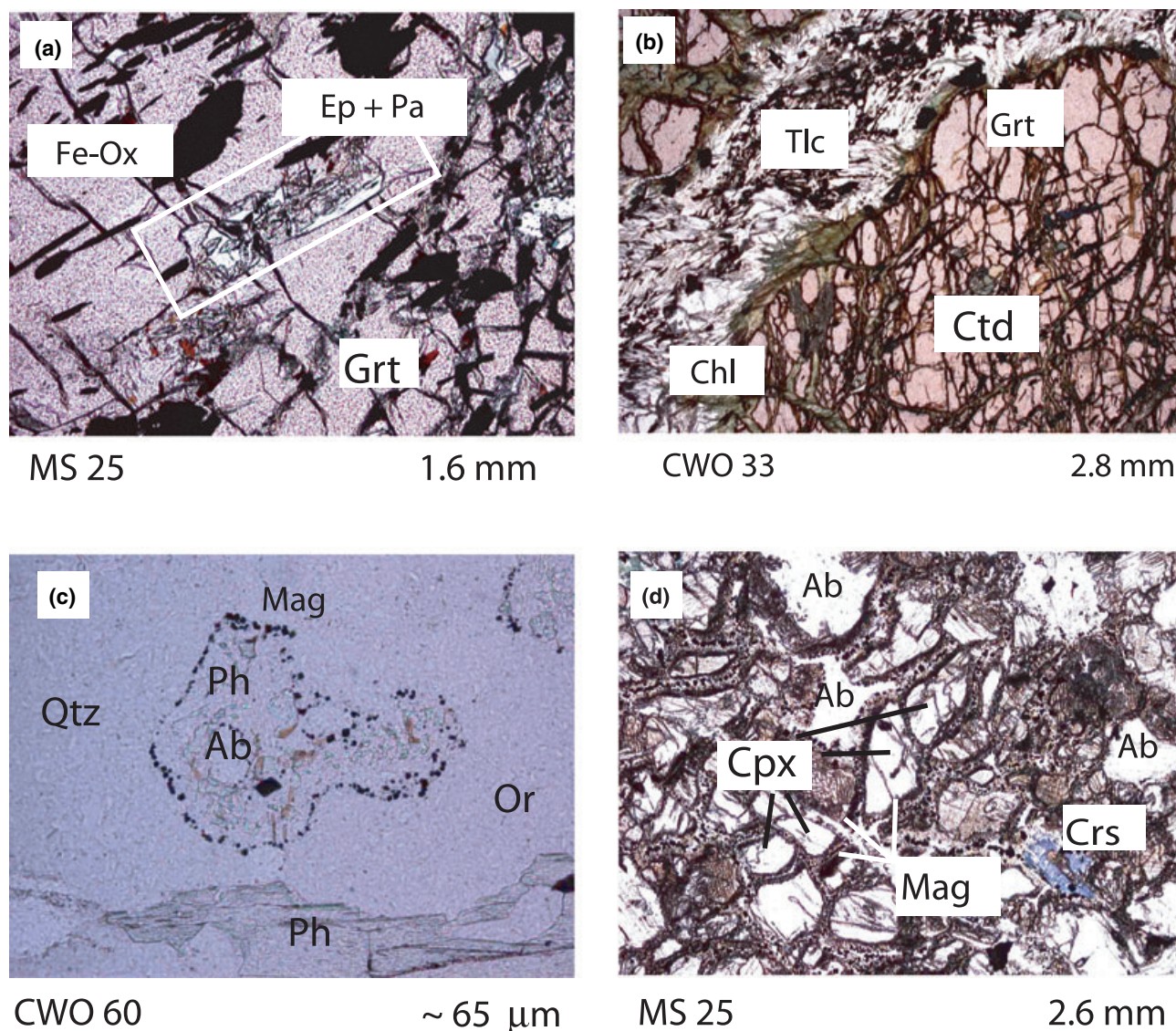


Fig. 4. Photomicrographs and back-scattered electron images of selected microtextures constraining the evolution of the Oman eclogites and garnet-blueschists. (a) Prismatic aggregates of paragonite and epidote in a garnet from chloritoid-eclogite sample MS 25, interpreted as pseudomorphs after lawsonite. (b) Talc-garnet-chloritoid rock (sample CWO 33) collected from a single outcrop amongst the garnet-blueschists (see Fig. 1). (c) Aggregates of albite and phengite rimmed with magnetite in quartzofeldspathic schist CWO 60, collected from an eclogite-bearing mafic lense on As Sifah beach. (d) Aegirine-jadeite clinopyroxene crystals breaking down to rims of albite and magnetite in modelled chloritoid-eclogite MS 25. Size refers to width of photomicrograph.

(Fig. 4c), have previously been recorded (El-Shazly, 2001) but not interpreted as pseudomorphs after HP phases. During the present study (and that of Martin, 1994), rims of magnetite around albite-quartz symplectites have been found around retrogressed aegirine-jadeite in chloritoid-bearing eclogites such as the modelled sample MS 25 (Fig. 4d). This suggests that the pseudomorphs in the quartzofeldspathic schists are after pyroxene, and hence mineral assemblages in cofacial units *could* have formed at >16 kbar.

Kyanite, paragonite and hornblende – common minerals in eclogites from other regions – have not

been recorded as part of the Oman HP assemblage. Albite, chlorite and paragonite, as well as blue-green sodic-calcic amphibole of actinolitic composition have grown as part of the retrograde overprint, but there is no evidence that they were stable at the metamorphic peak. Paragonite is predicted to be stable at eclogite facies pressures and temperatures on petrogenetic grids and pseudosections calculated in the NCFMASH system, but is not found as a major rock-forming phase in the Oman HP rocks. It has, however, been reported as the main white mica in a glaucophane-rich sample (El-Shazly *et al.*, 1990). Paragonite is normally found only as a minor phase, produced by the breakdown of

Table 2. Mineral data for garnet-blueschist CWO 211

	Grt Rim	Grt Mid	Grt Core	Ctd	Gln In grt	Gln Rim	Gln Core	Ep Ep	Ph Rim	Ph Core	Chl
No. of analyses:	5	5	6	5	3	8	7	6	3	3	3
SiO ₂	36.99	37.07	37.00	23.67	57.22	58.44	57.73	37.79	53.24	53.36	26.11
TiO ₂	0.06	0.06	0.08	0.04	0.05	0.03	0.06	0.07	0.25	0.23	0.06
Al ₂ O ₃	20.97	20.80	20.80	38.63	7.19	8.57	6.88	23.05	23.36	22.87	18.88
FeO	35.16	35.42	34.39	24.71	15.87	13.66	16.45	13.27	4.36	4.62	25.77
MnO	0.21	0.78	2.09	0.23	0.05	0.02	0.06	0.16	0.02	0.02	0.17
MgO	2.74	2.71	2.65	3.97	9.55	10.06	9.45	0.05	4.44	4.38	15.82
CaO	4.56	3.95	4.04	0.01	0.21	0.23	0.23	22.62	0.01	0.03	0.02
Na ₂ O	0.03	0.00	0.03	0.11	7.05	6.93	6.85	0.00	0.04	0.07	0.15
K ₂ O	0.00	0.02	0.01	0.00	0.00	0.01	0.00	0.03	10.19	9.95	0.00
Total	100.72	100.80	101.08	91.38	97.19	97.93	97.70	97.04	95.91	95.53	86.98
Si	2.95	2.96	2.95	1.97	7.97	8.00	8.00	3.01	7.10	7.14	2.79
Ti	0.00	0.00	0.00	0.00	0.01	0.00	0.01	0.00	0.03	0.02	0.00
Al	1.97	1.96	1.95	3.78	1.18	1.38	1.12	2.16	3.67	3.61	2.38
Fe ³⁺	0.13	0.12	0.14	0.29	0.89	0.71	0.95	0.82	0.00	0.00	0.00
Fe ²⁺	2.22	2.25	2.15	1.42	0.96	0.85	0.96	0.06	0.49	0.52	2.30
Mn	0.01	0.05	0.14	0.02	0.01	0.00	0.01	0.01	0.00	0.00	0.02
Mg	0.33	0.32	0.31	0.49	1.98	2.05	1.95	0.01	0.88	0.87	2.52
Ca	0.39	0.34	0.34	0.00	0.03	0.03	0.03	1.93	0.00	0.00	0.00
Na	0.00	0.00	0.00	0.02	1.90	1.84	1.84	0.00	0.01	0.02	0.03
K	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.73	1.70	0.00
Sum	8.00	8.00	8.00	8.00	14.93	14.87	14.87	8.00	13.91	13.89	10.04

Proportions of Fe³⁺ in clinopyroxene and sodic amphibole have been estimated from stoichiometric charge balance from electron microprobe analyses (Spear & Kimball, 1982; Droop, 1987).

Table 3. Mineral data for talc rock CWO 33

Place:	Tlc Matrix	Ctd In grt	Chl Matrix	Chl Grt breakdown	Grt Core	Grt Mid?	Gln Matrix
No. of analyses:	4	4	4	5	6	6	5
SiO ₂	60.36	23.69	25.84	27.49	36.31	36.40	57.47
TiO ₂	0.01	0.02	0.06	0.04	0.05	0.05	0.03
Al ₂ O ₃	0.02	38.81	20.58	19.66	20.40	20.59	7.41
FeO	8.28	24.67	25.67	21.39	31.69	35.05	15.51
MnO	0.01	0.10	0.26	0.12	6.25	1.31	0.07
MgO	25.31	4.05	14.94	18.78	2.12	2.67	9.76
CaO	0.00	0.00	0.11	0.04	3.48	3.86	0.19
Na ₂ O	0.00	0.09	0.03	0.05	0.01	0.06	7.00
K ₂ O	0.00	0.02	0.02	0.00	0.00	0.00	0.00
Total	93.99	91.44	87.52	87.58	100.32	100.00	97.44
Calculated ions							
Si	8.04	0.99	2.74	2.84	2.93	2.93	8.01
Ti	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Al	0.00	1.90	2.57	2.39	1.94	1.95	1.22
Fe	0.92	0.86	2.28	1.85	2.14	2.36	1.81
Mn	0.00	0.01	0.02	0.01	0.43	0.09	0.01
Mg	5.04	0.25	2.36	2.89	0.26	0.32	2.03
Ca	0.00	0.00	0.01	0.00	0.30	0.33	0.03
Na	0.00	0.01	0.01	0.01	0.00	0.01	1.89
K	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sum	14.00	4.00	10.00	10.00	8.00	8.00	15.00

other phases such as lawsonite, blue amphibole and clinopyroxene.

Mineralogical constraints on evolution

The major minerals (garnet, clinopyroxene and amphibole) in the Oman garnet-blueschists and eclogites commonly show chemical zonation from core to rim. This indicates that the effective bulk composition of the rocks must have been changing during evolution, and hence certain major assumptions must be made in order to calculate an effective bulk

composition for modelling. Mineral analyses for both rocks are given in Tables 1 and 2.

Figure 5 shows the garnet-zoning profiles of typical garnet from the chloritoid-bearing eclogites (e.g. MS 25; Fig. 5a), granoblastic eclogites (e.g. CWO 42; Fig. 5b) and blueschists (e.g. CWO 211 and 101; Fig. 5c,d). Garnet is almandine-dominated and, in the eclogites, commonly contains inclusion-rich cores (quartz, sodic clinopyroxene, sodic amphibole, pseudomorphs after lawsonite, rutile, ilmenite, zircon) overgrown by inclusion-free rims. Gray *et al.* (2004b) suggested that the inclusion patterns indicated that the cores were 'relict', perhaps from some earlier metamorphic event. However, where distinct garnet growth stages have been documented from other regions (e.g. Argles *et al.*, 1999), chemical zoning profiles show distinct jumps. Major element profiles for the Oman rocks, however, vary smoothly, with no distinct jumps in composition. Most of the garnet zoning profile is interpreted as representing the prograde path, culminating with the inner rim composition at the metamorphic peak. In some rocks garnet has been heavily replaced by chlorite and epidote, especially at the rims. In others, the garnet is very well preserved, with little evidence for diffusion or resorption at the rims.

Sodic clinopyroxene in the Oman eclogites and blueschists varies in composition depending on the rock type in which it is found (Fig. 5e; Lippard, 1983; El-Shazly *et al.*, 1990, 1997; El-Shazly, 2001). Clinopyroxene in the granoblastic eclogites typically has distinct chloromelanite cores and omphacitic rims. Martin (1994) studied the crystal chemistry of the Oman eclogite clinopyroxene in detail and concluded that although the core-rim boundary is optically, chemically and structurally abrupt, this is due to a miscibility gap rather than a break in crystallization

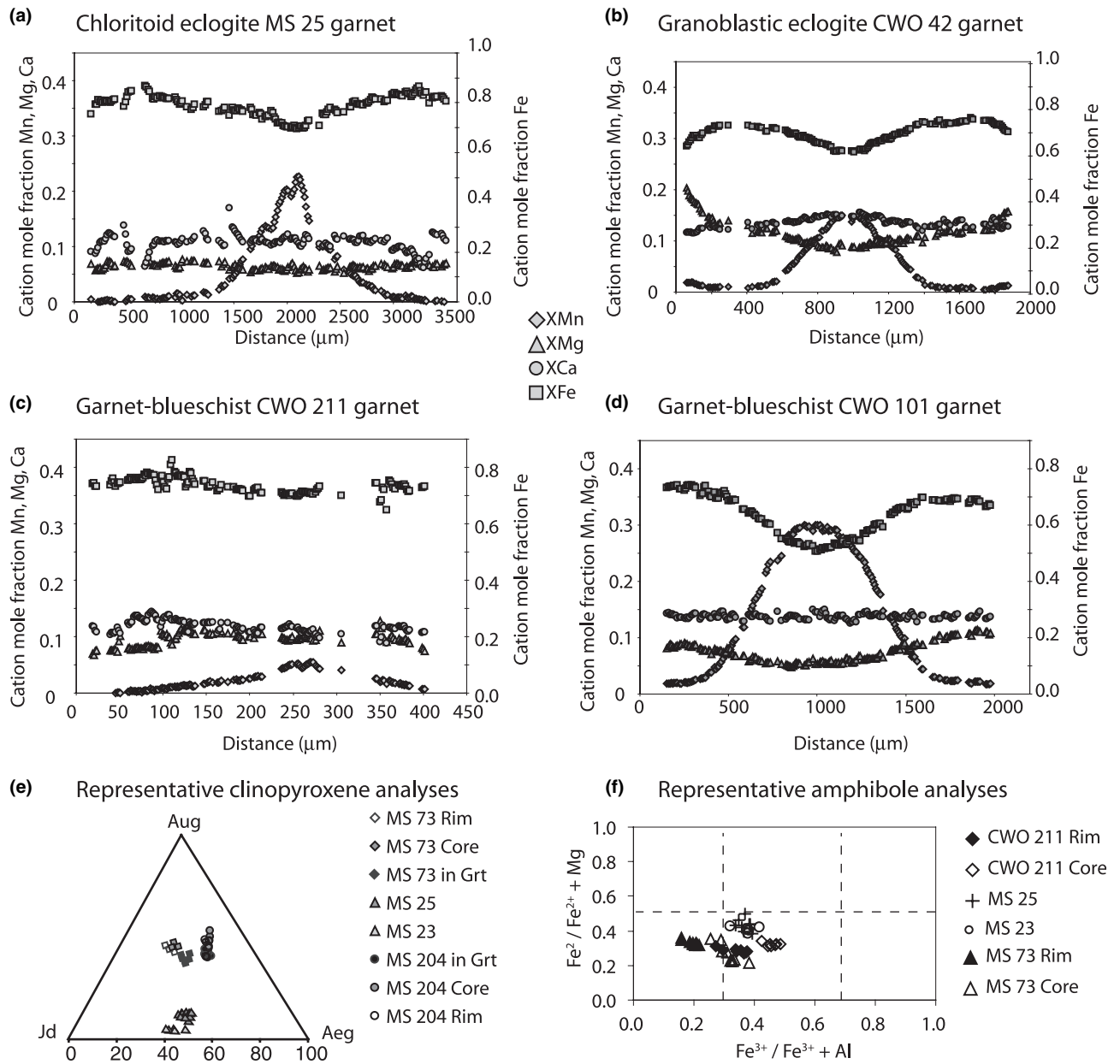


Fig. 5. Graphical representations of mineral analyses from selected rocks. (a–d) Major element traverses across selected garnet from the eclogites and garnet-blueschists. (e) Clinopyroxene compositions plotted onto a ternary Fe^{3+} (aegirine), Na (jadeite), Ca[Mg, Fe^{2+}] (hedenbergite, diopside) diagram. MS 204 is a garnet-blueschist sample containing chloromelanitic clinopyroxene. MS 23 and MS 25 are chloritoid-eclogites with aegirine-jadeite clinopyroxene. MS 73 is a typical granoblastic eclogite with chloromelanitic clinopyroxene (nomenclature after Essene & Fyfe, 1967, see text for explanation). (f) Representative amphibole compositions. Note that these analyses mostly plot in the 'crossite' field, see text for nomenclature explanation. Sample CWO 211 is a garnet blueschist.

(c.f. Carpenter, 1983). Aegirine-jadeite clinopyroxene in the chloritoid-eclogites is less zoned than the clinopyroxene in the granoblastic eclogites. Clinopyroxene is rare in the garnet-blueschist region, and is generally omphacite or aegirine-augite (Fig. 5e), although compositions lying on the aegirine-jadeite/omphacite boundary have also been reported from the blueschists (El-Shazly *et al.*, 1990).

Sodic amphibole in the granoblastic eclogites and garnet-blueschists is typically zoned, with optically and chemically distinct cores and rims (Fig. 5f). In the eclogites, the amphibole commonly has paler cores and darker rims, whereas the reverse is usually seen in the garnet blueschists (Searle *et al.*, 1994). The sodic amphibole in the chloritoid-eclogites is generally more homogeneous. Most of the amphibole

has crossitic compositions. Retrograde rims of green actinolite, winchite and barroisite are commonly present.

Epidote is a ubiquitous phase in both the eclogites and the garnet-blueschists, where it formed as part of the peak assemblage as well as during retrogression. Crystals are generally unzoned or weakly zoned, although in some granoblastic eclogites sharp compositional differences exist between the core and rim zones. Allanite is found coring epidote in some samples.

Chloritoid is present only in eclogites and blueschists which contain a high proportion of phengite and quartz. In the eclogites, chloritoid is present only in rocks which contain aegirine-jadeite rather than omphacite. In the modelled eclogite sample MS 25, chloritoid is found as inclusions in garnet, although in other samples it is also found in the matrix.

Phengite is commonly a major rock-forming mineral in the Oman eclogites and blueschists. It is the only K₂O-bearing phase, therefore K has not been included in the model system. Phengite is relatively enriched in celadonite, and potentially the celadonite exchange could affect the effective bulk composition defined by the other phases. Our focus here is only on the peak *P-T* assemblage rather than on the full *P-T* path, and our judgement is that omitting phengite will not significantly affect the Fe-Mg exchange behaviour in other phases. Minor minerals such as rutile, iron oxides (hematite, magnetite and ilmenite), zircon and titanite are common accessory phases.

PSEUDOSECTION CONSIDERATIONS

Pseudosections in the NCFMASHO (Na₂O-CaO-FeO-MgO-Al₂O₃-SiO₂-H₂O-Fe₂O₃) model system were calculated in order to derive more detailed information about the *P-T* evolution and the peak *P-T* conditions of the HP rocks in Oman. They were calculated using the software THERMOCALC 3.25 and the updated thermodynamic database 5.5 (Holland & Powell, 1998) using garnet, sodic clinopyroxene, sodic amphibole, epidote, lawsonite, paragonite, chloritoid and chlorite, with excess quartz and water.

Mineral activity coding

A new activity model coding for Fe³⁺-bearing minerals has been introduced for the expanded NCFMASHO system. These are generally extensions to the coded models supplied with the THERMOCALC documentation. Symmetric solid-solution models (Powell & Holland, 1993) in combination with Darken's quadratic formalism (DQF) corrections (Powell, 1987) were used for garnet, clinopyroxene, amphibole, chloritoid, chlorite and epidote. Paragonite, albite and lawsonite were included as pure end-members. Details of the mineral activity models can be found in the Appendix.

Table 4. Bulk compositions for THERMOCALC modelling, normalized to 100%

	Al ₂ O ₃	CaO	MgO	FeO	Na ₂ O	MnO	O
Garnet blueschist	18.08	7.29	25.67	31.66	11.62	0.00	5.68
Chloritoid-eclogite	31.13	11.70	7.01	42.64	4.61	0.00	2.91
Blueschist-Mn	18.08	7.28	25.67	31.65	11.62	0.02	5.68
Ctd-eclogite-Mn	31.07	11.68	7.00	42.57	4.60	0.18	2.90

Bulk compositions

Bulk compositions of the blueschists and eclogites were determined by combining mineral modes from thin-section measurements with microprobe analyses. Whole-rock XRF analyses were not used because of the highly zoned nature of the Oman blueschists and eclogite minerals, indicating that not all of the total bulk composition was available for equilibration at every step of the metamorphic history. The point-counting method for calculating effective bulk composition is an estimation, and the bulk composition thus calculated is valid only for the prograde-to-peak segment of the *P-T* path.

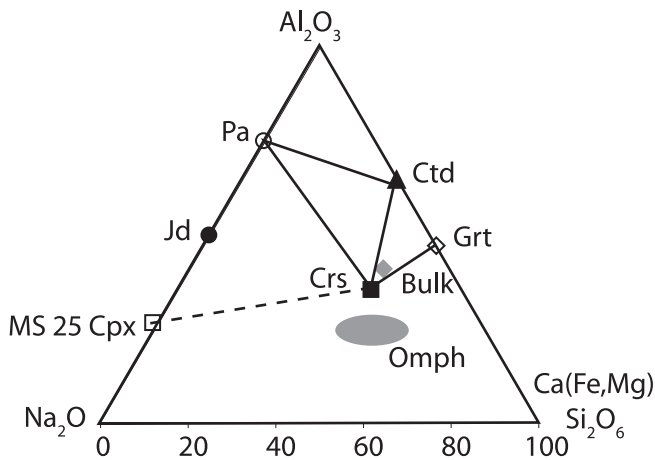
Bulk compositions were calculated using average chloritoid-eclogite and garnet-blueschist peak mineral-phase compositions and using the bulk composition calculation facility built into THERMOCALC. Modelled peak bulk compositions are given in Table 4 and are projected onto the Al₂O₃-Na₂O-Ca(Fe,Mg)Si₂O₆ plane from water, quartz, epidote and magnetite in Fig. 6. The garnet-blueschist bulk composition was calculated using 10% garnet with Fe²⁺/(Fe²⁺ + Mg) = 0.92 and Ca/(Ca + Fe²⁺ + Mg) = 0.2; 70% sodic amphibole with Fe²⁺/(Fe²⁺ + Mg) = 0.47 and Fe³⁺/(Fe³⁺ + Al) = 0.49; 5% chloritoid with Fe²⁺/(Fe²⁺ + Mg) = 0.75; 10% lawsonite and 2% magnetite. The chloritoid eclogite bulk composition was calculated using 50% garnet with Fe²⁺/(Fe²⁺ + Mg) = 0.85 and Ca/(Ca + Fe²⁺ + Mg) = 0.1, 20% clinopyroxene with Fe²⁺/(Fe²⁺ + Mg) = 0.6, Fe³⁺/(Fe³⁺ + Al) = 0.5 and Na/(Na + Ca) = 0.9; 15% chloritoid with Fe²⁺/(Fe²⁺ + Mg) = 0.85; and 15% lawsonite. Manganese was added to the bulk composition (Table 4) to calculate the *P-T* conditions for the first appearance of garnet.

The projection of peak metamorphic phases and calculated bulk compositions in Fig. 6 show that paragonite and chloritoid stability appears to be controlled by bulk composition. Bulk compositions richer in Al will grow chloritoid, whereas the absence of paragonite at the metamorphic peak in the Oman rocks is apparently a function of relatively low-bulk Al and Na.

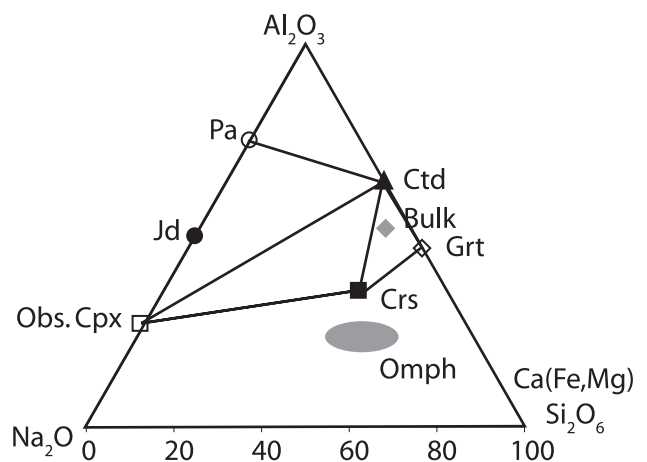
Calculation of Fe³⁺

Proportions of Fe²⁺ to Fe³⁺ in clinopyroxene and sodic amphibole have been estimated from stoichio-

(a) Garnet-blueschist CWO 211



(b) Chloritoid eclogite MS 25



(c) Granoblastic eclogite MS 73

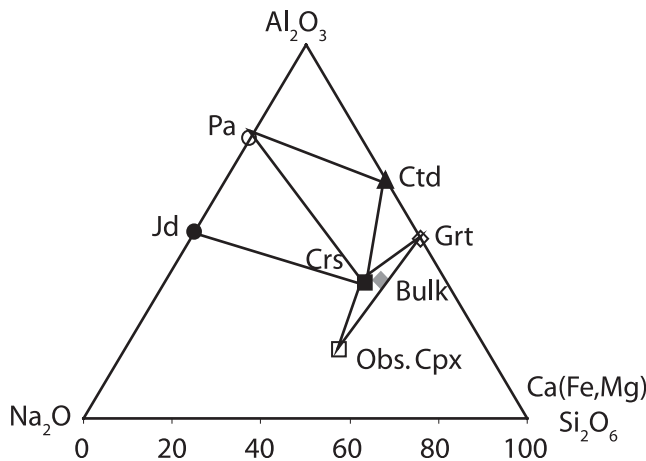


Fig. 6. Projection of modelled bulk compositions (grey diamonds) with observed mineral compositions onto the Al_2O_3 - Na_2O - $\text{Ca}(\text{Fe},\text{Mg})\text{Si}_2\text{O}_6$ (augite) plane projected from water, quartz, observed epidote and magnetite. The bulk composition appears to drive the clinopyroxene composition and presence or absence of paragonite at the metamorphic peak. Although the mineral compositions appear to plot in similar positions in all three diagrams, the actual mineral compositions given in Tables 1 and 2 are plotted. Although there is no clinopyroxene in the garnet-blueschists, the chloritoid-eclogite clinopyroxene composition has been plotted for schematic purposes: if the garnet blueschists were allowed to evolve further, would they become chloritoid eclogites? Granoblastic eclogite MS 73 with omphacitic clinopyroxene is plotted for comparison.

metric charge balance from electron microprobe analyses (Spear & Kimball, 1982; Droop, 1987). Published comparisons of $\text{Fe}^{3+}/\text{Fe}_{\text{total}}$ ratios estimated by charge balance and $\text{Fe}^{3+}/\text{Fe}_{\text{total}}$ ratios calculated by other methods such as Mössbauer spectroscopy (Canil & O'Neill, 1996), precise Mössbauer milliprobe determination (Sobolev *et al.*, 1999) and micro-X-ray absorption near-edge structure (micro-XANES) analysis (Schmid *et al.*, 2003), show that the charge balance method can be quite inaccurate. As the results of the present study are sensitive to the amount of Fe^{3+} in the system, and that amount has not been determined by a quantitative method such as Mössbauer spectroscopy, this is considered to be the largest source of error in the P - T results yielded by the calculated pseudosections.

There have been many recently published studies on pseudosections for eclogites and garnet-blueschists calculated in the NCFMASH system (e.g. Will *et al.*,

1998; Carson & Powell, 1999; Guiraud *et al.*, 2001; Klemm *et al.*, 2002; Rebay & Powell, 2002; Wei *et al.*, 2003; Hoschek, 2004), but none in the oxidized NCFMASHO system. The effect of adding Fe^{3+} into the model system is generally considered to be much more profound than the effects of adding TiO_2 or K_2O , because Fe^{3+} can enter many of the NCFMASH phases (White *et al.*, 2000). The incorporation of Fe^{3+} into epidote, sodic amphibole, chloritoid and clinopyroxene will lead to the enlargement of the stability fields of these phases, and to the stabilization of new NCFMASHO-invariant points.

There is a perceived lack of detailed thermodynamic data on Fe^{3+} -bearing end-members, particularly amphibole, in the THERMOCALC database. The present study uses the information in the THERMOCALC database 5.5 (Holland & Powell, 1998) to explore the effects of Fe^{3+} substitution into sodic pyroxene (aegirine or augite), sodic amphibole (riebeckite) and epidote.

The stability relations of riebeckite, aegirine and epidote in the THERMOCALC database were ascertained from published studies of both natural and experimental data (Ernst, 1962; Holdaway, 1972; Liou, 1972).

H₂O activity

Many of the key prograde reactions in the blueschists and eclogites, especially those which eliminate chlorite, are dehydration reactions. The presence of an impure aqueous fluid, with water activity less than unity, will affect the equilibrium temperature of the reactions. In Oman, the HP mafic units occur within a carbonate-rich sequence. Syn-metamorphic carbonate veins are common, and have been reported in many studies (El-Shazly *et al.*, 1990; Searle *et al.*, 1994; Miller *et al.*, 2002). Dissolved species and other fluid components are therefore thought to be present in the fluid at equilibrium with the rock at HP.

Measurements of the composition of fluid inclusions in the HP phases of the Oman eclogites (El-Shazly, 1999) show that the equilibrium fluid during growth of metamorphic phases such as garnet was predominantly aqueous. Most inclusions have a salinity of ≤ 10 wt% NaCl equivalent, in some samples reaching up to 17%. Activity of water, $a_{(\text{H}_2\text{O})}$, varies with the weight fraction of water in the solution, $x_{(\text{H}_2\text{O})}$, as $a_{(\text{H}_2\text{O})} = x_{(\text{H}_2\text{O})}/[2 - x_{(\text{H}_2\text{O})}]$ (Aranovitch & Newton, 1996; Tropper & Manning, 2004). A value of $x_{(\text{H}_2\text{O})} = 0.9$ has been used for the purpose of the present study, yielding a value of $a_{(\text{H}_2\text{O})} = 0.8$. The effect of lowering the water activity is to lower the temperature, at fixed pressure, at which certain dehydration reactions occur. Reactions differ in their sensitivity to water activity.

PREVIOUS PSEUDOSECTION CALCULATIONS OF SIMILAR ROCKS

Pseudosection modelling in the NCFMASH system has proved unsatisfactory for modelling oxidized rocks such as those of the Oman compositions. In addition to predicting relatively low pressures for rocks of a suitable model bulk composition, published pseudosections of similar rocks consistently predict the apparent stability of paragonite and/or lawsonite at the temperature and pressure values of interest. Paragonite is not a common rock-forming mineral in the HP assemblages from Oman, although it has been described as a breakdown product of lawsonite and chloritoid. Phengite is instead the common matrix-forming white mica.

An NCFMASH pseudosection for a garnet glaucophanite from Samos, Greece (Will *et al.*, 1998), used a bulk composition similar to that of the Oman garnet-blueschists and chloritoid-eclogites, and is useful for comparison. The key points of interest are that between 480 and 530 °C (the relevant temperature range

in Oman), lawsonite is the stable Ca-Al phase above ~ 20 kbar, with zoisite stable only below 15–16 kbar. Paragonite is predicted to be ubiquitously stable below ~ 20 kbar. Omphacitic sodic pyroxene appears at > 550 °C and > 20 kbar, with sodic amphibole, garnet and paragonite, but no chloritoid. The Oman assemblage of garnet, sodic amphibole, epidote (modelled as zoisite) and chloritoid (\pm pyroxene) is not stable on the Will *et al.* (1998) section. Paragonite, predicted to be ubiquitous, is not found as a peak phase in Oman, and in the rocks of interest, chloritoid is instead ubiquitous.

An NCFMASH pseudosection using a bulk composition similar to that of the Oman granulitic eclogites has been published for an eclogite from the Tien Shan, China (Wei *et al.*, 2003). This section indicates that garnet, sodic amphibole, sodic pyroxene, clinozoisite and paragonite (no chloritoid) are stable from 14 to 18 kbar and 530 to 590 °C. Apart from the pervasive presence of paragonite, these P – T conditions are similar to those predicted by El-Shazly (2001) for the Oman eclogites on the basis of NMASH and NFASH phase diagrams and pseudosections calculated using the TWEEQU program and the Berman (1991) database. Similar pseudosections for a variety of eclogite bulk compositions from localities world-wide also predict that paragonite is pervasively stable in the P – T region relevant to the Oman eclogites (Carson & Powell, 1999; Guiraud *et al.*, 2001; Klemm *et al.*, 2002).

Apart from the predicted presence of paragonite, NCFMASH pseudosections also fail to predict the correct mineral compositions or modal proportions of the phases of interest. Predicted garnet is too rich in calcium and magnesium, whereas the clinopyroxene is too poor in sodium.

RESULTS

Garnet-blueschist results

Calculations using the updated version of the THERMOCALC database and the Oman garnet-blueschist bulk composition in the NCFMASH system (no Fe^{3+}) yields a pseudosection which is very similar to that published by Will *et al.* (1998). Slight differences in pressure and temperature values arise from the use of a different database and differences in bulk composition, but the general topology is the same.

The major effect of adding Fe^{3+} into the system is the stabilization of epidote (Fig. 7a). The other Fe^{3+} -bearing phases (sodic amphibole and chloritoid) also show large stability fields. The epidote-lawsonite transition is shifted to relatively higher pressures (~ 4 kbar higher at 520 °C), whereas the chloritoid-paragonite transition is shifted to lower pressures (~ 4 kbar lower at 520 °C), which in turn means that chloritoid is now stable in the epidote field, as observed from natural samples from Oman.

Figure 7b shows isopleths of mineral composition across the field containing the peak P – T assemblage.

These show that garnet and chloritoid become richer in Mg with increasing temperature, whilst sodic amphibole becomes richer in Fe. There is minimal variation in the Fe^{3+} content of the sodic amphibole.

Figure 7c shows a plot of calculated mineral composition variation within the same P - T field plotted with the observed mineral compositions (see also Table 5). These plots show that there is a good match between observed and calculated compositions, with the best fitting temperatures in the range 500–530 °C, at pressures of 17–20 kbar. This is within the range of the previously published P - T estimate for the Oman blueschists (< 510 °C, > 6.5 kbar; El-Shazly & Liou, 1991). The best fit between observed and calculated volume percentages occurs between 18 and 20 kbar, and 510 and 530 °C (Fig. 7d), with a variation of $\pm 5\%$ on observed values. Note that on a one-oxygen basis, mol.% (from the calculated pseudosections) is approximately equal to volume percent, or mode, in the observed samples, and that we are directly comparing mol.% in the pseudosection with sample modes. Uncertainties on the calculated mol.% are 1–2%.

As garnet cores contain a high proportion of spessartine, manganese was added to the model system (in garnet, chloritoid and chlorite) to improve the P - T estimate of initial garnet growth. Bulk compositions are given in Table 4. The cores of the observed garnet are enriched with up to 20% spessartine, with the remainder consisting of 20% grossular, 4% pyrope and 56% almandine. Inclusion of manganese into the model system lowers the temperature of the first appearance of garnet by 10–15 °C. The observed garnet composition is best modelled at 23–24 kbar and ~ 450 °C (Fig. 7e). The manganese-bearing bulk composition was used only to calculate an estimated P - T for the first appearance of garnet, and was not used in further calculations, because of the refractory nature of garnet and the changing effective bulk composition during mineral growth.

The pseudosection for the modelled Oman blueschist composition predicts that clinopyroxene will appear at higher temperatures and pressures than the observed peak blueschist assemblage. The calculated pyroxene is aegirine-jadeite, similar to that seen in the chloritoid-eclogites. This indicates that although the predicted peak pressure difference between the blueschists and eclogites (1–2 kbar) is greater than the stratigraphic distance measurable on the ground today (2 km or < 1 kbar), a *major* tectonic discontinuity between the blueschists and eclogites is not required.

The entire eclogite and blueschist region is one of intense distributed shear, and this could be enough to account for the calculated P - T difference across the region. Discrete shear zones responsible for any apparent pressure difference are not traceable in the field, and are not required to explain the observed difference in metamorphic conditions.

Eclogite results

A projection of the calculated chloritoid-eclogite model bulk composition alongside the observed mineral compositions shows that in the oxidized system, paragonite stability is apparently controlled by the bulk composition (Fig. 6b). The compositions of the pyroxene, amphibole and garnet also control whether or not chloritoid is present. When the pyroxene is omphacite/chloromelanite (as in the granuloblastic and foliated eclogites; Fig. 6c), chloritoid is not present.

As with the blueschists, the inclusion of oxidized minerals into the model system increases the stability field of epidote, such that garnet, epidote, sodic amphibole, chloritoid and aegirine-jadeite clinopyroxene are predicted to be stable from ~ 490 to 550 °C and ~ 13 to 21 kbar. Comparison of calculated and observed phase compositions shows that the NCFMA-SHO system more closely predicts the observed mineral compositions than the NCFMASH system.

At $a_{(\text{H}_2\text{O})} > 0.8$, the best fit of calculated phase compositions and mol fractions with observed mineral compositions and modes occurs at about 520 ± 15 °C and 20 ± 1.6 kbar (Fig. 8a). Calculated $\text{Fe}^{2+}/(\text{Fe}^{2+} + \text{Mg})$ ratios agree less well with the observations (Table 6) than for the garnet blueschists, with the calculated clinopyroxene being too poor in Fe^{2+} and the calculated sodic amphibole being slightly too rich in Fe^{2+} . The uncertainties on calculated $\text{Fe}^{2+}/(\text{Fe}^{2+} + \text{Mg})$ ratios for clinopyroxene and sodic amphibole are $\sim 10\%$ in this region. The predicted mol.% of calculated phases satisfactorily matches the observed modes. Uncertainties on calculated mol.% in this region are 2–10% for garnet and 20–25% for epidote, clinopyroxene and sodic amphibole. The best fit between calculated mol.% and measured modes of peak phases is seen at $\sim 520 \pm 15$ °C and 20 ± 1.6 kbar with a rapidly worsening fit at higher and lower temperatures.

Isopleths of mineral composition have been calculated to investigate their variation across the peak P - T field (Fig. 8b). All minerals become more magnesian at

Fig. 7. (a) Pseudosection for garnet-blueschist sample CWO 211 showing part of the predicted P - T path (dashed line). The ellipse shows the best-fit estimate of peak P - T conditions. Darker field shading denotes indicates higher variance. (b) Enlarged section of the same pseudosection showing isopleths of constant mol fraction for the peak garnet-chloritoid-amphibole-epidote assemblage. The ellipse shows the best estimate of peak P - T conditions. (c) Modelled mineral composition variation within the garnet – chloritoid-sodic amphibole-epidote field plotted with observed mineral compositions. See Table 5 for actual data at the best fit conditions of 560 °C and 20 kbar. (d) Calculated mineral mol percentages in the best-fit region compared with observed mineral modes. (e) Comparison between modelled and observed garnet core compositions at the first appearance of garnet in the model. Conditions are 457 °C and 24 kbar and the MnNCFMASHO bulk composition (Table 4).

Table 5. Comparison between observed and calculated mineral data at best-fit pressures and temperatures (18 kbar, 520 °C) for garnet blueschist CWO 211.

	Garnet Rim		Amphibole Core		Chloritoid		Epidote	
	Obs	Calc	Obs	Calc	Obs	Calc	Obs	Calc
Si	2.95	3.00	8.00	8.00	1.97	1.00	3.01	3.00
Al	1.97	2.00	1.12	1.17	3.78	2.00	2.16	2.06
Ti	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00
Fe ³⁺	0.13	0.00	0.95	0.83	0.29	0.00	0.82	0.94
Fe ²⁺	2.22	2.01	0.96	1.06	1.42	0.72	0.06	0.00
Mn	0.01	0.00	0.01	0.00	0.02	0.00	0.01	0.00
Mg	0.33	0.29	1.95	1.94	0.49	0.28	0.01	0.00
Ca	0.39	0.70	0.03	0.00	0.00	0.00	1.93	2.00
Na	0.00	0.00	1.84	2.00	0.02	0.00	0.00	0.00
K	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe ²⁺ /Fe ²⁺ + Mg	0.87	0.87	0.33	0.35	0.74	0.72		
Fe ³⁺ /Fe ³⁺ + Al			0.46	0.41			0.28	0.31

higher temperatures, with glaucophane and clinopyroxene also becoming richer in Fe³⁺.

Eclogite garnet contains up to 25% spessartine in their cores. Manganese was therefore also added to the model system (the bulk composition is given in Table 4) to improve the *P–T* estimates for the first appearance of garnet in the eclogites. The Mn-bearing bulk composition grows garnet containing observed amounts of spessartine at $\sim 22 \pm 1$ kbar and $\sim 410 \pm 10$ °C. The observed amounts of pyrope, almandine and grossular match reasonably (Fig. 8e). The bulk composition was not further altered to reflect fractionation within mineral cores. Without independent knowledge of the *P–T* conditions of garnet core formation, the effective bulk composition at that time can only be an educated guess.

DISCUSSION

Peak *P–T* estimates

The calculated peak pressures and temperatures of the garnet-blueschists are consistent with field and petrological observations; they lie within the predicted stability range (Wei & Powell, 2004) for an assemblage containing garnet-talc-chloritoid which has been collected from a nearby outcrop. The Oman blueschists are predicted to have experienced slightly lower temperature and pressure values than the eclogites. The model results adequately match the observed phase compositions, and the match between observed and calculated compositions are only rarely outside the limits of analytical uncertainty.

The estimated peak pressure for the eclogites matches very well with previous estimates. The garnet-clinopyroxene-phengite geobarometer (Wills *et al.*, 1991; Waters & Martin, 1993; Waters, 1996) yielded peak pressures of 22–23 kbar for metabasic eclogite sample MS6 (Searle *et al.*, 1994). Thermal modelling of radial cracking around quartz inclusions in almandine garnet suggested peak pressures > 18 kbar (Wendt *et al.*, 1993). The pressure is significantly higher, however, than the peak pressures estimated in the NCFMASH system using either THERMOCALC (Wei *et al.*, 2003) or GEO-CALC (El-Shazly, 2001), both of which yield pressures < 16 kbar.

Pressure–temperature–time paths

The predicted *P–T* path of the Oman garnet blueschists is marked as a dashed line on Fig. 7a; the equivalent *P–T* path of the chloritoid eclogites is marked on Fig. 8a. Petrography suggests that the *P–T* paths should pass through the following mineral assemblage fields.

Garnet-lawsonite-sodic amphibole-chloritoid-(clinopyroxene in eclogites)

On the basis of the observed blueschist garnet core compositions, garnet is predicted to appear at around 450 ± 15 °C, although the modelled predicted pressures, at 23–24 kbar, are possibly too high. This may be a consequence of not adjusting the effective bulk composition for the initial stages of garnet growth. Garnet core compositions were not used in the bulk composition calculations. In the eclogites, garnet is predicted to appear at 22 ± 1 kbar and 410 ± 10 °C. Calculated grossular, almandine and pyrope contents of the garnet fit reasonably well with those observed, given the inaccuracies of the estimation of the bulk composition. In both rock types, garnet continued to grow in the stability field of lawsonite, as indicated by rectangular pseudomorphs of paragonite and epidote found included in the garnet.

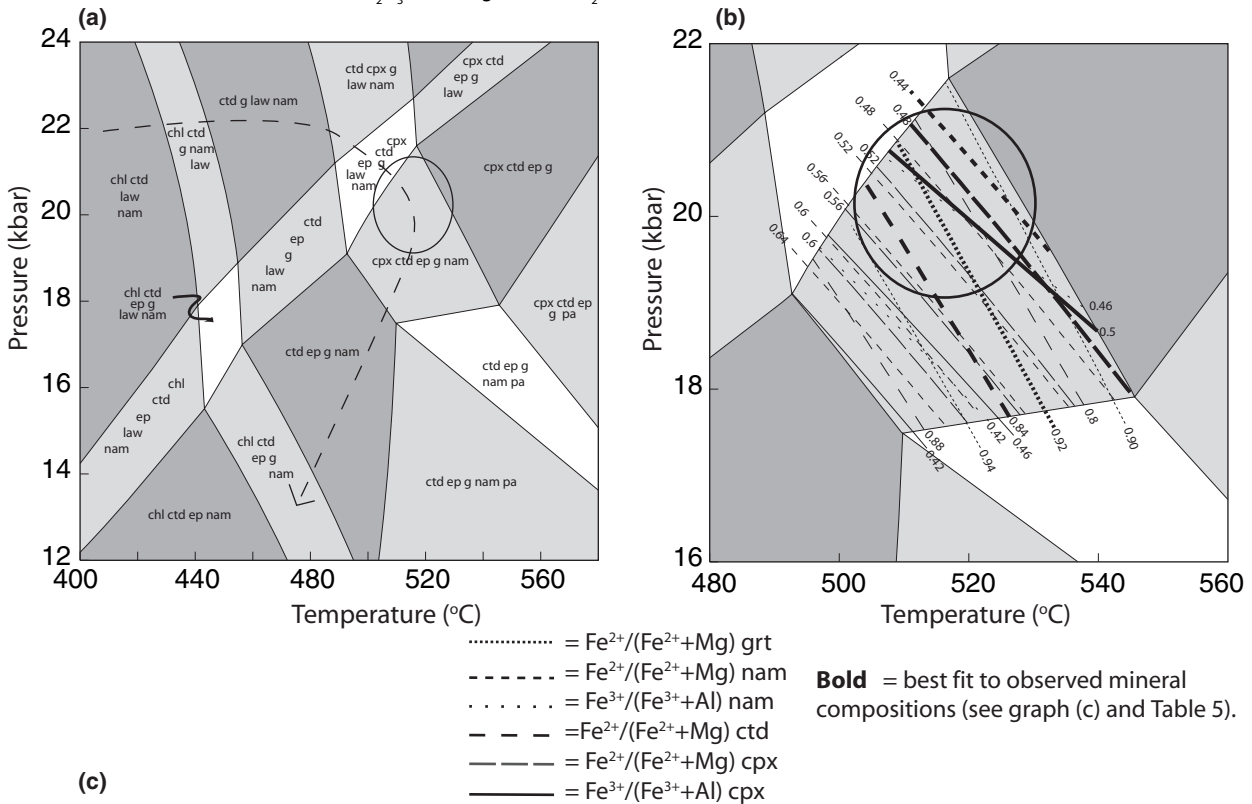
Garnet-epidote-sodic amphibole-chloritoid-(clinopyroxene in eclogites)

This is considered to be the peak assemblage. Epidote has replaced lawsonite as the stable Ca-Al silicate. The compositions and modal proportions of the peak blueschist metamorphic phases are best matched at

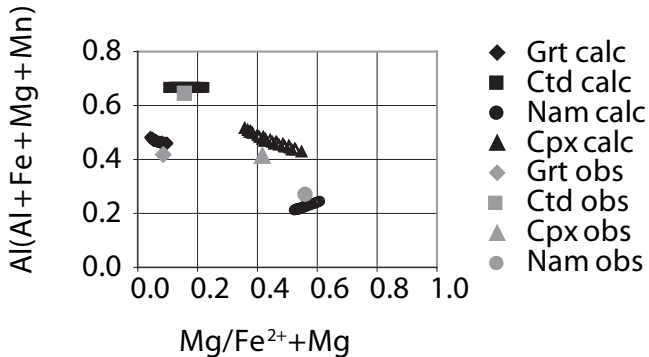
Fig. 8. (a) Pseudosection for chloritoid eclogite sample MS 25, showing part of the predicted *P–T* path (dashed line). The ellipse shows the best estimate of peak *P–T* conditions. Darker field shading denotes indicates higher variance. (b) Enlarged section of the same pseudosection showing mineral isopleths for the region of interest. The ellipse shows the best estimate of peak *P–T* conditions. Isopleths extend beyond the region of interest for clarity of labelling only. (c) Modelled mineral composition variation within the area of interest plotted with observed mineral compositions. (d) Calculated mineral mol percentages in the best-fit region compared with observed mineral modes. (e) Comparison between modelled and observed garnet core compositions.

Chloritoid-Eclogite NCFMASHO with $a(\text{H}_2\text{O}) = 0.8$ (excess quartz + H_2O)

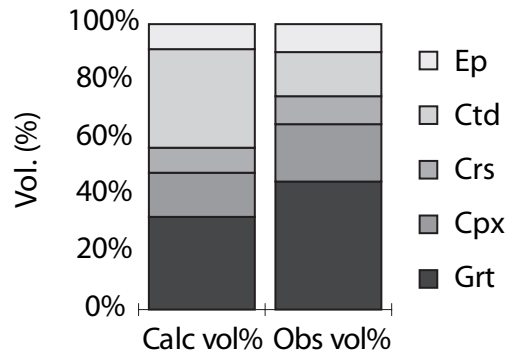
$\text{Al}_2\text{O}_3 : \text{CaO} : \text{MgO} : \text{FeO} : \text{Na}_2\text{O} = 31.13 : 11.70 : 7.01 : 42.64 : 4.61 : 2.91$



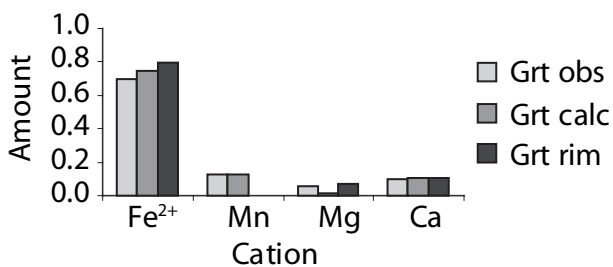
(c) Peak mineral composition comparison



(d) Peak volume % mineral comparison



(e) Garnet core composition comparison at 410 °C and 22 kbar



	Garnet Rim		Glaucofane Core		Clinopyroxene		Chloritoid		Epidote	
	Obs	Calc	Obs	Calc	Obs	Calc	Obs	Calc	Obs	Calc
Si	2.95	3.00	7.90	8.00	2.01	2.00	1.97	1.00	3.01	3.00
Al	1.97	2.00	1.37	1.08	0.42	0.44	3.89	2.00	2.16	1.97
Ti	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe ³⁺	0.13	0.00	0.76	0.92	0.42	0.44	0.17	0.00	0.81	1.03
Fe ²⁺	2.39	2.12	1.31	1.43	0.10	0.05	1.64	0.80	0.11	0.00
Mn	0.01	0.00	0.01	0.00	0.00	0.00	0.02	0.00	0.03	0.00
Mg	0.22	0.20	1.66	1.57	0.07	0.06	0.30	0.20	0.01	0.00
Ca	0.32	0.67	0.09	0.00	0.11	0.11	0.00	0.00	1.86	2.00
Na	0.00	0.00	1.88	2.00	0.87	0.89	0.00	0.00	0.00	0.00
K	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe ²⁺ /Fe ²⁺ + Mg	0.92	0.91	0.44	0.48	0.58	0.49	0.84	0.80		
Fe ³⁺ /Fe ³⁺ + Al			0.36	0.46	0.50	0.50			0.27	0.34

Table 6. Comparison between observed and calculated mineral data at best-fit pressures and temperatures (20 kbar; 520 °C) for chloritoid eclogite MS 25.

~510–530 ± 15 °C and 18–19 ± 1.2 kbar and peak eclogite phases at 520 ± 15 °C and 20 ± 1.6 kbar.

Chlorite-albite-calcic amphibole-epidote-(clinopyroxene in eclogites)

A greenschist overprint is seen in most of the garnet-blueschists and eclogites. A near-isothermal first stage of decompression is indicated by fluid inclusion studies (El-Shazly, 1999). The blue sodic amphibole has rims of green calcic-sodic amphibole, garnet is replaced by a chlorite-epidote mixture around rims and fractures, and porphyroblasts of albite overgrow the matrix. Fractionation of the bulk composition into the porphyroblasts during porphyroblast growth means that the bulk composition changes during rock evolution. The modelled bulk composition is estimated only for the metamorphic peak, and the effective bulk composition will have changed by the time the rock reached the greenschist stage (assuming a closed system). The compositions and modal proportions of the modelled greenschist minerals therefore do not match well with the observed greenschist minerals, especially the composition of chlorite. Paragonite is predicted as a stable phase in both rocks at pressures less than ~12–13 kbar, but is only found in small amounts in the Oman rocks – specifically in the lawsonite pseudomorphs and associated with chloritoid and sodic amphibole breakdown. Albite is predicted to be stable with chlorite in the absence of garnet at pressures < 7–8 kbar.

Uncertainties on model results

The THERMOCALC program includes the option of estimating uncertainties by propagating errors on database enthalpies throughout the calculations. Uncertainties may be calculated on pressure, temperature and phase composition values.

The expression of uncertainty on any field boundary depends on its slope in *P–T* space. Shallow slopes will have a larger uncertainty in temperature; steep slopes will have higher uncertainty in pressure. For the peak

garnet-sodic amphibole-chloritoid-epidote field on the blueschist pseudosection (Fig. 7a,b), there is ±20 °C, and 1.2 kbar (1σ) uncertainty on the epidote-in, lawsonite-out boundary, ±12–14 °C and 1.3 kbar (1σ) uncertainty on the garnet-in and chlorite-out boundaries, ±15 °C and 1.3 kbar (1σ) uncertainty on the clinopyroxene-in boundary and ±5–7 °C (1σ) uncertainty on the paragonite-in boundary.

For the peak garnet-sodic amphibole-sodic clinopyroxene-chloritoid-epidote field on the eclogite pseudosection (Fig. 8a,b), there is ±10 °C, and 1 kbar (1σ) uncertainty on the epidote-in and lawsonite-out boundaries, ±10 °C (1σ) uncertainty on the garnet-in and chlorite-out boundaries, ±8 °C, and 1 kbar (1σ) uncertainty on the amphibole-out boundary and ±5–7 °C (1σ) uncertainty on the paragonite-in boundary.

Uncertainties on compositions were calculated every 10 °C and every 0.5 kbar within the peak *P–T* fields. For the blueschists, the average uncertainty on garnet, chloritoid and sodic amphibole Fe²⁺/(Fe²⁺ + Mg) ratios is 1–4% (absolute uncertainty on the composition × 100), with 15–20% on garnet Ca/(Ca + Fe + Mg) and epidote Fe³⁺/(Fe³⁺ + Al). For the eclogites, the average uncertainty on garnet and chloritoid compositions is 1–8%, whereas on the clinopyroxene, epidote and sodic amphibole the uncertainty is 8–20%. Although the uncertainties on the Fe³⁺/(Fe³⁺ + Al) ratios look high, they are within reasonable agreement of the uncertainty on the estimation of calculated Fe³⁺ from stoichiometric balancing.

Application to Oman

Projections of the calculated model bulk composition and observed mineral compositions onto the Al₂O₃-Na₂O-Ca(Fe,Mg)Si₂O₆ plane (Fig. 6) show that the absence of paragonite at the metamorphic peak in the Oman rocks is apparently a function of relatively low Al and Na in the bulk composition. The presence or absence of chloritoid appears to affect which pyroxene composition is present – chloritoid is present in conjunction with aegirine-jadeite but not with omphacite.

Pseudosections in the MnNCFMASHO model system provide constraints on the evolution of a typical Oman garnet-blueschist. Calculated and observed phase compositions match satisfactorily, and the predicted sequence of mineral growth matches what is observed. Peak metamorphic conditions are predicted at ~510–530 °C and 17–20 kbar. Previous studies estimated (poorly constrained) peak temperatures of ~350–500 °C (El-Shazly *et al.*, 1990; El-Shazly & Liou, 1991), and peak pressures of > 10.2 kbar based on conventional thermobarometry and petrogenetic grid constraints.

Pseudosections in the NCFMASHO system for the Oman chloritoid-eclogite compositions indicate that the peak assemblage of garnet, glaucophane, chloritoid, aegirine-jadeite and epidote can exist stably in the absence of paragonite. Observed phase compositions and volume proportions best match at ~520 ± 15 °C and 20 ± 1.6 kbar. The similarity in predicted pressures suggests that the garnet-clinopyroxene-phengite geobarometer (Waters & Martin, 1993; Waters, 1996) is successful at predicting peak pressures even in highly oxidized rocks.

The results show that the blueschists and eclogites formed at very similar peak temperatures, with the eclogites forming at only 1–2 kbar higher pressure. Previous workers (e.g. Gray *et al.*, 2004b; Searle *et al.*, 2004) have inferred a structural break between the eclogites and blueschists, in part to account for the apparent difference in metamorphic grade. No evidence of a structural break is visible on the ground. The occurrence of a talc-chloritoid-garnet-bearing rock within the blueschist zone, itself an eclogite-facies assemblage, suggests that the conditions of formation of the eclogites and blueschists are similar; and that their peak assemblage is mainly controlled by bulk composition. The pseudosections predict that the chloritoid-bearing garnet-blueschist bulk composition will grow aegirine-jadeite if heated.

CONCLUSIONS

Pseudosection modelling in the NCFMASHO system, with only minor adjustments to the data for Fe-bearing end-members in the Holland and Powell database, satisfactorily predicts the mineral assemblages and phase compositions of the highly oxidized Oman garnet blueschists and eclogites. The activity models presented here are applicable to other oxidized high (and ultra-high) pressure mineral assemblages. At the metamorphic peak, pressure values are consistent with those estimated using conventional thermobarometry, and the modelled mineral phase compositions and modal volumes match well with those observed. The presence of Fe³⁺-bearing minerals such as crossitic amphibole and aegirine-rich clinopyroxene does not necessarily reflect lower peak *P–T* conditions.

The NCFMASHO pseudosections offer a significant improvement over modelling in the NCFMASH system. Estimations of peak pressures of oxidized assemblages using pseudosections, equilibrium phase diagrams and activity-calculated petrogenetic grids in the NCFMASH system may consistently underestimate peak pressures and do not correctly predict phase compositions and volume proportions of minerals in oxidized rocks.

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REFERENCES

- Aranovitch, L. Y. & Newton, R. C., 1996. H₂O activity in concentrated NaCl solutions at high pressures and temperatures measured by the brucite-periclase equilibrium. *Contributions to Mineralogy and Petrology*, **125**, 200–212.
- Argles, T. W., Prince, C. I., Foster, G. L. & Vance, D., 1999. New garnets for old? Cautionary tales from young mountain belts. *Earth and Planetary Science Letters*, **172**, 301–309.
- Berman, R. G., 1991. Thermometry using multi-equilibrium calculations: a new technique, with petrological applications. *Canadian Mineralogist*, **29**, 833–855.
- Canil, D. & O'Neill, H. S. C., 1996. Distribution of ferric iron in some upper mantle assemblages. *Journal of Petrology*, **37**, 609–635.
- Carpenter, M. A., 1983. Microstructures in sodic pyroxenes: implications and applications. In: *Application of Mineral Synthesis to High-Pressure Petrology: The Real and Average Structures of Synthetic and Natural Pyroxenes and Amphiboles*. Proceedings of the Meeting on Application of Mineral Synthesis to High-pressure Petrology; the Real and Average Structures of Synthetic and Natural Pyroxenes and Amphiboles. *Periodico di Mineralogia*, Vol. 52(3), pp. 271–301. Istituto di Mineralogia dell' Università di Roma.
- Carson, C. J. & Powell, R., 1999. Calculated mineral equilibria for eclogites in CaO-Na₂O-FeO-MgO-Al₂O₃-SiO₂-H₂O. *Journal of Metamorphic Geology*, **17**, 9–24.
- Carswell, D. A., O'Brien, P. J., Wilson, R. J. & Zhai, M., 1997. Thermobarometry of phengite-bearing eclogites in the Dabie Shan Mountains of central China. *Journal of Metamorphic Geology*, **15**, 239–252.
- Cuthbert, S. J., Carswell, D. A., Ravna, E. J. K. & Wain, A., 2000. Eclogites and eclogites of the Western Gneiss Region, Norwegian Caledonides. *Lithos*, **52**, 165–195.
- Dale, J., Holland, T. J. B. & Powell, R., 2000. Hornblende-garnet-plagioclase thermobarometry: a natural calibration of the thermodynamics of hornblende. *Contributions to Mineralogy and Petrology*, **140**, 353–362.

- Droop, G. T. R., 1987. A general equation for estimating Fe^{3+} concentrations in ferromagnesian silicates and oxides from microprobe analyses, using stoichiometric criteria. *Mineralogy Magazine*, **51**, 431–435.
- El-Shazly, A. K., 1999. Retrograde evolution of eclogite facies rocks from NE Oman: evidence from fluid inclusions and petrological data. *Chemical Geology*, **154**, 193–223.
- El-Shazly, A. K. & Liou, J. G., 1991. Glaucophane chloritoid-bearing assemblages from NE Oman: petrologic significance and a petrogenetic grid for high P metapelites. *Contributions to Mineralogy and Petrology*, **107**, 180–201.
- El-Shazly, A. K., 2001. Are pressures for blueschists and eclogites overestimated? The case from NE Oman. *Lithos*, **56**, 231–264.
- El-Shazly, A. K., Coleman, R. G. & Liou, J. G., 1990. Eclogites and blueschists from NE Oman: Petrology and PT evolution. *Journal of Petrology*, **31**, 629–666.
- El-Shazly, A. K., Worthing, M. A. & Liou, J. G., 1997. Inter-layered eclogites, blueschists and epidote amphibolites from NE Oman: a record of protolith compositional control and limited fluid infiltration. *Journal of Petrology*, **38**, 1461–1487.
- El-Shazly, A. K., Brocker, M., Hacker, B. & Calvert, A., 2001. Formation and exhumation of blueschists and eclogites from NE Oman: new perspectives from Rb-Sr and $^{40}\text{Ar}/^{39}\text{Ar}$ dating. *Journal of Metamorphic Geology*, **19**, 233–248.
- Ernst, W. G., 1962. Synthesis, stability relations and occurrence of riebeckite and riebeckite-arfvedsonite solid solutions. *Journal of Geology*, **70**, 689–736.
- Essene, E. J. & Fyfe, W. S., 1967. Omphacite in Californian metamorphic rocks. *Contributions to Mineralogy and Petrology*, **15**, 1–23.
- Goffé, B., Michard, A., Kienast, J. R. & Le Mer, O., 1988. A case of obduction-related high pressure, low temperature metamorphism in upper crustal nappes, Arabian continental margin, Oman. *Tectonophysics*, **151**, 363–386.
- Gray, D. R., Hand, M., Mawby, J., Armstrong, R. A., Miller, J. M. & Gregory, R. T., 2004a. Sm-Nd and zircon U-Pb ages from garnet-bearing eclogites, NE Oman: constraints on high-P metamorphism. *Earth and Planetary Science Letters*, **222**, 407–422.
- Gray, D. R., Miller, J. M., Foster, D. A. & Gregory, R. T., 2004b. Transition from subduction- to exhumation-related fabrics in glaucophane-bearing eclogites, Oman: evidence from relative fabric chronology and $^{40}\text{Ar}/^{39}\text{Ar}$ ages. *Tectonophysics*, **389**, 35–64.
- Guiraud, M., Powell, R. & Rebay, G., 2001. H_2O in metamorphism and unexpected behaviour in the preservation of metamorphic mineral assemblages. *Journal of Metamorphic Geology*, **19**, 445–454.
- Holdaway, M. J., 1972. Thermal stability of Al-Fe epidote as a function of $f\text{O}_2$ and Fe content. *Contributions to Mineralogy and Petrology*, **37**, 307–340.
- Holland, T. J. B., 1980. The reaction albite = jadeite + quartz determined experimentally in the range 600–1200 °C. *American Mineralogist*, **65**, 129–134.
- Holland, T. J. B. & Powell, R., 1996. Thermodynamics of order-disorder in minerals II: Symmetric formalism applied to solid solutions. *American Mineralogist*, **81**, 1425–1437.
- Holland, T. J. B. & Powell, R., 1998. An internally consistent thermodynamic dataset for phases of petrological interest. *Journal of Metamorphic Geology*, **16**, 309–343.
- Hoschek, G., 2004. Comparison of calculated P-T pseudosections for a kyanite eclogite from the Tauern Window, Eastern Alps, Austria. *European Journal of Mineralogy*, **16**, 59–72.
- Klemm, R., Schroter, F. C., Will, T. M. & Gao, J., 2002. P-T evolution of glaucophane-omphacite bearing HP-LT rocks in the western Tianshan Orogen, NW China: new evidence for “Alpine-type” tectonics. *Journal of Metamorphic Geology*, **20**, 239–254.
- Le Métour, J., de Gramont, X. & Villey, M., 1986. *Geological Maps of Muscat and Quryat and Accompanying Notes*. Ministry of Petroleum and Minerals, Sultanate of Oman, Muscat.
- Leake, B. E., Woolley, A. R., Arps, E. E. S., *et al.* 1997. Nomenclature of amphiboles: Report on the Subcommittee on Amphibole of the International Mineralogical Association, Commission on New Minerals and Mineral Names. *The Canadian Mineralogist*, **35**, 219–246.
- Liou, J. G., 1972. Synthesis and stability relations of epidote, $\text{Ca}_2\text{Al}_2\text{FeSi}_3\text{O}_{12}(\text{OH})$. *Journal of Petrology*, **14**, 381–413.
- Lippard, S. J., 1983. Cretaceous high pressure metamorphism in NE Oman and its relationship to subduction and ophiolite nappe emplacement. *Journal of the Geological Society, London*, **140**, 97–104.
- Marimoto, M., 1989. Nomenclature of pyroxenes. Subcommittee on pyroxenes, committee on new minerals and mineral names, International Mineralogical Association. *Canadian Mineralogist*, **27**, 143–156.
- Martin, H. N., 1994. Crystal chemistry of alkali pyroxenes, with applications to metamorphic thermobarometry. PhD Thesis, University of Oxford, Oxford, 222 pp.
- Miller, J. M., Gray, D. R. & Gregory, R. T., 2002. Geometry and significance of internal windows and regional isoclinal folds in Saih Hatat, Sultanate of Oman. *Journal of Structural Geology*, **24**, 359–386.
- Newton, R. C. & Haselton, H. T., 1981. Thermodynamics of the garnet-plagioclase- Al_2SiO_5 -quartz geobarometer. In: *Thermodynamics of Minerals and Melts* (eds Newton, R. C., Navrotsky, A. & Wood, B. J.), pp. 131–147, Springer-Verlag, New York.
- Nowlan, E. U., Schertl, H. P. & Schreyer, W., 2000. Garnet-omphacite-phengite thermobarometry of eclogites from the coesite-bearing unit of the Dora-Maira Massif, Western Alps. *Lithos*, **52**, 197–200.
- Powell, R., 1987. Darken’s quadratic formalism and the thermodynamics of minerals. *American Mineralogist*, **72**, 1–11.
- Powell, R. & Holland, T. J. B., 1993. On the formulation of simple mixing rules for complex phases. *American Mineralogist*, **79**, 120–133.
- Rebay, G. & Powell, R., 2002. The formation of eclogite facies metatrolites and a general petrogenetic grid in Na_2O - CaO - FeO - MgO - Al_2O_3 - SiO_2 - H_2O (NCFMASH). *Journal of Metamorphic Geology*, **20**, 813–826.
- Schmid, R., 2001. Geology of ultra-high-pressure rocks from the Dabie Shan, Eastern China. PhD Thesis, Universität Potsdam, 141 pp.
- Schmid, R., Wilke, M. & Oberhänsli, R., 2003. Micro-XANES determination of ferric iron and its application in thermobarometry. *Lithos*, **70**, 381–392.
- Searle, M. P., Waters, D. J., Martin, H. N. & Rex, D. C., 1994. Structure and metamorphism of blueschist-eclogite facies rocks from the northeastern Oman mountains. *Journal of the Geological Society, London*, **151**, 555–576.
- Searle, M. P., Warren, C. J., Parrish, R. R. & Waters, D. J., 2004. Structural evolution, metamorphism and restoration of the Arabian continental margin, Saih Hatat region, Oman Mountains. *Journal of Structural Geology*, **26**, 451–473.
- Sobolev, V. N., McCammon, C. A., Taylor, L. A., Snyder, G. A. & Sobolev, N. V., 1999. Precise Mössbauer milliprobe determination of ferric iron in rock-forming minerals and limitations of electron microprobe analyses. *American Mineralogist*, **84**, 78–85.
- Spear, F. S. & Kimball, C., 1982. RECAMP – a Fortran IV program for estimating Fe^{3+} in amphiboles. *Computational Geosciences*, **10**, 383–426.
- Tropper, P. & Manning, C. E., 2004. Paragonite stability at 700 °C in the presence of H_2O - NaCl fluids: constraints on H_2O activity and implications for high pressure metamorphism. *Contributions to Mineralogy and Petrology*, **147**, 740–749.
- Wain, A., 1998. Ultrahigh-pressure metamorphism in the Western Gneiss Region of Norway. PhD Thesis, University of Oxford, Oxford, 159 pp.
- Wain, A., Waters, D. J. & Austrheim, H., 2001. Metastability of granulites and processes of eclogitisation in the UHP region of

- western Norway. *Journal of Metamorphic Geology*, **19**, 609–625.
- Warren, C. J., 2004. *Continental subduction beneath the Semail Ophiolite Oman: Constraints from U-Pb geochronology and metamorphic modeling*. PhD thesis, University of Oxford, Oxford, 240 pp.
- Warren, C. J., Parrish, R. R., Searle, M. P. & Waters, D. J., 2003. Dating the subduction of the Arabian continental margin beneath the Semail ophiolite, Oman. *Geology*, **31**, 889–892.
- Warren, C. J., Parrish, R. R., Waters, D. J. & Searle, M. P., 2005. Dating the geologic history of Oman's Semail Ophiolite: constraints from U-Pb geochronology. *Contributions to Mineralogy and Petrology*, **150**, 403–422.
- Waters, D. J., 1996. *The Garnet-Cpx-Phengite Barometers: Recommended Calibration and Calculation Method*, updated 1 March 1996. <http://www.earth.ox.ac.uk/davewa/research/eclogites/ecbarcal.html>.
- Waters, D. J. & Martin, H. N., 1993. Geobarometry of phengite-bearing eclogites. *Terra Abstracts*, **5**, 410–411.
- Wei, C. J. & Powell, R., 2004. Calculated phase relations in high-pressure metapelites in the system NCFMASH (Na₂O-K₂O-FeO-MgO-Al₂O₃-SiO₂-H₂O). *Journal of Petrology*, **45**, 183–202.
- Wei, C. J., Powell, R. & Zhang, L. F., 2003. Eclogites from the south Tianshan, NW China: petrological characteristics and calculated mineral equilibria in the Na₂O-CaO-FeO-MgO-Al₂O₃-SiO₂-H₂O system. *Journal of Petrology*, **45**, 183–202.
- Wendt, A. S., D'Arco, P., Goffé, B. & Oberhänsli, R., 1993. Radial cracks around alpha-quartz inclusions in almandine: constraints on the metamorphic history of the Oman mountains. *Earth and Planetary Science Letters*, **114**, 449–461.
- White, R. W., Powell, R., Holland, T. J. B. & Worley, B. A., 2000. The effect of TiO₂ and Fe₂O₃ on metapelitic assemblages at greenschist and amphibolite facies conditions: mineral equilibria calculations in the system K₂O-FeO-MgO-Al₂O₃-SiO₂-H₂O-TiO₂-Fe₂O₃. *Journal of Metamorphic Geology*, **18**, 497–511.
- Will, T. M., Okrusch, M., Schmädicke, E. & Chen, G., 1998. Phase relations in the greenschist-blueschist-amphibolite-eclogite facies in the system Na₂O-CaO-FeO-MgO-Al₂O₃-SiO₂-H₂O (NCFMASH), with application to metamorphic rocks from Samos, Greece. *Contributions to Mineralogy and Petrology*, **132**, 85–102.
- Wills, H. N., Waters, D. J. & Searle, M. P., 1991. A clockwise P-T path at P > 20 kbar for eclogite and high-P schist beneath the Semail ophiolite, Oman. *Terra Abstracts*, **3**, 98.

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APPENDIX: MINERAL MIXING MODELS

Garnet

The garnet models used are similar to the models used in other published studies, e.g. Dale *et al.* (2000) and Wei *et al.* (2003).

A symmetric solution model is used for Mg-Fe-Ca mixing in ternary garnet in which only the Ca-Mg and Fe-Mg interactions are taken to be non-ideal with the interaction parameters $W(\text{py, gr}) = 41.4 - 0.0188T$ kJ mol⁻¹ (Newton & Haselton, 1981) and $W(\text{py, alm}) = 2.5$ kJ mol⁻¹ (Dale *et al.*, 2000). The end-members are pyrope (py; Mg₃Al₂Si₃O₁₂), almandine (alm; Fe₃Al₂Si₃O₁₂) and grossular (gr; Ca₃Al₂Si₃O₁₂), and the compositional variables are $x(\text{g}) = \text{Fe}/(\text{Mg} + \text{Fe})$ and $z(\text{g}) = \text{Ca}/(\text{Ca} + \text{Fe} + \text{Mg})$.

In the MnNCFMASHO system, a symmetric solution model is used for Mn-Mg-Fe-Ca mixing in quaternary garnet, with additional end-member spessartine (sps; Mn₃Al₂Si₃O₈). The interaction parameters are as above and the compositional variables are $\text{prp}(\text{g}) = \text{Mg}/(\text{Mg} + \text{Fe} + \text{Ca} + \text{Mn})$, $\text{grs}(\text{g}) = \text{Ca}/(\text{Mg} + \text{Fe} + \text{Ca} + \text{Mn})$ and $\text{sps}(\text{g}) = \text{Mn}/(\text{Mg} + \text{Fe} + \text{Ca} + \text{Mn})$.

Clinopyroxene

An experimental extension of the ordered omphacite NCFMASH symmetric mixing model is used, similar to that described in Holland & Powell (1996). The Fe³⁺-Al substitution is added. Five end-members are used to describe clinopyroxene in this system:

- Diopside (di) [Ca]_{0.5}^{M2a}[Ca]_{0.5}^{M2b}[Mg]_{0.5}^{M1a}[Mg]_{0.5}^{M1b}Si₂O₆,
- Hedenbergite (hd) [Ca]_{0.5}^{M2a}[Ca]_{0.5}^{M2b}[Fe]_{0.5}^{M1a}[Fe]_{0.5}^{M1b}Si₂O₆,
- Jadeite (jd) [Na]_{0.5}^{M2a}[Na]_{0.5}^{M2b}[Al]_{0.5}^{M1a}[Al]_{0.5}^{M1b}Si₂O₆,
- Omphacite (om) [Ca]_{0.5}^{M2a}[Na]_{0.5}^{M2b}[Mg]_{0.5}^{M1a}[Al]_{0.5}^{M1b}Si₂O₆,
- Acmite (ac) [Na]_{0.5}^{M2a}[Na]_{0.5}^{M2b}[Fe]_{0.5}^{M1a}[Fe]_{0.5}^{M1b}Si₂O₆.

The coding for this model comes from the omphacite example file with the documentation for THERMOCALC version 2.7. The interaction parameters used are $W(\text{jd,di}) = 26$ kJ mol⁻¹, $W(\text{jd,hd}) = 24$ kJ mol⁻¹, $W(\text{jd,om}) = 16$ kJ mol⁻¹, $W(\text{di,hd}) = 4$ kJ mol⁻¹, $W(\text{di,om}) = 16$ kJ mol⁻¹, $W(\text{hd,om}) = 17$ kJ mol⁻¹, $W(\text{di,acm}) = 26$ kJ mol⁻¹, $W(\text{hd,acm}) = 24$ kJ mol⁻¹ and $W(\text{acm,om}) = 16$ kJ mol⁻¹ (Holland & Powell, 1996 and the THERMOCALC documentation). $x(\text{cpx}) = \text{Fe}/(\text{Fe} + \text{Mg})$, $f3(\text{cpx}) = \text{Fe}^{3+}/(\text{Fe}^{3+} + \text{Al})$,

$\text{na}(\text{cpx}) = \text{Na}/(\text{Na} + \text{Ca})$ and $\text{N}(\text{cpx}) = 0.5(x_{\text{M1a}}^{\text{Al}} - x_{\text{M1b}}^{\text{Al}})$, which is half the order parameter Q . At complete disorder, Q has a value of 0. At complete order, Q has a value of 1.

The assumption is that Fe³⁺ does not participate in the ordering process, and is assumed to show no preference for either of the M1 sub-sites. Using this model, the activity-composition relationships imply a transition from ordered to disordered pyroxene at ~25% acmite in omphacite at 500–550 °C, in reasonable agreement with natural data from Oman (Martin, 1994) and elsewhere.

Chlorite

Ordered chlorite is modelled using a quaternary symmetric mixing model (Holland & Powell, 1998). The coding comes from example files included in the THERMOCALC download. The end-members used are:

- Al-free chlorite (afchl) [Mg]₄^{M2,3}[Mg]₄^{M1}[Mg]₄^{M4}[Si]₂^{T2} [Si]₂^{T1} O₁₀(OH)₈,
- Clinocllore (clin) [Mg]₄^{M2,3}[Mg]₄^{M1}[Al]₄^{M4}[Al]₄^{T2} [Si]₂^{T2}[Si]₂^{T1} O₁₀(OH)₈,
- Daphnite (daph) [Fe]₄^{M2,3}[Fe]₄^{M1}[Al]₄^{M4}[Al]₄^{T2} [Si]₂^{T2} [Si]₂^{T1} O₁₀(OH)₈,
- Amesite (ames) [Mg]₄^{M2,3}[Al]₄^{M1}[Al]₄^{M4}[Al]₄^{T2}[Si]₂^{T1} O₁₀(OH)₈.

The interaction parameters are $W(\text{afchl,clin}) = 18$ kJ mol⁻¹, $W(\text{afchl, daph}) = 14.5$ kJ mol⁻¹, $W(\text{afchl, ames}) = 20$ kJ mol⁻¹, $W(\text{clin, daph}) = 2.5$ kJ mol⁻¹, $W(\text{clin, ames}) = 18$ kJ mol⁻¹, $W(\text{daph, ames}) = 13.5$ kJ mol⁻¹. The compositional variables are $x(\text{chl}) = \text{Fe}/(\text{Fe} + \text{Mg})$, $y(\text{chl}) = x_{\text{Al}}^{\text{T2}} = \text{Al}/4$ and $Q(\text{chl}) = 0.5(x_{\text{Al}}^{\text{M4}} - x_{\text{Al}}^{\text{M1}})$.

In the MnNCFMASHO system, an additional end-member is used, $m(\text{chl}) = \text{Mn}/(\text{Fe} + \text{Mg} + \text{Mn})$. Substitution for manganese is assumed to be ideal.

Sodic Amphibole

A symmetric mixing model is used between three end-members: glaucophane (gl) Na₂Mg₃Al₂Si₈O₂₂, ferroglaucophane (fgl) Na₂Fe₃Al₂Si₈O₂₂ and riebeckite (rieb) Na₂Mg₃Fe₃Si₈O₂₂.

Interaction parameters are from the AX documentation (which accompany the THERMOCALC download) and are $W(\text{gl,fgl}) = 10$ kJ mol⁻¹, $W(\text{gl,rieb}) = 10$ mol⁻¹. A DQF adjustment of -4.4–

$0.012T$ kJ mol⁻¹ is made to ferroglaucophane to bring the calculated Fe/Mg ratios into concordance with those of coexisting actinolite, garnet and pyroxene in natural samples from Oman and the Western Gneiss Region in Norway. The entropy correction is applied to remove an incorrect and improbable K_D temperature dependence. A DQF adjustment is made to the (fictive) riebeckite end-member of 10 kJ mol⁻¹ to match the ferric iron contents of natural crossites coexisting with epidote and pyroxene. The compositional variables are $x(\text{nam}) = \text{Fe}/(\text{Fe} + \text{Mg})$ and $f3(\text{nam}) = \text{Fe}^{3+}/(\text{Fe}^{3+} + \text{Al})$.

Chloritoid

A simple binary solid solution model is used for chloritoid, using Mg-chloritoid (mctd) $\text{MgAl}(\text{OH})_4\text{Al}_3\text{O}_2[\text{SiO}_4]_2$ and Fe-chloritoid (fctd) $\text{FeAl}(\text{OH})_4\text{Al}_3\text{O}_2[\text{SiO}_4]_2$.

The interaction energy is $W(\text{ctd}) = 1.5$ kJ mol⁻¹ (from the AX documentation), and the compositional variable is $x(\text{ctd}) = \text{Fe}/(\text{Fe} + \text{Mg})$. A small DQF adjustment was made to simulate a lowering of activity due to a constant 5% Fe³⁺ substituting for Al.

This was $-0.001T$ kJ mol⁻¹ on the entropy term, calculated as $\ln(0.95)^2 \times R/1000$.

In the MnNCFMASHO system, an extra manganese-bearing end-member was added with the composition variables $x(\text{ctd}) = \text{Fe}/(\text{Fe} + \text{Mg} + \text{Mn})$ and $m(\text{ctd}) = \text{Mn}/(\text{Fe} + \text{Mg} + \text{Mn})$. The substitution of Mn is considered as ideal, with all other interaction parameters and DQF adjustments as above.

Epidote

Epidote is treated as a ternary solution of clinozoisite (czo), Fe-epidote (fep) $\text{Ca}_2\text{Fe}^{3+}\text{Al}_2\text{Si}_3\text{O}_{12}(\text{OH})$ and an ordered epidote solid solution (ep) (Holland & Powell, 1996). This approach has been taken from the epidote example file available with the THERMOCALC 2.7 download package. Al and Fe³⁺ are assumed to mix on only the M1 and M3 sites, with a strong tendency for Fe³⁺ to order onto the M3 site. Interaction energies are $W(\text{cz},\text{fep}) = 15.4$ kJ mol⁻¹ and $W(\text{fep},\text{ep}) = 3$ kJ mol⁻¹. The compositional variables are $f3(\text{ep}) = \text{Fe}^{3+}/(\text{Fe}^{3+} + \text{Al})$ and $N(\text{ep}) = X_{\text{Fe}}^{\text{M}_3} - X_{\text{Fe}}^{\text{M}_1}$ = proportion of ordered epidote.