

# Pressures and Temperatures of Ultrahigh-Pressure Metamorphism: Implications for UHP Tectonics and H<sub>2</sub>O in Subducting Slabs

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## Abstract

Kyanite–phengite eclogites can yield robust P–T equilibration conditions that do not depend on the ferrous/ferric ratios of the constituent minerals. Even rocks lacking kyanite or phengite—for which the ferrous/ferric ratios are calculated stoichiometrically—can yield equilibration conditions that differ by < 0.4 GPa. The range of robust P–T conditions for kyanite–phengite UHP eclogites is more restricted than that reported for eclogites generally, with most in the range 600–800°C and < 4 GPa; none fall in the “forbidden zone” defined by geothermal gradients of ≤ 5 K/km. Most UHP eclogites equilibrated at temperatures below the H<sub>2</sub>O-saturated solidus for crustal rocks. This is probably because hotter UHP terranes are sufficiently low in viscosity that they mix with their surroundings and lose their identity or re-equilibrate continuously during cooling until the solidus is reached. Lawsonite and chloritoid are not known from UHP eclogites.

## Introduction

THE DEPTHS AND temperatures to which continental crust can be subducted and exhumed are important to quantify because knowledge of these conditions affects our understanding of: (1) whether subducting sediment or crust contributes a melt component to arc magmatism (Ringwood, 1974); (2) the temperatures in subduction zones (Kelemen et al., 2003); (3) the fluxes and mechanisms by which material is exchanged between the crust and mantle (Walsh and Hacker, 2004); (4) maximum depths of subduction/exhumation; and (5) the degree of structural disruption of UHP terranes.

There have been many determinations of the equilibration conditions (temperature and depth) of UHP eclogites. The purpose of this paper is to: (1) assess whether those determinations are sufficiently accurate to answer the questions posed above; and (2) provide a reduced, but robust, data set of equilibration conditions for UHP eclogites.

## The Problem

P–T determinations on UHP–HP eclogites are inherently difficult because most eclogites contain only two silicate phases: garnet and clinopyroxene. Measuring the Fe–Mg exchange between these two

minerals enables calculation of temperature, but additional phases such as phengite or kyanite are required for barometry. There are two problems, however, even with simple Fe–Mg exchange reactions that render temperature calculation via this method tenuous: (1) diffusional re-equilibration during retrogression ensures that recovering the peak temperature is unlikely—especially at the highest temperatures; and (2) the position of an Fe–Mg exchange reaction cannot be calculated accurately unless the Fe<sup>3+</sup>/Fe<sup>2+</sup> ratios of the Fe-bearing phases—particularly clinopyroxene—are known. The former problem is well known (Pattison et al., 2003), but the magnitude of the latter problem is perhaps not widely appreciated. Ravna and Paquin (2003) summarized the results of half a dozen studies that compared ferrous/ferric ratios calculated by charge balance with ratios measured by Mössbauer, micro-XANES, or titration. They found that Fe–Mg garnet-clinopyroxene temperatures calculated without knowledge of mineral Fe<sup>3+</sup>/Fe<sup>2+</sup> typically have uncertainties of ±100°C. Proyer et al. (2004) used the Mössbauer milliprobe to demonstrate that the problem can be even worse—with temperatures calculated assuming no ferric iron as much as 300°C too high. Unfortunately, there have only been a handful of Mössbauer, micro-XANES or titration Fe<sup>3+</sup>/Fe<sup>2+</sup> measurements on UHP eclogites; these methods have not found general application.

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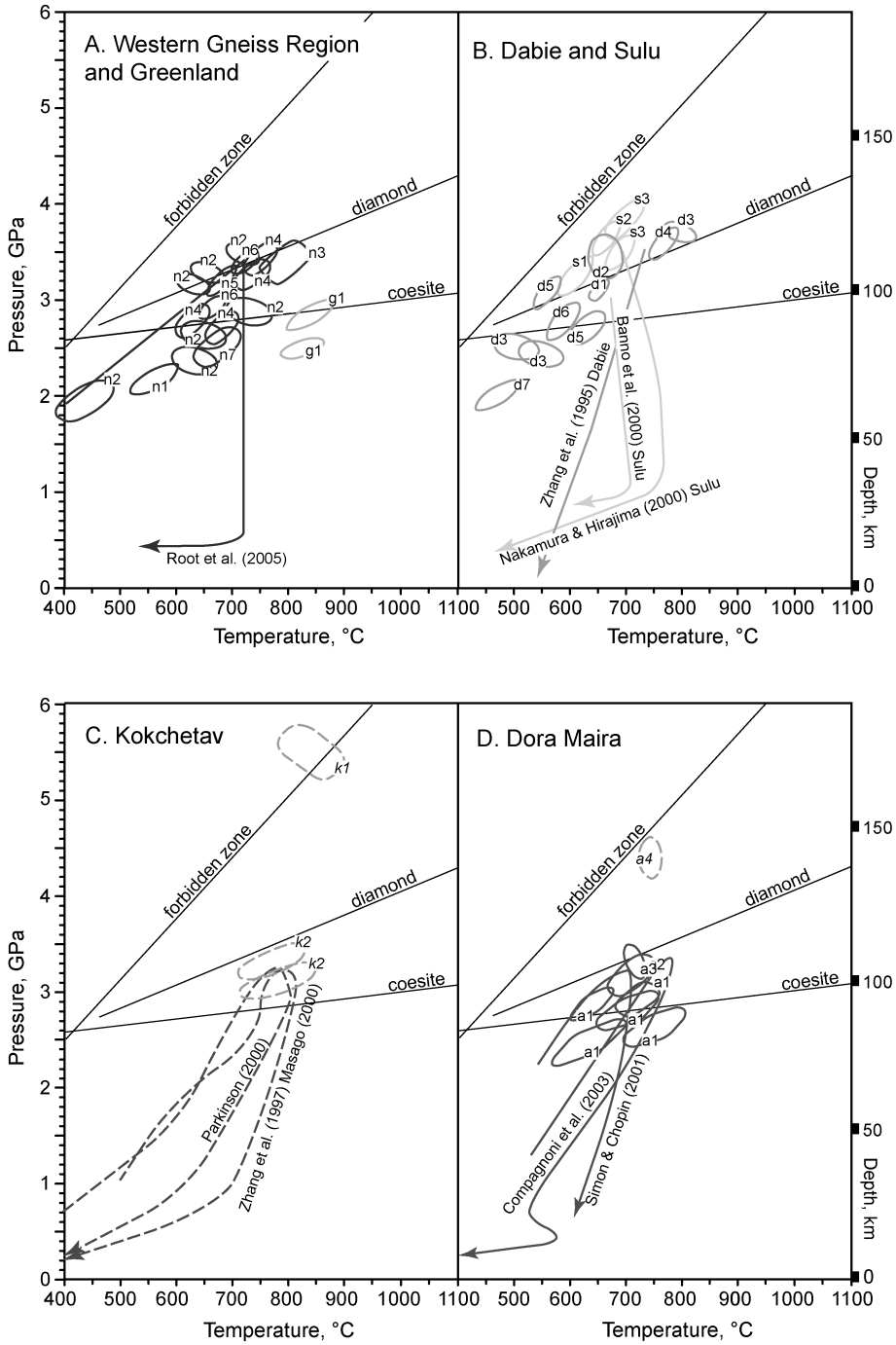


FIG. 1. P-T conditions of HP-UHP terranes. Solid lines show P-T for kyanite-phengite eclogites determined from intersections among garnet-clinopyroxene-muscovite-kyanite-quartz/coesite net-transfer equilibria and the solution models of Ravna and Terry (2004); the sizes and shapes of the uncertainty ellipses are from THERMOCALC and are represented at the  $\pm 0.25\sigma$  level for clarity. Using the solution models of THERMOCALC results in a similar, but slightly

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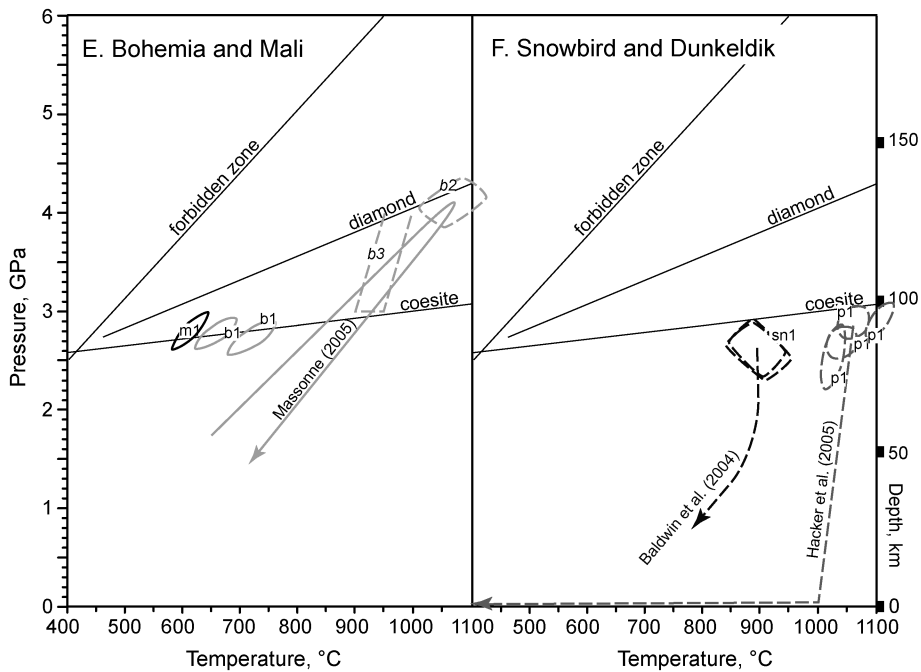


Fig. 1. *continued.* more dispersed set of pressures and temperatures. Dashed lines and italicized text show P-T determinations from other kinds of equilibria and reasoning (see text). Data from: a1 = Nowlan (1998), Dora Maira; a2 = Kienast et al. (1991), Dora Maira; a3 = Coggon and Holland (2002), Dora Maira; a4 = Hermann (2003); b1 = Massonne and O'Brien (2003), Saldenbach; b3 = Becker and Altherr (1992); d1 = Okay (1993), Dabie; d2 = Proyer et al. (2004), Dabie; d3 = Ravna and Terry (2004), using data from Carswell et al. (1997), Dabie; d4 = Zhang et al. (1995b), Dabie; d5 = Okay (1995), Dabie; d6 = Zhang and Liou (1994), Hong'an; d7 = Eide and Liou (2000), Hong'an; g1 = Gilotti and Ravna (2002), Greenland; k1 = Manning and Bohlen (1991), Kokchetav; k2 = Masago (2000), Kokchetav; n1 = Engvik et al. (2000), Norway; n2 = Ravna and Terry (2004), Norway; n3 = Terry et al. (2000), Norway; n4 = Wain (1998), Norway; n5 = Wain (1998), combined with an Fe<sup>3+</sup> measurement by Catherine McCammon of a David Root sample from Norway; n6 = Young et al. (2006), Norway; n7 = Krogh (1982), Norway; p1 = Hacker et al. (2005), Dunkeldik Pamir; s1 = Zhang et al. (1995a), Sulu; s2 = Mattinson et al. (2004), Sulu; s3 = Hirajima and Nakamura (2003), Sulu; sn1 = Baldwin et al. (2004), Snowbird tectonic zone.

### A Solution

The best solution to both of these problems with eclogite thermobarometry is to use net-transfer equilibria, rather than exchange equilibria. The retrograde diffusional re-equilibration problem is solved (rather, reduced) because the increase in diffusive length scale from grain scale (in net-transfer reactions) to grain-boundary scale (in exchange reactions) vastly increases the ability to recover peak temperature, and the problem with ferrous/ferric ratios is solved by using equilibria that involve Mg rather than Fe. In eclogites, the equilibria of choice, as noted by Nakamura and Banno (1997) and Ravna and Terry (2004), are:

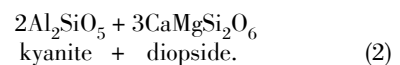
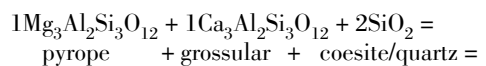
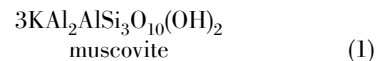
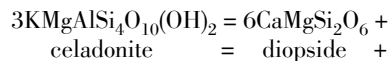
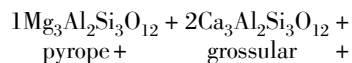


TABLE 1. P-T Data for Kyanite ± Phengite Eclogites

Reference	Area	Sample no.	(Mg)GC+GCKQ <sup>1</sup>		(Mg)GCM+GCKQ <sup>2</sup>		(Mg)GC+GCM <sup>3</sup>		Mode 2 with Fe <sup>4</sup>		Ravna & Terry <sup>5</sup>									
			P, kbar ± 1 s	T, °C ± 1 s	P, kbar ± 1 s	T, °C ± 1 s	P, kbar ± 1 s	T, °C ± 1 s	P, kbar ± 1 s	T, °C ± 1 s	P, kbar	T, °C								
Massonne and O'Brien, 2003	Bohemia	Munchberg	24.6	8.1	690	89	25.7	2.9	680	71	25.8	2.9	696	121	25.7	3.6	682	83	28.5	725
Massonne and O'Brien, 2003	Bohemia	Munchberg	26.6	7.7	554	65	24.6	2.5	570	58	24.4	2.4	544	87	24.5	3.2	565	71	28	660
Massonne and O'Brien, 2003	Bohemia	Saadenbach	bad fit				38.5	3.9	1046	93	bad fit				39.9	7.9	1182	197	41	1040
Zhang et al., 1995b	Dabie	Bixiling	31.8	4.6	808	121	35.1	3.1	717	51	37.1	4.6	839	158	35	3.8	723	64	36	770
Carswell et al., 1997	Dabie		37.1	4.3	757	144	38.7	13.4	788	185	35.7	16.2	750	211	37.4	3.8	770	68	37	800
Carswell et al., 1997	Dabie		15.2	7.7	582	70	24.1	2.6	516	60	24.7	2.9	630	96	25.2	3.5	548	79	24.5	545
Carswell et al., 1997	Dabie		26.4	2.8	515	59	26.1	2.5	468	75	23.7	4.2	459	86	26	3.8	503	79	25	505
Okay, 1993	Dabie		19.1	6	758	66	29.8	1.9	632	33	32	2.5	839	101	29.6	4.7	653	84	31.5	655
Okay, 1995	Dabie		24.8	4.5	660	87	31.8	2.8	528	41	34.4	4	710	116	31.7	5.5	542	84	30.5	565
Okay, 1995	Dabie		20.2	4.4	762	100	26.4	2.9	628	55	27.8	3.7	808	127	26.2	5.1	653	102	27	635
Zhang and Liou, 1994	Dabie	Henan	21.4	5	846	119	32	3.2	600	49	36.9	5.3	946	166	31.7	10.1	625	163	28	580
Eide and Liou, 2000	Dabie	Hong'an	bad fit				23	2.7	550	67	bad fit				bad fit				20	475
Hirajima and Nakamura, 2003	Sulu	Donghai	bad fit				38.3	3.4	702	56	bad fit				bad fit				35	690
Hirajima and Nakamura, 2003	Sulu	D-4	34	4.3	785	113	38.1	3.1	671	46	bad fit				bad fit				38	700
Hirajima and Nakamura, 2003	Sulu	Yangkou	bad fit				39.3	4.3	757	110	bad fit				bad fit				37.5	735
Hirajima and Nakamura, 2003	Sulu	Y-3/4	bad fit				34.7	3.1	607	43	bad fit				bad fit				34.5	650
Mattinson et al., 2004	Sulu	Qinlongshan	bad fit				34.7	3.1	607	43	bad fit				bad fit				31.5	17.2
Zhang et al., 1995a	Sulu	SL13c	18.1	4.8	963	143	33.5	3.4	583	53	bad fit				31.7	10.1	625	163	28	580
Kienast et al., 1991	Dora Maira	T66	28.4	10.1	638	145	34.8	12	730	179	31	3.3	651	109	31.4	3.7	679	69	32	720
Nowlan, 1998	Dora Maira	17595	24.5	7.1	635	81	25.4	3	627	80	25.5	3	640	98	25.5	4.2	631	112	24.5	615
Nowlan, 1998	Dora Maira	17726	28.5	4.2	751	101	29	3.1	738	65	29.1	3.5	755	122	28.9	3	740	87	29.1	720
Nowlan, 1998	Dora Maira	20093	25.1	7.4	672	83	28.4	3	642	68	28.9	3.2	692	111	28.2	4	642	75	30.2	675
Nowlan, 1998	Dora Maira	23423	31.9	7.7	717	92	25.8	3.5	786	99	25.2	3.1	681	110	25.5	4.9	758	133	28	710
Gilotti and Ravna, 2002	Greenland	434446 max P	25.8	8.8	1150	175	32.9	3.6	978	87	bad fit				33.5	5.2	1035	137	34.5	995
Gilotti and Ravna, 2002	Greenland	434446 min P	12.4	9.4	895	115	25	3.2	751	85	26.4	4	995	173	26	5.1	802	137	28.5	840
Gilotti and Ravna, 2002	Greenland	434454	14.1	6.9	844	111	21.4	3	762	95	21.7	3.4	895	141	21.6	3.6	798	127	25	825
Masago, 2000	Kokchetav	Zone D cps free	no kyanite				no kyanite				27.1	3.3	741	110	no kyanite				31	780
Masago, 2000	Kokchetav	Zone D cps bearing	no kyanite				no kyanite				27.6	3.2	713	103	no kyanite				33	770
Ravna and Terry, 2004	Norway	Kvin	17.1	7.4	507	63	22.1	2.5	473	60	22.3	2.6	530	80	22.7	3.5	494	86	19.5	440
Ravna and Terry, 2004	Norway	Levdal	17.9	7.3	581	70	20.5	2.5	561	66	20.5	2.5	598	89	20.9	5.8	558	151	23.5	640
Krogh, 1982	Norway	Verpenset	24.1	4.6	696	94	25.2	2.7	673	53	25.3	2.9	703	117	25.1	3.4	676	68	28.5	715
Engvik and Andersen, 2000	Norway	Vardalsneset	15.5	7.6	614	74	20.7	2.5	572	67	20.8	2.7	641	97	21.2	3.3	593	85	23.5	565
Ravna and Terry, 2004	Norway	Skavyt	23.7	7.5	689	87	26.3	3.1	664	79	26.5	3.2	705	112	26.5	4.5	674	113	25.5	670
Wain, 1998	Norway	Nordpollen S	19.7	4.4	737	96	26.9	2.8	590	51	28.5	3.6	589	124	26.7	5.6	615	109	28	635
Wain, 1998	Norway	Nordpollen W	21	4.6	749	99	26	2.8	640	52	27.1	3.4	784	127	27.1	5.3	666	101	28	685

Ravna and Terry, 2004	Norway	Haldes	HPM36	23.8	4.3	746	98	25.8	2.9	700	64	26.2	3.3	759	119	25.6	3.7	709	85	28.5	735
Young et al., 2006	Norway	Nordfjord	Y1616C2	26.4	4.3	679	89	28.5	2.9	633	56	29	3.3	686	109	28.4	4.1	637	81	30	680
Ravna and Terry, 2004	Norway	Maustad	UHPM13	25.5	4.3	669	87	29.9	2.7	581	45	31.3	3.5	699	112	30.2	4.3	591	71	32	640
Wain, 1998	Norway	Runderheim	aw389	29.8	4.3	730	101	31.4	2.9	691	51	32	3.6	743	127	31.5	4.2	695	75	32.5	740
Wain, 1998 + Fe <sup>3+</sup> analyses <sup>6</sup>	Norway	Flatraket	aw428	26.9	4.7	708	97	31	2.9	619	45	32.4	3.7	738	127	31.9	4.4	635	71	33	680
Wain, 1998	Norway	Flatraket	aw428	25.1	4.7	751	104	31.2	2.9	615	45	33.6	4.1	801	138	32.1	5.2	636	84	33	680
Ravna and Terry, 2004	Norway	Totland	UHPM70	28.4	4.2	700	94	31.9	2.9	624	51	33.2	3.8	725	119	31.5	4.2	629	75	33	670
Terry et al., 2000	Norway	Fjortoft	1066b	28.2	5.1	1070	201	33	3.2	897	72	35.8	5.6	1127	265	32.6	3.7	904	85	33.7	800
Young et al., in review	Norway	Nordfjord	Y1614B	27.4	4.4	836	117	33.3	3	683	52	36.3	4.6	891	155	32.5	5.2	691	94	34	720
Wain, 1998	Norway	Risnakkon	h127	25.4	4.4	833	117	31.1	2.9	690	51	33.4	4.2	882	154	30.5	4.5	698	82	34	760
Ravna and Terry, 2004	Norway	Dage	3/97	28.3	4.6	748	107	32	2.8	660	47	33.6	3.9	778	140	31.7	4.1	664	68	34.5	725
Baldwin et al., 2004	Snowbird		85A	11.1	9.3	1145	178	no phengite		no phengite		no phengite		no phengite		no phengite				26	885
Baldwin et al., 2004	Snowbird		99A	14	9.4	1061	153	no phengite		no phengite		no phengite		no phengite		no phengite				27	880

<sup>1</sup>Calculated conditions for equilibria among Mg-endmember garnet, clinopyroxene, kyanite, and quartz/coesite, using Thermocalc.

<sup>2</sup>Calculated conditions for equilibria among Mg-endmember garnet, clinopyroxene, muscovite, kyanite, and quartz/coesite, using Thermocalc.

<sup>3</sup>Calculated conditions for equilibria among Mg-endmember garnet, clinopyroxene, kyanite, and quartz/coesite, using Thermocalc.

<sup>4</sup>Thermocalc "mode 2" calculation using all equilibria among garnet, clinopyroxene, muscovite, kyanite, and quartz/coesite.

<sup>5</sup>Calculated conditions for equilibria among garnet, clinopyroxene, muscovite, kyanite, and quartz/coesite, using the method of Ravna and Terry, 2004.

<sup>6</sup>Fe<sup>3+</sup> by Catherine McCammon from a sample collected by David Root.

In other words, for kyanite–phengite eclogites in which all these phases are in equilibrium, the intersection between these reactions gives pressure and temperature without the need to measure Fe<sup>3+</sup>/Fe<sup>2+</sup>. Unfortunately, kyanite–phengite eclogites comprise only a small portion of the total eclogite population, gravely restricting the applicability of this method. This limitation is offset, however, by the huge advantage that the pressures and temperatures determined by this method are robust.

I applied this method to calculate accurate eclogite P–T conditions from microprobe mineral analyses presented in the literature (Fig. 1; Table 1). The positions of the net-transfer equilibria were calculated via two approaches: (1) using THERMOCALC v3.1 with the May 2001 database (Powell and Holland, 1988); and (2) using the spreadsheet of Ravna and Terry (2004), which is based on the same data set, but uses the Ganguly et al. (1996) garnet activity model rather than the Newton and Haselton (1981) model used by THERMOCALC. Only the P–T determination based on Ravna and Terry are shown in Figure 1; the P–T determinations based on THERMOCALC are similar for samples with good fits among the relevant equilibria—on average 0.1 GPa lower (Fig. 2A) and 30°C cooler. In samples for which a range of mineral compositions was reported, I calculated P–T conditions using the most jadeite-rich omphacite, the most siliceous white mica, and the garnet with the highest  $a_{\text{prp}} a_{\text{grs}}^2$ , following the logic outlined by Carswell et al. (2000). Where possible, these data were supplemented with other robust T determinations (e.g., the oxygen isotope T measurements from Dora Maira by Sharp et al. (1993). A few UHP localities do not have kyanite–phengite eclogites. For these, I calculated or reported P–T (dashed lines in Fig. 1) using other equilibria.

## Results

### Western Gneiss Region, Norway

The Western Gneiss region of Norway contains one of the two giant UHP terranes on Earth. Mineral compositions in more than a dozen kyanite–phengite eclogites have been analyzed (Krogh, 1982; Carswell et al., 1997; Wain, 1998; Engvik et al., 2000; Terry et al., 2000; Young et al., 2006) and yield good intersections among the relevant equilibria (Fig. 1). The P–T conditions range from ~400°C / 2.0 GPa to 800°C / 3.5 GPa, approximating a thermal gradient of ~7 K/km. No UHP melts or restites have been identified or postulated to exist.

Retrogression of the Western Gneiss region UHP rocks was near-isothermal to pressures of 0.5 GPa (Root et al., 2005). There is evidence of local melting after the UHP event. Widespread, minor amphibolite-facies melting of the gneiss hosting the UHP eclogites produced cm/dm-scale melt veins that locally coalesced into m-scale bodies (Labrousse et al., 2004). Strain shadows around some eclogite boudins are filled with pegmatitic trondhjemite that is spatially associated with amphibolitization of the eclogite, and interpreted to have been derived from the gneiss that hosts the eclogites (Cuthbert, 1995); some of these trondhjemites contain zircons that are significantly younger than zircon neoblasts within adjacent eclogite boudins (Krogh et al., 2004), supporting this interpretation.

#### *NEGEP, Greenland*

A few kyanite-phengite eclogites have been discovered and analyzed in the Northeast Greenland Eclogite Province (NEGEP) (Gilotti and Elvevold, 2002; Gilotti and KroghRavna, 2002). Two that yield good intersections among the relevant equilibria are shown in Figure 1.

#### *Dabie-Sulu*

The Dabie-Sulu region of China contains the second giant UHP terrane on Earth. More than a dozen kyanite-phengite eclogites have been analyzed (Okay, 1993, 1995; Zhang and Liou, 1994; Zhang et al., 1995a; Eide and Liou, 2000; Hirajima and Nakamura, 2003; Mattinson et al., 2004; Proyer et al., 2004) and some of these yield good intersections among the relevant equilibria (Fig. 1)—particularly those from Dabie. The P-T conditions range from ~450°C/2.0 GPa to 800°C/3.8 GPa, approximating a thermal gradient of ~6 K/km, a bit colder than Norway. No UHP melts or restites have been identified or postulated to exist.

Exhumation in Sulu involved near-isothermal decompression through 700–800°C and 0.7–1.2 GPa (Banno et al., 2000; Nakamura and Hirajima, 2000), whereas Dabie exhibits greater cooling during decompression (Zhang et al., 1995b). Anatectic textures and widespread, strongly deformed dikes that overlap in age with the UHP metamorphism imply melting during subduction in the Sulu area (Wallis et al., 2005).

#### *Dora Maira*

The Dora Maira locality in the Western Alps is one of two localities where coesite was first discovered (Chopin, 1984). The P-T determinations for Dora Maira shown in Figure 1 are calculations based on the data of Nowlan (1998) and Kienast et al. (1991), but also include the P-T determination of Coggon and Holland (2002), which makes use of an oxygen-isotope temperature determination by Sharp et al. (1993). The P-T conditions range from ~650°C/2.5 GPa to 750°C/3.2 GPa, approximating a thermal gradient of ~8 K/km, a bit warmer than Norway. Even higher pressures of 4.3 GPa in the diamond stability field have been suggested by Hermann (2003) for Dora Maira (dashed ellipse in Fig. 1), based on experiments in the KCMASH system, but diamond has not been found (Compagnoni and Rolfo, 2003).

A kyanite-garnet-phengite-quartz schist at Dora Maira has been considered by some (Schreyer et al., 1987; Sharp et al., 1993) to be a quenched melt produced from pyrope-coesite quartzite/white-schist (Compagnoni and Rolfo, 2003). Evidence in favor of this melt hypothesis comes from Fe + Na rich almandine-jadeite-kyanite layers that have a bulk composition similar to granitic melt (Massonne and Schreyer, 1987). Late-stage enstatite + sapphirine assemblages developed in garnet cracks at low  $a_{\text{H}_2\text{O}}$  combined with continued stability of the peak-P assemblage talc + phengite indicate cooling during decompression (Simon and Chopin, 2001).

#### *Kokchetav Massif, Kazakhstan*

Regional metamorphic diamonds were first discovered on Earth in the Kokchetav Massif (Sobolev et al., 1990). Assessing P-T conditions of the diamond-facies metamorphism is difficult because the eclogites contain no kyanite and little phengite. The absence of kyanite means that P-T estimates can only involve phengite, clinopyroxene, and garnet, and therefore suffer from the problems with Fe-Mg exchange outlined earlier. The estimated eclogite equilibration conditions fall below the diamond stability field (“k2” in Fig. 1), which led Masago (2000) to conclude that the eclogites were mixed into a higher-pressure host paragneiss, but the pressures differ from the diamond stability field by only a few kbar and can as easily be attributed to inaccuracy in barometry. Much higher pressures—up to 5–8 GPa—have been estimated from the presence of supersilicic titanite (Ogasawara et al., 2002), the amount of K<sub>2</sub>O in clinopyroxene

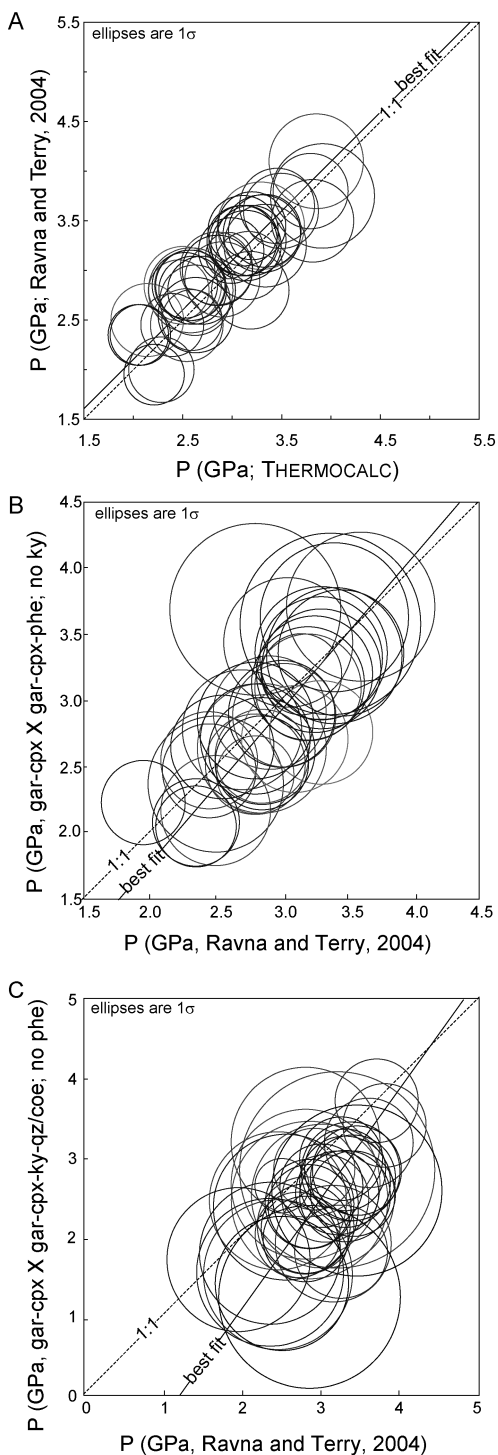
FIG. 2. Comparison of pressures at intersection temperature calculated (A) using THERMOCALC vs. Ravna and Terry (2004) for the assemblage garnet–kyanite–clinopyroxene–phengite–quartz/coesite; (B) using Ravna and Terry (2004) vs. the assemblage garnet–clinopyroxene–phengite–quartz/coesite with THERMOCALC; (C) using Ravna and Terry (2004) vs. the assemblage garnet–clinopyroxene–kyanite–quartz/coesite with THERMOCALC. Uncertainties for the Ravna and Terry (2004) pressure and temperature assumed equal to that for THERMOCALC.

(Katayama et al., 2002; Bindi et al., 2003), and rutile–titanite barometry (“k1” in Fig. 1; Manning and Bohlen, 1991). There are reasons for considering each of these claims with caution—large extrapolation of experimental solubility data in the case of the first two, and considerable extrapolation of the thermodynamic properties of the phases in the case of the latter. Temperatures in excess of 1000°C have been estimated from Ti solubilities in garnet (Massonne, 2003).

The prograde and retrograde path are reasonably well constrained through amphibolite- and greenschist-facies conditions by Zhang et al. (1997), Masago (2000), and Parkinson (2000). Massonne (2003) suggested that garnet–muscovite gneisses that host the eclogites formed by the melting of metasediments at high pressure. No melting of the host gneisses during decompression has been detected.

### Bohemian Massif

The Bohemian Massif is a Variscan basement uplift centered around Prague, long known to contain high-pressure granulites (O’Brien and Carswell, 1993). In recent years, diamond (Massonne, 1998) and then coesite (Massonne, 2001) have been found. A range of P–T conditions is expected for the Bohemian Massif simply because of the large number of nappes. For the Münchberg Massif I calculate 660–725°C/2.8 GPa using the data of Klemm et al. (1991) and O’Brien (1993) reported by Massonne and O’Brien (2003). For the Gföhl unit, Becker and Altherr (1992) estimated ~1100°C and >3 GPa for a marble containing clinopyroxene with K-feldspar exsolution lamellae; our recalculations using Fe–Mg exchange between garnet and clinopyroxene (Ravna and Terry, 2004) indicate cooler temperatures of 950–1000°C at an assumed pressure of 3–4 GPa for this same rock. For the Erzgebirge Massif, Massonne and O’Brien (2003) suggested P–T conditions of 1000°C at 4.5 GPa using the solubility of Ti in



garnet. The concentration of Zr in rutile suggests 900–1000°C (Zack et al., 2005) for the same rocks, and I calculate 1040°C and 4.1 GPa by applying garnet-clinopyroxene-phengite-coesite equilibria to the data of Massonne and O'Brien (2003). The discovery of nanometer-size  $\alpha$ -PbO<sub>2</sub>-structured TiO<sub>2</sub> in the Erzgebirge by Hwang et al. (2000) prompted suggestions of recrystallization at 7 GPa (Massonne, 2003), but Hwang et al. emphasized that the unknown effect of interfacial free energies on the stability of  $\alpha$ -PbO<sub>2</sub>-structured TiO<sub>2</sub> makes pressures of ~4 GPa more likely.

A number of localities within the Bohemian Massif have been interpreted to contain quenched high-pressure melts: Gföhl nappe metasedimentary rocks (Vrána, 1989; Kotková and Harley, 1999), north Moldanubian leucogranulites (Kotková and Harley, 1999), very potassium-feldspar rich garnet-bearing layers within a garnet-kyanite-biotite granulite in the Blansky les Massif (Vrána, 1989), and garnet-muscovite gneisses at Erzgebirge (Massonne, 2001, 2003).

The Bohemian Massif underwent cooling during decompression, showing granulite- and amphibolite-facies overprints from 800°C down to 500°C (O'Brien and Carswell, 1993; Massonne and O'Brien, 2003). Local melting, producing zoisite-bearing leucotonalites, occurred during decompression from ~2 to 1 GPa, prior to an amphibolite-facies overprint (Franz and Smelik 1995).

#### *Snowbird tectonic zone*

Garnet-kyanite gneiss in the Snowbird tectonic zone in Canada equilibrated under near-UHP conditions. Using mineral compositions from Baldwin et al. (2004) and garnet-clinopyroxene-kyanite-quartz equilibria, I calculated P-T conditions of 880°C/2.7 GPa for these rocks. Retrogression occurred at 900°C/1.6 GPa and 800°C/0.9 GPa (Baldwin et al., 2003). These rocks represent subducted or otherwise deeply buried continental crust.

#### *Xenoliths from Dunkeldik, Pamir*

Xenoliths erupted in Miocene ultrapotassic igneous rocks in the Southern Pamir also came from near-UHP conditions (Ducea et al., 2003; Hacker et al., 2005). Solid-phase thermobarometry (garnet-clinopyroxene  $\pm$  kyanite  $\pm$  quartz; Hacker et al., 2005), reveals recrystallization at temperatures of 1000–1100°C and pressures of 2.5–2.8 GPa. Textures, parageneses, mineral compositions, and Nd and O isotopic ratios indicate derivation of the xeno-

liths from subducted basaltic, tonalitic, and pelitic crust that experienced high-pressure dehydration melting, K-rich metasomatism, and solid-state re-equilibration.

### Implications for UHP Metamorphism

Figure 3 is a synopsis of the data in Figure 1 and therefore represents a worldwide compendium of the P-T conditions of HP-UHP eclogites with kyanite + phengite, plus a few particularly noteworthy eclogite localities that lack one or both of these phases. Also shown are the range of H<sub>2</sub>O-saturated solidi for crustal rocks (including granite, tonalite, basalt and sediment), the range of phengite-dehydration solidi, and the range of P-T conditions reported in the literature using *all* kinds of thermobarometry.

A number of important observations fall from this figure. As determined by the technique employed in this study, the temperature range of *UHP kyanite-phengite* eclogites is ~550 to ~850°C, although most are 600–800°C; the maximum pressure is <4 GPa. This P-T field is smaller than that determined for kyanite- or phengite-free eclogites (hachured region), which suffer from the various disadvantages outlined earlier. None of the robust P-T determinations fall on the high P/T side of the “forbidden zone” at a P-T trajectory of 5 K/km (Liou et al., 2000), suggesting that no eclogites can yet be proven to have experienced such conditions. Most of the robust P-T determinations fall at temperatures below the H<sub>2</sub>O-saturated solidi for crustal rocks, and, indeed, the majority of the robust P-T determinations cluster *along* the solidi. The only phengite-kyanite eclogites in Figure 2 that reveal equilibration conditions above the solidus are from Greenland, suggesting that those rocks are unique. This coincidence between eclogite P-T conditions and the crustal solidus likely reflects a geologic process. It may indicate that: (1) UHP rocks that experience hypersolidus temperatures recrystallize continuously in the presence of melt during cooling and then “freeze in” mineral compositions when they cross back below the solidus; (2) UHP rocks that experience hypersolidus temperatures are rarely exhumed because the UHP terrane disaggregates as a result of melt-induced weakening; or (3) UHP rocks rarely experience hypersolidus temperatures. Although the latter possibility is improbable, either of the first two are permissible.

There are, of course, a few HP-UHP occurrences—specifically Kokchetav, the Bohemian



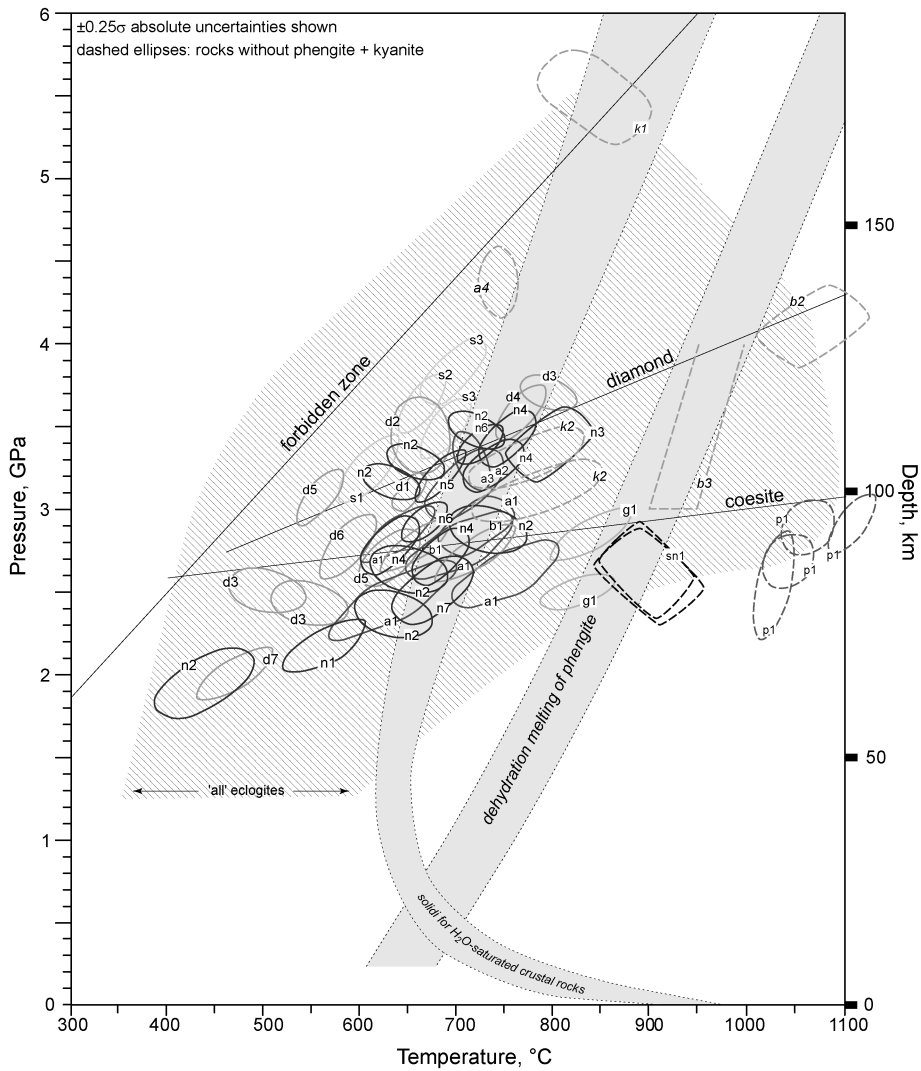


FIG. 3. Synoptic diagram of P-T conditions for HP-UHP eclogites. Range of solidi shown for H<sub>2</sub>O-saturated granite (Stern et al., 1975), tonalite (Stern et al., 1975), sediment (Nichols et al., 1994), MORB (Kessel et al., 2005), and phengite dehydration (Hermann and Green, 2001).

Massif, the Snowbird tectonic zone, and the Dunkeldik Pamir xenoliths—for which much higher temperatures or pressures have been calculated. Most of these localities lack phengite and cannot, therefore, yield “robust” (in the sense of this paper) P-T determinations from kyanite-phengite-clinopyroxene-garnet equilibria. The main issue is the ferrous/ferric ratio in clinopyroxene—if there is significant Ca-Eskola component (CA<sub>0.5</sub>AlSi<sub>2</sub>O<sub>6</sub>) in

the clinopyroxene, the calculated Fe<sup>3+</sup>, and thus temperature, will be underestimated (E. Ravna, pers. commun., 2006). Until better or new solution models can be determined, many of these P-T determinations will remain somewhat speculative. Perhaps the only exception to this is the Pamir rocks, which, because they are xenoliths, suffer from none of the retrogression issues that plague HP-UHP terranes.

### Implications for UHP Hydrous Phases

Considerable effort has been spent to assess the conditions under which oceanic lithosphere dehydrates during subduction. Experimental and theoretical studies (e.g., Connolly and Kerrick, 2002; Schmidt and Poli, 2003) suggest that lawsonite and chloritoid are stable at UHP conditions. However, no UHP rocks have been found that contain either chloritoid or lawsonite, and all known lawsonite eclogites were stable at non-UHP conditions (Altherr et al., 2004; Zack et al., 2004b; Tsujimori et al., 2005). These observations imply that chloritoid and lawsonite are not stable at UHP conditions. The only significant hydrous phase in UHP eclogite is phengite, which is typically present at 0–5 vol%, implying crystallographically bound H<sub>2</sub>O contents of ≤0.25 wt%.

### Implications for UHP Thermobarometry

Despite the concerns presented in the introduction to this paper, reasonably accurate pressures can be obtained from phengite eclogites. Figure 2B shows that the pressure determined by THERMOCALC from the intersection of the garnet–clinopyroxene thermometer (dependent on Fe<sup>2+</sup>/Fe<sup>3+</sup>) with reaction 1 (i.e., a kyanite-free eclogite) deviating from the intersection of reactions 1 and 2 (independent on Fe<sup>2+</sup>/Fe<sup>3+</sup>) determined using Ravna and Terry (2004) by <0.2 GPa over the pressure range of interest. The situation is not as good for kyanite eclogites. Figure 2E shows that the pressure determined by THERMOCALC from the intersection of the garnet–clinopyroxene thermometer (dependent on Fe<sup>2+</sup>/Fe<sup>3+</sup>) with reaction 2 (i.e., a phengite-free eclogite) is as much as ~0.4 GPa lower than the intersection of reactions 1 and 2 from Ravna and Terry (2004) (independent of Fe<sup>2+</sup>/Fe<sup>3+</sup>) in the 2–4 GPa range.

### Future Work

Four new trace-element thermometers—Ti in zircon, Zr in rutile, Ti in quartz, and Zr in garnet—enable major advances in our ability to recover peak temperatures in metamorphic rocks. These thermometers are imperfectly calibrated, but may be useful for eclogites because of the relatively low diffusivities of high-valence cations. Thus, where Fe–Mg exchange during cooling may have continued to 300°C or lower in many eclogites, the Ti and Zr

thermometers could still record higher temperatures. The requisite saturating phases—rutile, zircon, and/or quartz—are common in eclogites.

The Ti-in-zircon thermometer (Watson and Harrison, 2005) is experimentally and empirically calibrated. The effect of pressure has not been quantified, but appears to be small over the 0.2–2.0 GPa range of the calibration. Whether zircons are igneous or metamorphic can be assessed qualitatively with cathodoluminescence (metamorphic zircons in HP rocks tend to have mottled or patchy cathodoluminescence, rather different from igneous grains; Corfu et al., 2003; Root, 2003) and through measured REE and Th/U (Rubatto, 2002; Root et al., 2004).

The Ti-in-quartz thermometer, published in abstract form (Wark and Watson, 2004), is experimentally calibrated at 1 GPa. The effect of pressure has not been assessed, and the solubility of Ti in coesite has not been measured. Moreover, the effect of the coesite → quartz reaction on Ti zoning is unknown; despite the polymorphic nature of these minerals, transformation textures indicate that quartz nucleates on coesite grain boundaries and grows via grain-boundary propagation (Hacker and Peacock, 1995), a process likely to modify the Ti zoning of the precursor coesite.

Zr-in-rutile (Zack et al., 2004a, 2005) is empirically calibrated and, as a result, less precise (± 50–100°C). No pressure effect was quantified by Zack et al. All natural rutiles I have examined in UHP rocks contain plates of ilmenite, but Zack et al. (2004a) did not report this to be a problem.

Zr-in-garnet (Donohue et al., 2001) is experimentally calibrated in almandine only, as reported in a Ph.D. thesis (Donohue, 2002). The effect of pressure on Zr solubility in garnet is substantial, such that at 2 GPa, the Zr solubility does not reach 100 ppm until 1100°C. In summary, these thermometers are preliminary, but given the paucity of other thermometers available in eclogites, they should be exploited.

### Conclusions

Robust P-T determinations can be obtained from kyanite–phengite eclogites; surprisingly, even if kyanite or phengite are absent, the calculated equilibration conditions differ from the “robust” answer by <0.4 GPa. Most UHP terranes equilibrated at 600–800°C and < 4 GPa, along metamorphic field gradients of 6–8 K/km; none fall within the very low

T/P “forbidden zone.” Most of their eclogites record P-T conditions below the H<sub>2</sub>O-saturated solidus for crustal rocks, presumably because hotter UHP terranes disaggregate or undergo continuous re-equilibration during cooling; the few unusually hot UHP terranes deserve further study. By its very nature, this review has excluded a range of more speculative thermobarometric studies, which, if proven correct, will modify these conclusions.

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