

Available online at www.sciencedirect.com



EPSL

Earth and Planetary Science Letters 249 (2006) 74-89

www.elsevier.com/locate/epsl

The influence of H_2O on mantle wedge melting

Timothy L. Grove *, Nilanjan Chatterjee, Stephen W. Parman, Etienne Médard

Department of Earth, Atmospheric and Planetary Sciences, Massachusetts Institute of Technology, Cambridge, MA 02139, USA

Received 2 February 2006; received in revised form 16 June 2006; accepted 27 June 2006 Available online 14 August 2006 Editor: R.W. Carlson

Abstract

The solidus and near-solidus melting behavior of a primitive undepleted peridotite composition has been determined over a pressure range of 1.2–3.2 GPa at H₂O saturated conditions. Vapor-saturated melting (melting in the presence of an H₂O-rich supercritical fluid) begins at 940 °C at 1.2 GPa and the solidus temperature decreases continuously to 860 °C at 2 GPa and 800 °C at 3.2 GPa. This solidus is similar to the lower temperature results of previous investigations. The temperature discrepancies found in earlier studies could be a result of short run times used in several studies and the slower kinetics of olivine vs. diopside melting. The solidus phases include olivine, orthopyroxene, high-Ca clinopyroxene and Al-rich phases that change from spinel+amphibole (1.2-1.8 GPa) to spinel+chlorite over the pressure range of 2–2.4 GPa. Above 2.4 GPa garnet+chlorite+ilmenite are present along with olivine+orthopyroxene+clinopyroxene on the solidus. Chlorite may be a stable phase at the base of the mantle wedge and it may play a role in the onset of flux melting. Ilmenite might play a role in the development of HFSE depletions in arc magmas. Flux melting of the mantle wedge above the subducting oceanic lithosphere begins when an H₂O-rich component (either fluid or melt) released from the slab ascends within the overlying mantle. As it ascends into the mantle wedge the H₂O triggers melting at the vapor-saturated solidus at a depth shallower than the wedge-slab interface. Melting continues as the melt ascends into shallower, hotter overlying mantle. Melting in this part of the wedge occurs at vaporundersaturated conditions because the H₂O content of the melt is continually diluted as the melt ascends through the wedge, dissolving and re-equilibrating with shallower, hotter mantle. Final equilibration with the mantle wedge occurs at shallow depths near the top of the wedge. A model of this process is developed using the vapor-saturated phase relations as a starting point. © 2006 Elsevier B.V. All rights reserved.

Keywords: Subduction zone melting; Vapor saturated peridotite melting; Mantle wedge melting; Arc magma generation; Water in magmas

1. Introduction

In subduction zone settings, mantle melting occurs in response to the addition of an H_2O -rich component released from the subducted oceanic lithosphere. Arc magmas [1–4] inherit their high H_2O contents from this process. Melting might be initiated at the vapor-saturated solidus [5] near the base of the wedge at high pressure. The H_2O -rich melt that is initially produced continuously reacts with overlying

* Corresponding author. *E-mail address:* tlgrove@mit.edu (T.L. Grove). hotter, shallower mantle, diluting the magmatic H_2O content as the melt ascends [6]. To understand this process one needs to know the melting behavior of the mantle in the presence of excess H_2O and this study re-examines this melting process. Previous determinations of the solidus differ significantly, resulting in more than a 200 °C difference in the vapor-saturated solidus temperature over the pressure range of 2.5–3 GPa [7]. This study presents new experimental data, compares them with the results of the four previously published experimental studies, and critically reevaluates the wet peridotite solidus. Results of this study are similar to those of earlier investigators who

⁰⁰¹²⁻⁸²¹X/\$ - see front matter $\ensuremath{\mathbb{C}}$ 2006 Elsevier B.V. All rights reserved. doi:10.1016/j.epsl.2006.06.043

found lower melting temperatures for the peridotite solidus [8]. We use our results along with evidence from experimental studies of primitive arc magmas to model the mantle wedge melting processes and the evolution of primitive arc magmas.

2. Experimental methods

2.1. Starting materials

The experiments (Table 1) use a synthetic oxide mix with the composition of Hart and Zindler's primitive mantle [9]. This composition (Table 2, top row) was prepared by mixing high purity oxides or metasilicates and FeO was added by mixing metallic iron and hematite in the appropriate molar proportions. Brucite, Mg(OH)₂, was synthesized from high purity MgO [5,10,11] and used

Table 1

Experimental conditions, phase proportions and estimates of temperature and oxygen fugacity

as the source for MgO and H₂O. The H₂O present in brucite (\sim 31 wt.%) allowed the incorporation of \sim 14.5 wt.% H₂O in the starting mix.

2.2. Experimental procedures

All of the experiments were carried out at the MIT Experimental Petrology Laboratory in a 0.5" solid medium piston cylinder apparatus [12] using the hot piston-in technique [13]. The pressure medium was BaCO₃, and pressure was calibrated against the reaction: anorthite+gehlenite+ corundum=Ca-tschermak pyroxene [14]. Pressures are thought to be accurate to \pm 50MPa. Temperature was monitored and controlled using W₉₇Re₃–W₇₅Re₂₅ thermo-couples with no correction applied for the effect of pressure on the thermocouple EMF. Temperatures are thought to be accurate to \pm 10 °C. The sample was positioned in the center

Expt.	Р	Т	Duration	H ₂ O	Phases									r^2	%Fe loss	QUILF	f_{O_2}
	(GPa)	(°C)	(hours)	present?	ol	opx	cpx	sp	gar	ilm	amph	chl	melt		(or gain)	T (K)	(ΔQFM)
B993	1.2	930	73.1	yes	х	х	х	х			х						
B985	1.2	950	48.0	yes	х	х	х	х			х		х				
B804	1.2	980	50.0	yes	х	х	х	х			х		х				
B810	1.2	1000	54.9	yes	0.48	0.33	0.08	0.01			0.10		n.a.	0.07	-2.8	1327 (22)	-1.0
B814	1.2	1020	54.3	yes	0.58	0.21	0.09	0.01					0.11		-5.0	1362 (54)	
B816	1.2	1100	25.0	no	0.44	0.40	0.14	0.02					n.a.	а	а	1406 (11)	1.3
C249	1.6	980	139.0	yes	х	х	х	х			х		х				
C250	1.6	1000	120.0	yes	х	х	х	х			х		х				
C254	1.8	1000	121.8	yes	х	х	х	х					х				
C236	2.0	850	24.0	yes	х	х	х	х				х					
C237	2.0	850	75.9	yes	х	х	х	х				х					
C306	2.0	880	96.0	ves	х	х	х	х					х				
C239	2.0	940	72.5	ves	0.49	0.36	0.13	0.02					n.a.	0.10	1.4	1297 (35)	2.1
C241	2.0	960	98.0	no	х	х	х	х					х			()	
C255	2.0	1000	116.3	ves	0.49	0.31	0.10	0.01	0.09				n.a.	0.12	2.2	1303 (98)	0.6
C258	2.0	1020	123.0	ves	0.46	0.37	0.13	0.03					n.a.	0.51	6.8	1290 (54)	-0.0
B823	2.0	1050	78.0	ves	х	х	х	х					х			()	
C264	2.0	1100	95.5	ves	х	х	х	х					х				
C257	2.2	940	121.3	ves	х	х	х	х	х				х				
C256	2.2	1000	137.3	no	х	х	х	х	х				х				
C253	2.4	880	120.0	ves	х	х	х	х	х				х				
C252	2.4	900	120.0	no	0.51	0.29	0.10		0.10				n.a.	0.12	1.5	1269 (54)	
C238	2.4	900	144.9	no	х	х	х		х				х				
C245	2.4	960	98.8	ves	х	х	х		х				х				
C248	2.4	1100	24.0	no	0.44	0.39	0.13	0.03					n.a.	а	а	1367 (92)	2.0
D150	2.8	840	121.0	ves	х	х	х		х	х		х	х				
D97	2.8	870	122.3	ves	х	х	х		х				х				
C259	2.8	890	124.8	ves	х	х	х		х				х				
C260	2.8	910	120.6	ves	0.49	0.30	0.08		0.12				n.a.	0.09	0.9	1221 (27)	
C303	2.8	950	74.0	ves	x	x	x		x				x				
D148	3.2	780	147.9	ves	x	x	x		x	x		x					
D146	3.2	820	143.5	ves	x	x	x		x	x		x	x				
D151	3.2	840	147.4	yes	0.48	0.23	0.12		0.01	0.01		0.16	n.a.	0.08	-0.1	1279 (39)	

^a A large amount of melt was present in these charges, but could not be analyzed. n.a.=not analyzed.

of the graphite heater near the hot spot, and the thermocouple was positioned above the sample in the cooler upper part of the furnace. A correction of +20 °C was added to the thermocouple temperature. This temperature difference was obtained by direct measurement using offset thermocouples. We also mapped out the thermal gradient in our run assembly using the kinetics of the MgO+Al₂O₃=MgAl₂O₄ reaction [15]. We found that the hot spot in the furnace is 20 °C hotter than the thermocouple temperature and located at the top of our sample capsule 2 mm from the thermocouple junction. Over the length of the silicate sample (~1 mm) the temperature drops by 10 °C. Thus, the hottest part of the sample container is at the top of the charge, and the temperature is 10 °C lower at the bottom.

Au capsules were used for all of the experiments. The Au capsules were fabricated from 0.43" long Au tubes with a 0.01" wall thickness. The Au tube was triplecrimped, welded on one end and then flattened to make a uniformly thick capsule top. About 0.04 g of the starting material was loaded into the capsule. The bottom of this capsule was again triple-crimped and welded shut with an arc welder. This welded capsule was flattened in a die to produce a final capsule length ($\sim 0.15''$) similar to that of our conventional anhydrous graphite capsule assemblies. The resulting product was a small capsule that could be welded shut and still retain the 14.5 wt.% H₂O added as brucite. These capsules were centered in graphite furnaces in the same manner utilized in our conventional experimental assemblies [16]. Experiments were pressurized to 1 GPa at room temperature, and then the temperature was raised to 865 °C at 100 °C/min (if the final experimental temperature was <865 °C, the final experimental temperature was achieved during this step). The experiment was held at these conditions for 6 min, then the pressure was increased to the desired value and the temperature was raised to the final run conditions at 50 °C/ min. The sample was held at isothermal conditions for the duration of the experiment (Table 1). Experimental durations ranged from 25 to 148 h. At the end of the experiment the sample was quenched by turning off the power. A hole was made in the capsule using a small diameter hand drill, and the presence or absence of water was noted (Table 1). After this step the capsule was sliced using a diamond saw, dried out, vacuum-impregnated in epoxy and polished for further examination.

2.3. Analytical methods

Back scattered electron (BSE) images and wavelength dispersive X-ray elemental maps of the polished run products were collected with a JEOL JXA-733 Superprobe at Massachusetts Institute of Technology. An electron beam rastering and/or x-y stage translation technique (depending on the size of the image) was used to obtain large area spatial representations of the samples [17]. Secondary electron images of fractured surfaces of the sample were obtained using a JEOL 6320 field emission SEM at the Massachusetts Institute of Technology. These images and maps were extremely useful in examining the distribution of minerals in the sample, detecting the beginning of melting and to identify points for conventional spot analysis by wavelength dispersive spectrometry (WDS).

The experimental products were analyzed by WDS with the MIT five-spectrometer JEOL 733 Superprobe. The on-line data reduction utilized the CITZAF correction package [18]. The atomic number correction of Duncumb and Reed, Heinrich's tabulation of absorption coefficients, and the fluorescence correction of Reed were used to obtain a quantitative analysis [18]. Analyses of mineral and quenched liquid products are presented in Table 2. All analyses were performed with a 15 kV accelerating voltage and a 10 nA beam current. Spot size was 1 µm for the mineral analyses. Elements in the crystalline phases were measured for up to 40 s, depending on abundance level. In one experiment the glass phase was analyzed using a 10 µm beam size. Most of the Na in the glass was lost in the first second of counting (see Experimental results), despite the short counting time used for Na (5 s).

3. Experimental results

3.1. Mineral phase relations

The results of the experiments are shown on a pressuretemperature plot in Fig. 1. In all of the plotted experiments olivine+orthopyroxene+high Ca-clinopyroxene (oliv+ opx+cpx) are present. The symbols and boundaries demarcate the stability fields of aluminous and/or hydrous minerals that were stable along with oliv+opx+cpx. Fig. 2A,B shows a high pressure subsolidus (2 GPa, 850 °C) experiment where super-critical vapor coexisted with crystals. Fig. 2C shows the texture in a lower pressure experiment (1.2 GPa, 1020 °C, B814) when melt and a supercritical vapor phase are present. At 1.2 GPa amphibole+ spinel are present, with amphibole disappearing above 1010 °C. Above 1.7 GPa and 980-1000 °C amphibole breaks down and spinel becomes the stable aluminous phase. Garnet and spinel coexist in a small P-T region above the solidus between 2 and 2.4 GPa and between 880 and 1000 °C. Above approximately 2.2 GPa on the solidus, garnet becomes the only anhydrous aluminous phase to coexist with oliv+opx+cpx (Fig. 3). At the lowest temperatures (780-840 °C) and highest pressures

Table 2 Analyses of selected experiments

	No. of anals	SiO_2	TiO ₂	Al_2O_3	Cr_2O_3	FeO	MnO	MgO	CaO	Na ₂ O	K_2O	NiO	Sum
H&Z bulk		46.2	0.18	4.08	0.40	7.59	0.10	37.96	3.23	0.33	0.03	0.28	
B810													
oliv	6	40.4	0.01	0.08	0.03	9.55	0.13	49.1	0.10			0.66	100.01
		0.16	0.01	0.08	0.01	0.18	0.01	0.33	0.01			0.07	100.01
opx	11	54.6	0.23	5.21	0.48	6.17	0.13	32.3	0.91	0.02			100.01
CDY	10	0.44 52.2	0.02	0.58	0.06	2.00	0.02	0.42	0.13	0.01			100.46
срх	10	0.44	0.31	4.32 0.48	0.37	0.36	0.11	0.24	0.41	0.13	0.39		100.40
amph	12	44.4	1.01	14.4	0.39	3.58	0.05	18.9	11.9	1.85	0.16		96.73
		0.30	0.14	0.52	0.17	0.08	0.02	0.26	0.40	0.09			
spin	4	0.78	0.05	57.7	12.8	9.13	0.01	20.7	0.05			0.33	101.48
		0.44	0.02	2.1	0.36	0.07	0.01	0.61	0.06			0.13	
B814													
oliv	11	40.3	0.01	0.02	0.02	9.02	0.08	49.3	0.08			0.57	99.43
		0.27	0.01	0.01	0.02	0.16	0.02	0.24	0.02			0.13	
opx	16	54.2	0.16	4.49	0.54	5.98	0.13	32.8	1.01	0.01			99.33
	10	0.57	0.03	0.88	0.15	0.13	0.02	0.55	0.12	0.01			00.40
cpx	18	52.0	0.34	3.65	0.68	2.79	0.10	17.8	22.0	0.11			99.42
onin	3	0.44	0.04	0.44 30.4	28.2	12.3	0.01	0.28	0.58	0.02		0.16	100.00
spin	5	0.17	0.02	0.96	0.76	0.33	0.14	1 00	0.14			0.10	100.90
glass	10	50.6	0.52	19.9	0.06	2.54	0.09	4.32	8.07	0.75	0.20	0.09	87.26
8		1.11	0.08	1.20	0.02	0.41	0.02	1.91	0.62	0.12	0.15	0.06	
	norm	57.99	0.60	22.81	0.06	2.92	0.11	4.95	9.25	0.86	0.23	0.10	100.00
	wNa2Oa	56.98	0.59	22.42	0.06	2.87	0.11	4.86	9.09	2.80	0.22		
R816													
oliv	7	41.3	0.00	0.03	0.08	5 98	0.11	52.3	0.11			0.42	100.28
0117	,	0.25	0.00	0.02	0.01	0.15	0.02	0.55	0.01			0.05	100.20
opx	10	57.9	0.11	0.91	0.58	3.90	0.12	35.4	1.29	0.01			100.18
1		0.40	0.01	0.20	0.08	0.19	0.03	0.49	0.09	0.01			
cpx	10	54.7	0.14	0.95	0.89	2.15	0.09	20.1	21.0	0.10			100.14
		0.57	0.01	0.26	0.20	0.25	0.03	0.51	0.65	0.04			
spin	5	1.81	0.31	10.6	59.8	11.3	0.20	16.5	0.06			0.10	100.72
		0.33	0.01	1.0	1.1	0.24	0.03	1.3	0.03			0.06	
C239													
oliv	6	40.8	0.03	0.08	0.01	9.81	0.12	48.6	0.25			0.77	100.46
		0.20	0.02	0.02	0.01	0.25	0.02	0.59	0.05			0.10	
opx	7	54.4	0.18	5.74	0.32	6.35	0.10	32.3	0.66	0.07			100.07
	10	0.43	0.02	0.76	0.06	0.19	0.02	0.36	0.08	0.04			100 65
cpx	10	52.5	0.52	4.83	0.29	2.93	0.08	17.2	22.1	0.25			100.65
anin	7	0.79	0.10	0.81	0.09	0.31	0.02	0.51	0.66	0.07		0.69	00.91
spin	/	0.39	0.28	2.9	14.5	0.36	0.12	0.87	0.10			0.08	99.81
		0.00	0101	2.0	110	0.00	0102	0107	0102			0.10	
C248													
oliv	6	41.2	0.03	0.00	0.07	8.58	0.11	50.1	0.07			0.41	100.57
	10	0.20	0.01	0.00	0.01	0.17	0.02	0.24	0.01	0.00		0.12	101.10
opx	12	56.1	0.07	3.40	0.80	5.61	0.12	34.1	0.92	0.00			101.18
CDY	14	0.35	0.01	0.52	0.13	0.20	0.03	0.3/ 18/	0.06	0.07			100.92
срх	14	0.40	0.10	0.59	0.82	0.16	0.07	0.31	0 34	0.07			100.62
spin	2	0.50	0.34	26.4	43.2	13.1	0.18	17.1	0.11	0.02		0.18	101.03
r	-	0.08	0.01	0.37	1.3	0.30	0.02	0.04	0.04			0.00	

Table 2 (continued)

	No. of anals	SiO_2	TiO ₂	Al_2O_3	Cr_2O_3	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	NiO	Sum
C252													
oliv	6	41.1	0.05	0.05	0.02	9.39	0.11	49.7	0.05			0.75	101.17
ont	0	0.34	0.03	0.03	0.01	0.20	0.02	0.40	0.04			0.11	101117
opx	6	55.5	0.15	4.92	0.32	6.41	0.07	32.7	0.58	0.03			100.66
1		0.98	0.02	0.63	0.07	0.07	0.02	0.28	0.19	0.00			
cpx	10	53.6	0.36	3.33	0.47	2.56	0.03	17.8	22.6	0.26			100.94
		0.61	0.08	0.56	0.04	0.19	0.03	0.86	1.37	0.03			
garnet	6	42.2	0.76	23.1	1.13	8.63	0.26	16.5	8.68	0.02			101.26
		0.56	0.34	0.37	0.65	0.25	0.02	0.40	0.91	0.01			
C255													
oliv	6	40.9	0.02	0.03	0.02	9.07	0.12	49.4	0.08			0.52	100.23
		0.34	0.01	0.02	0.01	0.29	0.01	0.13	0.03			0.12	
opx	7	55.1	0.17	4.41	0.35	6.19	0.08	32.9	0.77	0.00			99.90
		0.66	0.01	0.85	0.07	0.32	0.03	0.48	0.22			NiO 0.75 0.11 0.52 0.12 0.31 0.17 0.20 0.05 0.14 0.01 0.05 0.07	
cpx	7	52.4	0.48	4.28	0.46	2.79	0.09	17.2	22.7	0.27			100.60
		0.56	0.07	0.63	0.11	0.27	0.04	0.30	0.46	0.02			
spin	4	0.44	0.31	48.1	21.0	10.73	0.12	19.1	0.05			0.31	100.17
		0.17	0.04	2.1	1.9	0.46	0.03	0.38	0.04			0.17	
garnet	7	41.8	0.67	23.0	1.00	7.72	0.27	17.9	8.20	0.01			100.64
		0.36	0.10	0.49	0.19	0.19	0.05	0.23	0.24	0.01			
C258													
oliv	7	41.0	0.00	0.01	0.02	9.02	0.13	49.8	0.05			0.20	100.24
		0.67	0.00	0.01	0.01	0.20	0.06	1.19	0.01			0.05	
opx	5	55.2	0.20	4.94	0.34	6.12	0.20	32.9	0.69	0.05			100.59
		0.67	0.05	0.69	0.05	0.16	0.17	0.44	0.04	0.01			
cpx	6	53.0	0.51	3.98	0.40	2.57	0.10	17.5	22.8	0.19			101.01
		0.55	0.07	0.52	0.07	0.13	0.03	0.28	0.55	0.01			
spin	3	0.09	0.29	50.5	18.0	9.60	0.06	19.9	0.00			0.14	98.64
		0.02	0.03	2.1	0.99	0.32	0.02	0.84	0.00			0.01	
C260													
oliv	5	40.7	0.00	0.10	0.03	9.29	0.10	49.7	0.06			0.62	100.57
		0.24	0.01	0.08	0.01	0.16	0.03	0.38	0.02			0.07	
opx	4	55.0	0.12	4.37	0.48	6.31	0.15	33.3	0.45	0.05			100.22
		0.77	0.03	1.02	0.09	0.15	0.04	0.38	0.04	0.02			
cpx	5	54.0	0.28	2.40	0.51	2.28	0.07	17.5	23.6	0.27			100.85
		0.60	0.07	0.32	0.02	0.10	0.05	0.13	0.25	0.03			
garnet	4	43.2	0.43	19.8	1.02	8.24	0.35	17.7	9.11	0.04			99.86
		1.7	0.15	1.7	0.84	0.73	0.05	1.6	2.5	0.03			
D151													
oliv	3	41.1	0.09	0.07	0.05	10.4	0.11	47.8	0.05			0.76	100.35
		0.93	0.04	0.08	0.02	0.20	0.02	0.77	0.02			0.07	
opx	b	56.4	0.08	1.96	0.20	6.86	0.16	33.5	0.80	0.00			99.91
cpx	b	54.6	0.08	1.26	0.11	3.01	0.10	17.1	24.2	0.21			100.59
garnet	9	41.2	0.92	21.0	1.46	10.5	0.61	15.5	9.40	0.03			100.52
		0.35	0.15	0.63	0.41	0.25	0.06	0.61	0.69	0.02			
chlorite	13	33.1	0.06	15.5	1.42	4.05	0.04	31.6	0.23	0.07			86.00
		1.43	0.01	0.91	0.33	0.29	0.02	1.3	0.25	0.05			
ilmenite	4	1.41	54.2	0.51	0.94	28.6	0.31	12.6	0.30			0.42	99.30
		0.43	1.1	0.29	0.57	0.47	0.04	0.99	0.14			0.04	

Number below each oxide is one standard deviation of mean of replicate analyses.

(a) Glass composition lost Na₂O during the analysis. The composition was recalculated by adding Na₂O to achieve mass balance.

(b) Pyroxenes in this sample were small and very difficult to analyze. The analyses represent single points of pyroxenes with lowest, Al and Ti contents.



Fig. 1. Vapor-saturated phase equilibria for the Hart and Zindler [9] primitive mantle composition. Symbols show phases present in addition to olivine+orthopyroxene+clinopyroxene. Grey curve is the vapor-saturated solidus.

investigated (2.8 and 3.2 GPa) magnesian chlorite [19,20] and geikielite–ilmenite solid solution (Table 2) coexist with garnet, oliv, opx and cpx near the solidus (Fig. 4).

3.2. Detection of melt

Two criteria were used to determine the presence of melt: (1) the presence of visible interstitial melt and (2) the simultaneous occurrence of variations in modal abundance in minerals in the charge along with regions of melt+ crystal segregation. The textural characteristics of the sample and the appearance of the guenched melt changes over the range of pressures investigated. In the pressure range of 1.2-2.0 GPa (Fig. 2C) the minerals form an open diktytaxitic network that was filled by supercritical H₂O and pockets of melt blebs (up to 10 µm in size) that are trapped between grain boundary junctions. At higher pressures (≥ 2 GPa) the porosity of the open crystal network decreases and the most common appearance of melt was as small bubble-filled regions that were ubiquitously present in the entire charge, but preferentially concentrated in the upper (hotter) portion of the charge with olivine or olivine+ orthopyroxene (Figs. 3A and 4C). The bubble-filled melt pockets were visible optically when the sample was first cut open. The melt-rich area appeared as a milky-white foamy region that consisted of a network of microscopic vesicles in the quench glass. These large regions were often difficult to preserve during vacuum-impregnation and subsequent polishing. The presence of glass has also been

determined by looking at broken pieces of the experiments with an SEM. Fig. 5 shows the quenched melt in the upper olivine+opx-rich zones of the charge in sample C260 (2.8 GPa, 910 $^{\circ}$ C).

At constant pressure, the lowest temperature (unmelted) experiments are texturally unzoned, with a homogeneous distribution of phases throughout the charge (Fig. 2A). With increasing temperature the charge (melt-bearing experiments) is no longer texturally homogeneous and porosity decreases from the hottest part (top) to the coldest part (bottom) of the charge (there is a 10 °C thermal gradient in the charge). We attribute this textural zonation to a thermal compaction effect [21] facilitated by the presence of melt, the small thermal gradient (~ 10 °C) and the long experimental run times. The low temperature reactant phases segregate to the cooler bottom of the sample, and the high temperature liquid+solid product phases segregate to the hotter top. This modal segregation does not occur when only crystals+vapor are present, either because the entropy reduction driving force is not high enough between the hot and cold ends or the element transport rates are not fast enough. In the modally zoned melted experiments clinopyroxene tends to concentrate in the cold end of the sample as clearly revealed in the Ca X-ray images (Figs. 3D and 4B). Olivine and melt (and the open pore spaceformerly occupied by supercritical H2O vapor) concentrate in the hot part of the charge (Figs. 3 and 4). The phases remain chemically homogeneous throughout the charge.

Samples that had not undergone melting also have very distinctive textural characteristics. Subsolidus experiments (Fig. 2A,B) show the characteristic uniformity in the distribution of phases throughout the charge. The textures of the minerals in the subsolidus experiments are also distinctive. Euhedral needles of pyroxene extend into a uniformly distributed open pore space (Fig. 2B) throughout the entire experimental charge.

As summarized in Fig. 1 and Table 1, the vapor-saturated solidus that would be inferred from these experiments is at 940 °C at 1.2 GPa, 865 °C at 2 GPa and 800 °C at 3.2 GPa within an uncertainty of ± 15 to 20 °C. The vapor saturated solidus shown in Fig. 1 is extrapolated to the 0.01 MPa dry solidus, according to the predictions of [22,23] for the Hart and Zindler peridotite composition. At 0.01 MPa, H₂O solubility in the melt would be negligible.

3.3. Mineral textures

The mineral shapes and textural characteristics of these experiments are a response to the nucleation and growth of the product phases from an oxide starting mix in the presence of H_2O . Olivine grew as equant, euhedral to subhedral crystals in all charges and ranged in size

from 10 to 100 μ m (Figs. 2–5). Orthopyroxene and clinopyroxene grew as elongate prismatic crystals that ranged in dimension from 20 by 100 μ m in higher temperature experiments (Figs. 2 and 4C) to needle-like laths with high aspect ratios and widths of 1–10 μ m (Fig. 4C) in the lowest temperature experiments. Amphibole crystallized as well developed euhedral crystals up to 100 μ m in longest dimension (Fig. 2D) that poikilitically enclose the olivine and pyroxene in high temperature experiments. Spinel was present as small subhedral to euhedral crystals that were rarely larger than 2 μ m in diameter. Garnet always grew as large subhedral crystals (up to 500 μ m in diameter, Figs. 3 and 4) that poikilitically enclosed oliv+opx+cpx. Garnet nucleated in all parts of the capsule regardless of the presence or absence of melt (Figs. 3E and 4A).

3.4. Mineral and melt composition

Multiple mineral grains were analyzed (Table 2) in the experimental charges to assess the extent to which the oxide starting mix had reacted to a set of homogeneous silicate products. In BSE images all phases appear to be compositionally uniform and homogeneous, and this observation is reinforced by the lack of compositional variability measured by analyzing multiple mineral grains. Olivine and orthopyroxene are the most chemically homogeneous phases and Fe and Mg are very homogeneous with variations in the means of replicate analyses that range from <1 to 2% relative. The minor element contents of pyroxenes show slightly more variation. The large poikilitic phases (amphibole and garnet) are also compositionally homogeneous, despite their large size. Spinel was difficult to analyze because of its small grain size and it showed the largest compositional variations. The phase compositions vary from sample to sample in response to variations in temperature, pressure and melt composition. Despite the variability in minor element contents of pyroxenes and in spinel in individual samples, a variation can be identified with increases in melt fraction and temperature of the sample.

Melt could be analyzed only in one experiment (e.g., B814, Table 2, Fig. 2C) because in most experiments, it



Fig. 2. (A) Back-scattered electron image of sub-solidus experiment C237 (850 °C, 2 GPa) shows entire sample with hot end up. (B) Example of uniformly distributed porosity and mineral assemblages in unmelted experiment C237. Chlorite (chl) is the darker, tabular phase. (C) Experiment B814 (1020 °C, 1.2 GPa) showing blebs of quenched melt (now glass) at grain junctions. Black regions are porosity, previously vapor-filled. (D) Amphibole-bearing experiment B810 (1000 °C, 1.2 GPa) showing inclusions of orthopyroxene (opx), clinopyroxene (cpx), olivine (ol) and spinel (sp) in amphibole (amp).

was present as micron-thick bubble walls in a quenched melt froth making it impossible to analyze with the electron microprobe. The melt in B814 is a high-Al₂O₃ andesite (57 wt.% SiO₂, 22.4% Al₂O₃). The high SiO₂ content of this melt and its occurrence with olivine in the hotter end of the charge is consistent with a peritectic melting reaction:

opx + cpx + spinel = olivine + melt

Although melt compositions could not be determined in the higher pressure experiments, the association of olivine+liquid is present up to 2.8 GPa, suggesting that melts remains SiO_2 rich. In the 3.2 GPa experiments orthopyroxene joins olivine and melt, suggesting that the first melt becomes olivine-normative at higher pressures [24]. We do not think that the quenched melt that we observe is an SiO₂-enriched fluid phase that formed below the solidus. The solubility of SiO₂ in H₂O at these conditions in the presence of olivine and orthopyroxene is very low [25,26], and our expectation is that a quenched fluid phase would produce spherical blebs of an SiO₂-rich component by unmixing from a dominantly fluid phase.

3.5. Oxygen fugacity

The oxygen fugacity of the spinel-bearing experiments was estimated using the olivine–orthopyroxene–spinel oxygen geobarometer [27]. The predicted values lie between -1 to +2 log units around the QFM buffer with an average of +0.8 log units above QFM (Table 1). Thus, the f_{O_2} of these experiments is similar to the f_{O_2} values inferred for the mantle wedge above subduction zones [28].



Fig. 3. Melt-bearing near-solidus experiment C260 (910 °C and 2.8 GPa). Hot end of the sample faces up. (A) Back-scattered electron (BE) image showing gold capsule with concentration of olivine+melt at top of charge. Black regions are porosity, previously vapor-filled. (B) BE image of close-up of melt and olivine at top of charge. (C) Large area BE image showing edges of Au capsule (bright regions) and poikilitic garnet (gt) crystals throughout the sample. (D) Large area Ca WDS X-ray image showing compaction of clinopyroxene toward bottom. (E) Large area Al WDS X-ray image highlighting the garnet crystals, present near the top and near the bottom of the charge.

3.6. Approach to equilibrium

The experiments reported here are synthesis experiments, no reversal-type experiments have been performed. Demonstration of equilibrium through a reversal experiment would be difficult (if not impossible) for an assemblage of phases with this compositional complexity. However, we will demonstrate that reaction among coexisting solids has proceeded sufficiently so that the coexisting minerals have approached near equilibrium values, and that the results are meaningful for investigating the systematics of peridotite melting. Three sets of observations indicate a close approach to equilibrium: (1) the growth of compositionally homogeneous, chemically unzoned minerals, (2) the achievement of 2pyroxene temperatures between coexisting orthopyroxene and high-Ca clinopyroxene (opx+cpx) that are similar to the experimental conditions and (3) maintenance of constant bulk composition.

As discussed above, the silicate minerals produced in these experiments are compositionally uniform, even when they are large, as in the case of garnet and amphibole. The combination of using oxide starting mixes, H_2O and the long duration of the experiments has led to the development of homogeneous experimental products. This has also been the conclusion of other experimental studies on dry peridotite melting [5,29] that compared the compositions of minerals using experiments that used both oxide and natural crystalline starting materials. In these dry experiments the oxide mixes grew more uniform products, whereas the mineral grains in the natural peridotite experiments retained compositional heterogeneities for much longer; even after the longest experiment durations [29].

For all of the experiments that were analyzed we calculated a 2-pyroxene temperature using the QUILF thermometer [30]. The temperatures predicted by QUILF are summarized in Table 1. Of the 10 experimental charges



Fig. 4. Melted near-solidus experiment D151 (840 °C and 3.2 GPa). Hot end of the sample faces up. (A) Back-scattered electron (BE) image of the entire sample. Au is black with white fringe as a result of image processing. Melt+bubble layer is visible at top of the charge. Poikilitic garnet (gt) is distributed throughout the charge. (B) Large area Ca WDS X-ray image showing gradation in cpx abundance away from the melt+olivine rich layer near the hot end. (C) Close up BE image near top of the charge.



Fig. 5. High-resolution secondary electron images of broken fragments in experiment C260 (2.8 GPa, 910 °C). White arrows in figures point to glass coatings and glass shards on olivine and orthopyroxene crystals. Glass is widespread in the upper (hot) part of the charge (compare to Fig. 3B). (A) The glass coatings on olivine/olivine grain boundaries are vesiculated. (B) Glass shards are attached to the terminations of orthopyroxene crystals. The temperature of this experiment is about 100 °C lower than the wet peridotite solidus estimated by Kushiro et al. (1968), Green (1973) and Millhollen et al. (1974).

analyzed, all but 3 predict the experimental temperatures within 1 sigma of the uncertainty in the estimate, and the other 2 are close, and would probably approach the experimental value more closely, if more analyses were made of the minerals. The exception is one of the lowest temperature experiments analyzed (D151). In this experiment it was not possible to obtain good quality analyses of the pyroxenes. The width of the pyroxene grains (Fig. 4C) is on the order of the electron beam size, and melt coating the grain edges interferes in the X-ray generation. Thus, the close correspondence of the experimental and estimated temperatures is judged to be sufficient evidence that the experiments approached equilibrium.

An approach to equilibrium requires that there be no loss or gain of mass between the starting material and the enclosing capsule. The analyzed experiments were mass balanced and with the exception of the highly melted experiment (B816, 1100 °C, where the melt phase was not analyzed) have low sum of squares of the residuals (<0.25). Also, the gain or loss of Fe to the enclosing capsule was calculated (Table 1) and was generally less than 5 wt.% relative. The element that did not mass balance well was Na, and this is because it is concentrated in the melt or fluid phase. For the melt analysis of B814 (w/Na₂O in Table 2), the result of the mass balance calculation was used to restore Na₂O in the liquid. We do not know whether some Na₂O was also partitioned into the super-critical fluid, and this restored value should be viewed as a maximum amount.

4. Discussion

4.1. Comparison with previous experimental studies

Four prior experimental studies investigated the lowerpressure vapor saturated melting of peridotite [8,31-34]. The earliest studies were made when the piston cylinder technique was in its infancy. The experiments of Kushiro et al. [33,34] and Millhollen et al. [32] were carried out in either Pt or Mo capsules, run durations were short (from 5 min to 3 h) and H₂O was added as a liquid to a starting material of natural perdotite powder. Green [31] utilized AgPd alloy capsules with experimental run times of up to 6 h and 10 wt.% H₂O was added to an oxide starting material. All three of these studies reached a similar conclusion for the melting behavior of peridotite. Their results show a curved concave-up P-T boundary with a minimum melting temperature of about 1000 °C at 2.5-3 GPa (Fig. 6A). Mysen and Boettcher [8] used AgPd alloy capsules but with much longer experimental run times of up to 64 h and their starting material of natural peridotite powder contained 20-30 wt.% H₂O. Their melting behavior differs substantially from the three other experimental studies. The melting point depression is significantly greater and reaches a minimum at 800 °C at 3 GPa (Fig. 6A) and is most similar to results of the present study.

The reason for the apparent discrepancy in results may be that the higher melting point experiments were all run for very short times, perhaps too short for melting of the natural minerals to be observed. Experimental studies have shown that the melting kinetics of olivine are significantly slower than those of diopside under similar temperature– pressure conditions [35]. Kinzler and Grove [22] found that this could explain discrepancies in basalt–peridotite sandwich melting experiments where olivine persisted with pyroxene and melt outside its equilibrium stability range. The melting behavior observed in the previous vapor-saturated peridotite experiments that found a higher



Fig. 6. (A) Water-saturated peridotite solidus comparison. M&B=[8] K&K, S&A=[33,34], M=[32], G=[31]. K&G=[23]. (B) Comparison of vapor-saturated melting of peridotite, with that of MORB basalt and terrigenous sediment. Basalt melting (dashed grey lines) from L&W [47] and L et al. [46]. Sediment melting studies (dashed black lines) are P&S [48] and N et al. [49].

temperature solidus may be similarly influenced by melting kinetics. The solidus depression in the older short duration experiments is most similar to that observed for pure diopside [36,37] (the mineral that melts faster) while the solidus depression found in the longer duration experiments [8] is more similar to that observed for the vapor-saturated melting of forsterite [38,39]. At 2 GPa, the melting point depression in diopside caused by the presence of H_2O is ~ 200 °C less than that observed for forsterite. A possible explanation of the high solidus temperature of the short duration experiments is that they were too short for equilibrium melting to occur. At the lowest temperature (e.g. 800 °C, 3 GPa), melting rates for diopside and olivine are so slow that neither phase melted during the short run time. Also, temperatures are too low for disequilibrium melting of diopside (the mineral with the fastest melting kinetics) to occur. At higher temperatures (1000 °C) diopside melted significantly during the experiment: some olivine may have melted as well. Enough disequilibrium melting occurred so that the melt could be observed in the run product. Thus, the melts in these experiments were not in equilibrium with the other mineral phases and the solidus determined was not the equilibrium solidus.

Another factor in two of the early studies was the use of Pt and Mo capsules. These containers are now known to lose H₂O rapidly by diffusion of H₂ through the capsule and to interact with the silicate starting material. It is possible that H₂O loss and Fe loss also influenced the experimental results. The expected effect on the solidus would be to move it to higher temperatures. The experimental results presented here are in close agreement with those obtained by Mysen and Boettcher [8]. We conclude that both sets of experiments provide a more accurate characterization of the vapor-saturated melting behavior of peridotite. Both studies used experimental durations significantly longer than the studies that found a higher temperature solidus. Both used capsule material that is inert to exchange of Fe with the starting material and both also added significant amounts of H₂O to the starting material, which may have facilitated the observation of the appearance of the first melt.

4.2. Phase equilibrium controls on melting in subduction zones

4.2.1. Amphibole stability in hydrated mantle peridotite

The amphibole stability in our experiments is most similar to that found by Mysen and Boettcher [8]. As discussed by Wyllie [40] and Niida and Green [41] peridotite bulk composition (alkalis and titanium contents) as well as oxygen fugacity influence the upper temperature and pressure limits of amphibole stability. The upper pressure limit of amphibole in this study (<2 GPa, Fig. 1) is at the low pressure end of the range found in previous investigations [40,41], and our peridotite also has the lowest Na₂O and TiO₂ of the ones that have been used in amphibole stability studies. Vapor-saturated melting in the presence of amphibole occurs from 940 °C at 1.2 GPa to 880 °C at 1.7 GPa.

4.2.2. Chlorite as a stable phase on the peridotite solidus

A high pressure chlorite phase has been found in mantle-analog [19] and in natural peridotite compositions [20]. We find a similar phase coexisting with melt at the peridotite solidus from 2 to 3.2 GPa ((Figs. 1, 2B)

and 4)C, Table 2). This hydrous phase contains 12 wt.% H_2O and is potentially stable at the peridotite solidus during mantle wedge melting. If so, then H_2O released from the slab into the overlying mantle wedge at P>2 GPa (~60 km) may be stored as chlorite that can be advected to greater depths by descending mantle flow at the base of the wedge. This hydrated mantle will be heated and then dewatered when chlorite breaks down, releasing its water and initiating hydrous melting.

4.2.3. Ilmenite as a residual phase—HFSE depletions

The low temperatures of the wet peridotite solidus result in a significant decrease in the solubility of "other" components (CaTi₂Al₂O₆, CaAl₂SiO₆, CaCrAlSiO₆, etc.) in high-Ca pyroxene. The consequence is the saturation of another oxide phase that is an ilmenite–geikielite solid solution (D151, Table 2). This oxide phase is a potential reservoir for high field strength elements (HFSE, e.g., Zr, Ti, Nb and Ta) [42] and its presence may lead to retention of HFSE elements during melting in arc systems [43]. In this case the HFSE retention would be a consequence of melt/mantle residue partitioning of these elements at the initiation of H₂O saturated peridotite melting, and not a consequence of melting of subducted ocean crust.

4.2.4. The source of H_2O for melting of the mantle wedge

In the following discussion we assume that H₂O is in abundance at the onset of melting in the mantle wedge. The dehydration of hydrous minerals in subducted oceanic lithosphere may be the source and H₂O may be supplied from hydrated sediment, basalt or mantle lithosphere [6,44]. Also, serpentinized mantle lithosphere underlying the top-most sediment and basalt layers of subducted lithosphere can be an important reservoir that fuels vapor-saturated flux melting. Recent observations of serpentinite formation at the locus of plate bending in the fore arc [45] indicate that serpentine can form at depths of 25 km within the subducted lithospheric mantle. Chlorite-bearing hydrated mantle above the slab may also carry H₂O into the melt generation zone. H₂O is supplied to the wedge by hydrous mineral breakdown throughout the subducted lithosphere wherever hydrous minerals become unstable. The vapor-saturated solidus of peridotite is compared to that of basalt [46,47] and sediments [48,49] from previous experimental studies in Fig. 6B. The solidi are separated by ~ 100 °C at pressures relevant to subduction zone melting. This depth is chosen as that corresponding to the average depth range to the slab-wedge interface in modern subduction zones (100-125 km). If the subducted basalt or sediment is heated sufficiently melting will occur. The resulting

siliceous and H₂O-rich melt (\sim 30 wt.% H₂O) would encounter solid mantle as it ascended into the overlying wedge, crystallize, converting olivine to orthopyroxene, and producing an alkali and trace element enriched supercritical fluid that would equilibrate with peridotite [6].

4.3. Mantle wedge melting processes

In the following discussion the vapor-saturated phase relations for peridotite are used as a starting point to develop a model of mantle wedge flux melting. The model assumes that the first melt generated along the base of the wedge is vapor-saturated, and that melting will occur everywhere above the slab where temperature exceeds the vapor-saturated solidus. After this melt forms and ascends into the wedge, melting will continue at H₂Oundersaturated conditions. This simplifying assumption neglects the potential controls that might exist on the release of H_2O into the mantle wedge [50]. At present we do not have a complete characterization of the melting behavior of natural hydrous mantle peridotite. However, we do understand that H₂O has a large influence on melting [44,51] characterized by a large temperature lowering effect that spreads melting out over a larger temperature interval. Thus, while realizing that there are complexities we are not accounting for in the model, a simplified melting model exploring the general influence of variations in H₂O may reveal some features that could be important in arc melt generation in the mantle wedge.

4.3.1. A simplified peridotite melting model

The relationship between melt H₂O content, temperature and pressure is approximated by taking advantage of the results of thermodynamic models for simple silicate-H₂O binary systems developed by Silver and Stolper [52]. Their model accounts for speciation of H₂O in the melt phase and its influence on melting behavior. Their prediction for the temperature-composition ($T-X_{H_2O}$) liquidus surface has been modified for natural peridotite. The input parameters needed are the H₂O content of the vapor-saturated solidus (X_{init}) and an approximation of the dry peridotite melting behavior. We use the phase relations determined here (Fig. 1) along with measured H₂O solubility vs. pressure in forsterite-H₂O [38,39] to predict the peridotite-melt boundary in $T-P-X_{H_2O}$ space. The expression is:

 $7290^* P - 810^* T - 24600^* H_2 O + 1093500 = 0 \tag{1}$

where *T* is in $^{\circ}$ C, *P* is in kilobars and H₂O content is in wt.%. The dry peridotite melting temperatures are reasonable approximations of sub-liquidus partial

melts of peridotite taken from [22,24] and the simplified melting boundary is essentially the liquidus in a binary system that extends from a eutectic-like vapor-saturated solidus to a dry liquidus (Fig. 7). This model represents the liquidus as a planar surface in $T-P-X_{\rm H_2O}$. This is the shape of the liquidus surface predicted by the Silver and Stolper model [52] for Diopside–H₂O and Albite–H₂O.

The fraction of melt produced at the vapor-saturated solidus (F_{init}) is assumed to be 2.5 wt.%. This is an unknown parameter and the distribution of H₂O-rich fluid at the base of the mantle wedge may influence the



Fig. 7. Flux melting pressure–temperature– $X_{\rm H_2O}$ paths. (A) Path taken by a melt produced at the vapor-saturated solidus (P1, T1) as it ascends vertically into shallow, hotter mantle (arrow). This path is dictated by the thermal structure in the mantle wedge and the path taken by the ascending melt. Grey arrow shows path from shallower part of the wedge. A series of vertical ascent paths is used to construct the melt distribution vs. depth shown in Fig. 8. (B) Re-equilibration of melts with surroundings during flux melting. Melt ascends to shallower, hotter mantle at lower pressure (P2, T2 and P3, T3). Melt is too H₂Orich under these conditions and dissolves silicates to come into equilibrium with its surroundings (Δ F2, Δ F3). At last depth of equilibration, the melt records only the shallow conditions (P3, T3).

initial melt fraction [50]. Estimates of equilibrium melt fraction for anhydrous melts in olivine-rich aggregates range from <0.1 to 2.5 wt.% interstitial melt [53] and up to 8–9 wt.% in olivine+pyroxene-bearing water-saturated systems [54]. We chose the value of 2.5 wt.% because it yields melts of comparable melt fractions (F=0.17–0.20) to melting amounts inferred by experimental petrology [6].

The first melt generated along the base of the wedge is vapor-saturated (P1, T1, Fig. 7). After this melt forms and ascends into the overlying mantle it continues to react and melt its surroundings. It will evolve along the H₂O undersaturated peridotite liquidus surface (Eq. (1)). The variation in melt fraction is calculated by determining the amount of crystalline material that needs to be dissolved in order to bring the melt at a higher temperature and lower pressure (P2, T2 in Fig. 7) into equilibrium with the surrounding solids (Δ F2 in Fig. 7). At P2, T2 the amount of melt ($F_{P2, T2}$) is given by:

$$F_{P2,T2} = ((X_{init} - X_{P2, T2}) / X_{init})^* F_{init} + F_{init}$$
(2)

where $X_{P2, T2}$ is the equilibrium H₂O content of the vapor-undersaturated melt on the crystal+melt boundary at P2, T2. P2 and T2 are specified by knowing the thermal structure of the wedge, thereby allowing estimation of $X_{P2, T2}$. The melting process continues and the melt ascends again to shallower depths, encounters hotter mantle (P3, T3) and melts (Δ F3 in Fig. 7). At each step the amount of melt can be estimated by calculating the amount of solid that needs to dissolve at the shallower, hotter depth to bring the melt into equilibrium with the enclosing mantle minerals:

$$\Delta F_n = ((X_{n-1} - X_n) / X_{n-1})^* F_{n-1},$$

where $X_n = f(T, P).$ (3)

The H₂O-rich melts would be very buoyant would leave the base of the wedge and ascend into the overlying mantle by porous flow or by coalescing into small upward moving diapirs [55]. Grove et al. [6,44] discuss the possible mantle flow mechanisms and favor reactive porous flow as the flux melting process. In either case, the melt or melt+crystal diapirs must come into thermal equilibrium with the surrounding mantle. We assume a reactive porous flow mechanism and also assume that the melt does not lose H₂O to the surrounding mantle as it ascends (essentially a closed system for H₂O, a reasonable assumption since only nominally anhydrous phases are stable in the wedge). The system is open to exchange of heat and all other elements between the melt and surrounding mantle. The melt is a relatively small mass distributed in grain boundaries and is thermally overwhelmed by its surroundings.

4.3.2. Pressure–temperature variations in the mantle wedge

The temperature distribution in the mantle wedge shown in Fig. 8 is taken from a numerical study by Kelemen et al. [56]. The exact temperature distribution, spacing of isotherms and maximum temperature achieved in the



Fig. 8. Temperature distribution and H2O fluxed melting processes in the mantle wedge. The temperature structure is taken from Kelemen et al. [56]. Melting is calculated for vertical trajectories above the slabwedge interface using the solidus parameterization (Eq. (1)) and the melting process described in the text (Eqs. (2) and (3)). The calculation was arbitrarily cut off below 108 km, and was extended to shallower depths until vertical trajectories no longer intersected the vaporsaturated solidus. Finit was taken as 0.025 and Xinit varies according to (1) for each vertical trajectory. Shaded and hatched regions show the parts of the mantle wedge that are above the vapor-saturated solidus. Shaded regions show the amount of melt present in the mantle (A) or H₂O content (B) for independent parallel vertical flux melting trajectories. The hatched region is drawn to enclose the part of the mantle where temperature decreases with decreasing depth but still remains above the vapor-saturated peridotite solidus. Dark lines are isotherms and small arrows are mantle flow lines from [56].

mantle wedge are model dependent and may vary with subduction geometry [57], and the Kelemen et al. [56] model was chosen because it has a temperature structure that is broadly consistent with phase equilibrium constraints from primitive arc magmas. An important characteristic of the lower part of the mantle wedge is the inverted thermal gradient (higher temperatures with decreasing depth) that extends from a cold base adjacent to the slab, to a shallow, hot low-viscosity core. Above this hot core, the thermal gradient assumes its normal configuration and temperature decreases toward the wedge–crust interface [6,44,58].

4.3.3. A flux melting model

The model flux melting process is mapped into the mantle wedge thermal model in Fig. 8. Melting has not been calculated at depths >108 km. This cut off is arbitrary, but it is assumed that below some depth H₂O will no longer be supplied to the overlying mantle wedge. Also, for the thermal model used in Fig. 8, the vaporsaturated solidus is at the wedge-slab interface at 108 km depth. Vertical melting paths are calculated from 108 km depth to 55 km on the slab interface. This shallower depth corresponds to the depth above which vapor-saturated melting no longer occurs, because the overlying mantle is too cool to exceed solidus temperatures. The base of the shaded regions in Fig. 8 marks the part of the wedge that is above the vapor-saturated solidus. Above that melting is vapor-undersaturated. The melt fraction increase is shown in Fig. 8A and the melt H₂O content is shown in Fig. 8B. The H₂O content of the first vapor-saturated melt is calculated to be 28 wt.% at 108 km and 20 wt.% at 60 km (Fig. 8B). A very H₂O-rich melt is predicted in a thin sliver at the base of the melting regime. Melt fraction is low all along the base and H₂O content drops as initial pressure of melting decreases. Melt fraction increases toward the hotter center of the mantle wedge. The maximum amount of melting (10-15 wt.%) occurs in the hot core of the mantle wedge that ranges from 40 to 63 km depth and H₂O contents of these melts vary from 3 to 5 wt.%. These melt fractions and H2O contents are consistent with evidence from experimental petrology [6,44]. Melting of the overlying wedge at progressively shallower depths occurs at lower temperatures and produces lower extents of flux melting with higher H₂O contents. The maximum amount of melting in the hot core of the mantle wedge in this region (30–40 km depth) is 3-5 wt.% and the H₂O contents of these melts vary from 10 to 15 wt.%.

The upper hatched region in Fig. 8A represents the part of the mantle with a normal thermal gradient and the hatched region is extended from the hot core up to the minimum depth and temperature of the vapor-saturated solidus. The melt passes into this part of the mantle, cools and reacts further with the mantle by dissolving olivine and crystallizing orthoproxene [58] and increase melt H_2O content. Alternatively, melts might pool, coalesce and ascend as diapirs evolving further by adiabatic melting processes.

4.4. Summary

In summary, our re-evaluation of the melting of peridotite in the presence of excess H₂O finds a solidus that is much lower (by ~ 200 °C at 3 GPa) than reported by some early experimental studies. The discrepancy in results is probably the result of short run times used in these early studies. Chlorite is a stable and abundant phase on the vapor-saturated peridotite solidus from 2 to 3.2 GPa and could be a potentially important reservoir for H₂O. The near-solidus peridotite assemblage contains 16 wt.% chlorite and could hold \sim 2 wt.% H₂O. The new phase diagram also allows the description of reactive porous flow flux melting in the mantle wedge. Melts produced by this process will undergo most of their melting at shallow mantle depths in the hottest part of the wedge. The maximum amount of melt (~ 15 wt.%) is in the hottest part of the mantle wedge over a depth range of 40-60 km.

Acknowledgements

The authors thank D. Johnston and D. Walker for thoughtful reviews. This research was supported by National Science Foundation Grants EAR-0073766, EAR-0440172 and EAR-0538179.

References

- T.W. Sisson, T.L. Grove, Experimental investigations of the role of H₂O in calc-alkaline differentiation and subduction zone magmatism, Contrib. Mineral. Petrol. 113 (2) (1993) 143–166.
- [2] T.W. Sisson, T.L. Grove, Temperatures and H₂O contents of low-MgO high-alumina basalts, Contrib. Mineral. Petrol. 113 (2) (1993) 167–184.
- [3] G.A. Gaetani, T.L. Grove, W.B. Bryan, The influence of water on the petrogenesis of subduction-related igneous rocks, Nature 365 (6444) (1993) 332–334.
- [4] I.S.E. Carmichael, The andesite aqueduct: perspectives on the evolution of intermediate magmatism in west-central (105-99 degrees W) Mexico, Contrib. Mineral. Petrol. 143 (6) (2002) 641–663.
- [5] G.A. Gaetani, T.L. Grove, The influence of water on melting of mantle peridotite, Contrib. Mineral. Petrol. 131 (4) (1998) 323–346.
- [6] T.L. Grove, S.W. Parman, S.A. Bowring, R.C. Price, M.B. Baker, The role of an H₂O-rich fluid component in the generation of primitive basaltic andesites and andesites from the Mt. Shasta region, N California, Contrib. Mineral. Petrol. 142 (4) (2002) 375–396.
- [7] BSVP, Volcanism on the Terrestrial Planets, Pergamon, 1981, 1931 pp.

- [8] B.O. Mysen, A.L. Boettcher, Melting of a hydrous mantle; I, Phase relations of natural peridotite at high pressures and temperatures with controlled activities of water, carbon dioxide, and hydrogen, J. Petrol. 16 (3) (1975) 520–548.
- [9] S.R. Hart, A. Zindler, In search of a bulk-Earth composition, Chem. Geol. 57 (3-4) (1986) 247–267.
- [10] S.W. Parman, T. Grove, Harzburgite melting with and without H₂O: experimental data and predictive modeling, J. Geophys. Res. 109 (2004) B02201.
- [11] M.C. Johnson, D. Walker, Brucite [Mg(OH)₂] dehydration and the molar volume of H₂O to 15 GPa, Am. Mineral. 78 (3-4) (1993) 271–284.
- [12] F.R. Boyd, J.L. England, Apparatus for phase equilibrium studies at pressures up to 50 kilobars and temperatures up to 1750 °C, J. Geophys. Res. 65 (1960) 741–748.
- [13] W. Johannes, D.W. Chipman, J.F. Hays, P.M. Bell, H.K. Mao, R.C. Newton, A.L. Boettcher, F. Seifert, An interlaboratory comparison of piston-cylinder pressure calibration using the albite-breakdown reaction, Contrib. Mineral. Petrol. 32 (1971) 24–38.
- [14] J.F. Hays, Lime-alumina-silica, Year Book- Carnegie Institution of Washington, 1967, pp. 234–239.
- [15] E.B. Watson, D.A. Wark, J.D. Price, J.A. Van Orman, Mapping the thermal structure of solid-media pressure assemblies, Contrib. Mineral. Petrol. 142 (6) (2002) 640–652.
- [16] M. Hesse, T. Grove, Absarokites from the Western Mexican volcanic zone: Constraints on mantle wedge conditions, Contrib. Mineral. Petrol. 146 (2003) 10–27.
- [17] D.E. Newbury, Chemical compositional mapping by microbeam analysis at the micrometer scale and finer, Microelectron. J. 28 (4) (1997) 489–508.
- [18] J.T. Armstrong, Citzaf- a package of correction programs for the quantitative Electron Microbeam X-Ray-Analysis of thick polished materials, thin-films, and particles, Microbeam Anal. 4 (3) (1995) 177–200.
- [19] A. Pawley, Chlorite stability in mantle peridotite: the reaction clinochlore plus enstatite=forsterite+pyrope+H₂O, Contrib. Mineral. Petrol. 144 (4) (2003) 449–456.
- [20] P. Fumagalli, S. Poli, Experimentally determined phase relations in hydrous peridotites to 6.5 GPa and their consequences on the dynamics of subduction zones, J. Petrol. 46 (3) (2005) 555–578.
- [21] C.E. Lesher, D. Walker, Cumulate maturation and melt migration in a temperature-gradient, J. Geophys. Res., Solid Earth Planets 93 (B9) (1988) 10295–10311.
- [22] R.J. Kinzler, T.L. Grove, Primary magmas of mid-ocean ridge basalts: 1. Experiments and methods, J. Geophys. Res., Solid Earth 97 (B5) (1992) 6885–6906.
- [23] R.J. Kinzler, T.L. Grove, Primary magmas of mid-ocean ridge basalts: 2. Applications, J. Geophys. Res., Solid Earth 97 (B5) (1992) 6907–6926.
- [24] R.J. Kinzler, Melting of mantle peridotite at pressures approaching the spinel to garnet transition: Application to mid-ocean ridge basalt petrogenesis, J. Geophys. Res., Solid Earth 102 (B1) (1997) 853–874.
- [25] Y.G. Zhang, J.D. Frantz, Enstatite-forsterite-water equilibria at elevated temperatures and pressures, Am. Mineral. 85 (7-8) (2000) 918–925.
- [26] R.C. Newton, C.E. Manning, Solubility of enstatite plus forsterite in H₂O at deep crust/upper mantle conditions: 4 to 15 kbar and 700 to 900 degrees C, Geochim. Cosmochim. Acta 66 (23) (2002) 4165–4176.
- [27] C. Ballhaus, R.F. Berry, D.H. Green, High-pressure experimental calibration of the olivine-orthopyroxene-spinel oxygen

geobarometer—Implications for the oxidation-state of the uppermantle, Contrib. Mineral. Petrol. 107 (1) (1991) 27–40.

- [28] I.J. Parkinson, R.J. Arculus, The redox state of subduction zones: insights from arc-peridotites, Chem. Geol. 160 (4) (1999) 409–423.
- [29] T.J. Falloon, L.V. Danyushevsky, D.H. Green, Peridotite melting at 1 GPa: Reversal experiments on partial melt compositions produced by peridotite-basalt sandwich experiments, J. Petrol. 42 (12) (2001) 2363–2390.
- [30] D.J. Andersen, D.H. Lindsley, P.M. Davidson, Quilf- a Pascal program to assess equilibria among Fe-Mg-Mn-Ti oxides, pyroxenes, olivine, and quartz, Comput. Geosci. 19 (9) (1993) 1333–1350.
- [31] D.H. Green, Experimental melting studies on a model upper mantle composition at high pressure under water-saturated and water-undersaturated conditions, Earth Planet. Sci. Lett. 19 (1) (1973) 37–53.
- [32] G.L. Millhollen, A.J. Irving, P.J. Wyllie, Melting interval of peridotite with 5.7 percent water to 30 kilobars, J. Geol. 82 (5) (1974) 575–587.
- [33] I. Kushiro, Stability of amphibole and phlogopite in the upper mantle, Carnegie Inst. Washington Yearbook 68 (1970) 245–247.
- [34] I. Kushiro, Y. Syono, S. Akimoto, Melting of a peridotite nodule at high pressures and high water pressures, J. Geophys. Res., B, Solid Earth Planets 73 (1968) 6023–6029.
- [35] Y.X. Zhang, D. Walker, C.E. Lesher, Diffusive crystal dissolution, Contrib. Mineral. Petrol. 102 (4) (1989) 492–513.
- [36] D.H. Eggler, C.W. Burnham, Solution of H_2O in diopside meltsa thermodynamic model, Contrib. Mineral. Petrol. 85 (1) (1984) 58–66.
- [37] D.H. Eggler, Role of CO₂ in melting processes in the mantle, Carnegie Inst. Washington Yearbook 72 (1973) 457–467.
- [38] I. Kushiro, H.S. Yoder Jr., Melting of forsterite and enstatite at high pressures under hydrous conditions, Carnegie Inst. Washington Yearbook 67 (1969) 153–158.
- [39] F.N. Hodges, Solubility of H₂O in forsterite melt at 20 kbar, Carnegie Inst. Washington Yearbook 72 (1973) 495–497.
- [40] P.J. Wyllie, Mantle fluid compositions buffered in peridotite-CO₂-H₂O by carbonates, amphibole, and phlogopite, J. Geol. 86 (6) (1978) 687–713.
- [41] K. Niida, D.H. Green, Stability and chemical composition of pargasitic amphibole in MORB pyrolite under upper mantle conditions, Contrib. Mineral. Petrol. 135 (1) (1999) 18–40.
- [42] Y.D. Jang, H.R. Naslund, Major and trace element variation in ilmenite in the Skaergaard Intrusion: petrologic implications, Chem. Geol. 193 (1-2) (2003) 109–125.
- [43] R.L. Rudnick, M. Barth, I. Horn, W.F. McDonough, Rutilebearing refractory eclogites: Missing link between continents and depleted mantle, Science 287 (5451) (2000) 278–281.
- [44] G.A. Gaetani, T.L. Grove, Experimental constraints on melt generation within the mantle wedge, in: Geophysical Monograph 138: Inside the Subduction Factory, J.M. Eiler, ed.

pp. 107–134, American Geophysical Union, Washington, D.C., 2003.

- [45] C.R. Ranero, J.P. Morgan, K. McIntosh, C. Reichert, Bendingrelated faulting and mantle serpentinization at the Middle America trench, Nature 425 (6956) (2003) 367–373.
- [46] J. Liu, S.R. Bohlen, W.G. Ernst, Stability of hydrous phases in subducting oceanic crust, Earth Planet. Sci. Lett. 143 (1-4) (1996) 161–171.
- [47] I.B. Lambert, P.J. Wyllie, Melting in the deep crust and upper mantle and the nature of the low velocity layer, Phys. Earth Planet. Inter. 3 (1970) 316–322.
- [48] S. Poli, M.W. Schmidt, Petrology of subducted slabs, Annu. Rev. Earth Planet. Sci. 30 (2002) 207–235.
- [49] G.T. Nichols, P.J. Wyllie, C.R. Stern, Subduction zone melting of pelagic sediments constrained by melting experiments, Nature 371 (6500) (1994) 785–788.
- [50] K. Mibe, T. Fujii, A. Yasuda, Control of the location of the volcanic front in island arcs by aqueous fluid connectivity in the mantle wedge, Nature 401 (6750) (1999) 259–262.
- [51] M.M. Hirschmann, P.D. Asimow, M.S. Ghiorso, E.M. Stolper, Calculation of peridotite partial melting from thermodynamic models of minerals and melts. III. Controls on isobaric melt production and the effect of water on melt production, J. Petrol. 40 (5) (1999) 831–851.
- [52] L. Silver, E. Stolper, A thermodynamic model for hydrous silicate melts, J. Geol. 93 (2) (1985) 161–177.
- [53] D.L. Kohlstedt, Structure, rheology and permeability of partially molten rocks at low melt fractions, in: J. Phipps Morgan, D.K. Blackman, J.M. Sinton (Eds.), Mantle Flow and Melt Migration at Mid-Ocean Ridges, Geophysical Monograph, vol. 71, American Geophysical Union, Washington, D.C., 1992, pp. 103–121.
- [54] N. Fujii, K. Osamura, E. Takahashi, Effect of water saturation on the distribution of partial melt in the olivine-pyroxene– plagioclase system, J. Geophys. Res., Solid Earth Planets 91 (B9) (1986) 9253–9259.
- [55] C. Kincaid, R.W. Griffiths, Laboratory models of the thermal evolution of the mantle during rollback subduction, Nature 425 (6953) (2003) 58–62.
- [56] P.B. Kelemen, J.L. Rilling, E.M. Parmentier, L. Mehl, B.R. Hacker, Thermal structure due to solid-state flow in the mantle wedge beneath arcs, in: J.M. Eiler (Ed.), Inside the Subduction Factory, Geophysical Monograph, vol. 138, American Geophysical Union, Washington, D.C., 2003, pp. 293–311.
- [57] P.E. van Keken, B. Kiefer, S.M. Peacock, High resolution models of subduction zones: Implications for mineral dehydration reactions and the transport of water into the deep mantle, Geochem. Geophys. Geosyst. 3 (10) (2003) 1056.
- [58] T.L. Grove, L.T. Elkins Tanton, S.W. Parman, N. Chatterjee, O. Muntener, G.A. Gaetani, Fractional crystallization and mantle melting controls on calc-alkaline differentiation trends, Contrib. Mineral. Petrol. 145 (2004) 513–533.