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# Mantle Melting as a Function of Water Content beneath the Mariana Arc

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Subduction zone magmas are characterized by high concentrations of pre-eruptive  $H_2O$ , presumably as a result of an  $H_2O$  flux originating from the dehydrating, subducting slab. The extent of mantle melting increases as a function of increasing water content beneath back-arc basins and is predicted to increase in a similar manner beneath arc volcanoes. Here, we present new data for olivine-hosted, basaltic melt inclusions from the Mariana arc that reveal pre-eruptive  $H_2O$ contents of  $\sim 1.5-6.0$  wt %, which are up to three times higher than concentrations reported for the Mariana Trough back-arc basin. Major element systematics of arc and back-arc basin basalts indicate that the back-arc basin melting regime does not simply mix with wet, arc-derived melts to produce the observed range of back-arc magmatic  $H_2O$  concentrations. Simple melting models reveal that the trend of increasing extents of melting with increasing  $H_2O$  concentrations of the mantle source identified in the Mariana Trough generally extends beneath the Mariana volcanic front to higher mantle water contents and higher extents of melting. In detail, however, each Mariana volcano may define a distinct relationship between extent of melting and the  $H_2O$  content of the mantle source. We develop a revised parameterization of hydrous melting, incorporating terms for variable pressure and mantle fertility, to describe the distinct relationships shown by each arc volcano. This model is used in combination with thermobarometry constraints to show that hydrous melts equilibrate at greater depths (34-87 km) and temperatures (>1300°C) beneath the Mariana arc than beneath the back-arc basin (21-37 km), although both magma types can form from a mantle of similar potential temperature (~1350°C). The difference lies in where the melts form and equilibrate. Arc melts are dominated by those that equilibrate within the hot core of the mantle wedge, whereas back-arc melts are dominated by those that equilibrate within the shallow zone of decompression melting beneath the spreading center. Despite higher absolute melting temperatures (>1300°C), Mariana arc melts reflect lower melt productivity as a result of wet melting conditions and a more refractory mantle source.

KEY WORDS: subduction; mantle melting; melt inclusions; magmatic volatiles

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### **INTRODUCTION**

Water plays a central role in subduction zone magmatism. Driven from the subducting plate during metamorphic dehydration, water enters and modifies the mantle wedge beneath arc volcanoes. The well-established effect of water in lowering the peridotite solidus (e.g. Kushiro et al., 1968; Gaetani & Grove, 1998; Grove et al., 2006; Hirschmann et al., 2009) is thought to be a principal cause of mantle wedge melting, which is ultimately expressed as volcanism at the surface. Arc lavas show characteristic enrichments in fluid-mobile trace elements that are believed to participate, along with water, in these mass transfer and melting processes (e.g. Tera et al., 1986; Morris et al., 1990; Plank & Langmuir, 1993; Elliott et al., 1997); however, the development of direct, quantitative relationships between H<sub>2</sub>O and key subduction zone processes in natural systems has been slow

Water contents of magmas have until recently been difficult to measure in arc systems because subaerially erupted lava degasses at low pressures, releasing most of the volatiles (e.g. H<sub>2</sub>O, CO<sub>2</sub>, S) that were dissolved in the liquid phase of the magma at high pressure. Melt inclusions, however, preserved as blebs of glass trapped in phenocrysts, often retain the pre-eruptive, dissolved volatiles that are lost from the bulk lava during degassing because they typically form when the magma was at depth. Enclosed within their crystalline containers, such inclusions were never exposed to low pressures on eruption. These tiny inclusions thus provide a means of bypassing the problem of volatile loss from conventional, whole-rock samples or from matrix glasses. Early evidence for high magmatic water contents in arc melt inclusions was found by Anderson (e.g. Anderson, 1979, 1982), who used the difference of the sum of major element oxides from 100% in glass inclusions from arc volcanoes to infer high dissolved H<sub>2</sub>O concentrations (2-7 wt %). Recent innovations in microbeam analytical techniques such as Fourier transform infrared spectrometry (FTIR) and secondary ionization mass spectrometry (SIMS) have since established and streamlined the direct micro-analysis of volatiles in glasses (e.g. Stolper, 1982; Sisson & Layne, 1993; Sobolev & Chaussidon, 1996; Hauri, 2002a). Now, a rapidly growing database of direct measurements and experimental predictions of high H<sub>2</sub>O contents in arc magmas has shown Anderson's original inferences to have been correct (e.g. Sisson & Grove, 1993b; Newman et al., 2000; Grove et al., 2002; Wallace, 2005), and current work continues to demonstrate the tremendous utility of igneous melt inclusions as messengers of deep magmatic and mantle processes (e.g. Sobolev & Shimizu, 1993; Nielsen et al., 1995; Sobolev & Chaussidon, 1996; Saal et al., 1998, 2002; Baker et al., 2005; Baker, 2008; Johnson et al., 2009).

A number of recent studies have investigated the pre-eruptive water contents of arc magmas using melt inclusion or glass data and experimental techniques, drawing important links between magmatic H<sub>2</sub>O and arc volcanic processes (e.g. Roggensack et al., 1997; Roggensack, 2001; Blundy et al., 2006), the bulk composition of arc magmas (e.g. Sisson & Grove, 1993a, 1993b; Grove et al., 2002; Gaetani & Grove, 2003; Wood, 2004) and fluid-mobile trace element signatures (e.g. Cervantes & Wallace, 2003; Sadofsky et al., 2008). Several studies have specifically examined the relationship between magmatic water concentrations and indicators of the extent of mantle melting in subduction zone settings. Stolper & Newman (1994) used natural pillow glass samples from the Mariana Trough back-arc basin to model a direct relationship between water content and the extent of mantle melting, as evidenced by the correlation of increasing magmatic H<sub>2</sub>O with decreasing TiO<sub>2</sub>. A number of studies have since supported and built upon these observations and models, using additional data for the Mariana Trough and other global back-arc basins (e.g. Gribble et al., 1996, 1998; Kelley et al., 2006; Langmuir et al., 2006), all in support of the paradigm that high water contents in the source regions beneath back-arc basins lead both to high overall extents of mantle melting beneath back-arc basins and elevated dissolved H<sub>2</sub>O contents in the resulting partial melts. Some recent work has also drawn similar links between melting processes and high magmatic H<sub>2</sub>O at arc volcanoes using minor and trace elements as proxies for melt fraction (e.g. Walker et al., 2003; Portnyagin et al., 2007; Johnson et al., 2009). Nevetheless, although geochemical data suggest a causal relationship between water flux and extent of mantle melting beneath arcs and back-arc basins, the connections between these two types of wet melting systems have not been fully developed.

Recent work has begun to forge a framework for realistic models of melting processes and melt transport in the mantle wedge. For example, models involving reactive transport of water (e.g. Davies & Stevenson, 1992) or reactive porous flow of melt through the wedge interior (e.g. Kelemen et al., 2003; Grove et al., 2006), mixing of melts from distinctly separate wet and dry melting regimes (e.g. Langmuir et al., 2006), and buoyant, coincident ascent of hydrated mantle plus melt (e.g. Hall & Kincaid, 2001; Gerya & Yuen, 2003; Kelley et al., 2006) have all been proposed to explain the observed range of melt compositions in specific arc and back-arc basin settings. Despite this progress, we still lack quantitative treatments that link these processes with the water flux from the subducting plate. Cross-arc traverses of subaerial volcanism in Guatemala, Kamchatka, and Mexico (Walker et al., 2003; Portnyagin et al., 2007; Johnson et al., 2009) suggest that the role of water in magma production generally diminishes with distance behind the volcanic front. This idea is supported by observations of back-arc basin basalts, which display an overall global decrease in magmatic

water content with distance from the trench (e.g. Kelley et al., 2006).

The premise of this study is to develop a broader understanding of the links and distinctions between arc and back-arc melting processes and how these relate to the behavior of water in the mantle source. We will show that this is possible based on several recent, comprehensive studies of back-arc basin magmatism (e.g. Taylor & Martinez, 2003; Kelley et al., 2006; Langmuir et al., 2006; Wiens et al., 2010), which permit both the sub-arc flux melting process and the role of related processes in back-arc basin magmatism to be compared for a single arc-back-arc basin pair such as the Marianas. In addition to using literature data in our analysis, we present new combined major element and volatile data for olivine-hosted glass inclusions from four islands of the Mariana arc. These data are then used to (1) evaluate the conditions and processes driving mantle melting beneath arcs, (2) explore how recent models of back-arc basin melting processes relate to processes beneath the Mariana arc, and (3) assess the relationship between the arc and back-arc melting regimes in the Mariana system. The melting processes in these systems are ultimately reflective of important contrasts in the shape of the geotherm, the fertility of the mantle wedge, and the amount of H<sub>2</sub>O added to the mantle wedge.

# SAMPLES AND METHODS

# Mariana Arc scoria samples

The glass inclusions analyzed for this study come from seven Mariana arc scoria samples provided by A. T. Anderson, some of which provided the melt inclusions that were the focus of prior work (Anderson, 1982). These scoria samples originate from the Mariana islands of Guguan (GUG 79-1), Pagan (PB-14, PB-62, and PB-64), Agrigan (AGR19 and AGR-Kimi), and Sarigan (SA93), located in the central island province of the active Mariana arc (Fig. 1). Major and trace element analyses of whole-rock powders of these scoria samples are provided in Electronic Appendix 2 (downloadable from http://pet rology.oxfordjournals.org/). From each scoria sample, we hand-picked olivine crystals from the available material, which came either as mineral separates that had been crushed, sieved, and separated using methylene iodide by Anderson or as bulk hand samples of centimeter-scale lapilli to fist-sized bombs that we then crushed and sieved. The olivine separates were immersed in mineral oil and examined under a binocular microscope to identify inclusion-bearing crystals. We selected only olivine-hosted inclusions consisting of clear, brown glass and petrographically determined to be fully enclosed within the host crystals (e.g. Fig. 2). Most of the studied inclusions contained a single vapor bubble and some inclusions contained co-entrained spinel crystals, determined to have been

present syn-entrapment rather than crystallized postentrapment because of their large sizes relative to the associated glass inclusions (see Electronic Appendix 3). In one rock in which naturally glassy inclusions were rare (AGR19), a subset of four crystallized inclusions were homogenized in a gas-mixing furnace for 10 min, following the technique of Hauri (2002*b*; see Table 1 and Electronic Appendix 3).

In addition to these new Mariana arc melt inclusion samples and data, we also incorporated data for olivine-hosted glass inclusions from these four Mariana islands from Shaw et al. (2008) in our dataset. Tephra samples yielding melt inclusions for the Shaw et al. (2008) study were collected during MARGINS-funded field expeditions to the Mariana islands in 2003-2004. Although their tephras are from the same islands as the samples examined in the present study, they are from different eruptive units. In detail, we expect that some samples from Shaw et al. (2008) may show compositional differences relative to the samples of the present study. We note that when subjected to the same screening criteria (see below), both sample sets give the same sense of variation in magmatic H<sub>2</sub>O content (Pagan < Guguan < Agrigan), with the exception of Sarigan. The compositional contrast between the two Sarigan suites, however, is not surprising given that the samples are from different eruptions and could represent different magma batches.

#### **Analytical methods**

Glass inclusions were exposed and polished on a single side for electron microprobe analysis at the Massachusetts Institute of Technology (MIT). Major element, S, and Cl concentrations of the glasses (Table 1 and Electronic Appendix 3) were measured on the MIT JEOL Superprobe following the techniques outlined by Parman & Grove (2004) for hydrous glasses, using a beam defocused to 20 µm to minimize alkali loss and calibrating against the hydrous glass reference materials 1140mf#18 and 87s35a#14 (Sisson & Grove, 1993b). Major element compositions of the host olivine crystals were also measured by electron microprobe at either MIT or the Carnegie Institution of Washington (CIW). Host olivine crystals were also examined using backscattered electron (BSE) imaging to evaluate whether the hosts showed evidence of complex magmatic processes (e.g. reverse zoning, reaction textures, etc.); all host olivines were found to be either homogeneous or slightly normally zoned in forsterite content, reflecting simple magmatic histories. Volatile concentrations  $(H_2O \text{ and } CO_2)$  in the glass inclusions were directly measured in one of two ways. Some inclusions were doubly intersected to make 30-100 µm thick wafers for analysis by FTIR at the California Institute of Technology, following the techniques of Newman et al. (2000; Table 1 and Electronic Appendix 3). Other inclusions were left with a single exposed side and

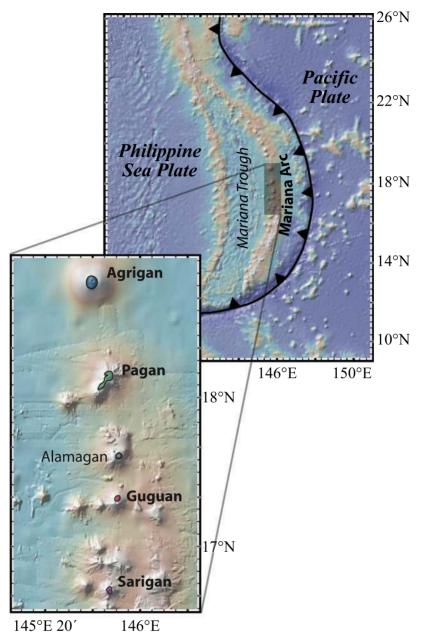
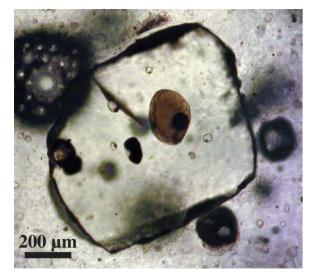


Fig. 1. Regional map of the Mariana subduction zone. The inset shows the locations of volcanoes (bold names) in the Mariana Central Island Province that provided the melt inclusion samples for this work.

the crystals were re-mounted in indium metal for volatile analysis (H<sub>2</sub>O, CO<sub>2</sub>, S, Cl, F) by ion microprobe at CIW using the procedures outlined by Hauri (2002*a*), using <sup>1</sup>H as the mass for determination of H<sub>2</sub>O. One inclusion (AGR 19) was analyzed using both techniques and yielded agreement between the two methods of <2% relative (i.e.  $5\cdot00$  wt % H<sub>2</sub>O by FTIR vs  $5\cdot08$  wt % H<sub>2</sub>O by ion probe; Table 1 and Electronic Appendix 3).

# DATA TREATMENT Correction for post-entrapment crystallization

As a melt inclusion and crystal cool under magmatic conditions, olivine may precipitate from the melt onto the walls of its olivine container. We corrected for this post-entrapment crystallization (PEC) of olivine by adding equilibrium olivine [using  $K_D^{\text{ol-liq}}(\text{Fe}^{2+}/\text{Mg}) = 0.3$ ]



**Fig. 2.** Photomicrograph of an olivine-hosted melt inclusion. The inclusion pictured is sample GUG-D, from Guguan island. The olivine crystal is embedded in resin and has been polished to expose the melt inclusion at the surface. The inclusion is made of clear, brown glass and contains a single vapor bubble.

to each glass inclusion composition in 1% increments until the melt composition reached equilibrium with the forsterite content of a reference point in the host olivine measured  $\sim 40 \,\mu m$  from the inclusion interface. This correction is sensitive to the Fe<sup>3+</sup>/ $\Sigma$ Fe ratio (i.e. Fe<sup>3+</sup>/[Fe<sup>2+</sup> + Fe<sup>3+</sup>]) of the melt. Although Fe<sup>3+</sup>/ $\Sigma$ Fe is unknown in these glass inclusions, we assume  $\text{Fe}^{3+}/\Sigma\text{Fe}$  of 0.25 for all arc samples, which represents an average of  $Fe^{3+}/\Sigma Fe$  ratios measured by micro-X-ray Absorption Near Edge Structure (XANES) spectroscopy for a separate suite of glass inclusions from sample GUG 79-1 (Kelley & Cottrell, 2009). These starting  $Fe^{+3}/\Sigma Fe$  ratios are carried through all subsequent calculations, assuming the total moles of Fe<sup>3+</sup> are conserved, which causes  ${\rm Fe}^{3+}\!/\Sigma{\rm Fe}$  to decrease when olivine is added to the melt compositions. On average, the PEC correction requires <2.5% olivine added back to a given melt composition. To be conservative, any inclusions indicating >5% PEC of olivine were not used in the melting model. The compositions of the AGR19 inclusions that were homogenized in a 1 atm furnace as described above indicate that these inclusions resorbed 1-13% of the host olivine during the homogenization procedure. To correct for this, the composition of the host olivine was subtracted from each homogenized melt composition in 1% increments, using the same approach as described above to correct for crystallization on the inclusion wall, until the reconstructed melt was calculated to be in equilibrium with the host olivine. In rare instances, other minerals (e.g. clinopyroxene) also precipitated from the melt after entrapment as evidenced by BSE images from the electron microprobe.

In cases where secondary or co-entrapped crystals were visible, we excluded those samples from further modeling, although we report the data in Electronic Appendix 3.

In some instances, post-entrapment processes may drive diffusional exchange of some elements (e.g. Fe) between the melt inclusion and the external magma. In the case of these Mariana arc melt inclusions, the results of Kelley & Cottrell (2009) rule out this potential complication. In their study, the Fe<sup>3+</sup>/ $\Sigma$ Fe of Guguan and Sarigan glass inclusions were measured directly by micro-XANES, and with these values, the Mariana inclusions are in near-perfect Fe–Mg exchange equilibrium with their olivine hosts. This indicates that post-entrapment Fe diffusion has not significantly modified the inclusion compositions.

#### Assessing the effects of degassing

Volatiles will partition into bubbles from the liquid component of magma as it decompresses on ascent and ultimately erupts. Despite the fact that melt inclusions are enclosed in crystalline hosts, they may trap melts after extensive degassing has already occurred, thus potentially compromising their utility as probes of the volatile contents of primitive melts and their mantle source regions, which is the goal of this study. Because of the differential solubilities of the various major volatile species, however, it is often possible to show that volatile loss was minimal and thus to ensure that the as-analyzed volatile contents of glass inclusions were not significantly affected by degassing during decompression. We evaluated the effects of degassing on the volatile contents of Mariana arc melt inclusions by examining the co-variation of volatile species (CO<sub>2</sub>, S,  $H_2O$ ). Of these,  $H_2O$  is the most soluble in basaltic magma at low pressure, and CO<sub>2</sub> is the least soluble (Dixon & Stolper, 1995); sulfur solubility in melt is a complex function of fO2 and fS, but recent empirical observations of the relationship between S and the concentrations of other volatile species in arc melt inclusions suggest that its solubility may be between those of H<sub>2</sub>O and CO<sub>2</sub> in basaltic arc magmas (e.g. Sisson & Layne, 1993; Wallace, 2005; Benjamin et al., 2007). Degassing is thus expected to remove  $CO_2$  from solution first, followed by S and H<sub>2</sub>O.

The volatile data presented in Fig. 3 show the extent to which degassing may have removed these volatile species from Mariana arc glass inclusion compositions. Because of the low solubility of CO<sub>2</sub> relative to H<sub>2</sub>O in silicate melt at low pressures, samples with >50 ppm CO<sub>2</sub> are considered to have retained enough CO<sub>2</sub> that H<sub>2</sub>O is unlikely to have been significantly lost by degassing. Below 50 ppm CO<sub>2</sub>, H<sub>2</sub>O concentrations are more scattered and H<sub>2</sub>O may or may not have significantly degassed (Fig. 3a). CO<sub>2</sub> may thus not be the most sensitive indicator of the overall effect of degassing on melt H<sub>2</sub>O concentrations, and in cases where CO<sub>2</sub> is below detection by FTIR, which is a function of both CO<sub>2</sub> concentration and sample thickness, JOURNAL OF PETROLOGY VOLUME 51 NUMBER 8 AUGUST 2010

Sample no .:		Agr19	Agr19C <sup>1</sup>	Agr19E <sup>1</sup>	Agr19F <sup>1</sup>	Gug#6b	GugA	GugC	GugD
Host rock:		AGR19	AGR19	AGR19	AGR19	GUG 79-1	GUG 79-1	GUG 79-1	GUG 79-1
Volcano:		Agrigan	Agrigan	Agrigan	Agrigan	Guguan	Guguan	Guguan	Guguan
Melt inclusion									
SiO <sub>2</sub>	wt %	46.43	45·87	47·31	47.04	46·51	46.10	47·17	45·70
TiO <sub>2</sub>	wt %	0.64	0.56	0.57	0.81	0.69	0.69	0.69	0.74
Al <sub>2</sub> O <sub>3</sub>	wt %	17·52	14·71	15.05	15·02	17.31	18·29	17.59	18·01
FeO*	wt %	10·18	13·07	12.04	12·67	11.03	11·21	11.19	11.32
Fe <sub>2</sub> O <sub>3</sub> †	wt %	2.83	3.63	3.35	3.52	3.06	3·11	3.11	3·15
FeO†	wt %	7.63	9.80	9.03	9.50	8·27	8.40	8.39	8.49
MnO	wt %	0.20	0.24	0.22	0.21	0.19	0.24	0.25	0.24
MgO	wt %	4.83	9.03	8·11	6.38	5.70	6.20	6.22	5.44
CaO	wt %	12·27	10.15	10.38	10.41	11.08	11.64	11.40	12·58
Na <sub>2</sub> O	wt %	1.83	1.66	1.94	2.25	2.29	1.95	1.99	1.95
K <sub>2</sub> O	wt %	0.59	0.53	0.29	0.45	0.38	0.21	0.33	0.30
$P_2O_5$	wt %	0.13	0.12	0.10	0.39	0.09	0.00	0.08	0.09
S <sup>2</sup>	ppm	1440	723	500	615	947		1644	1894
Cl <sup>2</sup>	ppm		580	705	934	895		647	678
$H_2O^3$	wt %	5.00					3.26	3.80	3.28
CO23	ppm	260					—	—	—
H <sub>2</sub> O <sup>4</sup>	wt %	5.08	4.69	3.88	3.99	2.92			
CO24	ppm	264	14	88		44			
S <sup>4</sup>	ppm	1380	973	575	860	1190			
Cl <sup>4</sup>	ppm	515	641	643	973				
F <sup>4</sup>	ppm	520	226	179	221	322			
${\sf Fe}^{3+}/\Sigma{\sf Fe}^{\dagger}$		0.25	0.25	0.22	0.25	0.25	0.25	0.25	0.25
Host olivine									
SiO <sub>2</sub>	wt %	39.32	39.75	39.90	39.83	39.24			
Al <sub>2</sub> O <sub>3</sub>	wt %	0.03	0.03	0.02	0.02	0.04			
FeO	wt %	17.99	18.33	18.40	19.34	19·45			
MnO	wt %								
MgO	wt %	42·12	41.75	41.38	40.86	40.64			
CaO	wt %	0.22	0.21	0.24	0.22	0.21			
NiO	wt %	0.06	0.02	0.02	0.02	0.07			
Total	wt %	99·73	100.09	99.97	100.32	99.66			
Fo		0.81	0.80	0.80	0.79	0.79			
PEC-corrected melt									
Olivine added	%	2	-13	-10	-1	0			
SiO <sub>2</sub>	wt %	46.28	46·79	48·14	47·11	46·51	46·10	47·17	45·70
TiO <sub>2</sub>	wt %	0.62	0.64	0.63	0.81	0.69	0.69	0.69	0.74
Al <sub>2</sub> O <sub>3</sub>	wt %	17.17	16.90	16.72	15·17	17.31	18·29	17·59	18·01
Fe₂O₃†	wt %	2.77	4·17	3.72	3.55	3.06	3·11	3·11	3·15
FeO	wt %	7.86	11.26	10.03	9.60	8·27	8·40	8.39	8.49
MnO	wt %	0.19	0.58	0.24	0.22	0.19	0.24	0.25	0.24
MgO	wt %	5.55	7.64	6.96	6·25	5.70	6·20	6·22	5.44
CaO	wt %	12.03	11.67	11·53	10.52	11.08	11.64	11.40	12.58
Na <sub>2</sub> O	wt %	1.80	1.91	2.16	2.28	2.29	1.95	1.99	1.95
K <sub>2</sub> O	wt %	0.58	0.27	0.32	0.46	0.38	0.21	0.33	0.30
P <sub>2</sub> O <sub>5</sub>	wt %	0.13	0.13	0.11	0.39	0.09	0.00	0.08	0.09
H <sub>2</sub> O	wt %	4.98	5.40	4.31	4.03	2.92	3.26	3.80	3.58
CO <sub>2</sub>	ppm	259	16	97	-	44	_	_	_
S	ppm	1353	1118	639	869	1190	2115	1644	1894
CI	ppm	504	737	714	983		624	647	678
F	ppm	510	259	199	223	322			

Table 1: Major and volatile element compositions of primitive, undegassed Mariana arc melt inclusions and host olivines

(continued)

Table 1:	Continued
100000 11	0.010000000

Sample no.: Host rock: Volcano:		GugF GUG 79-1 Guguan	GugXa GUG 79-1 Guguan	GugAB-1 GUG 79-1 Guguan	GugAE GUG 79-1 Guguan	PB14H PB14 Pagan	PB14Ka PB14 Pagan	PB14Kb PB14 Pagan	PB640-1 <i>A</i> PB64 Pagan
		Cuguan	Cuguun	Cagaan	Cuguan	i agan			
Melt inclusion									
SiO <sub>2</sub>	wt %	46.01	46.9	45.27	47·53	49.36	49·57	48·50	49·10
TiO <sub>2</sub>	wt %	0.80	0.93	0.79	0.75	0.75	0.90	0.83	0.62
Al <sub>2</sub> O <sub>3</sub>	wt %	18·14	17·66	16·29	17·62	15·46	15·87	15·83	14·60
FeO*	wt %	11.80	10.65	13.14	10·92	11·27	11.03	11·49	11.13
Fe₂O₃† F₂O‡	wt %	3.28	2.96	3.65	3.03	3·13	3.06	3·19	3.09
FeO†	wt %	8.85	7.99	9.85	8·19	8·45	8·27	8·62	8·35
MnO Mao	wt %	0.26	0·17	0·23	0·21	0·21	0.20	0·17	0.15
MgO	wt %	4·85	5·18	5·93	5·31	5·86	4·59	5·60	7·21
CaO	wt %	12.50	12·27	11.92	10.77	10.93	11.35	11.44	9·40
Na <sub>2</sub> O	wt %	1.98	2.09	1.77	2.03	2.54	2.39	2.30	2.80
K <sub>2</sub> O	wt %	0.33	0.23	0.33	0.31	0.51	0.48	0.44	0.59
P <sub>2</sub> O <sub>5</sub> S <sup>2</sup>	wt %	0.04	0.11	0.02	0.06	0·14	0·13	0.08	0.07
S <sup>-</sup>	ppm	2001	901	1309	820	756	445	487	
	ppm	763	841	988	898	477	610	620	0.00
$H_2O^3$	wt %	3.25							2.90
$CO_2^3$	ppm	_	0.40	4.40	0.00	0.00	0.50	0.05	_
H <sub>2</sub> O <sup>4</sup>	wt %		3·18	4.49	3.03	2.28	2·52	2·35	
CO <sub>2</sub> <sup>4</sup>	ppm		18	60	42	19	16	31	
S <sup>4</sup>	ppm		1247	1402	1105	810	613	592	
Cl <sup>4</sup>	ppm		768	796	754	432	575	565	
F <sup>4</sup>	ppm		213	203	197	216	240	241	
Fe <sup>3+</sup> /∑Fe†		0.22	0.525	0.25	0.25	0.25	0.25	0.25	0.25
Host olivine									
SiO <sub>2</sub>	wt %	38.74	40.01	39.29		40.03	40.04	39.60	38.96
Al <sub>2</sub> O <sub>3</sub>	wt %	0.02	0.03	0.02		0.37	0.03	0.19	0.02
FeO	wt %	19·97	17.64	22.61		19.69	18.38	19.74	19.94
MnO	wt %								0.30
MgO	wt %	39.83	42.84	38.35		40.22	41.80	40.57	40.23
CaO	wt %	0.21	0.21	0.24		0.41	0.24	0.31	0.30
NiO	wt %	0.06	0.06	0.06		0.06	0.07	0.02	0.10
Total	wt %	98.84	100.79	100.57		100.78	100.56	100.45	99.85
Fo		0.78	0.81	0.75		0.78	0.80	0.79	0.78
PEC-corrected melt									
Olivine added	%	2	2	0		0	3	0	0
SiO <sub>2</sub>	wt %	45.86	46·78	45·27	47.53	49.36	49·25	48·50	49·10
TiO <sub>2</sub>	wt %	0.78	0.91	0.79	0.75	0.75	0.87	0.83	0.62
Al <sub>2</sub> O <sub>3</sub>	wt %	17.78	17.31	16.29	17.62	15.46	15.41	15.83	14.60
Fe <sub>2</sub> O <sub>3</sub> †	wt %	3.21	2.90	3.65	3.03	3.13	2.98	3.19	3.09
FeO	wt %	9·10	8·20	9.85	8·19	8.45	8.64	8.62	8.35
MnO	wt %	0.25	0.17	0.53	0.21	0.21	0.19	0.17	0.15
MgO	wt %	5.53	5.90	5.93	5.31	5.86	5.64	5.60	7·21
CaO	wt %	12.26	12.03	11.92	10.77	10.93	11.02	11.44	9.40
Na <sub>2</sub> O	wt %	1.94	2.05	1.77	2.03	2.54	2.32	2.30	2.80
K <sub>2</sub> O	wt %	0.32	0.22	0.33	0.31	0.51	0.46	0.44	0.59
P <sub>2</sub> O <sub>5</sub>	wt %	0.04	0.11	0.02	0.06	0.14	0.13	0.08	0.07
H <sub>2</sub> O	wt %	3·19	3·11	4.49	3.03	2.28	2.45	2.35	2.90
CO <sub>2</sub>	ppm		18	60	42	19	15	31	-
S	ppm	1962	1223	1402	1105	810	595	592	1419
CI	ppm	748	753	796	754	432	559	565	716
F	ppm		209	203	197	216	233	241	

Table 1: Continued

Sample no.:		PB640-2	PB64G	SA93B	SA93D
Host rock:		PB64	PB64	SA93	SA93
Volcano:		Pagan	Pagan	Sarigan	Sarigan
Nelt inclusion					
SiO <sub>2</sub>	wt %	49·71	49·5	49·51	51·17
TiO <sub>2</sub>	wt %	0.74	0.56	1.01	0.90
Al <sub>2</sub> O <sub>3</sub>	wt %	14.95	15.45	16.57	15.99
FeO*	wt %	11.99	10.40	7.76	8.47
Fe <sub>2</sub> O <sub>3</sub> †	wt %	3.33	2.89	2.16	2.35
FeO†	wt %	8.99	7.80	5.82	6.35
MnO	wt %	0.18	0.16	0.14	0.18
MgO	wt %	7.27	7.17	4.59	4·91
CaO	wt %	9.46	9.58	11.89	10.14
Na <sub>2</sub> O	wt %	2.27	2.96	2.34	2.70
K <sub>2</sub> O	wt %	0.55	0.20	0.31	0.20
P <sub>2</sub> O <sub>5</sub>	wt %	0.04	0.00	0.02	0.08
S <sup>2</sup>	ppm		1652	1090	1172
Cl <sup>2</sup>	ppm		239	555	852
$H_2O^3$	wt %	2.83	3.45		
CO <sub>2</sub> <sup>3</sup>	ppm	_	123		
$H_2O^4$	wt %			5.09	6.14
CO <sub>2</sub> <sup>4</sup>	ppm			207	85
S <sup>4</sup>	ppm			1559	1378
Cl <sup>4</sup>	ppm			583	805
F <sup>4</sup>	ppm			265	362
$Fe^{3+}/\Sigma Fe^{\dagger}$		0.25	0.25	0.22	0.25
lost olivine					
SiO <sub>2</sub>	wt %	37.86	39.39	40.99	39.97
$AI_2O_3$	wt %	0.03	0.02	0.12	0.05
FeO	wt %	20.31	17.98	14.55	16.38
MnO	wt %	0.29			
MgO	wt %	40.40	41.61	43·56	43·18
CaO	wt %	0.58	0.53	0.22	0.19
NiO	wt %	0.02	0.08	0.10	0.10
Total	wt %	99.26	99.30	99.54	99.83
Fo		0.78	0.80	0.84	0.82
PEC-corrected melt		c	-	-	-
Olivine added	%	0	0	2	0
SiO <sub>2</sub>	wt %	49.71	49.54	49.32	51·17
TiO <sub>2</sub>	wt %	0.74	0.56	0.99	0.90
Al <sub>2</sub> O <sub>3</sub>	wt %	14.95	15.45	16.25	15.99
Fe <sub>2</sub> O <sub>3</sub> †	wt %	3.33	2.89	2.11	2.35
FeO	wt %	8.99	7.80	6.02	6.35
MnO	wt %	0.18	0.16	0.14	0.18
MgO	wt %	7.27	7.17	5.37	4.91
CaO	wt %	9.46	9.58	11.66	10.14
Na <sub>2</sub> O	wt %	2.27	2.96	2.29	2.70
K <sub>2</sub> O	wt %	0.55	0.50	0.30	0.50
P <sub>2</sub> O <sub>5</sub>	wt %	0.04	0.00	0.02	0.08
H <sub>2</sub> O	wt %	2.83	3.45	4.99	6·14
CO <sub>2</sub>	ppm	_	123	203	85
S	ppm	1464	1652	1529	1378
CI	ppm	536	239	572	805
F	ppm			259	362

Major elements for melt inclusions and host olivines were determined by electron microprobe (EMP) at MIT. A subset of host olivines were analyzed by EMP at CIW. PEC-corrected melts have been corrected for post-entrapment crystallization of olivine following methods described in the text; volatile compositions used in this calculation are SIMS data where available, and otherwise are FTIR + EMP data.

\*Total Fe reported as FeO.

<sup>†</sup>Fe<sub>2</sub>O<sub>3</sub> calculated as 25% of total Fe prior to correction for post-entrapment crystallization. <sup>1</sup>Crystallized inclusions re-homogenized in a gas-mixing furnace; compositions were corrected for excess olivine resorption by subtracting the host olivine composition from the melt as described in the text.

Concentrations determined by EMP at MIT.

<sup>3</sup>Concentrations determined by FTIR at Caltech.

<sup>4</sup>Concentrations determined by SIMS at CIW.

-, concentration below the detection limit.

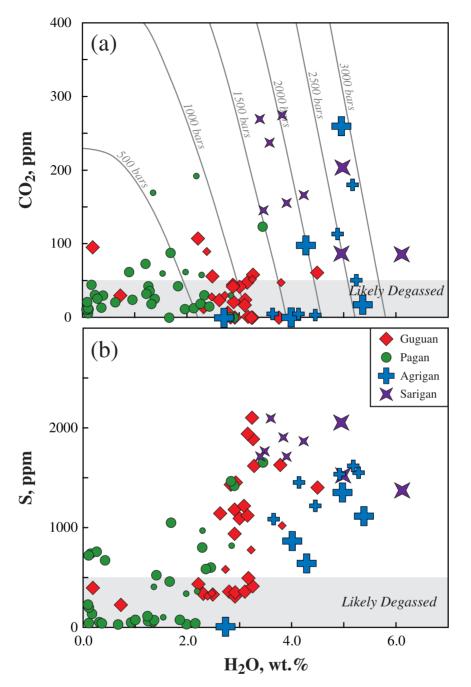


Fig. 3. Plot of volatile element concentrations,  $H_2O$ ,  $CO_2$  and S, in Mariana olivine-hosted melt inclusions. The larger symbols are data from this study; smaller symbols are data from Shaw *et al.* (2008). (a)  $H_2O$  vs  $CO_2$ . The shaded field identifies samples with 0–50 ppm  $CO_2$ , which are likely to have degassed some  $H_2O$  (see text). Isobars were calculated using the VolatileCalc vapor solubility model for basalt compositions (Newman & Lowenstern, 2002). (b)  $H_2O$  vs S. The shaded field identifies samples with 0–500 ppm S, which are likely to have degassed some  $H_2O$  (see text).

the extent of  $CO_2$  degassing could not be determined. We also examined the relationship of  $H_2O$  to S in these melt inclusions, which appears to show more systematic co-variations within each suite of inclusions (Fig. 3b). Other studies have shown similar degassing systematics between S and  $H_2O$  (e.g. Sisson & Layne, 1993; Wade *et al.*, 2006; Benjamin *et al.*, 2007). We thus established a secondary filter at 500 ppm S, considering those inclusions with <500 ppm S to be degassed enough that  $H_2O$  may have been lost; the highest  $H_2O$  contents appear generally

consistent within each sample above this S concentration, and H<sub>2</sub>O contents are more scattered below it.

Post-entrapment diffusion of H<sup>+</sup> could also potentially decouple melt H<sub>2</sub>O concentrations from those of other, less soluble, volatiles. We note, however, that diffusive loss of H<sup>+</sup> from a melt inclusion would also result in significant oxidation of the inclusion as  $O^{2-}$  is left behind. Such a process would disrupt the Fe<sup>2+</sup>–Mg exchange equilibrium between inclusions and their host olivines. As noted above, Mariana melt inclusions from these same samples are close to Fe<sup>2+</sup>-Mg equilibrium with their host olivines, when measured  $Fe^{3+}/\Sigma Fe$  ratios are accounted for, indicating that the redox conditions of the melt inclusions have not been significantly affected by H<sup>+</sup> diffusion (Kelley & Cottrell, 2009). There is thus no evidence that diffusive processes are the main cause of variability in H<sub>2</sub>O content relative to other volatiles in these melt inclusions.

### Assessing the effects of crystal fractionation

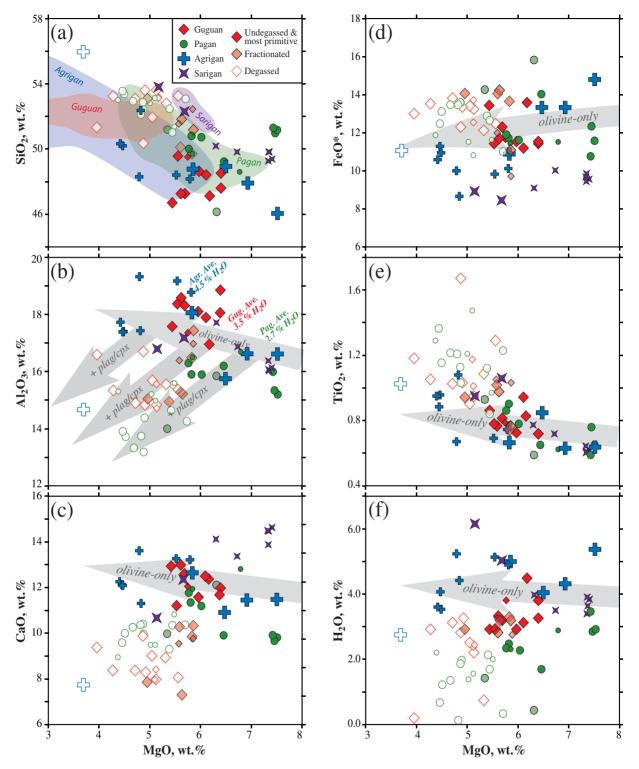
The PEC-corrected melt inclusions range in composition from basalt to basaltic andesite (~45-54 wt % SiO<sub>2</sub>). Melt compositions from each Mariana island show major element variations consistent with synchronous degassing and fractional crystallization (Fig. 4). All inclusions identified as minimally degassed are relatively MgO-rich, with <51.2 wt % SiO2 and >4.9 wt % MgO (Table 1 and Fig. 4a; note that glass inclusion data are plotted on an anhydrous basis in Fig. 4 for comparison with the whole-rock data), and generally have higher  $Al_2O_3$  than degassed inclusions from the same islands (Fig. 4b). In Fig. 4b, however, the data suites for each island show distinct variations consistent with crystal fractionation. The point at which plagioclase saturation occurs, as indicated by the change from increasing to decreasing Al<sub>2</sub>O<sub>3</sub> with decreasing MgO, is sensitive to magmatic H<sub>2</sub>O content. Water suppresses plagioclase crystallization by stabilizing the Ab component in the melt (e.g. Yoder, 1969; Sisson & Grove, 1993a). The data for each island are consistent with plagioclase saturation at distinct magmatic H<sub>2</sub>O concentrations, with the Pagan samples indicating earlier plagioclase saturation from a lower-H<sub>2</sub>O melt, and the Agrigan samples consistent with late plagioclase saturation caused by high magmatic  $H_2O$ . These observations are supported by the measured H<sub>2</sub>O concentrations of the most MgO-rich inclusions from each suite (filled symbols in Fig. 4), which are lowest at Pagan (average = 2.7 wt % H<sub>2</sub>O) and highest at Agrigan (average = 4.5 wt % H<sub>2</sub>O). This clear impact of water content on the liquid lines of descent of Mariana arc magmas has been developed as a magmatic hygrometer (Parman et al., 2010).

Figure 4 identifies those melt inclusions that preserve the least fractionated compositions. Undegassed melt inclusions that fall along plagioclase or clinopyroxene co-crystallization trends are identified in Fig. 4b and c

(<6 wt % MgO and <10.5 wt % CaO anhydrous), and are excluded from further modeling. The plag  $\pm$  cpxfractionated compositions are screened out to avoid large errors from back-tracking these more complex liquid lines of descent. To compensate for the effects of crystal fractionation on the least fractionated melt compositions, we also adopt the simplifying assumption that olivine is the only liquidus phase. Although there is some scatter in Fig. 4c, these least fractionated, undegassed melt inclusions are consistent with the olivine fractionation trend of increasing CaO with decreasing MgO, in support of this assumption.

The least fractionated melt compositions were back-corrected to primary melts in equilibrium with the mantle by adding equilibrium olivine to each inclusion composition in 0.1% increments, until equilibrium with Fo90 [as described by Stolper & Newman (1994) and Kelley et al., (2006)], giving concentrations of elements in the primary magma in equilibrium with mantle olivine (e.g. TiO<sub>2(Fo90)</sub>; see Electronic Appendix 4). On average, this step required addition of  $\sim 22\%$  olivine to the melt compositions. To test whether this extent of olivine-only crystallization is appropriate for these magmas, a subset of reconstructed primary melts was used as input to isobaric, forward fractionation models calculated using the Adiabat interface to the MELTS algorithm (Smith & Asimow, 2005). These models show 17-21% crystallization of olivine only for the primary melts from Guguan, Pagan, and Agrigan before saturation with plagioclase or clinoyroxene, consistent with the olivine-addition calculations. To avoid possible artifacts associated with over-correction, any inclusions requiring more than 30% olivine addition (n=3) were also screened out from further modeling. The melt inclusions passing all steps of data filtering for post-entrapment modification, degassing, and fractional crystallization are reported in Table 1 (n = 20 from this study; n = 15 from Shaw et al., 2008). The complete dataset for all samples is provided in the Electronic Appendix 3.

For direct comparison, similar filtering and correction schemes were applied to pillow glass compositions from the Mariana Trough back-arc basin, following steps modified from Kelley et al. (2006). After filtering for degassing, the Mariana Trough dataset (Stolper & Newman, 1994; Gribble et al., 1996, 1998; Newman et al., 2000) was subdivided by  $H_2O$  content into three groups: <1.0 wt %, 1.0-1.5 wt %, and >1.5 wt %. These groups also follow parallel liquid lines of descent, with visible offsets related to the delay in plagioclase crystallization caused by increasing magmatic H<sub>2</sub>O. The point of plagioclase-in for each group was identified based on inspection of the Mariana Trough data trends in MgO vs Al<sub>2</sub>O<sub>3</sub> (see Electronic Appendices 1 and 5). In this case, the Mariana Trough glass dataset is sufficiently large that fractionation trends are clearly defined for all major elements, and these melt



**Fig. 4.** Plot of major elements vs MgO for Mariana arc olivine-hosted melt inclusions, corrected for post-entrapment olivine crystallization and calculated on an anhydrous basis. The larger symbols are data from this study; smaller symbols are data from Shaw *et al.* (2008). (a) SiO<sub>2</sub> vs MgO. Shaded fields indicate the range of Mariana arc whole-rock lavas for each island (Larson *et al.*, 1974; Dixon & Batiza, 1979; Stern, 1979; Banks *et al.*, 1984; Woodhead, 1989; Elliott *et al.*, 1997). (b) Al<sub>2</sub>O<sub>3</sub> vs MgO. (c) CaO vs MgO. (d) FeO\* vs MgO, where \* indicates total Fe expressed as FeO. (e) TiO<sub>2</sub> vs MgO. (f) H<sub>2</sub>O vs MgO, where MgO is expressed on an anhydrous basis, but H<sub>2</sub>O is the concentration in the PEC-corrected melt inclusions. The symbol shading scheme in these panels is different from that in other figures. Open symbols indicate probably degassed samples, as identified in Fig. 3 and in the text. Lightly shaded symbols indicate compositions designated as undegassed but identified as fractionated in major element compositions, with <6 wt % MgO and <10.5 wt % CaO (anhydrous). Solid symbols identify the least fractionated, undegassed melt inclusion compositions from each island. Average melt H<sub>2</sub>O concentrations are calculated from the measured dissolved H<sub>2</sub>O contents of the samples represented by the solid symbols (Table 1).

compositions were corrected along average major element vs MgO slopes for these multi-saturated liquid lines of descent to the appropriate point of plagioclase-in, after which each melt was assumed to be saturated with olivine-only (see Electronic Appendices 1 and 5). As with the melt inclusions, these reconstructed primitive melts were traced back to primary mantle melts, assuming 17% Fe<sup>+3</sup>/ $\Sigma$ Fe [average of  $Fe^{+3}/\Sigma Fe$  ratios reported for Mariana Trough glasses by Kelley & Cottrell (2009)], by adding equilibrium olivine to each melt in 0.1% increments, until in equilibrium with Fo<sub>90</sub>. This approach to account for H<sub>2</sub>O-based differences in liquid lines of descent (LLDs) differs from that used by Langmuir et al. (2006), who used a model to predict LLD offsets for different melt H<sub>2</sub>O contents, but then grouped basalts from back-arc basins regionally by spreading segment, rather than strictly by H<sub>2</sub>O content, then identified an MgO value at plag-in for each segment. Our approach allows within-segment variations in primary magmatic H<sub>2</sub>O, which may produce different LLDs over smaller spatial scales.

### RESULTS

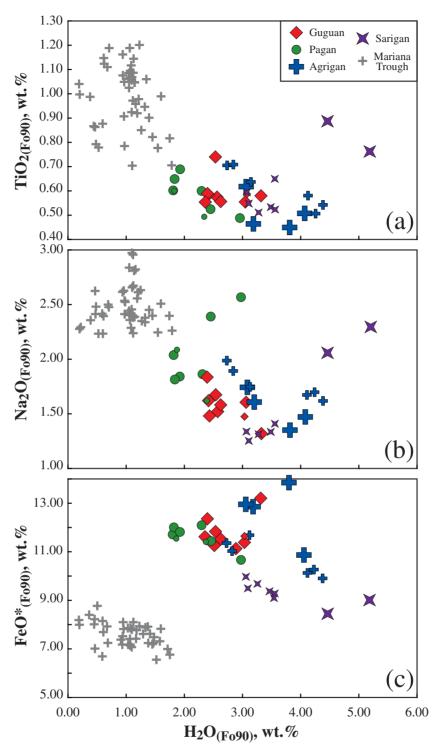
The olivine-hosted melt inclusions examined in this study show major element compositions typical of whole-rock basalts from the Mariana arc, although the leastfractionated compositions extend to higher MgO than whole-rock lavas (e.g. Fig. 4a). Although even the most MgO-rich basaltic melt inclusions are not very primitive. this is a characteristic of the Marianas as a whole (e.g. Larson et al., 1974; Dixon & Batiza, 1979; Stern, 1979; Banks et al., 1984; Woodhead, 1989; Elliott et al., 1997). The olivine hosts for the full data suite range in forsterite content from Fo<sub>69</sub> to Fo<sub>84</sub>, but the least degassed and least fractionated inclusions are hosted by the most forsteritic olivine from each island (Fo75-84). The least degassed inclusions reveal distinct pre-eruptive magmatic H<sub>2</sub>O contents characteristic of each island or eruptive unit, and magmatic H<sub>2</sub>O generally increases from Pagan ( $\sim 2.7$  wt %) to Guguan ( $\sim 3.5 \text{ wt } \%$ ) to Agrigan ( $\sim 4.5 \text{ wt } \%$ ). The two samples from Sarigan indicate distinct magmatic H2O for each sample [~3.7 wt % for SARI-15 (Shaw et al., 2008);  $\sim 5.6$  wt % for SA93].

The concentrations of incompatible minor elements (e.g.  $Na_2O$ ,  $TiO_2$ ) in basalts are particularly useful for evaluating mantle melting processes in certain systems. At low extents of melting of a homogeneous source, the melt will have relatively high concentrations of incompatible elements, and as the melt fraction (*F*) increases, their concentrations in the melt decrease progressively as they are diluted. Because of this simple behavior, and the abundance of measurements for these elements in most analyzed igneous rocks, both  $TiO_2$  and  $Na_2O$  are widely used to evaluate mantle melting processes beneath mid-ocean ridges (e.g. Klein & Langmuir, 1987; Langmuir *et al.*, 1992;

Johnson, 1998). In the Mariana Trough and globally among back-arc basins, increasing  $H_2O_{(Fo90)}$  correlates with decreasing  $TiO_{2(Fo90)}$  and  $Na_2O_{(Fo90)}$  (Fig. 5; Stolper & Newman, 1994; Gribble *et al.*, 1996; Kelley *et al.*, 2006; Langmuir *et al.*, 2006), suggesting a relationship between  $H_2O$  input and the extent of mantle melting that has been successfully modeled by several studies (e.g. Stolper & Newman, 1994; Gribble *et al.*, 1996; Wood, 2004; Kelley *et al.*, 2006).

After data filtering and corrections for crystallization, the Mariana arc melts contain higher  $H_2O_{(F_090)}$  (2–5 wt %) than the Mariana Trough basalts (<2 wt %), and the remaining variability among the data is interpreted as diversity in primary magmas at these volcanoes. This interpretation is supported by diversity in the ratios of incompatible minor elements (e.g. K<sub>2</sub>O/TiO<sub>2</sub>; Na<sub>2</sub>O/  $K_2O$ ) among the melt inclusions, which vary by a factor of two within each sample suite from each volcano. The simple trends from back-arc lavas would predict higher extents of melting and lower concentrations of Na<sub>2</sub>O and TiO<sub>2</sub> in Mariana arc melts. Indeed, TiO<sub>2(Fo90)</sub> decreases with increasing  $H_2O_{(Fo90)}$  in the calculated primary arc glass compositions, extending to lower TiO2(Fo90) and higher  $H_2O_{(Fo90)}$  relative to the Mariana Trough (Fig. 5a). Moreover, Na<sub>2</sub>O<sub>(Fo90)</sub> also generally decreases with increasing H<sub>2</sub>O<sub>(Fo90)</sub>, appearing to extend the trend defined by the Mariana Trough (Fig. 5b), although this trend is more diffuse than that of TiO<sub>2(Fo90)</sub>. Sarigan melts from sample SA93 appear independent of the overall trend of the other Mariana islands in Fig. 5, and their distinct compositions may relate to differences in physical variables beneath this volcano. Overall, the relationships shown in Fig. 5 are consistent with the hypothesis that higher magmatic H<sub>2</sub>O contents beneath the arc are connected to higher extents of mantle melting, as long as the mantle source beneath the arc is not extremely depleted relative to the back-arc mantle source.

At subduction zones, however, the mass flux from the dehydrating subducting slab transports not only H<sub>2</sub>O but also a veritable cocktail of fluid- and/or melt-mobile elements into the mantle source of arc magmas, potentially complicating the straightforward utilization of these incompatible elements as indicators of arc melting processes. For example, although Na<sub>2</sub>O has been identified as a gauge of the overall extent of melting beneath arcs (e.g. Plank & Langmuir, 1988), it is also a primary component of the slab-derived mass flux (e.g. Stolper & Newman, 1994; Kent et al., 2002; Eiler et al., 2005) making it difficult to separate explicitly mantle- vs slab-derived contributions to the Na<sub>2</sub>O content of arc melts. In this respect, TiO<sub>2</sub> may be a more sensitive indicator of the extent of melting beneath arcs because, like other 'conservative' high field strength elements (HFSE), TiO<sub>2</sub> has low solubility in low-temperature, rutile-saturated aqueous fluids



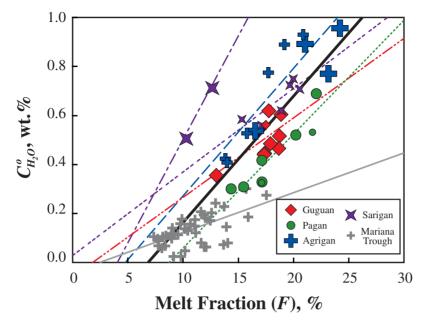
**Fig. 5.** Major element vs  $H_2O_{(Fo90)}$  systematics in calculated primary melt compositions from the Mariana arc and trough, derived from the least degassed and least fractionated melt inclusions identified in Fig. 4. The larger symbols are data from this study; smaller symbols are data from Shaw *et al.* (2008). (a)  $H_2O_{(Fo90)}$  vs  $TiO_{2(Fo90)}$ ; (b)  $H_2O_{(Fo90)}$  vs  $Na_2O_{(Fo90)}$ , and (c)  $H_2O_{(Fo90)}$  vs  $FeO*_{(Fo90)}$ . FeO\* is total Fe expressed as FeO.

(Antignano & Manning, 2008) and is less likely to be added in significant quantities to the wedge by the mass flux from the slab (e.g. Stolper & Newman, 1994; Kelley *et al.*, 2006). The characteristic deficiency of HFSE relative to other incompatible trace elements in arc magmas is generally recognized as related to this effect (e.g. Pearce & Parkinson, 1993). Although the TiO<sub>2</sub> flux from the slab is likely to be non-zero, for simplicity, in what follows we assume that TiO<sub>2</sub> is immobile in slab-derived materials, and that its concentration in arc melts is solely a function of the extent of mantle melting and the initial TiO<sub>2</sub> concentration of the mantle source.

Applying the model of Kelley et al. (2006), we use the TiO<sub>2</sub> contents of primitive arc magmas to place constraints on the extent of mantle melting and the H<sub>2</sub>O concentrations of their mantle sources beneath the Mariana arc. This model uses a simple batch melting relationship to invert melt  $TiO_2$  concentration (i.e.  $TiO_{2(Fo90)}$ ) into the mantle melt fraction (F). The calculated F may then be related to other elements in the melt (e.g.  $H_2O_{(F_090)}$ ) through the batch melting equation to yield the concentrations of these elements in the mantle source (e.g.  $C_{\text{HeO}}^{\text{o}}$ ). The constraints needed to apply this model are (1) the composition of the primary mantle-derived melt, (2) mantle-melt partition coefficients for TiO<sub>2</sub>, H<sub>2</sub>O, and any other elements of interest (i.e. D<sub>TiO2</sub>, D<sub>H2O</sub>, etc.), and (3) the TiO<sub>2</sub> concentration of the mantle source beneath the Mariana arc (i.e.  $C_{TiO_2}^{o}$ ). Primary melt compositions were calculated from the most MgO-rich melt inclusions analyzed in this study (see Table 1 and above). The values for  $D_{\rm H2O}$  (0.012) and  $D_{\rm TiO2}$  (0.04) are those used by Kelley et al. (2006). The  $TiO_2$  concentration of the Mariana arc mantle source is the variable to which this model is most sensitive. Plank (2005) used Th/La and Sm/La systematics to show that the Mariana arc taps a mantle source that is more depleted than the source of normal mid-ocean ridge basalt (N-MORB; or the Mariana Trough source, which is similar to N-MORB), and Stolper & Newman (1994) concluded that the Mariana arc mantle source is probably a residue of partial melting beneath the back-arc basin based on significant depletions in HFSE (Ti, Y, Zr) in primitive arc lavas relative to the Mariana Trough. Using whole-rock basalt compositions for Mariana arc lavas from Guguan, Pagan, Agrigan and Sarigan islands (Elliott *et al.*, 1997), we constrain  $C_{\text{TiO}_2}^{\text{o}}$  beneath the Mariana arc based on systematics in TiO<sub>2</sub>/Y ratios as described by Kelley et al. (2006). Because all four of the islands included in our study yield similar  $C_{\text{TiO}_2}^{\text{o}}$  contents based on this analysis (0.104-0.135 wt % TiO2), we use an average TiO<sub>2</sub> concentration of 0.123 wt % for the mantle source beneath these four islands from the Mariana arc (compared with 0.133 wt % for typical N-MORB sources; e.g. Salters & Stracke, 2004). A complete sensitivity test and Monte Carlo error analysis of this model is presented in Electronic Appendix 1, showing that maximum uncertainties in Fare  $\pm 0.03$  and in  $C_{\rm H_2O}^{\rm o}$  are  $\pm 0.10$  wt % (absolute), and that most of the model points for each island are statistically separated.

The results of these calculations are shown in Fig. 6a and provide constraints on the extent of melting and the concentration of H<sub>2</sub>O in the mantle sources of magmas beneath the Mariana arc, and how these factors may correlate with other physical parameters. Arc melt compositions indicate higher F (~15–25%) than the back-arc basin ( $\leq$ 15%). The concentration of H<sub>2</sub>O in Mariana arc mantle sources also reaches  $>3 \times$  higher than in the Mariana Trough (i.e. >0.9 wt % H<sub>2</sub>O for the Agrigan sources, vs a maximum of 0.3 wt % for the calculated Mariana Trough sources). Such high mantle H<sub>2</sub>O concentrations clearly exceed the storage capacity of H<sub>2</sub>O in nominally anhydrous mantle minerals (e.g. Hirschmann et al., 2005), but would be permissible if a hydrous phase is stable in the mantle wedge (e.g. chlorite; Grove et al., 2006) or if sub-arc melting is a fractional process driven by incremental water addition (e.g. Kelley et al., 2006).

The results of this modeling reveal a positive relationship between melt fraction and the water content of the mantle beneath these Mariana arc volcanoes (Fig. 6). Similar positive relationships are defined both for each volcano, and for the group of four volcanoes taken together (excluding glass inclusions from Sarigan sample SA93). Although distinct from the others, the Sarigan SA93 sample also indicates a positive relationship between  $C_{\rm H_{2}O}^{\rm o}$ and F. Previous studies have proposed linear (e.g. Stolper & Newman, 1994; Kelley et al., 2006) and non-linear (e.g. Katz et al., 2003; Langmuir et al., 2006; Portnyagin et al., 2007) shapes to the melting function relating mantle  $H_2O$ content and F, although the data range revealed here neither constrains the functional shape well nor supports a significantly non-linear shape. Although the Mariana arc melts indicate higher mantle H<sub>2</sub>O concentrations and higher extents of melting than the back-arc, the slopes are different and the arc is unlikely to be a simple extension (whether curved or linear) of the back-arc trend. Collectively and for single islands, the arc melts indicate a steeper slope (i.e. smaller  $\Delta F$  for a given increase in mantle H<sub>2</sub>O content) than the back-arc. We note, however, that consideration of a range of values for  $D_{\rm TiO2}$  and  $C_{\text{TiO}_2}^{\text{o}}$  strongly influences the value of the apparent *F*-axis intercept (i.e. melt fraction at  $C_{\text{H}_2\text{O}}^{\text{o}} = 0$ ) of the arc trends. Either a much higher value of  $D_{\text{TiO2}}$  (~0.16) or a much more depleted mantle source ( $C_{\text{TiO}_2}^{\text{o}} = \sim 0.06$ ) will result in a zero F intercept for the arc. Changes in these variables do not, however, have a significant influence on the slope of the arc or trough trends, and we thus emphasize that no value for either  $D_{\text{TiO}2}$  or  $C_{\text{TiO}2}^{\circ}$  will cause the arc to lie on a simple linear extension of the Mariana Trough trend.



**Fig. 6.** Plot of  $C_{H_2O}^o$  (i.e.  $H_2O$  concentration in the mantle source; see text) vs melt fraction (*F*) for Mariana arc and trough modeled data. The lines shown are least-squares linear regressions through the data for each island, the whole arc (excluding SA93) and the back-arc basin. The continuous gray line is the Mariana Trough ( $y = 1.63 \times -0.05$ ;  $r^2 = 0.40$ ), the dotted line is Pagan island ( $y = 5.10 \times -0.41$ ;  $r^2 = 0.87$ ), the dash-double-dot line is Guguan island ( $y = 3.21 \times -0.06$ ;  $r^2 = 0.43$ ), the long-dashed line is Agrigan island ( $y = 5.20 \times -0.26$ ;  $r^2 = 0.78$ ), the dash-dot line is Sarigan island sample SA93 from this study ( $y = 8.62 \times -0.38$ ;  $r^2 = 1$ ), the triple-dot line is Sarigan island data from Shaw *et al.* (2008) ( $y = 3.36 \times +0.03$ ;  $r^2 = 0.71$ ), and the bold black line is all of the Mariana arc data, excluding SA93 samples ( $y = 5.10 \times -0.35$ ;  $r^2 = 0.55$ ).

# DISCUSSION

Interpretation of the data with respect to melting processes taking place beneath the Mariana arc requires constraints on the physical state of the mantle wedge. In the following discussion, the arc and back-arc basin trends in the Mariana system are examined together, in the light of variables likely to play important roles in the mantle melting process. When viewed together, the arc and back-arc data support the interpretation of TiO<sub>2</sub> vs H<sub>2</sub>O trends as melting relationships, rather than mixing of end-member melts, which is further reinforced by seismic tomography models of the Mariana system. We show that the arc melt inclusion data ultimately reflect a combination of three key variables: the geotherm, the fertility of the mantle wedge (a function of source depletion), and the amount of H<sub>2</sub>O added to the mantle wedge. We develop a model that incorporates these variables and successfully reproduces melting trends shown by the Mariana data.

### Mixing vs melting

The modeled trends in  $C_{\rm H_2O}^{\circ}$  vs *F* for the Mariana arc and trough shown in Fig. 6 suggest a direct link between the magnitude of H<sub>2</sub>O addition to the mantle wedge and the extent of mantle melting. From one perspective, each melt inclusion or glass records a melt fraction driven by a certain amount of water addition to the mantle wedge (Kelley *et al.*, 2006). Alternatively, the trends in H<sub>2</sub>O vs TiO<sub>2</sub>, or  $C_{\rm H_2O}^{\circ}$  vs *F*, for back-arc basin basalts could result from mixing of melts produced by two separate endmember processes: (1) nominally anhydrous, pooled, fractional melting analogous to the melting processes beneath normal mid-ocean ridges, giving rise to a low-F, low-H<sub>2</sub>O, high-FeO\* (i.e. FeO\* is total Fe expressed as FeO), high-TiO<sub>2</sub> final melt, and (2) low-pressure, hydrous, equilibrium melting that produces a high-degree melt with high H<sub>2</sub>O, low FeO\*, and low TiO<sub>2</sub> (Langmuir *et al.*, 2006). In a physical sense, these two distinct melts could originate from the arc-distal, 'dry' side of a triangular ridge-like melting regime, and a shallower, water-rich melting regime on the arc side of the mantle wedge, and the compositional trends of back-arc basin basalts could be explained through variable, shallow mixing of magmas from these two separate melting systems.

These new melt inclusion data for the Mariana arc have particular bearing on the question of mixing vs melting relationships reflected in melt compositions across the Mariana arc-back-arc system. If the compositions of Mariana Trough basalts reflect mixing of MORB- and arc-like end-members, we would expect the Mariana arc to define a linear extension of the Mariana Trough data array, particularly in terms of H<sub>2</sub>O, TiO<sub>2</sub>, and FeO\*, and possibly to exemplify the shallow, 'arc-like' H<sub>2</sub>O-rich, end-member melt. Although the arc data certainly extend the back-arc trend in H<sub>2</sub>O vs TiO<sub>2</sub> (Fig. 5a), the transitions between the arc and back-arc basin basalts are nonlinear for these elements. Moreover, the difference between arc and back-arc basin melts in the Mariana system is clearly apparent in H<sub>2</sub>O vs FeO\* (Fig. 5c). Total FeO\* concentrations of water-rich Mariana arc melts are highly enriched  $(>2 \times in \text{ some cases})$  relative to hydrous melts from the Mariana Trough, and simple linear mixing between arc and back-arc magmas cannot explain the data array in Fig. 5c. If the FeO\* concentrations of the primary arc magmas contain a much greater fraction of Fe<sub>2</sub>O<sub>3</sub> than do back-arc magmas (i.e. arc magmas are significantly more oxidized than back-arc magmas), then the absolute FeO concentrations of magmas from the two settings may be more similar than the FeO\* content indicates on its own, but in this case the Fe2O3 variations would then not be explained through mixing. Furthermore, examination of the trace element and isotopic systematics of the Mariana arc and trough exclude simple mixing of arc components into the back-arc (e.g. Stolper & Newman, 1994; Gribble et al., 1996; Pearce et al., 2005). The observed geochemical trends among the arc and back-arc data are thus interpreted as melting relationships.

# Separate arc and back-arc basin melting regimes

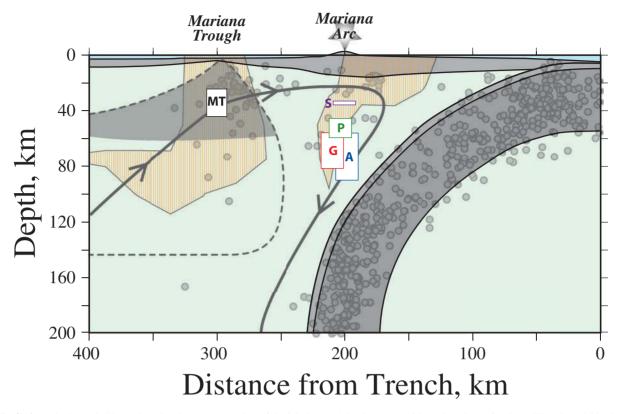
Conventionally, arc and back-arc basin melting regimes are often envisioned and modeled as physically separate. Prevailing models of magma generation for arcs vs back-arc basins invoke compositionally distinct mantle sources for each, with back-arcs sampling mantle that is broadly similar to the range of MORB sources (e.g. Stolper & Newman, 1994; Kellev et al., 2006; Langmuir et al., 2006) and associated arcs tapping mantle that is relatively more depleted in incompatible HFSE (e.g. Woodhead et al., 1993; Pearce et al., 2005). Mantle flow vectors and magma geochemistry suggest that mantle upwelling beneath back-arc spreading centers leads to an episode of melt extraction that 'preconditions' the mantle (e.g. Woodhead et al., 1993; Pearce, 2005; Pearce et al., 2005) before it then moves horizontally toward the wedge corner and melts a second time beneath the arc (e.g. Hawkins et al., 1990; Stolper & Newman, 1994; Kincaid & Hall, 2003). Despite broad similarities to mid-ocean ridges in terms of overall structure (e.g. Tamaki, 1985; Taylor & Martinez, 2003), mantle temperature (Klein & Langmuir, 1987; Kelley et al., 2006; Langmuir et al., 2006; Wiens et al., 2010), and the presence of relatively anhydrous MORBtype lavas, back-arc basin basalts (BABB) are geochemically distinct from MORB in many ways, including elevated H<sub>2</sub>O, large ion lithophile elements, and light rare earth elements, suggestive of an 'arc-like' component infiltrating the back-arc mantle source (e.g. Fryer et al., 1981). However, new seismic attenuation results for the Mariana mantle wedge (Pozgay et al., 2009), in addition to geochemical relationships in the Marianas (see above), generally support the view that the mantle sources of arc and back-arc magmas are physically separated from one another, particularly at shallow depths (Fig. 7).

Langmuir et al. (2006) show a correlation of increasing  $H_{(8:0)}$  with decreasing  $Fe_{(8:0)}$  (i.e.  $H_2O$  and FeO\* traced along a liquid line of descent to the concentrations equivalent at 8.0 wt % MgO) in the Mariana Trough, arguing that H<sub>2</sub>O-rich melts originate at shallower depths than anhydrous melts.  $Fe_{(8.0)}$  is a powerful indicator of melting pressure in mid-ocean ridge systems, where variations in primary MORB melt chemistry can be directly compared by choosing a single reference point along comparable LLDs (Klein & Langmuir, 1987). Adapting this approach for back-arc basin basalts, however, requires accurate constraints on the variations of the liquid line of descent caused by variations in H<sub>2</sub>O content (see above), and the selection of an appropriate reference point along the LLD. At 8.0 wt % MgO, most dry basalts are not directly comparable with hydrous basalts because of differences in the LLDs. Dry basalts would thus be under-corrected for crystal fractionation, yielding, for example, too high  $Fe_{(8.0)}$ relative to wetter basalts that originated from a parent magma with the same FeO\*. In the present study, we choose MgO = 8.5 wt % as the point of plagioclase-in for Mariana Trough basalts with < 10 wt % H<sub>2</sub>O (see above), which is consistent with MORB systematics (Kelley et al., 2006), and then correct all compositions back to primary melts in equilibrium with Fo<sub>90</sub> for direct comparison. These methods result in a weak correlation between FeO\* and H<sub>2</sub>O in Mariana Trough basalts (Fig. 5c) that could relate less to mean pressures of melting than to the expansion of the olivine liquidus volume and coincident decrease in normative olivine in the melt with increasing H<sub>2</sub>O and decreasing T (e.g. Kushiro, 1972; Stolper & Newman, 1994). The interpretation of co-variations in  $H_{(8\cdot0)}$ -Fe<sub>(8\cdot0)</sub> is thus ambiguous, and in a subsequent section we directly assess the relationship between melt composition and quantitative estimates of P-T conditions of melt equilibration.

# Modes and conditions of melting beneath the Mariana arc

### Wet melt productivity

Taken as a whole, the Mariana arc melt compositions indicate a positive correlation between water content in the magmas (and their sources) and proxies for melt fraction (e.g. TiO<sub>2</sub>; Fig. 5). The slope of each trend in Fig. 6, expressed as  $dF/dC_{\rm H_2O}^{\rm o}$ , is one indication of the productivity of water-fluxed melting. Differences in slope are unlikely to be the result of differences in model variables, such as  $C_{\rm TiO_2}^{\rm o}$  or  $D_{\rm TiO_2}$ , because the mantle source is not expected to vary significantly between these volcanoes (Plank, 2005; and see above), and changes in these parameters have only a minor influence on the slope (Kelley *et al.*, 2006, and see Electronic Appendix 1). Instead, if the



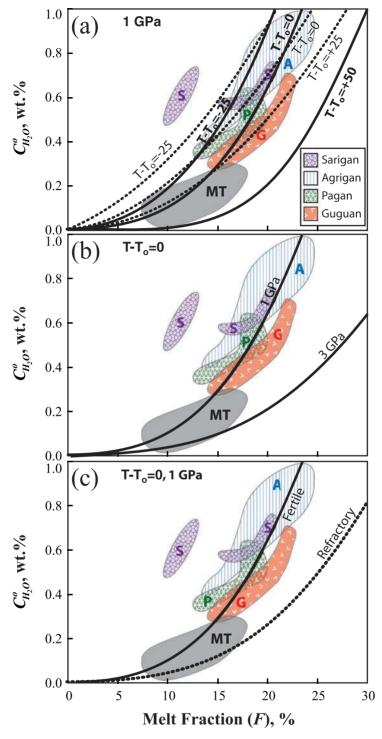
**Fig. 7.** Scaled schematic illustration showing a cross-section of the Mariana subduction zone, with the locations of melt equilibration within the mantle wedge for the Mariana arc and trough, as constrained by thermobarometry. The small, shaded circles are earthquake data from England *et al.* (2004), and the crustal thickness is taken from the seismic velocity model of Takahashi *et al.* (2007). The trace of the subducting plate is drawn to encompass the majority of the seismicity, and the asymmetric triangle beneath the Mariana Trough represents the anhydrous melting regime for the back-arc spreading center where vertical mantle upwelling is deflected towards the slab, guided by the numerical models of Conder *et al.* (2002), for a mantle  $T_p$  of 1350°C. The dashed line outlines the approximate melting triangle that would apply for  $H_2O$ -saturated mantle melting beneath the Mariana Trough. The gray line with arrows traces an approximate vector of solid flow through the mantle wedge. The vertically striped fields are regions of high seismic-wave attenuation in the mariana Trough; horizontal offsets of the arc boxes are not significant and the boxes are shown in this way only to distinguish the range for each island. A, Agrigar, G, Guguar, P, Pagar; S, Sarigar; MT, Mariana Trough.

mantle composition and the magnitude of the water flux are similar, then differences in wet melt productivity may be governed by physical conditions in the mantle wedge. For example, Kelley et al. (2006) showed an empirical correlation between  $dF/dC^{o}_{H_{2}O}$  and mantle potential temperature  $(T_p)$  among back-arc basin basalts. Following these systematics, the arc slopes could be interpreted as reflecting overall lower mantle temperatures under the arc than under the back-arc. Although this interpretation is consistent within back-arc basin data arrays, the arc data require the additional consideration of melting pressure and mantle fertility, for which we develop new models here (see below). The key parameter in recent hydrous melting models is the temperature (T) relative to the dry solidus  $(T_{0})$ . Comparisons of parameterizations of hydrous melting (Langmuir et al., 2006; Portnyagin et al., 2007) with the modeled arc data require temperatures near or

below the dry peridotite solidi specific to these models (e.g. Fig. 8a; curves for  $T - T_o = 0$  to -25). The arc melting trends require melting to occur largely below the dry solidus (i.e.  $T - T_o < 0$ ) and the back-arc melting to occur above the dry solidus (i.e.  $T - T_o > 0$ ). This appears to be a general feature of arcs vs back-arc basins, based on the data presented here and shown by recent studies (e.g. Langmuir *et al.*, 2006; Portnyagin *et al.*, 2007).

# Parameterizing hydrous melting

Previous hydrous melting models are largely isothermal and isobaric, or consider melting over a limited range of pressure and mantle composition (Gaetani & Grove, 1998; Hirschmann *et al.*, 1999; Katz *et al.*, 2003; Langmuir *et al.*, 2006). Here, we consider the specific effects of pressure and mantle fertility on wet melting productivity. Langmuir *et al.* (2006) developed a re-formulation of the



**Fig. 8.** Plots of  $C_{H_2O}^{\circ}$  vs melt fraction (F) showing melting curves derived from various models. (a) Wet melting models from previous studies, showing the effect of changing temperature at constant pressure and mantle composition. The continuous lines are the model of Langmuir *et al.* (2006) for a range of temperatures relative to the solidus  $(T - T_0)$  at 1 GPa. The dotted lines are the model curves of Portnyagin *et al.* (2007), which use the parameterization of Katz *et al.* (2003). (b) Wet melting model curves derived from equation (4), for fertile peridotite melting at the dry solidus (i.e.  $T - T_0 = 0$ ) over a 1–3 GPa range of pressure. The curvature of the model trend changes significantly as pressure increases. (c) Wet melting model curves derived from equation (4) for fertile and refractory peridotite models, at the temperature of the solidus (i.e.  $T - T_0 = 0$ ) for each case at 1 GPa.

melting parameterization of Katz *et al.* (2003), using the linear expression of F vs T for a set of 1GPa, anhydrous peridotite melting experiments (Baker & Stolper, 1994; Baker *et al.*, 1995; Hirschmann *et al.*, 1998) to parameterize F as a function of  $C_{\rm H_2O}^{\rm o}$  and T at 1GPa. One form of their equation is

$$C_{\rm H_2O}^{\rm o} = [D_{\rm H_2O}(1-F) + F] \left[ \frac{T - 1235 - 539F}{-60} \right]^{1.85}$$
(1)

where 1235 is the temperature in  $^{\circ}C$  of the dry solidus (i.e.  $T_{\rm o}$ ) at 1 GPa and 539 is  $[\partial T/\partial F]_{\rm P}$  (i.e.  $\sim 5^{\circ} {\rm C}/\%$ ) at 1 GPa, derived from the anhydrous experiments (see fig. 33 of Langmuir et al., 2006). Melting functions calculated using this model are isothermal and isobaric, applying to a specific solidus only at 1 GPa, and the approximate slope (i.e.  $dF/dC_{\rm HoO}^{\rm o}$ ) of the melting curve does not change significantly with changing T relative to the dry solidus at this pressure (Fig. 8a). Combining this analysis with the 3-7 GPa anhydrous peridotite melting experiments of Walter (1998), however, reveals a significant pressure dependence to  $[\partial T/\partial F]_P$  (Fig. 9a), which decreases with increasing P. This effect will lead to greater wet melting productivity at higher pressure, and can be incorporated into equation (1) in the following way. We use Walter's experiments to fit a simple expression for the pressure dependence of  $[\partial T/\partial F]_{\rm P}$  for fertile peridotite (Fig. 9b):

$$\left[\frac{\partial T}{\partial F}\right]_{\rm P} = x \ln(P) + y \tag{2}$$

where the coefficients x = -221.34 and y = 536.86 and *P* is pressure in GPa. We also adopt the recommended solidus for upper mantle peridotite from Hirschmann (2000) (Fig. 7c):

$$T_{\rm o} = aP^2 + bP + c \tag{3}$$

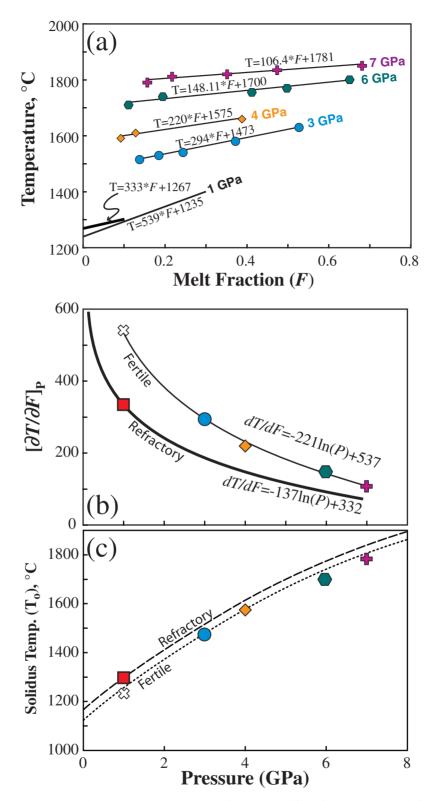
where  $T_{\rm o}$  is the temperature of the dry solidus in °C, *P* is pressure in GPa, and coefficients are a = -5.1404654, b = 132.899012, and c = 1120.66061. Hereafter, models using the coefficients provided here are referred to as the 'fertile' peridotite case. Substituting these terms into equation (1) gives the following:

$$C_{\rm H_2O}^{\rm o} = [D_{\rm H_2O}(1-F)+F] \\ \times \left[\frac{T - (aP^2 + bP + c) - (x\ln(P) + y)F}{-60}\right]^{1\cdot85}$$
(4)

Equation (4) is similar to the formulation of Langmuir *et al.* (2006) at 1 GPa, but allows pressure to be varied and thus provides a simple parameterization of hydrous melting that can be applied at different temperatures and pressures. Figure 8b shows the change in shape of this wet melting function along the dry solidus (i.e.  $T - T_0 = 0$ ) from 1 to 3 GPa, confirming that increasing pressure

results in a coincident increase in wet melt productivity. Such an effect may contribute to the observed increase in wet melting productivity with increasing mantle  $T_p$  beneath back-arcs globally (Kelley *et al.*, 2006; Langmuir *et al.*, 2006), because mantle of higher  $T_p$  will melt at higher mean pressures than mantle of lower  $T_p$  (Langmuir *et al.*, 1992). Figure 8b also predicts that wet melts may equilibrate at higher mean pressures beneath the Mariana Trough than the Mariana arc, given that the trough indicates a greater wet melt productivity than the arc (Fig. 6), although we will demonstrate below that the opposite is true when appropriate pressures, temperatures, and mantle fertility are considered together.

Mantle fertility is an important effect to include in the wet melting parameterization because refractory mantle (i.e. mantle from which melt has previously been removed) will melt at higher solidus temperatures and higher melt productivities than fertile mantle for a given pressure and water content (Asimow et al., 1997; Wasylenki et al., 2003). Many studies also provide constraints on the solidus of nominally anhydrous upper mantle, which may vary considerably with several compositionally dependent variables including alkali content (e.g. Hirschmann et al., 1998; Hirschmann, 2000) and prior melt depletion (e.g. Wasylenki et al., 2003). Substituting different dry solidus equations and melt productivities [i.e. alternative coefficients from equations (2) and (3) into equation (4) produces appropriate melting functions relevant to the specified mantle. Here, we use constraints from melting experiments on composition DMM1, intended to represent an upper mantle peridotite from which some melt has been removed (Wasylenki et al., 2003), to parameterize melting of a more refractory mantle composition. The solidus of DMM1 is constrained at 39°C higher than the recommended solidus of Hirschmann (2000) at 1 GPa [giving a new value for the coefficient c = 1159.66061 for equations (3) and (4)] and DMM1 anhydrous melt productivity in the lherzolite field at 1GPa is somewhat higher than the productivity of the more fertile MM3 peridotite (Fig. 9a and c; Wasylenki et al., 2003). We model the change in DMM1 melt productivity with pressure as proportional to the fertile case, giving coefficients for equations (2) and (4) of x = -136.88 and y = 332.01. Models using the coefficients provided here are hereafter referred to as the 'refractory' peridotite case. It is important to emphasize that both the fertile and refractory cases developed here are appropriate for lherzolite melting. The DMMl composition exhausts cpx in the residue at  $F \sim 0.1$ , at which point melt productivity decreases, reflecting less productive melting with a harzburgite residue (Wasylenki et al., 2003); the model developed here does not account for this additional complexity because our primary goal is to characterize first-order differences between melting lherzolite of contrasting fertility.



**Fig. 9.** Experimental constraints on melting parameters across a range of pressures. (a) Plot of temperature vs melt fraction for the 1GPa partial melting experiments cited by Langmuir *et al.* (2006; fine line labeled 1GPa), and for the 3–7 GPa experiments of Walter (1998). Symbols show these experimental data at 3 GPa (circles), 4 GPa (diamonds), 6 GPa (hexagons), and 7 GPa (crosses). Linear regressions through the datasets at each pressure, as written on the figure, provide constraints on  $[\partial T/\partial F]_P$  as a function of pressure. The bold line is the 1GPa depleted lherzolite trend of Wasylenki *et al.* (2003). (b) Plot of  $[\partial T/\partial F]_P$  vs pressure for the experiments shown in (a). The fertile 1GPa suite is shown as the 'x' symbol, the depleted 1 GPa suite is shown as the square symbol. The fine curve is a least-squares regression through the data (equation on the figure), which provides the coefficients for the fertile case of equation (2) in the text. The bold curve is proportional to the fertile case, constrained to pass through the square symbol, and provides coefficients for the refractory model. (c) Plot of solidus temperature ( $T_0$ ) vs pressure (i.e. P-T curves of the mantle solidus) for the experiments in (a) and (b). The recommended fertile solidus of Hirschmann (2000; dotted line) and the depleted mantle solidus of Wasylenki *et al.* (2003; dashed line) are shown.

The effect of melting fertile vs refractory lherzolite at a given P and T is illustrated in Fig. 7c for the two mantle compositions described above. These specific choices of peridotite composition are intended to provide examples of well-constrained mantle materials and phase relations that reflect variations in natural systems that arise from prior melt extraction. We do not develop here a model for how melt extraction quantitatively affects the solidus or productivity of the residual peridotite; rather we use these established examples to infer the first-order effects. The impact of the choice of peridotite on the melting function is clear in Fig. 8c, where the refractory case gives a much higher melt productivity relative to the fertile case. At first glance, this result predicts that melting refractory mantle beneath the arc should project to much higher extents of melting than those indicated by the melt inclusion data, but the effect of mantle fertility has not yet been integrated with the effects of temperature and pressure of melting. In the following sections, we will constrain relevant temperatures and pressures of melt equilibration beneath the Mariana arc and trough, and assess the competing effects of pressure, temperature, and mantle fertility on melting beneath the Mariana system.

### Thermobarometry

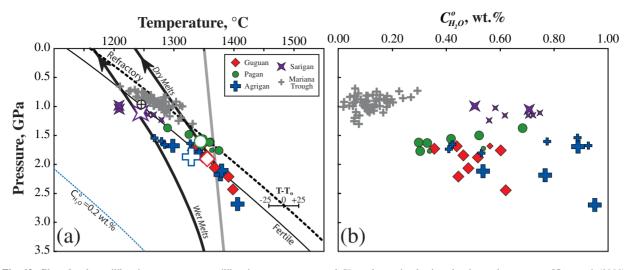
Thermobarometric information, as recorded by melt compositions and mineral-melt equilibria, provides a means to quantify the pressures and temperatures of equilibration of primary melts in the mantle wedge. To calculate P-Tconditions recorded by primary Mariana arc and back-arc melts, we use the recent model of Lee et al. (2009), which quantifies in a thermobarometer the well-known effects of pressure on the SiO<sub>2</sub> content and temperature on the MgO content of olivine+orthopyroxene-saturated mantle melts. These P-T constraints, however, are not necessarily straightforward to interpret. They may represent the final conditions of equilibration of a single batch melt. or a continuously interacting melt that percolates upward through the solid mantle and reacts constantly along its path, in which case these conditions are very different from the potential temperature of the mantle; in general they are substantially cooler than  $T_{\rm p}$  as a result of cooling from the heat of fusion. The P-T constraints could alternatively represent some intermediate P-T conditions along a melting path. In this case, P-T would be similar to the mean P and T of polybaric, fractional, pooled melts, although not an exact mean because the pooled melt is a mixture that would not invert back to any single point or mean.

The results of thermobarometry calculations for the Mariana Trough indicate pressures of equilibration of 0.6–1.2 GPa ( $\pm 0.2$  GPa), which are consistent in range with the polynomial SiO<sub>2</sub> barometer of Wang *et al.* (2002), but are systematically lower by ~0.4 GPa. The *P*–*T* conditions of the drier Mariana Trough melts lie along a melting

path for mantle with a potential temperature of  $\sim 1350^{\circ}C$ (Fig. 10a), identical to that estimated by Langmuir et al. (2006) and Wiens et al. (2006). In this case, the calculated absolute P and T are similar to the mean values along the melting path, consistent with pooling of polybaric melts, as for mid-ocean ridge basalts (Langmuir et al., 1992). On the other hand, the wet Mariana Trough melts record substantially cooler absolute  $T (\sim 1250 \pm \sim 40^{\circ} \text{C})$  at similar P (~l GPa), also nearly identical to that estimated by Langmuir et al. (2006) for their wet melt end-member, using a completely independent method. Despite some ambiguities in interpretation, the thermobarometer of Lee et al. (2009) returns intermediate P and T for the Mariana Trough, similar to those derived from other methods, consistent with polybaric pooling of melts along the melting path.

In contrast, the Mariana arc melts yield a larger pressure range, extending to much higher values than the Mariana Trough  $(1 \cdot 0 - 2 \cdot 4 \pm 0 \cdot 2 \text{ GPa})$ , as well as higher overall temperatures spanning a much broader range  $(\sim 1200-1400 \pm \sim 40^{\circ}C;$  Table 2; Fig. 10). The contrast in P-T conditions between the Mariana arc and trough indicates hotter, deeper melting beneath the arc than the back-arc. These results are suggestive of the different physical processes of melting and melt aggregation in these two settings. Beneath the Mariana Trough, H<sub>2</sub>O-fluxed melting could begin at great depth, where slab-derived H<sub>2</sub>O is introduced into the mantle wedge, but all melts from the Mariana Trough record P-T conditions at shallow depths, within the predicted pressure range of the anhydrous melting triangle (Fig. 7). Moreover, there is no strong correlation between pressure of equilibration and the H<sub>2</sub>O content of the mantle in the Mariana Trough (Fig. 10b). These observations suggest that wet melts passing through the anhydrous back-arc melting triangle equilibrate there at shallow depth, recording P-T conditions of mean or later stages of melting and retaining no record of their depth of origin in their major element composition.

If the ambient mantle  $T_{\rm p}$  beneath the Mariana Trough is ~1350°C (Langmuir *et al.*, 2006; Wiens *et al.*, 2006), then the base of the dominant (dry) melting triangle is ~2.0 GPa (Figs 7 and 10). A melting triangle extending from 2.0 to 0.2 GPa will generate melts with mean pressures of between 0.7 and 1.3 GPa, for equilibrium and fractional melting, respectively (Langmuir *et al.*, 1992; see their fig. 50). This is very similar to the range observed (Fig. 10), and suggests that the back-arc melts are dominated by the melting systematics driven by the upwelling mantle beneath the spreading center, much as at mid-ocean ridges. Absolute mantle temperatures colder than the mantle potential temperature of 1350°C are consistent with cooling effects during adiabatic melting, where temperature decreases during melting so as to



**Fig. 10.** Plot of melt equilibration pressure vs equilibration temperature and  $C_{H_2O}^{\circ}$ , determined using the thermobarometer of Lee *et al.* (2009). (a) Equilibration pressure vs temperature for Mariana arc and trough melts. Filled symbols are constraints from single glasses; large open symbols are averages of the glass results from each island (Table 2). The fine continuous curve is the recommended fertile anhydrous solidus of Hirschmann (2000), and the dashed curve is the depleted mantle (refractory) solidus of Wasylenki *et al.* (2003). The thick, continuous gray line is an adiabatic ascent path for  $T_p = 1350^{\circ}$ C. A  $T_p$  of  $1350^{\circ}$ C is assumed for the Mariana Trough. The thick, continuous black line with arrow, labeled 'Dry Melts,' is the adiabatic melting path for  $T_p = 1350^{\circ}$ C above the solidus of Hirschmann (2000). The analogous curve labeled 'Wet Melts,' is a schematic melting path for  $T_p = 1350^{\circ}$ C above a hydrated solidus with 0.2 wt % H<sub>2</sub>O (fine dotted line). The crossed circle at 1240°C and 1GPa represents the P-T conditions of the wet Mariana Trough melt end-member of Langmuir *et al.* (2006). The scale bar in the lower right of the panel illustrates the variable  $T - T_{oo}$  where negative values indicate that the temperature is below the reference solidus at a given pressure, and positive values indicate temperatures above the more fertile, anhydrous solidus, whereas the Mariana arc melts record conditions below the more refractory anhydrous mantle solidus. (b) Equilibration pressure solidus, whereas the Mariana arc and trough show no correlation between equilibration pressure and water content.

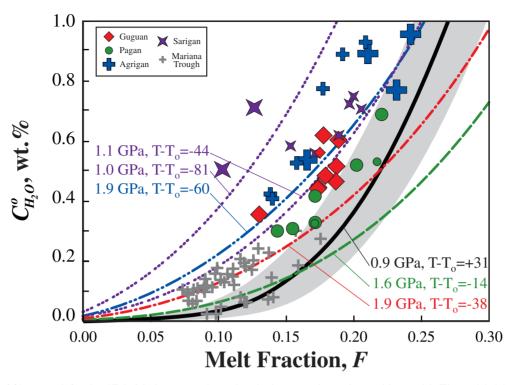
supply the heat of fusion. The Mariana Trough P-T range in Fig. 10a probably reflects cooling from melting mantle of  $T_{\rm p} = 1350^{\circ}$ C that intersects either the anhydrous solidus, melting to a lower extent and cooling less ('dry melts' curve in Fig. 10a), or a hydrated solidus at higher pressure, melting to a greater extent and cooling more ('wet melts' curve in Fig. 10a).

Beneath the arc, on the other hand, the conditions recorded by the melt inclusions are indicative of melts equilibrating over a very broad range of P-T conditions, extending to greater depths and higher absolute temperatures than the anhydrous back-arc melting triangle (Figs 7 and 10). Considering possible cooling during melting, the arc melts could be traced back along an adiabatic melting path to mantle of  $T_{\rm p} \sim 1400 - 1450^{\circ}$ C (Fig. 10). Melting paths beneath arcs, however, may not be adiabatic if melts or partially molten sources migrate upwards and increase in temperature through the lower half of the mantle wedge (e.g. Grove et al., 2006). Melting-induced cooling could thus be offset by the inverted geotherm in the lower half of the wedge, particularly if the volume of the mantle experiencing melting is small relative to the thermal reservoir of the mantle (Kelley et al., 2006). Small parcels of ascending melt or partially molten mantle could equilibrate thermally with the progressively hotter mantle through

Table 2: Average pressures and temperatures of equilibrationof Mariana melts

Volcano or region	Av. <i>T</i> (°C)	SD	$T-T_{o}$ (°C)	Av. P (GPa)	SD
Guguan	1360	24	-39	1.9	0.3
Pagan	1343	31	-12	1.6	0.1
Agrigan	1365	47	-57	2.2	0.4
Sarigan	1208	0	-81	1.0	0.0
Mariana Trough	1273	22	+31	0.9	0.1

which they rise, thus experiencing non-adiabatic heating, instead of cooling, during ascent and melting. The melt temperature would thus be fixed by the mantle temperature up to the maximum T in the hot core of the wedge, which would reflect the conditions of last equilibration of the arc melts with the arc mantle. In contrast to back-arc melting, which is driven by spreading and mantle up-welling, melting and melt equilibration beneath the arc may occur largely within the hot, central portion of the mantle wedge. When considering the average P-T conditions recorded by melts from each island (see Table 2), arc



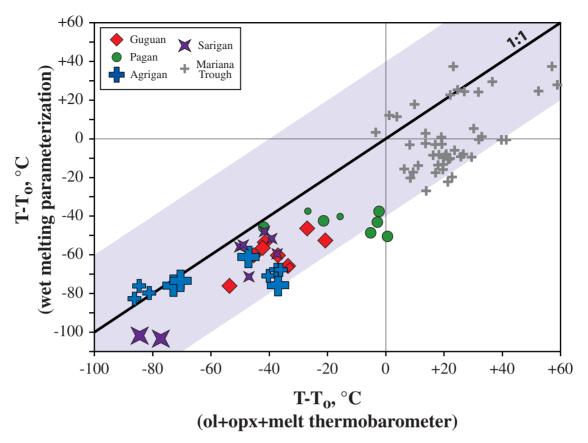
**Fig. 11.** Plot of  $C_{H_2O}^{\circ}$  vs melt fraction (F) in Mariana arc and trough melts, incorporating various melting models. The modeled data points and symbols are the same as those shown in Fig. 6. The curves shown are outputs of variations of equation (4), using coefficients for the fertile and refractory cases. The pressures and temperatures input into each model are shown in Fig. 9 and are provided in Table 2. The thick, continuous black curve describes melting for the average P-T conditions of the Mariana Trough, using coefficients for the fertile case  $(T - T_o = +3)$ . The shaded region surrounding this curve represents an uncertainty of  $\pm 20^{\circ}$ C on the fertile solidus. Models for the arc use coefficients for the refractory case. Arc model melting curves are shown for average P-T conditions of Pagan island (dashed curve;  $T - T_o = -38$ ), Agrigan island (dash–double-dot curve;  $T - T_o = -60$ ), and the two distinct samples from Sarigan island (triple dotted curves;  $T - T_o = -81$  and -44).

melting conditions are actually consistent with a maximum wedge core temperature of  $1350^{\circ}$ C or cooler (Fig. 10a).

### Melting in the Mariana system

Although the thermobarometric results make some sense with respect to the physical arc and back-arc melting regimes (Fig. 7), they stand in apparent disagreement with the inferences from the data arrays on the  $C_{\rm H_2O}^{\rm o}$  vs F diagram (Fig. 6), which indicate lower productivity of hydrous melting (i.e. lower  $dF/dC_{H_0O}^o$ ) suggestive of cooler temperatures beneath the arc than the back-arc. Resolving this apparent contradiction requires an integrated examination of the factors controlling melt formation and productivity in the Mariana system, including pressure, temperature, and the peridotite fertility appropriate to this system. To develop a comprehensive view of the conditions of melting, the role of H<sub>2</sub>O, and the influences over the form of the melting function for each location in the Mariana system, we combined our thermobarometric calculations with the fertile and refractory parameterizations of hydrous melting [e.g. equation (4)]. For the Mariana Trough, we use the fertile case, appropriate for MORB sources; for the Mariana arc, we use the refractory case to account for the increased depletion of the Mariana arc mantle relative to the Mariana Trough (see above). These choices utilize the best available constraints on solidi and melt productivities for fertile and comparatively depleted natural peridotite, and are intended to reflect the general characteristics of melting variably depleted mantle sources. We emphasize that the precise fertilities that apply to the mantle beneath the Mariana arc and trough are subject to debate. Those used here were chosen to illustrate the important first-order contrast between melting of fertile vs refractory lherzolite on melt productivity and on the form of the wet melting function.

Figure 11 shows the model melting curves output by equation (4) as described above, calculated for each location using P-T conditions determined from melt thermobarometry. For each island and for the whole Mariana Trough, pressures and temperatures given by each modeled glass were averaged (Table 2; Fig. 10a) to give a mean P-T condition for each location. In the case of Sarigan, where two samples yielded two distinct sets of P-T



**Fig. 12.** Plot of  $T - T_0$  derived from two independent methods. The *x*-axis represents  $T - T_0$  calculated relative to fertile (Mariana Trough) or refractory (arc islands) peridotite solidi, using temperatures and pressures calculated using the 0 + opx + melt thermobarometer of Lee *et al.* (2009). The *y*-axis represents  $T - T_0$  calculated relative to fertile (Mariana Trough) or refractory (arc islands) peridotite solidi by solving equation (4) for  $T - T_0$  (where  $T_0 = aP^2 + bP + c$ ), using the batch melting model results to supply *F* and  $C_{H_2O}^{o}$  (see Electronic Appendix 4), and using the pressure derived from the Lee *et al.* (2009) model. The shaded region is  $\pm 40^{\circ}$ C from the l:l line, which is the quoted error on temperatures derived from the Lee *et al.* (2009) model.

conditions, the conditions for each sample were averaged separately. These calculations yield the amount of melting expected over a range of H<sub>2</sub>O contents added to a fertile or refractory mantle wedge at the P-T conditions specified for each location. On the whole, the model curves are consistent with the modeled data points derived from TiO<sub>2</sub> systematics for the Mariana arc and trough. For example, the melts from Agrigan, Gugan, and Pagan islands show high equilibration pressures and temperatures (Figs 8 and 9), but also indicate temperatures below the anhydrous, refractory solidus  $(T - T_o = -12 \text{ to } -60^{\circ}\text{C})$ .

The P-T conditions indicated by these arc samples yield melting curves that broadly bracket many of the modeled data for these three islands, indicating that H<sub>2</sub>O-fluxed melting of relatively refractory peridotite at the modeled P-T conditions is an appropriate mechanism to explain the data trends. In detail, however, the model curves for the arc melting conditions show melt productivities systematically higher than indicated by the arc data. This outcome may be a result of the DMMI composition being too refractory relative to the true Mariana arc mantle

source, or a refractory solidus that is too cold, or both. Lower productivities of a slightly more fertile peridotite would yield closer agreement between the arc data and the models. Nevertheless, the sense of variation among the arc volcanoes is accurately captured by the melting models, regardless of the exact melt productivities used, with Sarigan (SA93) as the coldest and least productive, and Pagan as the warmest and most productive. Without adjusting solidi or melt productivities, however, independent constraints on  $T - T_0$  derived from the thermobarometry models (Lee et al., 2009) and from equation (4) [solved for  $T - T_{o}$ , using the batch melting results to supply F and  $C_{\text{H}_2\text{O}}^{\text{o}}$ , and given P from the Lee *et al.*, (2009) model] are remarkably consistent. Figure 12 compares  $T - T_0$  derived from both methods, and shows clear agreement, within error of the temperature model of Lee et al. (2009), although there is a systematic bias that may be resolved as discussed above with adjustments to solidi and/or melt productivities. Figure 12 also illustrates the consistency of the two models in resolving the strong temperature contrast beneath the arc (negative  $T - T_0$ )

relative to the back-arc basin (positive  $T - T_{\rm o}$ ), and among the arc islands, where  $T - T_{\rm o}$  decreases in the order Pagan > Guguan > Agrigan > Sarigan (SA93).

As a group, the melts from Sarigan indicate lower equilibration pressures than the other Mariana islands  $(\sim 1 \text{ GPa})$ , and the two inclusions from sample SA93, in particular, also record very low relative temperatures  $(T - T_0 = -80^{\circ}\text{C}; \text{ Fig. 9a})$ , consistent with the lowest melting productivities among the samples examined here. For the Mariana Trough, the combination of lower equilibration pressures ( $\sim$ l GPa) and a more fertile (i.e. colder; Fig. 9) solidus leads to super-solidus mean melts  $(T - T_0 = +31^{\circ}C)$  that are distinct from the sub-solidus mean melts of the Mariana arc. The model curve is not a good fit for many of the back-arc data, which suggests that the relevant solidus for the Mariana Trough may be  $\sim 10^{\circ} C$  warmer than the fertile solidus (uncertainties on this solidus are  $\pm \sim 20^{\circ}$ C from 0 to 3.5 GPa; Hirschmann, 2000), but the important systematics are nonetheless clear. The inferences drawn from simple observations of slopes defined by the data trends in Figs 6 and 11 are inadequate to constrain melting conditions because the effects of pressure, temperature, and relevant peridotite fertility all combine to influence the shape of the melting function. We show here that the modeled data trends are consistent with arc melts equilibrating at higher temperatures and pressures than back-arc basin melts, and vary in melt fraction as a function of temperature, pressure, mantle fertility, and H<sub>2</sub>O addition to the mantle source.

In summary, the relevant parameter for trends on the  $C_{\rm H_2O}^{\rm o}$  vs F diagram is  $T - T_{\rm o}$ , which is the relative temperature contrast with respect to the relevant solidus at a given pressure (e.g. relative to either the fertile or refractory solidus, as in Fig. 10a). This controls both the slope (particularly at negative  $T - T_0$ ) and horizontal translation of the melting curves on the  $C_{\text{H}_2\text{O}}^{\text{o}}$  vs F diagram, both of which are measures of the wet melting productivity (i.e.  $dF/dC_{H_2\Omega}^{o}$ ). Knowledge of  $T - T_o$ , however, requires independent constraints on the absolute P and T of melting, obtained here through thermobarometry, as well as independent constraints on the position of the anhydrous solidus. The quantitative consistency between these independent approaches demonstrates the utility of this framework for describing the melting relationships defined by natural arc and back-arc samples. For back-arc basins, where mantle fertility largely reflects that of the ambient convecting upper mantle, and where mantle  $T_{\rm p}$  largely controls the depth and extent of melting, the slope of melting trends on the  $C_{H_2O}^o$  vs F diagram is an adequate proxy for wet melting productivity, which increases with the mean pressure of melting and  $T_{\rm p}$ , as indicated in this study and previously (Kelley et al., 2006). For arcs, the mantle composition could be either more refractory or more enriched than normal MORB mantle, as a result of,

for example, the absence of back-arc spreading or ocean island basalt-like mantle sources (e.g. Woodhead et al., 1993; Eiler et al., 2005; Pearce et al., 2005), and the mantle may begin to melt near the slab, at higher pressures than it would melt under drier conditions, driven by a high water flux from below. This drives significant melting at temperatures below the dry solidus, but with smaller increases in the amount of melting per unit of added water than occurs beneath back-arcs, particularly if the arc mantle is more refractory. We thus expect that, as more water data are produced for arc systems, many arcs will define steeper slopes on  $C_{\text{H}_{0}\text{O}}^{\text{o}}$  vs F diagrams, with potentially lower average F, than back-arc basins. Recent work examining wet melting systematics for the Kamchatka, Central America, and Mexican arcs appear to substantiate this prediction (Portnyagin et al., 2007; Johnson et al., 2009).

#### CONCLUSIONS

The integrated approach developed here for describing the conditions of melting in the Mariana system predicts that the Mariana arc melts (excluding those from Sarigan) have equilibrated at greater depths (50-90 km), from more refractory mantle, and at higher absolute temperatures (>1300°C) and water contents ( $C_{H_2O}^o$ >2000 ppm) than back-arc basin melts from the Mariana Trough. Nonetheless, most of the melts beneath the arc are generated at temperatures below the dry solidus, and so by a less productive wet melting process than beneath the back-arc. The contrast in the arc and back-arc melting productivities reflects the different physical processes involved: low water concentrations within a dominantly spreadingdriven upwelling system beneath the back-arc vs higher water concentrations within the hot, central portion of the comparatively stagnant mantle wedge beneath the arc. This does not exclude a significant component of dry melting beneath the arc, but our data range is too limited to explicitly define the low-H<sub>2</sub>O ends of the arc melting trends and our thermobarometric approach relies on mean properties of the aggregate melts rather than the discrete melts that may exist within the mantle. However, the quantitative constraints on the pressures and temperatures of melting presented here allow us to describe the wet melting process within the Mariana arc-back-arc system in a self-consistent way, as a function of the combined effects of the geothermal gradient, mantle fertility, and the magnitude of H<sub>2</sub>O addition to the mantle wedge, providing a useful framework for the examination of other subduction systems.

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# SUPPLEMENTARY DATA

Supplementary data for this paper are available at *Journal* of *Petrology* online.

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