

# Volatiles in submarine basaltic glasses from the Ontong Java Plateau (ODP Leg 192): implications for magmatic processes and source region compositions

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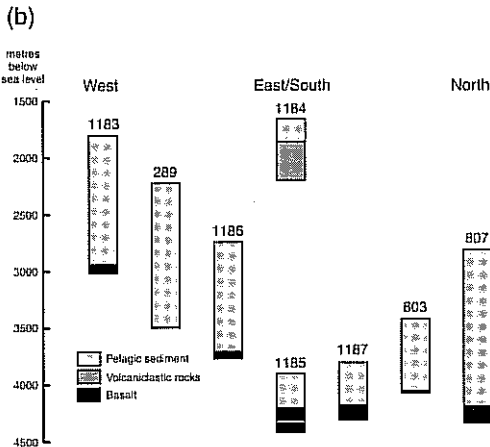
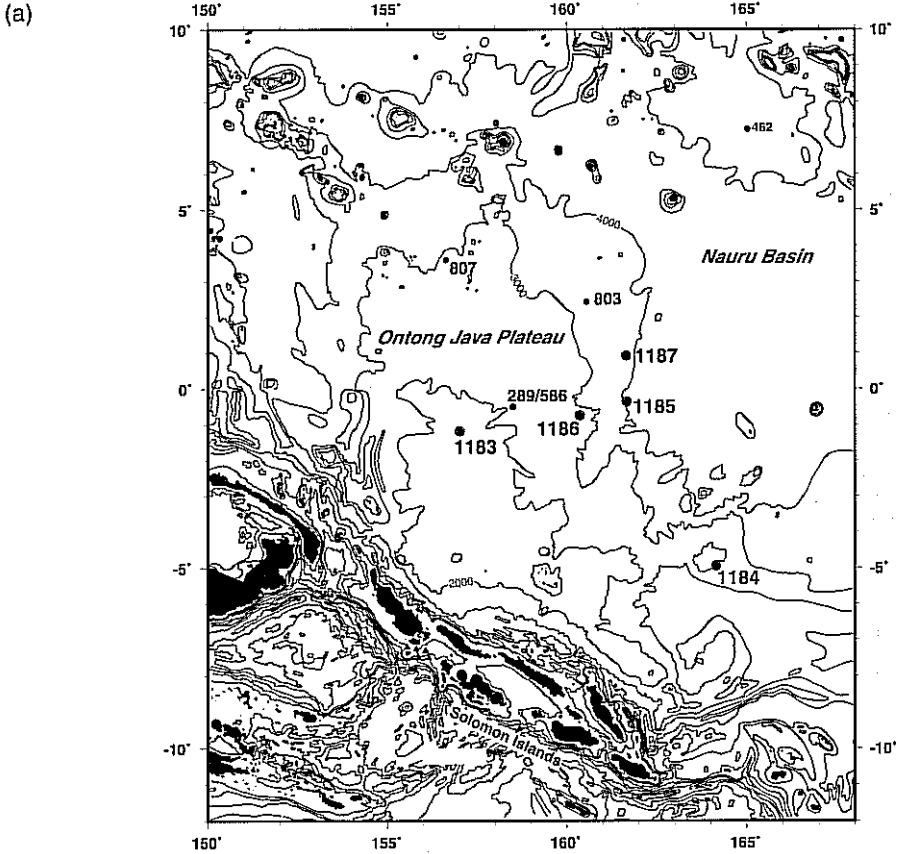
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**Abstract:** Submarine basaltic glasses from five widely separated sites on the Ontong Java Plateau (OJP) were analysed for major and volatile elements (H<sub>2</sub>O, CO<sub>2</sub>, S, Cl). At four of the sites (1183, 1185, 1186, 1187) the glass is from pillow basalt rims, whereas at Site 1184 the glass occurs as non-vesicular glass shards in volcanoclastic rocks. Glassy pillow rims from Site 1187 and the upper group of flows at Site 1185 have 8.3–9.3 wt% MgO compared with values of 7.2–8.0 wt% MgO for glasses from Sites 1183, 1184, 1186, and the lower group of flows at Site 1185. Low-MgO glasses have slightly higher H<sub>2</sub>O contents (average 0.22 wt% H<sub>2</sub>O) than high-MgO glasses (average 0.19 wt%), with the exception of Site 1184, where low-MgO glasses have lower H<sub>2</sub>O (average 0.16 wt%). Average S concentrations are 910 ± 60 ppm for the high-MgO glasses v. 1030 ± 60 ppm for the low-MgO glasses. When compared with mid-ocean ridge basalt (MORB), the OJP glasses have lower S at comparable FeO<sup>T</sup>. This suggests that OJP basaltic magmas were not saturated with immiscible sulphide liquid during crystallization, but small decreases in S/K<sub>2</sub>O and S/TiO<sub>2</sub> with decreasing MgO require some sulphide fractionation. Measurements of the wavelength of the S K $\alpha$  peak in the glasses indicate low oxygen fugacities comparable to MORB values. Chlorine contents of the glasses are very high compared with MORB, and Cl/K ratios for all glasses are relatively high (>0.7). This ratio is sensitive to assimilation of hydrothermally altered material, so the high values indicate assimilation during shallow-level crystallization of OJP magmas. Ratios of H<sub>2</sub>O to Ce, which have similar incompatibility to each other, are higher than most depleted and enriched MORB. However, these high H<sub>2</sub>O/Ce values are probably also caused by the same assimilation process that results in high Cl. The water content of the high MgO-magmas before contamination is estimated to be approximately 0.07 wt% H<sub>2</sub>O, corresponding to H<sub>2</sub>O/Ce of 135 for OJP basalts, a value at the low end of the range for Pacific MORB. There is no evidence for high H<sub>2</sub>O contents that would have significantly increased extents of mantle melting beneath the OJP, and the estimated H<sub>2</sub>O content of the OJP mantle source region (170 ± 30 ppm H<sub>2</sub>O) is similar to that of the depleted MORB source (140 ± 40 ppm H<sub>2</sub>O). Instead, large extents of melting beneath the OJP must have been caused by a relatively high mantle potential temperature, consistent with upwelling of a hot mantle plume.

The Ontong Java Plateau (OJP) is the largest volcanic oceanic plateau and may represent the largest magmatic event on Earth in the last 200 Ma. The OJP is located in the SW Pacific and is believed to have formed in response to the emplacement of a mantle plume head (e.g. Mahoney & Spencer 1991; Richards *et al.* 1991). Large igneous provinces such as the OJP are important because they provide information on mantle processes and compositions, and because their formation may have global environmental consequences (Larson & Erba 1999; Courtillot & Renne 2003). Magmatic volatiles are especially important in many aspects of large igneous province formation. Basaltic magmas

related to mantle plumes commonly have higher H<sub>2</sub>O than depleted mid-ocean ridge basalt (MORB), suggesting that the excess magmatism associated with mantle plumes could be caused, at least in part, by the effect of higher H<sub>2</sub>O on mantle melting (Schilling *et al.* 1980; Bonatti 1990; Nichols *et al.* 2002). A greater H<sub>2</sub>O content for the lower mantle, from which mantle plumes are probably derived (Hofmann 1997), could also indicate the involvement of undegassed primitive mantle (based on high <sup>3</sup>He/<sup>4</sup>He), or could result from recycling of subducted oceanic crust and sediments into the lower mantle. At the Earth's surface release of volatiles such as CO<sub>2</sub>, S, Cl and F during eruption of enormous



**Fig. 1.** (a) ETOPO5 bathymetric map of the Ontong Java Plateau showing locations of Leg 192 drill sites (large solid circles). Locations of previous ODP and DSDP drill sites that reached basement (small solid circles) are also shown. Depth contours are in metres below sea level. (b) Stratigraphic sections drilled during Leg 192 and at previous DSDP/ODP Ontong Java Plateau basement sites (modified from Mahoney *et al.* 2001).

volumes of basaltic magma in large igneous provinces may have significant environmental consequences.

During Ocean Drilling Program (ODP) Leg 192, igneous rock and sediment cores were obtained from five widely separated sites in previously unsampled regions across the OJP (Fig. 1). An exciting result of Leg 192 was the discovery that the basement at Site 1187 and the upper group of flows at Site 1185 are composed of high-MgO, incompatible-element-poor basalt that is unlike the more evolved basalts found elsewhere on the OJP. Because they are less differentiated, these high-MgO basalts are especially valuable in providing information on parental magma compositions. Basaltic lavas recovered during Leg 192, as well as lavas sampled previously in DSDP/ODP drill sites and on land in the Solomon Islands, were all erupted well below sea level, except for a basaltic volcanoclastic sequence erupted in shallow water at Site 1184 (Mahoney *et al.* 2001). Submarine-erupted lavas are particularly valuable for studying magmatic volatiles because quenched glassy pillow rims preserve information on pre-eruptive volatile contents.

In this chapter we present major- and volatile- ( $\text{H}_2\text{O}$ ,  $\text{CO}_2$ , S, Cl) element concentrations of fresh glass derived from pillow basalt rims (Sites 1183, 1185, 1186 and 1187) and non-vesicular glass shards in volcanoclastic rocks (Site 1184). Our results complement previously published data for glasses recovered from Sites 803 and 807 on the OJP (Michael 1999). We use the new and published data to infer the  $\text{H}_2\text{O}$  content of the source region for OJP basaltic magmas, to assess magmatic processes such as pressures of fractionation and assimilation in crustal magma chambers, and to discuss possible environmental effects of released volatiles during formation of the OJP. Volatile solubilities in magma are pressure dependent, and thus knowing the volatile content of the quenched glass also allows us to estimate the original eruption depth. A discussion of eruption depths and their implications for plateau subsidence will be presented elsewhere (Roberge *et al.* 2004).

### Geological setting and sample characteristics

The Ontong Java Plateau (OJP) covers an area of approximately  $2.0 \times 10^6 \text{ km}^2$  and is delimited by the Lyra Basin to the NW, the East Mariana Basin to the north, the Nauru Basin to the NE, and the Ellice Basin to the SE (Fig. 1).  $^{40}\text{Ar}$ - $^{39}\text{Ar}$  geochronology suggests that the bulk volume of the plateau was formed in a single episode around 122 Ma (Mahoney *et al.* 2001; Chambers *et al.* 2002). A second, volumetrically minor episode happened at about 90 Ma, but none of the lavas recovered during Leg 192 were of this age (Mahoney *et al.* 2001). After its formation, the OJP collided with the Solomon Islands arc and now lies between the Pacific and Australian plate, resisting subduction (Neal *et al.* 1997). The igneous rocks that form the OJP are now covered with thick accumulations of pelagic sediment. At its highest point, the upper surface of sediment on the plateau is approximately 1700 m below sea level, but elsewhere lies between a depth of 2 and 3 km.

During ODP Leg 192, five widely spaced sites were drilled (Fig. 1) (Mahoney *et al.* 2001). Site 1183 is located on the northern part of the high plateau. The sediment sequence overlying the basement is approximately 1130 m thick, and about 80 m of basement rocks consisting of pillow basalt were penetrated. Basaltic glasses analysed from this site come from throughout the recovered basement sequence. Site 1184 is on the northern ridge of the eastern lobe of the OJP. The recovered section at this site contains 337 m of volcanoclastic sequences formed by

hydroclastic eruptions in shallow water, but the hole did not penetrate into the underlying igneous basement, nor is the depth to basement known (Mahoney *et al.* 2001). The entire sequence recovered is altered to varying degrees. Unaltered, non-vesicular glass shards from Subunits IIA, IID and IIE were used for analysis; Subunits IIB and IIC do not contain any unaltered glass shards. At Site 1185, which lies on the eastern edge of the OJP, 216 m of basement rock was recovered beneath a 309 m-thick sediment sequence. The basement rocks at this site consist of pillow basalt and massive basalt; because abundant pillow basalt is present only in the first c. 150 m of the hole, most glasses sampled for analysis come from this interval. However, we did sample glass from two quenched margins associated with the underlying sheet flows. Site 1186 is located on the eastern slope of the OJP between Sites 1183 and 1185. The sediment sequence at this site is 968 m thick, and about 65 m of basement rocks were penetrated. The basement rocks consist of pillow basalt alternating with massive basalt. Again, because pillow basalt is present only in the upper part of the drill hole, the samples analysed from Site 1186 represent only the uppermost 50 m of the recovered sequence. Finally, Site 1187 is located about 100 km north of Site 1185 on the eastern edge of the OJP. At this site the sediment thickness is 372 m and the basement penetration was 135 m, consisting almost entirely of pillow basalt. Therefore, the samples analysed from this site represent the entire sequence of the recovered basement.

Based on whole-rock analyses (Mahoney *et al.* 2001; Fitton & Godard 2004), basalts at Sites 1183, 1186 and the lower part of 1185 are homogeneous, moderately evolved, low-K tholeiites, whereas the low-K basalts found in the upper part of Site 1185 and at Site 1187 have higher MgO (between 8 and 10 wt%).

### Analytical methods

#### Sample preparation

Fragments of visually unaltered glass from pillow margins or volcanoclastic sediment (Site 1184) were selected for infrared (IR) spectroscopy. Pieces of glass containing hair-like tubules that are the result of microbial alteration (Fisk *et al.* 1998; Banerjee & Muehlenbachs 2003) were avoided. The pieces of glass chosen were mounted on a glass slide using acetone-soluble cement. The samples were then doubly ground and polished into wafers with two parallel sides. The thickness of each glass wafer was

measured using a micrometer with a precision of  $\pm 2 \mu\text{m}$ .

### Infrared spectroscopy

A Nicolet Magna 560 Fourier transform IR spectrometer interfaced with a Spectra-Tech Nic-Plan microscope was used at Texas A&M University to obtain transmission IR spectra. Two individual spectra, taken on different areas of each glass sample, were acquired using a circular aperture  $100 \mu\text{m}$  in diameter.

Band assignments for dissolved water and carbonate in basaltic glass are based on Dixon *et al.* (1995). Quantitative measurements of dissolved total  $\text{H}_2\text{O}$ , molecular  $\text{H}_2\text{O}$  and carbonate ( $\text{CO}_3^{2-}$ ) were obtained using Beer's law:

$$c = \frac{MA}{\rho d \epsilon}$$

where  $c$  is the concentration (weight fraction) of the absorbing species,  $M$  is the molecular weight of  $\text{H}_2\text{O}$  (18.02) or  $\text{CO}_2$  (44.00),  $A$  is the absorbance intensity of the band of interest,  $\rho$  is room temperature density of the basaltic glass ( $2800 \text{ kg m}^{-3}$  was used for all glasses),  $d$  is the thickness of the glass wafer and  $\epsilon$  is the molar absorption coefficient.

Total dissolved  $\text{H}_2\text{O}$  was measured using the intensity of the band centred at  $3550 \text{ cm}^{-1}$ , which corresponds to the fundamental O-H stretching vibration (Ihinger *et al.* 1994). On a printed copy of the spectra the background was drawn as a smooth curve and graphically subtracted from the peak height to measure the absorbance intensity of the  $3550 \text{ cm}^{-1}$  band. The total dissolved water contents (Table 1) were calculated using a molar absorption coefficient of  $63 \pm 3 \text{ l mol}^{-1} \text{ cm}^{-1}$  from Ihinger *et al.* (1994).

To examine the speciation of water in the glasses as a means of screening for low-temperature hydration, concentrations of dissolved molecular  $\text{H}_2\text{O}$  were measured using the intensity of the  $1630 \text{ cm}^{-1}$  absorption band. Unlike the molar absorptivity for the  $3550 \text{ cm}^{-1}$  band, which is relatively independent of composition for basaltic glasses, the molar absorptivity for molecular water is compositionally dependent (Dixon *et al.* 1995). Using the method described in Dixon *et al.* (1995), the molar absorptivity of the  $1630 \text{ cm}^{-1}$  band for OJP basalt glasses is  $25 \pm 1 \text{ l mol}^{-1} \text{ cm}^{-1}$ .

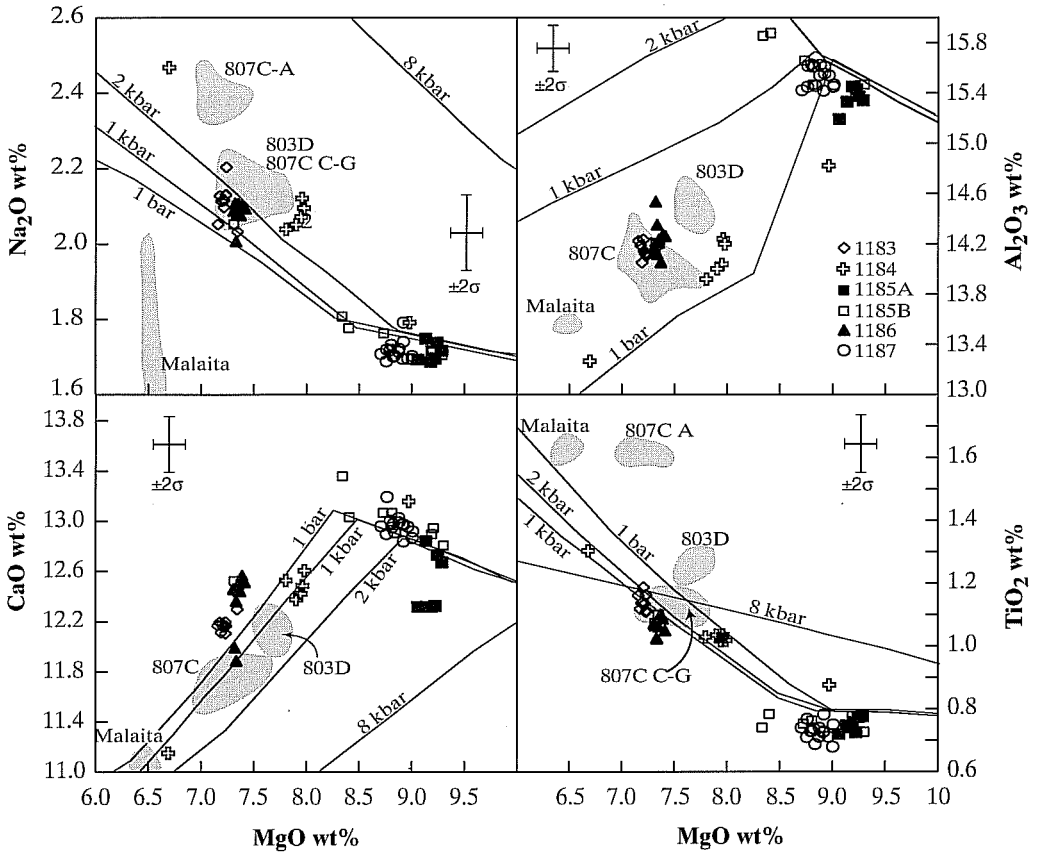
Dissolved carbonate was measured from the absorbance of the  $1515$  and  $1430 \text{ cm}^{-1}$  bands, which correspond to distorted asymmetric stretching of carbonate groups (Ihinger *et al.* 1994). Because the shape of the background in

the region of the carbonate doublet is complex, it is necessary to subtract a carbonate-free reference spectrum to obtain a flat background (Dixon *et al.* 1995). We measured absorbance intensities of the  $1515$  and  $1430 \text{ cm}^{-1}$  bands using a peak-fitting program that fits the sample spectrum with a straight line, a devolatilized basaltic glass spectrum, a pure  $1630 \text{ cm}^{-1}$  band for molecular  $\text{H}_2\text{O}$  and a pure carbonate doublet (unpublished program by S. Newman). The molar absorption coefficient of carbonate in basaltic glass is compositionally dependent and was derived using the average composition of the glasses and the linear equation reported in Dixon & Pan (1995). The dissolved carbonate content was calculated using a molar absorption coefficient of  $384 \text{ l mol}^{-1} \text{ cm}^{-1}$  for the high-MgO glasses and  $370 \text{ l mol}^{-1} \text{ cm}^{-1}$  for the low-MgO glasses.

Based on replicate analyses, precision ( $2\sigma$ ) for total  $\text{H}_2\text{O}$  is  $<16\%$  (relative) and  $<11\%$  for  $\text{CO}_2$ . Accuracy for these techniques is estimated to be  $\pm 10\%$  for total  $\text{H}_2\text{O}$  and  $\pm 20\%$  for  $\text{CO}_2$  (Dixon & Clague 2001).

### Electron microprobe

Major elements, S and Cl in most glass samples were analysed using a Cameca SX-50 electron microprobe at the University of Oregon (Table 1). The major elements were acquired using an electron beam diameter of  $10 \mu\text{m}$  with an accelerating voltage of  $15 \text{ kV}$  and a beam current of  $10 \text{ nA}$ . Both glass and mineral standards were used, and US National Museum glass standard VG-2 was used to assess analytical accuracy (Table 1). Sulphur was analysed using an anhydrite standard and an S  $K\alpha$  wavelength position measured on pyrite, which corresponds approximately to the  $\text{S}^{6+}/\Sigma\text{S}$  ratio expected for basaltic glass equilibrated at the fayalite-magnetite-quartz (FMQ) oxygen buffer (Wallace & Carmichael 1994). For all elements, five spots on each glass sample were analysed, and the average value is reported in Table 1. Chlorine was analysed using an electron beam diameter of  $20 \mu\text{m}$  with an accelerating voltage of  $15 \text{ kV}$  and a beam current of  $100 \text{ nA}$ . The counting time for chlorine was  $200 \text{ s}$  on peak and  $200 \text{ s}$  on background for each spot analysed. Sulphur speciation was also determined for selected samples by measuring the S  $K\alpha$  X-ray wavelength position as described by Wallace & Carmichael (1994), using sphalerite for  $\text{S}^{2-}$  and anhydrite for  $\text{S}^{6+}$ . The operating conditions for S speciation measurements were  $10 \mu\text{m}$  electron beam diameter with an accelerating voltage of  $15 \text{ kV}$  and a beam current of  $30 \text{ nA}$ . Wavelength scans were performed using counting times of  $40 \text{ s}$  per



**Fig. 2.** Major-element compositions of Ontong Java Plateau basaltic glasses. Data from Sites 803 and 807 and the island of Malaita are from Michael (1999). Lines show fractional crystallization paths for a parental magma with 17.6 wt% MgO calculated as described in the text. Crystallization of this parental composition at pressures of 1 bar–2 kbar can largely reproduce the observed range of major-element compositions. Under these conditions, the crystallization sequence is olivine, followed by olivine + plagioclase, followed by olivine + plagioclase + clinopyroxene.

wavelength step on unknowns and 5 s per step on standards. The sample was moved slightly relative to the beam after each step in the wavelength scan to avoid problems associated with beam damage to the glass (Wallace & Carmichael 1994). Major elements and S in the Site 1184 glasses were analysed at the University of Leicester using procedures described in White *et al.* (2004). Chlorine in Site 1184 glasses was measured at the University of Oregon as described above.

Two-sigma ( $2\sigma$ ) precision based on counting statistics is <2.5% (relative) for major elements and <30% for minor elements (K, Mn, Na, Ti, P). For Cl and S the  $2\sigma$  precision is <9% and <22%, respectively.

## Results

All 55 samples of unaltered basaltic glass, representing all sites drilled during ODP Leg 192, are tholeiitic basalts based on a total alkalis v. silica diagram (not shown). Two types of basalt could be observed based on MgO contents. Basement at Site 1187 and the upper group of flows at Site 1185 is composed of high-MgO basalt (average of 9 wt% MgO), compared to 7.2–8.0 wt% MgO for basalt found elsewhere on the OJP (Fig. 2). The low-MgO glasses from Sites 1183, 1186 and the lower part of 1185 are similar in composition to those found in the northern part of the OJP (Hole 803D and units C–G of ODP Hole 807C). All glasses have relatively low Na<sub>2</sub>O, K<sub>2</sub>O and

Table 1. Compositions of basaltic glasses from the Ontong Java Plateau

Sample	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	FeO <sup>T</sup>	MnO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	S (ppm)	Cl (ppm)	H <sub>2</sub> O (ppm)	CO <sub>2</sub> (ppm)	Total	Sat. P* (bars)
1183A-55R-1 32	50.58	1.12	14.19	11.25	0.19	7.18	12.19	2.13	0.11	0.09	948	673	0.24	45	99.42	
1183A-55R-2 134	50.46	1.14	14.23	11.33	0.21	7.21	12.18	2.12	0.11	0.08	1029	664	0.23	44	99.47	
1183A-56R-1 10	51.06	1.16	14.22	11.35	0.21	7.16	12.17	2.05	0.12	0.07	1156	601	0.20	43	99.97	
1183A-57R-2 97	50.54	1.19	14.14	11.26	0.21	7.21	12.16	2.10	0.10	0.09	1013	638	0.24	46	99.41	
1183A-58R-1 97	50.89	1.14	14.05	11.29	0.18	7.19	12.11	2.11	0.11	0.11	1131	667	0.23	47	99.59	
1183A-60R-1 36	51.00	1.11	14.11	11.25	0.22	7.23	12.19	2.13	0.11	0.09	957	666	0.22	46	99.82	
1183A-62R-2 1	50.86	1.14	14.18	11.12	0.21	7.34	12.30	2.03	0.11	0.08	1083	713	0.22	57	99.77	
1183A-64R-1 112	50.90	1.14	14.12	11.25	0.19	7.22	12.16	2.12	0.11	0.10	1139	691	0.23	51	99.72	
1183A-65R-2 19	51.15	1.16	14.10	11.13	0.22	7.23	12.10	2.13	0.11	0.10	982	678	0.23	43	99.83	
1183A-67R-3 60	50.97	1.11	14.13	11.27	0.22	7.24	12.16	2.20	0.11	0.08	1021	737	0.23	41	99.91	
<b>Average 1183A</b>	<b>50.84</b>	<b>1.14</b>	<b>14.15</b>	<b>11.25</b>	<b>0.21</b>	<b>7.22</b>	<b>12.17</b>	<b>2.11</b>	<b>0.11</b>	<b>0.09</b>	<b>1046</b>	<b>673</b>	<b>0.23</b>	<b>46</b>	<b>99.69</b>	<b>107±9</b>
1184A-13R-3 142	49.86	0.88	14.82	9.50	0.17	8.97	13.16	1.79	0.08	n.a.	641	495	0.17	19	99.52	
1184A-31R-7 53	50.63	1.30	13.27	12.32	0.23	6.70	11.15	2.47	0.14	n.a.	692	3171	0.14	47	98.73	
1184A-39R-7 95	49.82	1.03	13.92	10.24	0.18	7.81	12.53	2.04	0.10	n.a.	725	1708	0.16	31	98.07	
1184A-41R-6 67	50.81	1.04	14.20	10.59	0.17	7.98	12.61	2.09	0.11	n.a.	717	1678	0.16	27	99.99	
1184A-42R-5 69	50.21	1.04	14.01	10.44	0.20	7.91	12.37	2.05	0.10	n.a.	720	1685	0.16	24	98.73	
1184A-44R-3 78	50.80	1.04	14.23	10.59	0.17	7.96	12.49	2.12	0.10	n.a.	708	1690	0.16	30	99.91	
1184A-45R-2 75	50.35	1.02	14.03	10.46	0.19	7.95	12.42	2.07	0.10	n.a.	705	1699	0.17	29	99.01	
<b>Average 1184A</b>	<b>50.36</b>	<b>1.05</b>	<b>14.07</b>	<b>10.59</b>	<b>0.19</b>	<b>7.90</b>	<b>12.39</b>	<b>2.09</b>	<b>0.10</b>	<b>0.06</b>	<b>700</b>	<b>1700</b>	<b>0.16</b>	<b>30</b>	<b>99.13</b>	<b>54±21</b>
1185A-9R-1 130	49.43	0.75	15.33	9.64	0.18	9.13	12.84	1.75	0.07	0.06	895	812	0.18	94	99.56	
1185A-9R-3 88	49.74	0.78	15.34	9.69	0.17	9.28	12.67	1.72	0.07	0.05	922	778	0.19	106	99.90	
1185A-9R-4 100	49.94	0.77	15.38	9.73	0.17	9.24	12.73	1.74	0.07	0.06	876	777	0.19	100	100.19	
1185A-10R-1 10	50.41	0.73	15.43	9.64	0.18	9.22	12.33	1.70	0.08	0.07	902	756	0.18	92	100.13	
1185A-10R-1 40	48.87	0.72	15.20	9.91	0.17	9.06	12.32	1.69	0.08	0.07	814	798	0.18	98	98.45	
1185A-10R-2 1	50.33	0.74	15.46	9.67	0.20	9.18	12.32	1.69	0.07	0.06	867	759	0.20	102	100.10	
<b>Average 1185A</b>	<b>49.79</b>	<b>0.75</b>	<b>15.36</b>	<b>9.71</b>	<b>0.18</b>	<b>9.18</b>	<b>12.54</b>	<b>1.71</b>	<b>0.08</b>	<b>0.06</b>	<b>879</b>	<b>780</b>	<b>0.18</b>	<b>99</b>	<b>99.72</b>	<b>219±11</b>
1185B-3R-1 54	49.13	0.78	15.45	9.87	0.18	9.19	12.90	1.72	0.07	0.06	964	885	0.19	101	99.73	
1185B-5R-7 19	49.59	0.73	15.47	9.82	0.16	9.30	12.80	1.71	0.07	0.08	818	936	0.19	104	100.09	
1185B-6R-1 95	49.83	0.76	15.46	9.92	0.19	9.20	12.93	1.71	0.07	0.07	865	919	0.18	97	100.52	
1185B-9R-1 55	49.19	0.76	15.47	9.87	0.16	8.81	13.06	1.72	0.08	0.07	957	929	0.21	104	99.61	
1185B-9R-3 pc3	49.78	0.78	15.68	9.64	0.20	8.41	13.03	1.78	0.08	0.07	929	980	0.19	95	100.04	
1185B-15R-1 149	49.86	0.75	15.86	9.71	0.18	8.73	13.07	1.76	0.08	0.06	832	836	0.20	105	100.24	
1185B-16R-1 64	49.47	0.74	15.86	9.56	0.20	8.34	13.35	1.81	0.07	0.07	875	987	0.18	105	99.85	
<b>Average upper 1185B</b>	<b>49.55</b>	<b>0.76</b>	<b>15.61</b>	<b>9.77</b>	<b>0.18</b>	<b>8.85</b>	<b>13.02</b>	<b>1.74</b>	<b>0.08</b>	<b>0.07</b>	<b>891</b>	<b>924</b>	<b>0.19</b>	<b>102</b>	<b>100.01</b>	<b>221±7</b>

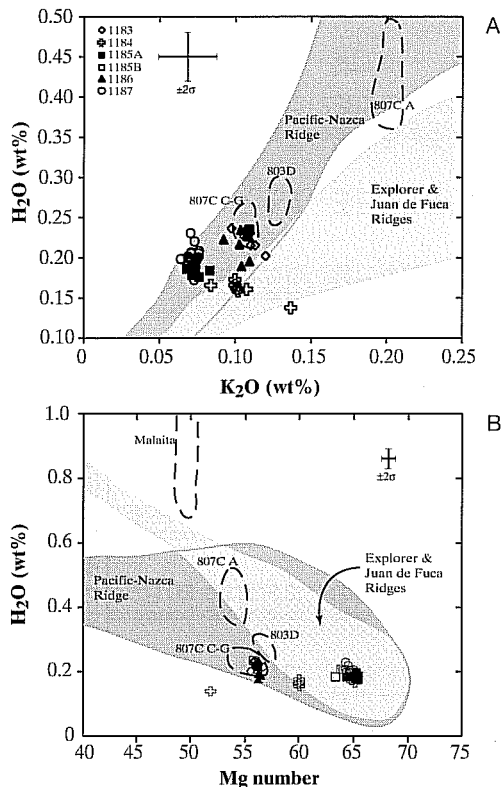
1185B-23R-1 4	50.58	1.07	14.21	11.48	0.17	7.31	12.52	2.05	0.11	0.10	1050	915	0.24	104	100.05
1185B-23R-1 78	50.71	1.10	14.20	11.35	0.19	7.35	12.44	2.10	0.11	0.09	1072	779	0.21	100	100.04
<b>Average lower 1185B</b>	<b>50.65</b>	<b>1.09</b>	<b>14.21</b>	<b>11.41</b>	<b>0.18</b>	<b>7.33</b>	<b>12.48</b>	<b>2.08</b>	<b>0.11</b>	<b>0.09</b>	<b>1061</b>	<b>847</b>	<b>0.22</b>	<b>102</b>	<b>100.05</b> 223±8
1186A-31R-2 47	50.87	1.07	14.18	11.15	0.21	7.31	12.46	2.09	0.10	0.08	1034	735	0.19	87	99.90
1186A-31R-3 34	51.01	1.06	14.24	11.34	0.22	7.35	12.50	2.11	0.10	0.11	1097	717	0.18	92	100.41
1186A-31R-3 47	51.06	1.09	14.28	11.38	0.18	7.39	12.57	2.10	0.10	0.07	972	717	0.23	107	100.62
1186A-32R-3 68	50.23	1.10	14.05	11.39	0.20	7.37	12.44	2.08	0.11	0.09	1041	740	0.23	101	99.49
1186A-32R-3 76	50.62	1.02	14.12	11.33	0.25	7.34	12.36	2.08	0.09	0.10	953	743	0.22	99	99.72
1186A-33R-1 27	52.07	1.07	14.54	11.29	0.21	7.32	11.99	2.11	0.10	0.10	962	687	0.22	97	101.19
1186A-34R-4 98	51.39	1.03	14.35	11.44	0.19	7.33	11.88	2.01	0.11	0.11	1031	693	0.23	102	100.25
1186A-34R-5 57	50.92	1.05	14.26	11.43	0.20	7.42	12.51	2.09	0.11	0.10	1023	907	0.19	89	100.49
<b>Average 1186A</b>	<b>51.05</b>	<b>1.06</b>	<b>14.27</b>	<b>11.38</b>	<b>0.21</b>	<b>7.36</b>	<b>12.29</b>	<b>2.08</b>	<b>0.10</b>	<b>0.10</b>	<b>997</b>	<b>748</b>	<b>0.22</b>	<b>99</b>	<b>100.29</b> 215±14
1187A-3R-2 104	49.70	0.73	15.42	9.54	0.17	8.91	12.98	1.70	0.07	0.06	881	946	0.17	118	99.64
1187A-4R-2 70	49.67	0.68	15.45	9.57	0.17	9.01	12.87	1.70	0.07	0.08	967	954	0.19	109	99.66
1187A-5R-7 62	49.65	0.71	15.54	9.54	0.17	8.97	12.96	1.69	0.07	0.05	962	955	0.21	117	99.76
1187A-6R-7 102	49.94	0.78	15.55	9.66	0.16	8.92	12.97	1.79	0.07	0.05	964	963	0.21	110	100.32
1187A-7R-2 53	49.63	0.74	15.42	9.56	0.16	8.71	12.96	1.71	0.07	0.09	769	998	0.18	87	99.42
1187A-7R-5 106	50.12	0.71	15.45	9.47	0.15	8.76	12.90	1.69	0.07	0.04	881	960	0.20	112	99.76
1187A-8R-2 133	50.04	0.69	15.45	9.52	0.14	8.84	12.91	1.70	0.08	0.06	799	974	0.21	116	99.83
1187A-9R-6 103	50.20	0.75	15.47	9.50	0.18	9.01	12.92	1.69	0.08	0.07	930	960	0.20	109	100.26
1187A-10R-4 63	49.82	0.74	15.62	9.73	0.18	8.88	12.99	1.72	0.07	0.05	972	980	0.20	109	100.22
1187A-11R-2 1	50.05	0.74	15.61	9.69	0.17	8.82	12.98	1.70	0.07	0.05	961	1016	0.20	115	100.29
1187A-12R-1 145	49.98	0.73	15.61	9.71	0.17	8.81	12.95	1.73	0.08	0.04	945	1005	0.21	115	100.22
1187A-13R-6 39	50.16	0.73	15.61	9.68	0.18	8.92	12.84	1.74	0.07	0.07	951	993	0.19	109	100.39
1187A-14R-4 35	49.75	0.71	15.54	9.63	0.15	8.87	13.03	1.71	0.07	0.06	969	1021	0.20	111	99.94
1187A-15R-1 83	50.11	0.77	15.62	9.54	0.17	8.76	13.19	1.72	0.07	0.07	980	1012	0.22	111	100.46
1187A-16R-5 96	49.94	0.73	15.62	9.68	0.17	8.80	13.00	1.72	0.07	0.08	935	999	0.23	111	100.25
<b>Average 1187A</b>	<b>49.92</b>	<b>0.73</b>	<b>15.53</b>	<b>9.60</b>	<b>0.17</b>	<b>8.87</b>	<b>12.96</b>	<b>1.71</b>	<b>0.07</b>	<b>0.06</b>	<b>924</b>	<b>982</b>	<b>0.20</b>	<b>111</b>	<b>100.03</b> 245±7
Average 803D	50.09	1.26	14.44	11.60	0.22	7.72	12.11	2.13	0.13	0.09	n.a.	370	0.27	201	100.12
Average 807CA	49.83	1.69	14.13	12.07	0.24	7.14	11.71	2.38	0.20	0.12	n.a.	580	0.41	54	99.99
Average 807CC-G	50.56	1.14	13.93	11.93	0.23	7.35	11.76	2.15	0.11	0.09	n.a.	850	0.24	158	99.59
Average Malaita	50.37	1.63	13.57	12.90	0.22	6.49	11.07	1.72	0.18	0.11		600	0.91		99.23
Analysed VG-2	50.44	1.89	14.04	11.82	0.21	6.77	11.23	2.68	0.20	0.20	1549	270			99.66
Standard deviation	0.54	0.10	0.26	0.24	0.04	0.11	0.26	0.07	0.02	0.03	166	57			
VG-2 USINM†	50.81	1.85	14.06	11.84	0.22	6.71	11.12	2.62	0.19	0.20					99.62

All data are in wt% except where noted. Data for glasses from Sites 803 and 807 and from the Island of Malaita are from Michael (1999).

n.a., not analysed.

\* Saturation pressures were calculated using VolatileCalc 1.1 (Newman & Lowenstern 2002).

† Data from Jarosewich et al. (1979)



**Fig. 3.** (A)  $\text{H}_2\text{O}$  v.  $\text{K}_2\text{O}$  and (B)  $\text{H}_2\text{O}$  versus Mg number for OJP basaltic glasses. For comparison, the shaded fields show data for MORB from the Pacific-Nazca, Explorer and Juan de Fuca ridges (Michael 1995), and the dashed lines represent data from Sites 803 and 807, and the island of Malaita (Michael 1999).

$\text{P}_2\text{O}_5$ , and high  $\text{FeO}^{\text{T}}$ , consistent with derivation of OJP basaltic magmas by large degrees of partial melting (Mahoney *et al.* 1993; Michael 1999; Fitton & Godard 2004).

Pillow rim glasses from a given site have a very restricted range of composition, except at Site 1185, which has both high- and low-MgO glasses (Fig. 2). Within each of these two chemical types, however, the glasses are homogeneous. A similar homogeneity of composition was found at Sites 803 and 807 by Michael (1999), who noted that the OJP shows considerably less geochemical variability than is found in drilled sections of MORB. The homogeneity suggests that the lavas recovered from a given site (except Site 1185) may represent single large eruptions with multiple flows or lobes, resulting in multiple glass-bounded cooling units and interbedded sheet flows within a given hole. In contrast to the

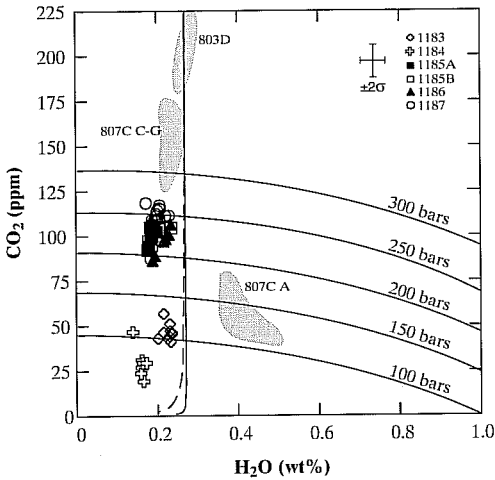
homogeneity observed for the pillow rim glasses from most sites, glass shards from the volcanoclastic sequence found at Site 1184 fall into three distinct compositional groups spanning a range of MgO contents (Fig. 2; see also fig. 4 of White *et al.* 2004).

Water concentrations are relatively low, similar to normal MORB (N-MORB) values, in all glass samples (Fig. 3A). Low-MgO glasses have slightly higher  $\text{H}_2\text{O}$  contents (average 0.22 wt%  $\text{H}_2\text{O}$ ) than high-MgO glasses (average 0.19 wt%), with the exception of Site 1184, where low-MgO glasses have lower  $\text{H}_2\text{O}$  (average 0.16 wt%; Fig. 3B). All glasses in Table 1 have very low amounts of molecular  $\text{H}_2\text{O}$  (mostly below detection), consistent with expectations for high-temperature equilibrium speciation in basaltic melts with low total  $\text{H}_2\text{O}$  (Dixon *et al.* 1995). Some of the glasses analysed had much higher molecular  $\text{H}_2\text{O}$  and anomalously high total  $\text{H}_2\text{O}$ , which we attribute to low-temperature hydration of the glass. These glasses were excluded from the data set in Table 1.

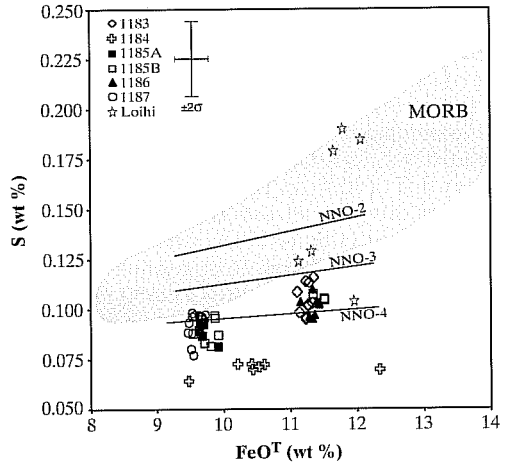
Carbon dioxide concentrations of OJP glasses average  $47 \pm 5$  ppm for Site 1183,  $30 \pm 9$  ppm for Site 1184,  $101 \pm 4$  ppm for Site 1185,  $99 \pm 7$  ppm for Site 1186 and  $110 \pm 7$  ppm for Site 1187 (Fig. 4). Using the method of Dixon *et al.* (1995), vapour saturation pressures were calculated for all sites (Table 1) and then converted into eruption depths (1 bar = 10 m of water depth) assuming that the volatiles were not supersaturated at the time of eruption. As expected, glass shards from the volcanoclastic deposits at Site 1184 have low saturation pressures, indicating an average quenching depth of approximately  $540 \pm 210$  m. Site 1183 glasses, which come from the shallowest water site on the crest of the plateau, also have relatively low saturation pressures of 107 bars (1070  $\pm$  90 m), whereas Sites 1185, 1186 and 1187 have saturation pressures of 215–245 bars, yielding estimated eruption depths of 2150–2450 ( $\pm 100$ ) m (Fig. 4). These estimated depths must be viewed with caution, however, because submarine basaltic pillow rims, particularly MORB samples, are typically supersaturated with  $\text{CO}_2$  (Dixon & Stolper 1995).

Compared with MORB, the OJP glasses have lower S (910  $\pm$  60 ppm for high-MgO glasses, 1030  $\pm$  60 ppm for low-MgO glasses) at comparable  $\text{FeO}^{\text{T}}$  (Fig. 5). Sulphur contents of MORB magmas are usually controlled by saturation with immiscible sulphide (Fe–S–O) liquid (Wallace & Carmichael 1992), so the lower S contents of OJP glasses suggest that OJP basaltic magmas may not have been saturated with immiscible sulphide liquid during crystallization. However, if OJP basaltic magmas had





**Fig. 4.**  $\text{CO}_2$  v.  $\text{H}_2\text{O}$  for OJP basaltic glasses. Shaded fields as in Figure 2. Vertical lines represent degassing paths for basaltic melts with initial  $\text{CO}_2$  contents of 225 ppm (solid line; value was chosen based on the maximum concentration in OJP glasses) and 2000 ppm (dashed line). Also shown are vapour-saturation curves for basaltic melts at pressures from 100 to 300 bars. All calculations were made using VolatileCalc 1.1 (Newman & Lowenstern 2002).

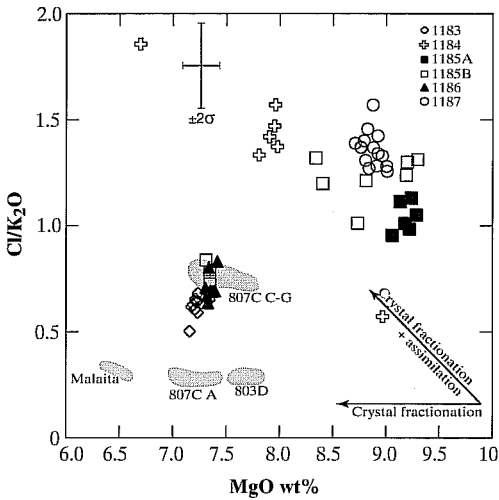


**Fig. 5.** S v.  $\text{FeO}^{\text{T}}$  for OJP basaltic glasses. The shaded field shows data for Pacific MORB glasses (MORB database, <http://petdb.ldeo.columbia.edu/petdb>), and small stars show Loihi glasses (Wallace & Carmichael 1992). Lines show 1 bar sulphide saturation limits for OJP basaltic melts at relative oxygen fugacities ranging from 2 (NNO-2) to 4 (NNO-4) log units more reduced than the Ni-NiO buffer. Saturation limits were calculated using the thermodynamic model of Wallace & Carmichael (1992) updated to incorporate the temperature dependence from Mavrogenes & O'Neill (1999).

lower oxygen fugacities than MORB, they could have been sulphide-liquid saturated because lower oxygen fugacity reduces the sulphur solubility in basaltic melts (Fig. 5). Measurements of the wavelength of the  $\text{S K}\alpha$  peak in the glasses indicate low oxygen fugacities ( $f_{\text{O}_2}$ ), broadly comparable to MORB values, but this technique lacks the precision at low  $f_{\text{O}_2}$  necessary to resolve whether the OJP glasses are more reduced than MORB (Wallace and Carmichael 1994). Ratios of S to other incompatible elements ( $\text{S}/\text{K}_2\text{O}$ ,  $\text{S}/\text{TiO}_2$ ) in the glass samples decrease slightly with decreasing MgO, consistent with some fractionation of sulphide liquid, but sulphides have not been observed in quenched glass samples and platinum-group element systematics show no evidence for sulphide-liquid fractionation (Chazey & Neal 2004). Given this contradictory evidence, the issue of whether or not OJP basaltic magmas were sulphide-liquid saturated remains unresolved at this time. The low S contents of OJP basalts are probably caused by the high degree of melting, which is estimated from major- and trace-element modelling to be approximately 30% (Fitton & Godard 2004). Such large degrees of melting would probably exhaust

residual sulphide in the mantle source during melting, in contrast to MORB magmas, which are generated by lower degrees of melting and probably form in equilibrium with residual mantle sulphide.

All OJP basaltic glasses have high Cl, and glasses from a given site are relatively uniform, except for Site 1184 (Table 1). Average values for each site are  $670 \pm 40$  ppm Cl (Site 1183),  $1470 \pm 600$  ppm (Site 1184),  $860 \pm 80$  ppm (Site 1185),  $750 \pm 70$  ppm (Site 1186) and  $980 \pm 25$  ppm (Site 1187). Melt inclusions in olivine from a high-MgO sample from Hole 1185A mostly have Cl contents (c. 900 ppm) similar to the glass, but some inclusions have lower Cl (c. 300 ppm; J. Roberge unpublished data). There is no correlation between Cl and  $\text{K}_2\text{O}$ , despite their similar incompatibility. OJP basaltic glasses are highly enriched in Cl relative to MORB, as was found previously for glasses from Sites 803 and 807 (Michael 1995). The cause of these very high Cl contents and their implications for OJP magmatic processes are discussed later.



**Fig. 6.** Cl/K<sub>2</sub>O v. MgO for OJP glasses showing the effects of crystal fractionation and assimilation of material with high Cl derived from a sea-water or brine component. Shaded fields as in Figure 2.

## Discussion

### Depths of crystallization

Basaltic glasses from the OJP preserve a record of quenched liquid compositions spanning a range of MgO contents, making them useful for constraining differentiation processes on the plateau. We estimated the composition of a primary magma by taking the most MgO-rich glass (9.3 wt% MgO; equilibrium olivine Fo<sub>86</sub>) and adding equilibrium olivine in 0.1 wt% increments until reaching a composition in equilibrium with mantle olivine of Fo<sub>91</sub>, a value that is constrained by modelling presented in Fitton & Godard (2004). This calculated primary magma contains 17.6 wt% MgO and requires addition of 27% olivine to the most MgO-rich glass. We modelled the liquid line of descent from this starting composition at a range of pressures (Fig. 2) using the MELTS program (Ghiorso & Sack 1995; Asimov & Ghiorso 1998). Previous modelling of crystallization used an assumed picritic composition with approximately 16 wt% MgO because of lack of information about primary magma compositions (Farnetani *et al.* 1996; Neal *et al.* 1997; Michael 1999).

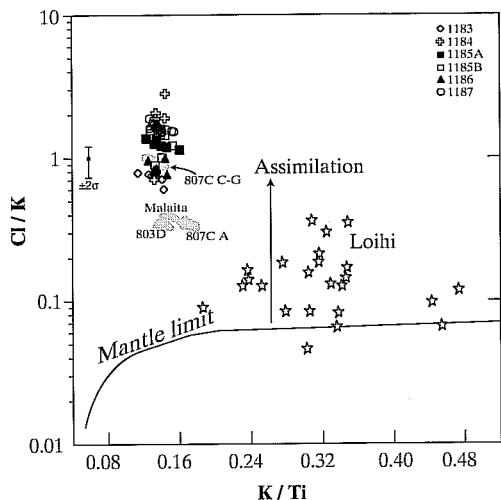
Equilibrium crystallization of the estimated primary magma (17.6 wt% MgO) at relatively low pressure (1 bar–2 kbar) yields residual liquids that match the compositions of OJP basalts (Fig. 2), in agreement with results based

on experimental phase equilibria (Sano & Yamashita 2004). These results indicate that derivation of OJP magmas from likely primary compositions could have occurred at low pressures within the upper crust. A similar conclusion was reached by Michael (1999) for glasses from Sites 803 and 807 using the crystallization program of Weaver & Langmuir (1990). These pressures are at the low end of the range found for MORB worldwide; specifically, they are similar to MORB from fast-spreading ridges and from robust slow-spreading ridges like the Kolbeinsey Ridge north of Iceland (Michael & Cornell 1998; Michael 1999). An alternative possibility is that crystallization took place in two stages, with crystallization of picritic liquids occurring first at deeper (e.g. Moho) levels followed by a second stage of crystallization in the upper crust (Farnetani *et al.* 1996; Michael 1999). However, as shown by Michael (1999), and reinforced by our results, no more than about 20–30% of crystallization of primary liquids could have happened at high pressures because the increase in clinopyroxene stability results in residual liquid compositions that do not match the observed values for OJP basalts. Thus, much of the crystallization of magmas parental to the erupted lavas must have occurred in shallow-level magma chambers, resulting in the formation of extensive volumes of cumulates within the OJP crust.

### Cause of high chlorine in Ontong Java Plateau basalts

Chlorine contents of normal MORB magmas are generally low (<50 ppm) reflecting low Cl in the upper-mantle source region (Michael & Cornell 1998). Like H<sub>2</sub>O, Cl is incompatible during partial melting in the mantle and crystallization of basaltic magmas (Schilling *et al.* 1980), so variations in Cl can be best understood by comparing them with other incompatible elements such as K (Fig. 6). The Cl/K ratio varies from below detection limits (c. 0.01) in normal MORB to approximately 0.07 in enriched MORB magmas (Michael & Cornell 1998). Both Cl contents and Cl/K ratios are highly sensitive to assimilation involving sea water or sea-water-derived brine because of their high Cl contents (Figs 6 and 7). Such assimilation is common in regions of the mid-ocean ridge system where magma chambers are relatively shallow, and in submarine oceanic islands (Michael & Cornell 1998; Kent *et al.* 1999).

The very high Cl contents of OJP basalts were first discovered by Michael (1999) from analyses



**Fig. 7.** Cl/K v. K/Ti showing the effect of contamination with hydrothermally altered materials containing sea water or sea-water-derived brines. Loihi data are from Kent *et al.* (1999). Uncontaminated MORB lavas generally plot below the line labelled 'mantle limit' (Michael & Cornell 1998; Michael 1999). K/Ti in MORB glasses generally correlates with La/Sm, and thus is an indicator of the relative enrichment or depletion of the mantle source (Michael & Cornell 1998). Shaded fields as in Figure 2.

of glasses from Sites 803 and 807. He attributed the high Cl to shallow-level assimilation, a hypothesis that we discuss further below. An alternative possibility is that the mantle source region for OJP basaltic magmas is enriched in Cl, perhaps by addition of subducted materials. It is well documented that mafic magmas associated with convergent plate margins have elevated Cl compared to MORB (Anderson 1974; Schilling *et al.* 1978; Ito *et al.* 1983). Elevated Cl contents are also found in back-arc basin basalts (e.g. Stolper & Newman 1994). However, basaltic magmas in oceanic islands with mantle source regions believed to contain a deeply recycled crustal component do not generally show elevated Cl/K compared to MORB, suggesting that this process does not strongly increase mantle Cl (Kent *et al.* 1999; Lassiter *et al.* 2002). Given this, and the observation that Sr–Nd–Pb–Hf isotope systematics of OJP basalts show little or no evidence of a recycled (enriched mantle (EM) or high  $\mu$ , where  $\mu = {}^{238}\text{U}/{}^{204}\text{Pb}$  (HIMU)) component (Tejada *et al.* 2004; next section), we think it is unlikely that the OJP source region contains elevated Cl relative to MORB and other ocean island basalt (OIB) mantle sources.

All OJP basaltic glasses have high Cl, so if this is caused by assimilation of material with a sea-water or brine component then such a process was a widespread phenomenon and relatively uniform in OJP magma chambers. It is possible to infer the composition of the contaminant by comparing Cl/K<sub>2</sub>O and H<sub>2</sub>O/K<sub>2</sub>O for basaltic glasses (Fig. 8) (Kent *et al.* 1999). The result suggests that the OJP basaltic magmas are typically contaminated with material that contains relatively concentrated brine with 50–60 wt% NaCl. Data from a few sites (803, 807 Unit C and 1184) indicate more or less concentrated brine. We find it remarkable that data from such geographically widespread sites all show evidence of interaction with brine of a similar composition. Interestingly, many of the contaminated basalts at the Loihi seamount also show evidence of interaction with similarly concentrated brine components, although the overall range of values at Loihi includes less concentrated brines and sea water as contaminants (Kent *et al.* 1999). It is important to note, however, that only very small amounts of this brine phase (<0.4 wt%) need to be incorporated to explain the range of variation in Cl/K<sub>2</sub>O and H<sub>2</sub>O/K<sub>2</sub>O for OJP basalts. Such small amounts are consistent with the hypothesis that the brine phase is present within inclusions and along grain boundaries in altered basalts that become assimilated (e.g. Michael & Schilling 1989).

Brines in subsurface hydrothermal systems form by high-temperature phase separation of sea water into gas plus a small amount of saline liquid (Bischoff & Rosenbauer 1987; Fournier 1987). One possibility is that OJP magmas became contaminated during eruption and transport on the seafloor, as magma moved through tube and/or sheet-flow systems. However, this is unlikely because the seafloor eruption pressures (<250 bars) for most sites (estimated from glass CO<sub>2</sub> data) are too low for brines with 50–60 wt% NaCl to form by phase separation (Fournier 1987). Moreover, contamination during eruption would be expected to result in a much wider variation of Cl contents. A more likely possibility is that the contamination occurred in well-mixed subsurface magma chambers. Fluid inclusions from ophiolites and altered mid-ocean ridge gabbros contain as much as 52 wt% NaCl (Kelley & Delaney 1987; Nehlig 1991), but the highest NaCl contents found for vent fluids are only about twice the sea water value of 3.5 wt% (Von Damm & Bischoff 1987). Owing to the difference in density of the saline fluid and gas that form during phase separation of sea water, hydrothermal systems commonly form layered

systems in which brine underlies fluid. However, mixing of these layers and further mixing with sea water probably occurs as fluids move to the seafloor, which might explain why high-salinity fluids have not been discovered at seafloor vents.

Formation of brine with >50 wt% NaCl by phase separation of sea water requires pressures greater than 250 bars and temperatures higher than 450°C (Fournier 1987; Nehlig 1991), which is consistent with contamination occurring either in the conduit system or in a shallow magma reservoir. The highest temperatures observed for hydrothermal fluids (*c.* 420°C; Berndt & Seyfried 1997) is believed to be limited by rock properties because at temperatures higher than about 450°C quasi-plastic behaviour closes off permeability (Fournier 1987). Higher temperatures for hydrothermal fluids are only possible if repeated magmatic intrusions pre-heat the surrounding wallrocks and repeated fracturing of the hot rock allows water to circulate (Fournier 1987). Given the large volume of OJP lava flows and the presumed large volumes and frequent magmatic recharge of subseafloor reservoirs, these conditions may be quite common, creating rocks surrounding the magma reservoirs with concentrated brine in fractures and along grain boundaries. Only small amounts of brine are needed to explain the Cl and H<sub>2</sub>O data. The very homogeneous nature of large volume flows on the OJP suggests convective homogenization in magma chambers during crystal fractionation, so this might explain the observation that glasses from a given site are rather uniformly contaminated.

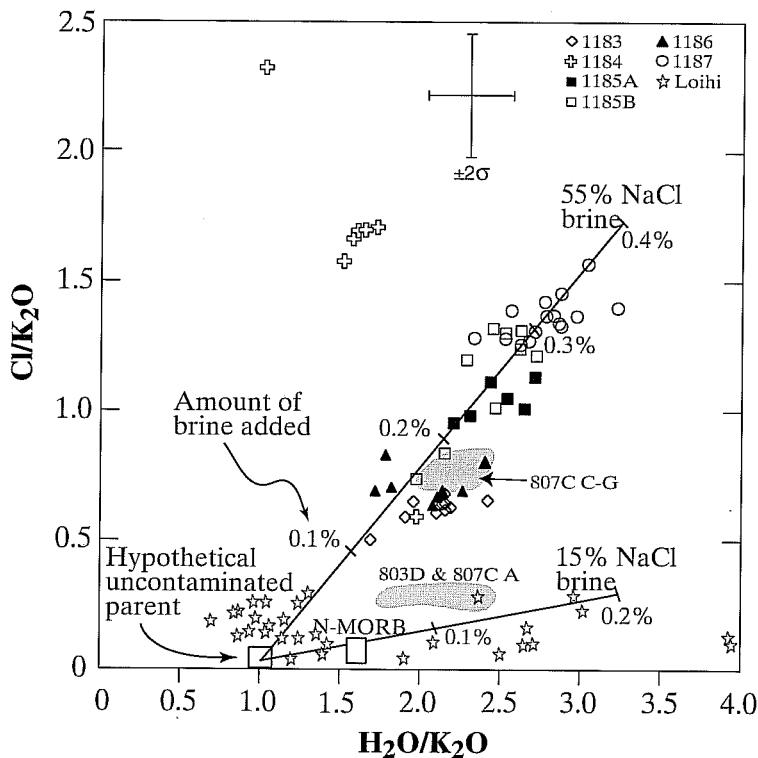
A final possibility is that the saline brines have a magmatic origin rather than being formed by phase separation of sea water (Nehlig 1991). Fractionation of olivine, plagioclase and clinopyroxene are required to derive the uniformly fractionated composition of OJP basalts from likely parent compositions, so enormous volumes of crystal mush must have been present within the OJP crust. Continued crystallization of crystal mush zones underlying magma chambers would result in exsolving H<sub>2</sub>O–CO<sub>2</sub>–Cl–S fluids that are relatively H<sub>2</sub>O-rich. A brine with 50–60 wt% NaCl could form from this fluid phase under a wide range of conditions (from 450 to 550°C and *c.* 400 bars to temperatures higher than 1000°C at pressures greater than 1.6 kbar; Fournier 1987). However, given that Cl isotopes in MORB glasses indicate that the brine contaminant in mid-ocean ridge environments is derived from sea water (Magenheim *et al.* 1997), and the likelihood of large hydrothermal systems associated with OJP magma chambers, we think it is more plausible that the brine

contaminants in the OJP were derived from sea water.

Glass shards from the shallow-water hydroclastic volcanic deposits at Site 1184 are anomalous in terms of Cl/K<sub>2</sub>O and H<sub>2</sub>O/K<sub>2</sub>O (Fig. 8). Their composition could be explained either by contamination involving a very concentrated brine or partial degassing of H<sub>2</sub>O during shallow-water eruption and quenching. The latter seems unlikely because the shards still contain some CO<sub>2</sub>, which has much lower solubility than H<sub>2</sub>O and should therefore be totally degassed before any significant H<sub>2</sub>O is lost. Disequilibrium degassing caused by the slower diffusion of CO<sub>2</sub> in the melt relative to H<sub>2</sub>O might allow H<sub>2</sub>O to be exsolved while CO<sub>2</sub> is retained, but such partial degassing of H<sub>2</sub>O is difficult to reconcile with the constant H<sub>2</sub>O/K<sub>2</sub>O and H<sub>2</sub>O/TiO<sub>2</sub> of most of the shards. Brines with >60 wt% NaCl would be difficult to form in hydrothermal systems for reasons of temperature and quasi-plastic rock behaviour, as discussed above. However, at the low hydrostatic pressures at the seafloor and upper part of the conduit system for this shallow-water eruption, contact of hot magma with sea water could cause flash vaporization of sea water to form either gas plus solid salt or gas plus highly saline brine (>80 wt% NaCl; Fournier 1987). Thus, contamination of the magma erupted at Site 1184 could possibly have happened in the very shallow conduit system. If so, one would expect this to be a common process in shallow-water hydrovolcanic eruptions, but we are not aware of Cl-rich glass shards having been reported from other such deposits.

#### *Water in the mantle source region for Ontong Java Plateau basaltic magmas*

Ocean island basaltic magmas typically have higher H<sub>2</sub>O than depleted MORB, suggesting that the excess magmatism associated with mantle plumes could be caused in part by the effect of H<sub>2</sub>O on mantle melting (Schilling *et al.* 1980; Bonatti 1990; Nichols *et al.* 2002). The higher H<sub>2</sub>O content of mantle-plume-derived magmas could result from either the involvement of undegassed primitive mantle (with high <sup>3</sup>He/<sup>4</sup>He) or deep recycling of subducted oceanic crust and sediments back into the mantle. The presence of such recycled lithospheric components in the source regions of mantle-plume-related basalts has been recognized on the basis of radiogenic Pb, Nd and Sr isotopes in some OIBs (Hofmann 1997). However, based on a detailed comparison of H<sub>2</sub>O in plume-influenced



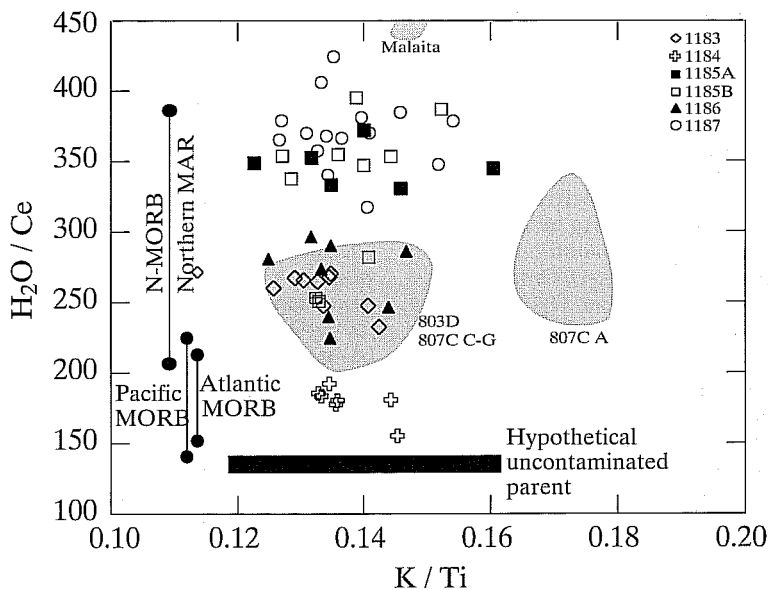
**Fig. 8.**  $\text{Cl}/\text{K}_2\text{O}$  v.  $\text{H}_2\text{O}/\text{K}_2\text{O}$  for basaltic glass from OJP. Lines show expected trends of composition for mixing between basaltic melt and small amounts of brine containing 15 and 55 wt% NaCl. The proportion of brine added (also in wt%) is noted by small tick marks along the lines. Loihi data are from Kent *et al.* (1999). Shaded fields as in Figure 2.

MORB glasses, it appears that basalts associated with mantle plume components containing recycled subducted lithosphere contain less  $\text{H}_2\text{O}$  than those without recycled components (Dixon *et al.* 2002). The likely explanation for this is that lithospheric components are efficiently dehydrated during subduction so that they are relatively poor in  $\text{H}_2\text{O}$ .

Before using the OJP glasses to constrain mantle volatile contents for the Ontong Java plume, it is important to ascertain whether significant  $\text{H}_2\text{O}$  was lost by degassing prior to eruption and quenching of the glass. Given the estimated pressures of eruption, the relatively low  $\text{H}_2\text{O}$  contents and the presence of  $\text{CO}_2$ , which has much lower solubility, it is unlikely that any significant loss of  $\text{H}_2\text{O}$  occurred before eruption. Closed-system degassing calculations (Fig. 4) suggest that less than 10% of the original primary  $\text{H}_2\text{O}$  would be lost by degassing, even if the primary magmas contained relatively high initial  $\text{CO}_2$ . However, the Cl and  $\text{H}_2\text{O}$  data (Fig. 8) show that assimilation

involving brine has increased the  $\text{H}_2\text{O}$  content of all OJP basaltic glasses, including those previously analysed from Sites 803 and 807. The effect of this enrichment in  $\text{H}_2\text{O}$  must be considered before making an assessment of mantle source concentrations.

To estimate the  $\text{H}_2\text{O}$  content of the uncontaminated parent magma, we assume that it had  $\text{Cl}/\text{K}$  of 0.03 ( $\text{Cl}/\text{K}_2\text{O} = 0.025$ ), intermediate between the values for uncontaminated normal (N-MORB) and enriched MORB. The basis for this assumption is that OJP basalts have incompatible-element abundances intermediate between those of N-MORB and many oceanic island tholeiites (Tejada *et al.* 1996; see also fig. 6 in Fitton & Godard 2004). Given the relations between  $\text{Cl}/\text{K}_2\text{O}$  and  $\text{H}_2\text{O}/\text{K}_2\text{O}$  for OJP basalts (Fig. 8), this requires that the parental magmas have  $\text{H}_2\text{O}/\text{K}_2\text{O}$  of approximately 1. Thus, for the high-MgO glasses, uncontaminated magmas would contain about 0.07 wt%  $\text{H}_2\text{O}$ . This is at the very low end of the range for N-MORB glasses that show no evidence of brine



**Fig. 9.**  $\text{H}_2\text{O}/\text{Ce}$  v.  $\text{K}/\text{Ti}$  for OJP basaltic glasses. Shown for comparison are  $\text{H}_2\text{O}/\text{Ce}$  ranges for MORB glasses from various regions (MAR, Mid-Atlantic Ridge). The horizontal black bar shows the  $\text{H}_2\text{O}/\text{Ce}$  ratio estimated as described in the text for uncontaminated OJP magmas. Shaded fields as in Figure 2.

contamination (Michael 1995; Michael & Cornell 1998). Using the large degrees of mantle melting estimated for OJP basalts (*c.* 30%; Fitton & Godard 2004), an estimate of 27% crystallization to get from a primary composition in equilibrium with mantle olivine to the high-MgO glasses, and a partition coefficient of 0.01 for  $\text{H}_2\text{O}$  (Michael 1995), we calculate a source region  $\text{H}_2\text{O}$  concentration of  $170 \pm 30$  ppm. This value is similar to the estimate for the depleted upper-mantle source for N-MORB ( $140 \pm 40$  ppm  $\text{H}_2\text{O}$ ) and much lower than estimates for enriched MORB sources ( $350 \pm 100$  ppm  $\text{H}_2\text{O}$ ; Michael 1988). Given the very low  $\text{H}_2\text{O}$  content inferred for the OJP mantle source, the large extents of melting (*c.* 30%) inferred from major- and trace-element data must have been caused by high mantle temperatures ( $>1500^\circ\text{C}$ ; Fitton & Godard 2004). Water does not appear to play a role in promoting large degrees of melting for the OJP.

To understand  $\text{H}_2\text{O}$  in mantle source regions it is useful to compare  $\text{H}_2\text{O}/\text{Ce}$  ratios because these elements have a similar incompatibility to one another during mantle melting and fractional crystallization (Michael 1995). Using our estimate of the  $\text{H}_2\text{O}$  content of high-MgO magmas at Sites 1185A and 1187 before contamination, and whole-rock Ce values (Fitton & Godard 2004; whole rock and glass from these

sites have identical  $\text{K}_2\text{O}$  and  $\text{TiO}_2$ , consistent with a very low phenocryst content), we calculate  $\text{H}_2\text{O}/\text{Ce}$  to be 135 for uncontaminated OJP basalts (Fig. 9). However, it is difficult to know the uncertainty in this value because it is essentially based on our assumption that uncontaminated  $\text{Cl}/\text{K}$  is 0.03 for these samples. Mean values of  $\text{H}_2\text{O}/\text{Ce}$  for Pacific MORB glasses with  $\leq 20$  ppm Ce (to exclude highly enriched samples) are  $145 \pm 12$  (Galapagos Spreading Centre),  $150 \pm 10$  (Easter microplate),  $180 \pm 37$  (Explorer and Juan de Fuca ridges),  $189 \pm 19$  (Pacific–Nazca Ridge) and  $194 \pm 44$  (East Pacific Rise; Michael 1995; Simons *et al.* 2002). Southern Mid-Atlantic Ridge MORB have comparable values ( $183 \pm 30$ ; Michael 1995), but MORB from the northernmost Mid-Atlantic Ridge and from around Iceland have distinctly higher values of 220–380 (Michael 1995). Our results suggest that  $\text{H}_2\text{O}/\text{Ce}$  for uncontaminated OJP basalts is at the low end of the range for Pacific MORB glasses.

Incompatible trace elements and Sr–Nd–Pb–Hf isotopic characteristics of the volumetrically dominant OJP basalt type (Kwaimbaita-type, named from occurrences in the Solomon Islands) show that they come from a mantle source region that is distinct in composition from the upper-mantle source for Pacific MORB, and there is no evidence for mixing

involving a MORB end member (Tejada *et al.* 1996, 2004). Mixing involving an EM-1-like recycled lithospheric component can explain OJP isotopic ratios, but the homogeneity of major- and trace-element data for the OJP basalts shows no evidence of such mixing between several end members (Tejada *et al.* 2004). If an EM-1-like component was involved, the proportion of this recycled component would be very small (J. Mahoney pers. comm.). The OJP basalts are also isotopically distinct from the common mantle component (focus zone (FOZO) or common mantle component (C)) for OIBs (Hauri *et al.* 1994; Hanan & Graham 1996), which Simons *et al.* (2002) suggest has  $H_2O/Ce$  of approximately 210. The simplest explanation that accounts for both trace-element and isotopic data is that the OJP basalts were derived from a primitive mantle source that underwent a minor fractionation event (removal of *c.* 1% partial melt) at approximately 3 Ga (Tejada *et al.* 2004). A partial melting event would not significantly fractionate  $H_2O$  from Ce because of their similar incompatibility. Our results suggest that there is a major Pacific mantle reservoir, probably in the lower mantle, that has  $H_2O/Ce$  lower than most Pacific and all Atlantic MORB, and lower than the common mantle plume component for OIBs. Alternatively, if the OJP source region does contain an EM-1-like recycled component, then the lower  $H_2O/Ce$  relative to most Pacific MORB could be caused by the near-total dehydration of this component during subduction, as has been inferred for other EM-plumes like Hawaii (Dixon *et al.* 2002).

#### *Volatile release to the environment during formation of the Ontong Java Plateau*

OJP basaltic lavas sampled at DSDP/ODP drill sites and on land in the Solomon Islands were all erupted well below sea level, except for the volcanoclastic deposits erupted in shallow water at Site 1184 (Mahoney *et al.* 2001). Even at Site 1183, which lies on the crest of the main plateau and should have originally had the greatest elevation, pillow lava rims are poorly vesicular and  $CO_2$  contents of the glass indicate eruption at about 1100 m water depth. Because nearly all of the plateau formed at substantial water depths, there would have been limited release of environmentally important volatiles such as S, Cl and F compared to subaerial flood basalt provinces or oceanic plateaus that formed subaerially, like the Kerguelen Plateau. High hydrostatic pressure during deep submarine eruptions

and low magmatic  $H_2O$  contents would result in very little vesiculation, and these volatiles would have remained quenched in glassy pillow rims or would have entered accessory phases like sulphide during crystallization of pillow and sheet-flow interiors. In contrast, the very low solubility of  $CO_2$  in silicate melts would result in most of the primary magmatic  $CO_2$  being degassed even during deep-water eruptions or intrusive solidification.  $CO_2$  released into the ocean would also affect atmospheric  $CO_2$  given that the ocean-atmosphere system equilibrates on a geologically short timescale.

If OJP basaltic magmas contained as much  $CO_2$  as other tholeiitic basalts derived from mantle plumes (Kilauea, Reunion), then the magmas may have contained as much as 7000 ppm  $CO_2$  (Bureau *et al.* 1999; Gerlach *et al.* 2002). Given a crustal volume of approximately  $5 \times 10^7 \text{ km}^3$  (Coffin & Eldholm 1993), formation of the OJP could have released a maximum of about  $1 \times 10^{21} \text{ g } CO_2$ . However, the time period over which the plateau was formed is poorly constrained. Isotopic data ( $^{40}\text{Ar}$ - $^{39}\text{Ar}$  and Re-Os) suggest that the uppermost part of the plateau formed over about 1 Ma or less (Chambers *et al.* 2002; Parkinson *et al.* 2002), but whether more deeply buried extrusive and intrusive rocks formed over a longer period of time is unknown. If most of the volume of the plateau formed during a 1 Ma time period, then the annual  $CO_2$  flux would have been approximately  $1 \times 10^{15} \text{ g } CO_2 \text{ year}^{-1}$ , equivalent to about 10 times the annual  $CO_2$  flux from the global mid-ocean ridge system. Note that we have made assumptions about magma  $CO_2$  content and eruption duration for the plateau that make our estimate for  $CO_2$  flux during formation of the OJP a maximum value.

Another major uncertainty in assessing the environmental effects of plateau formation and volatile release is lack of information on the magnitude and extent of hydrothermal systems associated with shallow-crustal magma chambers. Basalts recovered from the OJP show only relatively minor, low-temperature alteration, and there is no evidence from recovered materials or on-land sections for extensive hydrothermal alteration like that associated with mid-ocean ridge volcanism (Mahoney *et al.* 2001). This is likely to be due to the limited sampling of the plateau rather than an absence of such hydrothermal activity because the large volume and fractionated nature of OJP basalts both suggest the existence of large, relatively shallow-crustal magma reservoirs. These large hydrothermal systems are important for leaching metals from basalt and releasing them to the

ocean. Most importantly for assessing volatile release, hydrothermal systems precipitate carbonate and sulphate minerals in veins in altered basalt, resulting in significant transfer of C and S from sea water to altered crust. The magnitude of this transfer can be large, as there is good evidence from the oceanic crust that hydrothermal systems associated with mid-ocean ridge volcanism consume as much or more C and S from sea water than they release from magmatism (Staudigel *et al.* 1989; Alt & Teagle 1999).

## Conclusions

Submarine basaltic glasses from five widely separated sites on the Ontong Java Plateau all have relatively low H<sub>2</sub>O contents (0.16–0.24 wt%) that are similar to N-MORB values. In contrast, Cl contents and Cl/K ratios of the glasses are very high compared with MORB, probably as a result of assimilation involving small amounts of relatively concentrated brine. Such brines could have formed by high-temperature phase separation of sea water in large hydrothermal systems associated with shallow-crustal magma chambers on the OJP, and were stored in fractures and along grain boundaries of rocks that were assimilated by crystallizing magmas. The existence of large, upper-crustal magma chambers on the OJP is supported by crystal fractionation modelling, which shows that relatively low pressures (1 bar–2 kbar) are required to derive OJP basalts from likely primary magmas.

Ratios of H<sub>2</sub>O to Ce, which have similar incompatibility to each other, are higher than most depleted and enriched MORB. However, positive correlation between H<sub>2</sub>O/K<sub>2</sub>O and Cl/K<sub>2</sub>O in the glasses suggests that magmatic H<sub>2</sub>O contents were increased by the same assimilation process that results in high Cl. Therefore, the high H<sub>2</sub>O/Ce values of the glasses are probably an artifact of contamination. The water content of the high MgO-magmas before contamination is estimated to be approximately 0.07 wt% H<sub>2</sub>O, corresponding to H<sub>2</sub>O/Ce of 135 for OJP basalts, a value at the low end of the range for Pacific MORB. There is no evidence for high H<sub>2</sub>O contents that would have significantly increased extents of mantle melting beneath the OJP, and the estimated H<sub>2</sub>O content of the OJP mantle source region (170 ± 30 ppm H<sub>2</sub>O) is similar to that of the depleted MORB source (140 ± 40 ppm H<sub>2</sub>O). Large extents of melting beneath the OJP must have been caused by a relatively high mantle potential temperature, consistent with upwelling of a hot mantle plume.

OJP glasses have lower S (910–1030 ppm) at comparable FeO<sup>T</sup> than MORB glasses. This indicates that OJP basaltic magmas could not have been saturated with immiscible sulphide liquid during crystallization unless they had significantly lower oxygen fugacities than MORB. Available data from measurements of S K $\alpha$  peak positions in the glasses show that oxygen fugacities of OJP magmas are relatively low, but this technique does not offer the precision necessary to resolve whether OJP magmas are more reduced than MORB magmas. Small decreases in S/K<sub>2</sub>O and S/TiO<sub>2</sub> with decreasing MgO require some sulphide fractionation, but sulphides have not been observed in quenched glass samples, and platinum-group element systematics show no evidence for sulphide liquid fractionation. The low S contents of OJP basalts are probably caused by the high degree of melting (*c.* 30%) of the OJP source. Such large degrees of melting would probably exhaust residual sulphide in the mantle source during melting, in contrast to MORB magmas, which are generated by lower degrees of melting and probably form in equilibrium with residual mantle sulphide.

Because nearly all of the OJP formed at substantial water depths, there would have been limited release of environmentally important volatiles such as S, Cl and F compared to subaerial flood basalt provinces or oceanic plateaus that formed subaerially. However, the very low solubility of CO<sub>2</sub> in silicate melts would result in most CO<sub>2</sub> being degassed even during deep-water eruptions or intrusive solidification. The magnitude of CO<sub>2</sub> released during formation of the OJP is difficult to assess due to lack of information on primary magmatic CO<sub>2</sub> contents and magma output rates, but we estimate a maximum possible value that is about 10 times the annual CO<sub>2</sub> flux from the global mid-ocean ridge system.

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