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4. DATA REPORT: VOLATILES IN SUBMARINE BASALTIC GLASSES FROM THE AUSTRALIAN ANTARCTIC DISCORDANCE (ODP LEG 187)[1]

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INTRODUCTION

Basaltic lavas recovered from the Australian Antarctic Discordance (AAD) during Leg 187 provide a valuable record of mantle dynamics, mantle melting, and crustal formation in this unusual region of the global mid-ocean spreading system. In this paper, we report dissolved volatile (H_2O, CO_2, S, and Cl) concentrations of unaltered glass rims from submarine pillow basalts. The analyzed glasses come from 12 Leg 187 sites that include both Pacific Ocean (Sites 1153, 1154, 1158, and 1160) and Indian Ocean (Sites 1152, 1156, 1157, 1159, and 1161) isotopic types (Christie, Pedersen, Miller, et al., 2001; D. Christie, pers. comm., 2003). Detailed interpretation of these data and a comparison with recent on-axis Indian- and Pacific-type basaltic glasses from the AAD will be presented elsewhere (L.V. Danyushevsky et al., pers. comm., 2003).

ANALYTICAL METHODS

For analysis of volatiles, we selected glass chips that were visually free of alteration or hairlike tubules that are the result of microbial alteration (e.g., Fisk et al., 1998). 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 ±2 µm.

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Total H_2O and CO_2 (present as carbonate [CO_3^{2-}]) were measured for 27 glass samples using Fourier transform infrared (FTIR) spectroscopy. We used a Nicolet Magna 560 FTIR spectrometer interfaced with a Spectra-Tech Nic-Plan microscope at Texas A&M University (USA) to obtain transmission IR spectra. Two individual spectra, taken on different areas of each glass sample, were acquired using a circular aperture 100 µm in diameter.

Band assignments for dissolved water and carbonate in basaltic glass are based on Dixon et al. (1995). Quantitative measurements of dissolved total H_2O, molecular H_2O, and carbonate (CO_3^{2-}) were obtained using Beer's law:

$$c = (\mathrm{M} \times \mathrm{A})/(\rho \times d \times \varepsilon)$$

where

c = concentration (weight fraction) of the absorbing species,
M = molecular weight of H_2O (18.02) or CO_2 (44.00),
A = absorbance intensity of the band of interest,
ρ = room-temperature density of the basaltic glass (2800 kg/m^3 was used for all glasses),
d = thickness of the glass wafer, and
ε = molar absorption coefficient.

Total dissolved H_2O was measured using the intensity of the band centered at 3550 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-cm^{-1} band. The total dissolved water contents (Table **T1**) were calculated using a molar absorption coefficient of 63 ± 3 L/(mol·cm) from Ihinger et al. (1994).

T1. Volatile and minor element concentrations, p. 8.

We examined all spectra for the presence of dissolved molecular H_2O (1630 cm^{-1}). However, all glasses in Table **T1** have molecular H_2O concentrations that are below the detection limit (~0.05 wt%), consistent with expectations for high-temperature equilibrium speciation in basaltic melts with low total H_2O (Dixon et al., 1995).

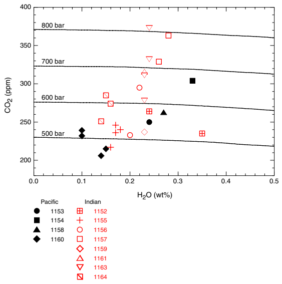
Dissolved carbonate was measured from the absorbance of the 1515- and 1430-cm^{-1} bands, which correspond to distorted asymmetric stretching of carbonate groups (Ihinger et al., 1994). Because the shape of the background in the region of the carbonate doublet is complex, it is necessary to subtract a carbonate-free reference spectrum to obtain a flat background (Dixon et al., 1995). The molar absorptivity for carbon dissolved as carbonate in basaltic glasses is compositionally dependent (Dixon and Pan, 1995). Dissolved carbonate contents (reported in Table **T1** and hereafter as the equivalent amount of CO_2, in ppm) were determined using a molar absorption coefficient of 350 ± 8 L/(mol·cm), calculated from the average composition of the glasses and the linear equation reported by Dixon and Pan (1995). Based on replicate analyses, average precision (±2σ) of the total H_2O measurements is ±8% and average precision for the carbonate analyses is also ±8%. Accuracy with these techniques is estimated to be ±10% for total H_2O and ±20% for CO_2 (Dixon and Clague, 2001).

For all glass chips analyzed by FTIR, Cl, S, K, and Ti were measured using a Cameca SX-50 electron microprobe at Texas A&M University using mineral and glass standards (Table T1). Chlorine was analyzed using procedures similar to those described in Michael and Cornell (1998). The electron beam was set at 15 kV, 100 nA, and a beam diameter of ~20 µm. Counting times were 200 s on peak and 200 s on background for each analyzed location. The values reported in Table T1 are the averages of analyses of five spots on each glass chip. Precision for the analyses was ±8 ppm (1σ). Sulfur, K, and Ti were also analyzed using 100-nA sample current and 200-s on-peak counting time. For S, we used an anhydrite standard and a K_α wavelength offset measured on pyrite, which corresponds approximately to the $S^{6+}/\Sigma S$ ratio expected for a basaltic glass equilibrated at the fayalite-magnetite-quartz (FMQ) oxygen buffer (Wallace and Carmichael, 1994). Analyses of glass standard VG-2 using this procedure yielded a S concentration of 0.147 wt%, slightly higher than the long-term average for VG-2 (0.137 ± 0.006 wt%) measured on the Texas A&M University probe using a lower sample current (10 nA instead of 100 nA). The lower value is similar to that reported for VG-2 by Dixon et al. (1991) and Dixon and Clague (2001).

RESULTS

Total H_2O contents of the glasses vary from 0.10 to 0.35 wt%, and the range of values is similar for both Indian- and Pacific-type glasses (Fig. F1). All H_2O contents are within the range typical for normal mid-ocean ridge basalt (N-MORB) glasses (e.g., Michael, 1995). CO_2 concentrations vary from 206 to 373 ppm and show a weak positive correlation with H_2O, although we note that there is a considerable range of CO_2 at a given H_2O (Fig. F1). Vapor saturation pressures calculated from the H_2O and CO_2 data vary from 450 to 810 bar (Newman and Lowenstern, 2002). Original eruption depths for the Leg 187 AAD glasses were probably mostly between 3300 and 4000 m below sea level based on sample recovery depths, the approximate age of basalts at each site (Christie, Pedersen, Miller, et al., 2001), and expected subsidence for oceanic lithosphere (Hayes, 1988). Given these depths and the range of vapor saturation pressures from the H_2O and CO_2 data, the basaltic magmas sampled in the Leg 187 cores would all have been supersaturated with CO_2 at the time of eruption and quenching. This is common for MORB basaltic magmas and occurs because ascent times from subridge magma chambers to the seafloor are relatively short compared to the time needed for CO_2 to diffuse through the melt to the sparse vapor bubbles in the melt (Dixon et al., 1995).

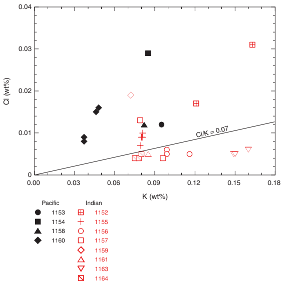
F1. H_2O vs. CO_2, p. 6.



Sulfur contents for Indian-type glasses average 1060 ± 110 ppm and those for Pacific-type glasses average 1280 ± 110 ppm. On a diagram of FeO^T vs. S (not shown; FeO^T data are from V. Balzar, C. Russo, and D. Christie, unpubl. data), the S contents for both types of glasses are similar to N-MORB values (Wallace and Carmichael, 1992). The S contents of MORB glasses are usually controlled by saturation with immiscible Fe-S-O liquid, so this similarity suggests that the AAD basaltic magmas were sulfide liquid–saturated at the time of eruption.

The range of Cl contents varies from 40 to 310 ppm for both Indian- and Pacific-type Leg 187 glasses (Fig. F2). These values are more variable and mostly much higher than the Cl contents (65 ppm Cl) (Michael and Cornell, 1998) of recent on-axis volcanism along the AAD. Chlorine behaves as an incompatible element during mantle melting and crystallization of basaltic magmas (Schilling et al., 1980), so variations in Cl can best be understood by comparing them with other incompat-

F2. K vs. Cl, p. 7.



ible elements such as K. Cl/K ratios vary from 0.03 to 0.19 for Leg 187 Indian-type glasses and 0.03 to 0.34 for Pacific-type glasses (Fig. F2). This ratio is sensitive to assimilation of hydrothermally altered material (Michael and Cornell, 1998), with Cl/K ranging from below detection limits (~0.01) in N-MORB to ~0.07 in enriched MORB (E-MORB) magmas that have not been affected by assimilation. The high Cl/K values for both Indian- and Pacific-type glasses indicate that assimilation during shallow level crystallization was relatively common along the AAD from 18 to 28 Ma (ages from Christie, Pedersen, Miller, et al., 2001), in contrast to the recent on-axis volcanism, for which most samples show no evidence of assimilation (Michael and Cornell, 1998).

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Figure F1. H_2O vs. CO_2 for AAD basaltic glasses in Table T1, p. 8. Lines show the H_2O and CO_2 contents of vapor-saturated basaltic melts at 500–800 bar and 1150°C (Newman and Lowenstern, 2002).

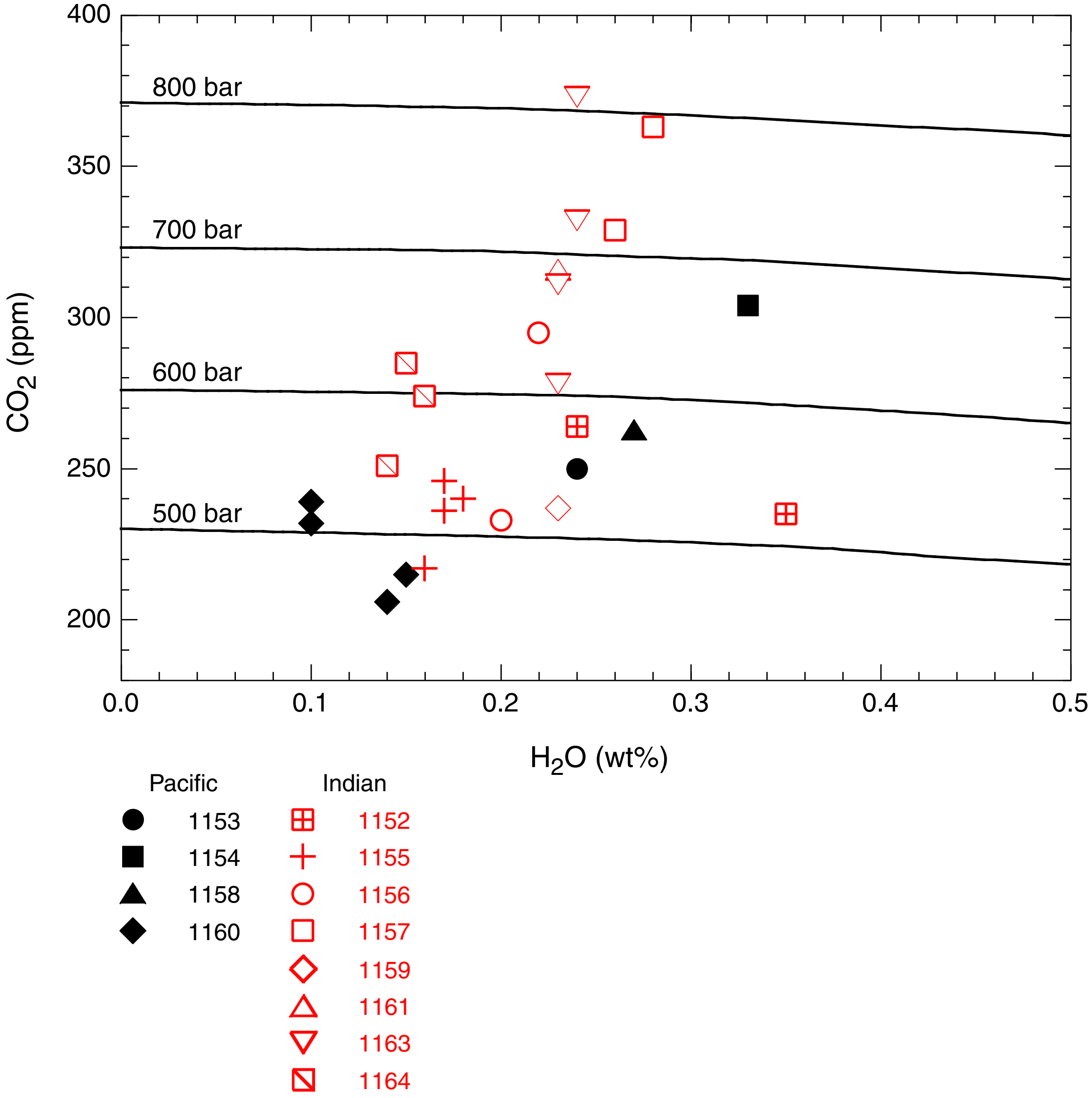

Figure F2. K vs. Cl for AAD basaltic glasses in Table T1, p. 8. Line shows the upper limit of Cl/K (= 0.07) for MORB magmas that have not been affected by assimilation of material with seawater-derived Cl (Michael and Cornell, 1998). Samples plotting above this line have likely been affected by such contamination.

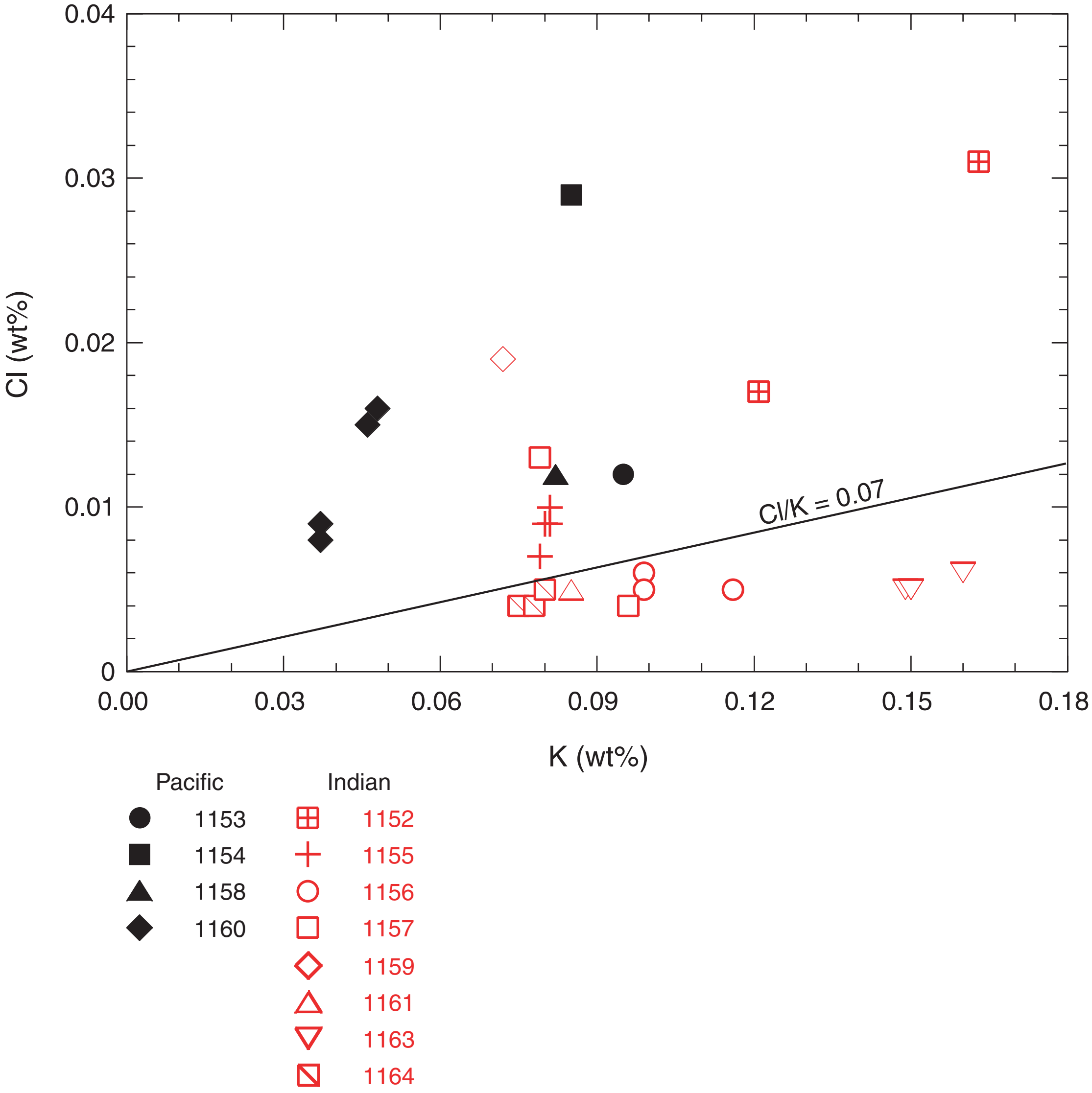

Table T1. Volatile and minor element concentrations in basaltic glasses.

Hole, core, section, interval (cm)	Volatiles				Minor elements (wt%)	
	H_2O (wt%)	CO_2 (ppm)	Cl (wt%)	S (wt%)	Ti	K
187-						
1152A-1R-1, 35–39	0.35	235	0.031	0.131	1.259	0.163
1152B-3R-1, 2–4	0.24	264	0.017	0.117	0.999	0.121
1153A-8R-1, 101–102	0.24	250	0.012	0.128	1.144	0.095
1154A-4R-1, 69–73	0.33	304	0.029	0.147	1.376	0.085
1155B-2R-1, 66–68	0.18	240	0.010	0.103	0.744	0.081
1155B-7R-1, 7–10	0.17	246	0.007	0.099	0.726	0.079
1155B-8R-2, 0–5	0.17	236	0.009	0.102	0.740	0.081
1155B-9R-1, 26–28	0.16	217	0.009	0.097	0.728	0.080
1156A-2R-3, 133–136	0.20	233	0.006	0.101	0.831	0.099
1156B-4R-1, 1–3	0.22	295	0.005	0.107	0.904	0.116
1156B-4R-1, 102–106	0.21	237	0.005	0.099	0.831	0.099
1157A-3R-1, 25–29	0.28	363	0.013	0.138	1.205	0.079
1157B-2R-1, 55–56	0.26	329	0.004	0.104	1.013	0.096
1158B-4R-1, 34–38	0.27	263	0.012	0.133	1.216	0.082
1159A-6R-2, 55–57	0.23	237	0.019	0.129	1.079	0.072
1160B-1W-1, 8–14	0.10	232	0.008	0.114	0.652	0.037
1160B-3R-1, 0–2	0.15	215	0.016	0.127	0.834	0.048
1160B-3R-1, 7–16	0.14	206	0.015	0.129	0.819	0.046
1160B-6R-2, 5–8	0.10	239	0.009	0.114	0.664	0.037
1161A-3R-1, 68–69	0.23	316	0.005	0.101	0.872	0.085
1163A-3R-1, 135–142	0.24	373	0.006	0.101	0.883	0.160
1163A-6R-3, 40–44	0.23	278	0.005	0.102	0.907	0.150
1163A-9R-1, 140–142	0.23	311	0.005	0.103	0.908	0.149
1163A-11R-2, 49–52	0.24	332	0.005	0.105	0.904	0.150
1164B-4R-2, 66–70	0.14	251	0.004	0.098	0.689	0.075
1164B-5R-1, 29–30	0.16	274	0.004	0.099	0.740	0.078
1164B-8R-1, 36–39	0.15	285	0.005	0.103	0.748	0.080

Notes: Volatiles were determined by FTIR spectroscopy using methods described in the text. The reported values are averages of data for two separate glass chips from the same sample. Other volatiles (Cl, S) and minor elements (Ti, K) were analyzed by electron microprobe at Texas A&M University. The values reported are averages of five analyses of each glass sample.