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# Stable isotopic composition of upper oceanic crust formed at a fast spreading ridge, ODP Site 801

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[1] ODP Legs 129 and 185 sampled the upper 474 m of ~170 Ma ocean crust in the western Pacific in order to investigate alteration processes in fast spread crust and to determine inputs to subduction. Fourteen composite bulk samples of altered upper oceanic crust from Site 801 have  $\delta^{18}O = 8.7-25.7\%$ ,  $\delta D = -69.4\%$  to -90.4%, and  $\delta^{13}C = -2.7\%$  to 1.8%. The intensity of alteration and the amount of sediment within the basement decrease with depth, leading to corresponding decreases in  $\delta^{18}O$  and  $\delta D$ . A SUPER composite, constructed to estimate the bulk composition of the upper crust, has  $\delta^{18}O = 12.0\%$ ,  $\delta D = -87.0\%$ , and  $\delta^{13}C = 0.7\%$ . Compared to core descriptions and geophysical logs, the SUPER composite contains too much  $\delta^{18}O$ -rich sediment ( $\delta^{18}O = 25.7\%$ ), and a corrected  $\delta^{18}O$  value of 10.8% is more reasonable for the upper crust at Site 801. These values are higher than those for other bulk upper oceanic basement sections ( $\delta^{18}O = 8.0-10.0\%$ ) and result in part from: (1) intense low-temperature (<100°C) hydrothermal alteration of the upper 100 m of tholeitic basement at Site 801 that may not be representative of material subducting in the western Pacific and (2) an aging effect, whereby progressive addition of  $\delta^{18}O$ -rich secondary carbonate in veins and breccia cements contributed to the high bulk  $\delta^{18}O$  of this old upper crustal section.

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**Theme:** Oceanic Inputs to the Subduction Factory

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#### 1. Introduction

[2] Low temperature interaction of seawater with the upper oceanic crust is an important sink for seawater alkalis, Mg, <sup>18</sup>O, C, and H<sub>2</sub>O [Muehlenbachs and Clayton, 1976; Alt et al., 1996; Staudigel et al., 1996; Alt and Teagle, 1999; Wheat and Mottl, 2000]. This process exerts a significant

control on the composition of seawater and the seawater component in altered crust is important for recycling of subducted material into the mantle or through arc volcanism. In particular, <sup>18</sup>O uptake in the upper ocean crust balances the <sup>18</sup>O source from high temperature axial hydrothermal systems, maintaining the oxygen isotopic composition of the oceans [Muehlenbachs and Clayton, 1976; Greg-



ory and Taylor, 1981; Jean-Baptiste et al., 1997; Wallmann, 2001]. The O and H isotopic compositions of altered oceanic crust can be retained during high-pressure metamorphism and recycling into the mantle [Eiler, 2002], and fluids released during subduction can modify the O and H isotopic compositions of subduction-related lavas [Kyser and O'Neil, 1984; Poreda, 1985]. The sink of carbon as carbonate minerals in the upper crust exceeds the source of carbon by degassing of CO<sub>2</sub> at mid-ocean ridges, and is an important component of metamorphic reactions and degassing in subduction zones [Staudigel et al., 1989; Alt and Teagle, 1999; Kerrick and Connolly, 2001].

[3] Most crust subducting today was generated at fast spreading ridges, but our knowledge of the composition of altered oceanic basement comes mainly from crust formed at slow and intermediate spreading rates because this is where most deep drilling has occurred. Hole 801C, on ∼170 Ma crust in the western Pacific, was deepened to 474 m into basement on ODP Leg 185 in order to investigate alteration processes in old crust generated at a fast spreading ridge and to determine inputs to subduction in the Mariana arc [Shipboard Scientific Party, 2000]. This paper presents results of a study to determine the bulk stable isotopic (O, H, C) composition of altered basement at Site 801. Because chemical and isotopic results for Site 801 will be used in models for subduction recycling, a major question to address is whether basement at Site 801 is representative of altered old Pacific crust.

#### 2. Site 801

[4] ODP Site 801 is located at 18°38.53798′N, 156°21.58813′E in the western Pacific (Figure 1). The crust at this site formed at ~170 Ma at a fast spreading ridge having an estimated spreading rate of 160 km/m.y. [Pringle, 1992; Shipboard Scientific Party, 2000]. The site was cored to 133 m subbasement on ODP Leg 129 in 1989 [Lancelot et al., 1990] and was extended to 936 mbsf (meters below seafloor) on ODP Leg 185 in 1999, for a total basement penetration of 474 m. Core recovery averages 50% and is slightly better in massive units

than in flows and pillows [Lancelot et al., 1990; Shipboard Scientific Party, 2000].

[5] Eight major sequences have been identified in the basement (Figure 2). Unit I consists of 60.2 m of late alkalic basalt sills that intruded into sediments at 157 Ma [Pringle, 1992; Shipboard Scientific Party, 2000]. The underlying ~404 m of tholeitic basalts have N-MORB compositions and contain 6–8 wt% MgO [Shipboard Scientific Party, 2000]. The massive flows of Units III and VI include minor pillows and thin flows. Units IV and VII consist mainly of thin flows and pillows. Thin (cm-dm) intervals of recrystallized sediments are common in Units III and IV. Also present are two hydrothermal silica-iron deposits, the ~20 m thick Unit II and a thin (~1 m thick) Unit V (Figure 2).

[6] Alteration of the basement section is described in detail elsewhere [Alt et al., 1992; Shipboard Scientific Party, 2000], and is briefly summarized here. Most of the tholeiites are characterized by slight (10-15%) recrystallization to smectite and carbonate, with minor celadonite, Fe oxyhydroxides, and pyrite. Volcanic glass at pillow rims and flow margins is extensively replaced by saponite and palagonite. Carbonate minerals (mainly calcite), smectite, and minor celadonite and quartz cement breccias and fill fractures. Alteration temperatures of 5-95°C are estimated from oxygen isotopic compositions of secondary minerals (J. C. Alt and D.A.H Teagle, Hydrothermal alteration of the upper oceanic crust formed at a fast spreading ridge: Mineral, chemical, and isotopic evidence from ODP Site 801, manuscript submitted to Chemical Geology, 2003, hereinafter referred to as Alt and Teagle, submitted manuscript, 2003). Although alteration of Site 801 basement is generally similar to that in other upper oceanic crustal sections, a major difference is the much lower abundance of oxidation effects at Site 801 than elsewhere, only 2 volume% versus 20-30% at other sites (Figure 2) [Alt et al., 1996; Alt, 2003]. A second major difference is the presence of the two silica-iron hydrothermal deposits and associated intense alteration at Site 801 (60-100% recrystallization of basalt to smectite, calcite, celadonite, and local K-feldspar; Figure 2). This alteration occurred by reaction with upwelling of distal, mixed hydrothermal fluids at the spreading axis, at

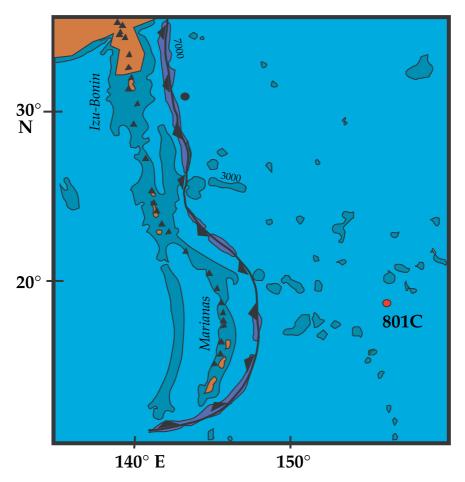


Figure 1. Map showing location of Site 801 in the western Pacific [from Shipboard Scientific Party, 2000].

temperatures <100°C [Alt et al., 1992]. High temperature (~350°C) hydrothermal fluids originating at depth mixed with seawater in the subsurface (probably in the uppermost sheeted dikes), resulting in precipitation of sulfides, while the resultant cooler (~10–100°C), mixed fluids remained enriched in Fe, Si and alkalies compared to seawater [Edmond et al., 1979]. The hydrothermal deposits formed where these fluids vented onto the seafloor, and the intense alteration in the upper 100 m of the basement is related to fluid pathways that were the feeder zones for the deposits at the surface.

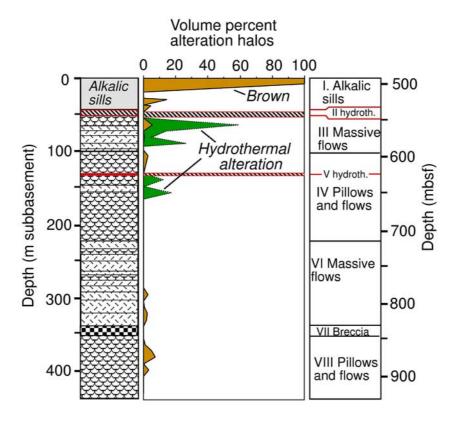
### 3. Sampling and Methods

[7] Altered ocean crust is heterogeneous at various scales, from the scale of centimeters to hundreds of meters. During Leg 185 a sampling approach was undertaken in an attempt to obtain bulk samples of altered crust at a scale of ~100 m. This was done by

sampling of the core at a small scale (cm) and combining numerous samples into composites for specific depth intervals at the scale of tens to hundreds of meters [Shipboard Scientific Party, 2000].

[8] A total of 116 "communal" samples from Site 801 were taken on board the JOIDES Resolution [Shipboard Scientific Party, 2000]. This was an attempt to representatively sample all parameters, including primary characteristics such as rock type and chemical composition, grain size and texture, as well as secondary parameters such as veins, different alteration types, and alteration halos along veins. The Site 801 basement was divided into four depth intervals based on primary geochemistry and alteration effects: the alkali basalt sills and three MORB intervals (Table 1). For each interval, communal samples were combined into one composite for submarine extrusives (FLO) and one for clastic rocks (VCL). Sample selections and proportions in the composites were based on detailed core descrip-





**Figure 2.** Schematic lithostratigraphy of Site 801 basement and distribution of alteration halos. "Brown" indicates oxidation halos along veins, and "Hydrothermal" indicates intense low-temperature hydrothermal alteration related to formation of the two silica-iron hydrothermal deposits (Units II and V). The disproportionately high proportion (100%) of brown alteration halos in the uppermost alkali basalts is an artifact of the extremely low recovery in these cores (<2%) and is not representative. Depth given as m subbasement and m below seafloor (mbsf). After *Shipboard Scientific Party* [2000] and Alt and Teagle (submitted manuscript, 2003).

tions and geophysical logging results, but it is nonetheless very difficult to get proportions correct because of the wide variety of features to be included, their heterogeneity of occurrence, and because incomplete core recovery (50%) results in biases in sampling by the core and uncertainties about the true proportions of various features.

- [9] Based on estimates of rock proportions from geophysical logs [Barret al., 2002], composites were combined in the proportions 30% VCL and 70% FLO to make a combined lithology composite for each depth interval (the MIX composites in Table 1). A SUPER composite was made for the entire MORB section by combining the three MORB depth composites in proportion to their total thicknesses, and a sediment composite was made for interflow sediments from the upper 230 m of the basement.
- [10] Each rock sample contributing to composites was ultrasonically cleaned for 10–20 minutes in

distilled water, air-dried, reduced to 2–4 mm particles in a hydraulic press, freeze-dried and then powdered for 15 minutes in an alumina ball mill. Multiple samples were weighed into a clean plastic bag, and homogenized by grinding for five minutes in an agate shatterbox.

- [11] Oxygen was extracted from bulk rocks and sediment by reaction with  $ClF_3$  and converted to  $CO_2$  gas for measurement of oxygen isotope ratios on a Finnegan Delta-S mass spectrometer [Clayton and Mayeda, 1963]. Repeated extractions and measurements of samples and standards were reproducible within  $\pm 0.2\%$ .
- [12] Hydrogen isotopic analyses were performed on selected composite samples [Venneman and O'Neil, 1993]. Rock powders were dried at 110°C in air, placed under vacuum overnight, and heated to 150°C under vacuum for 2 hours. Water



Table 1.	Stable	Isotopic	Data	for	Site	801	Com	posite	Samp	les
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		Depth Interval, m		$^{\#}\delta^{18}O$	$^{\#}\!\delta D$	$^{\#}\delta^{13}C$	#δ <sup>18</sup> O CO <sub>2</sub>	VCL, <sup>a</sup> %	Sed, <sup>a</sup> %	Veins, <sup>a</sup> %
801	TAB	0-50	FLO	14.6		-2.7	29.1	6.8	3.7	5.1
801	TAB	0 - 50	VCL	20.2		-0.2	29.5	100	55	
801	TAB	0 - 50	MIX	16.8	-69.4	-1.5	29.3	35	20	3.6
801	MORB	0 - 110	FLO	13.5		0.9	28.2	10	5.9	5.2
801	MORB	0 - 110	VCL	22.3		0.9	28.0	100	59	
801	MORB	0 - 110	MIX	15.3	-83.5	0.9	28.3	32	23	3.6
801	MORB	110 - 220	FLO	8.7		1.1	29.1	5.3	2.4	5.1
801	MORB	110 - 220	VCL	19.6		-0.2	27.5	100	45	
801	MORB	110 - 220	MIX	12.1	-88.3	0.0	27.8	34	16	3.6
801	MORB	220 - 420	FLO	9.2		0.5	26.6	2.6	0	7.7
801	MORB	220 - 420	VCL	13.4		0.9	27.1	100	0	
801	MORB	220 - 420	MIX	10.3	-90.4	0.6	26.9	32	0	5.4
801		SUPER		12.0	-87.0	0.7	27.9	35	9	4.4
801		SED		25.7		1.8	28.5			

 $^a$  From Shipboard Scientific Party, Leg 200 Preliminary Report, available at http://www-odp.tamu.edu/publications/prelim/200\_prel/200PREL.PDF, 2002. MIX includes sediment in VCL composite and in FLO composite. Sediment (Sed) in VCL and FLO composites estimated from composite recipes, sample descriptions and photographs of communal samples. Veins includes carbonate and silicate secondary mineral veins. # $\delta^{18}O$  and  $\delta D$  in per mil VSMOW,  $\delta^{13}C$  in per mil VPDB. Also given is the  $\delta^{18}O$  of CO $_2$  evolved from bulk carbonate in the composites.

was then extracted by melting the sample, and frozen into a quartz tube. Any  $H_2$  that was generated was converted to  $H_2O$  by reaction with hot CuO. The water was then converted to hydrogen for isotopic analysis by heating with Zn metal in a sealed quartz tube. Isotope ratios were measured on a Finnegan Delta-S mass spectrometer. Multiple extractions and measurements of standards over the course of these analyses were reproducible within  $\pm 2.8\%$  ( $1\sigma$ ; n = 7).

[13]  $CO_2$  from carbonate in bulk rock powders was liberated by dissolution in phosphoric acid at  $78 \pm 2^{\circ}$ C, and carbon and oxygen isotope ratios measured on a Finnegan MAT 251 mass spectrometer. Results are reported as  $\delta$  notation relative to VPDB and VSMOW for carbon and oxygen, respectively. Reproducibilty of standards is better than 0.1% for both carbon and oxygen isotope compositions.

#### 4. Results and Discussion

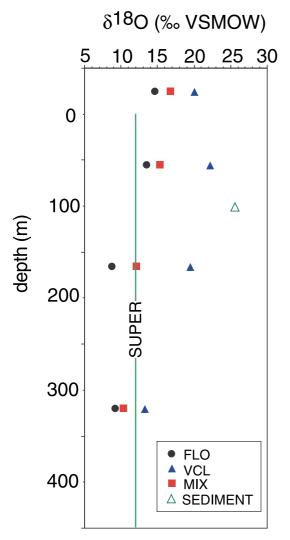
#### 4.1. Oxygen Isotopes

[14] The FLO composites have  $\delta^{18}O$  values of 8.7–13.5‰ and the VCL composites have values of 13.4–22.3‰ (Table 1; Figure 3). There is a general decrease in  $\delta^{18}O$  with depth (Figure 3), reflecting variations in rock types as well as alteration effects. The alkali basalt sills at the top of the section have high values because they are more

intensely altered (30–80%) than most of the tholeiites (10–15%). The greater alteration of the alkalic sills may be related to differences in their primary composition or texture compared to the tholeiites, or to a different mode of origin (injection into sediments rather than eruption onto the seafloor). The high  $\delta^{18}$ O value of 13.5% for the upper tholeiitic FLO composite is influenced by the highly altered rocks related to upwelling hydrothermal fluids and formation of the silica-iron hydrothermal deposits. The deeper FLO composites have lower values of 8.7–9.2%, reflecting their less intense alteration.

[15] The VCL composites have much higher  $\delta^{18}O$  than the FLO composites, and values generally decrease with depth. The upper three VCL composites contain  $\sim 50\%$  interflow sediments, resulting in high  $\delta^{18}O$  values of 19.6-22.3% that approach that of the sediment composite (25.7‰). The much lower  $\delta^{18}O$  of the deepest VCL composite reflects the lack of sediment and much greater proportion of igneous material in hyaloclastites and breccias in this interval. The MIX composites appropriately have values intermediate between the FLO and VCL composites, and the SUPER composite value, 12‰, is similar to the intermediate mixture.

[16] Core recovery at Site 801 averages 50%, and from comparison of recovered core material with



**Figure 3.** Oxygen isotope data for Site 801 composite samples. Late alkalic basalt sills are plotted at negative depth values because these intrude sediment overlying the tholeitic basement. Vertical line indicates SUPER composite composition, which does not include alkalic basalt sills. Unaltered MORB plot at  $\delta^{18}O = 5.8\%$  at the left side of the diagram [Muehlenbachs and Clayton, 1976].

geophysical logs, it is clear that there is preferential loss of vein and breccia material during drilling of oceanic volcanic basement [Barr et al., 2002; Haggas et al., 2002]. Barr et al. [2002] estimate that 31% of the cored basement at Site 801 consists of breccia, compared to 9.5% breccia in the recovered core. These authors also found 33% pillows and 33% massive flows in the 801 section versus 32% pillows and 58% massive units in the recovered core. Sediment estimated from combined logs

+ cores is the same as that in the recovered cores (2.5%). The unrecovered breccia material probably includes some sediment, but it is unlikely that the lost material contains as much sediment as the upper 3 VCL composites (~50% sediment; Table 1). Samples making up the VCL composite contain abundant interflow sediment, whereas the breccias documented by the logs are mainly highly fractured pillows and thin flows cemented by secondary minerals [Barr et al., 2002]. Thus, while 30% breccia appears reasonable for the Site 801 basement section, the amount of sediment mixed into the VCL (breccia) composites is too great. The MIX composites (30% VCL + 70% FLO) therefore also contain proportions of sediment that are too large (~20% sediment in the upper two MORB composites; Table 1).

[17] The 35% volcaniclastic material contained in the SUPER composite (Table 1) agrees nominally with the 33% breccia estimate from the logs [Barr et al., 2002], but the large amount of sediment contained in the VCL composites is propagated through the MIX composites and into the SUPER composite, leading to an excess of sediment in the latter (~9%; Table 1). Through comparison of geophysical and geochemical logs with drillcore, Révillon et al. [2002] came to a similar conclusion that the composite samples overestimate the K uptake by the Site 801 basement.

[18] A "corrected" SUPER composite value can be estimated by mass balance. To start, the 10% sediment ( $\delta^{18}O = 25.7\%$ ) is subtracted from the upper MORB FLO composite giving  $\delta^{18}O =$ 12.1‰ for the latter. The average 801 breccia contains 20% breccia cement [Shipboard Scientific Party, 2000], and if this breccia cement has the same  $\delta^{18}$ O as the sediment (25.7‰), then this can be combined with 80% corrected upper MORB FLO composite (12.1‰) to give an upper MORB VCL composite value of 14.8‰. The two lower MORB VCL composites can be similarly calculated: 20% matrix (25.7‰) + 80% FLO ( $\sim$ 9.0‰) = 12.3‰, in reasonable agreement with the measured value of 13.4‰ for the VCL 220-420 composite, which contains no sediment. Combining the calculated VCL and FLO composites in the 30:70 proportions observed from the borehole logs [Barr



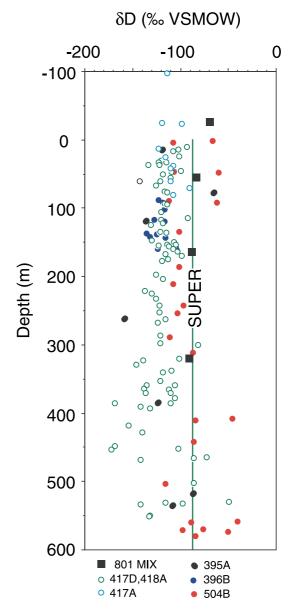
et al., 2002] then gives 12.9‰ for the 0–110 MIX, 10.0‰ for the 110–220 and 220–420 MIX composites, and a corrected SUPER composite  $\delta^{18}$ O of 10.8‰.

#### 4.2. Hydrogen Isotopes

[19] The MIX composites have  $\delta D$  values of -69.4% to -90.4% that decrease with depth, and the SUPER composite has a value of -87.0% (Table 1). These values are at the heavier end of the range of values for whole rocks from other deep volcanic basement sites, -76‰ to -135% (Figure 4). The slightly heavier  $\delta D$  values for the Site 801 composites may in part result from higher temperatures of alteration at Site 801 compared to the other sites. Another factor for the Site 801 composites is the presence of sediments, which at nearby Site 800 have relatively high δD values, -48.9 to -53.6% [France-Lanord and Sheppard, 1992]. Like in the basalts, the main water carrier in the sediments is smectite, and the slightly heavier δD of sediments is related to retention of some interlayer water that has estimated  $\delta D = -27\%$  to -44‰ [France-Lanord and Sheppard, 1992]. Decreasing the amount of sediment in the Site 801 composites would have the effect of decreasing the  $\delta D$  slightly, although the difference between the SUPER composite (-87%) and the deepest composite (-90.4%), which contains no sediment, may not be significant.

# 4.3. Comparison With Other Upper Oceanic Crust

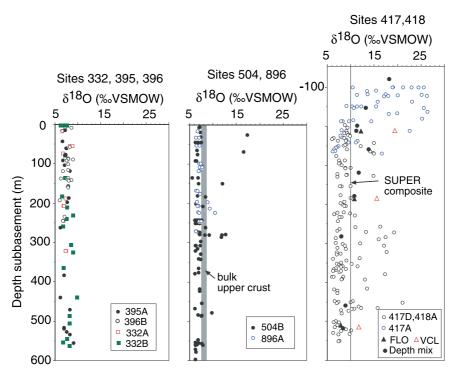
[20] Oxygen isotopic data for other deep holes in oceanic volcanic basement are compiled in Figure 5. Basalts from Sites 332, 395 and 396 (3.2–10 Ma) in the Atlantic have  $\delta^{18}$ O values of 6–10‰, with no apparent depth trends. These data do not, however, include analyses of more altered breccias or interflow hyaloclasite or sediment. Data for 6 Ma ODP Holes 504B and 896A in the eastern Pacific mostly fall in the range 6–9‰, with higher values (up to 18‰) in breccias and in local zeolite rich samples. Although there are few data for breccias, there is a decrease in the maximum values of bulk samples with depth. This has been attributed to lower seawater/rock



**Figure 4.** Hydrogen isotopic compositions of Site 801 MIX and SUPER composites. Shown for comparison are isotopic data for basalts from other deep basement holes. Data from *Hoernes and Friedrichsen* [1977, 1978], *Friedrichsen and Hoernes* [1979], and *Friedrichsen* [1985]. Alkalic basalt sill composite plotted as negative depth. Unaltered MORB plot at  $\delta D = -80 \pm 5\%$  [*Kyser and O'Neil*, 1984].

ratios and more evolved seawater fluids at depth [Alt et al., 1996].

[21] Holes 417A, 417D, and 418A lie in 110 Ma crust in the Atlantic. Hole 417A is sited on a basement hill, so samples that extend above the



**Figure 5.** Oxygen isotopic data for upper oceanic crust from other deep (>200 m) basement holes for comparison to Site 801 basement composites. Data for 3.2 Ma Site 332A–C in the Atlantic from *Gray et al.* [1977], *Hoernes and Friedrichsen* [1977] and *Muehlenbachs* [1977]; for 7 Ma Site 395 in the Atlantic from *Hoernes et al.* [1978] and *von Drach et al.* [1978]; for 10 Ma Hole 396B in the Atlantic from *Hoernes and Friedrichsen* [1978] and *Muehlenbachs and Hodges* [1978]; for 110 Ma Sites 417 and 418 in the Atlantic from *Muehlenbachs* [1979], *Friedrichsen and Hoernes* [1979], *Staudigel et al.* [1981] and *Bohlke et al.* [1984], and for 6 Ma Holes 504B and 896A in the eastern Pacific compiled in *Alt et al.* [1996] and from *Teagle et al.* [1996]. SUPER, FLO and VCL composite samples for Sites 417/418 constructed similarly to those for Site 801, and solid circles are depth composites (including veins, interflow material, etc.) for several intervals at those sites [*Staudigel et al.*, 1995]. Bulk upper crust estimate at Sites 504/896 from *Alt et al.* [1998] (see text). Unaltered MORB plot at δ<sup>18</sup>O = 5.8‰ at the left side of the diagrams [*Muehlenbachs and Clayton*, 1976].

surrounding basement are plotted at negative depth values in Figure 5. Rocks in the upper part of Hole 417A remained exposed to seawater for ~20 Ma and the outcrop was a site of prolonged and focused fluid flow leading to extreme alteration of the protruding rocks [Bohlke et al., 1984]. Rocks from the basement hill have  $\delta^{18}O$  values of 8-27‰, whereas the buried basement mostly has  $\delta^{18}O = 6-20\%$ . Excluding the high values from Site 417A there is no clear trend with depth, although there are decreases in scatter and maximum values in the bottom 100 m. Composite samples similar to those for Site 801 were made for Sites 417/418 [Staudigel et al., 1995]. These exhibit a general decrease in  $\delta^{18}$ O with depth, although the upper 6 composites include data from the highly altered Hole 417A, which may not be representative of the crust (Figure 5). Hole 896A also penetrates a basement hill, but, with the exception of thicker secondary mineral veins, alteration there is similar to the nearby basement at Hole 504B [*Alt et al.*, 1996].

[22] Differences in alteration temperatures at the various sites could contribute to differences in δ<sup>18</sup>O, but this does not appear significant for the sites in Figure 5. Temperatures estimated from oxygen isotopic analyses of secondary minerals at Sites 395 and 332 are 0–50°C, although temperatures locally ranged up to 150°C adjacent to an intrusive sill near the base of Hole 395A [*Muehlenbachs*, 1977; *Lawrence and Drever*, 1981]. Similar but slightly higher temperatures of 15–100°C are estimated for Sites 417/418 [*Muehlen-*



bachs, 1979; Staudigel et al., 1981; Bohlke et al., 1984], and temperatures were comparable at sites 504 and 896, mostly  $\sim$ 20–110°C [Alt et al., 1996].

[23] One of the main influences on the stable isotopic composition of the upper crust is the proportion of <sup>18</sup>O-rich material in veins, breccias, and interflow material (sediment, hyaloclastite, secondary minerals, etc.). Analyses of this material are missing from Sites 332, 395 and 396, leading to low overall  $\delta^{18}$ O values (mean  $\approx 7.5$  in Figure 5). In a mass balance approach, Alt et al. [1998] combined oxygen isotopic analyses with data for the distribution of different alteration types, veins, and breccias in Holes 504B and 896A to calculate a bulk  $\delta^{18}O$  of 7.6-8.0% for the upper crust at these sites. This calculation was based on the proportions of materials in recovered cores at  $\sim$ 30% core recovery, so breccias and interflow material were underestimated resulting in a low bulk  $\delta^{18}O$ . From comparison of cores and geophysical logs Haggas et al. [2002] suggest that breccias comprise 16% of the 896A section rather than the 9% determined in the recovered core. Using the higher proportion of breccia results in a slightly higher bulk  $\delta^{18}$ O for the upper crust of 8.0-8.5%. This estimate is based on the same type of data as that used to construct the Site 801 composites. Staudigel et al. [1995] constructed composite samples for Sites 417/418, similar to those for Site 801, and determined a bulk upper crustal  $\delta^{18}$ O of 10.0% for Sites 417/418. These composites include data from the highly altered basement hill penetrated by Hole 417A, which may not be representative of the upper crust, but subtraction of this material from the 417/418 SUPER composite only decreases its  $\delta^{18} O$  by 0.2% [Staudigel et al., 1995].

[24] These estimates of bulk upper crustal  $\delta^{18}O$  are lower than the Site 801 SUPER composite (12.0‰), which can be attributed in part to the high proportion of sediment in the VCL and SUPER composites. The corrected SUPER composite for site 801 calculated above, 10.8‰, is considered a better estimate for the upper crust at Site 801.

[25] A second factor leading to the high  $\delta^{18}O$  of the 801 SUPER composite is the intense alteration

associated with formation of the hydrothermal silica-iron deposits at Site 801. This occurred by upwelling low-temperature hydrothermal fluids at the spreading axis and differs from the ridge flank alteration that dominates at other sites. The highly <sup>18</sup>O-enriched rocks make up 10% of the upper 110 m of the tholeitic basement at Site 801 (Alt and Teagle, submitted manuscript, 2003), contributing to the high values of the upper tholeiite composites (Figure 3). Key questions here are (1) whether this is representative of the upper crust formed at fast spreading centers and (2) whether Site 801 is representative of basement subducting in this part of the western Pacific. Several holes penetrate at least the upper 100 m of oceanic basement generated at fast spreading rates, but these do not contain such hydrothermal deposits or associated intense alteration [Rosendahl, 1980; Lewis et al., 1983; Leinen et al., 1986; Alt, 1993; Shipboard Scientific Party, Leg 2000 Preliminary Report, available at http://wwwodp.tamu.edu/publications/prelim/200 prel/ 200PREL.PDF, 2002; Shipboard Scientific Party, Leg 206 Preliminary Report, available at http:// www-odp.tamu.edu/publications/prelim/206 prel/ 206PREL.PDF, 2003]. Thus, while perhaps a common component of crust from fast spreading rates, the hydrothermal deposits and associated intense alteration and <sup>18</sup>O-enrichment at Site 801 are not ubiquitous.

[26] An aging effect contributes to the differences between younger (≤10 Ma) and older (≥100 Ma) sites in Figures 3 and 5. Secondary carbonates are the last phases to form in the upper crust, and have the highest  $\delta^{18}$ O values. Alt and Teagle [1999] show that these phases continue to form in veins as the crust ages resulting in the progressive uptake of C by the crust. Addition of these <sup>18</sup>O-rich phases would result in a corresponding increase in  $\delta^{18}$ O of the upper crust. Starting with a bulk upper crust  $\delta^{18}$ O of 8.0% and adding 2.6% carbonate ( $\delta^{18}$ O = 30‰) to the upper crust, Alt and Teagle [1999] would increase the  $\delta^{18}O$  of the upper crust by 0.6%. Veins and breccias are preferentially lost during coring so carbonate addition and the aging effect are probably greater than this estimate based on recovered core. This carbonate aging effect can account at least in part for the progressively higher



 $\delta^{18}$ O of the upper crust from 6 Ma Sites 504/896 to 100 Ma Sites 417/418 and to 170 Ma Site 801.

#### 5. Conclusions

[27] Composite bulk samples of altered Jurassic upper oceanic crust from ODP Site 801 in the western Pacific have  $\delta^{18}O = 8.7-20.2\%$ ,  $\delta D = -69.4\%$  to -90.4%, and  $\delta^{13}C = -2.7\%$  to 1.1%. The intensity of alteration and the amount of sediment within the basement decrease with depth, leading to corresponding decrease in  $\delta^{18}O$  and  $\delta D$  values of the composites. A SUPER composite, constructed to estimate the bulk composition of the upper crust, has  $\delta^{18}O = 12.0\%$ ,  $\delta D = -87.0\%$ , and  $\delta^{13}C = 0.7\%$ .

[28] The  $\delta^{18}$ O of the SUPER composite is higher than values of 8.0-10.0% for other bulk upper oceanic basement sections based on similar data. Although constructed according to constraints from geophysical logs and from recovered cores, evaluation of the SUPER composite recipe suggests that it contains too much <sup>18</sup>O-rich sediment  $(\delta^{18}O = 25.7\%)$ . A corrected  $\delta^{18}O$  value of 10.8‰ is considered more reasonable for the Site 801 basement section. Other factors also contribute to the relatively <sup>18</sup>O-rich nature of the Site 801 basement: (1) intense low-temperature (<100°C) hydrothermal alteration occurred at the spreading axis associated with formation of hydrothermal silica-iron deposits and contributes to the strong <sup>18</sup>O-enrichment of the upper 100 m of basement, which is probably not representative of subducting material and (2) an aging effect, whereby progressive addition of <sup>18</sup>O-rich secondary carbonate in veins and breccia cements leads to increasing  $\delta^{18}O$  of the bulk upper crust with time.

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