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STABLE ISOTOPE EVOLUTION OF VOLCANIC ASH LAYERS DURING DIAGENESIS OF THE MIOCENE MONTEREY FORMATION, CALIFORNIA

J. S. COMPTON,[1] M. E. CONRAD[2] AND T. W. VENNEMANN[3]

[1] Department of Geological Sciences, University of Cape Town, Rondebosch 7700 South Africa
[2] Center for Isotope Geochemistry, Mailstop 70A-3363, Lawrence Berkeley National Laboratory,
Berkeley, California 94720, USA
[3] Institute for Geochemistry, University of Tuebingen, Wilhelmstr.56, 72074 Tuebingen, Germany

Abstract—The oxygen and hydrogen isotope compositions of volcanic ash layers from coastal outcrops of the Miocene Monterey Formation elucidate the progressive burial diagenesis of glass to bentonite and metabentonite. Volcanic glass that texturally appears unaltered is found to have $\delta^{18}O$ and δD values that are significantly higher than fresh volcanic glasses. The positive shift in $\delta^{18}O$ and δD values is proportional to the amount of hydration and chemical alteration of the glass samples. Initial hydration of the glass results in the exchange of Na for H; later hydration results in the loss of K and Fe in exchange for H and Na. The $\delta^{18}O$ values of the most hydrated glass, and clay minerals from bentonite and metabentonite layers are approximately in equilibrium with slightly modified seawater. The δD values of the hydrated glass, and clay minerals from bentonite and metabentonite layers, are significantly depleted in D relative to seawater and suggest meteoric exchange associated with tectonic uplift and erosion in the Pliocene and Pleistocene. Smectite from bentonite layers has $\delta^{18}O$ and δD values similar to the most hydrated glass samples, suggesting similar glass-water and smectite-water fractionation factors. Kaolinite and mixed-layered illite–smectite (I–S) altered from smectite have lower $\delta^{18}O$ and higher δD values than their precursor. The $\delta^{18}O$ and δD of nonvolcanic siliceous mudstones from the Pt. Arguello oil field show an unusual decrease in δD with increasing burial depth that probably reflects the presence of organic hydrogen in the analyzed samples as well as possible D-depleted formation waters from detrital illite-water and hydrocarbon-water exchange.

Key Words—Bentonite, Diagenesis, Monterey Formation, Stable Isotopes, Volcanic Ash.

INTRODUCTION

The Miocene Monterey Formation is composed primarily of organic-rich siliceous shale containing abundant biogenic (opal A) silica (mostly diatoms) that recrystallize to opal CT and diagenetic quartz with increasing burial metamorphism (Murata et al. 1977; Isaacs 1982). The Monterey also contains significant amounts of dolomite (Compton and Siever 1986). Discrete volcanic ash (tephra) layers in the Monterey Formation are preserved because much of the Monterey was deposited in deep, hemipelagic basins where low oxygen bottom waters allowed laminated sediment to accumulate undisturbed by bioturbation (Garrison and Douglas 1981). Rhyolitic ash layers in the Monterey Formation have undergone varying degrees of diagenesis resulting from lateral differences in burial and thermal histories (Isaacs 1980; Compton 1991). With increasing burial diagenesis the volcanic glass alters to smectite to form bentonite layers, and then the smectite alters to increasingly illitic mixed-layer I–S and kaolinite to form metabentonite layers (Compton 1991). The glass to smectite reaction coincides with the opal-A to opal CT transformation, and the smectite to illite plus kaolinite reaction overlaps the opal CT to quartz transformation.

Stable isotope analyses can provide important insight into the origin and diagenetic transformations of clay minerals (Yeh and Savin 1977; Eslinger et al. 1979; Savin and Lee 1988), as well as the isotopic evolution of associated pore waters that may no longer be available to sample (Fisher and Boles 1990; Wilkinson et al. 1992). Previous studies of the isotopic evolution of clay minerals during burial metamorphism and illitization of detrital-rich mudrocks show a general trend of ^{18}O-depletion and D-enrichment with increasing burial metamorphism (Yeh and Savin 1977; Eslinger et al. 1979; Yeh 1980; Primmer and Shaw 1991). The isotopic composition of clay minerals from the Monterey Formation is of particular interest because diagenetically altered siliceous mudstones are interbedded with bentonite and metabentonite layers (Compton 1991) which allows a comparison of clay minerals derived from detrital and volcanic glass precursors. The hydrogen isotope composition of clay minerals from the Monterey Formation may also be influenced by the presence of significant amounts of hydrocarbons (Compton et al. 1992).

This study examines the isotopic evolution of hydrated volcanic glass, authigenic clay minerals derived from volcanic glass and the clay-size fraction of interbedded siliceous mudstones with increasing diagenetic grade. The results have important implications for the marine diagenesis of rhyolitic glass in siliceous oil source and reservoir rocks of the Monterey Formation.

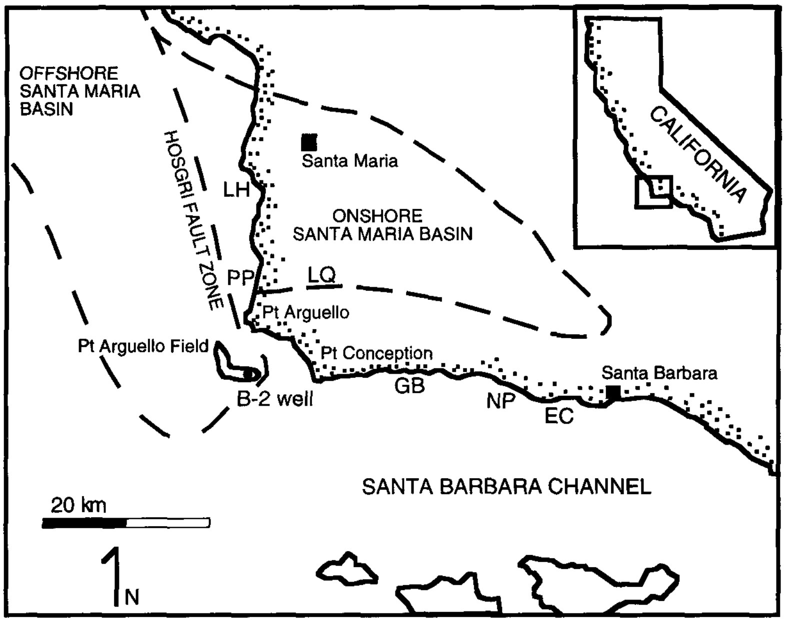

Figure 1. Location map of the areas studied in south-central coastal California. PP = Pt. Pedernales, LH = Lions Head, LQ = Lompoq (Celite Corp.) diatomite quarry, EC = El Capitan, GB = Gaviota Beach and NP = Naples Beach. The B-2 well is located in the offshore Pt. Arguello field.

METHODS

Bulk rock samples were collected from coastal outcrops in south-central California (Figure 1). Bulk drill cuttings were obtained from Chevron USA from the B-2 well located 20 km offshore in the Pt. Arguello field. Rock chips greater than 0.5 mm were sieved from the bulk cuttings, cleaned and pulverized before separation of the clay-size fraction. Bulk powders were suspended in water containing hexametaphosphate and disaggregated using a high-intensity ultrasonic probe. The clay-size fraction was then separated by centrifuge. The mineralogy of the clay-size fraction was determined by X-ray diffraction (XRD) using a Scintag XDS-2000 X-ray diffractometer. Photomicrographs of samples were taken with an ISI-D130 scanning electron microscope (SEM). Feldspar phenocrysts were separated from the volcanic layers by sieving and by suspension in heavy liquids. Major element compositions, expressed as oxides, were determined using X-ray fluorescence (XRF) spectroscopy, and total carbon and sulfur contents were determined using a Leco analyzer by X-ray Assay Laboratories (Ontario, Canada).

Oxygen isotope analyses were done at the Center for Isotope Geochemistry of the Lawrence Berkeley National Laboratory. After weighing and prior to analysis, the clay separates were stored for a minimum of 2 d in a desiccator with P_2O_5 to remove any atmospheric water adhering to the samples. Prior to reaction, the samples were heated to 150 °C in a vacuum for a minimum of 4 h. Oxygen from the samples was extracted by reaction with BrF_5 overnight in Ni vessels at 550–600 °C (Clayton and Mayeda 1963). The extracted oxygen was passed over a heated carbon rod to convert to CO_2 for isotopic analysis using a Prism Series II isotope ratio mass spectrometer. Corrections for systematic variations between sets ($\leq$0.4‰) were made by comparison with 3–4 samples of NBS-28 run in every set (at a value of 9.6‰). All samples were analyzed in duplicate. Additional analyses were done when the difference between the analyses exceeded ±0.2‰.

The δD values of the clay separates were measured at the stable isotope laboratory of the University of Michigan (Ann Arbor). Before extraction of water from the clays, the samples were heated to 150 °C in a vacuum for a minimum of 8 h to remove atmospheric water and most of the interlayer water. The hydrogen isotope compositions and wt% water of the clay separates were determined using the method of Vennemann and O'Neil (1993). The precision for δD analyses is ±2‰ and for the wt% water is ±0.2%. The $\delta^{18}O$ and δD values are reported as per mil variations relative to Vienna standard mean ocean water (SMOW).

RESULTS

Volcanic Glass

Friable, glassy volcanic (tephra) layers were sampled from Upper Miocene diatomite outcrops of the Monterey Formation. The age of the volcanic glass layers is between 7.4 and 5.6 Ma on the basis of di-

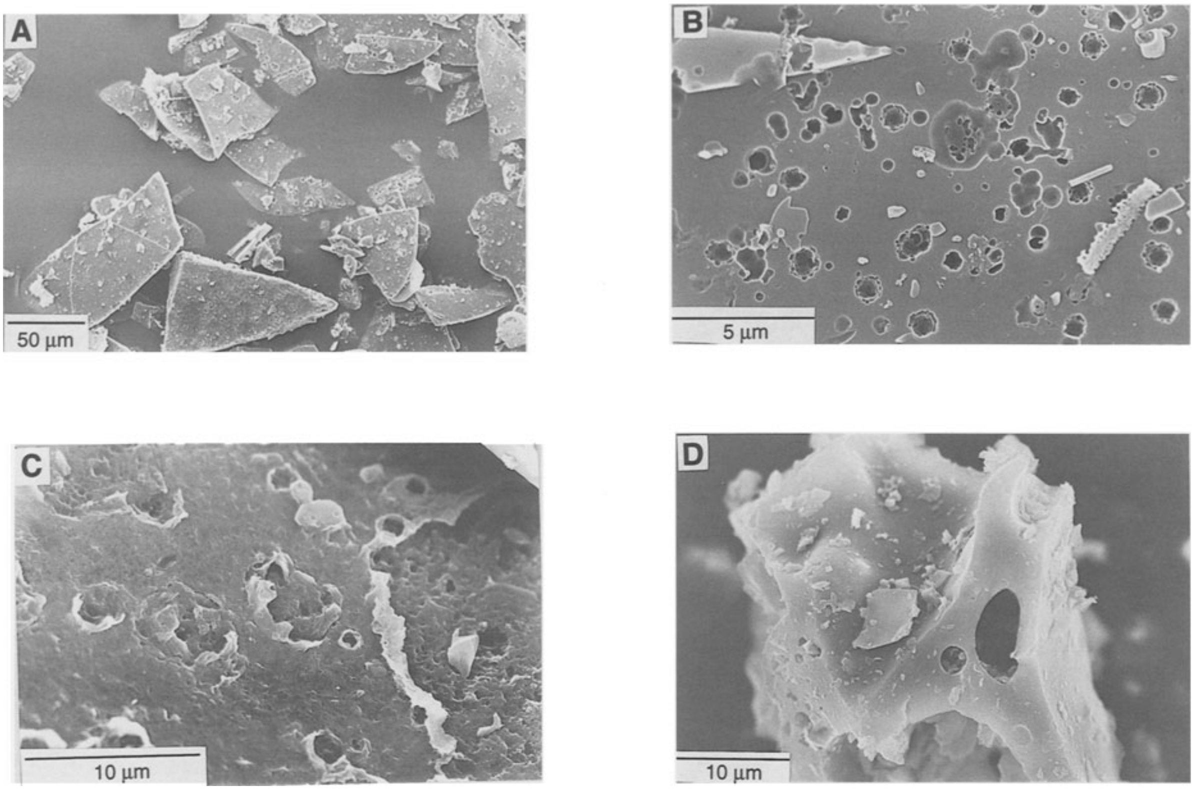

Figure 2. Scanning electron micrographs of glass shards from the volcanic ash layer PP-2. A) Overview of glass shards, B) close-up of vesicular surfaces of a glass shard, C) close-up of slightly altered shard surface and D) seemingly unaltered, vesicular glass shard.

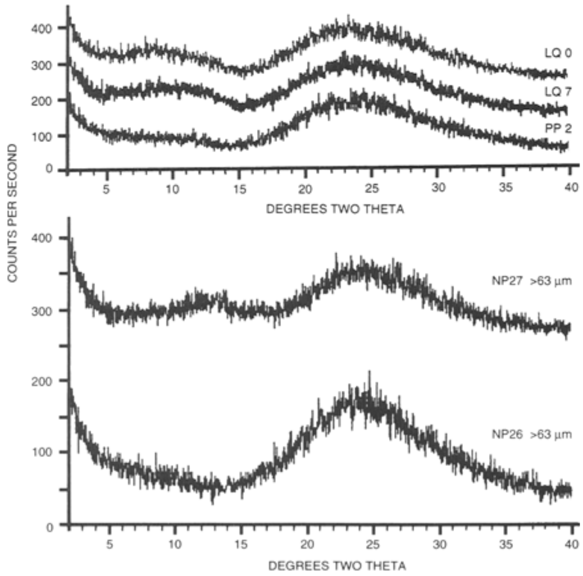

Figure 3. XRD profiles showing a large amorphous hump and no detectable crystalline peaks of bulk volcanic glass powders LQ0, LQ7 and PP2, and of the sand-size fraction of samples NP26 and NP27.

atom biostratigraphy of the host diatomite (Barron 1986). Sample LQ7 occurs 50 m stratigraphically below LQ0 in the Lompoc (Celite Corp.) diatomite quarry. SEM photomicrographs indicate that the ash samples are composed of vesicular glass shards, most of which appear fresh and unaltered (Figures 2a, 2b, and 2d). Some glass shard surfaces appear slightly altered but these are rare (Figure 2c). The volcanic glass layers consist of X-ray amorphous material with crystalline material below the XRD detection limit of 0.5 wt% (Figure 3). The δD and $\delta^{18}O$ values of the glass samples range from −95‰ and 14.0‰ for LQ0 to −90‰ and 17.1‰ for PP2 (Table 1; Figure 4). The glass contains 4.3–4.9 wt% H_2O.

Most older volcanic layers in the Monterey Formation have been altered to clay and zeolite minerals, but sand-size glass grains were separated from partially altered bulk samples of a basal, 1-m-thick tephra bed in the Naples Beach area (NP26 and NP27). Sample NP27 was collected from the base of the tephra bed and is coarser grained and contains less smectite than sample NP26 from the top of the bed. The age of sedimentary rocks directly above the basal tephra bed is 17.4 ± 0.4 Ma (DePaolo and Finger 1991). XRD profiles indicate that the sand fraction of both

NP26 and NP27 consists of amorphous material. The sand fractions of NP26 and NP27 have significantly higher δD and $\delta^{18}O$ values of −78‰ and −66‰, and 22.0‰ and 21.5‰, respectively, compared to the other glassy samples. The stable isotope compositions place the sand-sized glass of NP26 and NP27 in the defined isotopic field of smectite (see below). For comparison, the $\delta^{18}O$ values of feldspar phenocrysts from samples NP26 and NP27 range from 8.5‰ to 10.1‰.

For all 5 of the glassy samples, there is a general positive correlation between the $\delta^{18}O$ values and the water content of the samples (Figure 5a), and a negative correlation between $\delta^{18}O$ values and K_2O and Fe_2O_3 contents of the samples (Figure 5b). The major element compositions of the volcanic glass samples are similar, but sand-sized fractions of samples NP26 and NP27 contain more water (6.1 and >6.3 wt%) and less K_2O and Fe_2O_3 (Table 1).

Bentonite Layers

Bentonite layers in the Monterey Formation contain a mixture of glass and smectite with smectite flakes directly on the surfaces of volcanic glass shards (Figure 6). Bentonite samples are upper Miocene in age (11 to 7 Ma). The clay-size fractions (<1 or <2 μm) from bentonite layers of the Pt. Pedernales (PP), Gaviota Beach (GB) and El Capitan (EC) areas consist primarily of highly smectitic mixed-layer I–S with undetectable to trace amounts of opal CT, quartz or zeolite (0–2 wt%; Figure 7). Bentonite layers commonly contain diagenetic Fe-sulfide minerals (mostly pyrite). Two pairs of samples (EC1 and EC2, GB4 and GB421) were collected from within several meters of each other. Sample EC2 was separated into a <1 μm and 1–2 μm size fraction. The smectite samples have higher MgO and Al_2O_3, and lower K_2O and SiO_2 contents than the hydrated glass samples. The $\delta^{18}O$ values of the smectite samples range from 19.1‰ to 23.9‰ and the δD values range from −86‰ to −69‰ (Figure 4).

Metabentonite Layers

The clay-size fractions of metabentonite layers from the Lions Head area consist mostly of I–S and kaolinite with an average mineral composition of 60% kaolinite, 30% I–S (containing 40% illite layers) and 10% opal-CT/quartz. The clay minerals formed from precursor smectites and volcanic glass of bentonite layers during increased burial diagenesis (Compton 1991). Kaolinite is a common diagenetic mineral in the Lions Head area because of the limited amount of detrital K-bearing minerals such as K-feldspar (Compton 1991). Diagenetic Fe-sulfide minerals are also common in metabentonite layers. Sample LH3 is calcite cemented and sample LH163 is dolomite cemented. The depositional age of the metabentonite layers overlap with the bentonite layers (16–9 Ma; White 1989); however, no correlation is made between individual volcanic layers from the different areas. The $\delta^{18}O$ values of the metabentonite clay fractions range from 16.0‰ to 20.7‰ and are generally lower than the bentonite samples. The metabentonite δD values range from −58‰ to −35‰ and are significantly higher than the bentonite samples.

Siliceous Mudstones from the B-2 Well

The mineralogy of the clay-size fraction (<2 μm) of predominantly siliceous mudstones from the B-2 well is far more complex than the volcanic layers and includes variable amounts of detrital quartz, diagenetic opal CT and quartz, mica, feldspar, kaolinite and I–S (Table 2). Most clay minerals in the B-2 well samples are considered to have detrital rather than volcanic glass precursors (Bramlette 1946). The decrease in $\delta^{18}O$ values with burial depth from 23.1‰ at 1774 m to 21.9‰ at 2073 m generally corresponds to an increase in the percent illite layers of the I–S from around 20–25% to 40% and an increase in diagenetic silica content (opal CT plus quartz). The δD values decrease with depth from −55‰ at 1774 m to −76‰ at 2073 m (Figure 8).

DISCUSSION

Hydration of Volcanic Glass

Volcanic glass samples from the Monterey Formation all contain >4.3 wt% water, despite appearing to be essentially unaltered and uncrystallized (Figure 2). In addition, both the $\delta^{18}O$ and δD values of the glasses increase with increasing degrees of hydration, ranging from 14.0‰ to 22.0‰ and −95‰ to −66‰, respectively (Figure 5a). Obsidian clasts from air-fall tephra layers contain 0.5 to 3.0 wt% H_2O, $\delta^{18}O$ values of 7‰ to 10‰, and δD values of −90 to −60‰ (Taylor et al. 1983). Open-system degassing before eruption can result in loss of water and D, with water contents of obsidian flows of 0.3 to 0.1 wt% and δD values of −100‰ to −130‰ (Taylor et al. 1983; Newman et al. 1988; Taylor 1991; Turi et al. 1991). The range in $\delta^{18}O$ values of fresh rhyolitic tephra is much lower than the values measured for tephra layers in this study and indicates that the ^{18}O content of the glass increased during hydration (Figures 4 and 5a). The $\delta^{18}O$ values of separated feldspar phenocrysts from samples NP26 and NP27 (8.5‰ to 10.1‰) are characteristic of primary oxygen isotope compositions of feldspars in silicic volcanic rocks (Taylor 1968). This confirms that the glasses did not have anomalously high primary magmatic $\delta^{18}O$ values, which can result from assimilation of continental material into the magma prior to eruption (Turi et al. 1991). Primary magmatic compositions of around 8 to 10‰ are also consistent with extrapolated $\delta^{18}O$ values for glasses with a water content of about 2.5 wt% (Figure 5a). Measured δD values

Table 1. Element composition of Monterey Formation samples expressed as oxides.

Sample	Location	Depth (m)	Grain size	SiO_2 XRF	Al_2O_3 XRF	CaO XRF	MgO XRF	Na_2O XRF	K_2O XRF
Volcanic glass									
LQ0	Lompoc quarry		bulk	71.4	11.7	0.67	0.18	2.23	4.52
LQ0 (duplicate)	Lompoc quarry		bulk	71.7	11.7	0.65	0.17	2.15	4.52
LQ-7	Lompoc quarry		bulk	71.9	11.3	0.49	0.12	2.39	4.33
PP-2	Pt. Pedernales		bulk	71.0	11.6	0.50	0.16	2.65	4.07
NP26-63	Naples Beach		>63	74.4	11.3	0.67	0.16	2.24	3.00
NP27-63	Naples Beach		>63	72.9	11.3	0.67	0.16	2.37	3.16
Bentonite (smectite)									
PP6CLAY	Pt. Pedernales		<2	54.0	17.9	0.40	2.96	2.91	0.41
EC1-2C	El Capitan		<1	47.2	19.9	0.51	2.34	2.16	0.22
EC2-2C	El Capitan		<1	52.2	22.9	0.30	2.77	1.98	0.21
EC2-2B	El Capitan		1-2	54.3	23.8	0.14	2.79	2.20	0.25
GB421-2T	Gaviota Beach		<1	54.2	20.3	0.56	2.82	2.14	0.10
GB4-2C	Gaviota Beach		<1	50.1	20.9	0.12	2.42	3.40	0.46
Metabentonite (kaolinite + I–S)									
LHASHTC	Lions Head	50	<2	45.8	33.5	0.23	1.05	0.22	0.51
LH163†	Lions Head	150	<2	40.9	24.2	6.51	3.94	1.84	0.91
LH3 (calcite-free)	Lions Head	190	bulk‡	39.1	21.7	0.59	0.88	2.56	1.07
LH7BP	Lions Head	240	bulk‡	22.8	8.5	0.22	0.48	0.36	0.91
LH10-1	Lions Head	290	<1	47.0	27.4	0.13	1.48	1.36	0.95
LH11-2C	Lions Head	294	<2	45.0	28.2	0.25	0.73	1.40	0.58
Siliceous mudstone (cuttings)									
B2 5820	B-2 well	1774	<2	62.4	12.1	1.34	1.81	0.79	2.01
B2 6000	B-2 well	1829	<2	55.3	10.7	1.23	3.28	0.42	2.28
B2 6600	B-2 well	2012	<2	65.6	11.7	1.20	1.86	0.78	1.85
B2 6800	B-2 well	2073	<2	69.6	10.8	0.95	1.68	0.85	1.6

† LH163 contains dolomite, ‡ <1 μm size fraction analyzed for isotopes, NM = not measured, OC = organic carbon.

of tephra layers in this study overlap the range in δD values of fresh rhyolitic tephra (Figure 4). The δD values of the tephra layers in this study probably reflect an increase in D with increased hydration and alteration of the glass rather than variations in the δD values of the erupted tephra because δD values correspond to $\delta^{18}O$ values.

Previous workers have found similar shifts in the isotopic compositions of hydrated silicic glasses (Taylor 1968; Garlick and Dymond 1970; Cerling et al. 1985; Dobson and O'Neil 1987; Friedman et al. 1991a). In all cases, the isotopic shifts were not associated with detectable mineral formation. The low MgO contents of the glass samples in this study (Table 1) are consistent with the XRD analyses and indicate no significant smectite in the glass samples. The equilibrium stable isotope fractionations between hydrated glasses and associated pore fluids are estimated to be +23‰ or greater for $\delta^{18}O$ and −50‰ to −25‰ for δD (Cerling et al. 1985; Friedman et al. 1991b). Applying these isotopic fractionations to the most hydrated glass samples analyzed in this study (NP26/27) predicts approximate equilibrium isotope compositions of the fluid of −1‰ for $\delta^{18}O$ and −16‰ to −53‰ for δD. The estimated $\delta^{18}O$ values is within the range of values of late Miocene seawater, but the range in δD values is significantly lower than expected for late Miocene seawater. The low δD values suggest that these glasses may have exchanged with meteoric waters associated with regional uplift and erosion during the Pliocene/Pleistocene (Ingle 1980).

The increase in $\delta^{18}O$ with decreasing K_2O and Fe_2O_3 contents of the volcanic glass samples (Figure 5b) suggests that the change in the oxygen isotope composition is accompanied by chemical alteration. The depletion of K and Fe from the glass generally corresponds to increasing hydration (Figure 5a). Garlick and Dymond (1970) and Cerling et al. (1985) also noted significant depletion of K with increasing hydration. For samples LQ0, LQ7 and PP2, there is a progressive increase in Na_2O content of 0.45 mol% and decrease in K_2O content of 0.3 mol%. Pore water Na and H appear to exchange for K and Fe in the glass with increasing hydration. An approximate reaction representative of the progressive hydration of the glass samples LQ0, LQ7 and PP2 based on their elemental analyses (Table 1) is:

$$0.9Na^+ + 0.5H^+ + 1.6H_2O + \text{glass } (14.5H_2O)$$

$$= \text{glass } (16.3H_2O) + 0.6K^+ + 0.4Fe^{2+}. \qquad [1]$$

The high Na/K ion ratio of seawater would favor ex-

Table 1. Extended.

Fe_2O_3 XRF	MnO XRF	TiO_2 XRF	P_2O_5 XRF	Cr_2O_3 XRF	*LOI* XRF	*SUM* XRF	*OC* Leco	*S* Leco	H_2O >150 °C	Stable isotopes δ180 (‰ SMOW)	δD
2.13	0.06	0.39	0.07	NM	6.5	99.8	NM	<0.01	4.35	14.0	−95
2.00	0.06	0.38	0.07	NM	6.5	99.9	NM	<0.01	4.35	14.0	−95
1.84	0.05	0.24	0.03	NM	6.5	99.2	NM	0.01	4.31	15.6	−89
1.46	0.05	0.27	0.04	NM	6.9	98.7	NM	0.02	4.89	17.1	−90
0.70	0.05	0.17	0.06	0.03	7.2	100.1	NM	<0.01	6.08	21.5	−66
0.80	0.05	0.17	0.11	0.03	8.0	99.8	NM	<0.01	>6.29	22.0	−78
0.92	0.04	1.45	2.10	0.04	16.0	99.2	NM	NM	4.47	23.9	−84
0.79	0.04	0.96	1.51	0.06	16.3	92.1	NM	NM	5.35	19.1	−79
0.44	0.04	0.30	1.78	0.04	16.9	99.9	NM	0.13	4.55	19.8	−86
0.36	0.01	0.35	0.79	0.01	15.4	100.4	NM	0.18	4.19	20.3	−69
3.60	0.01	0.36	2.73	0.01	13.3	100.2	NM	0.23	5.36	21.8	−76
0.81	0.04	0.21	4.64	0.03	15.5	98.7	NM	0.04	5.28	22.1	−76
1.00	NM	0.95	0.06	0.02	17.9	101.2	0.00	0.25	8.66	17.8	−44
0.62	NM	0.31	0.5	0.01	19.4	99.1	0.08	0.00	>9.55	16.0	−35
10.90	0.06	1.24	0.15	0.04	20.3	98.7	NM	6.27	6.36	18.1	−49
22.20	0.07	0.82	0.29	0.06	44.3	101.1	NM	16.00	5.93	19.5	−58
0.99	0.04	0.37	1.67	0.03	16.8	98.4	NM	0.20	8.41	20.7	−49
2.44	0.04	1.15	2.46	0.03	16.3	98.6	NM	2.27	>10.06	17.8	−47
3.51	NM	0.64	0.66	0.03	14.5	99.8	3.20	NM	4.69	23.1	−56
2.92	NM	0.53	1.02	0.03	21.5	99.2	3.01	NM	4.06	23.2	−54
3.45	NM	0.59	0.74	0.03	12.6	100.4	2.88	NM	4.26	22.4	−63
3.46	NM	0.56	0.61	0.03	10.5	100.6	2.55	NM	2.74	21.9	−76

change of K in the glass for Na in seawater (White 1983). In samples NP26 and NP27, both K and Na contents decrease. Na was probably lost from the glass during early hydration since most previous studies have found Na to be highly labile (Lipman 1965; White 1983) and most fresh rhyolitic glasses contain an average of around 4 wt% Na_2O (Washington 1917). Assuming a starting composition of average fresh (nonhydrated) rhyolitic glass of 1.8 wt% H_2O and 4 wt% Na_2O, the initial hydration reaction to form the least hydrated glass sample LQ0 would be:

$$4H^+ + 6.3H_2O + \text{glass } (6.2H_2O)$$

$$= \text{glass } (14.5H_2O) + 4Na^+. \quad [2]$$

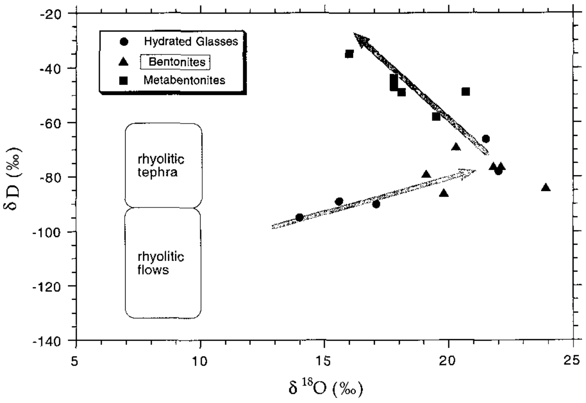

Figure 4. The $\delta^{18}O$ and δD values of the hydrated volcanic glass (tephra), clay-size fraction of bentonite samples (mostly highly smectitic I–S), and clay-size fraction of the metabentonites (mostly kaolinite and mixed-layer I–S). The fields of unaltered rhyolitic tephra and flows are outlined (Taylor et al. 1983; Taylor 1991) and the arrows indicate the trend in hydrogen and oxygen isotope compositions with increasing burial metamorphism.

Equation [2] suggests that most of the water is taken up by the glass during initial Na depletion. Of the 8.3 moles of water taken up by the glass in Equation [2], only 2 moles are by exchange of H for Na. Extrapolation of the $\delta^{18}O$ and K_2O trend (Figure 5b) to an average initial $\delta^{18}O$ value of +9‰ based on the $\delta^{18}O$ values of the separated feldspars gives a hypothetical initial K_2O content of the glass of around 5.5 wt%. However, the fact that most rhyolitic glasses have around 4.5 wt% (maximum of 5.2 wt%) K_2O (Washington 1917) suggests that the initial increase in the $\delta^{18}O$ of the glass from 9‰ to 14‰ was associated with the loss of Na. Loss of K and Fe from glass appears to occur during later hydration and corresponds to a greater increase in the $\delta^{18}O$ value of the glass than loss of Na and uptake of water. The difference in elemental composition between the moderately hydrated sample

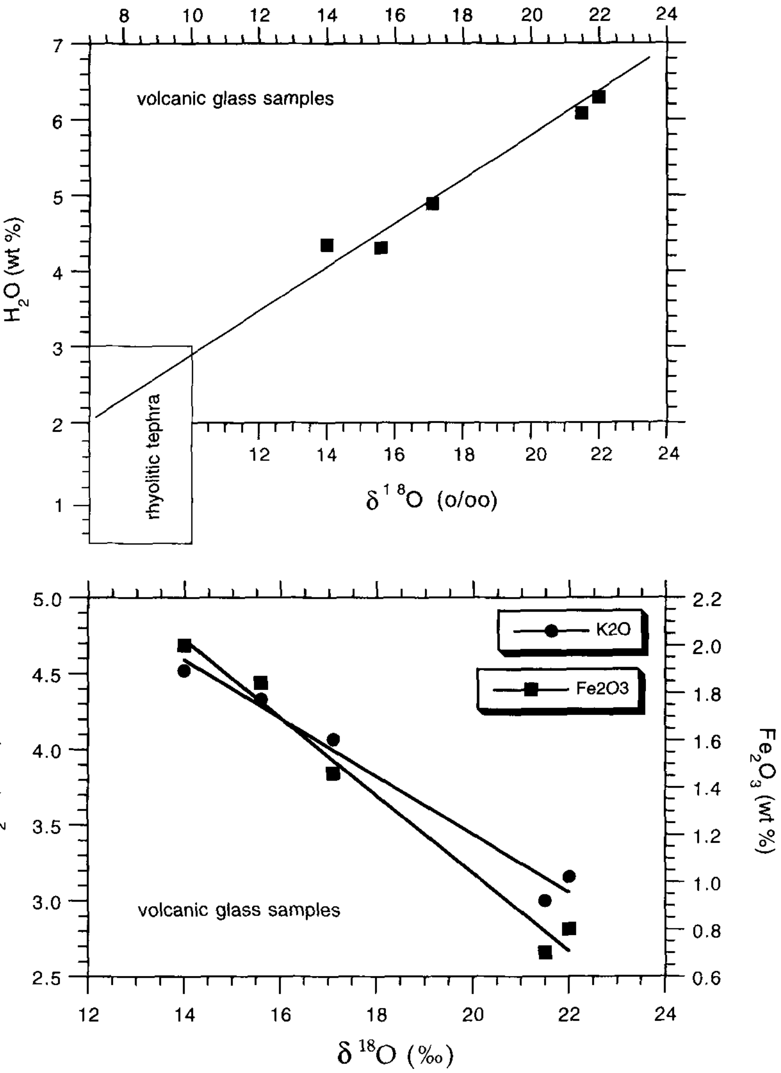

Figure 5. a) Increase in the weight percent H_2O of the volcanic glass samples with increasing $\delta^{18}O$ values. The field of $\delta^{18}O$ values and water contents of fresh rhyolitic tephra is outlined (Taylor et al. 1983). b) Decrease in the weight percent K_2O and Fe_2O_3 of the volcanic glass samples with increasing $\delta^{18}O$ values.

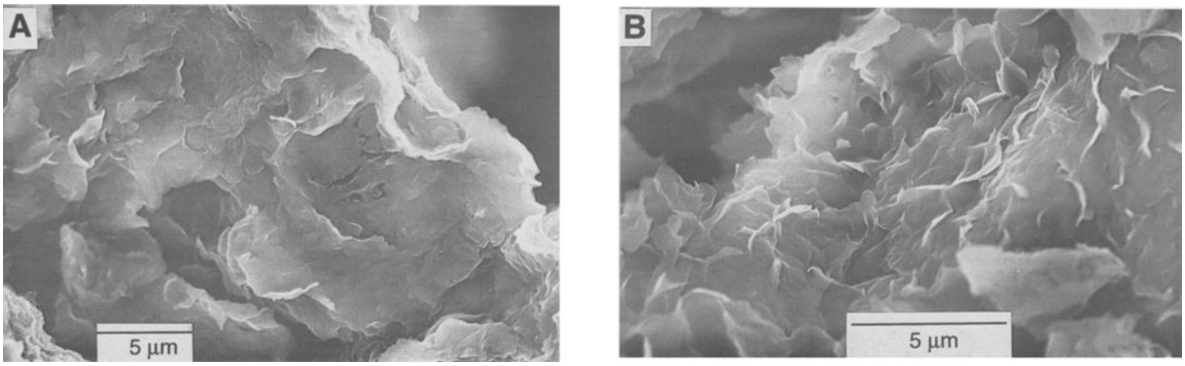

Figure 6. Scanning electron micrographs of bentonite samples showing A) smectite clay flakes forming on the surface of a volcanic glass shard precursor from sample PP6, and B) more extensive alteration of glass to smectite clay in sample GB421.

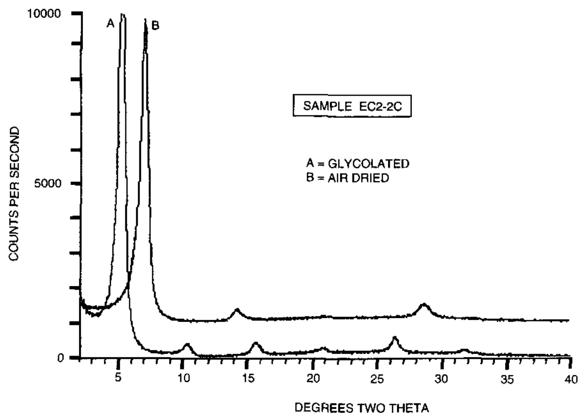

Figure 7. X-ray diffraction profiles of the A) glycolated and B) air-dried clay-size fraction of bentonite sample EC2-2C composed of highly smectitic I–S.

PP2 and the most hydrated samples NP26/27 indicates a greater exchange of H for K, Na, and Fe during late-stage hydration:

$$0.1Ca^{2+} + 3.2H^{+} + 1.4H_2O + \text{glass}\ (16.3H_2O)$$

$$= \text{glass}\ (19.3H_2O) + 1.4K^{+} + 0.8Na^{+} + 0.6Fe^{2+}. \qquad [3]$$

The silica content (on a near water-free basis) is at the upper end of the range of values for nonhydrated rhyolitic glasses and suggests that there was little or no loss of silica during hydration. Silica loss may have been inhibited by the high silica activity of the pore waters of adjacent diatomaceous rocks.

Alteration of Volcanic Glass to Smectite

The stable isotope compositions of the smectite samples are similar to those of the most hydrated glass samples (NP26/27) and suggests that glass-fluid and smectite-fluid fractionation factors are similar. The elemental composition and SEM textures indicate that the analyzed clay-size fractions of the bentonite samples are predominantly smectite clay and do not contain significant amounts of precursor glass. Using the smectite-water fractionation curve of Sheppard and Gilg (1996) for the estimated temperature of the glass to smectite reaction of 40 °C, the oxygen isotope compositions of waters in equilibrium with the smectites are between −3‰ and 2‰. Although the opal A to opal CT reaction is estimated to range from 17–50 °C (Murata et al. 1977; Matheney and Knauth 1993), an average temperature of 40 °C is assumed for the overlapping glass to smectite reaction because most bentonites occur in predominantly opal CT rocks rather than in predominantly opal A rocks that contain early, low-temperature opal CT chert nodules (Behl and Garrison 1994). The calculated $\delta^{18}O$ values for the formation water of between −3‰ and 2‰ bracket the $\delta^{18}O$ value of Miocene seawater, as well as possible increases in the $\delta^{18}O$ of pore waters from silica and carbonate diagenesis (Winter and Knauth 1992) or decreases from glass alteration or albitization of plagioclase (Fisher and Boles 1990). Variations in the isotopic composition of the smectite samples do not correspond to changes in the elemental compositions or to field evidence of approximate burial depths (temperature).

The hydrogen isotope fractionation for smectites is not well known for temperatures less than 100 °C (Sheppard and Gilg 1996). In the case of the low-iron smectites of this study, the hydrogen isotope fractionation with water at low temperatures is approximately −25‰ (Gilg and Sheppard 1995) and predicts δD values for the formation waters between −61‰ and −44‰. However, some studies indicate a trend of increasing hydrogen isotope fractionation with decreasing temperatures below 150 °C (Capuano 1992). Extrapolation of the fractionation trend of Capuano (1992) to the estimated temperature of the glass to smectite reaction of 40 °C predicts a greater hydrogen isotope fractionation of −45‰ which would correspond to formation water δD values of between −41‰ and −24‰. A greater hydrogen isotope fractionation of −45‰ at low temperatures is supported by smectite hydroxyl-porewater fractionations of −43 to −46‰ measured by France-Lanord and Sheppard (1992). Studies of marine pore waters indicate a decrease in δD values of 5 to 15‰ with depth that is interpreted to represent the lower δD values of seawater prior to major ice buildup since the middle Miocene (Friedman and Hardcastle 1988; France-Lanord and Sheppard 1992). Assuming a late Miocene seawater δD value of −5‰ still indicates that the δD values of the smectites are significantly lower (−36 to −19‰) than predicted for equilibrium exchange.

There are several possible explanations for the low δD values of the smectite samples. Contamination of the sample gas during analysis by D-depleted hydrogen derived from organic matter seems unlikely given the low organic matter content of the bentonite samples. Organic matter was not visually apparent in any of the volcanic layers studied and the organic carbon content of the few that were analyzed are <0.1 wt% (Table 1). Therefore, there is insufficient organic matter in the volcanic layers to produce the low δD values. Although the adjacent diatomites are organic-rich, the only slight decrease in δD values observed in marine pore waters (Friedman and Hardcastle 1988) suggests that pore water δD values are not significantly lowered by exchange with D-depleted products of organic matter diagenesis. Previous workers have attributed low δD values of clay minerals to exchange with low δD meteoric waters (Yeh and Savin 1976; Wilson et al. 1987; Bird and Chivas 1988). It is possible to have exchange of hydrogen isotopes at low temperatures

Table 2. Calculated mineralogy of B-2 well samples from Compton (1991) and Compton et al. (1992).

Siliceous mudstone (cuttings >0.5 cm)

Sample	Location	Depth (m)	Grain size	Opal CT	Qtz	Det Qtz	Feld-spar	Mica	Kaol	I–S	OM	Franc
B2 5820	B-2 well	1774	<2 μm	5	12	17	6	14	5	24	4.5	1
B2 6000	B-2 well	1829	<2 μm	2	13	15	4	15	5	21	4.2	1
B2 6600	B-2 well	2012	<2 μm	0	22	16	7	14	5	23	4.0	1
B2 6800	B-2 well	2073	<2 μm	0	30	15	5	10	5	23	3.6	1

Det Qtz = detrital quartz, I–S = mixed-layered illite–smectite, OM = organic matter, Franc = francolite, %NH_4 = NH_4/(NH_4 + K).

between meteoric waters and clay minerals without significant oxygen isotope exchange (O'Neil and Kharaka 1976). Monterey bentonite and metabentonite layers are considered to have formed in equilibrium with buried marine pore waters, but regional tectonic uplift and erosion in the Pliocene and late Pleistocene (Ingle 1980) probably exposed these rocks to meteoric waters.

Alteration of Bentonite to Metabentonite Layers

Bentonite layers alter to metabentonite layers with increasing burial diagenesis. The $\delta^{18}O$ values of the metabentonite samples decrease from 20.7‰ to 16.0‰ and their δD values increase from −58‰ to −35‰ away from the defined bentonite (smectite) isotopic field (Figure 4). The calculated $\delta^{18}O$ values of water in equilibrium with the metabentonites range from −0.6‰ to 4.3‰. The range in $\delta^{18}O$ values is calculated for an average temperature of 85 °C using the kaolinite-water, smectite-water, and illite-water fractionation curves of Sheppard and Gilg (1996), and assumes an average mineral composition of the metabentonite of 60% kaolinite, 30% I–S containing 40% illite layers, and 10% opal CT/quartz having a $\delta^{18}O$ value of 30‰ (Behl and Garrison 1994). The formation of illite and kaolinite from smectite occurs over a temperature range of approximately 50–120 °C and coincides with the opal CT to quartz transformation (Murata et al. 1977). The range in $\delta^{18}O$ values is somewhat higher than the range of values calculated for the smectite samples and consistent with the range of marine connate pore water $\delta^{18}O$ values estimated from the isotopic composition of dolomite from similar diagenetic grade Monterey rocks (Winter and Knauth 1992). An increase in the $\delta^{18}O$ value of the formation waters with increasing diagenetic grade is consistent with the decrease in the mineral $\delta^{18}O$ values during the illitization and opal CT to quartz reactions (Murata et al. 1977; Behl and Garrison 1994), assuming an approximately closed system. The possible δD values of the formation waters range from −33‰ to −5‰ using kaolinite-water and illite-water fractionation factors at 85 °C of −25‰ to −30‰ (Sheppard and Gilg 1996). These δD values are similar to or moderately lower than Miocene seawater and indicate somewhat D-depleted formation waters (see below) or possible exchange between the clays and meteoric waters.

Isotopic Trends of Siliceous Mudstones

The $\delta^{18}O$ values of the clay-size fraction of siliceous mudstones from the B-2 well decrease from 23.1‰ to 21.9‰ with depth (Figure 8). The decrease in $\delta^{18}O$ values is probably a result of increased illitization and recrystallization of opal CT to quartz and exchange with ambient fluids over the depths sampled. The overall higher $\delta^{18}O$ values of B-2 well samples compared to similar grade metabentonites from the Lions Head area probably reflect a greater abundance of diagenetic silica in the B-2 well samples (Table 2).

The decrease in δD values of the B-2 well samples from −54‰ to −76‰ with depth is opposite to the general increase in δD observed for the metabentonites from the Lions Head area and Texas Gulf Coast mudrocks, where δD values increase from −55‰ to −35‰ with increasing burial depth and illitization (Yeh 1980). The δD values of bulk samples are difficult to interpret because of the large number of potential mineral and organic sources of hydrogen having widely different δD values. Unlike the volcanic layers discussed above, the B-2 well siliceous mudstones contain appreciable amounts of organic matter (Table 2). The B-2 well is situated in the major hydrocarbon reservoir of the Pt. Arguello Field (Crain et al. 1985) and contains a mixture of marine organic matter and oil. Marine organic matter and oil have δD values of −76 and −89‰, respectively (Schiegl and Vogel 1970; Schoell 1983). No attempt was made to remove the organic matter or oil prior to isotopic analysis. The impact of organic hydrogen on the δD analyses can be estimated by assuming that the organic matter in the B-2 well samples contains 5 wt% hydrogen with an average δD value of −83‰. The amount of water (>150 °C) that could potentially be derived from organic hydrogen is estimated to be between 42 and 58%. If the balance of the water is derived from kaolinite and I–S hydroxyl having an isotopic fractionation factor of around −30‰ (Sheppard and Gilg 1996), then the calculated δD value of the water in equilibrium with samples 5820 and 6000 is similar to the δD value of seawater whereas the δD value of the

Table 2. Extended.

TiO_2	Excess Fe_2O_3	Excess H_2O	SUM	%illite layers	Fixed NH_4 wt%	$\%NH_4$
0.5	2.1	8	99	20	0.18	19
0.4	1.2	15	97	25	0.29	18
0.4	2.1	6	101	25	0.21	23
0.4	2.3	4	99	40	0.22	26

water in equilibrium with the deeper samples 6600 and 6800 is somewhat less (−11 to −15‰) than the δD value of seawater. These are considered maximum δD values of the formation water because complete conversion of organic hydrogen to water is unlikely. Another source of organic hydrogen in these samples is fixed ammonium in the diagenetic illite. The greater amount of illite layers in the I–S and $NH_4/(NH_4+K)$ ratios in the deeper samples 6600 and 6800 (Table 2) may explain in part their more negative δD values.

In addition to organic hydrogen, the unusual δD trend of the B-2 well samples may reflect low δD formation waters. Unfortunately, no isotopic data are available for waters from the B-2 well. The δD values of −17 to −35‰ have been documented in diagenetically modified connate waters from more proximal Miocene rocks of the San Joaquin Basin (Kharaka et al. 1973; Fisher and Boles 1990) and may reflect exchange between both detrital illite and water and hydrocarbons and water (Fisher and Boles 1990). Overlap of the illitization reaction with oil generation would allow for effective isotope exchange between clay minerals and hydrocarbon-exchanged fluids in the B-2 well and Lions Head samples. A meteoric influence is unlikely for the offshore B-2 well.

SUMMARY

The $\delta^{18}O$ and δD values of volcanic ash (tephra), bentonite and metabentonite layers in the Monterey Formation reflect distinct trends in the hydration of glass, the transformation of glass to smectite and the transformation of smectite to illite and kaolinite with increasing burial diagenesis. Although the volcanic glass visually appears to consist of mostly unaltered shards, an increase in $\delta^{18}O$ and δD values of the volcanic glass that corresponds to an increase in water content and depletion of K and Fe indicates that the glass is chemically altered. The extent to which isotopic compositions have changed appears to be directly related to the degree of hydration and the age of the volcanic glass as noted in earlier studies (Garlick and Dymond 1970; Cerling et al. 1985; Dobson and O'Neil 1987).

The $\delta^{18}O$ values of the most hydrated glass samples are approaching isotopic equilibrium with Miocene seawater. Smectite from bentonite layers has $\delta^{18}O$ and δD values in the same range as the most hydrated glass samples, suggesting that the glass-water and smectite-water fractionation factors are similar. The $\delta^{18}O$ values of the smectites are approximately in equilibrium with ocean water at 40 °C. Clay minerals from metabentonite layers have lower $\delta^{18}O$ values than precursor smectites, reflecting equilibration at higher temperatures and with more diagenetically modified (^{18}O enriched) formation waters.

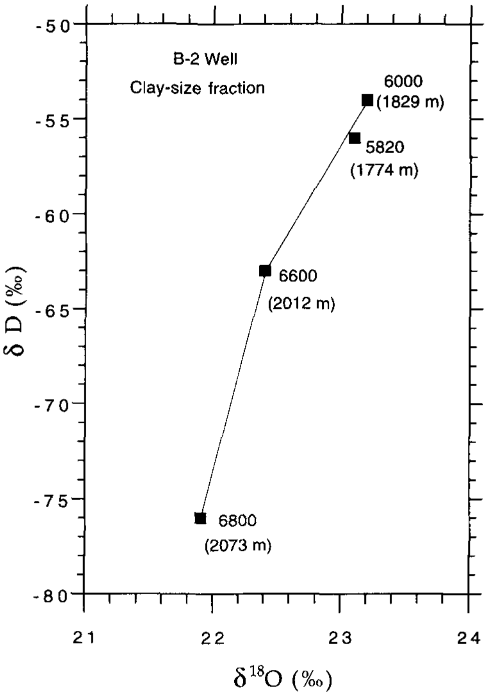

Figure 8. The $\delta^{18}O$ and δD values of the clay-size fraction (<2 μm) of siliceous mudstones from the B-2 well showing the decrease in both $\delta^{18}O$ and δD values with burial depth (indicated in parentheses).

The δD values of the smectites would be in equilibrium with waters having δD values of between −41‰ and −24‰, much lighter than expected for Miocene seawater. The overall lower δD values of volcanic glass, bentonite and metabentonite layers sampled from the coastal outcrops most likely reflect hydrogen exchange with meteoric waters associated with tectonic uplift and erosion during the Pliocene and Pleistocene.

The isotopic compositions of the clay-size fractions of siliceous mudstones from the B-2 well are significantly different from those of the metabentonite layers, despite being subjected to approximately the same diagenetic conditions. The higher $\delta^{18}O$ values of the mudstones and their slight increase with burial depth probably reflect greater diagenetic quartz contents. An unusual decrease in δD values with burial depth probably reflects a significant contribution of organic hydrogen to the analyzed water in addition to possibly D-depleted formation waters from detrital illite-water and hydrocarbon-water exchange.

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