ORIGIN OF CRETACEOUS AND OLIGOCENE KAOLINITES FROM THE IWAIZUMI CLAY DEPOSIT, IWATE, NORTHEASTERN JAPAN

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Abstract—Hydrogen- ($\delta D = -106$ to $-97‰$) and oxygen- ($\delta^{18}O = +14.0$ to $+16.6‰$) isotope compositions of kaolinite from late Cretaceous and Oligocene deposits at Iwaizumi, northeastern Japan, indicate that these clays formed by weathering of volcanic parent rocks, rather than during hydrothermal (>100 °C) alteration. The Iwaizumi kaolinites also are depleted of D and ^{18}O relative to kaolinite formed during modern, tropical weathering, suggesting that the kaolinite developed under cool or cool-temperate conditions. The oxygen-isotope compositions of the kaolinite increase slightly upward through the deposits, perhaps implying a modest increase in temperature from late Cretaceous to Oligocene time. The δD and $\delta^{18}O$ results for kaolinite from the Oligocene deposits closely follow the kaolinite weathering line. However, a small but systematic deviation from this line for the Cretaceous kaolinites is most simply explained by post-formational, hydrogen-isotope exchange between these clays and downward percolating meteoric water.

Key Words—Climate, Cretaceous, Hydrogen-isotopes, Iwate, Japan, Kaolinite, Oligocene, Oxygen-isotopes.

INTRODUCTION

The Iwaizumi clay deposit, located in northeastern Honshu, is one of several highly productive, late Cretaceous or Oligocene fire-clay and flint-clay deposits in Japan. These deposits are characterized by well-crystallized kaolinite, and are very pure and highly refractory. On the basis of mineralogical and paleobotanical data, Iijima (1972) and Tanai et al. (1978) suggested that this kaolinite formed by lateritic weathering and intensive desilication of parent volcanic rocks under warm-temperate to subtropical, humid conditions. This conclusion is consistent with the common view that extensive weathering, leading to kaolinite formation and enrichment in gibbsite and hematite, is indicative of such climates (Biscaye 1965; Ollier 1969). Bird and Chivas (1988) have challenged the universality of such an assumption, using oxygen isotopes to show that Permian kaolinitic weathering in eastern Australia occurred at relatively low temperatures.

A hydrothermal origin has also been proposed for the Iwaizumi clay deposits, based on the microscopic presence of dickite pseudomorphs after feldspar (Hu and Zhang 1988). Dickite is a common hydrothermal alteration product of volcanic rocks. However, it is difficult to demonstrate unequivocally the presence of dickite in the Iwaizumi clay deposits from the X-ray diffraction (XRD) and differential thermal analysis patterns of Hu and Zhang (1988). Furthermore, dickite formation under sedimentary conditions has been reported, for example, the Ashfield shale in Australia

(Davey et al. 1975) and Permo-Triassic sandstones in Spain (Ruiz Cruz and Moreno Real 1993).

In this paper, we use the hydrogen- and oxygen-isotope compositions of kaolinite from a stratigraphic section (Figure 1) through the Iwaizumi mine to determine the origin of these clays. Results for a single sample reported by Marumo et al. (1979, 1982) plot near the line that describes kaolinite formation during weathering (Savin and Epstein 1970). Our data confirm this earlier observation and provide further insight into the evolution of these kaolinites.

The hydrogen- and oxygen-isotope compositions of kaolinite are determined primarily by temperature and the isotopic composition of water present during crystallization (Savin and Epstein 1970; Lawrence and Taylor 1971, 1972). Because the δD and $\delta^{18}O$ values of meteoric water vary systematically with latitude and altitude (Craig 1961; Dansgaard 1964; Yurtsever and Gat 1981), the stable isotope composition of kaolinite formed during weathering is normally considered to reflect the location, and hence mean temperature, of the landscape surface (Lawrence and Taylor 1971, 1972). For example, lower kaolinite δ-values are characteristic of cooler regions, typically located at higher latitudes and/or altitudes. For oxygen, post-depositional isotopic exchange between kaolinite and water is virtually non-existent (O'Neil and Kharaka 1976). Thus, this climatic signature is almost always preserved. However, hydrogen-isotope exchange can occur under some conditions. These results should be interpreted more cautiously (O'Neil and Kharaka 1976; Bird and Chivas 1988; Longstaffe and Ayalon 1990).
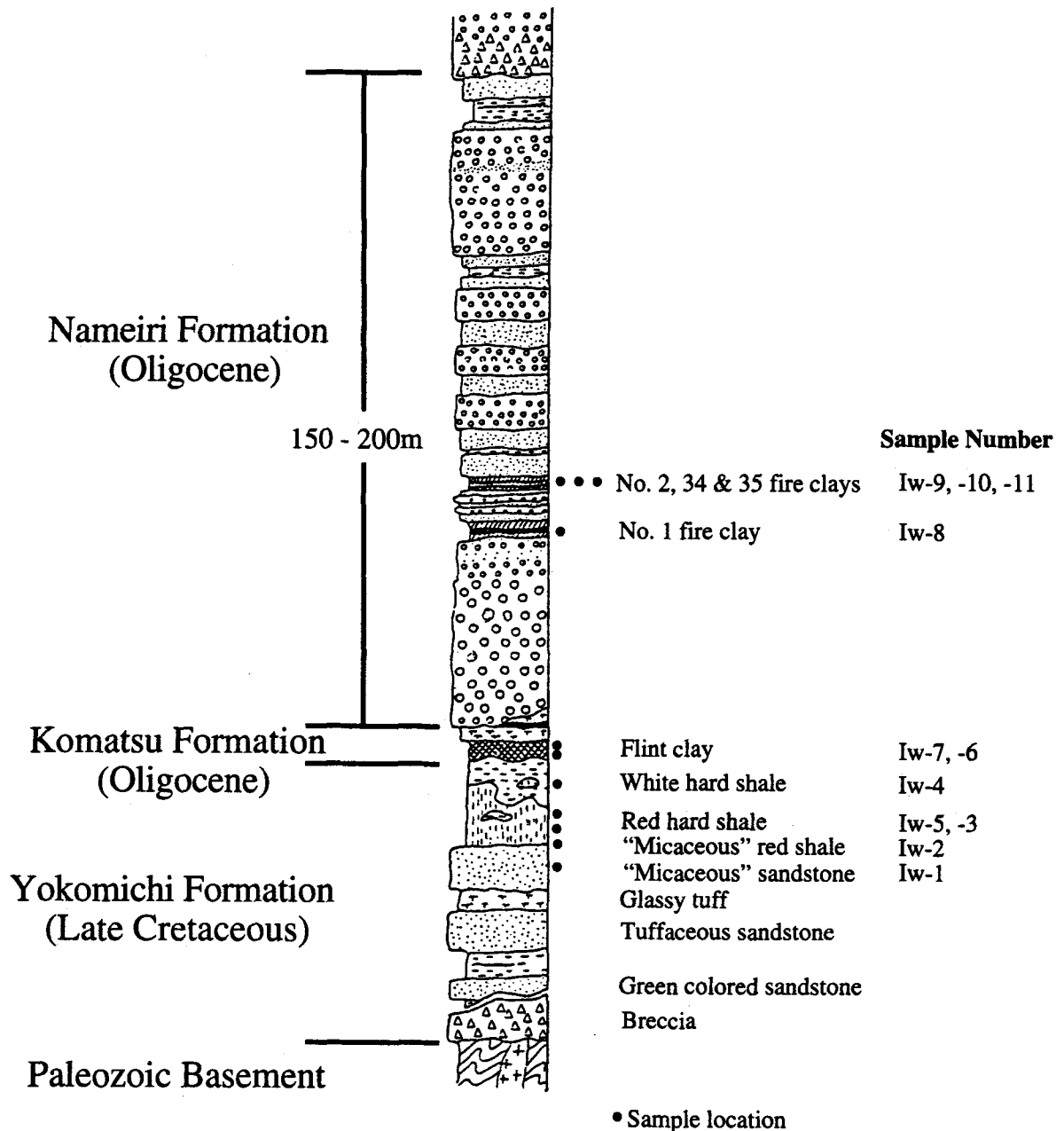
Figure 1. Schematic section through the Iwaizumi clay deposits (Fujii 1970).

GEOLOGIC SETTING AND SAMPLING

Basement rocks surrounding the Iwaizumi clay mine consist of Paleozoic sandstone, chert, shale and granodiorite, and are overlain unconformably by late Cretaceous and Paleogene volcanic rocks, which have a glassy texture and are highly permeable (Fujii 1970). The detailed stratigraphy, lithology and mineralogy of the kaolin deposits in the vicinity of the Iwaizumi clay mine (39°53'N, 141°38'E, 350 m above sea level) have

been described previously by Fujii (1970), Iijima (1972) and Tanai et al. (1978). Kaolinitic clays occur in 3 units, from oldest to youngest, the Yokomichi, Komatsu and Nameiri formations (Figure 1). An unconformity exists between the Yokomichi and Komatsu formations (Tanai et al. 1978). A fission-track zircon date of 71.2 ± 4.4 Ma has been reported for the Upper Yokomichi Formation (Kato et al. 1986).

Eleven samples representing the stratigraphic range of kaolinite in the Iwaizumi clay mine, plus a ground-

Table 1. Sample horizons and stable-isotope results for kaolinites from the Iwaizumi Clay Mine, northeast Japan.

Sample	Stratigraphy[1]	Age[1]	Lithology[2]	Color (moist)
Iw-11	Nameiri Fm.	Oligocene	No. 35 fire clay	10YR3/1
Iw-10	Nameiri Fm.	Oligocene	No. 34 fire clay	5Y1.7/1
Iw-9	Nameiri Fm.	Oligocene	No. 2 fire clay	5Y5/2
Iw-8	Nameiri Fm.	Oligocene	No. 1 fire clay	2.5Y4/2
Iw-7	Komatsu Fm.	Oligocene	Flint clay (upper unit)	7.5YR4/2
Iw-6	Komatsu Fm.	Oligocene	Flint clay (lower unit)	7.5YR6/2
Iw-5	Yokomichi Fm.	Late Cretaceous	Red shale (upper unit)	7.5R3/4
Iw-4	Yokomichi Fm.	Late Cretaceous	White shale	5Y7/1
Iw-3	Yokomichi Fm.	Late Cretaceous	Red shale (lower unit)	7.5R4/6
Iw-2	Yokomichi Fm.	Late Cretaceous	[3]"Micaceous" red shale	7.5R4/6
Iw-1	Yokomichi Fm.	Late Cretaceous	[3]"Micaceous" sandstone	5Y7/1

[1] After Tanai et al. (1978).
[2] After Fuji (1970).
[3] Vermicular aggregation of kaolinite.
† Calculated isotopic composition of meteoric water in equilibrium with kaolinite at 20 °C, and
‡ 15 °C, determined using the geothermometer of Lambert and Epstein (1980) for hydrogen: $10001n\alpha_{(kaolinite-water)} = -4.53(10^6)T^{-2} + 19.4$, and Land and Dutton (1978) for oxygen: $10001n\alpha_{(kaolinite-water)} = 2.50(10^6)(T^{-2}) - 2.87$.

water sample draining from the base of the Yokomichi Formation, which was collected in March 1993, were obtained for this study (Table 1, Figure 1). All samples are composed almost entirely of highly crystalline kaolinite. Contamination by other minerals is normally ≤5%. Dark grey to red, "micaceous" units (Yokomichi Formation) at the base of the section (samples Iw-1 and -2) consist almost entirely of granular and booklet-like mineral aggregates with a diameter of 0.5 to 1.0 mm, giving the material the texture of a sandstone. XRD analysis shows that the "micaceous" mineral is kaolinite. The overlying, hard, massive shale (samples Iw-3 to -5) comprises about 50 m of the section and is also rich in kaolinite. Lower portions of the shale are normally reddish, grading upward into bluish-grey to white material. About 1 to 2 m of dark grey to dark brown flint clays (Komatsu Formation, samples Iw-6 and -7) have developed directly on the shale. The shale and flint clays have similar textures, with the uppermost shale grading into the lowermost clays. The fire-clay deposits of the Nameiri Formation (samples Iw-8 to -11), located higher in the section, are associated with coal. Fujii (1970) suggested that the fire clays from seams 1, 2 and 34 are of sedimentary origin, whereas fire clay from seam 35 formed directly through alteration of dacitic or rhyolitic tuff (Figure 1).

ANALYTICAL METHODS

Two to 5 g of moist sample were disaggregated lightly using a wooden pestle in an iron mortar, and then treated with hydrogen peroxide (15%) at 80 to 95 °C. The clay suspension was agitated ultrasonically (28 Khz) for 15 min. The <2 μm size-fraction was separated by repeated centrifugation. To remove Fe oxides, the clay fraction was treated with a mixture of 0.3 M Na-citrate and dithionite at 25 °C, and shaken gently overnight. Excess salts were removed by dialysis and the clay suspension dried at 50 °C. A portion (10 to 20 mg) was air-dried on a glass slide and then examined by XRD using Co Kα radiation.

Stable isotope results are reported using the normal δ-notation relative to Vienna Standard Mean Ocean Water (V-SMOW). Hydrogen for isotopic analysis was obtained from 50 mg samples of pure kaolinite using a procedure modified after Bigeleisen et al. (1952) and Godfrey (1962). Samples were degassed at 150 °C for 2 h under vacuum, and then maintained under vacuum at room temperature for 12 h. The samples were then reheated under vacuum for 30 min at 200 °C prior to extraction of the hydroxyl group and hydrogen. During extraction, the samples were heated to 1000 °C for 30 min and the resulting gases passed first over Cu oxide at 500 °C and then U metal at 800 °C. The hydrogen gas was analyzed using a PRISM II dual inlet, gas-source mass-spectrometer. Precision of the kaolinite δD measurements was ±2‰.

Oxygen for isotopic analysis was liberated quantitatively from dried 20 mg samples of kaolinite by reaction with bromine pentafluoride at 600 °C (Clayton and Mayeda 1963). Prior to reaction, samples were degassed for 2 h under vacuum at 150 °C. Oxygen was converted to CO_2 by reaction with an incandescent carbon rod, and the $\delta^{18}O$ value of this gas was measured using an OPTIMA dual inlet, gas-source mass-spectrometer. An internal quartz standard calibrated to NBS-28 gave a $\delta^{18}O$ value of +11.47‰, compared to its average value of +11.5‰. A value of +9.66 ± 0.13‰ for NBS-28 is obtained routinely in our laboratory.

The $\delta^{18}O$ value of the water sample was determined using the conventional CO_2-H_2O equilibration method (Epstein and Mayeda 1953). The δD value of the water

Table 1. Extended.

Kaolinite (‰)		Water (‰)	
δD	δ¹⁸O	δD	δ¹⁸O
δD	$\delta^{18}O$	δD	$\delta^{18}O$
−97	+16.6	−66†	−9.7†
−98	+16.2	−67	−10.1
−103	+15.9	−74	−10.4
−101	+15.7	−71	−10.6
−106	+15.2	−76	−11.1
−100	+15.9	−70	−10.4
−100	+14.8	−70 (−68)‡	−11.5 (−12.5)‡
−100	+15.5	−70 (−68)	−10.8 (−11.8)
−102	+14.7	−72 (−70)	−11.6 (−12.6)
−103	+14.0	−73 (−71)	−12.3 (−13.3)
−103	+14.2	−73 (−71)	−12.1 (−13.1)

was obtained by reduction over hot metallic Zn (Coleman et al. 1982).

RESULTS

X-ray diffraction of clay separates treated to remove non-crystalline constituents, for example, ferrihydrite, organic matter, etc., showed that kaolinite was the only mineral constituent. Other crystalline matter was not observed, despite the <1% sensitivity to phases such as quartz and mica. We consider all kaolinite samples analyzed to be essentially free of contaminants. The purity of these separates rules out contamination as the major cause of variation in their isotopic compositions. The δD values of the kaolinite range from −106 to −97‰, and the $\delta^{18}O$ values, from +14.0 to +16.6‰ (Table 1). The $\delta^{18}O$ values show a systematic increase from the base to the top of the sampled section. The water sample from the mine has a δD value of −66.5‰ and a $\delta^{18}O$ value of −10.2‰.

DISCUSSION

To interpret the hydrogen- and oxygen-isotope compositions of the Iwaizumi kaolinites, it is first necessary to choose the most appropriate kaolinite-water isotopic fractionations from those that are currently available. The hydrogen-isotope fractionation between kaolinite and water is not particularly well-known. The divergent results of Savin and Epstein (1970), Taylor (1974), Lambert and Epstein (1980), and Liu and Epstein (1984) have been summarized by Kyser (1987) and Savin and Lee (1988). Fractionation factors for surficial to hydrothermal temperatures have also been reported by Lawrence and Taylor (1971, 1972), Suzuoki and Epstein (1976) and Marumo et al. (1979, 1980) among others. Fortunately for the purposes of this study, the spread among the reported values for the mineral-water fractionation is lowest at surficial temperatures, ≈±3‰ at 15 to 25 °C, (Kyser 1987, his Figure 18). Because of its widespread use, we have chosen the hydrogen-isotope geothermometer of Lambert and Epstein (1980) to calculate water compositions, but we note that other curves are unlikely to

produce significantly different values at surficial temperatures.

The oxygen-isotope fractionation between kaolinite and water has been reviewed by Kyser (1987) and Savin and Lee (1988). Consistent fractionations have been reported by Savin and Epstein (1970) and Lawrence and Taylor (1971, 1972) for natural kaolinites formed at surficial temperatures (~20 °C). Kaolinite-water fractionations for natural hydrothermal systems have been described by Eslinger (1971) and Marumo et al. (1982). In addition, empirical and semi-empirical derivations of the kaolinite-water fractionation equation have been provided by Savin and Lee (1988) and Zheng (1993). Land and Dutton (1978) combined the data of Eslinger (1971) and Savin and Epstein (1970) to produce an empirical kaolinite-water geothermometer that has been particularly useful for studies of lower temperature systems (Longstaffe 1983, 1989). We have adopted this equation because it utilizes reasonably well-constrained, low temperature fractionations obtained for natural kaolinite-water systems. For studies of kaolinite weathering, we place less confidence in equations produced by extrapolation of high temperature experiments, although the latter results may be more suitable for the study of hydrothermal systems (Marumo et al. 1995).

Isotopic Evidence for Cool-Temperature Weathering

The δD and $\delta^{18}O$ values of the Iwaizumi kaolinite are illustrated in Figure 2. The distribution of data do not support a hydrothermal origin for these clays. Instead, the samples plot on, or close to, the weathering (~20 °C) Kaolinite Line (Sheppard et al. 1969 after Savin and Epstein 1970). Detailed inspection exhibits that the Oligocene samples plot within error on the Kaolinite Line, whereas Cretaceous samples are slightly but systematically displaced to the left (Figure 3). All samples plot far to the right of the line that discriminates between clays of hydrothermal versus weathering origins (Supergene-Hypogene Line of Sheppard et al. 1969).

The Iwaizumi samples occupy a position along the Kaolinite Line that is well below the range known for kaolinite formed in tropical or warm-temperate climates. Kaolinite formed in hot climates generally has higher δD (−80 to −40‰) and $\delta^{18}O$ (+17 to +23‰) values (Savin and Epstein 1970; Lawrence and Taylor 1971, 1972; Sheppard 1977; Marumo et al. 1982; Hassanipak and Eslinger 1985). Lower δ-values, like those reported here, are acquired by kaolinites formed during weathering at high latitudes or altitudes, or at a large distance from the coast, where meteoric water was more depleted of D and ¹⁸O, and temperatures were generally lower. Previously reported examples include Permo-Triassic kaolinites from the Raniganj Basin of northeastern India ($\delta^{18}O$ = +7 to +11‰; Dutta 1985) and the Bowen (+3.5 to +6.5‰; Botz et
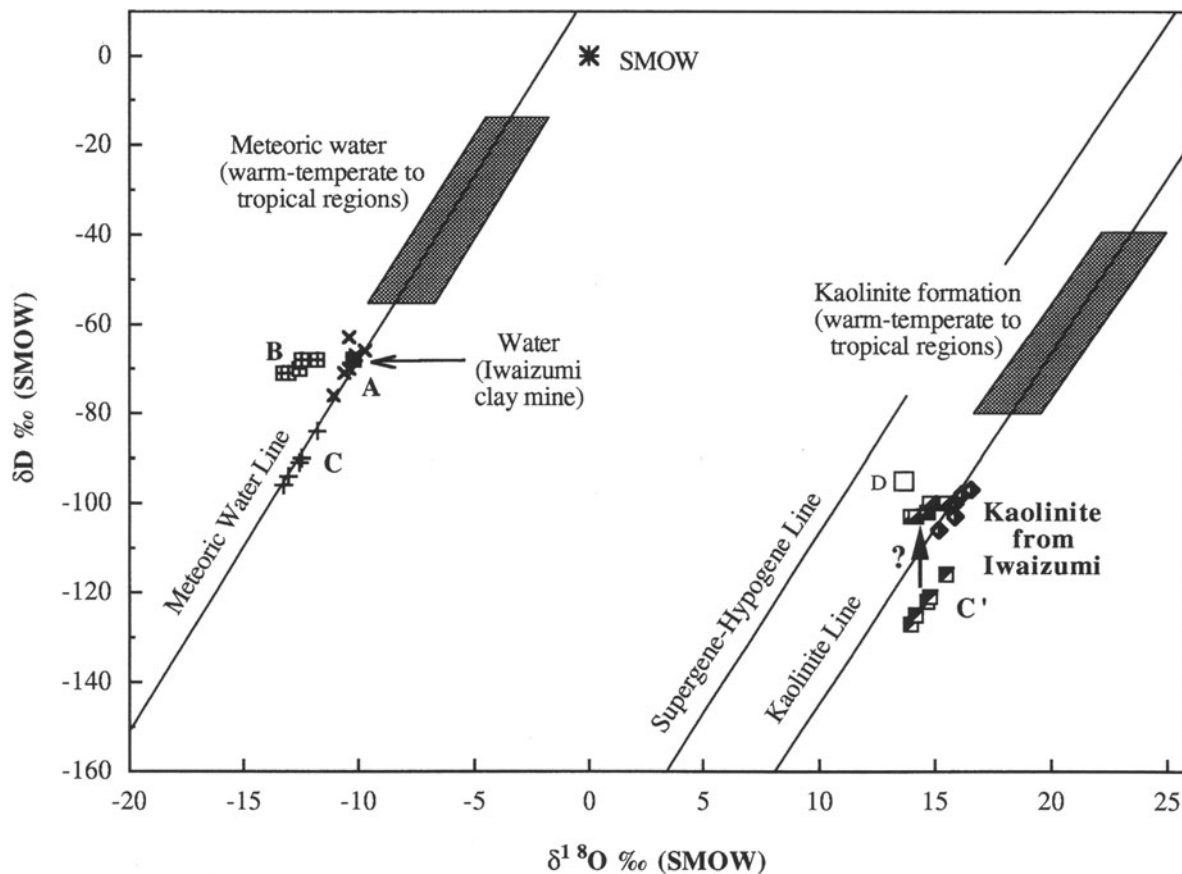
Figure 2. Hydrogen- versus oxygen-isotope plot for kaolinite and associated meteoric water from the Iwaizumi clay mine. The Meteoric Water Line is taken from Craig (1961). The Kaolinite and Supergene-Hypogene Lines are taken from Sheppard et al. (1969). The field (heavy stippled pattern) for kaolinite formed during weathering in tropical or warm-temperate climates and water in equilibrium with these kaolinites has been compiled from Savin and Epstein (1970), Lawrence and Taylor (1971, 1972), Sheppard (1977), Marumo et al. (1982) and Hassanipak and Eslinger (1985). Key: ◆ = kaolinite samples from Oligocene units. ◪ = kaolinite from upper Cretaceous units. D (□) = kaolinite reported by Marumo et al. (1982). Area A (×) = water compositions in equilibrium with Oligocene kaolinites at 20 °C; Area B (⊞) = water compositions in equilibrium with Cretaceous kaolinites at 15 °C, assuming no post-formational hydrogen-isotope exchange between the kaolinite and younger, downward percolating meteoric water. Area C (+) = calculated position on the Meteoric Water Line for water at oxygen-isotope equilibrium with Cretaceous kaolinites at 15 °C; the hydrogen-isotope composition for this water has been calculated using the equation for the Meteoric Water Line (Craig 1961). Area C' (◪) = Cretaceous kaolinites in equilibrium with water shown in Area C at 15 °C.

Most kaolinites formed in a weathering (supergene) environment plot along a trend close to the Kaolinite Line, with the Supergene-Hypogene line serving to separate kaolinite of supergene origin, on the right, from kaolinite of probable hypogene origin, on the left (Sheppard et al. 1969). Kaolinite from the Iwaizumi clay mine plots on or close to the kaolinite line, but below the range typical for tropical to warm-temperate climates. The heavy arrow indicates the proposed change within the δD values of the Cretaceous kaolinite resulting from low temperature, post-formational hydrogen-isotope exchange with meteoric water.

al. 1986) and Gunnedah (+6 to +9‰; Bird and Chivas 1988) basins of eastern Australia. The depleted compositions reflect the lower δD and δ^{18}O values of meteoric water at the higher latitude of the Gondwana landmass in the southern Hemisphere during weathering.

We suggest that the Iwaizumi data are also typical of a cooler climatic regime, with the small increase in δ^{18}O values from the Cretaceous to the Oligocene portions of the section (Table 1) indicating that the Oli-

gocene kaolinites (+15.2 to +16.6‰, av. = +15.9‰) formed under slightly different conditions than the Cretaceous kaolinites (+14.0 to +15.5‰, av. = +14.6‰). The δD values calculated for the meteoric water in equilibrium with the Iwaizumi kaolinites at 20 °C range from −76 to −66‰. At 15 °C, these values are 2‰ higher, and were calculated for Cretaceous samples only (Table 1). The water δ^{18}O values range from −12.3 to −9.7‰ at 20 °C, 1‰ lower at 15 °C (Table 1). The compositions (20 °C) calculated for wa-
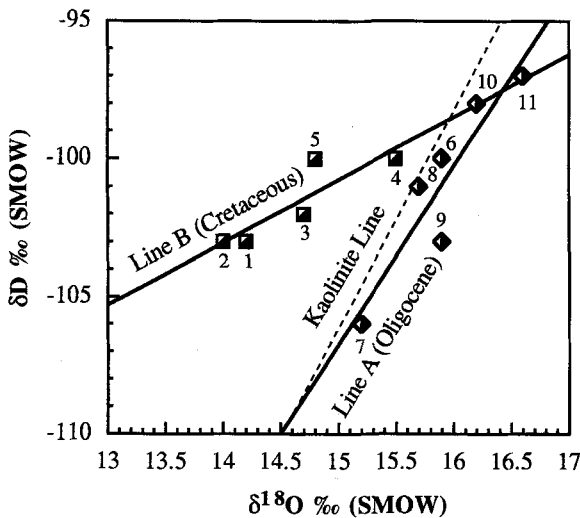
Figure 3. Hydrogen- versus oxygen-isotope plot for kaolinite from the Iwaizumi clay mine (magnified view of Figure 2). Key: ◆ = kaolinite samples from Oligocene units; and ◼ = kaolinite from upper Cretaceous units. Sample numbers (IW-1 to -11) are given next to each data point, corresponding to the information provided in Table 1 and Figure 1. Regression Line A describes the Oligocene kaolinite samples and closely matches the Kaolinite Line of Sheppard et al. (1969). Regression Line B describes the Cretaceous kaolinite samples and has a much shallower slope (~5) than Line A or the Kaolinite Line.

Post-Formational Hydrogen-Isotope Exchange?

The δD-$\delta^{18}O$ relationships among the Iwaizumi kaolinites are illustrated in more detail in Figure 3. Oli-gocene samples regress along a trend (Line A) that matches within error the Kaolinite Line of Savin and Epstein (1970). The small variation in the isotopic compositions of the Oligocene kaolinites probably reflects fluctuations in the isotopic composition of meteoric water as it percolated downward during Oligocene kaolinite formation. At the base of the Oligocene section (sample Iw-6), admixture of kaolinite derived from the underlying Cretaceous shale is also possible and consistent with the results illustrated in Figure 3.

As mentioned earlier, the lower $\delta^{18}O$ values of the Cretaceous kaolinites probably indicate that weathering occurred at lower average temperatures (<20 °C) than in Oligocene or younger times, assuming that the kaolinite oxygen-isotope compositions have remained unchanged since formation. Compared to the Oligocene kaolinites, the Cretaceous samples also exhibit a much lower slope (~5) on the δD-$\delta^{18}O$ plot (Figure 3, Line B). We do not believe that this difference arises from diagenetic alteration of the Cretaceous material, as overburden thickness probably never exceeded 300 m and maximum burial temperatures were ≤30 °C. Instead, we suggest that the lower slope reflects post-formational, hydrogen-isotope exchange between the Cretaceous kaolinite and downward percolating Oligocene and younger meteoric water. An alternative explanation is formation from evaporating meteoric water. However, this possibility seems unlikely for it requires the thick kaolinitic weathering and associated enrichment of hematite and gibbsite (Iijima 1972) to have occurred under very dry conditions, rather than the wet climates that typically promote the formation of such weathering products. Still other scenarios, such as Cretaceous kaolinite formation at higher temperatures than the younger equivalents, yet from meteoric waters with isotopic compositions typical of a cooler rather than warmer climate, require so many special circumstances that they are not considered further.

Figures 2 and 3 illustrate that both Oligocene and modern meteoric water have appropriate hydrogen-isotope compositions to produce the necessary, post-formational enrichment of D in the Cretaceous kaolinites. Bird and Chivas (1988) and Longstaffe and Ayalon (1990) have shown that post-formational hydrogen-isotope exchange between kaolinite and water can occur to temperatures ≤40 °C without disturbing the original oxygen-isotope compositions of these clays. Bird and Chivas (1988) documented a much larger shift to the left of the Kaolinite Line for surficial kaolinites of Permian to Tertiary age from eastern Australia. Their results extend the trend observed here for the Cretaceous Iwate kaolinites and convincingly demonstrated that such a pattern is best explained by hydrogen-isotope exchange with later, isotopically heavier meteoric waters.

For purposes of illustrating the effect of such hydrogen-isotope exchange, we have adopted a temper-

ter in equilibrium with Oligocene kaolinites (Figure 2, area A) plot directly on the meteoric water line of Craig (1961), overlapping measured values of groundwater from the Iwaizumi clay mine. Waters in equilibrium with the Cretaceous kaolinites at 20 °C, not shown in Figure 2, plot just to the left of the meteoric water line. This displacement increases if a lower temperature (15 °C) is used in the calculation (Figure 2, area B). Regardless of the exact temperature assumed for formation of these kaolinites, calculated water compositions remain typical of cool to cool-temperate climatic regions (Dansgaard 1964; Yurtsever and Gat 1981). Meteoric water with such δ-values is quite common in high latitude and/or altitude regions of central and northeastern Japan, as well as mid-latitude regions of eastern, inland China (Mizota and Kusakabe 1994). Cooler climates are not incompatible with kaolinite formation during weathering. Bird and Chivas (1988) emphasized that permeability of the parent rock, rather than temperature, is the most critical parameter in the development of thick kaolinite deposits. The highly permeable character of the parent materials at Iwaizumi (Figure 1) undoubtedly allowed effective leaching of silica and other cations.

ature of 15 °C for development of the Cretaceous weathering profile. Using this value, the isotope fractionation equations for kaolinite-water and the isotopic expression for the meteoric water line, we can constrain the hydrogen-isotope composition of the Cretaceous meteoric water to area C on Figure 2. From that, we have calculated the original, and substantially lower, δD values of the Cretaceous kaolinite, prior to post-formational exchange (Figure 2, area C'). The resulting isotopic compositions define a 15 °C surficial kaolinite line, which trends to the right of, but parallel to, the 20 °C line. Such results lie within the scatter known for surficial kaolinites about the Kaolinite Line. Most of this variation probably arises from the range of temperatures at which surficial kaolinite formation has occurred throughout the world.

Our model does not require that 15 °C be exactly the temperature of Cretaceous weathering at Iwate, or that this temperature was constant. But it does seem that interaction with younger, meteoric waters has preferentially reset the hydrogen-isotope compositions of these Cretaceous kaolinites. That the δD values of the Cretaceous kaolinites increase upward in the section may indicate that the lowermost samples have exchanged less completely or less continuously with downward percolating water, particularly later in the evolution of the profile. The Cretaceous samples may have possibly exchanged hydrogen primarily with older meteoric waters (Paleocene-Eocene precipitation on the Cretaceous unconformity?) that were less rich in D than their younger equivalents. Progressive development of the overlying Oligocene kaolinite led to decreased permeability, and lower water/rock ratios within the lower portions of the Iwate section. The Oligocene kaolinite samples show little effects of post-Oligocene hydrogen isotopic exchange, perhaps because less time was available, but more likely because Oligocene and modern meteoric waters apparently differed little in isotopic composition, making hydrogen-isotope exchange very difficult to discern.

Some minor but systematic variation in the conditions of Cretaceous kaolinite formation are indicated by the small but gradual increase in oxygen-isotope compositions stratigraphically upward through the Cretaceous kaolinite (Table 1). One explanation is a small but systematic change in temperature and hence the oxygen-isotope composition of meteoric water, as weathering progressed at the Cretaceous surface. Another possibility is progressive depletion of ^{18}O in the downward percolating groundwater because of water-rock interaction and neoformation of (^{18}O-rich) kaolinite. As noted by Clauer (personal communication 1995), our small data set points to the need for thorough study of water/rock ratios, and their implications for kaolin stable isotope compositions, during development of weathering profiles.

Associated Hematite and Gibbsite

In the Yokomichi Formation, samples Iw-3 and -5 are characterized by a red coloration (Table 1) that reflects abundant hematite. Upper horizons also contain up to 11% gibbsite (Iijima 1972). This mineral association has been interpreted as evidence for kaolinite development in a humid, subtropical climate (Iijima 1972; Tanai et al. 1978). However, in a study of glacial gravels from the European Alps, Schwertmann et al. (1982) showed that reddening (hematite formation) was possible in temperate climates with mean annual temperatures as low as 7 °C and that warmer, interglacial intervals are not required to explain rubification of soils. Rather, the prerequisite for hematite formation is coarse, highly permeable, parent materials.

Formation of gibbsite during weathering is also not restricted to tropical or subtropical climates. Excellent drainage and low-silica parent rocks are more important than climate in promoting the formation and persistence of gibbsite in natural environments (Juo 1980; Macias-Vasquez 1981). Gibbsite is known from Scottish soils, where cool climatic conditions prevail (Wilson 1969; Mellor and Wilson 1989; Hall et al. 1989), from alpine glacial environments of the northwestern USA (Reynolds 1971; Reynolds and Johnson 1972) and from coal measures flushed by glacial meltwaters in northern Canada (Van der Flier-Keller and Fyfe 1987). We conclude that the occurrence of gibbsite and hematite in the Iwaizumi area is not inconsistent with the cool-temperate conditions proposed here for weathering to kaolinite.

Our argument for a cooler climate rests upon the fact that meteoric waters with the isotopic compositions calculated here are atypical of tropical regions. But low-^{18}O and low-D precipitation can occur in tropical climates during monsoons (Yurtsever and Gat 1981; Aharon 1983; Bird 1988). Such an explanation for our results cannot be discounted out of hand. However, other observations also imply cooler climatic conditions during formation of the Iwaizumi clay deposits. First, isotopically depleted meteoric waters ($\delta D = -90$ to $-70‰$) have been proposed as the source of hydrothermal fluids responsible for late Cretaceous sericite deposits around the Kamioka mine in central Japan (Shimazaki and Kusakabe 1990). The calculated δD values are characteristic of cool-temperate to cool regions (Dansgaard 1964). Second, some paleogeographic reconstructions indicate that during the late Cretaceous to Paleogene, the Japanese Islands were located along the eastern margin of the mid-latitude region of the east Asian continent (Minato et al. 1965). Further paleomagnetic studies are needed to confirm this suggestion and to test our hypothesis of a cooler climate during formation of the Iwaizumi kaolinite deposits.

SUMMARY

The δD and $\delta^{18}O$ values of kaolinite from late Cretaceous and Oligocene deposits at Iwaizumi, northeastern Japan, suggest that these clays formed during weathering, rather than hydrothermal alteration. The kaolinites from the Oligocene deposits are sufficiently depleted of D and ^{18}O to suggest that weathering occurred under a cool to cool-temperate climate rather than during warm-temperate or tropical conditions. This observation adds to the growing body of thought that other variables such as permeability of parent materials are more critical than temperature to the development of thick kaolinite deposits. The kaolinites from the Cretaceous deposits are even more depleted of ^{18}O, suggesting formation under even cooler climatic conditions than the overlying Oligocene equivalents. However, the hydrogen-isotope compositions of these older kaolinites have a distribution that suggests exchange with younger, downward percolating meteoric water. These data provide further support for the view that hydrogen-isotope exchange between kaolinite and water can occur in sedimentary environments at quite low temperatures, independent of oxygen-isotope exchange. Any interpretation of hydrogen- and oxygen-isotope compositions for clay minerals from such systems must recognize such a possibility.

ACKNOWLEDGMENTS

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