FORMATION CONDITIONS OF AUTHIGENIC KAOLINITE AND CALCITE IN COALS BY STABLE ISOTOPE DETERMINATIONS

Authigenic kaolinite and calcite commonly occur as cleat (vertical fracture) fillings in coal (Ball, 1934; Gluskoter, 1967; Hughes, 1971; Hatch *et al.*, 1976; Ward, 1977). Although there is little doubt that these cleat-filling minerals are epigenetic, the nature of the aqueous solutions from which they precipitated and the temperatures of precipitation have not been well defined. In addition, Hatch *et al.* (1976) observed as many as five distinct veinlets of calcite filling a single cleat, suggesting that at least five periods of calcite deposition may have occurred. To obtain a better understanding of the conditions of formation, O^{18}/O^{16} and C^{13}/C^{12} ratios of 16 cleat calcites and O^{18}/O^{16} ratios of 20 cleat kaolinites have been determined from six coal mines in Indiana and Illinois, along with the O^{18}/O^{16} ratio of seepage water from one Indiana coal mine (Figure 1).

Kaolinite and calcite were hand-picked from cleats in Coal Beds III, V, VI, and VII of Pennsylvanian age. The cleats are typically 0.5 to 1 cm wide, 0.05 to 0.15 cm thick, and up to 3 cm long. The kaolinite is usually chalky white with occasional grey streaks and inclusions of coal. The calcite is clear to slightly cloudy and is generally free of coal inclusions. The kaolinite was identified by X-ray powder diffraction; calcite was identified by its vigorous reaction with H_3PO_4. Oxygen was extracted from the kaolinite using BrF_5 and was subsequently converted to CO_2. Calcite was reacted with 100% H_3PO_4 at 25°C to release CO_2; the acid-fractionation factor, $\alpha_{CO_2\text{-calcite}}$, was taken to be 1.01025. The oxygen-isotope analysis of water was performed by equilibration with CO_2 at 25°C; the fractionation factor, $\alpha_{CO_2\text{-}H_2O}$, was assumed to be 1.0412. The CO_2 was measured on an isotope-ratio mass spectrometer and reported in δ-notation in per mil relative to standard mean ocean water (SMOW) for δO^{18} and a belemnite standard (PDB) for δC^{13}.

RESULTS

The δO^{18} values of the kaolinites and calcites are plotted in Figure 2. Although the samples were collected from coal beds of four different stratigraphic horizons in six Indiana and Illinois coal mines, they show very little variation in δO^{18} values. This is particularly true for the kaolinites in which the δO^{18} values vary only from 16.5‰ to 17.6‰ (mean = 17.0, std. dev. = 0.2). For the calcites the variation is slightly greater: δO^{18} = 21.4 to 24.5‰ (mean = 22.8, std. dev. = 1.0); δC^{13} = −3.5 to −9.2‰ (mean = −6.1, std. dev. = 1.4). The O^{18}/O^{16} and C^{13}/C^{12} variation within each coal bed is almost as great as the variation within the entire area studied. No consistent change of δO^{18} and δC^{13} from top to bottom in a coal bed is noted.

The uniformity of the O^{18}/O^{16} and C^{13}/C^{12} ratios of the cleat-filling kaolinite and calcite in the coals examined suggests that the two minerals formed at or near isotopic equilibrium from an aqueous solution of a relatively uniform isotopic composition and temperature. The solution is most probably local groundwater which can easily percolate through the fractures in coal. If the isotopic composition of that groundwater can be estimated, the temperatures of deposition of the minerals may be calculated using the oxygen-isotope fractionation curves of calcite-water (O'Neil *et al.*, 1969) and kaolinite-water (Kulla and Anderson, 1978; Taylor, 1974).

The exact time of formation of the kaolinite and calcite is not known. However, their occurrence in fractures in the coal indicates that they must have formed after coalification and probably after the coal beds had been uplifted sufficiently close to the surface to allow for the development of cleat fractures and for percolation of groundwater through them. As a first approximation, it is therefore reasonable to assume that the groundwater from which the kaolinite and calcite were deposited had essentially the same composition as the present-day groundwater.

In estimating the temperatures of formation of kaolinite and calcite from the isotopic data, the isotopic composition of seepage water from the Minnehaha Mine was used (δO^{18} = −6.3). Calculated temperatures of calcite formation range from 28° to 13°C. In applying the kaolinite-water curve of Kulla and Anderson (1978), uncertainties have been compounded by extrapolating to low temperatures their results obtained between 172° and 319°C. Temperatures of kaolinite formation estimated from the measured isotopic values and the curve of Kulla and Anderson (1978) are between 5° and −1°C, unreasonably low values. Alternatively, using the empirical curve given by Taylor (1974), temperatures of 30°C to 24°C are obtained, values which are essentially within the temperature range obtained from the calcite-water curve. Thus, it is likely that the kaolinite formed in a somewhat more restricted temperature range than did calcite.

The temperature ranges for the precipitation of calcite and

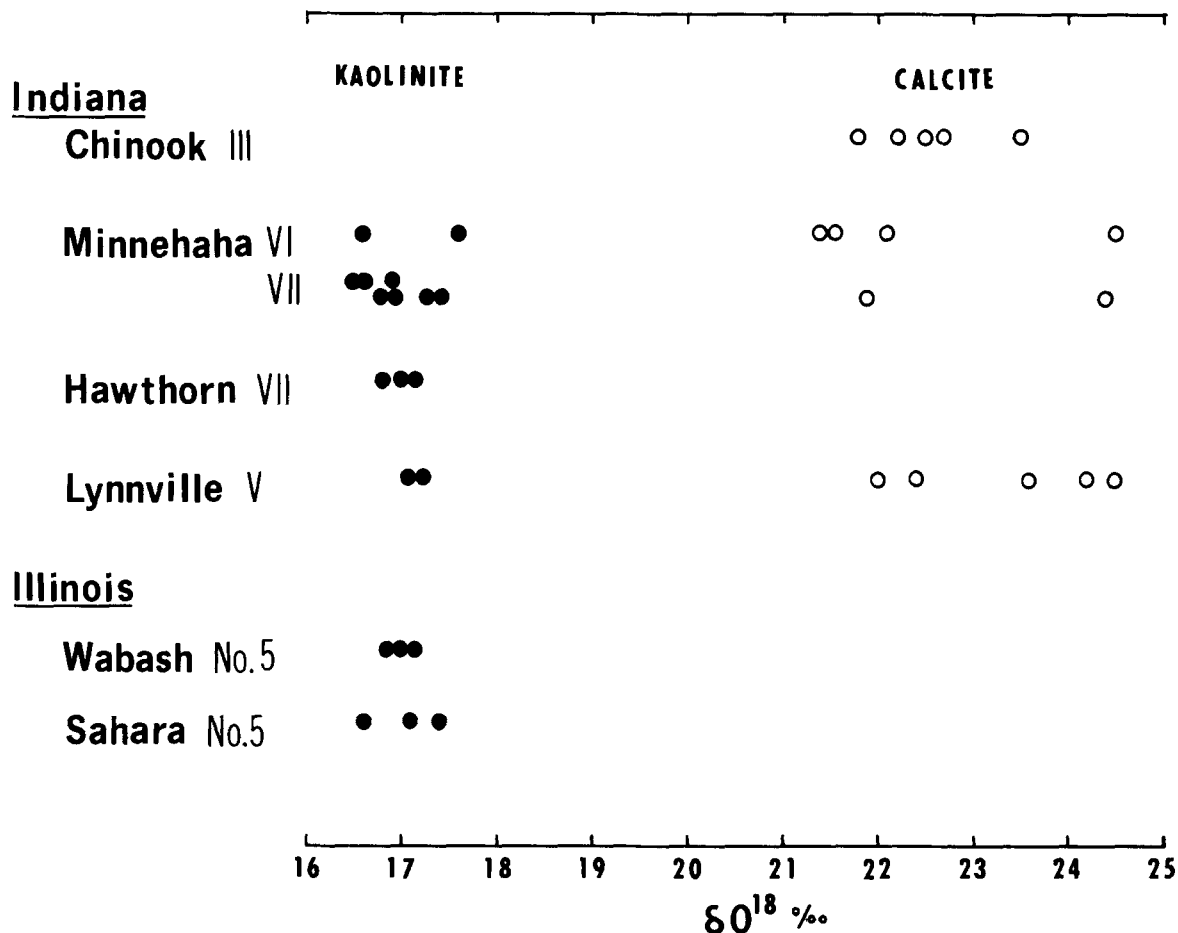Figure 1. Outline of the Illinois Coal Basin, showing locations of coal mines studied.

Figure 2. δO^{18} of cleat-filling kaolinite and calcite in coals from Indiana and Illinois.

kaolinite were obtained by assuming a uniform isotopic composition of groundwater for all localities studied; thus, these are *maximum* temperature ranges. In reality, the isotopic composition of the groundwater during the time span of deposition of kaolinite and calcite over the region of interest may have varied; therefore the temperature range of precipitation of the cleat-filling minerals must necessarily have been smaller than calculated.

CONCLUSIONS

Authigenic kaolinite and calcite which occur as cleat-fillings in coals from Indiana and Illinois have uniform oxygen and carbon isotope compositions, regardless of geographic or stratigraphic locations. Furthermore, the minerals are in, or close to, oxygen-isotope equilibrium with present-day seepage water. Negligible oxygen isotope exchange occurs between water and kaolinite or calcite at surface temperatures, even over tens of millions of years (Savin and Epstein, 1970; Lawrence and Taylor, 1971; Yeh and Savin, 1976; Urey *et al.*, 1951); therefore, the isotopic compositions observed in the kaolinite and calcite are most likely primary, representing the values at the time of precipitation of the minerals from groundwaters. The temperatures of formation of the calcites are estimated to be from 13° to 28°C and those of kaolinites from 24° to 30°C. These data suggest that the kaolinite and calcite were formed at or near the surface, perhaps in fairly recent geologic time.

Department of Geosciences   YUCH–NING SHIEH
Purdue University   TERRI G. SUTER
West Lafayette, Indiana 47907

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