Clays and Clay Minerals, Vol. 28, No. 5, 393–396, 1980.

OCCURRENCE OF CORRODED AUTHIGENIC KAOLINITE IN A DIAGENETICALLY MODIFIED SANDSTONE

Key Words—Authigenic, Corrosion, Dissolution, Kaolinite, Scanning electron microscopy.

Kaolinite is commonly studied texturally by scanning electron microscopy (SEM) (e.g., Keller, 1977). The occurrence of authigenic kaolinite in sandstones is widespread, and the textures of such kaolinites are illustrated in Wilson and Pittman (1977). Kaolinite is a persistent authigenic phase in sandstones, occurring metastably with porewaters in equilibrium with illite-chlorite assemblages (Siever, 1979). "Illitization" of kaolinite in sandstones has been recorded and interpreted as representing an increased grade of diagenesis (Hancock and Taylor, 1978). Corroded authigenic kaolinite is previously unrecorded from diagenetic environments. Its occurrence in a Jurassic sandstone is therefore of considerable interest, as the dissolution of kaolinite may be an important mechanism for the creation of secondary porosity in such rocks.

RESULTS

Corroded authigenic kaolinite was discovered during a routine petrographic study of Jurassic sandstones from core 11/30-1 of the Beatrice oilfield, Scotland (Figure 1). All authigenic kaolinite grains observed within a sandstone unit from 2004 to 2013 m below the seabed were characterized by varying degrees of corrosion (Figure 2).

X-ray powder diffraction of oriented mounts of <2-μm fractions of all samples produced sharp, 7-Å kaolinite peaks. Energy-dispersive analyses (LINK system mounted on a Cam Scan electron microscope) confirmed kaolinite chemistry. However, the analyses showed higher Si:Al ratios than most other authigenic kaolinites (Table 1).

The pseudohexagonal form commonly associated with authigenic kaolinite commonly appears to have been rounded to form isolated blobs (Figures 2a and 2b). If these authigenic kaolinites were initially more angular and recognizably hexagonal (like those shown in Figure 2a), the sequence of corroded morphologies shown in Figures 2b, 2c, and 2d can be interpreted as having formed due to differing amounts of dissolution or local reprecipitation of kaolinite during bulk dissolution.

DISCUSSION

Keller (1977) recorded weathered kaolinite from the Sparta saprolite which showed similar features to those recorded here, e.g., rounded, vermicular aggregates and particles with poorly developed crystal form. It is unlikely that weathering was responsible for the corrosion in the present case because the post-depositional history of these rocks suggests that they have never been sub-aerially exposed. It is pertinent to describe the sedimentary unit within which these textures were located.

The total thickness of the bed is ~10 m, and the rock varies in grain size from fine- to coarse-grained. It is marked at its base by a rapid gradation into sandy siltstones and at its top by the presence of a tightly carbonate-cemented sandstone with a very sharp base.

In the absence of downhole chemical data, textured evidence is the only available source of information concerning porewater–mineral equilibria. A reaction for the dissolution of kaolinite can be written:

$$6H^+ + Al_2Si_2O_5(OH)_4 = 2Al^{3+} + 2Si(OH)_4 + H_2O$$

for which the equilibrium constant is:

$$\text{K-equil.} = \frac{[Al^{3+}][SiOH_4]}{[H^+]^3}$$

where the aluminum species present is pH dependent (Hem, 1968). This relationship demonstrates that kaolinite stability is a function of the concentration of three dissolved species. In this example, $[SiO_4]$ is not responsible for the dissolution because the porewater is saturated with respect to quartz, as is demonstrated by the presence of quartz overgrowths (Figure 2).

The activity of H^+ is cubed; thus, pH is a dominant control of kaolinite stability. Kaolinite dissolves readily at pH < 5 or pH ≥ 8. The stability of other minerals present provides evidence as to the pH of the corrosive porewater. The overlying carbonate-cemented horizon suggests that porewater pH is likely to be buffered towards an alkaline composition. However, the carbonate content of the sandstone unit itself is zero. This is an atypical feature, as similar adjacent sandstones all contain some carbonate cement. The absence of carbonates implies that the porewater had a composition unsuited to the precipitation of carbonates or that the dissolution of carbonate has taken place; however, no relict structures or voids after carbonate cements were found. Feldspars are uncommon in this sandstone, but where present, show corroded textures similar to those illustrated by Berner and Holdren (1977). The absence of carbonates, the instability of feldspars, and the stability of quartz all imply that the porewater responsible for the corrosion of kaolinite had a pH ≥ 8 and suggest that an acidic porewater was indeed present.

May *et al.* (1979) showed that below pH 5.2 kaolinite sol-

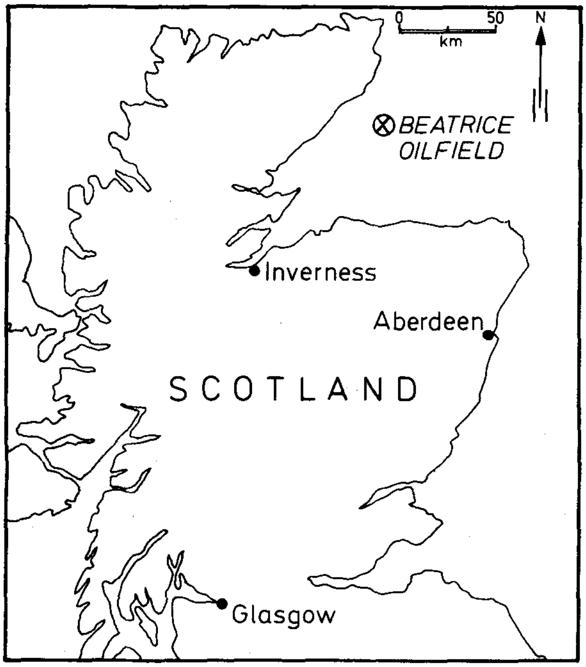

Figure 1. Location of the Beatrice oilfield.

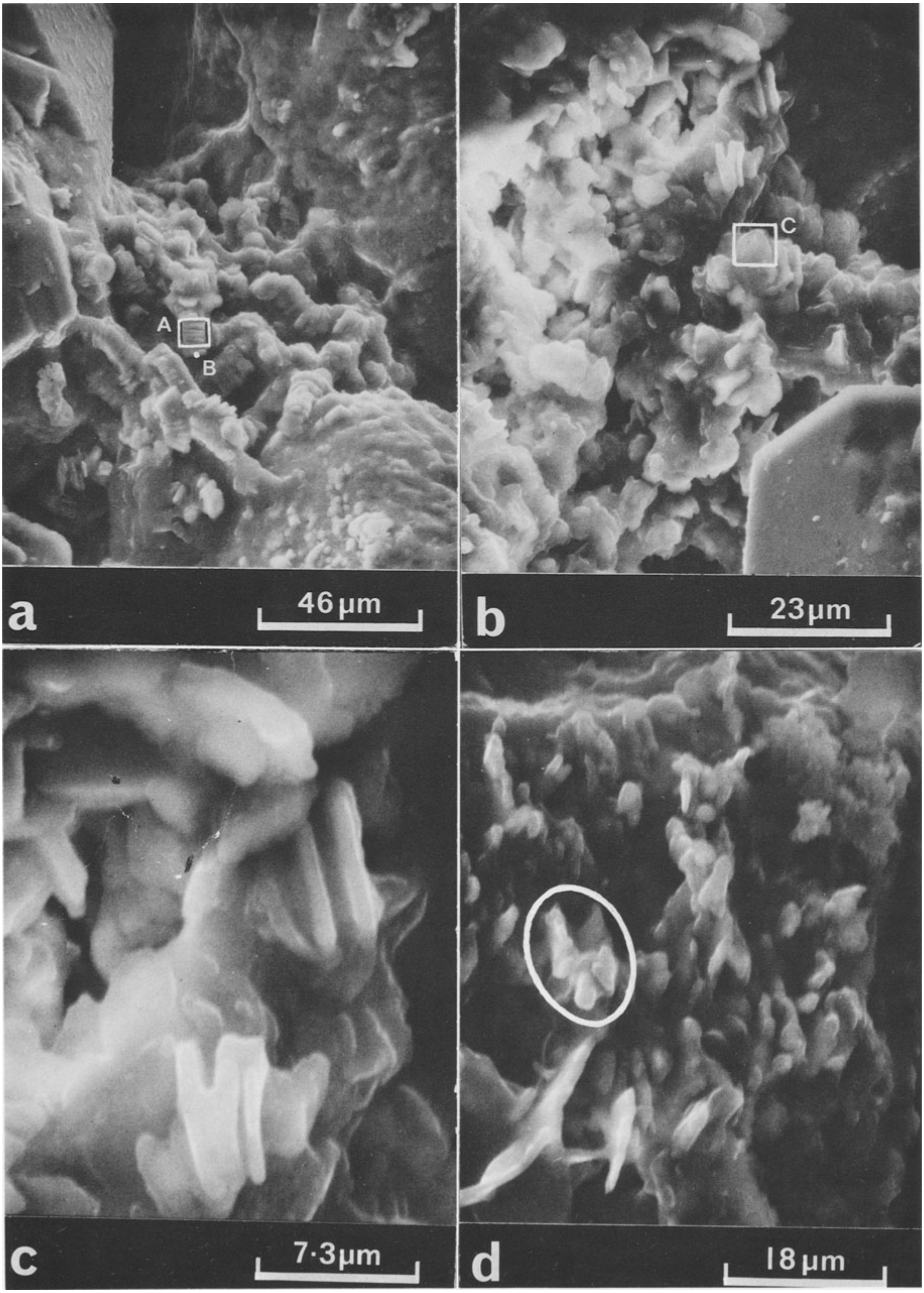
A
B
a
46 µm
C
b
23 µm
c
7·3 µm
d
18 µm

Table 1. Energy dispersive analyses of authigenic kaolinites in sandstones.

Sample	Si	Al	Si:Al	Total counts
A	19,390	12,841	1.510	32,231
B	25,174	15,425	1.632	40,572
C	12,739	8359	1.524	21,098
i	24,632	17,992	1.369	42,624
ii	10,332	7769	1.330	18,101
iii	14,748	11,816	1.248	26,564
iv	15,886	11,325	1.403	27,211
v	29,125	23,134	1.259	52,259
vi	35,336	24,588	1.437	59,924
vii	27,084	16,866	1.606	43,950

A, B, and C are analyses of areas and points shown in Figure 2. Analyses i to vii are samples analyzed from Middle Jurassic sandstones from the Moray Firth area (Hurst, Ph.D. thesis in preparation).

ubility increases quite rapidly. Porewaters of low pH are evolved during diagenetic breakdown of organic matter; however, this mechanism has never been recorded as causing kaolinite dissolution. Burial reactions generally increase the pH of porewaters after early diagenesis and acidic porewaters become more difficult to generate (Siever, 1979). For this reason, [Al^{3+}] may have been significant in determining the corrosion of this authigenic kaolinite.

Aluminum in natural waters usually occurs in concentrations below 100 μg/liter (Hem, 1968). If corrosion of kaolinite, such as recorded here, has taken place in the pH range where kaolinite is relatively insoluble as a direct consequence of undersaturation with respect to dissolved aluminum, a mechanism for maintaining a low concentration of dissolved aluminum to provide continuous undersaturation is required. Such a mechanism could be provided by a flux of porewater through the sandstone which was undersaturated with respect to kaolinite. This type of flux may originate as the result of a release of overpressure in the sandstone during burial.

Other possible mechanisms for producing these textures are the thermal instability of kaolinite, illitization, or coating by amorphous hydroxides. Thermal instability is unlikely in this instance as the mineralogy of adjacent shales establishes that the maximum temperature reached is 80°C (using the methods of Hower *et al.*, 1976). Experimental data (Eberl and Hower, 1975) and field examples (Hoffman and Hower, 1979) show that 80°C is well below the expected temperature for thermal decomposition of kaolinite. No evidence for the presence of illite was found and so illitization (Hancock and Taylor, 1978) has not taken place.

Coating by an amorphous precipitate is discounted on two grounds. Firstly, the textural evidence strongly suggests degradation of euhedral form by corrosion (Figure 2) rather than by addition of a coating (e.g., Sellwood and Parker, 1978). Furthermore no amorphous coating can be seen using SEM. Secondly, the chemistry of the amorphous coating is problematic. Analyses in Table 1 imply that the coating has an aluminum silicate composition in which the Si:Al ratio is greater than that of kaolinite. No crystalline (Chesworth, 1975) or noncrystalline (Wada, 1977) aluminum silicates are recorded as having such a composition. It is possible that an amorphous coating with a suitable chemistry could form, but the textural evidence suggests that no such coating is present.

This appears to be the first recorded example of corroded authigenic kaolinite from a diagenetic environment. If the bulk transfer of aluminum in porewaters is a feasible mechanism for precipitating authigenic clay minerals and feldspars in quartzose sandstone, the occurrence of corroded textures as recorded here is of significance. These textures show that porewaters have dissolved (and so transported) significant quantities of kaolinite. Consideration of the stability of other minerals present suggests that dissolution did not take place at a pH $\geqslant$ 8. However, no lower limit for pH can be defined.

ACKNOWLEDGMENTS

The British National Oil Company and its partners in the Beatrice oilfield are acknowledged for allowing publication of this paper. W. D. Keller is acknowledged for some early advice, and J. H. Stout, K. Bjørlykke, and A. Parker gave helpful advice and criticism. The technical facilities of the University of Reading and the tenure of a Natural Environment Research Council studentship are gratefully acknowledged.

Sedimentology Research Laboratory ANDREW R. HURST
Department of Geology
University of Reading
Reading R66 2AB, United Kingdom

REFERENCES

Berner, R. A. and Holdren, G. R., Jr. (1977) Mechanism of feldspar weathering: Some observational evidence: *Geology* **5,** 369–372.

Chesworth, W. (1975) Soil minerals in the system Al_2O_3–SiO_2–H_2O: Phase equilibrium model: *Clays & Clay Minerals* **23,** 55–60.

Eberl, D. and Hower, J. (1975) Kaolinite synthesis: The role of the Si/Al and (alkali)/(H^+) ratio in hydrothermal systems: *Clays & Clay Minerals* **23,** 301–309.

Hancock, N. J. and Taylor, A. M. (1978) Clay mineral diagenesis and oil migration in the Middle Jurassic Brent Sand Formation: *J. Geol. Soc. Lond.* **135,** 69–72.

Hem, J. D. (1968) Aluminum species in water: in *Advances in Chemistry* **73,** 98–114.

Hoffman, J. and Hower, J. (1979) Clay mineral assemblages as low grade metamorphic geothermometers: Application to the thrust faulted disturbed belt of Montana, U.S.A.: in *Soc. Econ. Paleontol. Mineral. Spec. Pub. 26,* P. A. Scholle and P. R. Schluger, eds., 55–80.

Hower, J., Eslinger, E. V., Hower, M. E., and Perry, E. A. (1976) Mechanism of burial metamorphism of argillaceous sediment: 1. Mineralogical and chemical evidence: *Geol. Soc. Amer. Bull.* **87,** 725–737.

Keller, W. D. (1977) Scan electron micrographs of kaolins

←

Figure 2. (a) Pore filling of authigenic kaolinite between quartz grains. Vermicular and booklet forms of kaolinite are present, but show rounding. "Blobs" of kaolinite occur as coatings on the surfaces of some quartz grains. Area A and point B were analyzed using the LINK system (see Table 1). (b) A considerably corroded kaolinite pore filling. All authigenic forms are degraded; only traces of pseudohexagonal form remain. Area C was analyzed using the LINK system (see Table 1). (c) Detail of booklet corrosion, enlarged from Figure 2b. (d) Elongate, rounded forms. A relict vermicular aggregate is present within the encircled area.

collected from diverse origins, Part IV: *Clays & Clay Minerals 25,* 311–345.

May, H. M., Helmke, P. A., and Jackson, M. L. (1979) Gibbsite solubility and thermodynamic properties of hydroxy-aluminium ions in aqueous solution at 25°C: *Geochim. Cosmochim. Acta* **43,** 861–868.

Sellwood, B. W. and Parker, A. (1978) Observations on diagenesis in North Sea reservoir sandstones: *J. Geol. Soc. Lond.* **135,** 133–135.

Siever, R. (1979) Plate tectonics and sandstone diagenesis: *Jour. Geol.* **87,** 127–155.

Wada, K. (1977) Allophane and imogolite: in *Minerals in Soil Environments,* J. B. Dixon and S. B. Weed, eds., Soil Sci. Soc. Amer., Madison, Wisconsin, 603–638.

Wilson, M. D. and Pittman, E. D. (1977) Authigenic clays in sandstones: Recognition and influence on reservoir properties and paleoenvironmental analysis: *J. Sediment. Petrology* **47,** 3–31.

(Received 25 October 1979; accepted 8 April 1980)