

## NOTE

### Persistence of gibbsite in deep sea sediments of Tertiary age

(Received 27 December 1971)

IN THE course of a study of siliceous sediments obtained from the Deep Sea Drilling Program, I found gibbsite in 5 samples out of 17 from Site No. 13-13A, 600 km off the coast of Sierra Leone at 6° 02.4' N and 18° 13.71' W (Maxwell *et al.*, 1970, p. 27). The hole is in 4585 m of water, on a local uplift in the abyssal plain. Samples are unconsolidated oozes, principally calcareous in the upper 24 m, clay-rich from 25 to 30 m, and radiolarian and diatomaceous in the lower section (Table 1).

Gibbsite has previously been reported from clays on the ocean floor adjacent to West Africa and Brazil, presumably derived by wind transport and ocean currents from land areas of lateritic weathering (Biscaye, 1965, p. 819). We would expect burial and diagenesis of such material to result in conversion of gibbsite to aluminosilicate minerals. In off-shore waters of Hawaii, for example, gibbsite from fluvial sediments has been

observed in process of conversion to chlorite (Swindale and Fan, 1967).

According to Garrels and Christ, (1965, pp. 353-362) the gibbsite-kaolinite equilibrium is fixed near 1 ppm of dissolved SiO<sub>2</sub>, therefore gibbsite is not to be expected in association with quartz and kaolin, particularly not in a clay-sized sediment with ample pore water to promote chemical exchange. Other workers have pointed out (Millot, 1970, p. 343) (Gastuche *et al.*, 1961) that the formation of gibbsite is favored by a high Al/Si ratio and low pH. A more recent study (Linares and Huertas, 1971) puts the upper limit of gibbsite formation at pH 6 when no silica is present and pH 4 when SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> (molal) = 0.5. The pore waters of the marine muds in Hole No. 13, associated with abundant quartz and kaolin, and little organic matter, are far too alkaline and siliceous to meet the requirements for stability of gibbsite. 6.5 ppm Si is an average figure for pore waters of this

Table 1. Data from Hole 13-13A, DSDP Leg IV

Sample No.	Sub-bottom depth (m)	Age	Gibbsite	Calcite	Quartz	Kaolin	Other minerals	Lithology
13-1-1,	30 cm	0	U. Pliocene	X	X	X		Calcareous mud
13-1-2,	40	2	U. Pliocene	X	X	X		Calcareous mud
13-1-3,	30	4	U. Pliocene	X	X	X		Calcareous mud
13-1-4,	30	5	U. Pliocene	X	X	X		Calcareous mud
13-1-5,	30	6	U. Pliocene	X	X	X		Calcareous mud
13-1-6,	30	8	U. Pliocene	tr.	X	X	X	Calcareous mud
13-2-2,	12	24	L. Pliocene	tr.	X	X	X	Calcareous mud
13-2-4,	7	27	?	0.7%	X	X	Mica, K-spar	Brown clay
13-2-4,	76	27	?	1.0%	X	X	Mica, K-spar	Brown clay
13-2-5,	79	29	?	0.5%	X	X	Mica	Brown clay
13-3-2,	15	138	M. Eocene		X			Radial. & diatom ooze
13-3-4,	135	142	M. Eocene				Amorph.	Radial. & diatom ooze
13-3-5,	7	142	M. Eocene				Amorph.	Radial. & diatom ooze
13-3-6,	8	143	M. Eocene				Amorph.	Radial. & diatom ooze
13A-1-1,	90	178	M. Eocene		X		Cristob.	Chert
13A-3-4,	8	310	U. Cret.		X	X	Cristob.	Pale green ooze
13A-4-1,	120	380	U. Cret.		X	X	Cristob.	Pale green ooze

type (Bischoff and Kuh, 1970); 9 ppm Si have been reported from interstitial water of No. 13-2-4 (Maxwell *et al.*, 1970, p. 666); Al was not reported but is probably well below 1 ppm.

Gibbsite at Site No. 13, in unconsolidated sediments of Lower Pliocene or older age (10–15 million yr), demonstrates a far longer life as a metastable phase than would be predicted from the physico-chemical data. Lodding (in press) believes that gibbsite may form in the presence of quartz under special conditions of dynamic disequilibrium, but these conditions do not occur in deep sea muds. In the present instance, the low temperature of the sediments may have prevented the attainment of equilibrium, despite their large specific surface and thorough permeation by pore waters.

#### Procedures

Samples were air-dried from aqueous slurries to achieve preferred orientation of platy minerals, and scanned on a Siemens X-ray diffractometer with  $\text{CuK}\alpha$  radiation. Calcareous samples were re-run after HCl treatment and removal of calcite. I confirmed the presence of gibbsite by DTA at  $10^\circ\text{C}/\text{min}$  in a Fisher Differential Thermaliser, using a bare chrome-alumel thermocouple. In both X-ray diffraction analysis and DTA, I estimated the amount of gibbsite by adding 6% of pure stalactitic gibbsite to a duplicate sample, and comparing the areas under the respective peaks. Gibbsite has one very strong diffraction peak at  $4.85 \text{ \AA}$  ( $18.3^\circ 2\theta$ ) corresponding to its (001) basal spacing; in these dilute mixtures of poorly ordered material it is the only peak recorded. In DTA runs, both the deep-sea samples and the stalactitic gibbsite showed one endotherm beginning near  $310^\circ \pm 5^\circ\text{C}$  (point of inflexion). Lodding (1969) using a heating rate of  $8^\circ/\text{min}$ , found that the endotherm of Brazilian gibbsite began near  $280^\circ\text{C}$ .

X-ray diffraction analysis (Table 1) confirms previous estimates (Maxwell *et al.*, 1970, p. 537) of the mineralogy, except for the addition of gibbsite and the fact that I find no cristobalite in Core No. 2. Gibbsite here cannot be recognized under the petrographic microscope because of the extremely fine grain size of all constituents of the sample.

*Acknowledgment*—Research was supported by National Science Foundation Grant GA-14553.

ROBERT GREENWOOD

*Department of Geology  
Rutgers University, Camden College of Arts and Sciences  
Camden, New Jersey 08102  
U.S.A.*

#### REFERENCES

- Biscaye, P. (1965) Mineralogy and sedimentation of Recent deep sea clay in the Atlantic Ocean and adjacent seas and oceans: *Bull. Geol. Soc. Am.* **76**, 803–832.
- Bischoff, J. L. and T. Kuh (1970) Pore fluids of Recent marine sediments: I—oxidizing sediments of  $20^\circ\text{N}$ , Continental Rise to Mid-atlantic Ridge: *J. Sed. Petrol.* **40**, 960–972.
- Garrels, R. M. and Christ, C. L. (1965) *Solutions, Minerals & Equilibria*, 450 pp. Harper & Row, New York.
- Gastuche, M. C. *et al.* (1961) La genèse des minéraux argileux de la famille du kaolin. I—Aspect colloïdal: *Colloq. Intern. Cent. Nat. Rech. Scient. Paris* no. **105**, 57–65.
- Linares, J. and Huertas, F. (1971) Kaolinite: synthesis at room temperature: *Science* **171**, 896–897.
- Lodding, W. (1969) The gibbsite dehydroxylation fork: In *Thermal Analysis* (Edited by Schwenker, R. and Garn, P.), Vol. 2, pp. 1239–1250, Academic Press, New York.
- Lodding, W. (1972) Conditions for direct gibbsite formation from K-feldspar—Discussion: *Am. Mineralogist* **57**, pp. 292–294.
- Millot, G. (1970) *Geology of Clays*, Springer, New York.
- Drilling Project, Vol. III, (U. S. Govt. Printing Office, Washington).
- Millot, G. (1970) *Geology of Clays*, Springer, New York.
- Swindale, L. O. and Fan, P. F. (1967) Transformation of gibbsite to chlorite in ocean-bottom sediments: *Science* **157**, 799–800.

*Note added in press.* See also Gardner, L. R. (1972).