CLAY MINERAL FORMATION IN SEA WATER BY SUBMARINE WEATHERING OF K-FELDSPAR

by

$R. W. Rex and B. D. MARTIN*$

Chevron Research Company, La Habra, California

and

U,S. Navy Oceanographic Office, Washington, D.C.

ABSTRACT

A SU1TE of granodiorite samples was collected by dredging from depths of about 1000 m from the walls of Carmel and Monterey submarine canyons, Monterey Bay, California. One surface of each of the various granodiorite slabs was weathered and encrusted with marine organisms. The weathering is maximum at the surface and penetrates to a depth of about 20 em and selectively alters the feldspars to clay. Potassium feldspars are most severely altered. Mineral selective attack, shallow depth of weathering, restriction of biological growth to weathered surfaces, and regional geological setting are interpreted to mean that the samples were broken from bedrock and that this granodiorite probably weathered in the marine environment.

Authigenic clays formed as a result of the submarine weathering of the granodiorite are kaolinite, K-mica, montmorillonite, and halloysite.

These data suggest that the assemblage K-mica, montmorillonite, and kaolinite have a phase join that may lie on or close to the composition of sea water. Furthermore, kaolinite may be unstable in sea water and gradually break up to form halloysite tubes. The possible influence of biologic agents is suggested in the formation of marine halleysite.

INTRODUCTION

CLAy minerals are often thought to be sensitive chemical indicators of their environment of formation. For this reason variations in clay mineralogy with depth in modern sediments have been ascribed to diagenesis. However, provenance differences may provide equally reasonable or even more satisfactory explanations of observed mineral variations. Consequently, clay equilibria with sea water can better be studied by careful examination of weathering products of various minerals exposed to sea water for long periods of time. This type of study presupposes satisfactory verification of submarine weathering. We wish to report an example of submarine weathering of feldspars in granodiorite exposed continuously to sea water for a long period of time.

* Present address: Dept. Water Resources, Annapolis Maryland.

235

236 FOURTEENTH NATIONAL CONFERENCE ON CLAYS AND CLAY MINERALS

FIELD WORK

During 1961 and 1962 cruises (numbers 468 and 502) of the R/V VELERO IV to Monterey Bay, California (Fig. 1)* dredge hauls yielded granodiorites from the south wall of Monterey submarine canyon and the east wall of Carmel submarine canyon (Martin, 1964). Many specimens of granodiorite showed, on one side only, a brown oxidized coating to which were attached

FIG. 1. Generalized geologic map of Monterey Bay area.

various flora and fauna. This weathered surface is considered to have been in contact with the ocean, i.e. forming the wall rock surface of the sub. marine canyon. The size of the total fragmented samples, angularity of fragments, and the oxidized surface indicate that the rocks were in-place material. Fragments of granodiorite range in size from approximately 10 em to 40 cm in maximum diameter and came from a depth of approximately

* The authors wish to acknowledge the support of these cruises by funds of the National Science Foundation (contract 15747).

PLATE 1. Clays forming within feldspar. A broken cleavage flake of orthoclase showing anomalous diffraction effects probably caused by strain associated with clay mineral growth.

PLATE 2. Kaolinite crystal showing curling edge as a consequence of severe weathering.

PLATE 3. Kaolinite crystal showing shrinkage cracks. This effect is not observed in kaolinite from deep sea red clays in the eastern Pacific.

100O m. All dredged material is stored and catalogued at the Smithsonian Oceanographic Sorting Center, Washington, D.C.

Almost all fragments of granodiorite exhibited varying degrees of alteration to white to buff clay. The larger fragments showing a surface of oxidation have greetest alteration to clays near the oxidized surface.

LABORATORY INVESTIGATIONS

Thin sections cut from various grandiorite samples show that orthoclase is the principal mineral altered to clay. In the alteration zone closest to the wall rock-ocean contact, little or no trace of unaltered orthoclase remains. Alteration also appears to progress from the edges of individual grains toward their centers; thus, it appears that clay formation is caused by reaction of orthoclase with pore water and/or organisms present in the interstices between grains.

Four samples of granodiorite (7462-1, 7470-3, 7470-5 and 8152-1: R/V VELERO IV samples) (Martin, 1964) from which thin-sections had been cut were studied in greater detail by X-ray diffraction and electron microscopy.

Clay Mineralogy

Authigenie clays in the granodiorite occur both as microvugs (Plate 1) and vein fillings. The clay rugs in the orthoclase crystals grow until a reticulated network is formed. Careful extraction of single orthoelase crystals yielded sufficient material for X-ray analysis of three stages of weathering. The trend is shown in Fig. 2. Both kaolinite and K-mica appear to form initially with the typical morphology of kaolinite and K-mica growing along the kaolinite-K-mica-K-feldspar phase boundary (Rex, 1965). This is the first evidence for this crystal habit in sea water. The preparation of sufficient sample material to provide the data points of Fig. 2 was exceedingly difficult; how. ever, the data available suggest that the ratio of mica to kaolinite increases with weathering. Two hypotheses are suggested. One is that because the silica-alumina ratios of kaolinite and muscovite are the same, a selective increase in mica implies addition of potassium and/or ammonium to the clays from sea water and biologic material such as bacteria, protozoa, and other microorganisms. This parallels the observed uptake of potassium from sea water by clays during glauconitization. The clays of the highly weathered crust still are predominantly kaolinite and mica in the orthoclase crystals. However, their morphology has changed. The authigenic mica laths are usually eroded and largely disintegrated. The kaolinite crystals are badly corroded or etched. Peeling layers are evident (Plate 2). Some kaolinite crystals are covered with shrinkage cracks (Plate 3).

Evidently, the pore system has become undersaturated with respect to one or more ions contained in the clays. The relative increase of mica with weathering could therefore also be explained by the hypothesis of preferential

FIe. 2. Triangular plot of relative weight abundance of kaolinite, K-mica, **and** orthoelaso present in weathered orthoelase crystals extracted from granodiorite, dredge haul 7470.

destruction of kaolinite. The electron micrograph data indicate weathering of both kaolinite and authigenie mica suggesting that the second hypothesis is possible. It is strongly supported by the observation that the original igneous micas are relatively unweathered and would be concentrated ff the authigenic clays were increasingly removed by later stages of solution.

Some of the weathered granodiorite and associated felsite from dredge haul 7490 contain small amounts of high erystallinity chlorite of undoubted igneous-metamorphic origin. All of these samples weather to yield abundant montmorillonite. In these specimens the authigenic clay assemblage is montmorillonite-K-miea-kaolinite with montmorillonite the main component. Thin-section studies show that some of the plagioclase as well as the orthoclase crystals weather to clay.

The second type of clay habit encountered is as vein fillings. These are predominantly halloysite. Small amounts of corroded ordered kaolinite and secondary mica occur with the halloysite. The identification of the halloysite is based on the broadened asymmetric (001) X-ray line and the tubular habit shown in the electron micrographs.

A white vein-filling clay is also common. It has the thermal properties and (001) and (002) lines of talc but lacks other lines to assist in identification. The electron micrographs show platy flakes of crystals lacking distinctive crystal morphology. Studies on this material are continuing.

The above data indicate that weathering of feldspars in equilibrium with sea water proceeds by stages and depends on the mother material. Montmorillonite was not observed to form by the sea water-orthoelase reaction while it formed from weathering of chloritic plagioclase. Normal kaolinite and a K-mica formed within the pore spaces embedded in the microenvironment of orthoclase crystals. However, on more direct exposure to the marine environment, kaolinite was converted to halloysite while mica was only slightly destroyed.

These data may be interpreted either in the context of a marine "soil" or as the equilibrium reaction between igneous silicates and sea water at low temperatures to form equilibrium clay mineral assemblages. The "soil" concept draws upon the ubiquitous presence of marine microorganisms and their metabolites to dissolve and transport into the free sea water phase those components that can be solubilized. If this process is of major importance then we must consider marine weathering as another class of soil-forming processes that produce clays. If we wish to assume biologic processes to be of lesser importance, then the observed clay mineral formation suggests that the composition of sea water lies close to the montmorillonite-kaolinite (halloysite) phase join and not too distant from the K-mica-kaolinite join. This study has not resolved which of these two hypotheses is more realistic. It is possible that both are valid.

GEOLOGIC EVIDENCE FOR SUBMARINE WEATHERING

Martin (1964) concluded that Monterey Canyon in the region of dredged granodiorite was cut in the submarine environment during the late Pliocene or early Pleistocene. The time of cutting of Carnel Canyon is less well-known owing to a more complex history of development, but is probably Pleistocene or earlier.

Granodiorites in Monterey and Carmel Canyons are within the same fault block as the Santa Lucia Mountains (Santa Cruz sheet, California Division of Mines and Geology) ; therefore, the geologic history of this range should be a criterion to judge whether the granodiorites exposed in Monterey and Carmel Canyons ever were subaerially weathered.

Beginning in middle Miocene and ending at the close of late Miocene the Santa Lucia block was downdropped, permitting the deposition of thick deposits of the Monterey Formation. Marine Pliocene, Pleistocene, and Recent rocks and sediments are unknown in the Santa Lucia Mountains except along the immediate coastline; thus at these times, the range was in the process of being elevated and eroded to its present relief (approximately 1000 m) and topographic expression.

If the granodiorites in the submarine canyons were ever exposed to subaerial weathering during the middle and later Tertiary and the Recent, the period would of necessity be from the Pliocene to Recent, owing to general uplift of the Santa Lucia Mountains. Assuming subaerial cutting of Monterey Canyon followed by subsequent downdropping of the granodiorite block containing the canyons below sea level, there would have been a transgressive phase of marine water (and resultant marine sedimentary units) over all or parts of the Santa Lucia Range. No such transgressive phase is recorded in Pliocene to Recent sediments of the Santa Lucia Mountains. It therefore 240 FOURTEENTH NATIONAL CONFERENCE ON CLAYS AND CLAY MINERALS

appears that the structural history of Monterey and Carmel canyons requires that they were cut in the submarine environment and that the granodiorites were altered in this environment.

CONCLUSIONS

Submarine weathering of granodiorite in Monterey Canyon produces kaolinite, K-mica, halloysite, and montmorillonite from the dissolution of feldspars. This weathering process may be either inorganic or assisted by the local biota and their metabolites.

REFERENCES

- MARTIN, BRUCE D. (1964) Monterey submarine canyon, California: Genesis and relationship to continental geology: Unpub. Ph.D., diss., University of Southern California, Los Angeles, 249 pp.
- REx, R. W. (1965) Authigenie kaolinite and mica as evidence for phase equilibria at low temperatures: *Clays and Clay Minerals*, Proc. 13th Conf., Pergamon Press, London, 95-104.