

# ALTERATION AND FORMATION OF CLAY MINERALS DURING CAT CLAY DEVELOPMENT

*by*

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## ABSTRACT

THE natural tidelands sediments along the north shore of San Pablo Bay, California, are neutral in reaction and subjected to a wet, reducing environment conducive to ferrous sulfide accumulation. When the sediments are diked and drained, the environment rapidly becomes oxidizing and generally dry. Oxidation of the ferrous sulfide results in extremely acid cat clays within a year or two.

Undrained sediments from the area contain montmorillonite, chlorite, mica, and kaolinite that all give sharp X-ray diffraction patterns. Sediments drained for 6 years, although strongly acid, have virtually the same clay mineralogy as the undrained sediments. However, sediments drained for 60 years show a general deterioration of crystalline clay minerals, particularly chlorite. The deterioration decreases with depth until the deeper zones closely resemble the undrained sediments.

In separate laboratory experiments, chlorites were formed in an oxidized soil that was subjected to reducing conditions simulating the environment of the undrained tidelands sediments. The possibility exists, therefore, that chlorites in the undrained sediments may have formed subsequent to deposition.

## INTRODUCTION

IN the presence of organic matter and sulfate and under reducing conditions, iron sulfides accumulate in marsh sediments. Cat clays, or acid sulfate soils, develop if such sediments subsequently oxidize. The diking of reduced sediments along the north shore of San Pablo Bay, California, to exclude tide water, has provided the necessary oxidizing conditions. Cat clays with characteristic yellow mottling and a soil pH between 3.0 and 3.5 are common.

The acid environment as well as some of the processes involved in cat clay formation may affect clay minerals. Changes during the oxidizing phase were studied by comparing the clay mineralogy of cat clays and nearby reduced sediments. Changes in clay mineralogy during the reducing phase were followed in laboratory experiments.

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## REDUCED TIDELAND SEDIMENTS

The study area extends along the north shore of San Pablo Bay, California, from the Napa River on the east to Petaluma Creek on the west (Fig. 1). The area is at near sea level and would be mostly inundated except for the protecting levees. Shallow mud flats extend a considerable distance southward

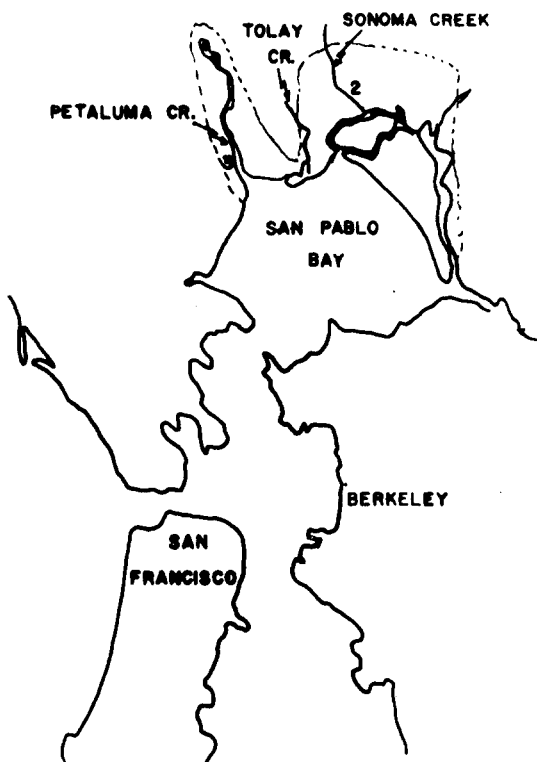


FIG. 1. Map of sampling area along the north shore of San Pablo Bay, California.

into the bay. Samples for study were taken from the zone of tidal fluctuation in the Tolay Creek, Sonoma Creek, and Petaluma Creek drainage ways (designated areas 1, 2, and 3, respectively, in Fig. 1). Two samples were collected in the Petaluma Creek area, one farther from the water than the other. Beneath the brown surface skin, the sediments are bluish-grey to black. Zones adjacent to organic matter remains are jet black. Hydrogen sulfide gas is often apparent or it will evolve upon addition of hydrochloric acid.

The particle size distribution in sediments from each of the three drainage ways is similar (Table 1). The clay ranges from 52 to 64%, and sand is less

than 1%. The clay is about evenly divided between coarse ( $0.2\text{--}2\ \mu$ ) and fine ( $< 0.2\ \mu$ ) clay. The higher clay percentage in the one Petaluma Creek sample represents the location farther from the creek, and probably is a reflection of decreased stream flow.

The X-ray diffraction patterns (diffractometer scans of oriented samples, copper  $K\alpha$  radiation) of the coarse and fine clay from each of the drainage ways are also similar. The patterns in Fig. 2 from the Petaluma Creek sediments are typical. Several well crystallized clays are present. In the coarse

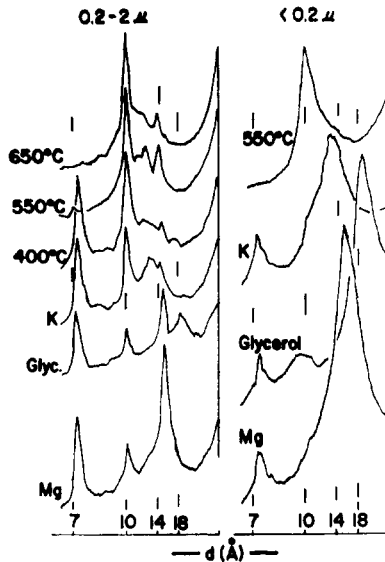


FIG. 2. X-ray diffraction patterns of clays from reduced sediments of the Petaluma Creek drainage way.

clay, mica is identified by the  $10\ \text{\AA}$  peak in the magnesium-saturated sample; montmorillonite by the  $18\ \text{\AA}$  peak in the glycerol-solvated sample; vermiculite by the enhanced  $10\ \text{\AA}$  peak in the potassium-saturated sample; chlorite by the  $14\ \text{\AA}$  peak that persists after heating; and kaolinite by the  $7\ \text{\AA}$  peak that disappears when the sample is heated to  $550^\circ\text{C}$ . The  $12.5\ \text{\AA}$  peak in the potassium-saturated sample after heating to  $550^\circ\text{C}$  is chlorite interstratified with vermiculite. The fine clay is mostly montmorillonite, with some kaolinite and a trace of mica.

The similar particle size distribution and clay mineralogy indicate the sediments are deposited via the San Pablo Bay rather than the separate drainage systems. This supports the contention of Grass, Aronovici, and Muckel (1962) that the Sacramento-San Joaquin River system is the source of sediments in the San Pablo Bay.

TABLE 1.—PARTICLE SIZE DISTRIBUTION OF SEDIMENTS ALONG THE NORTH SHORE OF SAN PABLO BAY, CALIFORNIA

Drainage way	Per cent				
	50–100 $\mu$	20–50 $\mu$	2–20 $\mu$	0.2–2 $\mu$	0.2 $\mu$
Tolay Creek	tr.	3.8	39.6	27.2	29.4
Sonoma Creek	tr.	9.0	38.8	24.9	27.0
Petaluma Creek					
A	tr.	5.8	33.7	27.5	33.7
B	tr.	2.8	32.5	29.0	35.7

A. 30 ft from creek bank, under reed cordgrass, *Spartina foliosa*.

B. 55 ft from creek bank, under pickleweed, *Salicornia ambigua*.

### CHANGES IN CLAY MINERALS UPON OXIDATION

Locations of cat clay profiles from the Tolay Creek area and the Sonoma Creek area are shown in Fig. 1 as areas 1 and 2, respectively. The sediments are light gray as deep as they are oxidized. At a depth of from 2 to 6 ft the sediments are still reduced with properties as described above. Jarosite  $[\text{KFe}_3(\text{OH})_6(\text{SO}_4)_2]$  gives characteristic yellow mottling that generally begins within a foot of the surface and may extend to a depth of 2 ft. Red mottles containing amorphous iron hydroxides or oxides accompany the yellow mottling and generally extend to a greater depth. The mottling occurs on ped surfaces and as concentric yellow and red rings around root channels.

The profile near Tolay Creek on Tubbs Island was exposed to an oxidizing atmosphere for 6 years prior to sampling. The pH is between 3.0 and 3.5. The diffraction patterns (Fig. 3) of the coarse and fine clay from a zone of maximum cat clay expression are similar to those from the reduced sediments. The same mineral suite is present: mica, montmorillonite, vermiculite, chlorite, kaolinite, and interstratified chlorite-vermiculite. The diffraction peaks are sharp, although chlorite is less pronounced than in the reduced sediments after 650°C heating.

The site in the Sonoma Creek area was diked over 60 years prior to sampling. The zone of oxidation and the yellow mottling extend to a greater depth than in the profile from the Tolay Creek area. The pH of the sediments is about the same, however. The same suite of minerals is present in the zone of maximum cat clay expression, but the peaks (Fig. 4) are not so sharp and generally less intense. Very little chlorite is present and the proportion of vermiculite is reduced.

A more complete picture of how the acid environment affects the chlorite is apparent when diffraction patterns of the entire Tolay Creek and Sonoma Creek profiles are compared. Patterns of the coarse clay, saturated with potassium and heated to 550°C, are shown in Fig. 5. The 14 Å chlorite peak

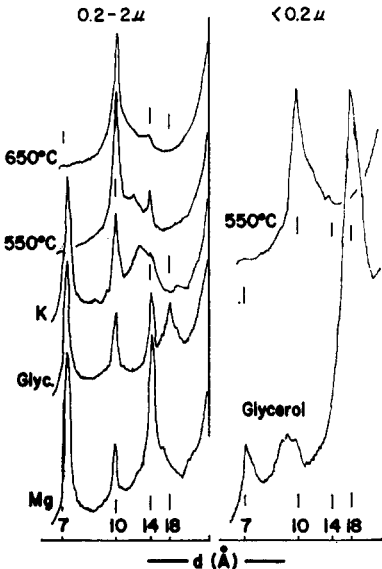


FIG. 3. X-ray diffraction patterns of clays from the zone of maximum cat clay development in sediments oxidized for 6 years, Tolay Creek area.

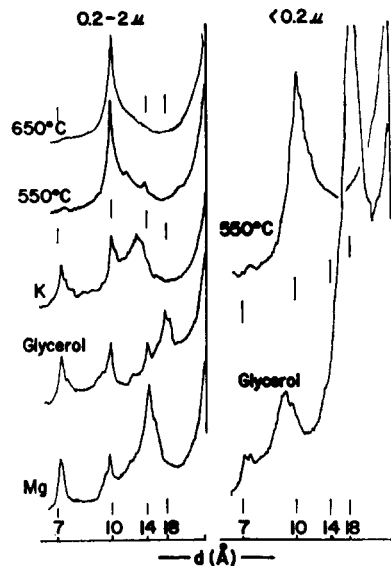


FIG. 4. X-ray diffraction patterns of clays from the zone of maximum cat clay development in sediments oxidized for 60 years, Sonoma Creek area.

remains the same throughout the profile oxidized for 6 years, or may be diminished a little in the surface layer. However, chlorite distinctly increases with depth in the profile oxidized over 60 years. The lowest depths presented in each profile are in the fringe of the reduced sediments.

The question arises as to the fate of the chlorite. An examination of Figs. 2, 3, and 4 shows an increase in montmorillonite relative to other 14 Å minerals as the length of time in the acid environment increases. Compare the 18 Å and 14 Å peaks in the glycerol-solvated samples of the coarse clays, and note the general increase in the fine clay montmorillonite. Apparently the "brucite" layer of the chlorite is selectively removed and the "mica" layer remains. The residual negative charge is evidently in the montmorillonite range and the mineral then responds to solvation and heating as montmorillonite.

#### CLAY MINERAL CHANGES DURING REDUCTION

Mineralogical and chemical changes during sulfide accumulation could not be studied directly because adequate time sequences were not available in the field. Therefore, laboratory experiments were designed to simulate reducing conditions in the bay area. Material from the B<sub>1</sub> horizon of Berrendos, an upland soil low in organic matter, was subjected to reducing conditions.

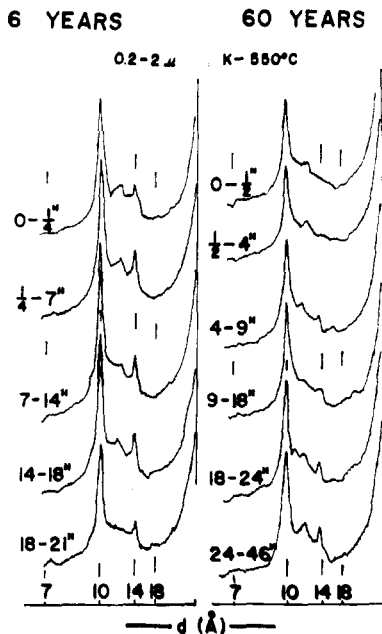


FIG. 5. A comparison of the coarse clay from Tolay Creek cat clays (oxidized 6 years) and Sonoma Creek cat clays (oxidized 60 years).

Ground plant materials and simulated brackish water were added to the experimental soil samples; the mixtures were incubated for 5 to 21 weeks under anaerobic conditions, with periodic changing of the brackish water solution.

The coarse clay minerals of the Berrendos (Fig. 6a) include kaolinite, mica, vermiculite, a little montmorillonite and some interstratified chlorite-vermiculite. After 5 weeks of incubation, a definite chlorite peak appeared (Fig. 6b). After 21 weeks of incubation, however, chlorite was barely detectable (Fig. 6c). The remainder of the clay minerals appear to be unchanged by the reducing environment. The apparent increase in talc in the incubated samples (9.2 Å spacing) is unexplained. The presence of chlorite after 5 weeks incubation, but not after 21 weeks, at first seemed incongruous. However, the same pattern occurred with each of six types of organic matter used in the experiments. The experiments included periodic chemical analyses of leachates from the incubating samples. The concentration of ferrous iron in the leachates reached a maximum between 5 and 10 weeks after initiation of incubation (Fig. 7). By 15 weeks the ferrous iron concentration was down to a low level. The trends were amplified more with oats as the source of organic matter than with tule (*Scirpus acutus*). The high ferrous iron concentration

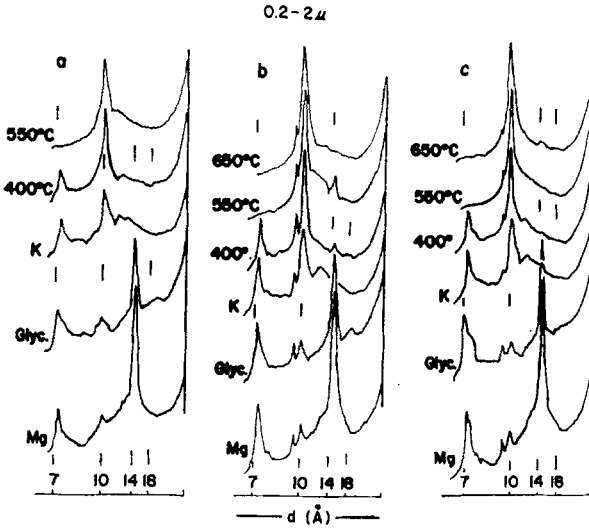


FIG. 6. X-ray diffraction patterns of the coarse clay (2-0.2  $\mu$ ) from the B<sub>1</sub> horizon of (a) Berrendos, and the same soil after (b) 5 weeks and (c) 21 weeks of anaerobic incubation.

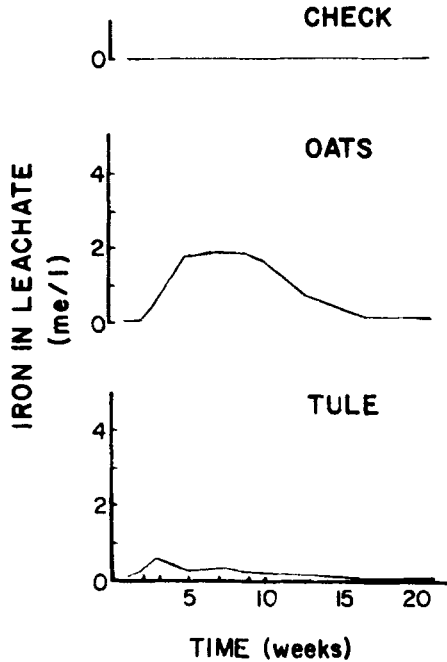


FIG. 7. Ferrous iron in leachates from anaerobically incubated mixtures of Berrendos soil and organic matter.

correlates with the presence of chlorite in the incubated samples. With soil alone (check), no ferrous iron was found and no chlorite formed. This strongly suggests the "brucite" layers of the synthesized chlorite are at least partially iron hydroxides. The destruction of the chlorite after heating to 650°C is additional evidence of a high iron content.

Disappearance of the chlorite after longer incubation is puzzling. Perhaps oxidation in the preparation of the sample for X-ray analysis, stabilized the chlorite, and this could occur only when the soluble iron content was high. On the other hand, continued precipitation of ferrous sulfide during the longer incubation period and periodic sulfate addition in the brackish water deplete the soluble iron available for chlorite formation. An equilibrium imbalance in favor of a more insoluble external iron sulfide may cause removal of interlayer iron and its precipitation as an insoluble ferrous sulfide.

The formation of chlorites in laboratory experiments cited above suggests that chlorites may have formed in the reduced tideland sediments subsequent to deposition.

## DISCUSSION

The extent to which cat clay formation has influenced present-day soils is open to question. The sea level fluctuations during Wisconsin and earlier glaciations would provide considerable opportunity for marsh development and sulfide accumulation. A receding sea level would expose sediments to oxidation and acid formation. If the sea level has been 50 to 100 ft above the present level, a number of present-day soils and their clay minerals may have been affected.

## SUMMARY

The reducing conditions required for sulfide accumulation may cause interlayers to form in expansible 2 : 1 layer silicates, resulting in synthesized chlorites. The acid environment of the oxidized cat clays has no apparent effect on clay minerals for the first few years, but after 60 years the clay minerals show a general deterioration in crystallinity, and chlorite shows a marked destruction, probably altering to montmorillonite.

The fluctuation in sea level during the Pleistocene may have influenced a number of present day soils through the processes of cat clay development.

## REFERENCE

- GRASS, LUTHER B., ARONOVICI, V. S., and MUCKEL, DEAN C. (1962) Some chemical characteristics of submerged and reclaimed sediments of the San Francisco Bay System, *Proc. Soil Sci. Soc. Amer.* **26**, 453-5.