divided siderite at moderate temperatures in hydrothermal or dry environments resulted in the formation of gamma-Fe_2O_3. In experiments with the same materials and at the same temperatures alpha-Fe_2O_3 was the final product when the oxidation rate was retarded by CO_2 in the system. Apparently rapid oxidation favors the type of mimicry which results in the magnetite structure being preserved in the ferric oxide.

The rate of oxidation of magnetite at a given temperature and oxygen pressure is a function of the specific surface of the material and of the degree of perfection of the crystal lattice. The most pronounced difference in natural and synthetic magnetite is grain size. This alone could easily account for the differences that have been found in the behavior of the two materials during rapid oxidation. Minor structural irregularities of synthetic magnetite proposed by Starke (8) have been invoked to account for the fact that it oxidizes to gamma-Fe_2O_3, but these irregularities are probably only of secondary importance.

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THE SEPARATION OF CLAY MINERALS FROM CARBONATE ROCKS

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The separation of the clay mineral fraction of a carbonate rock is accomplished ordinarily by acid digestion. Hydrochloric acid often is preferred because it is a strong acid, forms soluble compounds and facilitates rapid solution. When insoluble silica residues are not the primary objectives of carbonate rock solution, the extent of acid reaction with the

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minerals of interest, i.e. the clays, must be considered. Grim, Lamar and Bradley (1937) suggested placing the ground rock sample in two liters of distilled water and adding a few drops at a time of concentrated HCl, in order to keep a low concentration of acid and not destroy the clay minerals. The pH of such a solution is very low, however; and the present authors have observed that in such a procedure the reaction will start in a very low strength acid, but it is necessary to increase the acid concentration considerably toward the end of the process in order to dissolve all of the sample. During a study of the mineralogy of the Ordovician Jacksonburg cement rock formation of eastern Pennsylvania (a fine-grained, argillaceous, black limestone) the problem of destruction of clay minerals by acid was avoided by using cation exchange resins to effect solution of the carbonate in a very weakly acidic solution of relatively high pH.

Acid-insoluble residues from carbonate rocks contain clay minerals and quartz, chert, and other insoluble minerals. Strong acids are capable of dissolving some clay minerals such as ferri-ferrous chlorites, various members of the montmorillonite family such as hectorite, probably some of the hydrated micas and possibly others. Few quantitative data are available on rates of solution of identified clay minerals in acids. In order to minimize the probability of losing significant minerals from the Jacksonburg clay mineral suite by acid decomposition, a method was developed that did not decompose or dissolve a highly acid reactive clay mineral, hectorite, while completely dissolving the carbonate fraction.

Various mechanical mixtures of quartz, calcite, dolomite, and hectorite were prepared to simulate impure calcitic and dolomitic limestones. These mixtures were treated with solutions of hydrochloric, formic and acetic acids and with the cation-exchange resins, Amberlite IRC-50 and IR-120. IRC-50 derives its exchange activity from carboxylic acid groups, the IR-120 from sulfonic acid groups. A slurry in distilled water of the hydrogen form of the IRC-50 resin has a pH of about 6 or a hydronium ion concentration of about 10^{-6} molar. This compares with a hydronium ion concentration of about 9×10^{-3} molar for a 4.4 molar solution of acetic acid (1:3 by volume); about 3.3×10^{-2} molar for a 6 molar solution of formic acid (1:3 by volume); and about 3 molar for a 1:3 solution of hydrochloric acid, all at room temperature. The significant variable controlling the rates of reaction of the various acid solutions with the clay minerals, the hydronium ion concentration, is, therefore, of the order of a million times smaller in the case of the resin than in the hydrochloric acid solutions. If the reaction of clay minerals with acids were a first-order reaction, the clay would be decomposed by the resin at one-millionth the rate of decomposition in hydrochloric acid solutions.

In the cases of acetic and formic acids the corresponding rates would be several thousand times slower. Although the pH of the resin slurry decreases with increasing temperature (pH 5.9 at 28° C. vs. pH 5.3 at 70° C.) the slurry hydronium ion concentration is still markedly lower than those of the acids.

The clay mineral hectorite, a magnesium end-member of the montmorillonite family, was used in the simulated limestone mixtures because it reacts more rapidly with acids than other clay minerals. If it could be shown that detectable amounts of hectorite were not lost from the sample mixtures while the calcite was consistently dissolved at a controlled pH, this would serve as an acceptable criterion for an improved clay mineral separation procedure. If only negligible amounts of hectorite were decomposed by the solution procedure under test, this procedure could be relied upon for separations of all clay minerals in any carbonate rock. *X*-ray diffraction analysis was used to determine the amount of hectorite in the dried residues of the mineral mixtures after digestion. Quartz in the original sample mixtures and in the residues served as an internal standard for assignment of "*d*" spacings. Only semi-quantitative estimates of the amount of clay mineral were made with respect to the amount of quartz, because of the possibility that colloidal silica released in the breakdown of hectorite, would coat the quartz grains and decrease quartz line intensities.

Four different mineral mixtures were prepared: Mix 1: 50% quartz, 50% hectorite; Mix 2: 20% quartz, 20% hectorite, 60% calcite; Mix 3: 2½% quartz, 2½% hectorite, 95% calcite; and Mix 4: 2½% quartz, 2½% hectorite, 95% dolomite. The proportion of quartz to hectorite was the same in each mix. All materials were ground to pass a 270-mesh sieve. A powder pattern of Mix 1 showed, among many lines, a diffuse but strong line at 14.5 Å representing hectorite.

Mix 2 was split into four fractions. Three were treated respectively with 3 molar hydrochloric acid, 4.4 molar acetic acid (pH 1.9) and 6 molar formic acid (pH 1.5). Excess of acid was added in each case. The three samples were heated during digestion over a low gas flame at about 80–85° C. for about 1½ hours. The *x*-ray powder patterns of the hydrochloric and formic acid residues showed no trace of the 14 Å line but did show faint diffuse zones from about 12 Å to about 6.7 Å. Apparently the hectorite was destroyed. The acetic acid residue showed a strong line at 16.2 Å indicating that hectorite was not destroyed by acetic acid.

The fourth fraction of Mix 2 was treated with Amberlite IRC-50 by the batch technique. Theoretically 2½ grams of calcite in the mix would require 15 cc. of resin for dissolution but an excess was used (70 cc.). Sufficient water was added for the reaction to proceed. The resin-water-

sample slurry was heated on a water bath (70° C.) and stirred intermittently. The bulk of the calcite was dissolved in two hours. Resin and residue were separated by screening on 116-mesh cloth screen. The resin was regenerated with 10% solution of hydrochloric acid and the residue put through a second cycle. All effervescence ceased during the second cycle. An *x*-ray pattern of the dried residue showed a sharp, strong line at 16.2 Å, which was assigned to hectorite.

The increase in the "*d*" value from 14.5 Å to 16.2 Å is attributed to a total conversion of the hectorite to the H^+ form with partial dehydration as a result of drying the residue. This "*d*" value lies within the range of 19.3 Å to 14.5 Å given by Barshad (1950) as characteristic of an "immersed in water" and a "dry" condition of H^+ montmorillonite. The sharpness of the line of the resin residue compared with the broad diffuse line of Mix 1 is considered to be due to (1) conversion of the hectorite to an all H^+ form from a largely Ca^{++} form, (2) partial but uniform dehydration of the individual layers and (3) a similar arrangement of the water molecules in the layers. The 16.2 Å value obtained here is closest to one given by Barshad (1949) for montmorillonite with three monomolecular layers of water with the water molecules forming tetrahedra at the water-oxygen interfaces and octahedra at the water-water interfaces.

To test if hectorite could be recovered from a mixture containing a minor amount of the mineral, several fractions of Mix 3 were treated with acids and resin. A four gram sample was digested with Amberlite IRC-50 following the procedure for Mix 2, except that the first cycle was four hours long and the second cycle was three hours. The bulk of the calcite was digested in the first cycle. The *x*-ray powder pattern showed the hectorite line at 14.6 Å.

Other fractions of Mix 3 were treated with acids but at lower concentrations than those used for Mix 2. A six gram sample was treated with 850 cc. of .2 molar hydrochloric acid (pH = .9) for four hours at room temperature (20° C.). The powder pattern of the residue showed the hectorite line. However, a five gram sample treated with 700 cc. of .2 molar hydrochloric acid on a water bath for four hours showed only a very faint line in the vicinity of 14 Å, indicating almost complete destruction of the hectorite.

A six gram sample of Mix 3 was treated with 500 cc. of one molar formic acid (pH 1.95) for nine hours and an eight gram sample was treated with 170 cc. of 4.4 molar acetic acid (pH 1.9) for 6½ hours, both at room temperature. Powder patterns of these two residues showed strong lines at 14.9 Å. No calcite lines were present. Treatment of the formic acid residue with fresh one molar formic acid for four hours over a low flame destroyed almost all of the hectorite. The acetic acid residue was treated

with 100 cc. of fresh 4.4 molar acetic acid but heated on a water bath for $3\frac{1}{2}$ hours. The powder pattern showed a strong hectorite line.

The solution of dolomite (Mix 4) with the IRC-50 resin was a slower process than that of calcite, but it was accomplished by heating the resin-sample-water slurry gently over a flame and continuing through four two-hour cycles. Some hectorite may have been destroyed because of the length of the treatment at elevated temperatures (80–85° C.), but the characteristic lines for hectorite were definitely present in the diffraction patterns of the residue.

These experiments indicate that the use of hydrochloric and formic acids for extraction of acid-sensitive clay minerals from limestone and dolomite is restricted to solutions at room temperature with a pH no lower than 2. Under these conditions digestion is slow, particularly for dolomite. Amberlite IRC-50, however, can be used at elevated temperatures and despite the lower concentration of hydronium ions in its slurry, the reaction times are about comparable for limestone and apparently faster for dolomite. Acetic acid seems to be as effective as the resin for calcite but less so for dolomite. Gault and Weiler (1955) report that an excess of 4.4 molar acetic acid dissolves only about 10% of a sample of dolomite in 30 hours compared with 60% of a limestone sample in five hours and 80% in 30 hours.

Amberlite IR-120 in its NH_4^+ form has also been tried with Jacksonburg limestone samples.[2] The reaction in this case leads to the formation of $(NH_4)_2CO_3$ which is soluble and passes through the cloth screen with the residue. Heating on a water bath decomposes the $(NH_4)_2CO_3$ and the dried residue is free of it. The reaction with the IR-120 resin takes place at a pH of about 6.1. The chlorite and illite lines are well preserved in the *x*-ray diffraction patterns.

The IR-120 in the NH_4^+ form is less desirable than the IRC-50 in the H^+ form because of the slower reaction. Even after four two-hour cycles of treatment, the residue showed calcite lines. Dolomite would require even more cycles for dissolution.

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TITANCLINOHUMITE FROM THE WICHITA MOUNTAINS, OKLAHOMA

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Significant megascopic quantities of titanclinohumite have been identified in two rock specimens presented by J. V. Smith, a local ranger, found near the U.S. Post Office at Meers in 1950, when the writer first visited the gabbro-granophyre complex of Precambrian age in the Wichita Mountains of southwestern Oklahoma. Later, in 1952, titanclinohumite was again found in magnetite gabbro and troctolite at Iron Mountain, Sec. 28, T.4N., R.16W, and a diallagite exposure six miles northwest of Meers, NW$\frac{1}{4}$, Sec. 30, T.4N., R.14W., while the writer undertook the investigation of the Wichita Mountains igneous complex.

The gabbroic rocks at Iron Mountain and diallagite in the area six miles northwest of Meers are contaminated with granitic materials and veined with pegmatites, as both localities lie in the contact zone between gabbro and granophyre of the igneous complex. The ramifying quartzofeldspathic veinlets, stringers, and pegmatite patches are flecked by small black titanclinohumite grains. Many blackish brown titanclinohumite grains are sparsely distributed in the diallagite, and at Iron Mountain brown titanclinohumite is admixed with olivine crystals both in magnetite gabbro and troctolite.

Alteration is pronounced in the gabbroic rocks, and the severe alteration could not be attributed to atmospheric weathering alone. The distribution of alteration products is patchy and irregular, as if caused by a granophyric melt and volatiles which migrated through the rocks and altered the minerals in their paths. Olivine is altered to iron minerals. Plagioclase has been partly replaced by aggregates of prehnite. The aggregates form irregular patches and are associated with chlorite, zeolite, and iron ores. Alteration of augite indicates a tendency to form pale-