trace elements between coexisting phases observed in metamorphic sequences, and (2) the laws governing the inclusion of a trace element in different coexisting crystal lattices are more than those based on any single parameter such as ionic radius.

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INTERCRYSTALLIZED APATITE AND ANKERITE FROM THE NEW ALBANY SHALE OF INDIANA[1]

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A core that penetrated the New Albany Shale (upper Devonian and lower Mississippian) was obtained from Clark County in southeastern Indiana. An unusual specimen of intercrystallized apatite and ankerite was found within the black shale. This sample, which is 0.1 foot thick, was obtained approximately 1 foot stratigraphically below the top of the New Albany Shale. Similar material has been seen in approximately the same stratigraphic position at five other localities in Indiana; the sample from Clark County best illustrates the relationships described in this note.

More than 90 per cent of a thin section cut from this sample is composed of intercrystallized apatite and ankerite. Pyrite, quartz and gypsum(?) as well as separately crystallized ankerite and apatite, also are present. The intercrystallized apatite and ankerite has wavy extinction, a birefringence between apatite and ankerite, and refractive indices ranging from 1.648 to 1.576 (Na light). Discrete areas of intercrystallized

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[1] Published with permission of the State Geologist, Geological Survey, Indiana Department of Conservation, Bloomington, Ind.

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ankerite and apatite extinguish at the same position but at different positions from adjacent areas (Fig. 1). The boundaries between areas are interlocking. Pyrite is found as spheres or as a replacement of fossils. Quartz grains are less than 0.04 mm, and gypsum(?) is associated with the pyrite.

The intercrystallized ankerite and apatite were formed by the incomplete replacement of apatite by ankerite. The discrete grains of apatite and ankerite represent areas that were unaltered or completely replaced, respectively. Much of the pyrite has been replaced by the intercrystallized ankerite and apatite, by the apatite or by the ankerite. The gypsum
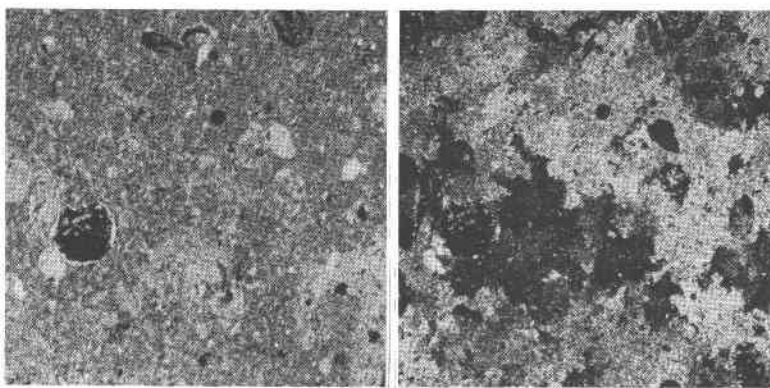

FIG. 1. Photomicrographs of thin section of sample from New Albany Shale.
A. (left) single nicol, ×36. B. (right) crossed nicols, ×36.

(?) that is associated with the pyrite may have been formed during the alteration of the latter. Relict fossil textures (Fig. 1) indicate that the sample originally was a limestone. The postulated paragenesis is summarized in Fig. 2.

Neither apatite nor ankerite could be separated for x-ray or chemical analyses because of their small size, intergrown relationships and similar resistance to solvents. Table 1 gives the d-spacings and intensities of the measurable ankerite lines; the apatite lines are identical to those produced by N.B.S. samples No. 56b (Tennessee phosphate rock) and No. 120 (Florida phosphate rock). The only other diffraction peak that was observed was due to the (101) reflection of quartz. The d-spacings were measured on a General Electric slow speed (0.2° per minute) x-ray trace and corroborated by measurements on a film that was taken with a Norelco camera (radius=114 cm), using CuKα radiation. Quartz was used as an internal standard. Precise measurements were impossible because of the broad, low intensity characteristics of the carbonate peaks.

TABLE 1. CELL DIMENSIONS, d-SPACINGS AND INTENSITIES OF ANKERITIC MINERALS

hkl	Carbonate (this paper)		Ankerite (Howie and Broadhurst, 1958)		Theoretical CaFe(CO₃)₂ (Graf, 1961)	
	dÅ	I	dÅ	I	dÅ	I
100	4.05	5			4.0577	12.7
110	3.72	7	3.704	15	3.7233	48.1
211	2.915	100	2.899	500	2.9141	231
222	not observed		2.685	15	2.7031	1.15
101	2.42	5	2.411	15	2.4197	41.3
210	2.21	11	2.199	30	2.2085	42.5
200	2.03	7	2.020	15	2.0277	41.6
a	4.835± .005		4.819		4.8393	
c	16.245± .015		16.10		16.218₅	
c/a	3.36		3.341		3.3514	
a_{rh}	6.10± .05		6.045		6.0855	
	46° 36′±06′		47° 00′		46° 51.5′	

A differential thermal curve of the sample is shown in Fig. 3. This trace depicts the thermal reactions of the ankerite, because apatite undergoes no reactions below 950° C. (Silverman *et al.*, 1952). The broad exothermic hump from 300° to 600° C. probably is due to the organic material (Mac-Kenzie, 1957) in the sample (Table 2). After the sample has been heated to about 650° C. for 2 hours, only peaks for apatite are present on the *x*-ray trace, an indication that the intercrystallized ankerite and apatite is composed of two different mineral phases. The approximate cell dimensions that best fit the observed d-spacings of the measurable ankerite lines were calculated by means of trial and error on a Bendix G-15 digital computor (Table 1).

Chemical analyses (Tables 2 and 3) suggest that this ankerite is similar to the ankerite Ca(Mg, Fe)(CO₃)₂ described by Howie and
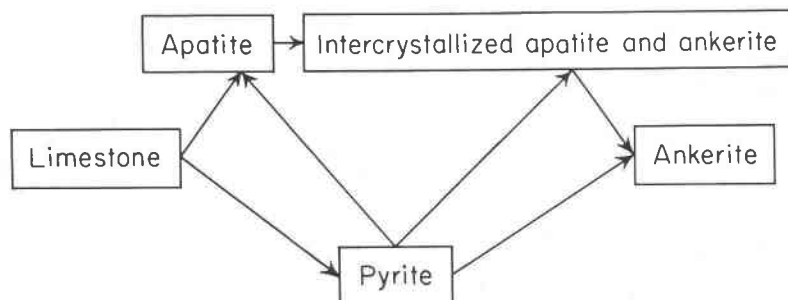

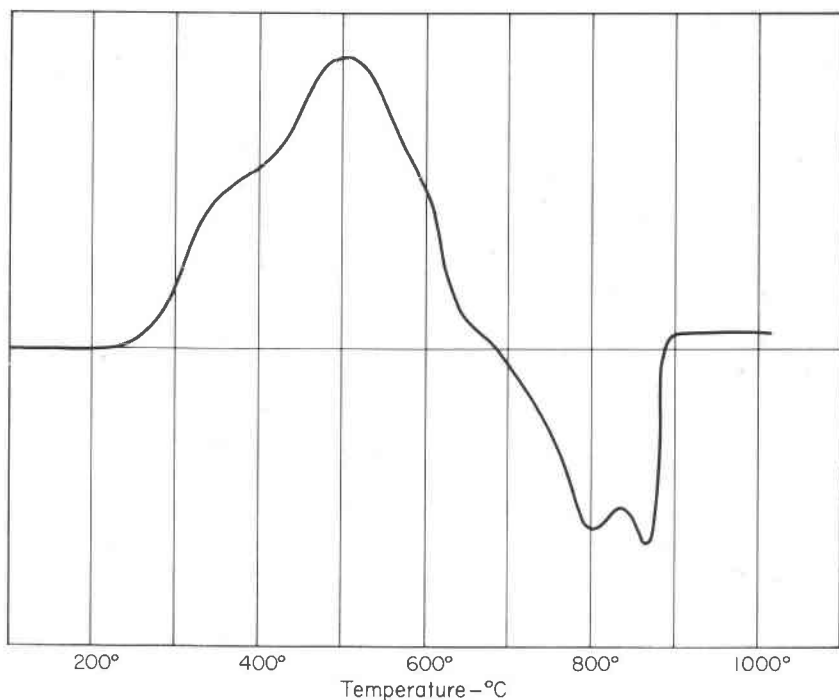FIG. 2. Diagram showing postulated paragenesis.

FIG. 3. Differential thermal curve of sample from New Albany Shale.

TABLE 2. CHEMICAL ANALYSIS OF APATITE-ANKERITE SAMPLE

(Analyst, M. E. Coller)

Oxide or element	Weight per cent
SiO_2	4.5
Al_2O_3	2.1
Fe_2O_3	—
FeO	6.5
MgO	4.65
CaO	37.5
CO_2	18.5
P_2O_5	18.4
S	2.12
C (organic)[1]	1.9
F	2.1

[1] Obtained by subtraction of C in CO_2 (5 per cent) from determined total C (6.9 per cent).

TABLE 3. CARBONATE ANALYSES

Calculated analysis of carbonate in Indiana sample			Ankerite of Howie and Broadhurst (1958)	
Oxide	Per Cent	Recalculated to 100 per cent	Oxide	Per cent
CaO[1]	13.5	33	CaO	29.23
CO$_2$	18.5	45	CO$_2$	44.70
FeO[2]	4.3	10.5	FeO	12.06
MgO	4.7	11.5	MgO	12.85

[1] Obtained after removal of 24 per cent Ca to form apatite (with 18.4 per cent P$_2$O$_5$)

[2] Obtained after removal of 1.85 per cent Fe to form pyrite (with 2.12 per cent S).

Broadhurst (1958), except that the Indiana ankerite contains more calcium. This increase in calcium should tend to increase the d-spacings and could explain the discrepancies between the cell dimensions of this sample and those of the ankerite described by Howie and Broadhurst (Table 1). Table 1 also shows that the cell dimensions and d-spacings for the ankerite described in this note are similar to those given by Graf (1961) for theoretical CaFe(CO$_3$)$_2$; excess calcium in an ankerite could account for this similarity. Furthermore, the DTA trace is similar to those for ankerite (Beck, 1950; Kulp *et al.*, 1951). Therefore the ankerite in the intercrystallized phase is probably an ankerite enriched in calcium.

During the formation of the intercrystallized ankerite and apatite, magnesium and iron replaced calcium. This replacement did not go far enough to produce the ankerite described by Howie and Broadhurst, and therefore the resultant carbonate mineral is enriched in calcium. The pyrite could have supplied the iron; dolomitic rocks, which are found stratigraphically just above this sample, may have provided the magnesium.

Possibly some reported occurrences of apatite containing carbonate are actually a carbonate mineral intercrystallized with apatite. If the amount of CO$_2$ in a chemical analysis of an apatite is small and the grain size is very small, a carbonate mineral would be virtually undetectable.

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ELECTRONOSCOPIC STUDIES OF ACID-TREATED KAOLINITE

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INTRODUCTION

The purpose of this paper is to present the results of a study of the
nature of the detailed morphological changes, if any, that take place
when a well-crystallized kaolinite is subjected to treatment with three
common acids.

EXPERIMENTAL TECHNIQUE

A sample of well-crystallized Georgia kaolinite was selected for in-
vestigation. A small amount of the clay was first dispersed ultrasonically
in distilled water but was not size fractionated. The three acids used
were: HCl, H_2SO_4 and H_3PO_4. Approximately 10 ml of the kaolinite dis-
persion was mixed with 20 ml of each of the above acids in its concen-
trated form. The sulfuric and phosphoric acid-clay mixtures were
allowed to stand for 24 hours; the hydrochloric acid for 72 hours. Each of
the mixtures was then washed three times in a centrifuge, redispersed and
sedimented on each of two glass microscope slides to air-dry. An un-
treated kaolinite dispersion was similarly prepared. One of the oriented
aggregates was used for x-ray diffraction analysis and the other for
electron microscopy.

The self-shadowed carbon replica technique was employed for the
electronoscopic studies. Carbon was evaporated *in vacuo* at an angle of
60° to the oriented aggregate slides. The kaolinite was then dissolved
from beneath the carbon using HF. The resulting replicas were washed in
distilled water and picked up on copper 200 mesh electron microscope
grids. Electron photomicrographs were taken of selected fields.

EXPERIMENTAL RESULTS

Examination of the x-ray diffractometer traces of each of the samples
shows that in no case is there an indication of a reaction product. All of