

## ANOMALOUS GYPSUM IN CLAYS AND SHALES\*

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Most clay mineral investigators are aware that gypsum may be formed artificially by the treatment of samples containing pyrite and calcite—such as common bituminous shales—with oxidizing agents such as hydrogen peroxide. It is shown here that anomalous gypsum may be produced by less obvious laboratory procedures and that caution is necessary in reporting this mineral in clay and shale analyses.

This problem first came to our attention during a mineralogical (and rehydration) study of ceramic clays and shales from near New Glasgow, Nova Scotia (Dean, 1975). Weak X-ray reflections for gypsum from the minus 5-micron size fraction of one of these samples (New Glasgow "B") were very strongly enhanced by overnight hydration at 100% r.h. following 1/2 hour heat treatments at 450 or 580°C. The high humidity conditions were obtained within a closed container partially filled with warm distilled water. Cooling to room temperature resulted in condensation throughout the interior of the vessel, including the mount surface. Following transfer of the mount to the X-ray diffractometer, a flow of nitrogen gas and water vapor (100% r.h.) was maintained around the sample (Dean, 1975, p. 13) after visible excess moisture had been allowed to evaporate.

It was initially suspected that migration of gypsum to the mount surface was responsible for the observed intensity increase. However, further experiments with artificial mixtures of clays and ground gypsum yielded ambiguous results, and the validity of this supposition became doubtful. An alternative possibility seemed more likely—the synthesis of artificial gypsum by reactions among the constituents of the New Glasgow sample, which included calcite and minor amounts of pyrite.

### PYRITE-CARBONATE REACTIONS

To investigate this possibility, a large crystal of pyrite was crushed and mixed with both powdered calcite and dolomite in the approximate proportions by weight of 60% pyrite and 40% carbonate. The mixtures were hand-ground in alcohol, portions were dried as thin films on borosilicate glass slides and stored in a desiccator. The untreated dry mixture of pyrite and calcite yielded the diffractogram illustrated in Fig. 1(a). The irradiated mount was then heated in air for 1/2 hour at 450°C and subsequently allowed to stand overnight at 100% relative humidity. The Fig. 1(b) diffractogram indicates the formation of a substantial amount of artificial gypsum by this procedure.

These results show that pyrite, heated beyond its decomposition temperature in air, will react with calcite, leading to the formation of gypsum following subsequent hydration. This mechanism provides a likely explanation for the gypsum which was apparently formed on the New Glasgow "B" sample mount. Similar results were obtained from the pyrite-dolomite mixture.

To see whether heating is necessary for gypsum formation, unheated mixtures of pyrite and carbonate minerals were held at 100% r.h. for varying periods of time. Overnight high humidity treatment resulted in the formation of a minor amount of gypsum within pyrite-dolomite, but none could be detected on the pyrite-calcite mount. How-

ever, after 6 days in moisture-saturated air, a minor amount of gypsum was also found in the pyrite-calcite mixture. In both cases the amount of gypsum produced in this manner was far less than had been observed on the mounts which had been heated to 450°C, suggesting that gypsum formation within the unheated mixtures may have been confined to pyrite-carbonate grain contacts. Finally, it was ascertained that the formation of gypsum within pyrite-calcite mixtures could be initiated without either heating or prolonged moisture-saturation. This was established when traces of gypsum were detected in a pyrite-calcite mount which had stood uncovered in the laboratory for 6 weeks.

### PYRITE-CLAY REACTIONS

Conditions under which clay (bentonite) may react with pyrite to form gypsum were investigated in the following experiments. The minus 5-micron size fraction was separated from Morrin bentonite (Ross, 1964, p. 40) by centrifugation. The clay was found to consist largely of smectite. No traces of pyrite or carbonate minerals were detected and examination by X-ray powder diffraction following

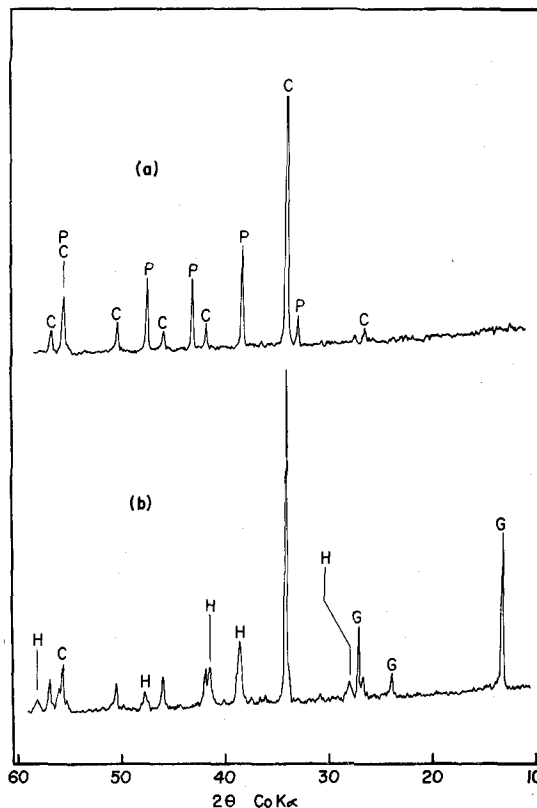


Fig. 1. X-ray diffractograms of hand-ground pyrite-calcite mixture spread thinly on glass substrate: (a) Dry, unheated (b) Heated 1/2 hour in air at 450°C, subsequently moisture-saturated overnight and scanned at 100% r.h. P—pyrite, C—calcite, H—synthetic hematite, G—synthetic gypsum.

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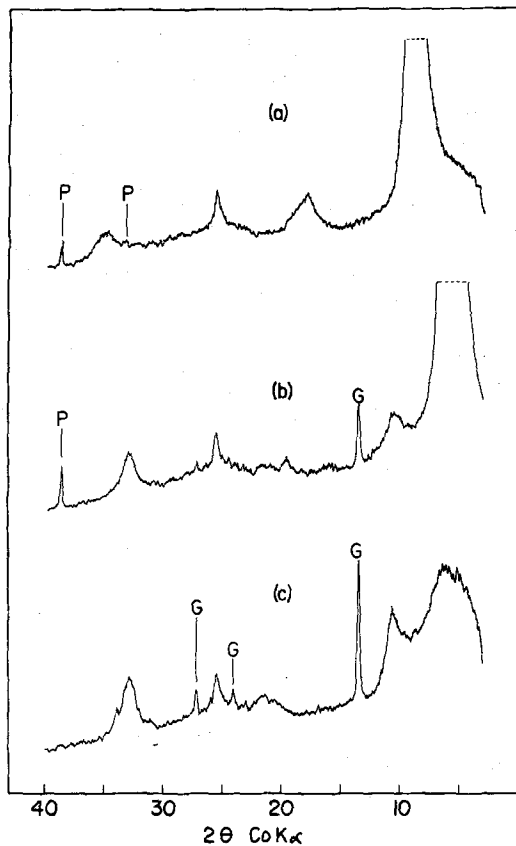


Fig. 2. X-ray diffractograms of oriented mount of minus 5-micron fraction of Ca-saturated Morrin bentonite containing 8% pyrite: (a) Dry  $N_2$  atmosphere (b) Scanned at 100% r.h. following overnight moisture saturation (c) Heated 1/2 hour in air at  $450^\circ C$ , subsequently moisture-saturated overnight and scanned at 100% r.h. P—pyrite, G—synthetic gypsum.

equilibration for several days at 100% r.h. showed no sign of gypsum.

Separate portions of the Morrin clay were saturated with  $Ca^{2+}$  and  $Mg^{2+}$  by means of 1M solutions of the appropriate salts. Excess salt was removed by four washings with demineralized distilled water and the clay recovered at each stage by high speed centrifugation. The treated Morrin clays were dried at about  $50^\circ C$ . Oriented mounts were prepared from mixtures consisting of 92% clay and 8% freshly ground pyrite.

Figure 2(a) is a diffractogram of Ca-saturated Morrin clay and pyrite from a mount which had been stored in a desiccator and scanned in a dry nitrogen atmosphere. Overnight 100% r.h. treatment of the same mount resulted in the formation of considerable gypsum (Fig. 2b) and heating at  $450^\circ C$  followed by rehydration caused a further increase in gypsum (Fig. 2c). The evidence indicates that gypsum was readily formed by reactions between ground pyrite and Ca-saturated bentonite at room temperature under moist conditions. As would be expected, no gypsum formation was observed in the mixture of pyrite and Mg-saturated Morrin clay following identical treatment.

Studies of possible reversal of these reactions suggested that, with heating, naturally occurring gypsum might be eliminated from clays saturated with cations other than  $Ca^{2+}$ . This was observed in a mount of the Mg-saturated

Morrin clay, to which 5% ground gypsum had been added. Heat treatment at  $450^\circ C$  followed by overnight rehydration resulted in a very sharp decrease in the observed gypsum reflections, and these disappeared completely following a subsequent heating cycle at  $500^\circ C$ . By contrast, a similar mixture of gypsum and Ca-clay showed little if any loss in gypsum peak intensities after identical treatment, and the New Glasgow "B" gypsum, repeatedly decomposed by heat treatments within the range  $450$ – $580^\circ C$ , was invariably fully reconstituted by overnight hydration. It would appear, however, that at room temperature, the reactions leading to the elimination of gypsum from Mg-clay either do not operate or are sufficiently slow to be of no practical importance within the laboratory. Four months after the first tests were made, a mount prepared from the previously-utilized distilled water suspension of Mg-clay and ground gypsum showed no evidence of gypsum removal.

#### DISCUSSION

In assessing the possibility that gypsum observed in a clay mineral mount may have been formed synthetically, a major factor to be considered must be the natural environment of the sample material. If water-saturation has occurred periodically by natural processes, as is the case with most clays, then it is unlikely that the mineralogy of the sample can be altered by wetting within the laboratory. On the other hand, the pyrite-carbonate reactions could conceivably occur in disaggregated shales or in clays from arid regions. It also appears unwise to saturate any pyrite-bearing clay or shale with calcium ions. The freshly-ground pyrite utilized in this investigation was, however, undoubtedly much more reactive than pyrite occurring naturally in clays or shales.

Synthetic gypsum formed in rehydration studies of clay minerals should be easily recognized and thus present few difficulties. However, the apparent high reactivity of gypsum with Mg-clay, pyrite with Ca-clay and pyrite with carbonate minerals during heat treatments above  $450^\circ C$  suggests that unforeseen cation-exchange effects likely will occur within samples containing these phases during rehydration (or dehydration) investigations.

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