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# ON THE SYNTHESIS OF GREIGITE

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Skinner *et al.*, (1964) have discovered a magnetic iron sulfide with the formula $Fe_3S_4$ and a spinel structure in a natural sedimentary occurrence, and named it greigite. Prior to the discovery, Yamaguchi and Katsurai (1960) have succeeded in the hydrothermal synthesis of a magnetic iron sulfide with a spinel-like structure. They have postulated, by analogy with linnaeite $Co_3S_4$, that the sulfide is cubic $Fe_3S_4$. Several attempts to synthesize a magnetic iron sulfide which is obviously greigite have been carried out: Lepp (1957), Piggott and Wilman (1958), and Berner (1964). However, no one has yet succeeded in obtaining greigite without accompanying contaminants.

In relation to the discovery of well-defined mineral greigite, the synthesis of pure $Fe_3S_4$ with a spinel structure seems to be of great interest. From a series of experiment, a procedure was found to obtain satisfactory greigite. The procedure was a modification of the method of Yamaguchi and Katsurai (1960). It was found that the quenching after autoclaving is necessary in order to obtain greigite free from contaminants. The structure of the autoclaving product was confirmed by means of electron diffraction and *x*-ray diffraction. Investigations of magnetic property and infrared absorption spectra were also carried out.

A black, non-magnetic iron sulfide was prepared by mixing 100 cc each of 0.15 M Mohr's salt and 0.2 M sodium sulfide. The mixture was shaken and 3 cc of the resulting suspension was taken out and it was transferred to a pyrex tube, 10 mm in diameter, 150 mm in length and 1 mm in thickness. The tube was then evacuated and sealed. It was left to stand 5 or 6 days. The precipitate settled completely. The contents of the tube consisted of two layers, black compact precipitate and clear upper liquid. The sealed tube was subjected to autoclaving by immersion in an oil bath at 190° C. for 1 hour. Quenching was then carried out by putting the sealed tube into water.

The result of electron diffraction study is listed in Table 1 in comparison with the *x*-ray data of mineral greigite. A diffraction pattern was taken with Hitachi HS-7 electron microscope having an accelerating voltage of 50 kV. We see that the diffraction pattern contains only the reflections allowed for the crystal with a spinel structure. No other reflections and no anomalous diffraction intensities are observed, indicating that the synthetic greigite prepared here with contains no contaminant.

Table 1. Electron Diffraction Data for Synthetic Greigite in Comparison with *X*-Ray Data for Mineral Greigite
(Skinner, Erd and Grimaldi, 1964)

Calculated d for a cubic cell with $a=9.90$ Å. Intensities were estimated visually. Electron beam with the wave length 0.0548 Å was used.

| hkl | Synthetic Greigite | | | Natural Greigite | |
|---|---|---|---|---|---|
| | $d_{calc}$ | $d_{obs}$ | I | $d_{obs}$ | I |
| 111 | 5.72 | 5.70 | 3 | 5.720 | 8 |
| 220 | 3.50 | 3.50 | 5 | 3.498 | 32 |
| 311 | 2.98 | 2.99 | 10 | 2.980 | 100 |
| 222 | 2.86 | 2.97 | 2 | 2.855 | 4 |
| 400 | 2.48 | 2.48 | 8 | 2.470 | 55 |
| 331 | 2.27 | — | | 2.260 | 1 |
| 422 | 2.02 | 1.02 | 1 | 2.017 | 9 |
| 511,333 | 1.91 | 1.90 | 4 | 1.901 | 29 |
| 440 | 1.75 | 1.75 | 9 | 1.746 | 77 |
| 531 | 1.67 | 1.67 | <1 | 1.671 | 1 |
| 620 | 1.57 | 1.57 | <1 | 1.5625 | 4 |
| 533 | 1.51 | 1.51 | 1 | 1.5058 | 10 |
| 622 | 1.49 | — | | 1.4883 | 2 |
| 444 | 1.43 | 1.43 | 3 | 1.4253 | 9 |
| 711,551 | 1.39 | — | | 1.3826 | 1 |
| 642 | 1.32 | 1.33 | <1 | 1.3204 | 4 |
| 731,553 | 1.29 | 1.29 | 3 | 1.2859 | 13 |
| 800 | 1.238 | 1.240 | <1 | 1.2349 | 9 |
| 733 | 1.210 | — | | 1.2097 | <1 |
| 644 | 1.201 | — | | 1.1975 | <1 |
| 822,660 | 1.167 | — | | 1.1640 | <1 |
| 751,555 | 1.143 | 1.145 | 2 | 1,1401 | 2 |
| 840 | 1.107 | 1.105 | 4 | 1.1051 | 16 |
| 911,753 | 1.087 | — | | 1.0844 | <1 |
| 664 | 1.055 | — | | 1.0544 | 2 |
| 931 | 1.038 | 1.040 | <1 | 1.0351 | 7 |
| 844 | 1.010 | 1.011 | 3 | 1.0080 | 31 |

For the sake of confirmation, the crystal structure of the product was examined also by means of *x*-ray diffraction. For this purpose a diffractometer with the scanning speed of goniometer, 0.5°, $2\theta$ per minute and unfiltered FeK radiation was used. The result coincided with that of the electron diffraction. The sample was prepared as follows. The autoclaved precipitate was separated from liquid phase by filtration, washed several times with water and then dried rapidly in an evacuated chamber.

Magnetization and coercivity were measured by means of a magnetic balance. The results: $M_s = 24$ gauss·cm$^3$/g at room temperature. Saturation induction = 1200 gauss. The calculation was carried out using the value of $M_s$ mentioned above and assuming that the density of the product is 4.1 g/cm$^3$ as taken from the $x$-ray data. No noticeable coercivity was found at room temperature, indicating that the product is magnetically soft.

Infrared absorption spectra of the product were studied by Perkin-Elmer 521 type spectrometer in the range of wave length 2.5–40$\mu$. Continuous absorption and no characteristic absorption peak were observed throughout the range. The result is similar to that of pyrrhotite, but differs from that of pyrite and marcasite (pyrite and marcasite have several characteristic absorption peaks in the range 23–32$\mu$).

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# PREPARATION OF PURE ARAGONITE AND ITS TRANSFORMATION TO CALCITE

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## INTRODUCTION

By varying the conditions of preparation different polymorphic modifications of calcium carbonate have been obtained in comparatively pure state. The methods suggested for the preparation of aragonite, the orthorhombic modification of calcium carbonate make use of

(1) the precipitation of calcium carbonate at or above 60° C., from a solution of calcium salt by alkali carbonate (Faivre, 1946; de Keyser, 1950; Wray and Daniels, 1957),

(2) passage of carbon dioxide through calcium hydroxide solution (Ievins *et al.*, 1955) or (3) removal of carbon dioxide from a solution of calcium bicarbonate (Kitano *et al.*, 1962).