THE AMERICAN MINERALOGIST, VOL. 49, NOVEMBER-DECEMBER, 1964

MINERALOGICAL NOTES

ELECTRON PROBE MICROANALYSIS OF SOME CARBONATE, SULFATE AND PHOSPHATE MINERALS IN THE ORGUEIL METEORITE

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INTRODUCTION

Electron probe microanalysis of petrographic thin sections of the Orgueil carbonaceous meteorite has led to the determination of the chemical composition of some mineral constituents. The presence of breunnerite, an iron-magnesium carbonate mineral $(Mg_{0.8}Fe_{0.2})CO_3$, has been confirmed in Orgueil. Gypsum has been tentatively identified in Orgueil; this is in agreement with published results on the presence of this mineral in another carbonaceous meteorite (DuFresne and Anders, 1962). A phosphate mineral, possibly merrillite, $Na_2Ca_3(PO_4)_2O$, which is known to occur in some stony meteorites (Tschermak, 1883; Shannon and Larsen, 1925), has also been identified in Orgueil.

The electron probe microanalyzer, first developed by Castaing and Guinier (1949), permits a nondestructive quantitative chemical analysis by means of *x*-ray emission spectra to be carried out on a volume of only a few cubic micra on the surface of a sample. In this instrument the surface of the sample is bombarded with a finely focused beam of high energy electrons and the resultant characteristic radiation is analyzed for wavelength and intensity by dispersive detection systems. The instruments used in this study were two Applied Research Laboratory electron microprobe *x*-ray analyzers, located at the University of California in La Jolla and at Hasler Research Center in Goleta. These instruments have a mimimum electron probe diameter of less than a micron, giving rise to a linear resolution of approximately two micra for *x*-ray data (Davidson *et al.*, 1962). Quantitative measurements can be made on as little as 10^{-13}g amounts of the elementary components with a relative error of approximately ± 2 per cent. Electron probe microanalysis has been repeatedly used in recent mineralogical and metallurgical studies and has been found to be well suited for the analysis of petrographic thin sections from which the cover slips have been removed and on which thin conductive coatings have been deposited (carbon was used in this study). Microprobe analysis of an optically examined, petrographic thin section ensures that the particles analyzed are indigenous to the meteorite.

The Orgueil carbonaceous meteorite was observed to fall in southern France in 1864. Under its thin "burnt" crust, the meteorite consists of hydrous, iron-magnesium, layer-lattice silicates, magnetite, limonite, magnesium sulfate, elemental sulfur and bituminous organic matter in addition to the minerals discussed in this report. (It should be pointed out, however, that not all of the constituent minerals have yet been analyzed.) The Orgueil meteorite contains approximately 20 per cent water; Boato (1953) found that most of this water has a deuterium content which is significantly different from that of terrestrial waters. The minerals are arranged in a brecciated texture of angular aggregates traversed by what appear to be magnesium sulfate veins. The results of the various mineralogical studies have been summarized by Mason (1962), Anders (1963), and Nagy (1963) *et al.*

Microanalysis of Petrographic Thin Sections

The carbonate mineral analyses were made on selected areas of large euhedral crystals 2–3 mm long and arranged in an aggregate 7 mm in diameter. Figure 1a shows a petrographic thin section in which these crystals are seen to be embedded in the fine grained, micaceous matrix. The crystals show well developed rhombohedral cleavage pattern (Figure 1b) and under polarized light 4th or higher order interference colors. A drop of cold 6N HCl placed on their surfaces from a micropipette caused the slow development of a few bubbles in the solution which became increasingly greenish-yellow in color. Portions of these crystals have been analyzed with the electron probe microanalyzer. First, the grains were analyzed qualitatively for Ca, Mg, Fe, Mn, Si, S, Cl, Ni, Zn, Al, Sr, Rb, P and K. Following this, semi-quantitative analyses were performed by scanning selected 300×300 μ-sized and smaller areas with the electron beam and displaying the backscattered electron as well as the Fe, Mg, Ca, Mn, Ni, Si, and S $K\alpha$ x-ray images on a cathode ray tube. Some of the results are shown in Figs. 1c–g. Quantitative analyses were made by performing point integrations for Fe, Mg, Mn, Ca and Si at 10 μ intervals on long traverses crossing the tips of the carbonate grains and extending into the micaceous matrix. These results are presented in Table 1. Semi-quantitative analyses for oxygen and carbon were also made with newly developed soft x-ray, dispersive detection systems, which utilize analyzing crystals of large d spacings and thin window detectors. Both carbon and oxygen were found to be present in these grains, verifying their carbonate character. Quantitative determinations could not be accomplished, however, due to the lack of the necessary mass absorption data for the long wavelengths. Control experiments were also carried out which show that the conductive carbon coating

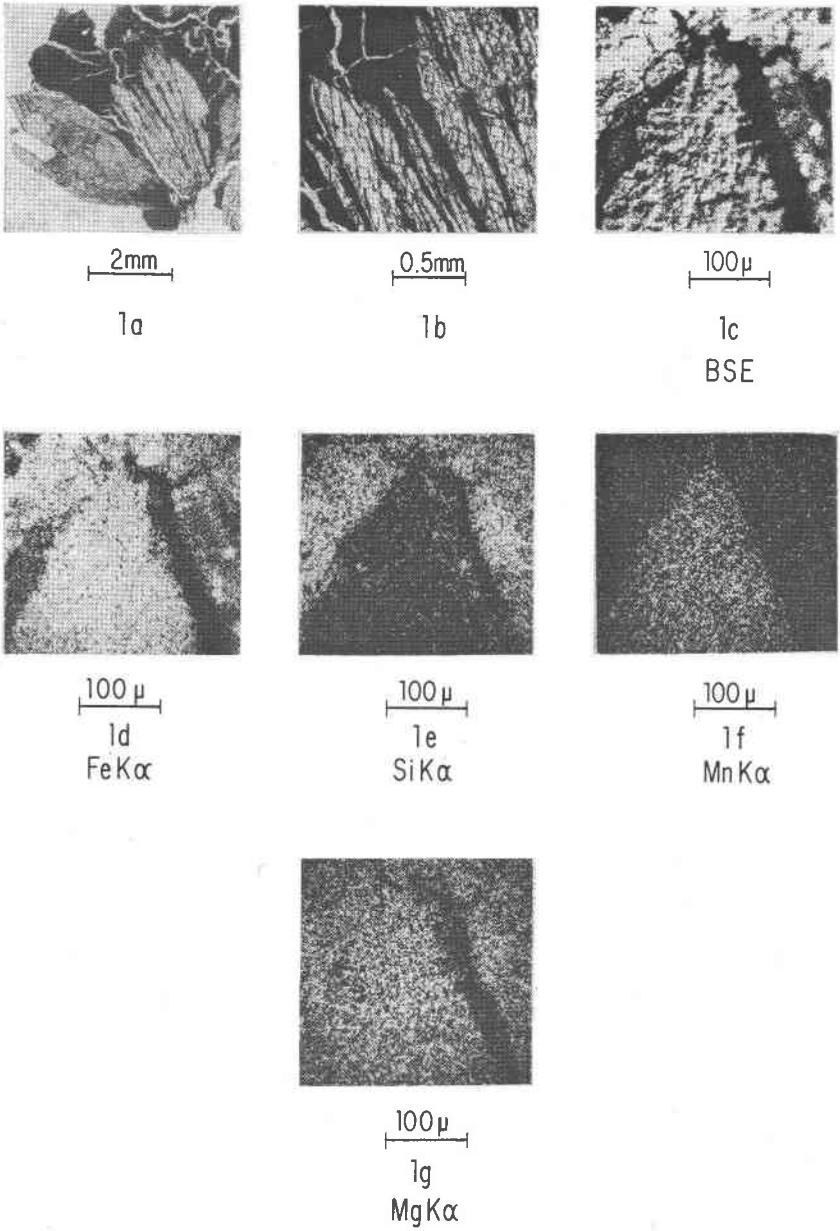

FIG. 1. Breunnerite, $(Mg_{0.8}Fe_{0.2})CO_3$ in a petrographic thin section of the Orgueil meteorite. 1a–b are photomicrographs; 1c–g show the backscattered electron (BSE) and x-ray images. Light areas on the x-ray images indicate abundances of the corresponding elementary components.

TABLE 1. CHEMICAL COMPOSITIONS OF BREUNNERITE, GYPSUM AND A CALCIUM PHOSPHATE MINERAL AS DERIVED FROM CHARACTERISTIC x-RADIATION INTENSITY RATIOS[1]

Breunnerite				Gypsum			Calcium Phosphate Mineral		
Breunnerite theoretical[2]		Orgueil carbonates: Grain Edge	Orgueil carbonates: Grain Interior	Gypsum theoretical[3]		Orgueil mineral[5]	Merrillite theoretical[4]		Orgueil mineral[6]
Mg	21.5	16.5	20.4	Ca	23.3	19.0	Ca	32.3	27.4
Fe	12.3	14.0	12.0	S	18.6	15.5	P	16.6	14.0
Ca	—	0.4	0.4	Fe	—	3.1	Fe	—	2.3
Si	—	0.4	0.4	O	55.8	present	Si	—	4.0
Mn	—	2.0	2.0						
C	13.3	present	present						
O	53.0	present	present						
				Ca/S	1.25	1.23	Ca/P	1.95	1.96

[1] Values are given in weight per cent and have been corrected for detector dead time, background and mass absorption. Well analyzed minerals were used as standards.
[2] $(Mg_{0.8}Fe_{0.2})CO_3$.
[3] $CaSO_4 \cdot 2H_2O$.
[4] $Na_2Ca_3(PO_4)_2O$. Derived from an insufficient analysis in the literature.
[5] A qualitative spectrum of the mineral also showed the presence of some Si, Al and Mg.
[6] A qualitative spectrum of the mineral also showed the presence of minor amounts of Ti, Mg and S.

placed on the specimen does not offer a significant source of error in the analysis of carbon. This is because the depth of penetration of the electron beam into the sample is orders of magnitude greater than the thickness of the coating film. The electron probe analyses show that the interiors of the crystals contain approximately 12 per cent Fe, 12–20 per cent Mg, 2 per cent Mn, and about one half per cent Ca by weight with small and varying quantities of Si. The rims of the crystals contain approximately 2 to 3 per cent more Fe than the interiors (Fig. 3). These chemical analyses confirm and extend the earlier mineralogical studies of Pisani (1864) and Mason (1962) which reported the presence of breunnerite in the Orgueil meteorite. On the other hand, DuFresne and Anders (1962) named dolomite as a carbonate mineral from Orgueil; their report could not yet be confirmed by the microprobe analysis.

The calcium sulfate and calcium phosphate minerals were found in Orgueil as the result of displaying the backscattered electron and the Ca, Mg, Si, Al, S and P $K\alpha$ x-ray images of parts of the thin sections on a cathode ray tube (Figs. 2a–f). Following these semi-quantitative surveys, complete qualitative spectra as well as quantitative analyses of the major components were obtained on the grains. The mineral containing Ca and S was quantitatively analyzed for Ca, S and Fe at various points in the particle and semi-quantitatively analyzed for oxygen. These grains were identified as gypsum by the absolute mass concentrations of Ca and S, which do not indicate anhydrite, and by the presence of O. The mineral containing Ca and P was analyzed for Ca, Si, Fe, and P at 1 μ steps in a one dimensional traverse. This mineral could not be positively identified because of its extreme rarity in the section. The measured mass concentrations of Ca and P, however, and their ratio suggest that the mineral is possibly merrillite. Apatite which was used as a reference standard is not indicated. The results of these investigations are presented in Table 1 and show reasonably good agreement between the analytical data and the theoretical values, particularly if the differences

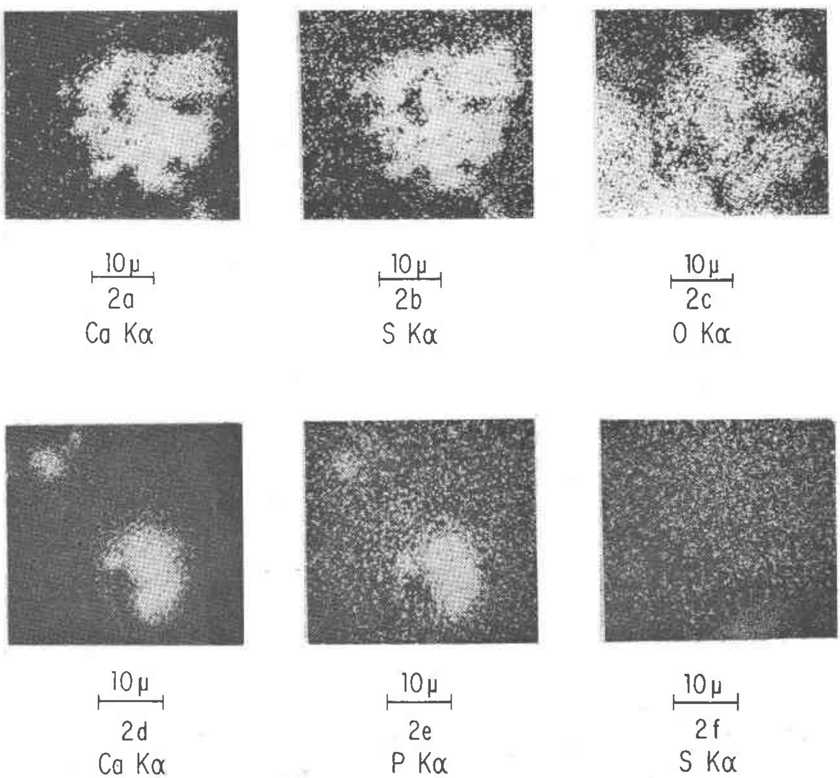

FIG. 2. X-ray images of gypsum, 2a–c, and a calcium phosphate mineral, 2d–f, in a petrographic thin section of the Orgueil meteorite.

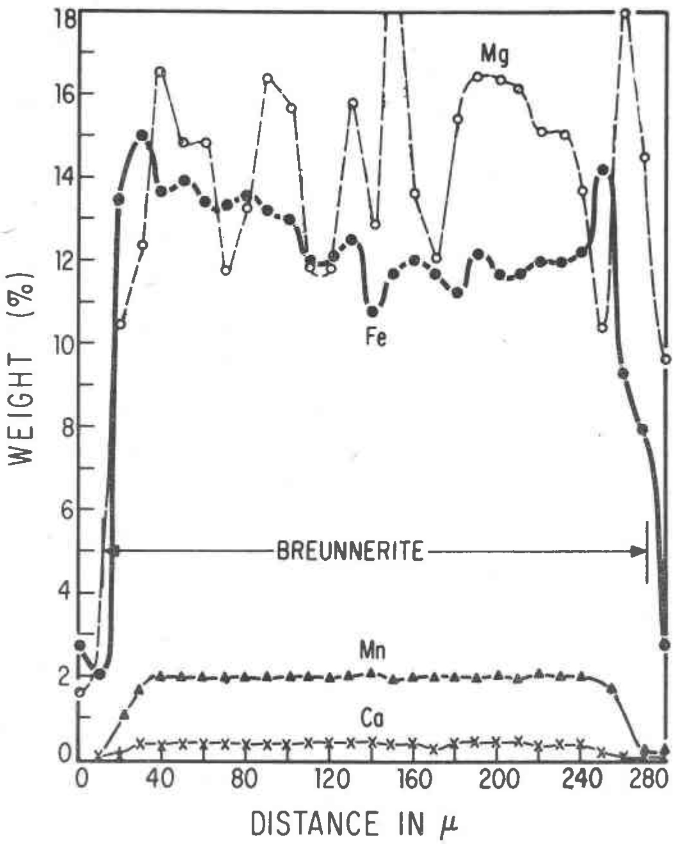

FIG. 3. The results of quantitative analyses for Fe, Mg, Mn and Ca across a carbonate grain.

can be accounted for by foreign mineral inclusions or by scattered x-radiation from underlying and surrounding mineral grains. Because the careful optical examination of the gypsum and calcium phosphate particles was prevented by thickness of the corresponding parts of the thin sections, the positive identification of these two minerals in the Orgueil meteorite must await future confirmation. One must also consider the possibility that gypsum was formed from anhydrite through hydration in the earth's atmosphere. However, regardless of the origin of the water content of these grains, this mineral as well as breunnerite and calcium phosphate are indigenous to the Orgueil meteorite.

ACKNOWLEDGMENTS

The authors would like to thank Prof. Harold C. Urey and Dr. Kurt Fredriksson of the University of California for their comments and for reading the manuscript. Prof. Gustaf Arrhenius of the University of California provided the use of one of the electron microprobe x-ray analyzers. Part of this investigation was supported by the National Aeronautics and Space Administration, Grant NsG-541.

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THE AMERICAN MINERALOGIST, VOL. 49, NOVEMBER–DECEMBER, 1964

CENOSITE FROM PORTHILL, IDAHO[1]

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Cenosite, a hydrous calcium yttrium carbonate-silicate mineral, has been discovered in a thorium vein 4 miles east-southeast of Porthill, Idaho. This mineral has been reported from only a few localities in the world, and the Porthill occurrence is the second known in the United States. Because cenosite is one of a small group of minerals in which yttrium is a major constituent, its occurrence is both of scientific and economic interest. Furthermore, as cenosite at Porthill closely resembles quartz, it may be overlooked in other thorium veins.

Cenosite, originally called kainosite, was first described by Norden-

[1] Publication authorized by the Director, U. S. Geological Survey.