tions will reach the southern limit of the lobster's range in the vicinity of Cape Hatteras during the middle 1970's.

Cyclic and geographic trends in lobster abundance and demonstrated fluctuations in other commercially important populations with climatic trends serve to identify probable maximum limits of inshore marine resource yield under natural conditions.

ROBERT L. DOW
Department of Sea and Shore Fisheries, Augusta, Maine 04330

References and Notes

1. W. Welch, *Monthly and Annual Means of Surface Seawater Temperature, Boothbay Harbor, Maine, 1905 through 1966* (U.S. Bureau of Commercial Fisheries, Boothbay Harbor, Maine, 1967).
2. L. M. Lauzier, *Special Publication No. 6* (International Commission for the Northwest Atlantic Fisheries Environmental Symposium, Rome, 1964).
3. H. C. Willett and J. T. Prohaska, *Final Scientific Report, NSF Grant 14077* (Cambridge, Mass., 1 Oct. 1963).
4. *Monthly Review of Canadian Fisheries Statistics, 1964 to 1968* (Dominion Bureau of Statistics, Ottawa), vols. 1 to 21.
5. *Fishery Statistics of the United States, 1921 to 1967* (U.S. Bureau of Commercial Fisheries, Dept. of Interior, Washington, D.C.).
6. R. L. Dow, *Commer. Fish. Rev.* **23** (9), 1 (Sept. 1961).
7. I thank Hurd Willett of the Dept. of Meteorology, M.I.T., for advice and comments on climatic trends; D. G. Wilder, Fisheries Research Board of Canada, St. Andrews, N.B., for catch data from the Canadian Provinces; and Charles Lyles of the U.S. Fish and Wildlife Service for differentiated data on U.S. lobster landings.

13 February 1969

■

Basic Ferric Phosphates: A Crystallochemical Principle

Abstract. *A polyatomic complex of iron-oxygen octahedral face-sharing triplets corner-linked to four other octahedra occurs in the atomic arrangements of the basic iron phosphates dufrenite, rockbridgeite, beraunite, and laubmannite. This complex is further knit together by the phosphate tetrahedra. The family of basic ferric phosphates arises from the variety of ways in which the complexes can be linked along a third "variable" crystallographic axis.*

The basic ferric phosphates, perplexing substances in the mineral kingdom, occur as replacements of organic products, such as wood and bones; as nodules in marls and soils; as secondary minerals in "limonite" beds and deposits of iron ore; and as hydrothermally reworked products of primary lithium-iron-manganese phosphates in pegmatites. Conflict and contradiction have frequently appeared in the nomenclature and data reported for these phosphates. Frondel (*1*) presented a historical survey as well as information on the physical and chemical characters of these minerals. Fanfani and Zanazzi (*2*) reported on the atomic arrangement of one member, beraunite.

The basic ferric phosphates include the species dufrenite [$Fe_3(OH)_3(H_2O)(PO_4)_2$], rockbridgeite [$Fe_5(OH)_4(O)(PO_4)_3$], laubmannite [$Fe_9(OH)_{15}(PO_4)_4$], beraunite [$Fe_6(OH)_6(H_2O)_3(PO_4)_4 \cdot 2H_2O$], and cacoxenite [$Fe_4(OH)_3(PO_4)_3 \cdot 12H_2O$] (*3*). With the exception of cacoxenite, all occur as fibrous greenish-black to brown nodules, concretions, and mammillary aggregates. Their chemical analyses often show minor and irrational amounts of ferrous iron. Single crystals of suitable dimension for crystallographic study are rare since the fibers usually consist of minute individuals in twisted bundles. Because the compositions and densities of these minerals are similar, physical, optical, or chemical characteristics alone do not suffice for certain identification. The list of species may be more extensive than the aforementioned, since Frondel documented two possibly new species and one new species is being studied in my laboratory.

Single crystals for all these species were isolated by carefully splitting fibers in acetone with a dissecting needle until an optically uniform individual could be found. Since the individuals were usually about 30 to 50 μ in mean diameter, long-exposure rotation and Weissenberg photographs were required to obtain the data reported in Table 1. Three-dimensional analysis of the crystal structure was undertaken on dufrenite and rockbridgeite (*4*). Intensity data were collected on a manual counter-diffractometer that operates on the basis of Weissenberg geometry with Zr-filtered Mo radiation for dufrenite, and on Weissenberg films with the same radiation for rockbridgeite. Atomic arrangements for these two species were determined by Patterson syntheses and vector set analysis of these data. Early refinement of atomic coordinates offers $R_{hkl} = 0.18$ (based on 1400 independent observed structure amplitudes) and 0.19 (340 independent observed structure amplitudes) for dufrenite and rockbridgeite, respectively. Their octahedral frameworks are illustrated in Fig. 1, A and B.

A remarkable polyatomic complex common to the atomic arrangements of beraunite, dufrenite, and rockbridgeite (Fig. 2) consists of an iron-oxygen

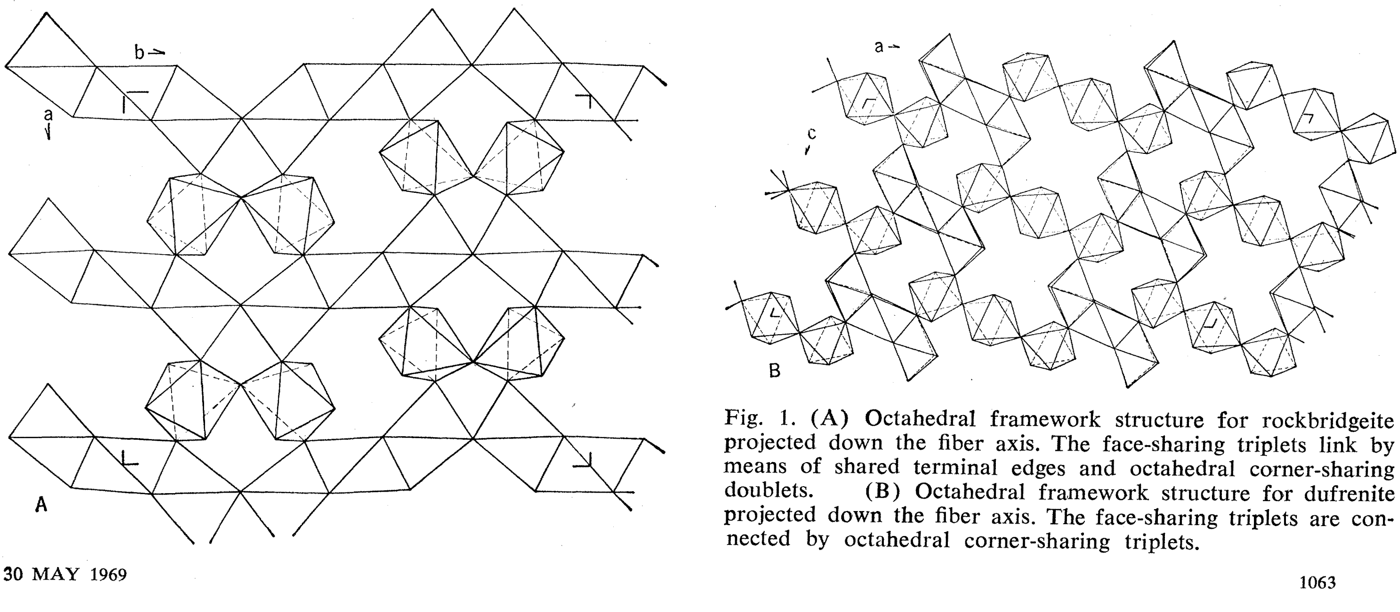

Fig. 1. (A) Octahedral framework structure for rockbridgeite projected down the fiber axis. The face-sharing triplets link by means of shared terminal edges and octahedral corner-sharing doublets. (B) Octahedral framework structure for dufrenite projected down the fiber axis. The face-sharing triplets are connected by octahedral corner-sharing triplets.

Table 1. Crystal data for the basic ferric phosphates (*5*).

Basic ferric phosphate	*a* (Å)	*b* (Å)	*c* (Å)	*β*	Space group	Specific gravity	No. of formula units per cell (Z)
Dufrenite	25.59	5.14	13.78	111°24′	*C*2/*c*	3.34	8
Rockbridgeite	13.85	16.82	5.18		*Bbmm*	3.49	4
Laubmannite	13.91	30.60	5.15		*Pbma*	3.33	4
Beraunite	20.646	5.129	19.213	93°37′	*C*2/*c*	3.08	4
Cacoxenite	27.66		10.65		*P*6/*mmm*(?)	2.26	12

octahedral face-sharing triplet, linked by corner-sharing to four other octahedra. The cluster of seven octahedra is knit together by phosphate tetrahedra. In fact, all the phosphate tetrahedra in these minerals are linked to the polyatomic complex.

This complex appears to occur in the other basic ferric phosphates as well. Inspection of the cell data (Table 1) reveals that all members have a common fiber axis of ~ 5.1 Å as well as another crystal axis of ~ 13.8 Å. Preliminary Patterson synthesis on the *hk*0 data of laubmannite reveals the same polyatomic complex in projection as that found for the three other species studied.

The family of basic ferric phosphates arises from the variety of ways in which the complex can be linked along the third "variable" crystallographic axis. The linking units are corner-sharing octahedral chain segments, extending along the directions of the four arrows shown in Fig. 2. In beraunite, the chain segments are one and two octahedra in length; in rockbridgeite, two octahedra; in dufrenite, three octahedra; and, tentatively, in laubmannite, four octahedra.

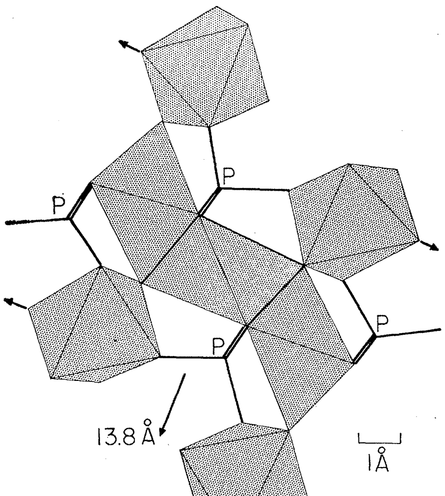

Fig. 2. The polyatomic complex common to the crystal structure of the basic ferric phosphates projected down the fiber axis. The seven octahedra are stippled; shared faces in the octahedral triplet are drawn bold. The phosphate tetrahedra are centered on phosphorus and the P-O distances are drawn bold. The direction of the ~ 13.8-Å cell repeat is designated; the directions of the octahedral corner-sharing chain segments are shown by four short arrows. The locations of the phosphorus atoms in Fig. 1, A and B, can be found by superimposing Fig. 2 upon them.

Once these data have been refined so that accurate interatomic distances can be obtained, the oxidation states of the iron atoms over the independent sites can be determined. It appears likely that the deep greenish-black color and pronounced pleochroism of these minerals arise from mixed valences in the face-sharing triplet, and this cluster may also result in peculiar magnetic and electric properties for these substances. Since their crystal chemistry can be placed on an absolute basis, perhaps even a direct link can be established between their paragenesis and their crystallochemical interrelations.

PAUL B. MOORE
Department of Geophysical Sciences,
University of Chicago,
Chicago, Illinois 60637

References and Notes

1. C. Frondel, *Amer. Mineral.* **34**, 513 (1949).
2. L. Fanfani and P. F. Zanazzi, *Acta Crystallogr.* **22**, 173 (1967).
3. Since the valence states of the iron are not known, compositions are quoted as the ferric end-members.
4. C. R. Stern assisted in the solution of the dufrenite structure. Specimens were donated by A. Kidwell and J. K. Nelson. Computation expenses were provided by the Advanced Research Projects Agency contract awarded to the University of Chicago.
5. The crystal data for beraunite are from Fanfani and Zanazzi (*2*). The cacoxenite data were reported by D. J. Fisher, *Amer. Mineral.* **51**, 1811 (1966). Approximate specific gravities are from Frondel (*1*). I am responsible for the remaining data and the crystallochemical interpretations. In cacoxenite *a*/2 = 13.83 Å and *c*/2 = 5.32 Å. In beraunite, one-half the obtuse diagonal for *a* and *c* = 13.65 Å, in agreement with the orientation of the polyatomic complex in that structure.

6 January 1969

Cuprous Complexes Formed with Isonicotinic Hydrazide

Abstract. *Chelate formation by Cu(II) and isonicotinic acid hydrazide has been postulated as an important step in the antitubercular activity of isonicotinic hydrazide (Isoniazid). Reevaluation of the copper–isonicotinic hydrazide system gives evidence for the formation of a Cu(I) species rather than a Cu(II) species. The reduction of Cu(II) to Cu(I) and the subsequent formation of an isonicotinic hydrazide complex with the latter ion, therefore, may be the critical reaction responsible for the efficacy of isonicotinic hydrazide against* Mycobacterium tuberculosis.

Isonicotinic acid hydrazide serves as a fundamental drug in the treatment of tuberculosis. Cupric ion enhances the in vitro activity of isonicotinic acid hydrazide against *Mycobacterium tuberculosis* (*1*). Studies of the cupric ion–isonicotinic hydrazide system (*1–3*) have indicated that cupric ion forms 1:1 and 2:1 bidentate complexes (chelates) with isonicotinic hydrazide. These reports point to a copper–isonicotinic hydrazide complex as the curative agent (*3*) or as a critical agent in the antitubercular activity.

Early reports on the existence of cupric–isonicotinic hydrazide chelates (*1, 2*) were based on spectrophotometric measurements (according to Job's method) and an observed drop in *p*H on mixing the metal ion and hydrazide. An equilibrium constant for the overall formation of the 2:1 chelate was calculated from the data ($K = 1.7 \times 10^5$); the constant was dependent on *p*H, however. The same system was studied (*3, 4*) by a potentiometric *p*H method, and the stability constant for the charged 1:1 complex (1×10^8) was obtained. Three other metal ions also were studied, Ni(II), Co(II), and Zn(II); the stability constants for all three ions were several orders of magnitude smaller than that for copper.

All of the reports cited thus far indicate that isonicotinic hydrazide complexes by a chelation mechanism; that is, the anion is the complexing species and protons are released in the overall complexation reaction

$$2RH + M^{2+} \rightleftarrows R_2M + 2H^+ \qquad (1)$$

where RH is isonicotinic hydrazide and M represents metal ions such as Cu(II), Ni(II), Co(II), and Zn(II). However,