American Mineralogist, Volume 67, pages 1258–1264, 1982

Sedimentary pachnolite and fluorite from Tampa Bay, Florida

SAM B. UPCHURCH, RAYMOND A. REA AND RALPH G. STEVENSON, JR.[1]

Department of Geology
University of South Florida
Tampa, Florida 33620

Abstract

Deltaic deposits of pachnolite and fluorite occur in Tampa Bay, Florida, as a result of chemical precipitation from a fluoride-rich effluent from a phosphate chemical plant. The deposits are crusts up to 8 cm in thickness and cover a total of 5 ha. Crusts range from discontinuous masses to a solid shield with superimposed distributaries. These deposits are the only known deposits where pachnolite and fluorite can be shown to have formed in a marine sedimentary environment.

Introduction

This study describes two deposits of sedimentary fluorite (CaF_2) and pachnolite ($NaCaAlF_6 \cdot H_2O$) in Tampa Bay, Florida. These deposits, which occur as small deltaic lenses, were formed at outfalls from a chemical fertilizer plant. Both minerals are generally hydrothermal in origin (Palache *et al.*, 1957). The deposits described herein represent the only known occurrence of pachnolite in sedimentary rocks. Although fluorite is found in sedimentary rocks, precipitation in a modern marine environment has not been previously documented.

Location of study area

The study area consists of 2.3 km of shoreline on the eastern shore of Hillsborough Bay, the northeastern extension of Tampa Bay, Florida. The site is north of the mouth of the Alafia River, near the community of Gibsonton. The study area is contiguous to the only phosphate chemical plant on the bay.

Phosphate (fluorapatite) has been processed at the chemical plant for five decades. Sulfuric acid is used to dissolve the fluorapatite in anticipation of producing phosphoric acid and several chemical fertilizer formulations. The major waste product of the plant is a spent sulfuric acid–gypsum slurry, which is retained on the property under normal conditions. Periods of heavy rainfall overloaded the system, and the acid was released to the bay. This runoff is now contained on site.

During the processing, some of the liberated fluoride was discharged into the atmosphere, despite fluoride extraction for sale. After installation of stack scrubbers in 1963, fluorite was discharged into Tampa Bay. Routine fluoride discharge ceased in 1973, so the deltas accumulated in the ten year interval from 1963 to 1973. This study was conducted in 1975, after chronic release of fluorides had ceased.

Environment of deposition

The deltas are located in water less than 60 cm in depth and the upper surfaces are emergent at low tide. Average tide range is 0.7 m, with a spring tide of 1 m. The bay is a shallow, sandy platform less than 1 m deep in this area. Waves are normally insignificant. Owing to discharge of the Alafia River to the south and net circulation in the bay, there is a slow, southerly current nearshore in the vicinity of the deltas.

The effluent from the outfalls has been studied by Taft and Martin (1974) and Martin and Taft (1975), who compared the effluent before and after cessation of fluoride release. Table 1 summarizes the results of this comparison. No other analyses of the effluent are available. Clearly, the effluent was greatly enriched in fluorides prior to cessation. The largest fluoride concentration reported was 43 ppm. Martin and Taft (1975) concluded that the fluoride was present as a fluosilicic acid complex. They also recognized the presence of the fluorite in the deltas.

[1]Present address: Gulf Science & Technology Co., P.O. Box 26506, Houston, Texas 77036.

0003–004X/82/1112–1258$02.00

Table 1. Summary of physical and chemical conditions in Tampa Bay near the fluoride outfalls before and after abatement. Based on data from Martin and Taft (1975).

Variable	Before abatement, near outfall		After abatement, near outfall		Undiluted effluent
	Mean	Std. Dev.	Mean	Std. Dev.	
Date of sampling	August, 1963		July, 1974		July, 1974
Number of samples	15		5		1
Salinity (°/₀₀)	26.1	4.8	17.8	6.9	32.0
Temperature (°C)	31	2.8	30.2	1.9	32.0
pH	4.2	1.2	7.1	0.4	2.28
PO_4-P (ppm)	29.1	9.8	----	----	----
SiO_2-Si (ppm)	26.7	15.7	2.0	1.7	61.2
F^- (ppm)	27.2	9.1	2.2	0.4	338.
Average sample distance from discharge canal (m)	223	106	147	189	0

In addition to the fluoride discharge, acid runoff was a chronic problem. Taft and Martin's (1974) data indicate that average pH offshore, in bay water, was 4.2. At the time of our sampling, acid runoff continued to be a problem during periods of high rainfall, when the on-site storage capacity of the plant was exceeded. There were no macroinvertebrates near the outfalls, and offshore, in areas of minimal influence, barnacles and other organisms had calcium carbonate tests that were thin and crumbly.

Occurrences of sedimentary pachnolite and fluorite

There are no known instances where pachnolite has been attributed to authigenesis in sedimentary environments. Palache *et al.* (1957) attribute pachnolite to fluorine-rich pegmatites, where it may be an alteration product of thomsenolite or cryolite.

Fluorite has been found in sedimentary rocks throughout the world. Most of these deposits, however, are clearly of hydrothermal origin and constitute replacement or void-fillings in a host rock. Barnes (1979) and Richardson and Holland (1979) have summarized the geochemistry and origin of these types of deposits.

Fluorite also occurs in sedimentary rocks where there seems little doubt that it is authigenic. This fluorite occurs in two major facies. The most widespread fluorite deposits in sedimentary rocks are found in Tertiary and Quaternary lacustrine deposits in association with tuffs and zeolite formation (Studer, 1967; Sheppard and Gude, 1969; Surdam and Eugster, 1976; Tourtelot and Meier, 1976; Sheppard and Gude, 1980). Fluorite has also been found in older, marine, carbonate rocks where the fluorine is derived from nearby igneous rocks (Schneider, 1954; Kruger, 1962; Akaiwa and Aizawa, 1979).

Procedures

Description of the fluoride-rich sediments required collection of sediment cores and description of the strata within the cores, including the mineralogy and composition of the sediment.

Sample sites

Fifty-six cores (Fig. 1) were taken between October and December, 1975. These cores were taken using a "fan-shaped" sampling grid centered on each known, major source of fluorides—Ditches 2 and 4. In addition, cores were taken along two traverses that are approximately perpendicular to the coast line and offshore of the gypsum-disposal field. By means of two plane tables and use of a stadia rod at each core site, the sites were carefully located by triangulation and by range-and-bearing techniques. Aerial photographs taken in 1974 were used to develop base maps used in this study.

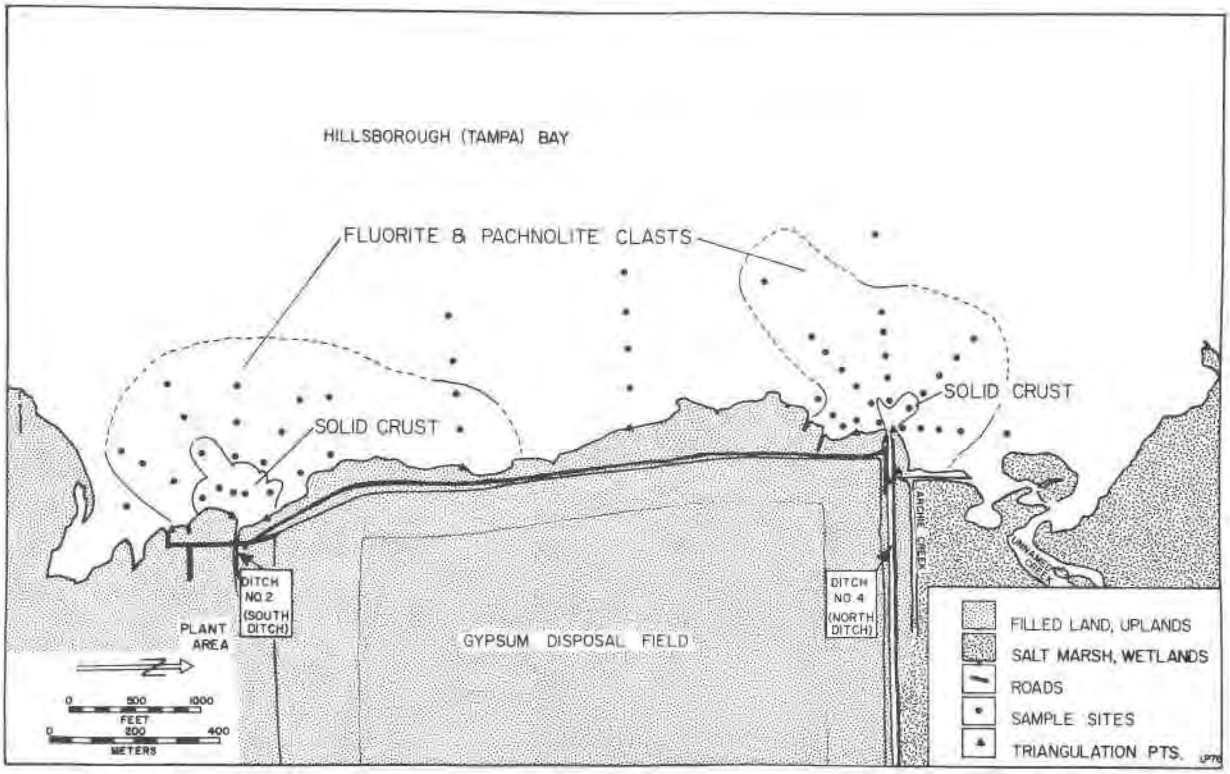

Fig. 1. Distribution of fluorite and pachnolite crusts and clasts.

Cores

Cores were taken by driving 1.5 m lengths of 5 cm OD, schedule 40, PVC pipe into the bottom sediments with a hammer. An expanding seal was then inserted into the pipe to insure a vacuum and reduce loss of material during removal. Core tubes were capped in the field and returned to the lab for cutting or extrusion.

Mineralogy

The mineral distribution was determined by petrographic analysis and by X-ray diffractometry. Samples were prepared for X-ray analysis by grinding bulk material to a maximum grain size of 0.125 mm and then packing in aluminum carriers for analysis. In many of the samples the content of sulfate or fluoride minerals is low and limited to the finer size fractions, in these cases unground sediment samples were sieved at 0.125 mm to concentrate the material of interest before X-ray analysis. All analyses were done on a Phillips-Norelco X-ray Diffractometer with a graphite monochrometer and Cu$K\alpha$ radiation.

Results

South ditch

Adjacent to the southern edge of the chemical plant is a fluorite and pachnolite delta. This environment receives discharges of thermally-enriched plant effluent, storm runoff, and in the past, fluoride-rich water (Taft and Martin, 1974; Martin and Taft, 1975). The latter discharge has produced a large (approximately 13 hectare (ha)) delta that includes a 4 ha crust (Figs. 1, 2A) of the minerals fluorite and pachnolite.

The intertidal area adjoining the south discharge ditch (Ditch No. 2) is part of an embayment limited by the gypsum disposal area and gypsiferous, fine sands to the north and by maritime vegetation bordering the Alafia River to the south. The embayment is exposed to minimum wave action, sediment influx from the Alafia River, and discharges from minor creeks and ditches draining the plant area. Three lithotopes are found in the embayment: a bare, fine quartz sand bottom, that is broadest to the north and south; a bare, solid fluorite/pachnolite delta immediately west of the ditch, and a fragmen-

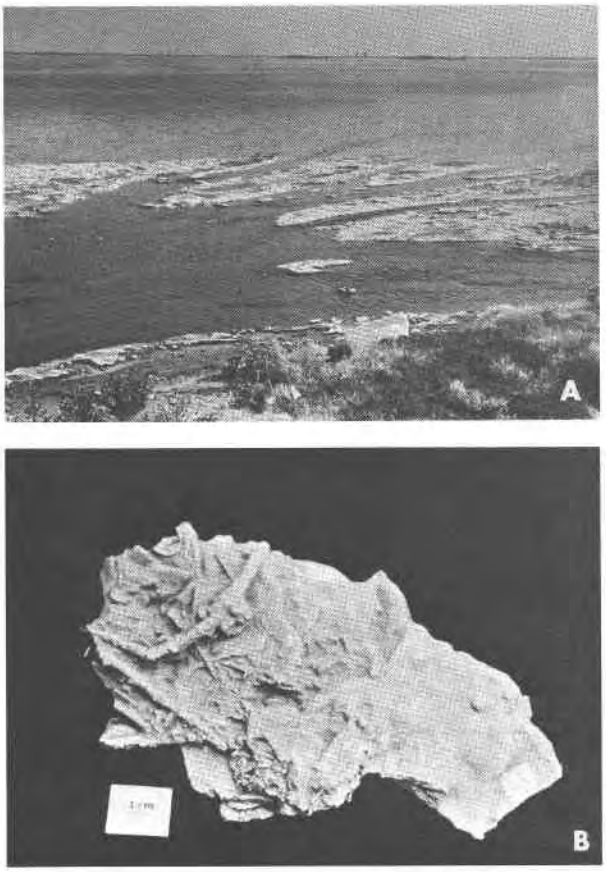

Fig. 2. (a) Delta of fluorite and pachnolite at the south ditch. Note distributary development and apparent thickness of crust. Surface is exposed during spring low tide. (b) Hand sample of fluorite and pachnolite. Note encrustation of fluorite/pachnolite clasts and plant fragments by fluorite and pachnolite.

tal fluorite/pachnolite/quartz sand covered by flocculent organic matter. The latter lithotope occurs as a thinning wedge extending from atop the delta to below mean low water. The delta is traversed by several distributaries which extend seaward to a depth of −0.6 m msl (Fig. 2A). The fluorite/pachnolite crust is solid near the mouth of the south ditch and ranges from a thin crust less than 1 cm to 8 cm in thickness.

In all of the environments studied, the contaminated sediments extend offshore for a maximum distance of 300 m. Since the slope of the bottom is less than one percent, this extends only a short distance below the intertidal zone.

North ditch

North of the gypsum-disposal field a second drainage ditch has created another fluoride-enriched area (Fig. 1). This ditch, Ditch No. 4, receives runoff from the gypsum disposal field and, even though efforts were made to buffer the acidity of the runoff, there was frequent discharge of acid waters to the Bay. Fluorides and gypsum have also been discharged here so that a smaller (1 ha) discontinuous crust of fluorite, pachnolite and gypsum has resulted. The total area affected by the north ditch is approximately 7 ha.

The intertidal zone adjoining the north ditch is a sandy shore exposed to moderate wave action, mid-estuarine salinites (22–30%), and high levels of organic nutrients. The affected areas range in elevation from +0.8 m msl to below mean low water (−1.0 m msl) and have an average slope of 0.4%. The horizontal extent of sedimentary fluorite and pachnolite crust below mean high water is 4 ha, and the crust is restricted to a shallow channel at the ditch mouth. A broad expanse of fine sand with admixed gypsum is the predominant lithotope of the area. Sediments are well to very well sorted, and are clean except for occasional pockets of petroleum products.

The topography of the intertidal zone at the north ditch shows the presence of the delta of fluorite and pachnolite. A prominent ridge that extends offshore from the mouth of the ditch consists of a discontinuous, thin veneer of fluorite and pachnolite, which undoubtedly adds to the resistance of the ridge to wave destruction. In addition, continuing discharge of particulates and water may tend to enhance the development of the ridge. On either side of the delta ridge, water depths increase 0.3 m or more.

Fluorite and pachnolite

Fluorite and pachnolite are the most obvious contaminants in the study area. The fluoride discharges have been briefly described by Taft and Martin (1974) and Martin and Taft (1975). In July 1973, Taft and Martin (1974) reported 10,886 kg of fluorides being introduced to the Bay each day by the plant.

As effluent entered the Bay, where pH of the water is higher and calcium is abundant, the minerals fluorite and pachnolite precipitated as a hard crust. The crust is best developed at the south ditch (Fig. 2A), where it is slightly-to-moderately laminated, and very fine grained. Where the crust thickness is over 1 cm, the crust is solid enough to bear the weight of a person. The delta is traversed by a number of distributaries. The bottoms of the distributaries have thin crusts or no crust at all.

Fluorite is the dominant mineral of the crust. Pachnolite is disseminated throughout the rock in minor amounts relative to fluorite (Fig. 3). Quartz occurs primarily as loose sand lamina within the crust.

The north ditch is different in mineral abundance and crust distribution. The crust is thinner and is solid only in the mouth of the ditch itself. Much of the solid crust shows evidence of repeated brecciation and recementation owing to thin crust development and slightly higher wave exposure (Fig. 4). The crust is laminated and individual laminae give the rock a fissile structure (Fig. 2B). Outside of the ditch there are discontinuous patches and nodules that encrust plants and other debris (Fig. 2B). Maximum crustal thickness observed was 2 cm. Fluorite and pachnolite are present in approximately equal proportions (Fig. 3) and thin laminae of gypsum are present in the crust.

Outside of the ditch areas there are thin, opaque to translucent flakes of fluorite and pachnolite, which are concentrated in the surface sediments (Fig. 1). These chips are not volumetrically important and represent material broken from the deltaic crusts by wave action.

In thin section both pachnolite and fluorite appear fine grained (Fig. 5). Fluorite is most abundant and consists of paired layers that are convoluted and that incorporate intraclasts of the same material. The upper layer is very fine grained, turbid and isotropic with a sharp upper contact and a gradational lower contact. This turbid layer includes grains that are less than 1 μm in diameter. Pachnolite may be included in this layer but is not visible. The lower layer consists of coarse fluorite with no visible pachnolite. In this layer the fluorite consists of interlocking grains from 5 to 75 μm in diameter. Larger grains have small, purple spots which probably reflect lattice disruption by radionuclides. North ditch crust contains up to 809 picoCuries per gram (pCi/g) radium-226. South ditch crust contains

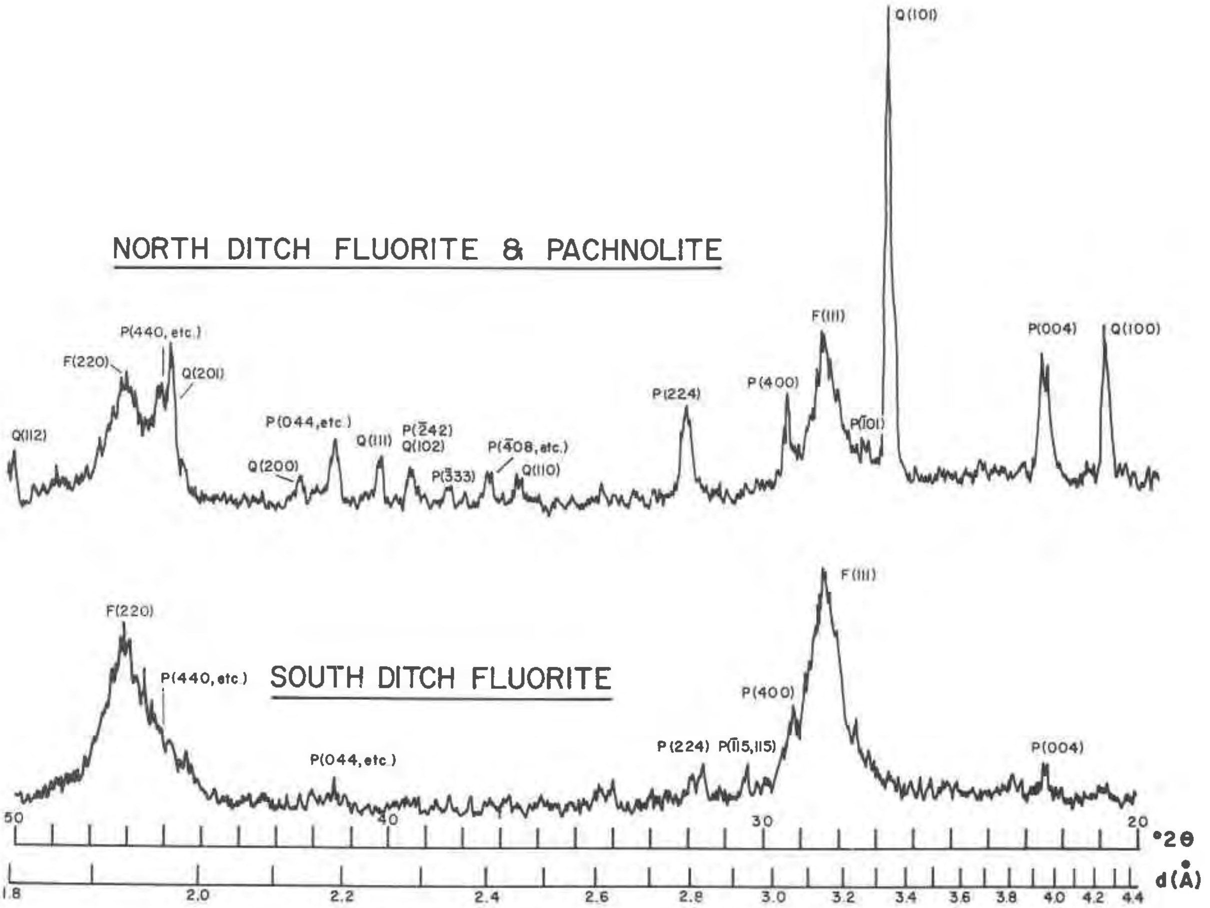

Fig. 3. X-ray diffractograms of fluorite/pachnolite samples from the north and south ditches. F(*hkl*), P(*hkl*), and Q(*hkl*) give the indices of fluorite, pachnolite, and quartz peaks, respectively.

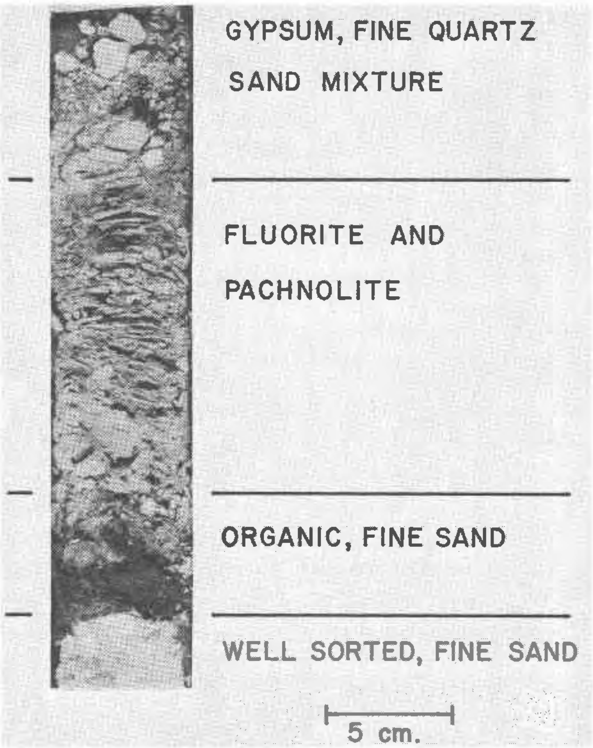

Fig. 4. Relief peel of core taken at north ditch. Note fissility of crusts and absence of evidence of biotic activity near top of core.

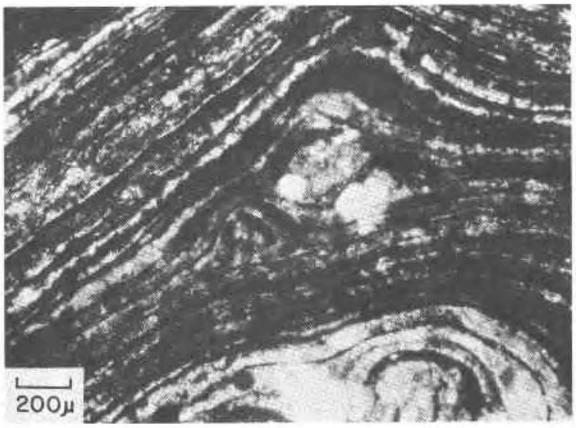

Fig. 5. Thin section of fluorite/pachnolite from north ditch. Note pairing of layers. Dark layers are fine-grained fluorite. Light laminae are coarse crystals of fluorite. Light layers with sharp upper and lower contacts are pachnolite. Plane polarized light.

up to 24 pCi/g radium. Uranium-238 was up to 123 pCi/g and uranium-235 was 6 pCi/g in north ditch fluorite.

Scattered, thin layers of pachnolite can be identified in thin section. These layers are fibrous with long axes perpendicular to the growth surface. The fibers are 20 to 40 μm in length and less than 1 μm in thickness. The scattered pachnolite layers are conformable to the layers of fluorite, and the upper and lower contacts are sharp.

Apparently, the paired layers of fluorite represent individual discharge events with coarse fluorite being deposited first and a turbid, fine grained layer following. It is probable that the turbid, upper surfaces of the layers are turbid because of incorporation of clay-sized detritus in the waning stages of the discharge event. The pachnolite layers undoubtedly have the same origin. The source of the aluminum for pachnolite layers is not clear. Sodium and small quantities of aluminum are present in the water of Tampa Bay. The phosphate ore is usually aluminum deficient after beneficiation. There are, however, sources of aluminum, such as wavellite and crandallite, in the ore.

Martin and Taft (1975) have noted that the plant has made an effort to reduce the discharge of fluorides to the Bay. Therefore, there is little reason to expect additional growth of the deltas. Wave action can be expected to slowly destroy exposed portions of the crusts.

Conclusions

The area offshore of the phosphate chemical plant is contaminated by fluorite and pachnolite crusts at two ditches that drain waste from the area. The crusts cover an area of 1 ha at the north ditch and 4 ha at the south ditch. The crust at the south ditch is up to 8 cm thick and solid. The crust at the north ditch is discontinuous and up to 2 cm thick. Fluorite and pachnolite have been identified by X-ray analysis. This occurrence represents the only known sedimentary pachnolite and the first known occurrence of modern, authigenic fluorite in a marine environment.

Acknowledgments

Portions of this study were funded by the Florida Department of Environmental Regulation. We thank E. D. Estevez, W. H. Taft, A. Rosenzweig, M. Bryant and the students who helped us.

References

Akaiwa, H. and Aizawa, S. (1979) Fluorine contents of Permian carbonate rocks in central Japan. Chemical Geology, 27, 157–169.

Barnes, H. L. (1979) Geochemistry of Hydrothermal Ore Deposits, second ed. John Wiley & Sons, New York.

Kruger, P. (1962) Occurrence of syngenetic sedimentary fluorite in the Platten dolomite of the Gera Basin. Bergakademie, 14, 742–750.

Martin, D. F. and Taft, W. H. (1975) Occurrence and implication of sedimentary fluorite in Tampa Bay, FL. In T. R. P. Gibb, Jr., Ed., Analytical Methods in Oceanography, p. 202–210. American Chemical Society, Advances in Chemistry Series, No. 147.

Palache, C., Berman, H., and Frondel, C. (1957) Dana's System of Mineralogy, Vol. II, Halides, Nitrates, Borates, Carbonates, Sulfates, Phosphates, Arsenates, Tungstates, Molybdates, Etc. John Wiley & Sons, New York.

Richardson, C. K. and Holland, H. D. (1979) Fluorite deposition in hydrothermal systems. Geochimica et Cosmochimica Acta, 43, 1327–1335.

Schneider, H. J. (1954) The sedimentary formation of fluorite in the Upper Wetterstein limestone of the northern Limestone Alps. Abhandlungen, Bayerische Akademie der Wissenschaften, Mathematisch–Naturwissenschaftliche Klasse, 66, 1–37.

Sheppard, R. A. and Gude, 3d., A. J. (1969) Authigenic fluorite in Pliocene lacustrine rocks near Rome, Malheur County, Oregon. In Geological Survey Research, U.S. Geological Survey Professional Paper 650-D.

Sheppard, R. A. and Gude, 3d., A. J. (1980) Diagenetic fluorite in the Eastgate zeolite deposit, Churchill County, Nevada. U.S. Geological Survey Open File Report 80-506.

Studer, H. P. (1967) Mineral analysis of natural zeolite deposits. (abstr.) In S. W. Bailey, Ed., Clays and Clay Minerals—Proceedings of the 15th Clay Minerals Conference, Pittsburgh, Pennsylvania, p. 187. Pergamon Press, New York.

Surdam, R. C. and Eugster, H. P. (1976) Mineral reactions in the sedimentary deposits of the Lake Magadi region, Kenya. Geological Society of America Bulletin, 87, 1739–1752.

Taft, W. H. and Martin, D. F. (1974) Sedimentary fluorite in Tampa Bay, Florida. Environmental Letters, 6, 167–174.

Tourtelot, E. B. and Meier, A. L. (1976) Lithium in the Gila Conglomerate, southwestern New Mexico. In J. D. Vine, Ed., Lithium Resources and Requirements by the Year 2000, U.S. Geological Survey Professional Paper 1005, 123–127.

Manuscript received, December 10, 1979;
accepted for publication, July 6, 1982.