



Ambient Pyrite in Precambrian Chert: New Evidence and a Theory

The Harvard community has made this article openly available. Please share how this access benefits you. Your story matters.

Citation	Knoll, Andrew H., and Elso S. Barghoorn. 1974. Ambient pyrite in Precambrian chert: New evidence and a theory. Proceedings of the National Academy of Sciences of the United States of America 71, no. 6: 2329-2331.
Published Version	doi:10.1073/pnas.71.6.2329
Accessed	February 17, 2015 8:11:53 PM EST
Citable Link	http://nrs.harvard.edu/urn-3:HUL.InstRepos:3294653
Terms of Use	This article was downloaded from Harvard University's DASH repository, and is made available under the terms and conditions applicable to Other Posted Material, as set forth at http://nrs.harvard.edu/urn-3:HUL.InstRepos:dash.current.terms-of-use#LAA

(Article begins on next page)

Ambient Pyrite in Precambrian Chert: New Evidence and a Theory

(pressure solution/pseudofossils)

ANDREW H. KNOLL AND ELSO S. BARGHOORN

Department of Biology and Botanical Museum, Harvard University, Cambridge, Massachusetts, 02138

Contributed by Elso S. Barghoorn, April 2, 1974

ABSTRACT Ambient pyrites of two distinct types were described from middle Precambrian rocks of the Lake Superior area. A new class of this phenomenon is here described from middle Precambrian chert from western Australia. The newly found ambient pyrites are quite minute and characteristically occur in groups forming a "starburst" pattern. All three types of ambient pyrite may be explained in terms of pressure solution initiated by gas evolution from organic material attached to the pyrite. Thermal degradation of the kerogen produces the gases which, due to the impermeability of the encompassing chert, build up the pressures necessary to initiate solution. Pyrite appendages bear a striking resemblance to microorganisms and, thus, constitute the smallest pseudofossils known.

In 1963, Tyler and Barghoorn (1) described two distinct classes of pyrite crystals with quartz or iron-carbonate appendages. From various petrological and geometrical considerations, it was apparent that the pyrites had moved through the microcrystalline chert matrix, leaving mineral trails in their wakes. We here report a third class of this phenomenon, as well as new occurrences of the smaller of the previously described types, in chert from the base of the 2.2 billion-year-old Fortesque Group of the Hammersly Iron Province of western Australia. We further present a theory for the origin of ambient pyrite and its apparent restriction to organic-rich Precambrain cherts.

A brief review of the salient features of the known ambient pyrites will facilitate the present discussion. Iron-carbonate appendages ranging up to 100 µm in length trail from minute (1-10 µm) pyrite gains set in the organic-rich chert matrix of the Precambrain Biwabik formation of Minnesota (Fig. 1, C-F). A wide variety of appendage morphologies have been observed, including straight, curved, coiled, and pseudobranching patterns; the width of the appendage always conforms to the diameter of the attached pyrite crystal. Quartz appendages observed in the well-known Gunflint chert (2) of southern Ontario differ from the carbonate trials mainly in their much larger size and multicrystalline nature (itself a probable derivative of the size difference). These pyrite grains range in diameter from 0.65 to 1.4 mm, the quartz appendages also having precisely the same width as the attached grain (Fig. 1, A and B). Quartz appendages may reach almost three millimeters in length. Crystals forming the border of the appendages are quite small and appear to be in optical continuity with the adjacent matrix grains. This would imply that chert microcrystals bordering the trails served as nucleation sites for reprecipitating quartz, the small size being indicative of rapid early growth. Later, as growth slowed, certain crystals grew at the expense of others.

The newly discovered appendages are of the same composition as those of the Biwabik chert, but are an order of magnitude smaller, having fairly consistent widths of 0.5–0.8 μ m. Length can exceed 60 μ m, but is more commonly 10–25 μ m. Although individual, isolated trails exist, the appendages are generally found as "starbursts" radiating, apparently randomly, from a central locus (Fig. 2). On occasion, the smaller type previously described ambient pyrite may be found associated with such an aggregation. These forms are ubiquitous in our sample; 308 groups were counted in a single square centimeter of thin-section area.

How were the ambient pyrite trails formed? An ultra-thin aqueous film at the chert-pyrite interface would provide the necessary medium for pressure solution and transportation of silica to recrystallization sites behind the advancing iron-sulfide. Pyrite itself is quite inert, immiscible, and has a hydrophobic surface, so it is particularly well suited for pressure dissolution of chert without diminishing itself in the process. The great variety of appendage morphologies probably reflects more rapid crystal growth on one side than the other.

But by what mechanism was pressure solution effected? H₂S is a product of the early stages of organic decomposition, and iron in solution would readily react with the evolving gas to form iron-sulfide. The newly formed pyrite would be encompassed by an opaline silica "gel", often with partially decomposed organic matter attached to it. (We know that the Biwabik, Gunflint, and Fortesque cherts were crystalline at the time of ambience because the pyrite trails cut through quartz crystals and oolites.) Increased temperature and pressure following crystallization would complete the breakdown of remaining organic matter to gaseous endproducts, notably CO₂ and, at higher temperatures, CH₄. Chert is incredibly impermeable; permeabilities of less than 0.1 millidarcy were measured for the Biwabik and Gunflint cherts by Robert Clarke of the Mobil Research and Development Corp. (3), so that evolving gas would have no outlet and would build up pressure. Unequal distribution of carbonaceous material about the pyrite would lead to differential pressure buildup. This explains the random orientation of motion, as well as the lack of movement of some grains (equal distribution or loss of organic matter about the grain).

The sizes of the two iron-carbonate-appendaged pyrite classes are consistent with those expected to form from the decomposition of single cyanophytes (the larger) or bacteria (the smaller). Further, the smallest trails occur in clusters, as may be expected for a bacterial colony. The larger quartz-appendaged pyrites require a much larger source of organic matter. Such sources are the oolites with which the grains are

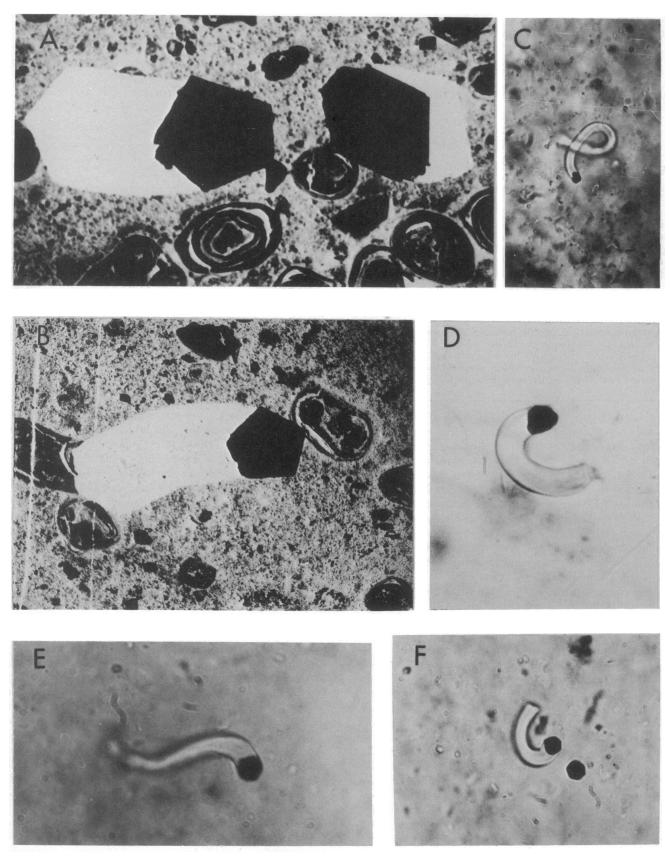


Fig. 1. (A and B) (\times 31) Quartz-appendaged pyrite crystals from the Gunflint chert, Ontario. The appendages appear white because the reprecipitated quartz contains no iron coloration or inclusions. Note the numerous colites in the chert matrix. (C-F) (D and E \times 1500; C and F \times 1000) Iron-carbonate-appendaged pyrite crystals from the Biwabik chert of Minnesota. Only a few of the many trail morphologies are shown. Note in F that one crystal has moved while an adjacent grain has not (or at best has moved in a direction perendicular to the sense of the first).

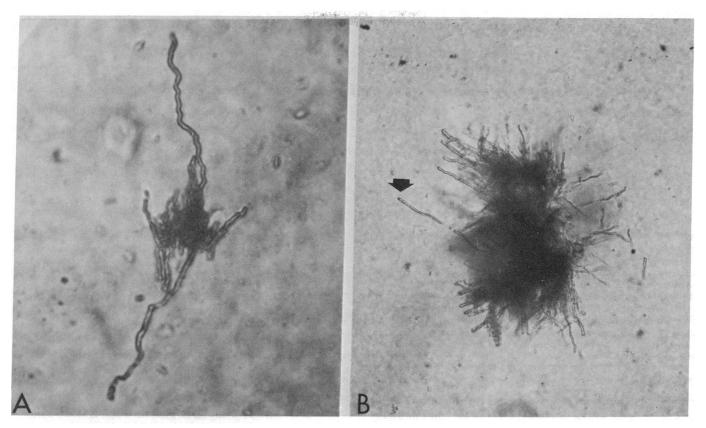


Fig. 2. (A and B)(\times 1150) Minute clusters of ambient pyrite trails from the Fortesque Group of western Australia. The arrow in B points to a tiny pyrite grain at the terminus of a well-developed appendage.

intimately associated. Numerous oolites can be observed to have burst and been filled by reprecipitated quartz lacking inclusions or iron coloring.

The apparent restriction of this phenomenon to organic-rich Precambrian cherts is in accord with the above outlined theory. The importance of organic matter is obvious, but the role of primary silica deserves further mention. The theory requires that the carbon-bedecked pyrite be enclosed rapidly, before bacterial respiration can completely degrade the organic material. Impermeability of the enclosing medium is a further requisite of the theory, and in this respect, chert stands alone among sedimentary rocks. Primary cherts are not restricted to the Precambrian (e.g., the Rhynie chert of Scotland or the Caballos novaculite of Texas), but in Phanerozoic cherts the necessary pyrite accumulations or post-depositional metamorphic effects are lacking.

A note of caution should be raised. The resemblance of ironcarbonate trails of both types to prokaryotic organisms is remarkable. In all probability, they constitute the smallest pseudofossils described or describable. Indeed, it seems that Gruner (4) fell victim to this similarity in describing "microfossils" from the Biwabik chert. His was a perfectly natural error, but care should be taken lest such physical phenomena be taken for microorganisms in the future. [For an illuminating review of the problems caused by incorrect interpretations of Late Precambrian pseudofossils, see the excellent paper by P. E. Cloud, Jr. (5).] In summary, three distinct classes of ambient pyrite crystals are known from Precambrian cherts. The associated appendages are the product of pressure solution initiated by gases evolved from metamorphically decomposed organic matter attached to the pyrite. The restriction of this phenomenon to organic-rich Precambrian chert is consistent with the theory developed. In fact, the cogency of the theory lies in its accounting for all observed facts. Finally, the similarity of ambient pyrite appendages to microfossils can be quite misleading and should be reemphasized.

We thank Dr. Ralph Iler, of E. I. du Pont de Nemour and Co., for suggestions concerning the physical and chemical relations of pyrite and silica. This work was partially supported by NASA Grant NGL-22-007-069. A.K. is a NSF Graduate Fellow.

- Tyler, S. A. & Barghoorn, E. S. (1963) "Ambient pyrite grains in Precambrian cherts," Amer. J. Sci. 261, 424-432.
- Barghoorn, E. S. & Tyler, S. A. (1965) "Microorganisms from the Gunflint chert," Science 147, 563-577.
- Barghoorn, E. S. (1973) in Origins of Life: Chemistry and Radio Astronomy, Proc. Fourth Conf. Origins Life, ed. Margulis, L. (Springer Verlag, New York), p. 72.
- Gruner, J. W. (1923) "Algae, believed to be Archean," J. Geol. 31, 146-148.
- Cloud, P. E. (1968) in Evolution and Environment, ed. Drake,
 E. T. (Yale University Press, New Haven, Conn.), pp. 1-72.