INHIBITION OF PYRITE GROWTH BY AMORPHOUS CARBON

EMANUEL E. LAUFER†, J. DOUGLAS SCOTT* AND ROD PACKWOOD

Canada Centre for Mineral and Energy Technology, 568 Booth Street, Ottawa, Ontario K1A 0G1

ABSTRACT

Evidence gathered in the course of an electron-microscope study of so-called "earthy pyrite" bands appears to substantiate a hypothesis that growth of pyrite crystals within such bands is inhibited by thin coatings of material rich in amorphous carbon.

Keywords: earthy pyrite, amorphous carbon, graphite, exploration geophysics, electron-microscope study, crystal growth, massive sulfide orebody.

SOMMAIRE

Une étude par microscopie électronique des bandes de pyrite terreuse semble confirmer l'hypothèse que la croissance des cristaux de pyrite dans ces bandes aurait été inhibée par un mince liséré riche en carbone amorphe.

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Mots-clés: pyrite terreuse, carbone amorphe, graphite, géophysique d'exploration, étude par microscopie électronique, croissance cristalline, gisement de sulfures massifs.

INTRODUCTION

Electromagnetic prospecting for massive-sulfide orebodies is severely complicated by the presence of other natural conductors in the earth. The most common of these in the Flin Flon belt of central Manitoba are the so-called "earthy pyrite" bands (Gale *et al.* 1976). These stratiform bands are highly conductive, much more so than their apparently minor content of graphite would indicate, to the extent that a 20-cm length of AX core from the Big Island zone is capable of short circuiting a standard 110 V line. It has therefore been standard practice in the mineral exploration community that when such an "earthy pyrite" conductor is intersected by diamond drilling, the drill hole is immediately abandoned. However, a hole was drilled beyond one such conductor, and a zone of base-metal mineralization was found stratigraphically beneath it (G.Y. Gale, pers. comm. 1976). This has led to a reappraisal of such conductors and, indirectly, to the present study of their nature and origin.

SAMPLE DESCRIPTION

Specimens of drill core from three types of ear-

†Present address: Department of Mining and Metallurgical Engineering, Technical University of Nova Scotia, Halifax, Nova Scotia B3J 2X4.
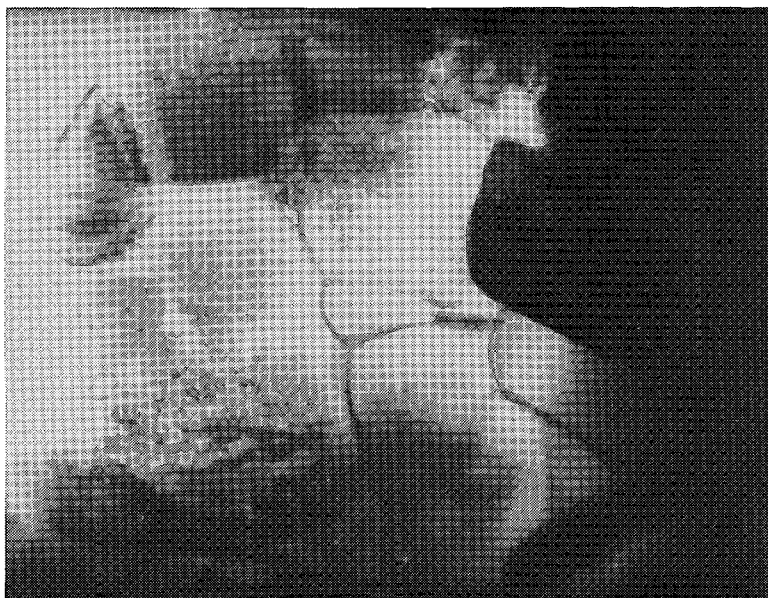*Present address: Kidd Creek Mines Limited, Commerce Court West, Toronto, Ontario M5L 1E7.

thy pyrite bands were examined in this study. They cover the range in pyrite grain-size from homogeneous very fine grained (Big Island, 01/03/76) through material with alternating bands of fine-grained and partly recrystallized pyrite (Pine Bay Mine, Pby 123–329') to a more fully recrystallized graphitic pyrite band cut by veinlets of massive granular pyrite (Eppa 9–579'). Hand specimens of "earthy pyrite" are generally dull greenish brown to black, very fine grained and compact. They display no readily identifiable minerals except occasional small crystals of pyrite and thin veins of quartz; all are universally and pervasively cut by anastomosing graphitic shear-zones (which appear to represent pressure-solution residues). In polished section, the material is seen to be composed of a host of tiny subhedral to rounded pyrite grains; these are isolated in a quartz matrix that is cut by thin shear-zones lined with crystalline graphite or iron-chlorite (chamosite) or both.

Quantimet image analysis of the Big Island specimen shows that all of the pyrite exists as subhedral cubes. These are closely packed but isolated in the quartz matrix. No crystals are larger than 10 μm, and half are smaller than 3 μm. Identical textures are observed in the fine-grained bands of the Pine Bay specimen; however, in the partly recrystallized bands the pyrite can be seen to be agglomerated in a highly ordered fashion. Groups of four to eight of the smaller (2 μm) cubes have grown together *at their corners* to form "cumulates", then two to five of these aggregates have begun to grow together in a linear string in the direction of fracturing. The planes of fracture are discontinuous and, in general, outlined by a thin graphitic, chamosite-rich band. There is also more quartz around the pyrite grains in these recrystallized bands. This quartz commonly contains large numbers of tiny euhedral chamosite crystals that tend to be aligned parallel to a faintly defined "fibrosity" in the quartz, radially outward from larger pyrite crystals; they probably outline partly coalesced pressure-shadows. Both of the above two processes are enhanced in the more fully recrystallized Eppa specimen, in which the pyrite occurs as pronounced braided bands in the quartz, and traces of old fracture-planes are visible as discontinuous bands of relict chlorite in the pyrite.

EXPERIMENTAL

Transmission-electron-microscope studies were made on these three specimens in order to investigate the hypothesis that a thin coating of graphite, or

FIG. 1. TEM photograph (40000×) of a pyrite crystal in quartz from Big Island. Quartz grains are to the left and at the top; pyrite, showing internal grain-boundaries outlined by thin curved lines, is on the right. The sharply defined dark grey band between quartz and pyrite grains is an expression of the amorphous carbon layer.

chlorite, around the pyrite crystals inhibited their growth, except at points of local breakdown of the layer, during metamorphic recrystallization. An ultrasonic drill was used to cut 3-mm disks from doubly polished thin sections. The disks were then glued to copper supporting-rings and thinned by argon-ion bombardment for examination in JEOL JEM 200B and Philips EM300 electron microscopes.

Pyrite, quartz, Fe-chlorite (in shear zones only) and trace pyrrhotite were identified in all samples by electron diffraction and X-ray-emission spectroscopy (XES). Figure 1 shows a sample of the fine-grained material from Big Island. Here, the intra-grain pyrite–pyrite and intergrain pyrite–quartz interfacial zones both contain a layer of a third phase. Figure 2a shows detail on an intergrain boundary-layer, and Figure 2b the corresponding selected-area diffraction pattern. The diffuse rings observed are typical of amorphous material. Figure 2c, a dark-field micrograph obtained using a portion of the diffuse ring (cf. Ruhle et al. 1977), shows clearly that the boundary layer is responsible for the diffuse diffraction-ring and is therefore an amorphous substance, distinct from the crystalline pyrite and quartz that it separates.

The thickness of the intergrain amorphous layer is estimated to be about 100 nm. Such layers appear to be continuous around the pyrite cubes in both the Big Island sample and the fine-grained portion of the Pine Bay sample, but were not observed on more coarsely crystalline Pine Bay and Eppa material,

where all + 100-μm crystals of pyrite appear to have sharp clean boundaries with both the surrounding quartz matrix and each other. Tilting of the Big Island sample, combined with selected-area electron diffraction, also revealed that a portion of the interfacial diffraction-pattern (Fig. 2b) was caused by a continuous layer some 6 nm thick of 1C-pyrrhotite single-crystal platelets. These are in apparent epitactic growth on the outer surface of the pyrite crystals.

Figure 3 shows the XES spectra observed in the TEM on, and on either side of, a similar boundary-layer separating two pyrite subgrains within a 4-μm cube of pyrite. Since the finest spot-size obtainable in our microscope is slightly wider than the amorphous layer, the spectrum from this region is influenced by the pyrite on either side. The spectrum from the amorphous layer shows no elements other than the iron and sulfur of the pyrite, and these elements are much reduced in intensity. The amorphous layer is therefore composed of carbon (or other elements lighter than fluorine, the lightest element that can be detected by XES in our microscope). Examination of intragrain boundaries of pyrite in the recrystalized Pine Bay and Eppa samples did not reveal a similar amorphous layer.

An electron-microprobe examination was made of broken surfaces of Pine Bay (mainly coarse-grained) and Big Island (fine-grained) materials. Under identical conditions, the fine-grained crystals of pyrite in the Pine Bay sample show 1500–2000 carbon counts, and the more common coarse-grained crys-
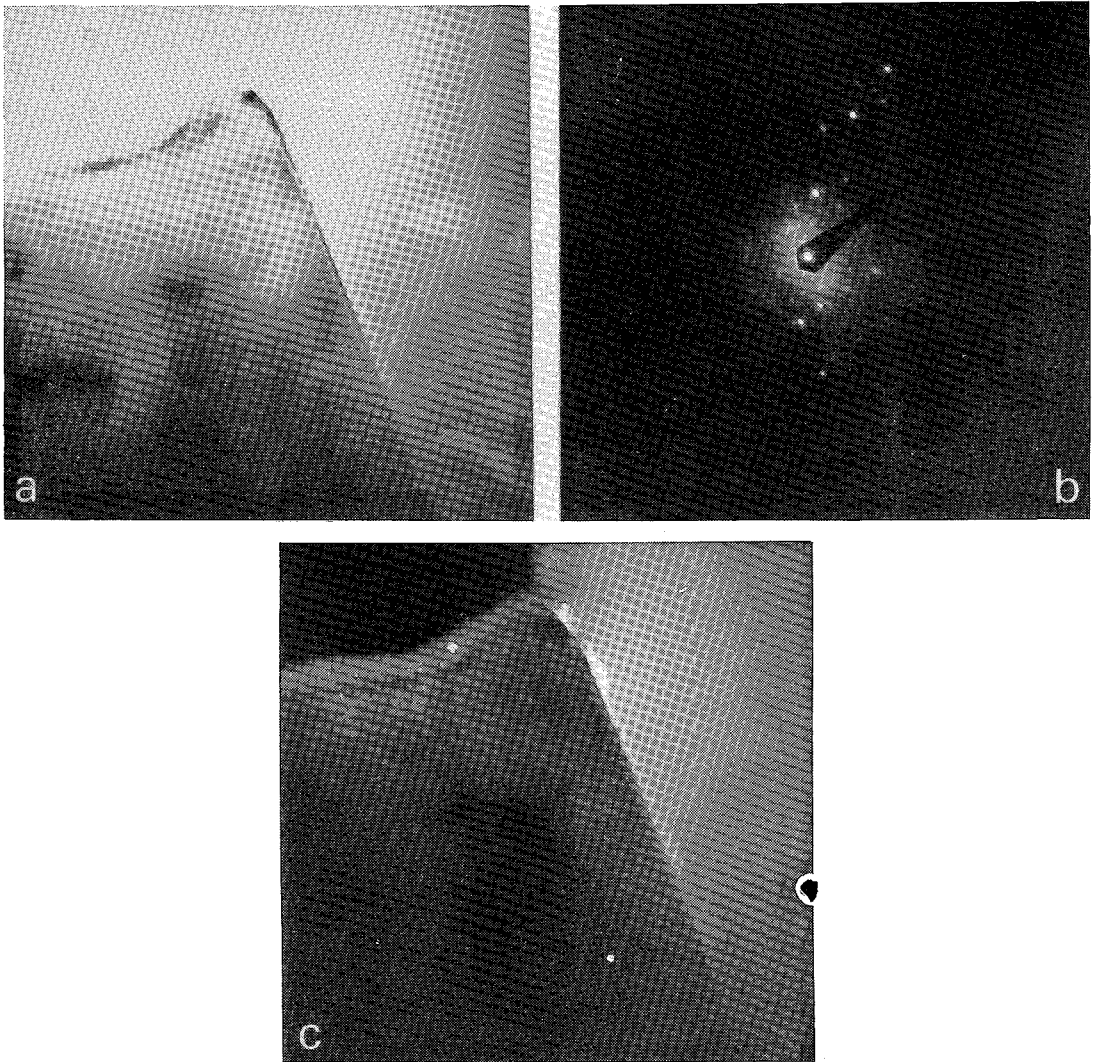
FIG. 2. TEM photographs (60000×) of a quartz–pyrite boundary in the Big Island sample. Figure 2a is a bright-field image, with pyrite on the left; part of the amorphous interfacial layer can be seen as a faint white streak at the lower right. Figure 2b is a selected-area electron-diffraction pattern of the interfacial layer; note the diffuse diffraction-rings. Figure 2c is a dark-field image of the interface, based on one of the diffuse rings; this shows that portion of the amorphous layer as a white streak.

tals 150–200 counts. The fine-grained pyrite from Big Island, examined under the same conditions, gave 5000–6000 carbon counts per crystal. Leaking a small amount of air onto the sample during the electron-microprobe observation would effectively remove any carbon film from the surface of the grain boundaries along which the sample was broken. When this was done, the carbon counts dropped by an order of magnitude in all cases. From this observation, together with the TEM observations, we conclude that a layer of amorphous carbon is present at the pyrite–pyrite and pyrite–quartz boundaries and that

it decreases in thickness with increasing metamorphic crystal-growth of the pyrite. This is taken as corroboration of the hypothesis that the pyrite grains in "earthy pyrite" bands are inhibited in their growth by a thin layer of amorphous carbon (not crystalline graphite or chlorite) situated at the grain boundaries. Note also that as the extent of metamorphic recrystallization of the pyrite increases, both the total surface-area of the pyrite and the thickness of the carbon layers decrease. The "excess" carbon appears to be locally redepositing as optically anisotropic crystalline platelets of graphite in the microfractures.
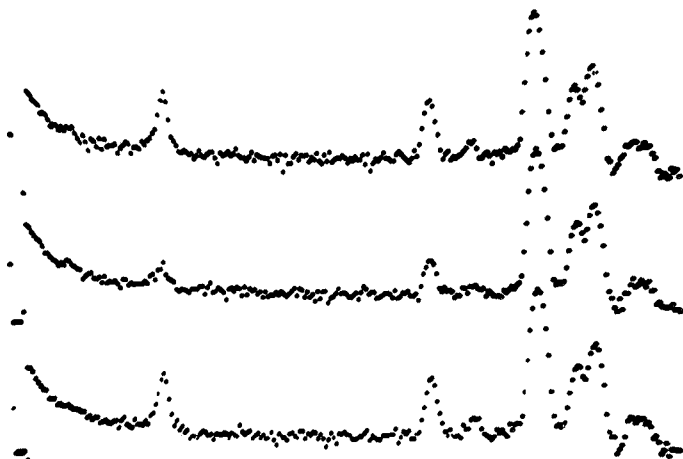
FIG. 3. TEM–XES spectra in the vicinity of a pyrite–pyrite grain-boundary in the Big Island sample. Noise at the low-energy ends (left) and the Cu and Zn peaks at the right are instrumental artifacts. The upper and lower curves were taken on the two pyrite grains and the central curve on the interfacial region; it shows reduced S and Fe peaks (central pair), relative to the pyrite spectra, but no additional lines.

DISCUSSION

This phenomenon and its attendant problems with geophysical prospecting are not restricted to the Flin Flon area. In the Norwegian Caledonides, very similar thin stratiform horizons of fine-grained pyrite and carbonaceous matter, locally known as "Vasskis", are commonly observed in the vicinity of both the Lokken and Skorovass mines (J. Guha, pers. comm., 1984).

An unpublished study of the Howards Pass deposit, Yukon (by I.R. Jonasson of the Geological Survey of Canada) may provide a clue as to the method of formation of "earthy pyrite" bands. He reports that: "Recrystallization of pyrite framboids in algae-rich cherty-carbonaceous shale in that deposit is a process of pressure solution. Algal cores are preserved within the recrystallizing pyrite grains except when shearing is strong and a pervasive anastomosing cleavage is developed. Under those circumstances the product of pressure solution and recrystallization followed by transposition of grains is a cleavage filled with carbonaceous residues. These residues effectively surround each pyrite grain. The grains may develop a preferred shape but tend to remain separated. Further deformation, accompanied by pressure solution, would be expected to take place as a result of grain-boundary slip along graphitic surfaces, and likely would not result in further recrystallization and growth of pyrite, i.e., the carbon "protects" pyrite grains from applied strain and would also minimize diffusive transfer of FeS_2 molecules (or their dissociates). Furthermore, development of quartz-fibre pressure shadows around individual framboids may also have helped to isolate them."

It should also be noted that such recrystallized pyritic shales, where they have been intensely deformed under pressure with the development of closely spaced (1–5 mm) anastomosing cleavages, display no vestige of their original bedding. The result is rather a pseudobedding of pyrite anhedra. This would seem to describe very well the genesis of the observed relationships in the "earthy pyrite" bands, when allowance is made for their formation in a Precambrian argillitic environment, rather than one of lower Silurian cherty-carbonate shale.

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