Framboidal pyrites in antique books

During the Middle Ages and the Renaissance, ink was commonly manufactured by mixing tannin with iron sulphates. The anoxic environment inside ancient books favours the reduction of the sulphate in the ink and allows spherical aggregates (framboids) of submicrometre-sized pyrite crystals (iron sulphide) to be formed.

Framboidal pyrites are ubiquitous in a variety of conditions and geological environments such as hydrothermal veins and sedimentary rocks. The meaning of the term ‘framboid’ has changed significantly since the beginning of the century, when it was used to emphasize a bacteriogenic origin. Since then, non-organic formation of framboids has been shown experimentally. The term ‘framboid’ is now used to describe spheroidal aggregates of microcrystals with a diameter of up to 150 μm (ref. 3).

For the formation of framboïds, the precipitation of iron and sulphur ions in a reducing environment is required. We have found that such an environment exists in books from the sixteenth and seventeenth centuries that have been stored in archives for hundreds of years. We discovered these authigenic framboidal pyrites in books during a restoration programme at the Archivo Histórico Nacional in Madrid. We found a shiny black powder in the seams joining the pages to the spines of the books. Studying this powder, by transmitted and reflected light microscopy, X-ray diffraction and scanning electron microscopy, revealed it to be solid remnants of the ink. This was corroborated by the presence of the same remains adhering to the writing itself (Fig. 1a).

The mineral phases included quartz, haematite, K-feldspar, allochthon pyrites, calcite, gypsum, rutile, magnetite and ilmenite, with crystal sizes ranging from 50 to 400 μm; additives commonly used to improve the finish of inks at that time (Fig. 1a). Autigenous pyrite was found in this black powder as framboïd aggregates of ~140 μm in diameter, made up from tiny, subbedral, pyrite microcrystals. These framboïds (Fig. 1b) are nearly perfect spheroids with smooth, homogeneous surfaces, caused by the coalescence of the pyrite microcrystals, indicating a certain degree of framboïd evolution.

It has recently been stated that: framboïd size is controlled by the residence time near the oxic–anoxic boundary; growth times for framboïds in the water columns of eucinic basins are less than three months; and diagenetic framboïds grow for about three times longer than syngenetic framboïds. The large size of our framboïds (140 μm) indicates that optimum growth conditions occur in these old books. The presence of red rot on the cover and some of the pages shows that there are eusinic micro-environments inside, and oxic–anoxic boundaries could have been maintained by the seasonal changes in Madrid (temperatures from −10 °C to 44 °C). The period inside the books was long considering the calculated framboïd growth rate (4 μm yr−1) in euxinic environments.

The chemical elements of these pyrite framboïds almost certainly came from the components of the ink: tannin, gum arabic, iron salts, additives and solvents. Iron gall inks used at the time were made by the reaction of tannins, derived from gallic acid (C₆H₄(OH)₂COOH) with iron sulphates (melanterite FeSO₄·7H₂O). Cellulose in the paper and gum arabic used in the ink provided carbon and nitrogen needed to develop iron- and sulphate-reducing bacteria. These, in turn, contributed to the formation of framboïd pyrites: framboïd pyrite has been found in the similar cellulose-rich environment of several species of fossil woods.

As organic matter is present in the closed environment of the books, the possibility of sulphate- and iron-reducing bacteria (such as Desulfovibrio desulfuricans, Desulfovomaculum nigrificans) being responsible for pyrite mineralization should also be considered.

The detection of processes of pyrite mineralization in this singular environment shows that unusually large pyrite framboïds, displaying a high degree of evolution, can be formed under intermittent oxic and anoxic conditions over hundreds of years. This discovery supports the recently published hypothesis that the formation of framboïd pyrites does not require a narrow set of physical or chemical conditions.

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Intercropping increases parasitism of pests

As part of a programme for controlling lepidopteran stem-borers in cereal crops in Africa, we have investigated the effectiveness of combined cropping regimes of cultivated and wild plants for reducing stem-borer damage. Intercropping with the non-host molasses grass, Melinis minutiflora, significantly decreased levels of infestation by stem-borers in the main crop and also increased larval parasitism of stem-borers by Cotesia sesamiae. Volatile agents produced by M. minutiflora repelled female stem-borers and attracted foraging female C. sesamiae. One of the volatile components released by intact M. minutiflora which attract parasitoids is also produced by herbivore-damaged plants and is implicated more widely as a cue for stimulating predation and parasitism.

Maize (Zea mays) and sorghum (Sorghum bicolor) are the most important cereal crops for the people of Africa. Lepidopteran stem-borers are ubiquitous pests that attack these crops throughout their growth stages and the larvae cause damage ranging from 20 to 80% loss of yield. One approach to pest control in resource-poor regions is to develop management systems.
using the ‘push–pull’ or stimulodeterrent diversionary strategy, whereby insects are repelled from a harvestable crop and simultaneously attracted to a ‘discard’ or ‘trap’ crop. For maximum efficacy, these systems should also exploit natural enemies, particularly hymenopteran parasitoids, which can be important in suppressing pest populations. Indeed, reductions in such beneficial organisms frequently trigger pest outbreaks.

To develop a diversionary strategy for small-scale African cereal production, we assessed a range of cultivated and wild plants in the Gramineae family (Poaceae) in field trials in Kenya for susceptibility to stem-borers, particularly the indigenous Bissoula fusca (Lepidoptera, Noctuidae) and the introduced Chilo partellus (Lepidoptera, Pyralidae). In these trials, molasses grass planted in alternate rows with maize significantly reduced stem-borer infestations. Indeed, reductions in such beneficial predators and parasites9 have been suggested as an explanation for the increased parasitism observed. In behavioural assays using a Y-tube olfactometer4, we showed that foraging female C. sesamiae were indeed attracted to live M. minutiflora plants and also responded in a dose-dependent manner to the hydrodistillation extract (Table 1), and to the nonatriene alone.

The prospects for understanding and exploiting the interaction of hymenopteran parasitoids with their hosts have advanced rapidly, particularly with the discovery that semiochemicals released during herbivore damage can stimulate parasitoid foraging11–13. Our study suggests that intact plants with an inherent ability to release such stimuli could be used in new crop protection strategies.

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| Table 1 Response of C. sesamiae to plant or plant extract |
| Treatment | Control | Significance (P) |
| Live plant (30 g) | 39 | 7 | <0.005 |
| Extract (0.2 mg) | 22 | 18 | Not significant |
| Extract (2 mg) | 32 | 18 | <0.05 |
| Extract (20 mg) | 44 | 9 | <0.005 |
| Nonatriene (0.1 mg) | 35 | 18 | <0.05 |
| Nonatriene (1 mg) | 36 | 14 | <0.005 |

Response of female Cotesia sesamiae in the Y-tube olfactometer to Melininia flava (live plant or extract) and (E)-4,8-dimethyl-1,3,7-nonatriene. Number of females choosing each ‘arm’ of the Y-tube is given. Control was clean air.

1 mg plant extract(+1g (wet mass) plant material.

Stochastic resonance at the single-cell level

Does the electricity with which we power our world pose significant health hazards from the resulting electromagnetic fields? Several authors have speculated that ‘stochastic resonance’—a nonlinear phenomenon in which the addition of noise to a system increases its response to an external signal—may allow biological cells to detect and respond to very weak external electric fields far below the thermal noise limit14, and thus possibly cause harmful effects. Here we examine this question using a recent theory of Bezrukov and Vodyanoy8 for the effect of non-equilibrium noise on a voltage detector (such as a biological ion channel). We show that with parameters appropriate for typical biological cells, adding noise does not make a far-from-detectable signal detectable.

Bezrukov and Vodyanoy imagine a Poisson process (for example, the entry of a toxic molecule through a protein gate), the rate of which is modulated by an external low-frequency signal voltage with dimensionless amplitude \( V_s \) and a zero average gaussian noise voltage \( V_n(t) \). For a small-amplitude signal, the signal-to-noise ratio (SNR) is:

\[
SNR = \frac{V_s^2}{2\Delta f} \frac{r(0)}{r(0)} \exp \left( \frac{\sigma^2}{2} \right) \sum_{n=1}^{k} \frac{\sigma^2}{n!} \tag{1}
\]

where \( r(0) \) is the basal rate of the Poisson process, \( \Delta f \) is the bandwidth of the detector, and \( f_c \) is the corner frequency and \( \sigma \) the dimensionless r.m.s. amplitude of the external noise.

The SNR is a non-monotonic function of \( \sigma \). The amplification (as compared to the SNR in the absence of added noise) can be quite large, particularly for small values of \( r(0)/f_c \) (ref. 6). Here we address a related but separate issue. With realistic biological parameters, can the addition of noise render detectable (SNR > 1) a signal that without added noise has a SNR much less than unity?

For a biological cell with radius \( r_{cell} \) in an external electric field \( E_{ext} \), the dimensionless signal amplitude is \( V_s = (E_s x_{cell}/k_BT) \), where \( z \) (a gating charge for an electrically sensitive protein) parametrizes the sensitivity of the biophysical detection mechanism to the applied field \( k_B \) is the Boltzmann constant and \( T \) the temperature. The cutoff \( f_c \) is approximately the inverse of the charging time for the membrane (less than 10 MHz) so we use \( f_c = 10^7 \) s\(^{-1}\). In Fig. 1, a