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[1,2]. 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 framboids, 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 remains 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[4]. Authigenic pyrite was found in this black powder as framboidal aggregates of ~140 μm in diameter, made up from tiny, subhedral, pyrite microcrystals. These framboids (Fig. 1b) are nearly perfect spheroids with smooth, homogeneous surfaces, caused by the coalescence of the pyrite microcrystals, indicating a certain degree of framboidal evolution[2].

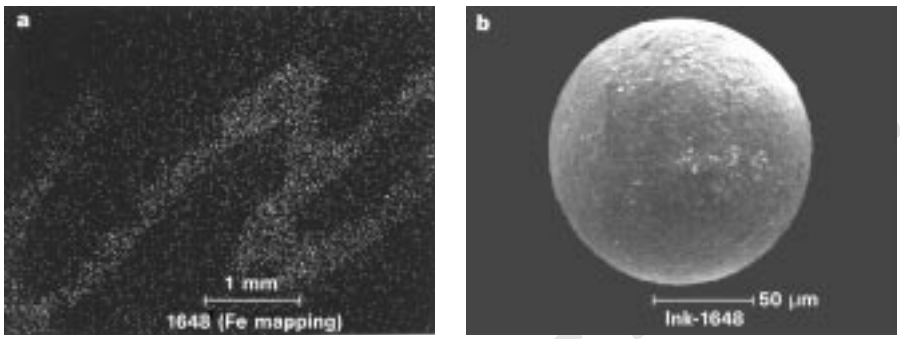

Figure 1 Scanning electron micrographs **a,** Iron mapping (SEM-EDAX) which clearly follows the shape of a letter in the text. **b,** Framboidal pyrites formed within the book.

It has recently been stated[5] that: framboid size is controlled by the residence time near the oxic–anoxic boundary; growth times for framboids in the water columns of euxinic basins are less than three months; and diagenetic framboids grow for about three times longer than syngenetic framboids. The large size of our framboids (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 euxinic 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 framboid growth rate (4 μm yr^{-1}) in euxinic environments[5].

The chemical elements of these pyrite framboids almost certainly came from the components of the ink: tannin, gum arabic, iron salts, additives and solvents. Iron gallic inks used at the time were made by the reaction of tannins, derived from gallic acid ($C_6H_2(OH)_3COOH$) with iron sulphates (melanterite $FeSO_4 \cdot 7H_2O$)[6]. 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 framboidal pyrites: framboidal pyrite has been found in the similar cellulose-rich environment of several species of fossil woods[7]. As organic matter is present in the closed environment of the books, the possibility of sulphate- and iron-reducing bacteria (such as *Desulfovibrio desulfuricans*, *Desulfotomaculum nigrificans*) being responsible for pyrite mineralization should also be considered[8].

The detection of processes of pyrite mineralization in this singular environment shows that unusually large pyrite framboids, 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 framboidal pyrites does not require a narrow set of physical or chemical conditions[1].

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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

Table 1 Response of *C. sesamiae* to plant or plant extract

Stimulus	Response		Significance (*P*)
	Treatment	Control	
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 *Melinis minutiflora* (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≡20.1g (wet mass) plant material.

using the 'push–pull' or stimulodeterrent diversionary strategy[1], 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[2]. Indeed, reductions in such beneficial organisms frequently trigger pest outbreaks[3].

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 *Busseola fusca* (Lepidoptera, Noctuidae) and the introduced *Chilo partellus* (Lepidoptera, Pyralidae). In these trials, molasses grass showed no colonization by stem-borers. Further, volatiles extracted by hydrodistillation of the plant repelled gravid female stem-borers in a laboratory oviposition assay (for *C. partellus*, eggs laid per filter-paper disc: control 40.9, 100 μg *M. minutiflora* extract 2.2; $P < 0.005$, $n = 8$). In field trials at Mbita Point on Lake Victoria, *M. minutiflora* planted in alternate rows with maize significantly reduced stem-borer infestation of the main crop (damaged maize plants: single crop 39.2%, intercropped with *M. minutiflora* 4.6%; $P < 0.01$). We also saw a significant increase in parasitism by the larval parasitoid *C. sesamiae* (Hymenoptera, Braconidae) (parasitized larvae in maize: single crop 5.4%, maize with *M. minutiflora* intercrop 20.7%; $P < 0.01$).

To identify the chemicals mediating this behaviour of stem-borers and parasitoids, we isolated volatiles from live *M. minutiflora* plants by entrainment into porous polymer[4]. Electrophysiologically active components in the solvent-eluted samples were located by coupled gas chromatography and electroantennography[5]. We tentatively identified active peaks by gas chromatography–mass spectrometry and confirmed their identity by co-injection with authentic compounds on two columns of different polarity, and using behavioural studies[6]. Characterized semiochemicals included α-terpinolene, the ocimene isomers, β-caryophyllene, humulene and (*E*)-4,8-dimethyl-1,3,7-nonatriene.

Production of some of the compounds released by intact *M. minutiflora* can also be induced in plants damaged by herbivorous insects[7–9]. The nonatriene in particular has been implicated as an 'SOS' signal recruiting predators and parasites[10]. The presence of such compounds in the *M. minutiflora* intercropping system could provide an explanation for the increased parasitism observed. In behavioural assays using a Y-tube olfactometer[6], 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 foraging[11–13]. 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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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[1,2] have speculated that 'stochastic resonance'[3] — 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 limit[4,5], and thus possibly cause harmful effects. Here we examine this question using a recent theory of Bezrukov and Vodyanoy[6] for the effect of non-equilibrium noise on a voltage detector (such as a biological ion channel[7]). 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[8]), 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:

$$\mathrm{SNR} = \frac{\frac{V_s^2}{2\Delta f_a} r(0) \exp\left(\frac{\sigma^2}{2}\right)}{2 + \frac{r(0)}{f_c} \exp\left(\frac{\sigma^2}{2}\right) \sum_{n=1}^{\infty} \frac{\sigma^{2n}}{n!\,n}} \qquad (1)$$

where $r(0)$ is the basal rate of the Poisson process, Δf_a is the bandwidth of the detector, and f_c is the corner frequency and σ the dimensionless r.m.s. amplitude of the external noise.

The SNR is a non-monotonic function of σ. 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_{rms}, the dimensionless signal amplitude[8] is $V_s = (zE_{rms}r_{cell}/k_BT)$, 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 cut-off f_c is approximately the inverse of the charging time for the membrane (less than 10 MHz) so we use $f_c = 10^7\ \mathrm{s}^{-1}$. In Fig. 1, a