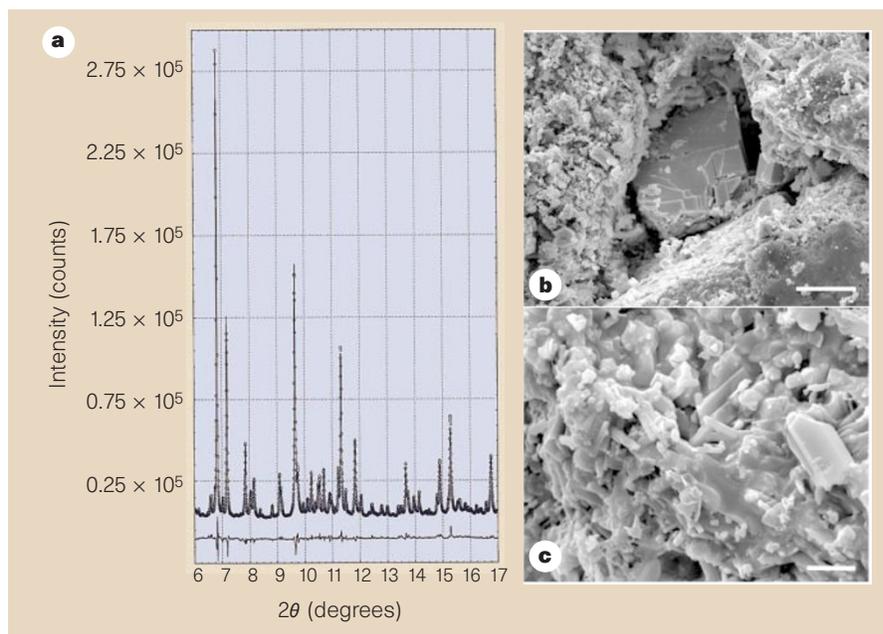


# Making make-up in Ancient Egypt

The extensive use of green, white and black make-up has been known since the earliest periods of Egyptian history<sup>1,2</sup>. We have investigated cosmetic powders dating from between 2000 and 1200 BC that were preserved in their original containers. Quantitative crystallographic and chemical analysis of the powders enabled us to identify two natural lead-based compounds: crushed ore of galena (PbS) and cerussite (PbCO<sub>3</sub>). We also found two unexpected constituents: laurionite (PbOHCl) and phosgenite (Pb<sub>2</sub>Cl<sub>2</sub>CO<sub>3</sub>). Because they are neither natural extracted ores nor products resulting from subsequent ageing or chemical modification, laurionite and phosgenite appear to be synthetic products manufactured by the Egyptians using 'wet' chemistry.

The cosmetic powders were exceptionally well conserved in containers made of stone (alabaster, haematite, marble), ceramic, wood and reed, which are housed in the Egyptian department of the Louvre Museum in Paris<sup>3</sup>. The powders contained the lead chloride compounds laurionite and phosgenite (Fig. 1a), which are both very rare in nature. They are found as corrosion products of lead artefacts<sup>4</sup> or in lead slags from ancient silver-mining operations that have been weathered by sea water<sup>5</sup>.

Phosgenite is naturally formed by the oxidation of minerals containing lead, but only in those few locations where the ore comes into contact with carbonated and chlorinated waters. Provided that such natural products were extracted, their abundance is far too small to account for their extensive use in cosmetics over a period spanning at least eight centuries (Table 1). Even if running water provided chlorides, chemical weathering of the powders in their original containers is also an unlikely source of these compounds, as the reed containers are very well preserved and some have intact hieroglyphics in black ink describing their contents. Moreover, no foreign cations or identified chlorinated phases could be detected in the powders, and the coarse galena grains have cleaved faces that are free of any surface damage



**Figure 1** Analysis of cosmetic powders. **a**, X-ray diffraction patterns for powder sample 4. Circles, experimental data points; top trace, calculated by Rietveld refinement; bottom trace, difference (observed minus calculated). **b**, Scanning electron micrograph (SEM) of sample 5. Compounds of lead and chloride are aggregated with cubic crystals of galena that have well developed faces free of alteration. Scale bar, 20  $\mu\text{m}$ . **c**, SEM of sample 5. Laurionite grains have a fine morphology, Scale bar, 2  $\mu\text{m}$ .

(Fig. 1b). The alteration of natural lead minerals within the make-up is therefore unlikely. The presence of large amounts of laurionite and phosgenite in the Egyptian cosmetics cannot therefore be explained by weathering or alteration. This evidence indicates that laurionite and phosgenite were synthesized artificially.

Support for this statement comes from recipes of medicinal products reported by classical authors<sup>6,7</sup> in which purified silver foam (PbO) was crushed and mixed in water with rock salt and sometimes natron (mainly Na<sub>2</sub>CO<sub>3</sub>) and then filtered; the procedure was repeated every day for several weeks. We repeated these chemical reactions in our laboratory by mixing PbO and NaCl powders in carbonate-free water. The corresponding slow reaction produces an alkaline solution that can be maintained at a neutral pH to simulate the daily replacement of water. The end precipitate was then

identified as laurionite by X-ray diffraction. Analysis of scanning electron micrographs reveals that our crystals and the Egyptian ones (Fig. 1c) have a similar fine morphology. It should be pointed out that, in the presence of carbonates, the reaction produces phosgenite<sup>4</sup>.

Taken together, these results indicate that laurionite and phosgenite must have been synthesized in Ancient Egypt using wet chemistry. The Egyptians manufactured artificial lead-based compounds, and added them separately to the cosmetic product. The underlying chemical reactions are simple, but the whole process, including many repetitive operations, must have been quite difficult to achieve.

Analysis of the organic constituent of the powders shows the presence of significant amounts of fatty acids. A variable amount (up to 7%) of lipids, identified by gas chromatography, was presumably added to the dry powder to yield a variety of textures (see Supplementary Information). The choice of the original minerals, the subsequent chemical process, the variable proportions of the mineral components, and the addition of lipids enabled the Egyptians to produce a wide range of cosmetics for specific purposes. Hieroglyphic inscriptions found on reed receptacles kept in a wooden box (from the XVIIIth dynasty) make a distinction between the one containing the black make-up 'mesdemet' and

**Table 1** Proportion of the four main mineral phases

Sample	Galena	Cerussite	Phosgenite	Laurionite
1	100			
2	50	13	37	
3	28	48	24	
4	43	27	29	1
5	12		72	16
6	62	28		10
7	24	25	16	35

Data were obtained by Rietveld refinement of the powder diffraction patterns. The samples were taken from containers made of alabaster (samples 1, 5, 6 and 7) and reed (samples 2, 3 and 4). See Supplementary information for a more detailed description.

two others with “eye lotion to be dispersed, good for eyesight”. Analysis<sup>8</sup> has shown that the former product was galena and the latter were mixtures of lead chloride and carbonate. Moreover, Egyptian medical papyrus lists one hundred recipes for treating problems of the eyelids, iris and cornea, as well as trachoma and conjunctivitis. Some of these materials have been identified as malachite, galena and their derivatives, although several others have not yet been identified<sup>9</sup>.

Fire-based technology has been used to manufacture Egyptian blue pigments since about 2500 BC (refs 1,2). We have now shown that wet chemistry was used as long ago as 2000 BC. This finding shows that the chemical technology of Ancient Egypt was more sophisticated than previously thought.

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Supplementary information is available on Nature's World-Wide Web site (<http://www.nature.com>) or as paper copy from the London editorial office of Nature.

## Josephson effect and a $\pi$ -state in superfluid $^3\text{He}$

Evidence has been reported for Josephson-type behaviour in the flow of superfluid helium-3 ( $^3\text{He}$ ) through an array of 4,225 apertures<sup>1,2</sup> and for a metastable  $\pi$ -state at low temperature<sup>3</sup>. Here we show that an array of holes cannot be expected to act as a single weak link in such a system, and that these results can be explained without invoking the superfluid analogue of the much-debated ‘ $\pi$ -junction’ in other systems.

Convincing experimental evidence for the Josephson effect in superfluid  $^3\text{He}$  was first reported ten years ago<sup>4,5</sup>. The mass current  $J$  and the quantum-mechanical phase difference  $\Delta\phi$  across a single microscopic orifice are well represented by the relations  $J = J_c \sin \zeta$ , and  $\Delta\phi = \zeta + \alpha \sin \zeta$ , where  $J_c$  is the critical current,  $\zeta$  is an auxiliary phase angle and  $\alpha$  is a non-ideality parameter. These relations describe both the ideal Josephson regime,  $\alpha \approx 0$ , observed close to the superfluid transition temperature, and the phase-slippage regime,  $\alpha > 1$ , which occurs at lower temperatures. This relation is represented by the solid line in Fig. 1a for  $\alpha = 2$ . In this hysteretic regime, the current is double-valued around  $\Delta\phi = \pi$ . In an array of holes, if half of the holes sit on the upper branch,  $J_+$ , and the other half sit on the lower one,  $J_-$ , the measured current through the array is  $(J_+ + J_-)/2$ , as represented by the dotted line in Fig. 1a. Numerical simulations indicate that a suitable excitation drive can set an array of holes into this state.

The time evolution of the membrane displacement,  $X$ , monitoring the flow through an array of  $N$  apertures, is obtained by solving numerically the set of equations

$$\Delta\phi = \zeta_i + \alpha_i \sin \zeta_i, \quad (1)$$

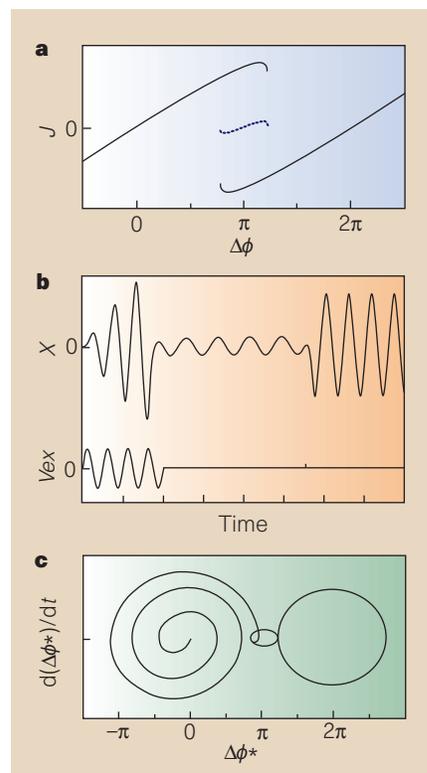
$$dX/dt = C \sum_{i=1}^N \sin \zeta_i, \quad (2)$$

$$\frac{d(\Delta\phi)}{dt} = V \sin(\omega t) - X - \frac{1}{\omega_0 Q} \frac{dX}{dt} \quad (3)$$

where  $C$  is related to the small signal oscillation frequency,  $\omega_0^2 = C \sum_{i=1}^N (1/\alpha_i)$ ,  $V \sin(\omega t)$  is the external drive of maximum amplitude  $V$  at frequency  $\omega$ , and  $Q$  is the quality factor of the resonator.

The result of such a simulation is shown in Fig. 1b. We used 200 holes with a gaussian distribution of  $\alpha_i$  values with mean value 2 and standard deviation 0.1. Apertures in different regions of the array experience different series hydraulic inductances, and the spread in  $\alpha_i$  in the previous experiments<sup>1–3</sup> could actually be larger. The  $Q$  value of the resonator was set at 1,000. The external drive,  $V \sin(\omega t)$  in equation (3), was made of four periods at a frequency  $\omega = 1.1\omega_0$  and the amplitude was adjusted until a stable low-amplitude state was reached. In this state, about half of the holes have experienced a phase slip. The kinetic energy is then stored in the circulating currents in the array and a small perturbation can drive the system out of this state, in one direction or in the other, as shown in Fig. 1b for a positive perturbation.

A plot of  $d(\Delta\phi^*)/dt$ , defined as  $-X(t)$ , versus  $\Delta\phi^*$ , defined as  $-\int_0^t X(t)dt$ , is represented in Fig. 1c. According to equation (3), these  $\Delta\phi^*$  are not the true  $\Delta\phi$ , but such a procedure was used to plot Fig. 3a in ref. 3,



**Figure 1** Numerical simulations. **a**, Current–phase relationship for  $\alpha=2$ . Dotted line, artefact of the measurements in an array of holes discussed in the text. **b**, Time evolution of the membrane amplitude  $X$  in response to an external drive  $V_{ex}$ . **c**, Corresponding trajectory in the  $d(\Delta\phi^*)/dt$  versus  $\Delta\phi^*$  plane.

with which our numerical data must be compared. The agreement with real data is striking, taking into account that there is neither noise nor filtering in the simulated data.

With these input parameters, the excitation window leading to a stable low-amplitude state is very narrow. Slight variations in the distribution of  $\alpha_i$ , in the shape of the applied drive, or in the details of the current–phase relationship around  $\pi$  could widen this window.

In conclusion, our analysis shows that direct measurements of the current–phase relationship in an array of holes should be interpreted with care. The data in refs 1–3 can be reproduced by simple numerical simulations that involve only physical mechanisms previously demonstrated to take place in a single aperture. By themselves, these data do not reveal the existence of an exotic  $\pi$ -junction, hidden degrees of freedom, or any influence of textural effects.

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