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News and Views

Material witness: Birth of the blues

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Painters wanted a cheap source of ultramarine blue ever since the natural pigment, made from the semiprecious stone lapis lazuli, was first exported east and west from the famous mines of Badakshan in Afghanistan — a process that seems to have been under way at least by the 6th century, when the pigment appears in Byzantine manuscripts.

So when the French chemist Jean-Baptiste Guimet found a way to synthesize ultramarine in 1826, it should have been cause for rejoicing among artists. Indeed, it appears Dominique Ingres was pleased enough: Guimet attested the following year that "M. Ingres who is an excellent judge in these matters has repeatedly assured me that my ultramarine leaves nothing to be desired."

But other painters were less easily persuaded that their finest pigment could be reproduced by a chemist. In England, J. M. W. Turner seems to have resisted using the artificial pigment in his oil paintings, and it is said he was deterred from helping himself to a blob of blue on the palette of another artist, during the 'varnishing days' at the British Royal Academy when works hung for display were given the final touches, by the cry that it was 'French'.

No one was quite as dismayed as Christian Gottlob Gmelin, professor of chemistry at Tübingen. If he'd had his way, synthetic ultramarine would have been known not as French but as German. Gmelin devised a synthesis independently, probably in 1827, and was incensed when Guimet was awarded the prize of 6,000 francs offered by the Société d'Encouragement pour l'Industrie Nationale in 1824 for an industrial route to ultramarine. The story of controversy and industrial secrecy is recounted by Joost Mertens of the University of Maastricht (*Ambix* **51**, 219–244; 2004).

The remarkable thing about ultramarine, which 19th-century chemists were reluctant to accept, is that the rich blue colour is not produced by a metal ion. Rather, it is the result of electronic transitions of polysulphur ions encaged in the sodalite framework of a sodium aluminosilicate. So sulphur is an essential ingredient: Guimet's and Gmelin's syntheses are similar, involving baking a mixture of china clay (the aluminosilicate kaolin), soda, charcoal, quartz and sulphur.

But the 19th-century arguments might be in some sense moot, judging from a recent analysis of ancient Chinese glazed beads (H. Berke *et al. Proc. 2nd Int. Conf. Conservation of Grotto Sites* Getty Conserv. Inst.; in the press). This reveals ultramarine in artefacts from the late Western Zhou dynasty, around the 8th century BC: about a thousand years before the first known reports of ultramarine in Chinese art, which is

assumed to have been imported along the Silk Road from Afghanistan. The pigment was mixed with other blues in a glaze formed from calcium and barium copper silicates, which are evidently synthetic materials related to Egyptian blue. It seems likely that sulphate impurities in the raw materials and charcoal in the kilns may have led to the inadvertent synthesis of ultramarine — yet another technological 'first' for China.