Current need for identifying and preserving pigments in the prehistoric cave paintings of India

The history of cave paintings in India ranges from the upper Palaeolithic to the early historic period. There are more than 10,000 locations in the country where these cave paintings can be found[1]. The remnants of rock shelter arts are found on sandstone or sedimentary rocks of Karnataka and Andhra Pradesh[2]. In North India, many rock engravings are in the upper reaches of the Karakoram Hills and Zanskar Valley. Several rock paintings are reported in Varanasi, Prayagraj and Agra, Uttar Pradesh[3]. In Eastern India, Odisha has the richest repository of rock arts. The Bhimbetka group of rock shelters in Madhya Pradesh is one of the most famous rock arts of the country and is a World Heritage Site. The scenes reflected in these paintings usually depict hunting and dancing humans, and fighting animals like antelopes, bisons, lions and tigers[4] (Figure 1). Though archaeologists have extensively interpreted the cave arts, systematic scientific studies are lacking on the use of paints and pigments in these engravings. These painted figures were found to be done in monochrome, mostly in red and white, or sometimes a combination of different colours. Even though the paints are durable, efforts must be undertaken to preserve them from fading as they are directly exposed to rainfall, sunlight and various anthropological activities from time immemorial.

Palaeolithic artists used two colour pigments or 'ochres' dominantly in their paintings. These were natural black (charcoal or manganese oxide) and natural red (hematite or heated goethite). To prepare the ochre pigments, the materials were finely grounded and mixed with water. The heavier granules settled at the bottom, leaving the coloured oxides as suspension[5]. The pigments were then mixed with a binder of plant or animal origin for further processing. The ancient people clearly understood particle size and the use of fluids to separate pigments by density. Many of these mineral pigments were mined from rocks near the settlements. In the Lascaux cave of France, red and yellow haematite ochres were used, while in Altamira, Spain, red haematite was dominantly used[6]. In Provence, southern France, haematite along with bauxite was used[7]. The minerals used in these paintings were usually found in local areas or were transported from far-away places. This indicates that these pigments might be traded over large distances.

Apart from mineral pigments, organic binders or colourants were used in some of the wall paintings in the Asian cultures from the late Bronze Age to the Roman era[8]. Arrays of organic binders have been reported from paintings of the Greek–Roman age to the Renaissance[9]. However, organic colourants were in restrictive use as they were expensive. The Getty Conservation Institute, USA and Dunhuang Academy, China, jointly surveyed the organic colourants used in different rock paintings of Asia during 2006–2010. The information generated and spectral database helped to identify the organic compounds used in the paintings of Mogao caves, Dunhuang, China[10]. A survey of the scientific literature from India revealed that the use of organic colourants in wall paintings has a long tradition as compared to European cultures[11]. Yü *et al.*[12] catalogued the organic colourants used in ancient Chinese paintings. The extensive use of organic colourants in Asia might be due to the major distribution and availability of raw natural materials in this region.

Anthraquinones were the most important group of red colour dyes extracted from the roots of the madder plants (*Rubia tinctorum*, *Rubia peregrina* and *Rubia cordifolia*)[13] and the scale insect (*Kermes vermilio* or *Kerria lacca*), popularly the Indian lac or lac dye. They were typically available in India and Southeast Asia, and considered expensive. The use of these materials has been recently reported by Osticioli *et al*.[14] in the famous painting of Leonardo da Vinci, viz. *The Last Supper*. There are descriptions of the import of lac from India to the Mediterranean basin by Aceto[10]. Apart from the anthraquinone dyes, extracts from the bark of *Caesalpinia sappan* (Southeast Asian origin), *Caesalpinia echinata* and *Haematoxylum brasiletto* (South American species) were widely used in the 14th-century choir screens at Cologne Cathedral, Germany. Safflower red was extracted from *Carthamus tinctorius* and found to be used in the caves of Mogao, China.

Jorge-Villar *et al.*[15] identified green colour in some rock paintings, which was an admixture of blue colour with a dye extracted from *Reseda luteola*. Akrawi and Shekede[16] reported a yellow organic matrix in the wall paintings of Petra, Jordan. The plant extract of *Flemingia macrophylla* was used to extract Asian orange dye. The Indian yellow was produced from cows' urine[17]. Gamboge, a yellow dye, was isolated from the latex of the *Garcinia* species. Some green dyes were prepared from the petals of *Iris germanica*, and the sap and ripe berries of *Rhamnus cathartica*.

Identifying organic colourants on wall paintings is generally more complex than inorganic colourants. The analysis of colourants from the paintings will provide information on their composition, preparation and geographic origin. The application and employment of powerful microinvasive chromatographic techniques (SERS, HPLC-MS, GC-MS, DAD, FTIR) will help to identify the use of metabolites in these wall paintings. This will subsequently provide more information on the artistic techniques, design, biological sources and trade routes, as well as the use of different colourants in the cave paintings. Organic compounds have lower physical and chemical stability with high molecular extinction

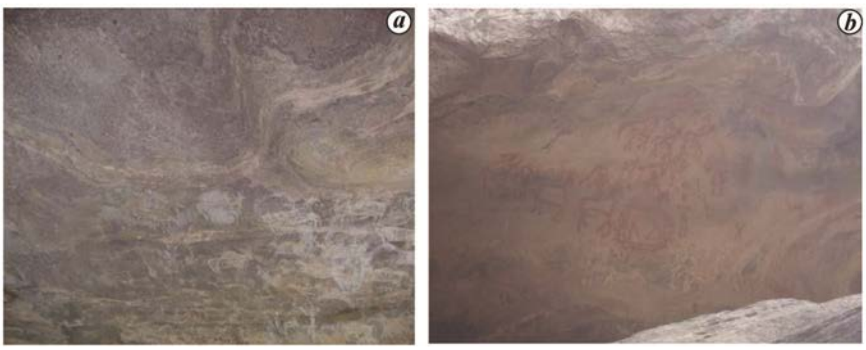

Figure 1 ***a*, *b*.** Cave paintings of Bhimbetka rock shelters, Madhya Pradesh, India.

coefficients. An effective and efficient strategy must be used for the heritage paintings of India in view of their chemical composition and long-term preservation; otherwise they will permanently fade.

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Coloured bivalves from the Middle Eocene of Kutch, India

Fossiliferous, shallow marine Palaeogene rocks are well exposed in Kutch, Gujarat, India[1]. Among diverse Paleogene fossils of Kutch, the Middle Eocene bivalves have been studied by several workers in the context of systematics, ontogeny and biostratinomy[2–5]. In the present study, we report pigment-bearing Middle Eocene ostreid bivalve *Flamingostrea* sp. Vredenburg from western Kutch (Figure 1). The previously reported coloured mollusc from Kutch was from the Jurassic age[6].

Spats (L = 0.54–1.13 cm, H = 0.52–1.37 cm) of pigment-bearing *Flamingostrea*[5] were collected from the *obtusus* bed (a marker bed) occurring in the upper part of the Harudi Formation[1] in Harudi village (23°30′30″, 68°41′10″), western Kutch (Figure 2). The present collection consists of 25 pigment-bearing, dissociated, left-valve specimens of *Flamingostrea*. This bivalve grows by cementing its left valve on a hard substratum. Tests of larger foraminifera *Nummulites obtusus* (Sowerby) Form B are commonly used as a substrate by *Flamingostrea*[5]. The attachment site of the left valve is markedly thin compared to the rest of the valve. The pigment-bearing valves of *Flamingostrea* exhibit various shades of red colour; darker specimens exhibit deep purple colour. The shell coloration is restricted to the inner surface of the valves. Portions of the valves lacking the pigment appear dull brown. External factors such as taphonomic iron staining of the *Flamingostrea* specimens may be ruled out as a possible cause for valve colouration because such staining would equally affect both the inner and outer surfaces of the bivalve along with the foraminiferal substrate[7]. In this context, it may be noted that the outer valve surface of the bivalve and the foraminiferal substrate are devoid of colour and appear dull brown. Platinum-coated SEM study of the pigment-bearing *Flamingostrea* specimens revealed the presence of preserved, elongated, block-like melanosomes within the valve (Figure 3). Such melanosomes are conspicuously absent in the non-pigmented shells (Figure 4).

In fossilized shells spanning the entire Phanerozoic, pigment preservation has been a rare phenomenon[8]. Traces of original pigment could be preserved as molecular fossil[9]. Shell pigments in the living molluscs are considered as metabolic waste that gets incorporated within the shell[10,11]. It has been observed that in the present-day gastropod *Haliotis asinine*, pigments originate from the invaginations of the epithelial

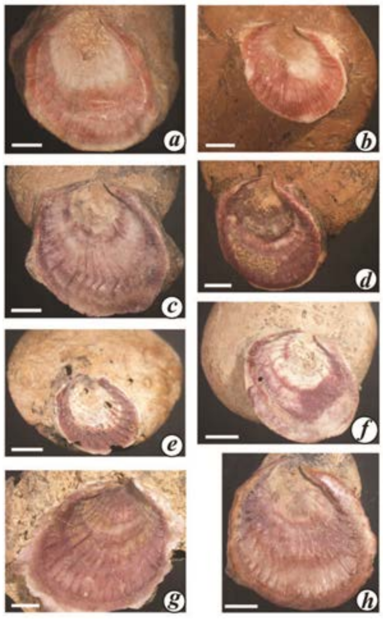

Figure 1. Various shades of red colour preserved in the left valve of *Flamingostrea* sp. Specimens collected from the *obtusus* bed of Harudi Formation, Harudi village area, western Kutch, Gujarat, India. ***a–f***, ***h***, *Flamingostrea* sp. attached to larger foraminifera *Nummulites obtusus* (Sowerby) Form B. ***g***, *Flamingostrea* sp. attached to a broken bioclast (fragmented bivalve?). Specimens in (***a***) and (***e***) were earlier illustrated in grey scale[5]. Scale bar = 2 mm for all figures.