

Assessing the photoprotective effects of red ochre on human skin by in vitro laboratory experiments

AUTHORS:

Riaan F. Rifkin^{1,2}
 Francesco d'Errico^{1,3}
 Laure Dayet-Boulliot³
 Beverley Summers⁴

AFFILIATIONS:

¹Institute for Archaeology, History, Culture and Religion, University of Bergen, Bergen, Norway
²Evolutionary Studies Institute, University of the Witwatersrand, Johannesburg, South Africa
³CNRS-UMR 5199 PACEA, Préhistoire, Paléoenvironnement, Patrimoine, University of Bordeaux, Talence, France
⁴Photobiology Laboratory, Department of Pharmacy, University of Limpopo, Pretoria, South Africa

CORRESPONDENCE TO:

Riaan Rifkin

EMAIL:

riaanrifkin@gmail.com

POSTAL ADDRESS:

AHKR, University of Bergen, Oysteingate 3, Bergen Hordaland 5020, Norway

DATES:

Received: 12 June 2014

Revised: 04 Aug. 2014

Accepted: 05 Aug. 2014

KEYWORDS:

red ochre; Ovahimba; Middle Stone Age; UVR; sunscreen; in vitro SPF assessment; visible spectroscopy

HOW TO CITE:

Rifkin RF, d'Errico F, Dayet-Boulliot L, Summers B. Assessing the photoprotective effects of red ochre on human skin by in vitro laboratory experiments. *S Afr J Sci.* 2015;111(3/4), Art. #2014-0202, 8 pages. <http://dx.doi.org/10.17159/sajs.2015/20140202>

© 2015. The Author(s).
 Published under a Creative Commons Attribution Licence.

Archaeological indicators of cognitive complexity become increasingly prevalent during the African Middle Stone Age, with the habitual exploitation of red ochre widely viewed as a key feature of the emergence of modern human behaviour. Given that some of the uses of ochre remain ambiguous, we present the preliminary results of an ongoing study in which we explore the efficacy of red ochre as a photoprotective device or sunscreen. The capacity of ochre to inhibit the susceptibility of humans to the detrimental effects of ultraviolet radiation was confirmed through the in vitro calculation of the sun protection factor values of samples derived from the Kunene Region in Namibia and the Bokkeveld Group deposits, Western Cape Province, South Africa. Visible spectroscopy was employed to determine colourimetric parameters of samples and assess the correlation between ochre colour and sun protection factor. The possible role of ochre as a sunscreen agent for hominin populations, including modern humans, during the Middle Stone Age in Africa is explored. We conclude that the habitual use of red ochre as a photoprotective agent likely played a role in the ability of prehistoric humans to adapt to novel environmental circumstances.

Introduction

Environmental variables have been shown to exert a substantial influence on ecosystems, communities and populations.^{1,2} Of the various climate-driven selective pressures that operated during the evolutionary history of *Homo sapiens* in Africa, negotiating the risks and benefits of persistent exposure to sunlight presented an enduring challenge. Most important in terms of human health are longwave ultraviolet A (UVA) (400–315 nm) and medium-wave ultraviolet B (UVB) (315–280 nm) radiation.³ Excessive UVA exposure results in DNA damage, skin aging and mild erythema, whereas UVB is responsible for sunburn with subsequent DNA damage and skin cancers. Shortwave UVC (280–200 nm) is potentially the most dangerous type of UV radiation (UVR) for humans, but is largely absorbed by the ozone layer.⁴

Sunlight is an essential environmental factor in most ecosystems and the beneficial effects of moderate exposure to sunlight are well known.⁵ Positive correlations exist between adequate UVR exposure, vitamin D synthesis, calcium absorption and human fertility.⁶ Vitamin D (1.25 dihydroxyvitamin D₃) in turn reduces the incidence of rheumatoid arthritis, coronary heart disease, diabetes, multiple sclerosis, osteomalacia, rickets, schizophrenia, autoimmune diseases and also several types of cancer.⁷ Conversely, excessive UVR exposure can lead to malignant skin diseases including cancer and mitochondrial (mtDNA) and nuclear (nDNA) molecule damage.^{8,9}

It has furthermore been proposed that excessive UVR may have had far-reaching effects on mammalian evolutionary processes. UVR has been implicated in several extinction events, including the disappearance of megafauna during the late Pleistocene^{10,11} and the extinction of a number of hominin species^{12,13}. These hypotheses are difficult to test because of the uncertainties concerning the dating of extinction events and in calculating the impact of UVR changes at different latitudes and among different populations. The absence of the MC1R gene variant (R307G) in analysed Neanderthal and Denisovan genomes further indicates that extensive variability in skin colour existed among archaic hominids, and that at least some of these individuals had darker and therefore more UVR-resistant skin tones.^{14,15} Fluctuations in UVR may nevertheless have generated a selective pressure on human populations, which could have influenced the life expectancy, particularly in the case of colonisation of different territories or altitudes within a given region, of at least some individuals within such populations.

Ultraviolet radiation protective mechanisms

Several theories have been proposed to explain the variation in human skin pigmentation.^{16,17} At present, the most widely accepted factor explaining the geographic distribution of autochthonous human skin pigmentation is UVR exposure.¹⁸ Evidence for natural selection operating at low latitudes (establishing and maintaining dark pigmentation under high UVR conditions) and high latitudes (which favours the development of light pigmentation under low UVR conditions), suggests that human skin colouration is a Darwinian adaptation.^{7,16} The gradient of skin colours observed from the equator to the poles consequently results from two clines operating over a spatially varying optimum of UVR distribution.¹⁹ The association between skin pigmentation in indigenous populations and latitude is therefore traceable to the correlation between skin colour and the intensity of UVR exposure.

That darker skin pigmentation conferred significant adaptive benefits is confirmed by the preservation, amongst modern human populations, of the MC1R, SLC45A2 and 70 other genetic mutations at loci implicated in pigment production.^{17,20} Unlike SLC45A2, which occurs only amongst Europeans, the SLC24A5, TYRP1 and KITLG mutations are present in a number of sub-Saharan populations. Although these alleles in all probability arose within and spread from Africa during early modern human migrations, some may result from a series of admixture events with groups containing Eurasian genetic ancestry.²¹

In behavioural terms, cultural innovations seeking to reduce the impact of UVR, such as the topical application of powdered clays including ochre, could also have reduced the pressure induced by increasing exposure to UVR. Changes in climate and ecology have been shown to provoke speciation and extinction²² and it has been proposed that these may have acted as selective pressures for enhanced cognition^{23,24}. Given that darker-skinned individuals

are also susceptible to the harmful effects of UVR,¹⁹ the development of effective sun-protection strategies may have been essential in prehistory.

Ochre as a sunscreen

Ochre is a pervasive artefact in historical, Iron Age, Later Stone Age (LSA) and Middle Stone Age (MSA) contexts throughout southern Africa. The term 'ochre' is widely used by archaeologists to designate any earthy materials comprising anhydrous iron (III – ferric or Fe³⁺) oxide such as red ochre (which includes unhydrated haematite or Fe₂O₃) and partly hydrated iron (III) oxide-hydroxide such as brown goethite (FeO(OH)).^{25,26}

The habitual exploitation of red ochre by *H. sapiens* has been interpreted as evidence for colour symbolism²⁷, as a proxy for the origin of language^{27,28} and as an essential element of symbolic and fully modern human behaviour^{29,30}. Although the collection and processing of ochre is not limited to our species^{31,32}, the routine exploitation of red ochre may represent a species-specific behavioural trait for *H. sapiens*^{27,28}.

There is sufficient archaeological evidence for the use of red ochre as a body cosmetic during the MSA. Examples comprise the adherence of red ochre residues to perforated marine shell beads derived from African MSA and Levantine Mousterian contexts dated from 92 000 years ago (ka) to 60 ka.³²⁻³⁴ As strung beads are generally worn around the neck or wrists,³⁵ these residues almost certainly derive from direct contact with red pigments applied to human bodies. But because evidence regarding the exact motives for red ochre exploitation during the MSA and LSA is not freely available, diverse interpretations for its usage have been proposed. The most familiar explanation concerns the use of red ochre as a body decoration in largely symbolic contexts.²⁷ In the absence of direct evidence, this inference is based largely on an analogy with modern hunter-gatherer societies.^{36,37} Red ochre was also used as a constituent in paint³⁸, for knapping stone implements³⁹, as an element in lithic hafting mastics⁴⁰ and possibly as a hide-processing ingredient⁴¹.

Ethnographic accounts illustrating the use of red ochre as a cosmetic substance have been reported for southern African San hunter-gatherers³⁷, Tswana³⁶ and Xhosa⁴² agro-pastoralists and also Khoe pastoralists⁴³. While these examples relate largely to the intermittent topical application of red ochre in symbolic contexts, foremost modern examples of the habitual use of red ochre as a body cosmetic comprise the Cushitic-speaking Hamar in Southern Ethiopia⁴⁴ and the Ovahimba of northwestern Namibia (Kunene Region; Figure 1) and southwestern Angola (Kunene and Namibe Provinces)^{45,46}.

Ovahimba women are renowned for covering their bodies, hair and personal attire with a red ochre-based substance (Figure 2). This substance is known as *otjise* and is comprised of clarified butter (*omaze uozongombe*) and red (*otjiserundu*) ochre powder. Ochre powder is produced by crushing and grinding ochre chunks between round upper and flat lower grinding stones. Clarified butter is produced by shaking cream-rich milk in a *Lagenaria* sp. calabash gourd to separate fatty substances from the watery solution. The extract is boiled in an iron pot above an open fire and the resultant greasy substance is recovered and stored. Whereas ochre processing forms part of the sociable settings of daily life, the application of *otjise* occurs in the confines of women's huts. *Otjise* also features prominently in initiation ceremonies, is applied by men when they are to be wed or undertake long journeys and is applied to human corpses prior to interment.^{45,47} Ethnographic interviews recently conducted amongst the Ovahimba furthermore reveal that, besides the intrinsic social and inexorably symbolic significance of *otjise*, it also fulfils several secondary functions, including that as a topical sun-protection element or sunscreen.

Materials and methods

Ochre

We used 24 ochre samples derived from ethnographic and non-archaeological geological sources likely to have been exploited during the MSA. Of these samples, 12 were collected from the Okamanga,



Figure 1: The location of the Kunene Region of northern Namibia within southern Africa.



Photos: Riaan F. Rifkin

Figure 2: The production and application of *otjise*. (a) Red ochre powder is obtained by grinding chunks between a round upper and a flat lower grindstone, (b) after which it is mixed with milk-derived clarified butter and (c) applied to the hair, body and ornaments.

Ovinjange and Otjongoro villages in the Kunene Region of northern Namibia. Half of these samples (Samples 1–6) were processed into powder by Ovahimba women. Samples 7–12 were acquired in Opuwo and were processed experimentally by direct grinding onto a coarse quartzite stone surface. This method closely resembles the technique used to produce ochre powder during the MSA.⁴⁸ Informed consent was obtained from all research participants and the principles of the Declaration of Helsinki were strictly adhered to. Ochre Samples 13–24 – comprising yellow, grey and red specimens – were collected from the Palaeozoic Bokkeveld Group shale deposits of the Cape Supergroup (South Africa). Six of these samples were processed into powder by direct grinding onto a coarse sandstone surface, and the remaining six by way of the technique employed by Ovahimba women (Table 1).

Ultraviolet irradiation

The assessment of the efficiency of a sunscreen is based on the value of its sun protection factor (SPF), which reflects the degree of protection against UVR-induced erythema. SPF values most generally denote the efficiency of a sunscreen to protect the skin from UVB. A sunscreen with an SPF of 2 filters out 50% of UVB, an SPF of 15 filters out 93% UVB and an SPF of 50 filters out 98% UVB.^{4,49} Theoretically, the application of a product with an SPF of 5 provides sun protection for five times longer than unprotected skin.

The UVR protection capacities (SPF values) of ochre samples were established by means of a series of in vitro experiments performed on ochre samples in dry powder form. The experiments were carried out at the Photobiology Laboratory (Department of Pharmacy, Medunsa Campus) of the University of Limpopo, South Africa.⁵⁰ A calibrated multipoint solar simulator (Solar Light Co., Glenside, PA, USA) was used as the UV irradiation source. In accordance with the SANS 1557/ISO 24444 SPF testing protocol, ochre powder samples were applied to Transpore[®] tape at a ratio of 2 mg/cm² and analysed in compliance with the SANS 1557:1992 procedure. Although Ovahimba women typically apply 4.2 mg *otjise* per cm², it was decided to adhere to the standard 2 mg/cm² ratio to acquire comparable SPF values. Actual SPF values are therefore likely to be significantly higher than the results reported here. Critical wavelength was determined using the Optometrics SPF 290 method. The critical wavelength is that below which 90% of the UV protection

is situated and the higher the critical wavelength, the higher the UVA protection ranges of the products.

Visible spectroscopy

It has been shown that clays exhibiting high UVR protection rates and low UVR-transmission values are most generally red.⁵¹ To determine whether colour does in fact play a role in the UVR reflectance and absorption capabilities of ochre, visible spectroscopy was employed to obtain L*a*b* values for each sample. An Avantes AvaSpec 2048 spectrometer (Avantes Inc., Broomfield, CO, USA) equipped with a 2048-pixel charge-coupled device detector, and set to operate in the retrodiffusion mode, was used for this purpose. This instrument is fitted with an optical fibre probe which is positioned 2 mm from the sample surface at an angle of 2°. An AvaLight-HAL illumination source (Avantes Inc., Broomfield, CO, USA) was used. The equipment was calibrated with a Halon D65 white reference sample in the same lighting conditions as for the archaeological samples. The colour parameters were obtained by Avasoft 7.5 software.

Results

Sun protection factor assessment

The in vitro SPF values of experimental ochre samples ranged from 1.9 (±0.1) to 13.1 (±1.3). The yellow (13 and 19) and grey (14 and 20) samples had the lowest in vitro SPF values, and the red samples the highest. When compared by processing method, samples processed by Ovahimba women had the highest mean SPF (8.9±1.2), those experimentally ground directly onto a grindstone had a mean SPF of 6.2±2.4 and those ground using the method employed by Ovahimba women had a mean SPF of 3.4±0.8. When comparisons were made of the direct grinding method (onto a coarse stone surface) and the simulated traditional grinding method (that employed by the Ovahimba), the former produced in vitro SPF values of the order of 0.5 to 4.0 units higher than the latter. The critical wavelengths of the samples are comparable, falling within the range of 387.7–390.0 nm. In contrast to the increase in SPF produced by the direct grinding method when compared with the simulated traditional method, the critical wavelengths are marginally lower (± 1 nm) in the directly ground samples (Table 2).

Table 1: Experimental ochre samples subjected to in vitro ultraviolet radiation analyses

Sample	Source	Description	Processing method
1	Okamanga	Ground red ochre powder	Ethnographically ground (by Ovahimba)
2	Okamanga	Ground red ochre powder	Ethnographically ground (by Ovahimba)
3	Okamanga	Ground red ochre powder	Ethnographically ground (by Ovahimba)
4	Okamanga	Ground red ochre powder	Ethnographically ground (by Ovahimba)
5	Ovinjange	Ground red ochre powder	Ethnographically ground (by Ovahimba)
6	Otjongoro	Ground red ochre powder	Ethnographically ground (by Ovahimba)
7	Opuwo	Fine-grained red ochre	Ground directly onto quartzite slab
8	Opuwo	Fine-grained red ochre	Ground directly onto quartzite slab
9	Opuwo	Fine-grained red ochre	Ground directly onto quartzite slab
10	Opuwo	Fine-grained red ochre	Ground directly onto quartzite slab
11	Opuwo	Fine-grained red ochre	Ground directly onto quartzite slab
12	Opuwo	Fine-grained red ochre	Ground directly onto quartzite slab
13	Napier	Soft yellow limonite	Ground directly onto quartzite slab
14	Bredasdorp	Soft grey shale	Ground directly onto quartzite slab
15	Napier	Medium hard red shale	Ground directly onto quartzite slab
16	Napier	Medium hard red shale	Ground directly onto quartzite slab
17	De Hoop	Soft light red shale	Ground directly onto quartzite slab
18	Cape Point	Hard orange shale	Ground directly onto quartzite slab
19	Napier	Soft yellow limonite	Experimentally ground (like Ovahimba)
20	Bredasdorp	Soft grey shale	Experimentally ground (like Ovahimba)
21	Napier	Medium hard red shale	Experimentally ground (like Ovahimba)
22	Napier	Medium hard red shale	Experimentally ground (like Ovahimba)
23	De Hoop	Soft light red shale	Experimentally ground (like Ovahimba)
24	Cape Point	Hard orange shale	Experimentally ground (like Ovahimba)

Table 2: Sun protection factor (SPF) values of ethnographic and experimental ochre powder samples obtained by in vitro analyses

Sample	Source	Colour	SPF	σ	UVAPF	σ	Critical wavelength (nm)	σ
1	Okamanga	Dark red	13.1	1.1	4.0	0.3	389.2	0.1
2	Okamanga	Dark red	8.6	0.6	8.0	2.7	389.1	0.1
3	Okamanga	Dark red	6.8	0.5	3.5	0.4	389.6	0.0
4	Okamanga	Dark red	7.0	0.9	3.4	0.4	389.6	0.3
5	Ovinjange	Dark red	12.4	2.6	13.7	2.8	389.4	0.0
6	Otjongoro	Dark red	6.3	1.3	6.3	1.3	389.5	0.1
7	Opuwo	Dark red	10.5	3.9	11.5	3.7	389.4	0.2
8	Opuwo	Dark red	7.3	3.2	8.8	3.5	389.7	0.1
9	Opuwo	Dark red	5.5	0.9	6.3	0.9	389.8	0.2
10	Opuwo	Dark red	8.3	1.0	10.3	1.0	389.8	0.2
11	Opuwo	Dark red	4.0	0.5	4.7	0.4	390.0	0.0
12	Opuwo	Dark red	3.8	0.3	3.3	0.3	388.2	0.3
13	Napier	Yellow	6.4	2.2	5.9	1.9	387.7	0.3
14	Bredasdorp	Light grey	2.4	0.3	2.1	0.2	387.5	0.1
15	Napier	Light red	4.1	0.3	4.0	0.3	389.2	0.1
16	Napier	Maroon	7.7	3.1	8.0	2.7	389.1	0.1
17	De Hoop	Dark red	3.0	0.5	2.9	0.4	389.1	0.0
18	Cape Point	Orange-red	7.5	0.4	7.9	0.5	389.4	0.0
19	Napier	Yellow	5.6	0.2	5.4	0.2	388.4	0.1
20	Bredasdorp	Light grey	1.9	0.1	1.8	0.1	388.4	0.2
21	Napier	Light red	3.3	0.4	3.5	0.4	389.6	0.0
22	Napier	Maroon	3.2	0.4	3.4	0.4	389.6	0.3
23	De Hoop	Dark red	2.6	0.1	2.7	0.1	389.5	0.2
24	Cape Point	Orange-red	4.6	0.3	5.2	0.3	389.7	0.1

Colourimetry

As calculated from the $L^*a^*b^*$ coordinates (ΔE), Ovahimba ochre samples exhibit negligible differences in colour (Table 3). The colour distance between samples falls below 5 ΔE , the limit above which a colour difference is significantly perceived by humans. Ovahimba samples display the same range of hue and chroma (similar a^* and b^* values) as the other red ochre samples. Only lightness (L^*) values are dissimilar, with Ovahimba red ochres being darker. Hues are not markedly different, with the ratios of a^* to b^* being relatively constant, but the brightness of Ovahimba samples is less pronounced (Table 3).

Table 3: Colourimetric $L^*a^*b^*$ values for experimental ochre samples

Sample	Colour	L^*	a^*	b^*	Delta E
1	Dark red	39	32	30	
2	Dark red	37	29	28	4.1
3	Dark red	40	30	28	3.0
4	Dark red	37	29	28	4.1
5	Dark red	40	32	30	1.0
6	Dark red	40	31	29	1.7
7	Dark red	39	31	29	1.4
8	Dark red	41	32	31	1.2
9	Dark red	40	32	30	1.0
10	Dark red	39	31	29	1.4
11	Dark red	41	29	28	1.1
12	Dark red	46	24	21	13.9
13	Yellow	81	9	43	49.6
14	Light grey	88	-1.5	8	63.6
15	Light red	47	30	30	8.2
16	Maroon	52	28	28	18.7
17	Dark red	59	24	25	22.1
18	Orange-red	47	33	35	9.5
19	Yellow	71	11	43	40.4
20	Light grey	84	-1	8	60.0
21	Light red	46	24	21	13.9
22	Maroon	51	22	18	19.7
23	Dark red	56	19	18	24.5
24	Orange-red	42	30	30	3.6

Whereas red experimental samples display a mean SPF value of 6.9 and a UVAPF value of 6.3, non-red samples exhibit mean SPF and UVAPF values of 4.5. Given that the red ochre samples from Okamanga, Ovinjange and Opuwo exhibit higher in vitro SPF values than those derived from the Bokkeveld shales, it is likely that higher Fe_2O_3 contents correlate with increased in vitro SPF values. However, it is not only elemental composition that determines the colour of ochre.⁵² Mineralogical and elemental composition and structural morphology, including grain size and crystallography, also influence colourimetric properties.¹⁷

It has been demonstrated that different ochre processing techniques result in differences in pigment powder consistency and colour⁴⁸ – an observation confirmed in this study. Powder extracted by direct grinding

presents higher chroma (a^* and b^* values) than powder obtained by conventional grinding. Noticeable differences in colour resulting from different processing techniques are exhibited by the Napier 15 sample (ground directly onto a coarse quartzite slab as evidenced by examples from MSA and LSA contexts) and Napier 21 sample (ground between an upper and lower grindstone as done by the Ovahimba) and the Napier 16 (direct) and 22 (conventional) samples. With the exception of samples 16 and 18, SPF values increase significantly when L^* is lower than 45 (Figure 3a). However, L^* remains stable while SPF values increase. SPF values also increase when a^* is higher than 25, although a^* remains stable when SPF values increase (Figure 3b).

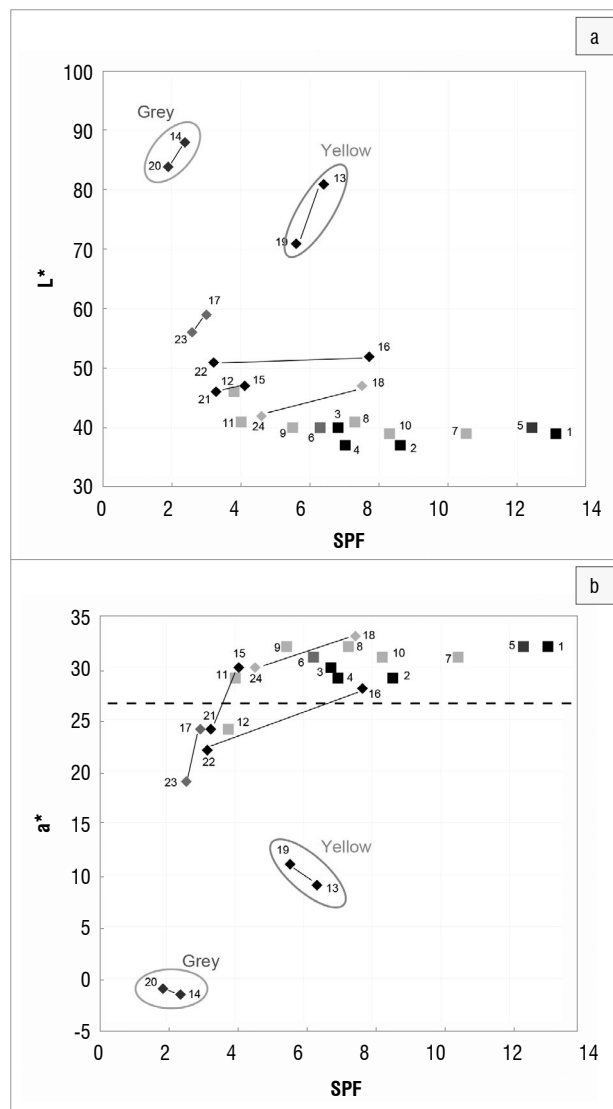


Figure 3: Bipolar plots of sun protection factor (SPF) values in relation to the colourimetric values (a) L^* (the lightness–darkness axis) and (b) a^* (the red–green axis).

Discussion

Hypotheses abound for human variation in skin pigmentation, with most models focusing on human depigmentation and not on the state of pigmentation of our hominin ancestors.¹⁶ The epidermis of most primates is unpigmented because of the absence of melanocytes, suggesting that this is the primitive condition for primates. Darker skin tones conceivably emerged as a characteristic trait of *H. erectus* ca 1000 ka, possibly because a darker complexion provided superior protection against UVR for increasingly hairless hominins. As *Homo* left the African tropics, lighter skin pigmentation evolved to facilitate the synthesis of vitamin D.⁵³ This cline of depigmentation is evident along

the southeastern edge of southern Africa, where adequate vitamin D production can occur throughout most, but not all, months of the year. In this region, the mean daily minimum erythral dose is not sufficient to produce vitamin D in darker (V and VI) skin types. Reduced UVR exposure and decreased potential for vitamin D biosynthesis therefore generated positive selection for skin depigmentation.

In addition to the incidence of lighter skin types amongst autochthonous groups along the southern and eastern coastline of South Africa and Mozambique⁵⁴, the preservation of the SLC24A5, TYRP1 and KITLG alleles amongst sub-Saharan populations²⁰ suggests that these are ancestral southern African mutations. The skin colour of southern African MSA *H. sapiens* is therefore likely to have resembled the olive-brown 'Capoid' skin type IV (Von Luschan 16 to 21) typical of some indigenous southern African groups. This skin type is characteristic of more than 90% of southern San individuals,⁵⁵ has a natural SPF of 3.5, a high tanning capacity and low susceptibility to UVR-induced damage. In terms of avoiding vitamin D deficiencies and the detrimental effects of UVR, and given the positive correlations between adequate UVR exposure and human health, an olive-brown skin tone represents the optimum skin type for inhabitants of southeastern sub-Saharan Africa. It stands to reason that, given the natural SPF of 3.5 for skin type IV, ochre samples exhibiting SPF and UVAPF values of >10 are likely to provide sufficient protection from UVR without generating vitamin D deficiencies. Additional *in vivo* experimental assessment is required to confirm this notion.

Conclusion

It is possible that the habitual exploitation of ochre during the MSA reflects some form of cultural adaptation to rapidly changing environmental circumstances. The habitual use of red ochre as a sunscreen may have presented an advantage for populations that migrated from higher into lower latitudes. As is the case for the positive impact of technological innovation in enhancing early human subsistence strategies,^{40,56} the topical application of ochre may have served to limit the adverse effects of increasing UVR exposure. While it is difficult to establish a precise scenario for the emergence of such an innovation, one could envision a tentative situation in which the habitual use of red ochre as a sunscreen may have originally arisen locally, and perhaps in response to changing UVR exposure rates produced by alternating orbital climatic cycles,⁵⁷ subsequently providing an adaptive advantage for migrating populations. Ochre might therefore have acted as a means by which migrant populations could have traversed and settled within new ecological niches and regions incompatible with their constitutive skin colour.

It is also possible that the intensification in the exploitation of red ochre during the MSA reflects a technologically mediated response to increasingly complex social circumstances, and that this response may have resulted from efforts to satisfy a growing demand for ochre implicated in innovative functional applications. The use of red ochre as an ingredient in novel pigment-based compounds, similar to lithic hafting mastics for which direct evidence exists in MSA contexts,^{39,40} strengthens the perception that the use of red ochre as a sunscreen may also be indicative of the cognitive complexity of MSA *H. sapiens*. In social terms, the ability to create and maintain durable cooperative relationships during the MSA is illustrated by the relatively extensive geographic distribution of Still Bay and Howieson's Poort sites across southern Africa.⁵⁸ This distribution signifies that human groups were integrated into structured social networks similar to those documented for ethnographically known foragers from at least 75 ka. It must, however, be brought to mind that the exploitation of ochre is not limited to *H. sapiens* and that the capacity to attribute specific meaning to conventional signs is not unique to our species.³⁰⁻³² Moreover, although current evidence concerning ochre exploitation supports proposals for socially complex and emotionally driven prehistoric lifestyles, it does not provide explicit evidence for symbolic thought and behaviour.⁵⁹

While suggestions concerning the efficacy of red ochre as a sunscreen are intriguing, the results presented here should be regarded as preliminary. As an initial screening method, *in vitro* tests provide a reasonable comparison of the relative SPF protection offered by the

ochre samples. To obtain confirmation that red ochre does provide a significant degree of protection from UVA and UVB radiation, ongoing research is exploring the sun protection efficacy of ochre by way of *in vivo* SPF assessment. The effects of chemical and physical characteristics besides colour, including mineralogical and elemental composition and structural morphology, also necessitate further exploration before the efficacy of ochre as a sunscreen for early *H. sapiens* can be validated. The establishment of analytical baselines for modern pigment-based compounds is expected to enhance current understandings of the applications for which prehistoric mixtures may have been used. Evidence for knowledge concerning the chemical and physical properties of ancient ingredients, and how these may change when mixed together, can add valuable insight into the minds of our ancestors.⁶⁰ Future research should endeavour to identify correlations between increased periods of ochre exploitation and known instances of sudden changes in climate. It is conceivable that increases in the amount of ochre may coincide with periods during which amplified rates of UVR may have posed an increased risk to human health.

Acknowledgements

We thank the Ovahimba participants from Okamanga, Ovinjange and Otjongoro for sharing their knowledge with us. Anzel Veldman (National Museum of Namibia) and Sennobia Katjiuogua (National Heritage Council of Namibia) are acknowledged for their support in the field. We acknowledge financial support provided by the PROTEA French–South Africa exchange programme and the European Research Council Advanced Grant, TRACSYMBOLS no. 249587, awarded under the FP7 programme.

Authors' contributions

R.F.R. developed the research concept; R.F.R. and F.D. undertook the field research; R.F.R. and B.S. performed the experimental research; F.D., B.S. and L.D. performed the analyses; and R.F.R. and F.D. wrote the paper.

References

1. Condamine FL, Rolland J, Morlon H. Macroevolutionary perspectives to environmental change. *Ecol Letters*. 2013;16:72–85. <http://dx.doi.org/10.1111/ele.12062>
2. Ziegler M, Simon MH, Hall IR, Barker S, Stringer C, Zahn R. Development of Middle Stone Age innovation linked to rapid climate change. *Nat Comm*. 2013;4, Art. #1905, 9 pages. <http://dx.doi.org/10.1038/ncomms2897>
3. Gasparro FP. Sunscreens, skin photobiology and skin cancer: The need for UVA protection and evaluation of efficacy. *Environ Health Perspect*. 2000;108(1):71–78. <http://dx.doi.org/10.1289/ehp.00108s171>
4. Lautenschlager S, Wulf HC, Pittelkow MR. Photoprotection. *Lancet*. 2007;370:528–537. [http://dx.doi.org/10.1016/S0140-6736\(07\)60638-2](http://dx.doi.org/10.1016/S0140-6736(07)60638-2)
5. Paul ND, Gwynn-Jones D. Ecological roles of solar UV radiation: Towards an integrated approach. *Trends Ecol Evol*. 2003;18(1):48–55. [http://dx.doi.org/10.1016/S0169-5347\(02\)00014-9](http://dx.doi.org/10.1016/S0169-5347(02)00014-9)
6. Yuen AWC, Jablonski NG. Vitamin D: In the evolution of human skin colour. *Med Hypotheses*. 2010;74:39–44. <http://dx.doi.org/10.1016/j.mehy.2009.08.007>
7. Juzeniene A, Setlow R, Porojnicu A, Hykkerud Steindal A, Moan J. Development of different human skin colours: A review highlighting photobiological and photobiophysical aspects. *Photochem Photobiol B*. 2009;96:93–100. <http://dx.doi.org/10.1016/j.jphotobiol.2009.04.009>
8. Biniek K, Levi K, Dauskardt RH. Solar UV radiation reduces the barrier function of human skin. *Proc Natl Acad Sci USA*. 2012;109(42):17111–17116. <http://dx.doi.org/10.1073/pnas.1206851109>
9. Gendron SP, Bastien N, Mallet JD, Rochette PJ. The 3895-bp mitochondrial DNA deletion in the human eye: A potential involvement in corneal ageing and macular degeneration. *Mutagenesis*. 2013;28(2):197–204. <http://dx.doi.org/10.1093/mutage/ges071>
10. Faith JT, Surovell TA. Synchronous extinction of North America's Pleistocene mammals. *Proc Natl Acad Sci USA*. 2009;106(49):20641–20645. <http://dx.doi.org/10.1073/pnas.0908153106>
11. LaViolette PA. Evidence for a solar flare cause of the Pleistocene mass extinction. *Radiocarbon*. 2011;53(2):303–323.

12. Valet J-P, Valladas H. The Laschamp-Mono lake geomagnetic events and the extinction of Neanderthals: A causal link or a coincidence? *Quaternary Sci Rev*. 2010;29:3887–3893. <http://dx.doi.org/10.1016/j.quascirev.2010.09.010>
13. Grove M. Amplitudes of orbitally induced climatic cycles and patterns of hominin speciation. *J Archaeol Sci*. 2012;39:3085–3094. <http://dx.doi.org/10.1016/j.jas.2012.04.023>
14. Cerqueira CC, Páixa-Côrtes VR, Zambra FM, Salzano FM, Hünemeier T, Bortolini MY. Predicting *Homo* pigmentation phenotype through genomic data: From Neanderthal to James Watson. *Am J Hum Biol*. 2012;24:705–709. <http://dx.doi.org/10.1002/ajhb.22263>
15. Meyer M, Kircher M, Gansauge M, Li H, Racimo F, Mallick S, et al. A high coverage genome sequence from an archaic Denisovan individual. *Science*. 2012;338(6104):222–226. <http://dx.doi.org/10.1126/science.1224344>
16. Jablonski NG, Chaplin G. Human skin pigmentation as an adaptation to UV radiation. *Proc Natl Acad Sci USA*. 2010;107(2):8962–8968. <http://dx.doi.org/10.1073/pnas.0914628107>
17. Elias M, Williams ML. Re-appraisal of current theories for the development and loss of epidermal pigmentation in hominins and modern humans. *J Hum Evol*. 2013;64(6):687–692. <http://dx.doi.org/10.1016/j.jhevol.2013.02.003>
18. Jablonski NG. The evolution of human skin colouration and its relevance to health in the modern world. *J Roy Coll Physicians Edinburgh*. 2012;42(1):58–63. <http://dx.doi.org/10.4997/JRCPE.2012.114>
19. Wagner JK, Parra EJ, Norton HL, Jovel C, Schriver MD. Skin responses to ultraviolet radiation: Effects of constitutive pigmentation, sex and ancestry. *Pigment Cell Melanoma Res*. 2002;15:385–390. <http://dx.doi.org/10.1034/j.1600-0749.2002.02046.x>
20. Beleza S, Johnson NA, Candille SI, Absher DM, Lopes J, Campos J, et al. Genetic architecture of skin and eye color in an African European admixed population. *PLoS Genet*. 2013;9(3):e1003372. <http://dx.doi.org/10.1371/journal.pgen.1003372>
21. Pickrell JK, Patterson N, Loh P, Lipson M, Berger B, Stoneking M, et al. Ancient west Eurasian ancestry in southern and eastern Africa. *Proc Natl Acad Sci USA*. 2013;111(7):2632–2637. <http://dx.doi.org/10.1073/pnas.1313787111>
22. Hancock AM, Alkorta-Aranburu G, Witonsky DB, Di Rienzo A. Adaptations to new environments in humans: The role of subtle allele frequency shifts. *Philos Trans R Soc B*. 2010;365(1552):2459–2468. <http://dx.doi.org/10.1098/rstb.2010.0032>
23. Kumm M, Varis O. The world by latitudes: A global analysis of human population, development level and environment across the north-south axis over the past half century. *Appl Geogr*. 2011;31:495–507. <http://dx.doi.org/10.1016/j.apgeog.2010.10.009>
24. Rindermann H, Woodley MA, Stratford J. Haplogroups as evolutionary markers of cognitive ability. *Intelligence*. 2012;40(4):362–375. <http://dx.doi.org/10.1016/j.intell.2012.04.002>
25. Cornell RM, Schwertmann U. The iron oxides: Structure, properties, reactions, occurrences and uses. New York: VCH; 2003. <http://dx.doi.org/10.1002/3527602097>
26. Popelka-Filcoff RS, Robertson JD, Glascock MD, Descantes C. Trace element characterisation of ochre from geological sources. *J Radioanalytical Nucl Chem*. 2007;272(1):17–27. <http://dx.doi.org/10.1007/s10967-006-6836-x>
27. Watts I. Red ochre, body-painting, and language: Interpreting the Blombos ochre. In: Botha R, Knight C, editors. *The cradle of language*. Oxford: Oxford University Press; 2009. p. 62–92.
28. Henshilwood CS, Dubreuil B. Reading the artefacts: Gleaning language skills from the Middle Stone Age in southern Africa. In: Botha R, Knight C, editors. *The cradle of language*. Oxford: Oxford University Press; 2009. p. 41–61. <http://dx.doi.org/10.1016/j.jhevol.2009.01.005>
29. Henshilwood CS, d'Errico F, Watts I. Engraved ochres from Middle Stone Age levels at Blombos Cave, South Africa. *J Hum Evol*. 2009;57:27–47.
30. d'Errico F, Salomon H, Vignaud C, Stringer C. Pigments from the Middle Palaeolithic levels of Es-Skhul (Mount Carmel, Israel). *J Archaeol Sci*. 2010;37(12):3099–3110. <http://dx.doi.org/10.1016/j.jas.2010.07.011>
31. Roebroeks W, Sier MJ, Nielsen TK, De Locker D, Parés J, Múcher HJ. Use of red ochre by early Neanderthals. *Proc Natl Acad Sci USA*. 2012;109(6):1889–1894.
32. d'Errico F, Vanhaeren M, Henshilwood CS, Lawson G, Maureille B, Gambier D, et al. From the origin of language to the diversification of languages: What can archaeology and palaeoanthropology say? In: d'Errico F, Hombert J-M, editors. *Becoming eloquent: Advances in the emergence of language, human cognition, and modern cultures*. Amsterdam: John Benjamins; 2009. p. 13–68. <http://dx.doi.org/10.1075/z.152.02ch1>
33. Vanhaeren M, d'Errico F, Stringer C, James SL, Todd JA, Mienis HK. Middle Palaeolithic shell beads in Israel and Algeria. *Science*. 2006;312:1785–1788. <http://dx.doi.org/10.1126/science.1128139>
34. Bouzouggar A, Barton N, Vanhaeren M, d'Errico F, Collcutt S, Higham T, et al. 82 000-year-old shell beads from North Africa and implications for the origins of modern human behaviour. *Proc Natl Acad Sci USA*. 2007;104:9964–9969. <http://dx.doi.org/10.1073/pnas.0703877104>
35. Vanhaeren M, d'Errico F, Van Niekerk KL, Henshilwood CS, Erasmus RM. Thinking strings: Additional evidence for personal ornament use in the Middle Stone Age at Blombos Cave, South Africa. *J Hum Evol*. 2013;64(6):500–517. <http://dx.doi.org/10.1016/j.jhevol.2013.02.001>
36. Campbell J. *Travels in South Africa: Undertaken at the request of the London Missionary Society*. London: Flagg and Gould; 1815.
37. Bleek WHI, Lloyd L. *Specimens of Bushman folklore*. London: George Allen; 1911.
38. Henshilwood CS, d'Errico F, Van Niekerk KL, Coquinot Y, Jacobs Z, Lauritzen S, et al. A 100,000-year-old ochre-processing workshop at Blombos Cave, South Africa. *Science*. 2011;334(6053):219–222. <http://dx.doi.org/10.1126/science.1211535>
39. Soriano S, Villa P, Wadley L. Ochre for the toolmaker: Shaping the Still Bay points at Sibudu (KwaZulu-Natal, South Africa). *J African Archaeol*. 2009;7(1):41–54. <http://dx.doi.org/10.3213/1612-1651-10121>
40. Wadley L, Hodgskiss T, Grant M. Implications for complex cognition from the hafting of tools with compound adhesives in the Middle Stone Age, South Africa. *Proc Natl Acad Sci USA*. 2009;106(24):9590–9594. <http://dx.doi.org/10.1073/pnas.0900957106>
41. Rifkin RF. Assessing the efficacy of red ochre as a prehistoric hide-tanning ingredient. *J African Archaeol*. 2011;9(2):1–28. <http://dx.doi.org/10.3213/2191-5784-10199>
42. Gordon JR. *Cape Travels*. Johannesburg: Brenthurst Press; 1786.
43. Thunberg CP. *Travels at the Cape of Good Hope*. Cape Town: Van Riebeeck Society; 1775.
44. Lydell J, Strecker I. *The Hamar of southern Ethiopia*. Hohenschäftarn: Renner Verlag; 1979.
45. Tönjes H. Ovamboland: Country people mission with particular reference to the largest tribe, the Kwanyama. Windhoek: Namibia Scientific Society; 1911.
46. Vedder H. The Herero. In: Hahn CHL, Vedder H, Fourie L, editors. *Native tribes of South West Africa*. Cape Town: Cape Times; 1928. p. 153–211.
47. Galton F. *The narrative of an explorer in tropical South Africa*. London: John Murray; 1853.
48. Rifkin RF. Processing ochre in the Middle Stone Age: Testing the inference of prehistoric behaviours from actualistically derived experimental data. *J Anthropol Archaeol*. 2012;31:174–195. <http://dx.doi.org/10.1016/j.jaa.2011.11.004>
49. Bernerd F, Vioux C, LeJeune F, Asselineau D. The sun protection factor (SPF) inadequately defines broad spectrum photoprotection: Demonstration using skin reconstructed *in vitro* exposed to UVA, UVB or UV-solar simulated radiation. *Eur J Dermatol*. 2003;13:242–249.
50. Summers B. Sun protection factor of South African-tested sunscreens. *S Afr Med J*. 2012;102(12):897. <http://dx.doi.org/10.7196/samj.6484>
51. Hoang-Minh T, Le TL, Kasbohm J, Gieré R. UV-protection characteristics of some clays. *Appl Clay Sci*. 2010;48:349–357. <http://dx.doi.org/10.1016/j.clay.2010.01.005>
52. Elias M, Chartier C, Prévot G, Garay H, Vignaud C. The colour of ochres explained by their composition. *Mat Sci Eng*. 2006;127:70–80. <http://dx.doi.org/10.1016/j.mseb.2005.09.061>
53. Jablonski NG, Chaplin G. Epidermal pigmentation in the human lineage is an adaptation to ultraviolet radiation. *J Hum Evol*. 2013;65:671–675. <http://dx.doi.org/10.1016/j.jhevol.2013.06.004>

54. Chaplin G. Geographic distribution of environmental factors influencing human skin coloration. *Am J Phys Anthropol.* 2004;125:292–302. <http://dx.doi.org/10.1002/ajpa.10263>
55. Wells LH. Physical measurements of Northern Bushmen. *Man.* 1952;52:53–56. <http://dx.doi.org/10.2307/2795077>
56. Dusseldorp GL. Tracking the influence of technological change on Middle Stone Age hunting strategies in South Africa. *Quaternary Int.* 2012;270:70–79. <http://dx.doi.org/10.1016/j.quaint.2011.02.011>
57. Blome MW, Cohen AS, Tryon CA, Brooks AS, Russell J. The environmental context for the origins of modern human diversity: A synthesis of regional variability in African climate 150,000–30,000 years ago. *J Hum Evol.* 2012;62(5):563–592. <http://dx.doi.org/10.1016/j.jhevol.2012.01.011>
58. Henshilwood CS. Late Pleistocene techno-traditions in southern Africa: A review of the Still Bay and Howiesons Poort, c. 75–59 ka. *J World Prehist.* 2012;25(3–4):205–237. <http://dx.doi.org/10.1007/s10963-012-9060-3>
59. Mithen S. The cognition of *Homo neanderthalensis* and *H. sapiens*: Does the use of pigment necessarily imply symbolic thought? In: Akazawa T, Ogiwara N, Tanabe HC, Terashima H, editors. *Dynamics of learning in Neanderthals and modern humans.* New York: Springer; 2014. p. 7–16. http://dx.doi.org/10.1007/978-4-431-54553-8_2
60. Wadley L. Recognizing complex cognition through innovative technology in Stone Age and Palaeolithic sites. *Cambridge Archaeol J.* 2013;23(2):163–183. <http://dx.doi.org/10.1017/S0959774313000309>

