

Explanation of the Colour Change in Alexandrites

Fei Xie,^{1,7} Yu Cao,^{1,2,7} Cindy Ranchon,^{1,3} Alan Hart,⁴ Robin Hansen,⁴ Jeffrey E. Post,⁵ Coralyn W. Whitney,⁵ Emma Dawson-Tarr,⁶ Alan J. Drew¹ and David J. Dunstan^{1*}

¹*School of Physics and Astronomy, Queen Mary University of London, London E1 4NS, UK*

²*College of Physical Science and Technology, Sichuan University, Chengdu, 610064, China*

³*Polytech Grenoble, Saint-Martin-d'Hères, 38400, France*

⁴*Natural History Museum, Cromwell Rd, London, SW7 5BD, UK*

⁵*National Museum of Natural History, Smithsonian Institution, Washington, DC, 20560, U.S.A.*

⁶*Absolute Action Ltd, Horns Oak Farm, Meopham, DA13 0BX, UK*

⁷These authors contributed equally: Fei Xie, Yu Cao.

* e-mail d.dunstan@qmul.ac.uk

Abstract

Alexandrites are remarkable and rare gemstones. They display an extraordinary colour change according to the ambient lighting, from emerald green in daylight to ruby red in incandescent light from tungsten lamps or candles. While this colour change has been correctly attributed to chromium impurities and their absorption band in the yellow region of the visible light spectrum, no adequate explanation of the mechanism has been given. Here, the alexandrite effect is fully explained by considering the von Kries model of the human colour constancy mechanism. This implies that our colour constancy mechanism is real (objective) and primarily attuned to correct for the colour temperature of black-body illuminants.

Introduction

Alexandrites are rare and highly-prized gemstones, which were first discovered around 1830 in Russia, and named after the future Czar, Alexander II, and later found in other countries such as Brazil and Sri Lanka.¹ They are prized for their dramatic colour change under different illumination: that is ruby-red under candlelight or incandescent lamplight, and emerald-green under natural daylight.¹ This is attributed to the Cr^{3+} impurities in the BeAl_2O_4 atomic structure which have strong optical absorption centred at the wavelength of yellow light. While the stones scatter blue, red and green light in proportions which vary with the illuminant,^{2,3,4} this is not sufficient to explain the colour change in alexandrites as it is as true of any coloured object as it is of alexandrites. Here we give a complete explanation of the alexandrite effect. Taking into account the responses of the cone photoreceptors in the human eye, we show that the ratio of green to red stimuli under the different illuminants changes much more for an alexandrite than it does for normal coloured objects, which have broad absorption bands (inks, pigments, paints, fruit and flowers, etc). This overrides the mechanism by which the human visual system corrects for illuminance and helps understand the working of this mechanism for colour constancy. We expect these findings to have implications for theories of the colour perception of the human visual system in the somewhat disparate fields of traditional colour science,⁵ the science of optical illusions,⁶ and the study of individual perceptions, as in Impressionist paintings⁷ or the dress that went viral.⁸

Figure 1 near here

Results and Analysis

We studied some alexandrites from the collections of the Natural History Museum, London, and picked out two with a particularly pure and vivid alexandrite effect. One of these stones is shown in Fig.1, under different illuminants, daylight and tungsten (incandescent) light. It was

placed on a print of a CIE colour chart⁹ and moved to be on the matching colour as judged by eye (see Methods). With the camera's colour-balancing software switched off, the effect on normal colours of the daylight is seen by the slightly bluish white paper (Fig. 1a) and of the incandescent light by the yellow-brown white paper (Fig. 1b). It is worth emphasising that to the observers under both illuminants the white paper appeared white, and the colours of the background colour chart appeared largely independent of the lighting. The brownish cast of the paper reflects only the brightness of the image, in that RGB yellow is close to (1, 0.9, 0) and just a 10% reduction in brightness to (0.9, 0.8, 0) gives brown. Colour balancing was optimised to create the corrected images (Fig. 1c-d, see the Methods section). The blue cast around the stone in Fig. 1d is discussed in the Supplementary §1.

A wide variety of physical phenomena from interference and diffraction to spectrally selective absorption can give rise to dramatic colour effects such as iridescence.¹⁰ Explanations of the colour change in alexandrites have been given which correctly invoke the spectrally-selective Cr³⁺ absorption band in the yellow region of the spectrum.¹⁻³ Liu et al.² took their explanation further, invoking also colour constancy. Experimentally, they said, the human visual system corrects for hue angle changes only up to 20° under different illuminations (hue angle is explained in the Supplementary §2). Calculating the change in hue angle for alexandrites and finding it to be greater than 20°, they attributed the absence of colour constancy in the alexandrite effect to that. However, the blue-to-brown hue angle change of the white paper in Fig. 1a and b is about 180°, yet colour constancy occurs. Recently a similar analysis of a weak alexandrite effect in purple flowers and low-quality alexandrite stones has been reported.¹¹

It is necessary to consider more carefully what colour constancy does. Crucially, it works to the extent that to the human eye, the colours of the CIE chart under each lighting are almost unchanged. To get colour matches under the two illuminants, the stone has to be moved, and

the colour matches are then recognisable to the eye and to the camera before and after correction. Objectively, to the camera as much as to the eye, the stone changes colour under different lighting. In contrast, pieces of blue, green, yellow or red paper do not have to be moved around the chart to keep the colour matches under different illuminations. Objectively, to the camera as much as to the eye, the pieces of paper do not change colour under different lighting.

Absorption spectra of two alexandrites R1 (BM41177) and R2 (BM41178) were recorded in a UV-VIS photospectrometer (Supplementary §3, Fig.S2). While these spectra were of low quality, because the stones are not optical flats, they confirmed the key features. Converted to transmission spectra, they show the Cr^{3+} absorption line centred on 572 nm with widths of approximately zero transmission of 90 and 120 nm, respectively, and also a strong absorption in the blue, cutting off all wavelengths less than about 480 nm, in agreement with the literature.^{1-4, 11-13} These data permit the prediction of what will be seen by the eye.

Figure 2 near here

The human retina has three kinds of colour photoreceptors, or cones. The S cones detect short-wavelength light (blue), the M, medium wavelengths (green) and the L, long wavelengths (red). See Supplementary §4. In Fig. 2, the spectra of the responses of the cones, the illuminants and the transmittance of the stones (SI) are combined, in order to find out what is perceived. Fig. 2 shows the spectral responses of the L, M and S cones,¹⁴ with, Fig.2a, the standard daylight spectrum D65,¹⁴ and Fig.2b, the candlelight spectrum (black body with a colour temperature of 1850K, which is approximately the standard illuminant A¹⁴). In Fig. 2c and 2d, the products of the illuminant spectra and the L, M and S spectra are plotted. The integrals of these curves correspond to the signals sent by the cones, and their values (normalised so the largest is 1) are marked. These LMS values are converted using an LMS-RGB conversion matrix (see Supplementary §5, Eq. S1) to the RGB colours used in the fill. These are

approximately the colours that a white object would be perceived to have if we did not have colour constancy; they are also approximately the colours that an uncorrected camera records, as in Fig. 1a and b. In Fig. 2e and 2f, the wavelengths absorbed by the stones are removed from the illuminant spectra; what remains are the spectra of the light scattered by the stones. By daylight, the green (and some blue) dominates and the red is weaker; conversion to RGB gives the green used as fill in Fig.2e. By candlelight the red dominates (Fig.2f). Now we apply colour constancy, using a standard model of the mechanism, the von Kries correction.¹⁵ See Supplementary §6 for details of our calculations and Supplementary §7 for a discussion of more advanced models.^{16,17} The correction makes the colours of Fig. 2c and 2d white. Applied to the data of Fig. 2e and 2f, we get the data of Fig. 2g and 2h, where conversion to RGB again gives the fill colours.

The key point here is that the colour-constancy correction hardly affects the daylight raw data (Fig.2e), as D65 is close to flat across the visible spectrum, leaving the alexandrite green in Fig.2g), and also does not affect the incandescent light raw data (Fig.2f) sufficiently to change the colour of the alexandrite from red (Fig.2h). In contrast, in Fig. 2i and 2j, the corresponding results are shown for a yellow object (absorbing short wavelengths to 480 nm and scattering all longer wavelengths through green, yellow and red). Here the uncorrected red in incandescent light is actually somewhat overcorrected beyond yellow to a greenish-yellow (due to uncertainties in the choice of RGB colour space, see Supplementary §5).

Figure 3 near here

It is now clear what the physics of the alexandrite effect is. The daylight D65 spectrum is approximately flat, while 1850K blackbody falls off exponentially from the red to the blue (Fig. 2a). The M spectral response is so close to the L, only about 25nm towards the blue, that this exponential weakens the M signal little (about one-third) relative to the L signal. In contrast, the S spectral response is so much further away, 120nm, that it drops by nine-tenths

relative to the L. These are the changes the colour-constancy mechanism corrects when it has detected the illuminant. Under D65, the green light around 500 nm in the alexandrite spectrum dominates and the stone is green. Under the 1850K black-body illumination, after the alexandrite absorption has removed the light around 580 nm, the remaining green light around 500 nm and the remaining red light around 650nm are so far apart that the green drops relative to the red enormously – much more than colour constancy will correct. Alexandrites do have many other interesting optical properties that may contribute to or detract from the effect, such as polarisation-dependent pleochroism,¹⁸ but the wider separation of the remaining green and red in the spectrum after the stones have absorbed the yellow is clearly the fundamental explanation of the alexandrite effect.

To directly see the alexandrite effect with different absorption peak positions and widths, a mapping based on Fig.2 of calculated RGB colours is shown in Fig. 3a. Both stones R1 and R2 are positioned where clear red/green colour contrast occurs (for more details see Supplementary §8 Fig.S4). The importance of the blue absorption is shown by the map in Fig. 3b, where the blue cut-off has been removed from the absorption spectrum. Now, the alexandrite effect is largely eliminated. Only the weak blue/purple and blue/green colour transitions characteristic of the chrysoberyls² – and some purple flowers¹¹ – remain.

The importance of the yellow absorption for the alexandrite effect is confirmed by our analysis. The very narrow limits on both its position and its strength (i.e. width) if a true red – green alexandrite effect is to be observed are striking. Taking these requirements together with the previously unreported requirement for a blue absorption, it is not surprising that natural alexandrites are so rare, and so prized. Indeed, given this analysis, for large stones or stones with too high a chromium doping in which the true red-green alexandrite effect is weakened by too little red and green transmission compared with the blue, we can conclude that by

reducing the yellow absorption-band width, one would be able to increase the alexandrite effect. This could be achieved by cutting the stones thinner (Supplementary §10).

Discussion

These results have impact for traditional colour science, in which colour constancy and the related ability to discount the illumination, are sometimes considered to be approximate at best, or even fundamentally non-existent.¹⁹ Yet the alexandrite effect may be described as an objective colour change just as the appearance of yellow under different illuminants may be described as objective constancy. Both can be verified by colour matching by eye and by RGB values (as in the raw and corrected photographs in Fig. 1), consistent with the colorimetry matching that underpins colour science. This questions why a yellow object does not show a colour change but alexandrites do. For people with normal colour vision, yellow is a different *quale* from red and green,²⁰ i.e. “yellow” is a basic colour term describing a unique rather than a binary hue such as greenish-blue or bluish-green.²¹ There is no reddish-green or greenish-red. Physiologically, yellow is perceived only when the amount of the L and M stimuli to the eye are very close to equal (and greater than the S stimulus).²² Yet the eye-brain system is so sophisticated that it normally sees a yellow object as yellow even when incandescent light or candlelight swing the red and green stimuli far away from their ratio under daylight. The precision of this correction can be judged from Fig.2. The ML ratio of 0.66 in Fig.2d is corrected to white, and would be corrected to yellow if the S signal were weaker, while the (not dissimilar) ML ratio of 0.59 in Fig.2f is corrected to ruby-red. From Fig.2c and Fig.2l we see that the correction is made to an accuracy of 1% or better. It is plausible that the input data is the ratio of S to L+M, for a rough estimate of that will give a very good estimate of the ML ratio for black-body illumination.²³ So we conclude that the human visual system does have – must have – a very efficient colour constancy mechanism, *provided* that it is black-body colour

temperatures that are to be corrected, and that the mechanism acts *before* the L and M signals are compared.

This also links to the question: whether colour constancy (to the extent it exists) is innate or learned. One might expect that millions of years of evolution of dichromatic mammals with only two kinds of cones, S and ML) under essentially black-body illumination would lead to innate colour correction based on the ratio of the S to ML. Following this reasoning to consider trichromacy, we test how the required changes in the sensitivities of the M and L cones, for black-body white-light illuminants, might be related to the S signal. Calculations (as for Fig.2, and detailed in Supplementary §7) give the curves of the three signals S, M and L as a function of colour temperature from 1850K to 12000K. Rather surprisingly, the corrections for M and L turn out to be linearly related to the logarithm of the change in S (Supplementary Fig.S3). Noting that most human sensations scale logarithmically with the stimulus (cf. the decibel scale for sound), we speculate that this adaptation of the M and L sensitivities, linear with the S sensation and arising only relatively recently with trichomacy, would be implemented at a higher level of the processing of the signals than the raw S v. ML correction.

Another important correction that our visual system does, that silicon-based colour correction does not normally do, is to correct the colour in a shadow to the colour of the unshadowed parts of the same object. The Impressionists were the first artists to observe that shadows are in fact different colours (by overriding their own colour-constancy mechanism) and to paint shadows accordingly.⁷ Initially, in the 1870s, this shocked the critics and the public; now we view the shadows in these paintings without any sense of shock, implying that there is a learned component to colour constancy. One aspect that could be learned rather than innate is the ability when viewing a painting, a photo or a screen to let colour constancy operate within the picture independently of ambient lighting and the surrounding colours. The extent to which different people learn to do this could account for the different responses to the picture

of the dress that went viral.⁸ Specifically, the white parts of the dress are a blue very similar to the blue of the white paper in Fig. 1a. Some peoples' colour constancy (or ambient lighting) may correct this to white if they are used to such images, and the same correction then takes the other parts to gold. Others, with different visual histories (or ambient lighting), clearly seeing the blue, will then rescale the other parts of the dress to black. However, following Foster,¹⁶ we suppose that all these corrections come after the initial von Kries correction for the illuminant colour temperature.

In summary, the colour balancing and correction of the photographs of alexandrites and the calculations of the colour change based on colorimetry and colour space theories indicate that the precision of the colour-constancy mechanism in the human eye-brain system and its overriding by the alexandrites play the key role for the alexandrite effect. These results provide a broader insight into colour constancy and colour perception in the human eye-brain system.

Methods

The alexandrite stones (BM41177 and BM41178, both from Russia) were from the collection of the Natural History Museum, London, UK. They were observed and photographed under natural daylight (north light, in the shadow of a large building on a summer day with sun and scattered clouds) and in a darkroom with only incandescent light for illumination. Candlelight and a tungsten lamp were both used with very similar results; the images in Fig.1b&d were made with the tungsten lamp. The stones were placed on a printout of a CIE 1976 UCS colour chart⁹ as a background, and a piece of white paper was placed in the picture. The position was selected by five judges (CR, AH, EDT, AJD and DJD for one session and AH, RH, EDT, AJD and DJD for another session). Each judge moved the stone as they thought best to improve the colour match to the chart; this process converged each time on a position at which no-one proposed a further move, i.e. a position to which all judges consented. A digital camera (Nikon D5100, 16 MP CMOS detector) was used with all colour-balance and selective-colour software

switched off, and flash and autofocus also off. Images were exported from the camera as NEF files (raw 14-bit data from the image sensor) and converted to JPGs by opening them in Microsoft Photos and saving a JPG copy.

These files were then imported into *Mathematica*[®] notebooks using `image = Import[filename]`, and converted to two-dimensional tables of triplet {R, G, B} values using `data = ImageData[image]`. Parts of the images could be selected using `Part[data, {indices}]`.

Colour balancing was applied to create the corrected images (Fig. 1c-d). For Fig. 1, we used a simple approximate technique for RGB image files. These photos were corrected by dividing all pixel (R, G, B) values by the (R, G, B) values of the white paper. Then the image was re-created using `image = Image[data]`. This makes the paper RGB-white, (1, 1, 1), in the colour space of the camera and of any RGB or CMYK display unit or printer (see Supplementary §1). The procedure is not very accurate for other colours because the response curves of the R, G and B photodetectors in the camera are not known nor used, and nor are the spectra of the R, G and B light sources in a computer monitor or the corresponding spectra of the inks in a colour printer. In particular, the blue cast of the red CIE chart in Fig.1d around the stone, where the light was brightest, appears to arise from a sub-linearity of the photodetectors at high light levels (see Supplementary §1).

References

1. Schmetzer, K. Russian Alexandrites (Schweizerbart Science Publishers, Stuttgart, 2010).
2. Liu, Y., Shigley, J., Fritsch, E. & Hemphill, S. The “alexandrite effect” in gemstones. *Color Res. Appl.* **19**, 186–191 (1994).
3. Liu, Y., Shigley, J. E., Fritsch, E. & Hemphill, S. Relationship between the

- crystallographic orientation and the ‘alexandrite effect’ in synthetic alexandrite. *Mineral. Mag.* **59**, 111–114 (1995).
4. Pinheiro, M.V.B. *et al.* The cause of colour of the blue alexandrites from Malacheta, Minas Gerais, *Brazil. J. Gemm.* **27**, 161-170 (2000).
 5. Fairchild, M. D. *Color Appearance Models*. (Wiley, 2005).
 6. Adelson, E. H. & Pentland, A.P. The perception of shading and reflectance in *Perception as Bayesian Inference* (ed. Knill, D.C. & Richards, W.) ch.11 (Cambridge University Press, 1996).
 7. Dunstan, B. *Painting methods of the Impressionists*. (Watson-Guptill, 1992).
 8. Melgosa, M., Gómez-Robledo, L., Isabel Suero, M. & Fairchild, M. D. What can we learn from a dress with ambiguous colors? *Color Res. Appl.* **40**, 525–529 (2015).
 9. Available at: <https://www.reef2reef.com/threads/understanding-spectrographs-and-chromaticity-graphs.120273/> (accessed 20/10/2019).
 10. Goodling, A.E. *et al.* Colouration by total internal reflection and interference at microscale concave interfaces. *Nature* **566**, 523-527 (2019).
 11. Kasajima, I. Alexandrite-like effect in purple flowers analyzed with newly devised round RGB diagram. *Sci Rep* **6**, 29630 (2016).
 12. White, W. B., Roy, R. & McKay Crichton, J. The “Alexandrite Effect”: An Optical Study. *Am. Mineral.* **52**, 867–871 (1967).
 13. Powell, R. C., Xi, L., Gang, X. & Quarles, G. J. Spectroscopic properties of alexandrite crystals. *Phys. Rev. B* **32**, 2788–2797 (1985).
 14. The database of the Colour and Vision Research Laboratory, University College London, at <http://www.cvrl.org/> (accessed 20/10/19).
 15. Wandell, B.A. *Foundations of Vision*. (Sinauer Associates Inc., Sunderland MA, U.S.,, 1995).

16. Foster, D.H.. Colour constancy. *Vision Research* **51**, 674-700 (2011).
17. Ramanath R. & Drew M.S. Von Kries Hypothesis in *Computer Vision*, ed. Ikeuchi K. (Springer, Boston, MA, 2014).
18. Schmetzer, K. Pleochroism and color change in faceted alexandrite: Influence of cut and sample orientation. *Gems Gemol.* **55**, 61–71 (2019).
19. Fairchild, M. D. *Color Appearance Models* (2nd ed.) (Wiley, Chichester, 2005).
20. Tye, M. Qualia, content, and the inverted spectrum. *Noûs* **28**, 159-183 (1994).
21. Unwin, N. Why do colours look the way they do? *Philosophy* **86**, 405-424 (2011).
22. Hurvich, L.M.& Jameson, D. (November 1957). An opponent-process theory of color vision. *Psychological Review* **64**, 384–404 (1957).
23. Weiss, D., Witzel, C. & Gegenfurtner, K. Determinants of colour constancy and the blue bias. *I-Perception* **8**, 2041669517739635 (2017)

Author Contributions: J.E.P., C.W.W. and E.D.T. posed the problem and enabled the study. D.J.D. and A.J.D. conceived and designed this work. R.H., A.H. and J.E.P. provided material and gemstones from National Collections. C.R. performed the transmission spectroscopy. A.H., R.H., E.D.T., C.R., F.X., A.J.D. and D.J.D. took the photographs. Y.C., F.X. and D.J.D. analysed the images and theories. F.X., A.J.D. and D.J.D. wrote the paper. All the authors participated in discussion of the results and preparation and review of the manuscript.

Additional Information

Competing interests: E.D.T. owns Absolute Action Ltd which has supplied lighting adapted for alexandrites to the Smithsonian Institution (Washington) and the Natural History Museum (London). D.J.D. acts in an unpaid advisory role to Absolute Action Ltd. A.H., R.H. and J.E.P. are staff of the museums and were involved in the procurement of the lighting from Absolute Action Ltd. C.W.W. donated valuable alexandrites to the Smithsonian, of which she is a member of the Board.

Supplementary Information is available for this paper.

Correspondence and requests for materials should be addressed to D.J.D.

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Figures and Legends

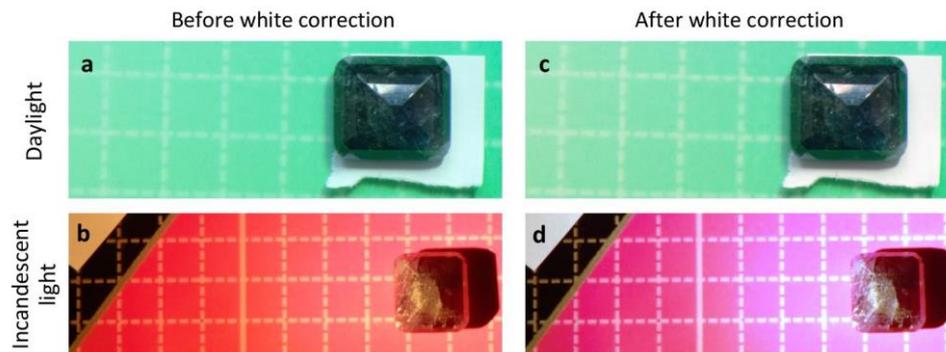


Figure 1. An alexandrite changing colour. The Russian alexandrite BM41178 from the collection of the Natural History Museum, London was photographed in **a**, daylight and **b**, incandescent light with the camera colour-correction feature switched off. The stone was placed on the matching colour on a printout of the CIE 1976 colour chart. A piece of white paper was included in the pictures, under the stone in **a**, and nearby (top left) in **b**. The corresponding images after colour balancing to make the paper white are shown in **c** and **d**.

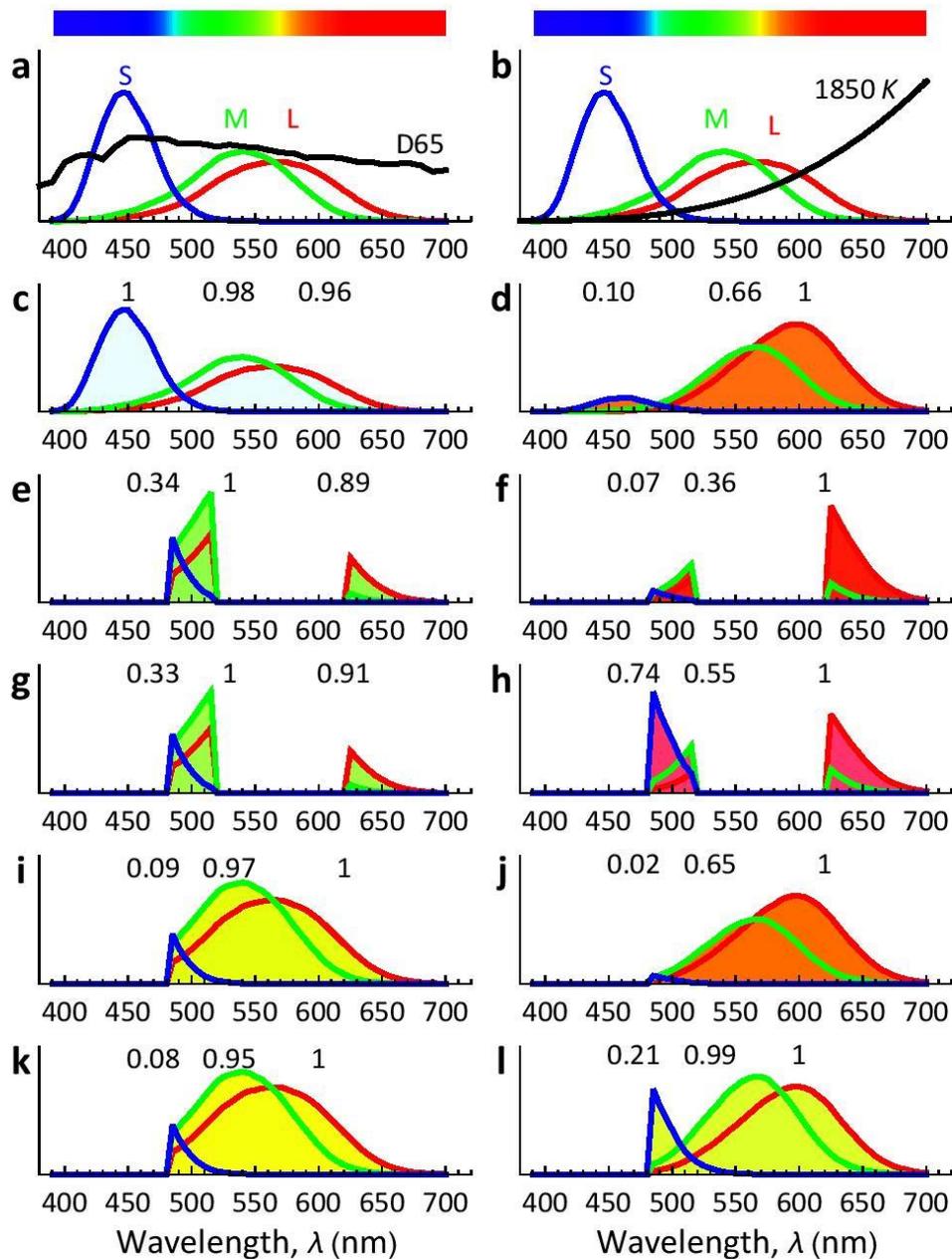


Figure 2. Analysis and explanation of the alexandrite effect. The CIE spectral response curves of the L, M and S cones are shown,¹⁴ together with, (a) the daylight CIE D65 spectrum (colour temperature 6500K)¹⁴ and (b) the candlelight black-body spectrum (1850K). In the panels below, for **c** and **d**, a white object, for **e – h**, the alexandrite R2, and, for **i – l**, a yellow object, the filling colours are the colours calculated in LMS and converted to RGB, before colour constancy correction is applied in (**c – f**, **i**, **j**), and after (**g**, **h**, **k**, **l**). The LMS signals are marked above each component in **c – l**. At the top, the visible spectrum calculated using monochromatic light and the same LMS-RGB correction is shown.

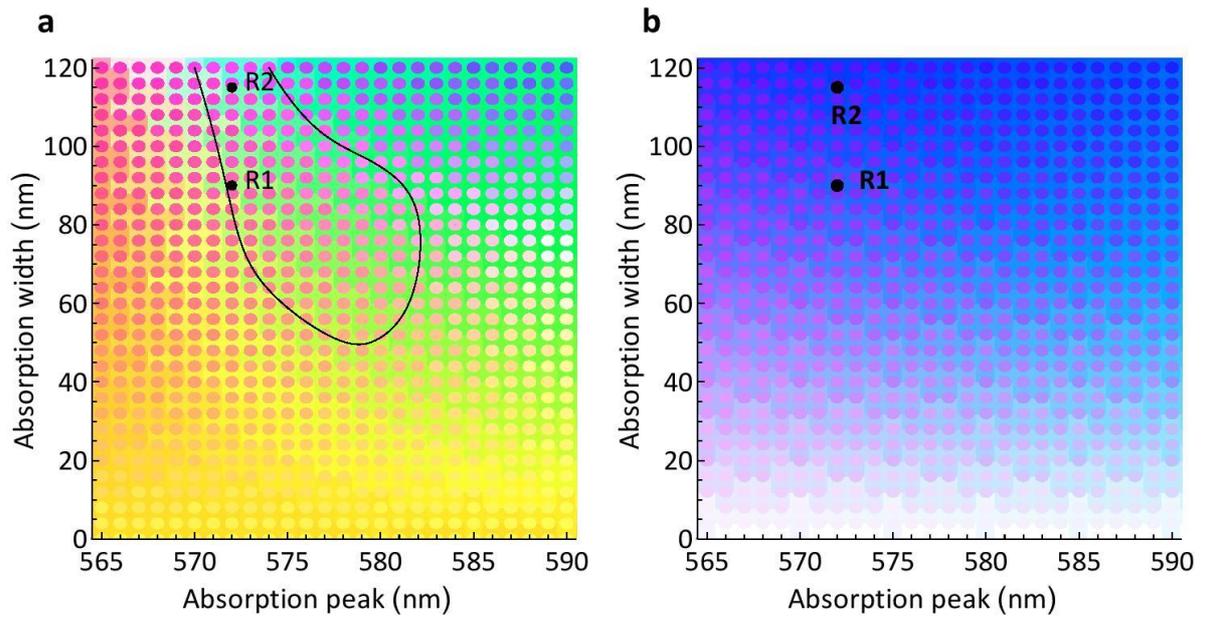


Figure 3. Mapping of the alexandrite effect. In (a), the colours calculated as for Fig. 2 for daylight (D65) and incandescent light (BB1850K) are plotted as a function of absorption peak position and peak width as background and overlaying spots, respectively. The small region where the full alexandrite effect occurs is outlined. The alexandrite stones R1 and R2 are marked on the map and fall within the outlined region. In (b) the map is calculated as for (a) but with the blue absorption band removed.

Supplementary Information

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§1. Colour balancing in Fig.1. None of our photos showed evidence of over-exposure. The correction factors were division by the white paper RGB values, daylight (0.80, 0.96, 0.96) and incandescent (0.84, 0.58, 0.31), followed by normalisation to avoid values greater than 1. However, there is a blue cast around the stone in the corrected Fig.1d. Fig.S1 shows plots of the RGB components across the uncorrected photographs. The uncorrected white paper and the corrected stone are shown in each plot at the relevant positions. The stones are lightened by multiplying all RGB values by 3 to make the green or red colour of the darker parts more obvious. In Fig.S1a, there is no evidence of saturation or non-linearity of the photodetectors. In contrast, in Fig.S1b for incandescent light, it is clear that the red photodetector is saturating, with a very sublinear response above 0.8. However, there is no green or blue in the stone.

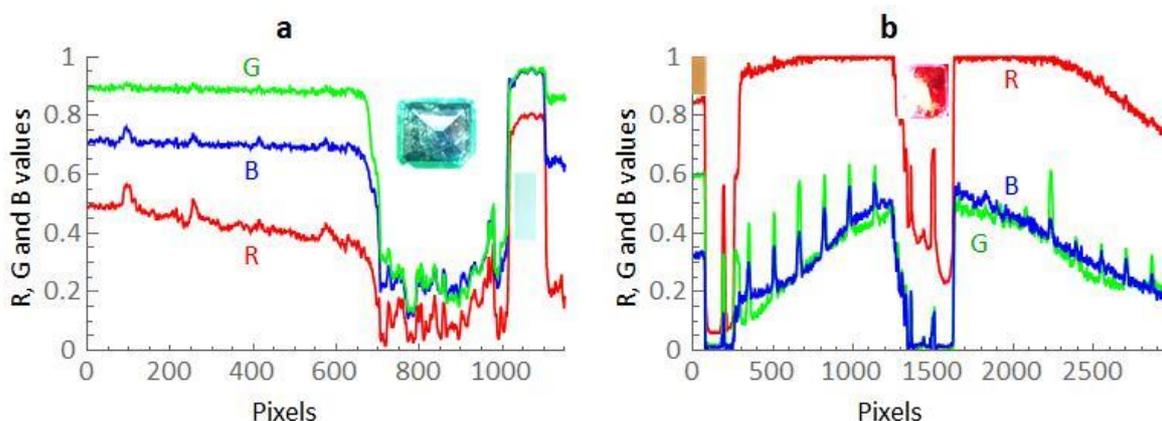


Fig. S1. RGB values from Fig.1. A line of pixels from left to right from the uncorrected images Fig.1a (a) and Fig.1b (b) are plotted. The lightened corrected images of the stones are shown, at $3 \times$ RGB, centred on pixel 900 (a) and 1500 (b). Uncorrected images of the white paper are centred on pixel 1100 (a) and 50 (b).

§2. Hue angle and colour theory: Newton proposed five, and later seven primary colours; pure colours which he identified in the rainbow.^{S1} Yellow was one of these. With paints, pigments and printers, blue (or cyan), yellow and red (the CMY subtractive colour space) are primary colours from which others, e.g. green can be made by mixing yellow and blue. However, looking at the light coming from a yellow pigment such as chrome yellow, it is not for the most part yellow light; instead the pigment works by absorbing (subtracting) the blue component of white light and scattering the rest of the spectrum (predominantly green and red light). In natural white light, there is a little yellow light, in the remarkably narrow spectral range around 575 – 585 nm, but generally a pure yellow object looks pure yellow not because it scatters yellow light (though it does) but because it scatters green and red light equally. Indeed, a pigment that absorbed all other light and scattered only the yellow light in the 575 – 585 nm range would not look yellow, but rather dark brown (brown is dark yellow). For emissive displays, in contrast to pigments, colours are added. Generating yellow for a display is done by generating green and red; adding blue as well gives white. This is the basis of the RGB additive colour space.^{S3}

The hue, saturation, lightness (HSL) model is a representation of colour spaces in which colours are arranged in a circle opposite their complementaries and a colour can be described by a single number, the angle.^{S3, S4} Typically, if blue is centred at 0°, yellow is centred at 180°, with green and red centred near 90° and 270°, cyan is between blue and green, orange is between yellow and red, and purple is between red and blue.

§3. Absorption Spectra

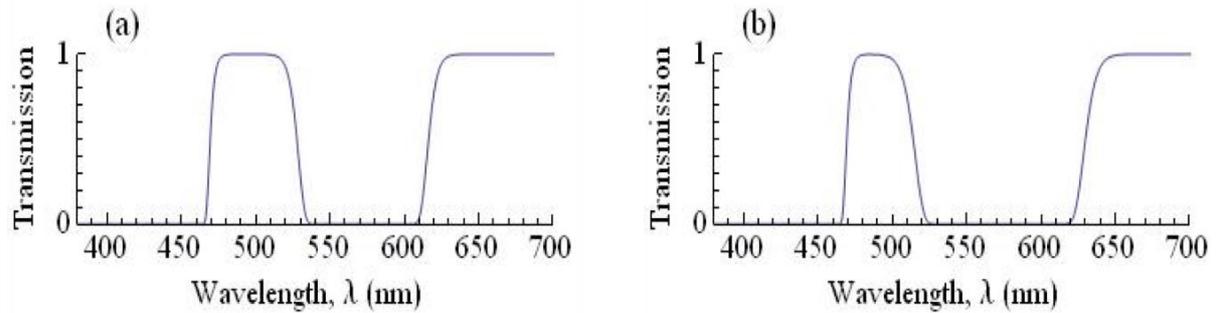


Fig. S2. The transmission spectra of alexandrite stones from the Natural History Museum, for (a) stone R1 (BM 41177) and (b) stone R2 (BM 41178). These spectra are calculated from fits to the noisy experimental absorption spectra.

§4. LMS colour space: While the human eye has red, green and blue receptors (cones), they are not well described as a simple RGB sensor system (as in a camera). Instead, the cones are better described as long, medium and short wavelength receptors (LMS colour space). Their spectral sensitivities $L(\lambda)$, $M(\lambda)$ and $S(\lambda)$ are known.¹⁴ They are plotted in Fig.2 (a), normalized to equal areas so that white will be $(L, M, S) = (1, 1, 1)$. The response curves of the red (L, long wavelength) and green (M, medium wavelength) cones are surprisingly close together. Only near equality (to a few %) of the L and M responses gives yellow, while even small excesses of the M or L responses give green or red.

§5. LMS-RGB conversion matrix: Conversion of colours calculated in the LMS colour space to an RGB colour space requires an RGB-LMS conversion matrix. There are many definitions of the RGB colour space and consequently numerous conversion matrices exist in the literature. The first well-defined RGB colour space used primaries based on three sharp lines of monochromatic light from discharge lamps.^{S2} Solid-state laser projectors can have other choices of sharp wavelengths, but on the other hand visual display units and colour printers necessarily use broad wavelength ranges for the primaries. We used the three wavelengths $\lambda_B = 450$ nm, $\lambda_G = 515$ nm and $\lambda_R = 620$ nm. First the RGB-LMS matrix is found. Taking each of the three monochromatic RGB sources in turn, the nine terms $L(\lambda_i)$, $M(\lambda_i)$, and $S(\lambda_i)$, $i = R, G, B$, are written as a 3×3 matrix. The inverse of this matrix is the RGB-LMS matrix,

$$\begin{bmatrix} R \\ G \\ B \end{bmatrix} = \begin{bmatrix} 2.71667 & -1.77027 & 0.05360 \\ -0.34944 & 1.53261 & -0.18317 \\ 0.00956 & -0.04194 & 1.03238 \end{bmatrix} \begin{bmatrix} L \\ M \\ S \end{bmatrix} \quad (S1)$$

§6. Von Kries correction: For Fig. 2, we used the von Kries method.^{16,18} Daylight may be approximated by a black-body curve for 6000K (BB6000K), but is more accurately represented by various standard CIE illuminants, of which we used D65 (average daylight) with a colour temperature of 6500 K.¹⁵ Incandescent light (ordinary tungsten filament bulbs) corresponds quite accurately to black-body spectra, and the CIE standard illuminant A for tungsten bulbs

has a colour temperature of 2850K (BB2850K). There is no standard for candlelight but black-body 1850K (BB1850K) is a reasonable approximation.

The L, M and S responses are calculated by multiplying the illuminant spectra by the response curves and integrating to get I_L , I_M and I_S . The reciprocals of these numbers are the diagonal elements of the correction matrix; the off-diagonal elements of which are zero. Then an LMS colour is corrected for the illuminant by multiplying the (L, M, S) vector by the correction matrix.

Our use of monochromatic RGB sources to generate the LMS-RGB conversion matrix is probably responsible for the slight overcorrection for candlelight (the yellow is a bit too green in Fig. 2l). That is due to the width of the real display unit or print RGB spectra, and it will be what creates the difficulty in getting a pure red for the alexandrite in Fig.2h.

§7. Other corrections: Much more complicated and accurate models of colour constancy have been developed, most of which however have the von Kries hypothesis as their basis.^{17,23} They generally address two points that von Kries leaves unspecified. First, how the human visual system might establish what the illuminance is. Examples are the “bright is white” assumption, and the space-average chromaticity or grey-world assumptions.¹⁶ Second, context and interactions between spatially-separated parts of the visual field. Also mechanisms have been proposed, such as that the cone responses adapt to the stimulus – but Foster notes that this can have the difficulty that it would predict perfect colour constancy for all changes in the illuminant.¹⁶

In our work, we know the illuminants and we include white paper in the photographs. We make only local, not global measurements. Accordingly, the von Kries rule applied as we do should be sufficient.

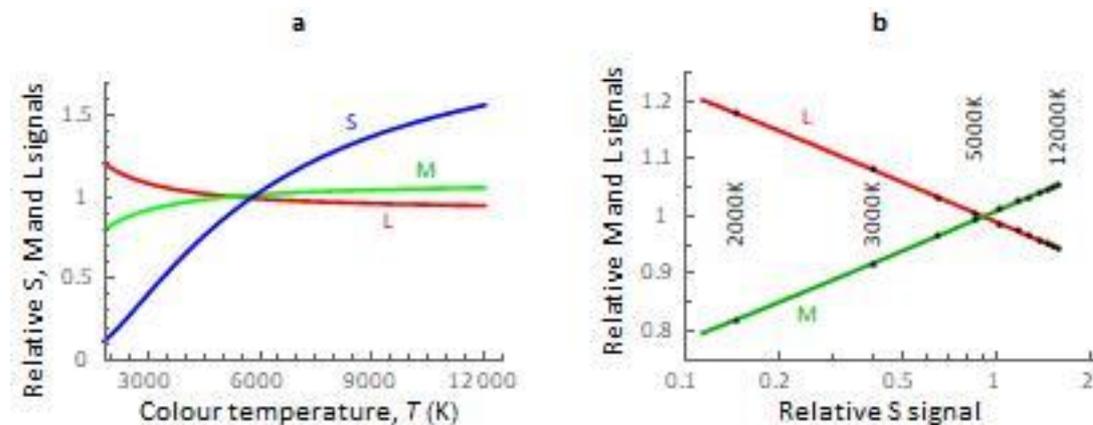


Fig. S3. Cone responses and corrections for black-body colour constancy. In (a), the cone signals $S(T)$, $M(T)$ and $L(T)$ are normalised to (1,1,1) at 5500K. In (b) $M(T)$ and $L(T)$ are plotted against $\log_{10}S(T)$; the black points mark the temperatures 2000K – 12000K. The data fit accurately straight lines, $1 \pm 0.23 \log_{10}S(T)$, indicating that the required changes to the M and L sensitivities are proportional to the perceived blue content of the scene or the light.

It is noteworthy – with implications for mechanisms of colour constancy - that the Alexandrite effect is very robust and independent of the rest of the field of view, with black-body or near-black-body illuminants – daylight, tungsten lamps and candles. In contrast, it is difficult or impossible to obtain with other white light illuminants (see §9 below), under which stones may fail to change colour or change colour unpredictably. Thus our colour-constancy mechanisms do not work reliably for non-black-body illuminants. We speculate that this

implies a robust colour-constancy mechanism that will have evolved specifically for black-body illumination, and which will underly the other corrections mentioned above. Given the relatively recent evolution of trichromacy, it is plausible that this black-body von Kries mechanism is functionally equivalent to changing the gain (sensitivity) of the L and M cones in proportion to the ratio of the S signal to the L and M signals. Calculating the S, M and L responses as in Fig.2, but for black-body white light as a function of colour temperature we get the curves of Fig.S1a. Replotted as the parametric plot of Fig.S1b, the M and L responses turn out to vary linearly with the logarithm of the S response, or linearly with the sensation. Many human sensations are logarithmic with the stimulus (hence the decibel for sound). M and L cone responses adapting in this way to the blue sensation would indeed correct perfectly for black-body illuminants but not others.

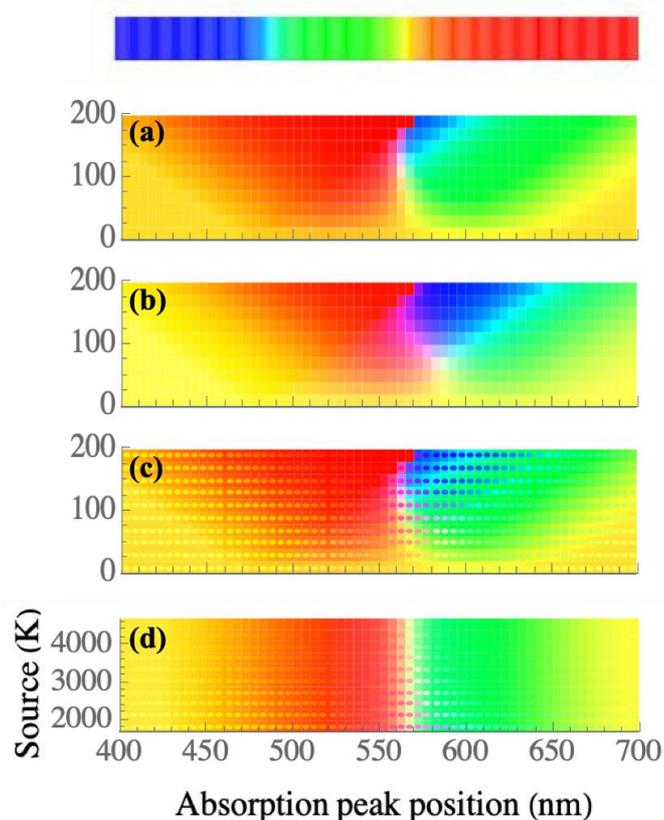


Fig. S4. Mapping the Alexandrite Effect. In (a), the colours calculated as for Fig.2 for daylight (D65) are plotted as a function of absorption peak position and peak width. The corresponding colours by candlelight (BB1850K) are plotted in (b). In (c), the candlelight colours of (b) are shown in small spots overlaying the background of daylight colours of (a). Finally, the effect of the candlelight colour temperature is shown in (d), in which the vertical axis is the colour temperature for the candlelight spots while the background is for the D65 daylight. Here, contrast disappears at about 4000K. The inaccuracy of the colour rendering in this Figure can be estimated by comparing the calculated spectrum shown above (a) with any true rainbow. In (d) the effect of the choice of colour temperature for incandescent illumination is shown.

§8. Mapping: Using the same method as for Fig. 2, the perceived colours have been calculated as a function of the peak position and widths of the yellow absorption band, with the results shown in Fig. S3. Figure S3a is for a stone illuminated by daylight, and it is clear that if the

absorption peak is narrow or weak the stone is yellow, as expected for anything with a dominant blue absorption. When the absorption peak is wide, strong, and in the green, the stone is red, while if it is in the red, the stone is green (see the rainbow spectrum above Fig. S3a). The transition between these is remarkably sharp. If the absorption is too broad, the red and green are both removed sufficiently to leave the stone blue. The same analysis describes Fig. S3b, which is the same map but calculated for candlelight. The only significant difference from Fig. S3a is that the transition through yellow is shifted to longer wavelengths. The blue portion at large peak widths is also larger. Although the alexandrite effect is seen by comparison of the two maps shown in Figs. S4a and b, a more much intuitive way to observe it is to superimpose the two maps on top of one another. This is done in Fig. S3c, where the candlelight map of Fig. S4b is superimposed as small spots on the daylight map of Fig. S3a. The most relevant part of this plot is shown at higher resolution in Fig. 3a in the main text. It is apparent that the true alexandrite effect (red spots on green background) is observed only for a very limited range of peak positions and widths, as marked on the Figure. A larger region of green – blue contrast is also observed, and there are regions of red – yellow and purplish contrast.

§9. Non-Incandescent Lamps:

This analysis also explains why alexandrites are in practice difficult to light. Lighting in museums and galleries has changed in recent years from largely daylight and incandescent light, to much more efficient and reliable artificial sources – fluorescent tubes and more recently LEDs. Absolute Action Ltd. used metal-halide arc lamps with optical fibre to light various coloured gemstones with excellent results, using 4000°C lamps for the Hope diamond (blue) and the Dresden diamond (green), and 3000°C lamps for the Hooker starburst diamonds (yellow), the Steinmetz diamond (pink) and the Mousaieff diamond (red), among others. However, with these lamps and colour temperature correction filters, it was difficult to obtain the alexandrite colour transition to red. Much of the light from these lamps is concentrated into a few sharp peaks as in Fig. S2. A wider range of colour temperatures is achieved using commercial filters. Generally these, too, have quite peaky spectra (Fig. S2), so while they achieve their nominal colour temperature change accurately on black-body light, and more-or-less well on other white light such as metal-halide, there is no guarantee that the final ratios of the light intensity in the two rather narrow bands of relevance in Fig. 2c are as required to replicate either daylight or candlelight. Getting the illumination correct to show the alexandrite effect is therefore challenging. A key issue is the 475nm peak in the lamp spectrum (Fig. S2), and whether a particular stone attenuates it a little or a lot.

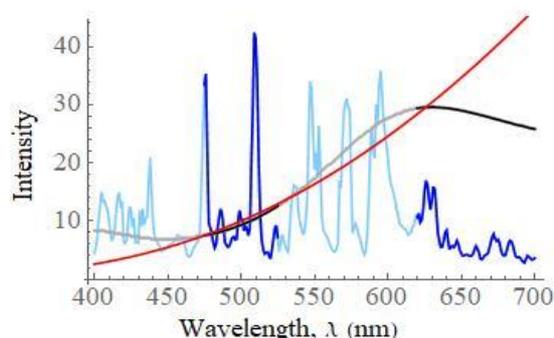


Fig. S5. A metal-halide arc-lamp spectrum is shown in blue; the two bands of relevance around 500 nm and 650 nm are in dark blue. The absorption spectrum of a typical commercial filter for changing colour temperature is shown in grey, black in the regions of relevance. This filter is designed to convert 5500K white light to 2700K. The red curve is the theoretical spectrum for this colour temperature

change. With this lamp and the actual spectrum of the filter, it converts the colour temperature defined by just the 500 nm and 650 nm bands from about 20000K to about 6000K.

§10. Thinning: The chromium absorption in Fig.S1 is saturated, i.e. strong enough that the transmission is effectively zero around the peak absorption. In this case, decreasing the chromium content, or equivalently thinning the stone, weakens the absorption and has the effect of narrowing the band of zero transmission. This could improve the performance of stones showing a purplish – green-blue alexandrite effect.

Supplementary References (other references are in the list in the main text).

- S1. Newton, I. A letter of Mr. Isaac Newton, Professor of the Mathematicks in the University of Cambridge; containing his new theory about light and colors: sent by the author to the publisher from Cambridge, Febr. 6. 1671/72; in order to be communicated to the R. Society. *Philos. Trans. Roy. Soc.* (1671). doi:<https://doi.org/10.1098/rstl.1671.0072>
- S2. Wright, W. D. A re-determination of the trichromatic coefficients of the spectral colours. *Trans. Opt. Soc.* **30**, 141–164 (1929).
- S3. Schanda, J. *Colorimetry: Understanding the CIE System*. (Wiley Interscience, 2007).
- S4. Fairchild, M. D. *Color Appearance Models*. (Wiley, 2005).