Photochromism and Photochromic Gems: A Review and Some New Data (Part 1)

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ABSTRACT: Photochromism is defined as the reversible change of colour caused by exposure to 'light' (visible and UV wavelengths, sometimes extended to X-rays). The species covered in part 1 of this article include sodalite (hackmanite), marialite (scapolite group), tugtupite, spodumene (kunzite), diopside and zircon. We review available data on such gems and provide a systematic approach to their photochromic behaviour, describing the discovery of the colour variation, the photochromic colours known, their corresponding UV-visible absorption spectra, and facts or hypotheses regarding the origin of the phenomenon. Where available we include new data to supplement the information available in the literature. Sulphur-based polyanions are thought to be responsible for photochromism in some aluminosilicates (i.e. hackmanite, marialite and tugtupite). More generally, the phenomenon can be explained by movement of an electron (either an electron centre or a hole centre) from one 'defect' ('colour centre') to a different one. However, the exact nature of the defects involved at the atomic and electronic levels are essentially unknown. This article also discusses proper use of terminology, and we propose that *photochromism* is more accurate than, for example, *tenebrescence*, *colour change* or *chameleon* effect.

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Photochromic gem varieties change colour, reversibly, upon exposure to visible light or UV radiation and sometimes X-rays (Figure 1). Such gem materials are rare, yet they are cherished by discriminating collectors and gemmologists who often prefer the unusual to the readily available. There is no indication that the colour cycling in such gems is limited either in time or in the number of cycles. The phenomenon is also known by various, less appropriate terms, such as *tenebrescence* or *colour change* (see below).

The gemmological community might not be fully aware that photochromic materials are used in everyday applications, such as light-sensitive glasses. However, the field of applications for these materials is expanding and could include, for example, erasable optical data storage and switching components (Irie 1989, 2000; Tian & Zhang 2016). Thus, photochromic gem materials might have industrial applications if they could be synthesised and made quickly reversible. In the large range of photochromic materials, distinction is commonly made between organic, inorganic and hybrid compounds. Organic (e.g. spiropyrans molecules) and hybrid (material with mixed organic and inorganic components, such as metal-organic frameworks) compounds are fairly well studied and present interesting photochromic characteristics, such as a rapid or marked change in colour (Dessapt *et al*. 2009; Tian & Zhang 2016). Inorganic photochromic materials are much less numerous but some have been extensively studied, such as silver-doped glass (Armistead & Stookey 1964). Others are understood in considerably less detail. This is particularly true for photochromic gem materials.

The aim of this article is to review our knowledge of inorganic photochromic gem materials. Those discussed in part 1 are the silicates sodalite (hackmanite), marialite (scapolite group), tugtupite, spodumene (kunzite), diopside and zircon. (Part 2 covers non-silicates: corundum, diamond and barite.) It is not the purpose of a review article to significantly add to existing knowledge, so our input is minor (mostly photographs with corresponding UV-visible absorption spectra). For each gem material, its photochromic property is described in the following order: (1) history of discovery, and possibly locality and first mention in the literature; (2) description of the photochromic colours (sometimes including several behaviours); (3) absorption spectroscopy; (4) hypotheses for cause of photochromism, if available; and (5) other information and optical properties possibly linked to photochromism.

Definition

For the purpose of this article, we define photochromism as the reversible change of colour observed in gems after exposure to visible light or UV radiation of any kind (long- or short-wave, using standard gemmological UV lamps as one example, but also the UV component of daylight).

There are many subtleties associated with defining this phenomenon. The word *photochromism* was apparently introduced by Hirshberg (1950) to name what he observed in a series of organic molecules (see also Bouas-Laurent & Dürr 2001). This generated scientific study of what is now known as *X-chromes*, *chromism* or *chromic phenomena*, terms that can also be found in the literature (Bamfield 2010), which concern changes of colour produced by some kind of excitation, generically referred to as *X* (photochromism, thermochromism, electrochromism, solvatochromism, tribochromism, etc.). In the case of photochromic behaviour, it is a change of colour caused by exposure to light (photons; hence *photo*chromic).

From a strict scientific point of view, according to the International Union of Pure and Applied Chemistry (IUPAC; see Bouas-Laurent & Dürr 2001, p. 642), photochromism is defined as follows:

> A reversible transformation of a molecular [or solid] entity between two forms, A and B, having different absorption spectra, induced in one or both directions by absorption of electromagnetic radiation. The spectral change produced is typically, but not

Figure 1: Some remarkable photochromic gems are shown in this composite image before (left) and after (right) exposure to UV radiation. Clockwise from top: sodalite (hackmanite; 0.48 ct), tugtupite (1.10 g), near-colourless zircon (0.43 ct), red zircon (21.3 ct) and marialite (0.91 ct). Photos by Thomas Hainschwang and Féodor Blumentritt.

> necessarily, of visible color and is accompanied by differences in other physical properties. The thermodynamically stable form A is transformed by irradiation into form B. The back reaction can occur thermally (photochromism of type T) or photochemically (photochromism of type P).

Although the IUPAC definition is fairly detailed, one point remains unclear: Which 'electromagnetic radiation' is concerned? Most examples of photochromic materials involve UV and visible light as the electromagnetic radiation of interest. However, some publications include X-rays (Claffy 1953), while infrared and lower energies are never mentioned. Although the IUPAC definition still applies, exposure to high-energy X-rays would be considered a treatment in gemmology, even if some loss of the induced colour might be observed over very long periods of time. Some historic discoveries of photochromic behaviours have been made under X-ray irradiation (see, e.g., the section on corundum in part 2 of this article) and later confirmed with UV radiation. However, we consider, at least for the purpose of gem materials, that near-UV (200–400 nm) is the highest-energy spectral range to induce a photochromic reaction.

Other details not included in the IUPAC definition (again, see Bouas-Laurent & Dürr 2001) concern the number of possible colouration-to-discolouration cycles. The notion of fatigue—progressive degradation of the induced colour, eventually leading to loss of the property—which is commonly associated with organic and hybrid materials (Zhang *et al*. 2013, 2014), does not appear in the literature for inorganic gems. Thus, photochromic minerals can be cycled a considerable number of times, which is of great interest for potential industrial applications.

Another point not explicitly discussed in the IUPAC definition is the speed of the colouration-to-discolouration process. This factor is key for many industrial applications (e.g. optical storage; Irie 2000), but it is not commonly mentioned for photochromic minerals in the gemmological literature.

An additional aspect not considered in the IUPAC definition, but which we faced during our research, is the notion of photon flux. This represents the quantity of energy (here, UV photons) reaching the sample per surface unit. For some gems, a 'classic' UV lamp, either short-wave or long-wave, is not able to induce photochromism. However, the property can be triggered by a more powerful UV source of similar wavelength (or energy). For example, a change in colour has been observed for blue sapphires that turn yellow on the outside, and yellow sapphires that turn orange, after illumination with a concentrated broadband near-UV 300 W xenon lamp (Thomas Hainschwang, pers. comm. 2020). This aspect of photon flux is also discussed in the spodumene section below, where three colour states (colourless, pink and green) are possible. With high-photon flux, a sample can change directly from the stable colourless state to the green state. With low-photon flux, the reaction is slowed, and a pink state is seen between colourless and green.

Terminology

From the point of view of terminology, the technical literature on minerals and gem materials is not always consistent. Some authors use the term *reversible photochromism* (Pizani *et al*. 1985; Tardío *et al*. 2003; Ramírez *et al*. 2005; Gaft *et al*. 2009; Williams *et al*. 2010; Friis 2011; Warner & Hutzen Andersen 2012; Byrne *et al*. 2014; Carvalho *et al*. 2018), which appears redundant in view of the IUPAC definition, in which reversibility is implicit.

Another term employed is *tenebrescence* (Claffy 1953; Kirk 1955; Chang 1974; Gaft *et al*. 2009; Williams *et al*. 2010; Friis 2011; Warner & Hutzen Andersen 2012; Norrbo *et al*. 2015; Renfro 2016; Carvalho *et al*. 2018). Although this term describes a change from a lighter to a darker colour, it does not include the key concept of reversibility. The same explanation applies to the term *darkening* also used in the literature (Medved 1953). Other descriptions that have been used but are obsolete today include *transichromism* (Copeland *et al*. 1960), *evanescence* (Miser & Glass 1941) and *phototropy* (Exelby & Grinter 1965).

Colour change has a very specific meaning in gemmology: a change of hue corresponding with a change of illumination or lighting (i.e. the *alexandrite effect*). Thus, although *colour change* is a convenient way to describe photochromism, this use is misleading, as it applies specifically to the alexandrite effect.

General Model

One accepted explanation for photochromism in solid crystals is linked with the presence of a defect in the crystal lattice (Medved 1953). This defect creates an electronic level in the band gap, which in this case makes visible-light absorption, and thus colour, possible. (For a definition of *band gap* and the related notions of *valence band* and *conduction band*, the reader is referred to classic physics texts such as Kittel [2004] or the summary at https://en.wikipedia.org/wiki/Electronic_band_structure.) This 'classic' model is convenient to explain photochromism at the atomic and electronic levels. The energy level of the defect in the lattice would, in fact, trap electrons (trap level; see Figure 2, left). When exposed to relatively high energy such as UV, electrons can fall in

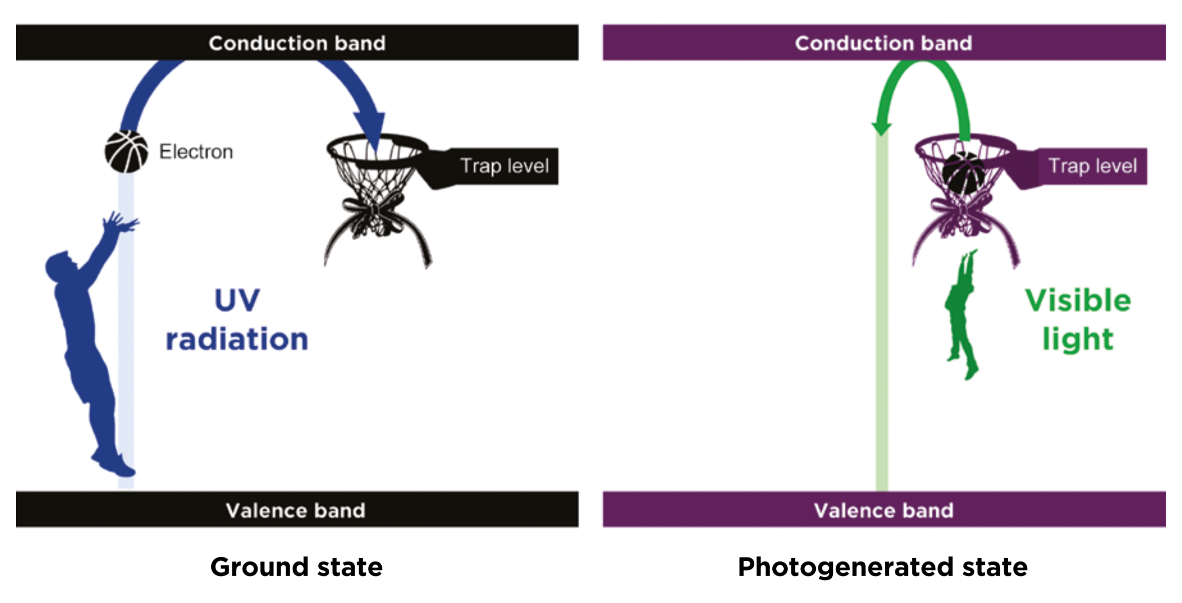


Figure 2: The 'classic' model of photochromism proposed by Medved (1953) involves two states. Left: High-energy (UV) radiation causes an electron to move from the valence band to the conduction band and then into a trap level at an energy slightly lower than the conduction band (the metastable position), yielding the photogenerated, coloured state. Right: Lower-energy visible-light radiation provides enough energy to enable the electron to escape from the trap level and return to its ground state, restoring the original colour.

this trap. This generates a colour centre—designated 'F' for *Farbe*, which means 'colour' in German (see definition in Fritsch & Rossman 1988)—responsible for a change in the absorption spectrum and, thus, a change in colour. In this coloured, photogenerated state, the electron in the trap level can absorb lower-energy visible-light radiation (Figure 2, right) and return to its initial position via the conduction band—the discolouration process.

However, there is no general, all-encompassing theory, and the above 'classic' model could be adapted or completely modified with future discoveries. For synthetic or industrial photochromic materials (mostly organic or hybrid compounds), the cause of photochromism often involves a change in the shape of an organic molecule (e.g. Tian & Zhang 2016). However, we do not yet have a full understanding of this photochromic mechanism for most of the gem materials presented in this work.

MATERIALS AND METHODS

We obtained natural, photochromic mineral samples (Table I) primarily to characterise their colours and absorption spectra for comparison with published literature and to provide a consistent presentation of the spectra in this article. The identification of the specimens studied was verified by standard gemmological techniques, Raman spectroscopy, and sometimes further chemical and structural analysis (including energy-dispersive X-ray spectroscopy and X-ray diffraction).

In addition, synthetic hackmanite powders were produced using the structure conversion method (Warner & Hutzen Andersen 2012) for comparison with natural samples and the existing literature.

Stable colours were observed using a daylight-equivalent (D65) lamp. The colours were modified using a UV lamp (Vilber-Lourmat VL-215-LC) with a total power of 30 W distributed between two UV tubes approximately 30 cm long and 15 W each. Exposures were performed at a fixed distance of 7 cm from the lamp, in a dark room and against an inert black background to avoid daylight contamination.

For this study, we limited the analysis of photochromism to ultraviolet-visible-near infrared (UV-Vis-NIR) absorption spectra. The larger opaque samples were analysed with a PerkinElmer Lambda 1050 instrument in reflectance mode, while the smaller transparent samples were analysed with a Magilabs GemmoSphere spectrometer. Details of the experimental conditions are provided in Table II. The GemmoSphere records luminescence together with absorption, so additional features due to luminescence are visible in the scapolite spectra that do not participate in the photochromic behaviour.

Table I: Photochromic samples collected for this study.

Gem material	Chemical formula	Stable colour	Weight	Type	Origin (*lender**)
Diopside	$CaMgSi_2O_6$	Greenish yellow	8.37 g	Rough	Bazenovskoe, Russia (*J. Hyršl*)
Marialite (scapolite)	$Na_4Al_3Si_9O_{24}(Cl,S)$	Near-colourless	2.58 ct	Faceted pear	Afghanistan
Sodalite (hackmanite variety)	$Na_8Al_6Si_6O_{24}(Cl,S)_2$	White or near-colourless	1.15 ct	Cabochon	Mogok, Myanmar
Spodumene (kunzite variety)	$LiAlSi_2O_6$	Near-colourless	51.6 g	Rough	Afghanistan
Tugtupite	$Na_8Al_2Be_2Si_8O_{24}Cl_2$	Pink	1.27 g	Rough	Greenland (*B. Mocquet*)
Zircon (behaviour 1)	$ZrSiO_4$	Near-colourless	0.43 ct	Faceted round	Unknown
Zircon (behaviour 2)	$ZrSiO_4$	Orangey red	21.3 ct	Rectangular cushion	Cambodia (*M. Daufresne*)

* Samples for which no lender is indicated are in the collection of the University of Nantes.

Table II: Experimental details for UV-Vis-NIR spectroscopy.

Parameter	Magilabs GemmoSphere	PerkinElmer Lambda 1050
Spectral range used	365–1000 nm	365–1000 nm
Collection mode	100 mm PTFE[a] integrating sphere (transmission mode)	150 mm PTFE[a] integrating sphere (transmission mode)
Sampling interval	1 nm	1 nm
Spectral bandwidth	Automatic	1 nm
Integration time	0.54 s	0.54 s
Reference spectra[b]	0% and 100% lamp spectra	0% and 100% lamp spectra

[a] Abbreviation: PTFE = polytetrafluoroethylene (also known as Teflon).

[b] Two reference spectra were recorded without the sample to correct for the spectral characteristics of the lamp (100%) and for any residual light in the sphere (or light 'pollution'; 0%).

For the sake of consistency, the Kubelka-Munk approximation (Kubelka & Munk 1931; Yang & Kruse 2004) was implemented to transform the reflectance spectra to absorbance. Absorbance (A) is proportional to reflectance (R; absolute value) through the relationship:

$$A \propto \frac{(1-R)^2}{2R}$$

For each sample, we obtained spectra corresponding to the stable and excited colours in the photochromic reaction. We also calculated the difference spectrum between the most coloured state and the least coloured state to highlight the absorption feature(s) created by photochromism. A summary of the properties of the photochromic gems discussed in this article can be found in Table III.

SODALITE (HACKMANITE)

The first mention of a change in the colour of sodalite was made by Robert Allan (Allan 1834; Friis 2011) on samples from Greenland that were sent to his father, Thomas Allan, by Karl Ludwig Giesecke in 1806 (De Bournon 1811; Friis 2011). Allan (1834) reported that the light purple to pink colour shown by hackmanite upon being excavated disappeared with exposure to sunlight, thus returning the sample to its initial colourless, pale pink or green colour. The purple colour of sodalite (hackmanite) can then be induced by exposing it to short-wave UV radiation for a few seconds to a few minutes (Figure 3), depending on the specific sample (Kondo & Beaton 2009; Milisenda *et al.* 2015). The purple colour is due to a photogenerated absorption band with a maximum at about 545 nm

Table III: Properties of the photochromic gems sodalite, marialite, tugtupite, spodumene, diopside and zircon.

Gem material	Stable/ metastable colour(s)	Photo-generated colour(s) induced by	Approximate time to induce photo-generated colour	Photo-generated colour(s) reversed by	Approximate time to fade photo-generated colour	Proposed mechanism (or suggestions, if possible)[a]	Principal reference[b]
Sodalite (hackmanite variety)	Colourless to pale pink/purple	Short-wave UV	Seconds to minutes	White light (or ~545 nm)	Seconds to minutes	$S_2^{2-} + V_{Cl}^0 \leftrightarrow S_2^- + V_{Cl}^-$	Curutchet & Le Bahers (2017)
				Darkness	Several days		
Marialite (scapolite)	Colourless/blue	Short-wave UV	Seconds to minutes	White light (or ~610 nm)	Seconds to minutes	$X_n^{y-} + V_{Cl}^0 \leftrightarrow x_n^{(y+1)-} + V_{Cl}^-$	Blumentritt *et al.* (2020)
				Darkness	Several days		
Tugtupite	Colourless to red/ dark red	Short-wave UV	Seconds to minutes	White light (or ~500–545 nm)	Seconds to minutes	$X_n^{y-} + V_{Cl}^0 \leftrightarrow x_n^{(y+1)-} + V_{Cl}^-$	Observation only: Sørensen *et al.* (1971)
				Darkness	Several days		
Spodumene (kunzite variety)	Colourless/ pink, green	Short-wave UV (and X-rays for green colour)	Minutes to hours	White light	Minutes to hours	$Mn^{2+} \leftrightarrow Mn^{3+} \leftrightarrow Mn^{4+}$	Schmitz & Lehmann (1975)
				Darkness	Several days		
Diopside	Yellow/green	Short-wave UV	Several minutes	White light	Seconds to minutes	Unknown	Hyršl (2016)
				Darkness	Several days		
Zircon (behaviour 1)	(1) Colourless/brown to orange; (2) blue/ blue with brownish component	Long-wave UV	Seconds to minutes	White light	Minutes to hours	Intrinsic defect	Zeug *et al.* (2018)
		Darkness	Several days				
Zircon (behaviour 2)	Orangey red/dark reddish brown	Long-wave UV	Seconds	Heat (around 100°C)	Minutes to ~1 hour	Intrinsic defect	Smith & Balmer (2009)
		Daylight	Minutes	Darkness	Several days		
Zircon (behaviour 3)	Colourless or light brown/brown to brownish yellow	Long- or short-wave UV	Minutes (partial regeneration)	Heat	Minutes	Intrinsic defect	Michael Gray, pers. comm. (2019)

[a] For marialite and tugtupite, X_n^{y-} and $x_n^{(y+1)-}$ refer to different polyanions of sulphur or another, as yet unknown, electron donor.

[b] For clarity, only the major reference is cited in this table for each gem material, but additional articles are cited in the main text.

(Figure 3). We observed a relatively large number of hackmanites for which this photogenerated band is independent of the absorption spectrum of the sample in its stable state, whether it was near-colourless, pale pink, green or light blue. This indicates that the photogenerated colour centre responsible for the purple colour is not related to other colour centres present in the sodalite.

The photochromic variety of sodalite was named hackmanite by Leon H. Borgström in 1901 (Friis 2011) in honour of Victor Axel Hackman, who gave him a photochromic sample from the Kola Peninsula, Russia. The formula of hackmanite is $Na_8Al_6Si_6O_{24}(Cl,S)_2$, with sulphur as a minor component. The presence of sulphur is thought to be linked to the photochromism of hackmanite (Gaft *et al.* 2009; Williams *et al.* 2010; Norrbo *et al.* 2015, 2016; Carvalho *et al.* 2018). Detailed determination of the colour centre at the atomic level could confirm this by providing a clearer link between the element sulphur and the photochromism.

The structure of sodalite, including hackmanite, is formed by chains of SiO_4 and AlO_4 tetrahedra (Figure 4, left). These chains organise in a cubic system and form cavities, or 'cages', between them, big enough to admit one large anion at the centre (Cl^-, Br^-, I^-, SO_4^{2-}, SO_3^{2-}, SO_3^-, SO_2^-, CO_3^{2-}, etc.) surrounded by a tetrahedron of four alkali cations (Ca^{2+}, Na^+, K^+, Li^+, etc.; Zahoransky *et al.* 2016). In nominal sodalite, these cages are filled with one chlorine anion surrounded by a tetrahedron of four sodium atoms. In hackmanite, the central chlorine ion is partly substituted by a sulphur ion. This substitution is thought to be responsible for the photochromic property (Kirk 1955).

Since the quantity of sulphur in each sample of sodalite can change the intensity of absorption, and thus the colouration (Norrbo *et al.* 2015), the current and most accepted theory links the photochromism of hackmanite to the S_2^{2-} sulphur polyanion replacing a chlorine (Cl^-) anion in the structure (see details on sulphur anions in Box A). This defect requires the formation of a neighbouring chlorine vacancy for charge compensation (Norrbo *et al.* 2015, 2016; Carvalho *et al.* 2018; Norrbo

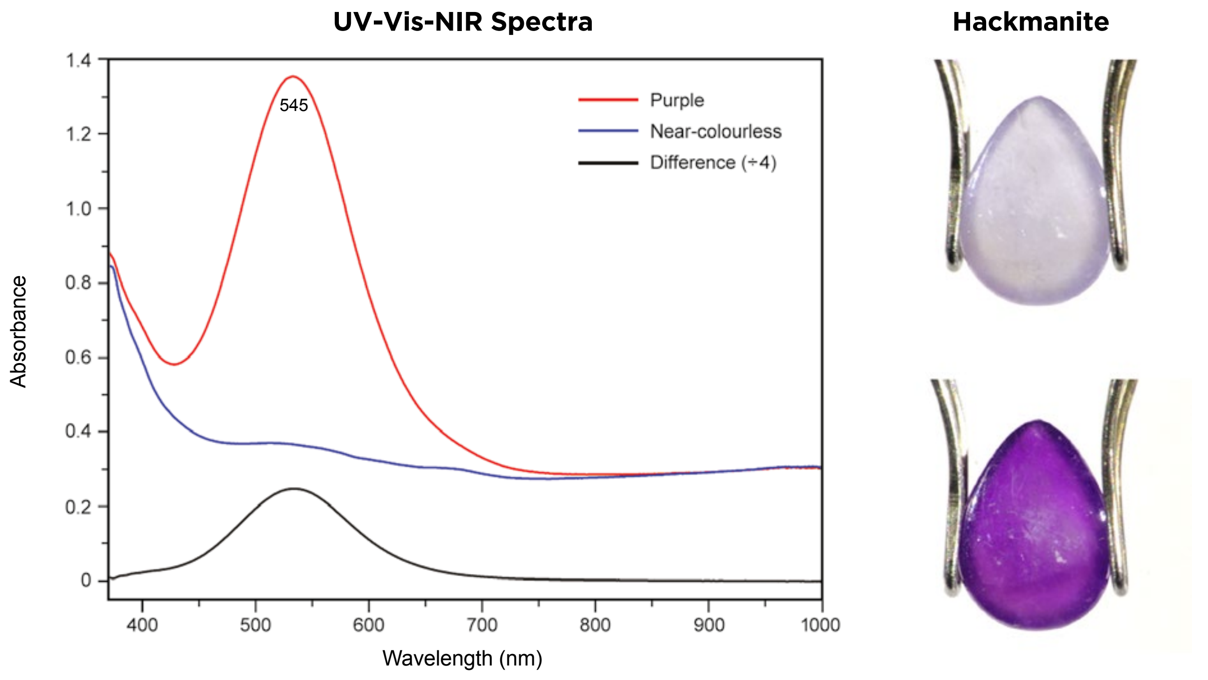


Figure 3: The absorption spectra of a 1.15 ct hackmanite cabochon from Mogok, Myanmar, before (near-colourless) and after (purple) exposure to UV radiation, correspond with the radical change in the sample's colour. The path length of the beam was approximately 3.1 mm, and the difference spectrum is divided by a factor of 4 for clarity. These spectra are consistent with others found in the literature (Ballentyne & Bye 1970; Chang 1974; Kondo & Beaton 2009; Milisenda *et al.* 2015). Photos by F. Blumentritt.

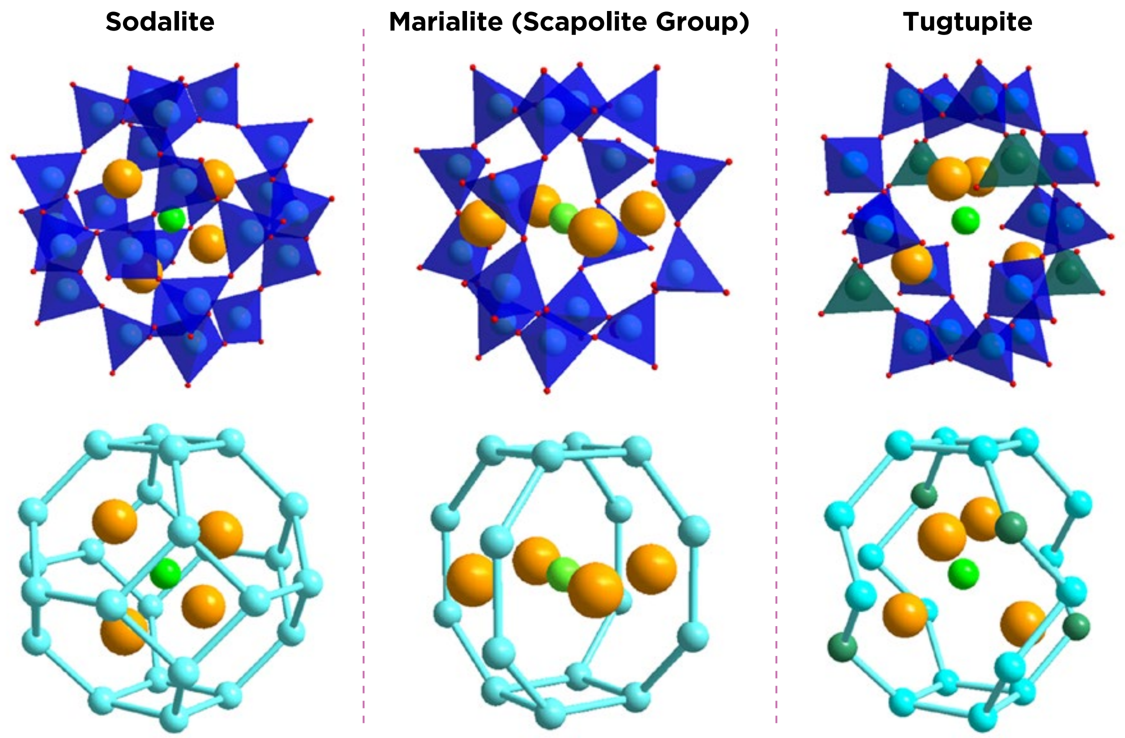


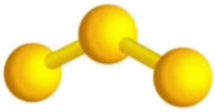
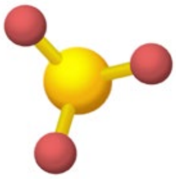
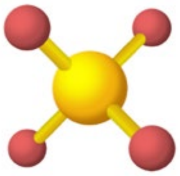
Figure 4: Photochromic aluminosilicates are characterised by the presence of 'cages' in their structures. These structural units enclose a large central area, as shown here (left to right) for sodalite, marialite and tugtupite. Top row: The cages are built of SiO_4 and AlO_4 tetrahedra (blue) and, for tugtupite, BeO_4 tetrahedra (dark green). Oxygen atoms are symbolised by small red dots. Each cage is nominally filled with four atoms of sodium (orange) around a central atom of chlorine (green). Bottom row: The cages are shown without oxygen atoms to highlight structural similarities. Drawings by F. Blumentritt.

BOX A: SULPHUR ANIONS IN SILICATES AND OTHER GEM MATERIALS

Sulphur is an important major or minor component of many mineral structures, and may occur as various ions (Table A-1), always with a negative charge (i.e. as an anion). Those that contain more than one sulphur atom are often referred to as sulphur polyanions. The polyanions S_2^- and S_3^- play a role in the colour or fluorescence of gems. For example, the S_3^- ion is responsible for the blue colour of lapis lazuli (lazurite) and several ultramarine minerals such as sodalite, haüyne, nosean, possibly afghanite, etc. (Fleet & Liu 2010). The S_2^- ion is responsible for the orange luminescence of sodalite, scapolite and tugtupite (Povarennykh *et al.* 1971; Blumentritt *et al.* 2020; Colinet *et al.* 2020).

Sulphur has a large number of oxidation states, resulting in many anions, as shown in Table A-1. These ions can be either impurities acting as colour centres, such as S_3^-, or constituents of the material, such as SO_4^{2-} in sulphate minerals.

Table A-1: Principal sulphur polyanions.

Sulphur anion	Schematic representation (S = yellow, O = red)	Main characteristics
S_2^-		Ion responsible for yellow-orange emission with vibronic structure found in the luminescence spectra of sodalite (hackmanite) and scapolite. Also gives a yellow colour to sodalite when present at elevated concentrations (Seel 1984).
S_2^{2-}		Ion theoretically responsible (i.e. lacking experimental evidence) for the photochromic property of hackmanite, acting as an electron donor.
S_3^-		Ion responsible for the blue colour of ultramarine, as seen in lazurite, sodalite, nosean, etc.
SO_3^{2-}		Ion possibly responsible for the light blue colour of celestite (Bernstein 1979) and barite.
SO_4^{2-}		Ion that constitutes sulphate minerals such as barite. It is also often present in the cages of the sodalite and scapolite structures.

2019). Hence, the photochromism could be due to a charge transfer between the sulphur polyanion and the associated chlorine vacancy (V_{Cl}):

$$S_2^{2-} + V_{Cl}^{0} \leftrightarrow S_2^{-} + V_{Cl}^{-}$$

This hypothesis has not yet been fully justified experimentally; in particular there is no physical evidence that S_2^{2-} in the above equation is, in fact, involved in the process. A recent study tends to support this mechanism with theoretical calculations (Curutchet & Le Bahers 2017), but it still provides no actual proof of the presence of S_2^{2-}. On the contrary, the presence of S_2^- has been proved experimentally, by the study of its associated orange luminescence in natural and synthetic hackmanite (Colinet *et al.* 2020), similar to the presence of S_2^- in scapolite (Blumentritt *et al.* 2020).

The colour centre—supposedly an electron trapped in the chlorine vacancy—is somehow naturally stabilised in some natural samples in which the purple colour remains even after long exposure to visible light or laser radiation (with a wavelength around the absorption maximum at 545 nm).

However, this model has been undermined by some authors, who consider that sulphur is not necessary for the photochromic property of hackmanite (Bye 1970; Bye & White 1970; Goettlicher *et al.* 2013). If sulphur can be considered an electron donor, then it could easily be replaced by another, as yet unknown, electron donor that is not related to sulphur.

The synthesis of sodalite is relatively easy, in theory, since the aluminosilicate framework already exists as a zeolite, used mostly as a molecular sieve and commercially available in powder form (Kowalak *et al.* 1995). This aluminosilicate framework makes it possible to replace the ions present in the sodalite cages with some unusual ones. Hence, it has been possible to synthesise bromosodalite ($Na_8Al_6Si_6O_{24}Br_2$) and iodosodalite ($Na_8Al_6Si_6O_{24}I_2$), for example. According to Williams *et al.* (2010), both of these are photochromic owing to the presence of sulphur as an impurity. Williams *et al.* (2010) further observed that the replacement of the major anion (Cl by Br, I, etc.), as well as substitution of atoms inside the aluminosilicate structure (Al for Ga; Si for Ge), induces a change in sodalite's photochromic colour, as illustrated in Figure 5.

The control of photochromism in sodalite is promising for its use in industrial applications such as a switching material (Irie 2000), optical data storage material (Irie 1989), and UV and X-ray dosimetry (Tian & Zhang 2016; Norrbo *et al.* 2018; Vuori *et al.* 2021). Research on hackmanite is probably the most advanced and closest to attaining industrial applications compared with other photochromic gem materials.

MARIALITE (SCAPOLITE GROUP)

Photochromic marialite was reported for the first time in 2005 and was originally mistaken for hackmanite because of its 'comparable' photochromism (McClure *et al.* 2005). This scapolite came from Afghanistan, and is colourless in its stable state but turns deep blue upon UV irradiation (Milisenda *et al.* 2015), preferentially with short-wave UV (Figure 6). The blue colouration disappears when the stone is illuminated with visible light. Chemical analyses revealed these gems to be marialite (McClure *et al.* 2005).

Marialite is the NaCl-rich member of the scapolite group with the ideal formula $Na_4Al_3Si_9O_{24}Cl$. However, the pure end-member composition does not appear to exist naturally because pure marialite has never been found (Shaw 1960). Gems of the scapolite group always have an intermediate composition in the solid solution between marialite (NaCl-containing pure end member) and meionite ($CaCO_3$-containing pure end member). Yet, the name *marialite* is not only used to define the NaCl-containing end member, but is also usually extended to samples containing less than 20% meionite (Shaw 1960). All the natural samples examined by Shaw (1960) plotted between these two end members with a composition that mostly ranged between two intermediate species, formerly known as 'dipyre' (20–50% meionite) and 'mizzonite' (50–80% meionite).

Nevertheless, the properties of the photochromic samples studied by McClure *et al.* (2005) showed them to be close to the ideal marialite end member, consistent with our own laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) analyses of the sample presented in Figure 6 and the many other photochromic scapolites in our collection. The main difference between the UV-Vis-NIR absorption spectra of the two colour states is a broad band centred at around 600 nm in the

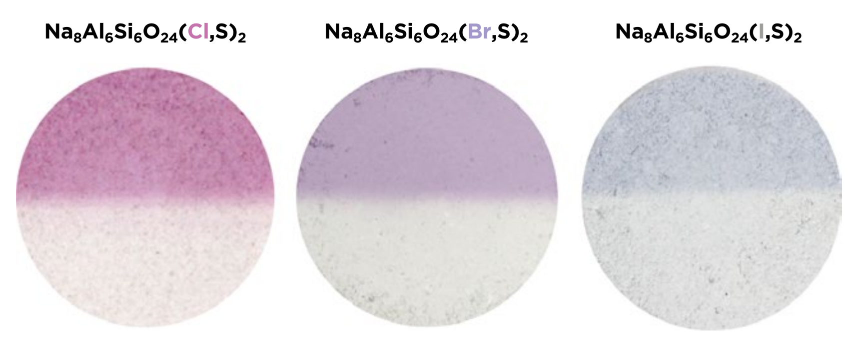


Figure 5: From left to right, synthetic powders of chlorosodalite, bromosodalite and iodosodalite (synthesised by F. Blumentritt), all containing a sulphur impurity, show photochromism. The images were taken after the top half (coloured) was exposed to short-wave UV radiation for 20 minutes, while the bottom half (near-colourless) was masked. Photos by F. Blumentritt.

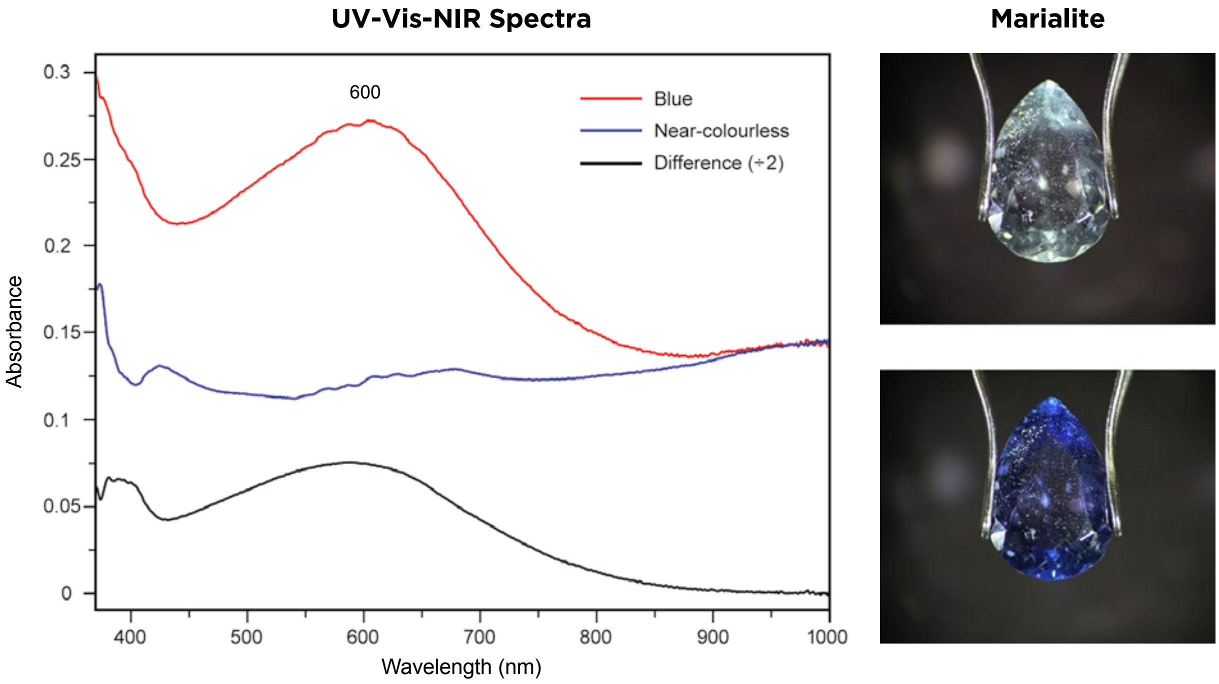


Figure 6: Photos and absorption spectra for a 2.58 ct photochromic marialite from Afghanistan are shown before (near-colourless) and after (blue) exposure to short-wave UV radiation. The wiggly vibronic structure around 600 nm is caused by trapped S_2^{2-} and is present due to the mode of operation of the spectrometer (see Materials and Methods section). The path length of the beam was approximately 4.2 mm, and the difference spectrum is divided by a factor of 2 for clarity. The spectra are consistent with those presented by Milisenda *et al.* (2015). Photos by F. Blumentritt.

excited state that absorbs in the orange-to-red region and thus produces the blue colour (again, see Figure 6).

Allen *et al.* (2014) documented increased photochromism in Afghan marialite that had reportedly been irradiated, in which the treated samples exhibited a deeper blue colouration under UV radiation than untreated ones. The exact details of the treatment are unknown, but it is believed that a nuclear reactor was used (Dudley Blauwet, pers. comm. 2021), so neutrons could have been involved, but gamma rays are also a possibility.

Marialite has been studied less than hackmanite but presents some similarities. As with sodalite, the scapolite structure can be described as a stacking of cages formed by intertwining chains of SiO_4 and AlO_4 tetrahedra (Figure 4, centre). In these cages the central anion is surrounded by a planar square of four cations. Regarding the solid solution of the scapolite group, marialite has cages filled mostly by chlorine surrounded by four atoms of sodium, and meionite mostly has carbonate surrounded by four atoms of calcium (Lin & Burley 1973).

Because the discovery of photochromic scapolite is relatively recent, earlier research targeted other properties such as its yellow-orange luminescence (Burgner *et al.* 1978) and its thermal expansion (Baker 1994). The characteristic yellow-orange luminescence of scapolite was first ascribed to the presence of uranium (Iwase 1937), but the currently accepted explanation is the presence of polysulphides (Kirk 1955; Burgner *et al.* 1978; Sidike *et al.* 2008). In particular, recent research has shown that the yellow-orange luminescence is caused by S_2^- ions (Blumentritt *et al.* 2020; Colinet *et al.* 2020), which could indirectly contribute to the understanding of the photochromism. One model proposed to explain the photochromic reaction in hackmanite includes sulphur polyanions and vacancies (Norrbo 2019). We recently demonstrated with chemical and spectroscopic considerations that photochromism in marialite also fits a reaction involving a vacancy (Blumentritt 2021). Even if sulphur has been conclusively shown to induce photochromism, it is still possible that sulphur might not be necessary in all cases.

TUGTUPITE

Henning Sørensen first discovered tugtupite in southern Greenland in 1957 (Sørensen *et al.* 1971). He immediately noticed the colour instability of this mineral: samples that were initially white, pink or deep red all took on a dark red appearance after X-ray irradiation (Sørensen *et al.* 1971). It was later realised that UV

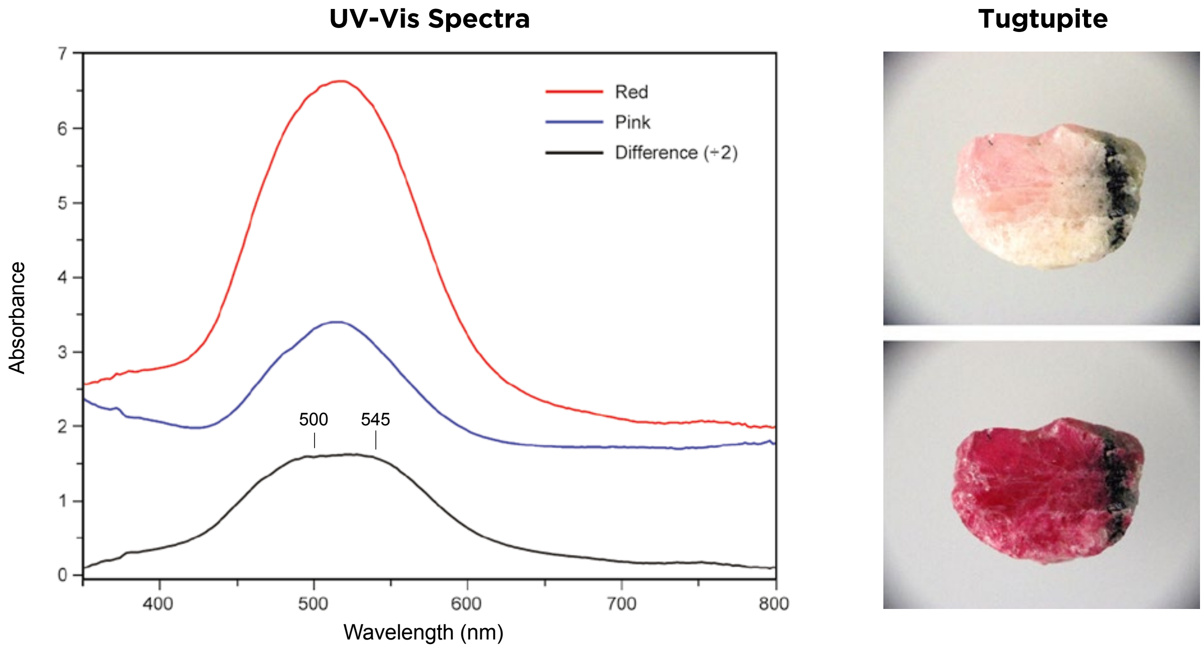


Figure 7: Photos and absorption spectra for a 1.27 g tugtupite from Greenland illustrate the difference in colour before (pink) and after (red) UV exposure. The absorbance was calculated from reflectance spectra using the Kubelka-Munk approximation. The difference spectrum is divided by a factor of 2. The red colouration seems to be due to two almost completely overlapping bands peaking at about 490 and 535 nm. This observation is consistent with published spectra (Milisenda *et al.* 2015). Photos by F. Blumentritt.

radiation also produces photochromism in tugtupite (Tunzi & Pearson 2008; Milisenda *et al.* 2015). The darkened gem returns to its initial colour when kept in the dark, or exposed to artificial visible-light radiation or standard natural daylight (D65) for a few minutes (Figure 7). The large photogenerated feature seen on the difference spectrum (black curve) in Figure 7 could be explained by two Gaussian contributions, thus two photogenerated colour centres. One of these Gaussian contributions is similar to the one observed in the spectrum of photogenerated purple hackmanite (again, see Figure 3) with a maximum at about 545 nm. However, unlike hackmanite, a second Gaussian contribution is photogenerated with an absorption maximum at about 500 nm. This second contribution explains the difference between the photogenerated purple colour of hackmanite and red colour of tugtupite.

Gem-quality tugtupite samples (Dragsted 1970; Jensen & Petersen 1982)—mostly as cabochons but exceptionally as transparent faceted gems—are relatively rare. Only three localities are known for tugtupite: the Ilímaussaq complex in Greenland, Kola Peninsula in Russia, and eastern Canada (Dragsted 1970; Sørensen *et al.* 1971; Jensen & Petersen 1982; www.mindat.org/min-4044.html). This could explain a relative lack of scientific studies on the mineral. However, tugtupite is of a great interest because the photochromic property seems to be intrinsic to this mineral. To the best of our knowledge, there is no documented natural, colour-stable tugtupite. The photochromic property has even been reported in rare light blue to very light blue tugtupite, with exposure to UV radiation causing a reddish purple to purplish red colouration (Jensen & Petersen 1982).

Tugtupite, $Na_8Al_2Be_2Si_8O_{24}Cl_2$, is a member of the helvite group, which can be considered a subgroup of the sodalite group because of structural similarities (Danø 1966; Jensen & Petersen 1982). In tugtupite, which shares the same 'cage' structure with sodalite (Figure 4, right), two Al^{3+} ions are replaced by one Si^{4+} and one Be^{2+} ion (Semenov & Bykova 1960). The majority of elemental analyses have revealed the presence of a sulphur impurity, some with replacement of up to 5% of chlorine in samples probably from Greenland (Danø 1966). Sørensen *et al.* (1971) proposed the structural formula $Na_8Al_2Be_2Si_8O_{24}(Cl,S)_2$, but sulphur does not appear to be a basic constituent of tugtupite, so the International Mineralogical Association has kept the formula without sulphur (IMA 2021).

The published literature does not provide any explanation for tugtupite's photochromism. However, its luminescence properties have been extensively studied. Gaft *et al.* (2009) reported at least five different emissions: yellow-orange, red, green, blue and violet. The yellow-orange luminescence is well known for related minerals such as sodalite and scapolite. It has long been suggested to be due to S_2^- (Povarennykh *et al.* 1971; Gaft *et al.* 2009; Friis 2011). The red luminescence is ascribed to the substitution of tetrahedral Al^{3+} or Si^{4+} by Fe^{3+}, as in feldspar (White *et al.* 1986; Krbetschek *et al.* 2002) or sodalite (Gaft *et al.* 2009). The other emissions—green, blue and violet—are ascribed to the presence of Mn^{2+}, Ce^{3+} and Eu^{2+} impurities, respectively (Gaft *et al.* 2009).

Investigations of tugtupite photochromism could help consolidate data on photochromic aluminosilicates (sodalite, scapolite and tugtupite). Synthetic tugtupite has been produced (Armstrong & Weller 2006), but since tugtupite contains beryllium, synthesis of such a material presents many Be-related health risks. In addition, synthetic tugtupite has not been tested for photochromism. Because of many similarities with the previously discussed aluminosilicates (structure, composition and presence of sulphur), the cause of tugtupite's photochromism is possibly similar, if not identical, to that of sodalite and scapolite—that is, an electron trapped in a Cl vacancy and associated sulphur polyanions, possibly S_2^{2-} and/or S_2^-. If so, the two photogenerated Gaussian contributions in the absorption spectrum of tugtupite (Figure 7) could be related to two different environments around the electron trapped in the Cl vacancy, and more research is needed to elucidate these two environments.

SPODUMENE (KUNZITE VARIETY)

George F. Kunz, after whom this variety is named, noted that the 'spodumene crystals are beautiful in their colour tones, varying from deep rosy lilac at some depth to pale or almost colourless, doubtless due to weathering or to the action of sunlight, in striking contrast to the rich deep pink-purple found in a greater depth' (Kunz 1903, p. 264). He was the first to indicate that sunlight could have an influence on the colour of spodumene.

Claffy (1953) reviewed the photochromic behaviour of spodumene, and mentioned that it can rapidly change from pink to green due to exposure to a high-energy source such as X-rays. In addition, the present authors have verified that this also happens with only UV radiation, although it takes much longer. Some giant gem-quality spodumene crystals found in Laghman Province, Nuristan, Afghanistan, were green upon discovery and turned pink shortly after being excavated (Bariand 2008). This modification of the colour can continue to near-colourless if exposed for a very long time to direct sunlight.

The photochromism of spodumene is unique because it has three colour states—colourless, pink and green—rather than the two of 'classic' photochromism (Claffy 1953). According to Claffy, any colourless spodumene exposed to X-rays turns green. This green colouration is completely different from the 'emerald-green' stable colour of hiddenite caused by Cr^{3+} (Cohen & Janezic 1983; Liu *et al.* 2017). In rare cases, hiddenite exposed to X-rays turns blue (Claffy 1953), but the reversibility of this colour behaviour has not been established. According to Claffy, after a colourless sample has been X-ray irradiated to green, it then returns to its initial state with visible-light exposure or heating, but a third (pink) state can be observed between the green and colourless states (Figure 8). However, these processes of colouration and discolouration are

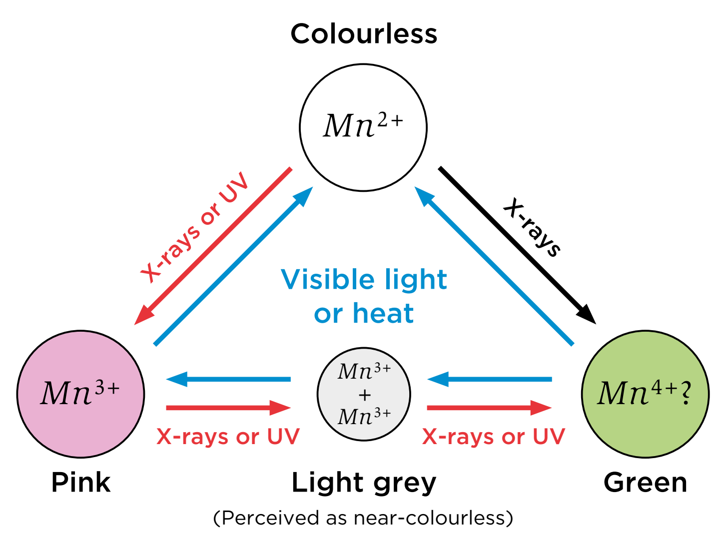


Figure 8: The relationship between the colours of photochromic spodumene is shown here, adapted from Claffy (1953) and Schmitz and Lehmann (1975). Depending on the X-ray energy and flux, the colourless state can change directly to green (high energy and flux) or pass through the pink and light grey states (low energy and flux). The return from the green state to the colourless state, in both ways, is achieved by visible-light exposure or heating.

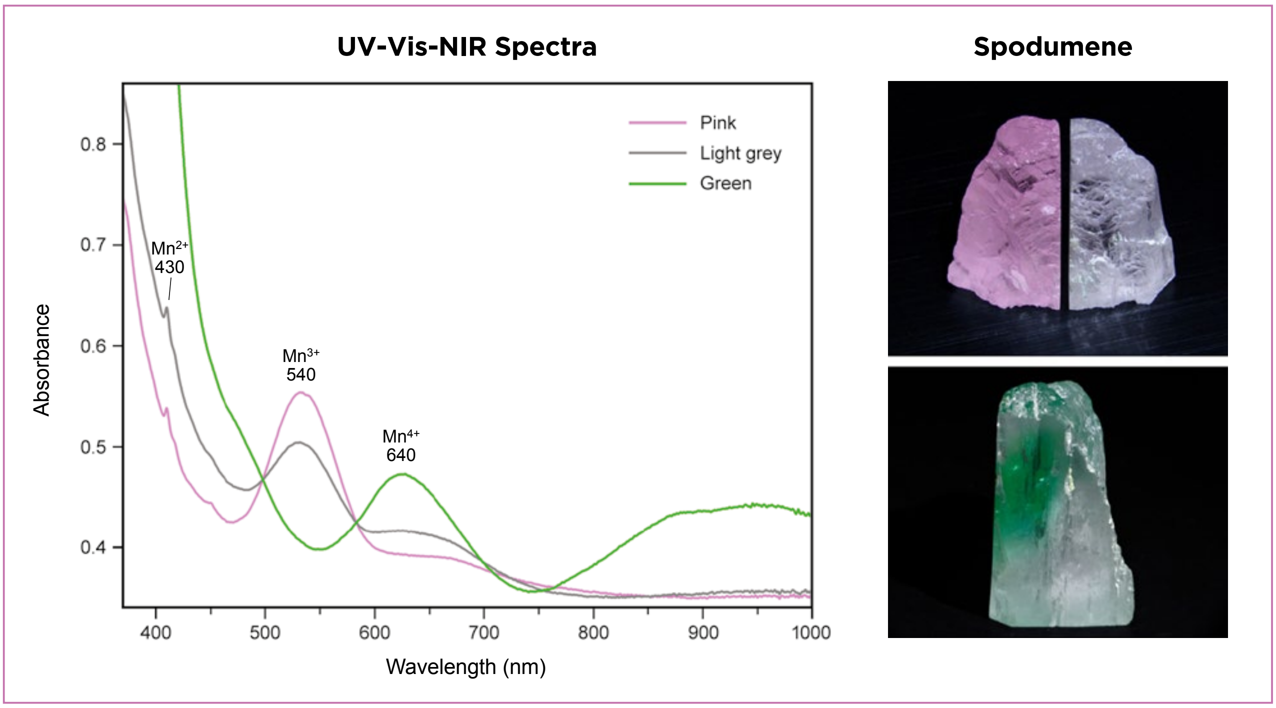


Figure 9: Photos and absorption spectra of a 51.6 g photochromic spodumene from Afghanistan that was cut into two parts show one half, initially near-colourless, which was exposed to short-wave UV until the deepest possible pink colouration was attained (1 hour), alongside the other part, which underwent more UV exposure until the pink colouration disappeared and it thus appeared light grey (4 hours). The latter half of the sample was then partly exposed to X-ray irradiation for 48 hours to obtain the 'emerald-green' colour. The pink colouration is due to the prominent Mn^{3+}-related band at about 540 nm. The green spectrum results from a dominant Mn^{4+}-related 640 nm band, absorbing the red spectral region. The sharp feature at about 430 nm is due to Mn^{2+}. The path length of the beam was approximately 26 mm. Photos by F. Blumentritt.

quite slow compared to other photochromic gems such as sodalite or scapolite. Also, according to Claffy (1953), the photochromism appears only in samples with very low Cr content.

For our own sample from Afghanistan (which was originally near-colourless; locality details unknown), the pink colour is due to a 540 nm band, attributed to Mn^{3+} produced by UV irradiation from Mn^{2+} (the latter seen in the spectrum mostly as a sharp band at about 430 nm).[1] Irradiation with X-rays turned the sample 'emerald green' (Figure 9), coincident with the disappearance of a persistent orange luminescence (commonly called phosphorescence) after several hours. This comes from decay of the Mn^{3+} band in favour of a band at 640 nm, classically linked to Mn^{4+} (see discussion below). The green colour faded slowly (over weeks to months) in artificial light, and at some point there was a combination of green and pink which appeared light grey, which could be perceived as near-colourless (again, see Figure 9, light grey trace). Then the colour of the stone changed further to purplish pink.

Spodumene is a member of the clinopyroxene subgroup, with the formula $LiAlSi_2O_6$. It is mainly exploited for its high Li content (Salakjani *et al.* 2017), but most interestingly, the photochromism of kunzite has been used for dosimetry (Oliveira *et al.* 2009; Olivieri 2011). The pink colour of kunzite is due to the presence of small amounts of Mn (about 0.07 wt.%; Schmitz & Lehmann 1975). Manganese is also suspected of participating in the photochromic reaction. Stuhlman and Daniel (1928) proposed a redox reaction to explain the different colour states. This was later supported by Schmitz and Lehmann (1975) and Hassan and Labib (1978), who proposed that the 536 nm broad band of Mn^{3+} in distorted Si^{4+} sites is responsible for the 'lilac' tint, and Mn^{4+} for the green colouration (again, see Figure 8). In the colourless state, the manganese would be present as Mn^{2+} (Hassan & Labib 1978), and possibly responsible for the orange luminescence classically associated with Mn^{2+} in octahedral coordination in spodumene and other minerals (Aguilar & Osendi 1982). Thus the substitution of Si^{4+} in the tetrahedral

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[1] Pink colouration in kunzite is typically due to natural gamma-ray irradiation from surrounding minerals in the granitic pegmatite environment in which it forms.

site by Mn^{3+} (or Mn^{2+}) is unlikely and has not been proven. The Mn^{2+} ion is more likely to substitute in the Al^{3+} octahedral site, as in tourmaline or beryl (Neiva & Neiva 2005; Sugiyama *et al.* 2016), which necessitates a charge compensation of +1.

Hassan and Labib (1978) and Bosshart *et al.* (2011) pointed out that the increase of the Mn^{4+} absorption band (about 640 nm; see Figure 9, green trace) that occurs upon irradiation is linked to adjacent Fe^{3+}, which possibly acts as a charge compensator by trapping the holes produced during irradiation, although no charge compensation has been proposed. Further, Bosshart *et al.* (2011) showed a correlation between the area under the Mn^{3+}-related peak at about 540 nm (see Figure 9, pink trace) and the amount of MnO + Fe_2O_3—a correlation that is not found for the 640 nm band. Thus the role of Mn is undeniable in the photochromism mechanism, while that of Fe remains to be clarified.

Recently, Czaja *et al.* (2020) proposed an alternate explanation by hypothesising that the octahedral M2 site (among M1 and M2 crystallographic octahedral sites), in which Mn substitutes for Al, changes dimension as a consequence of irradiation. This work also excludes the possibility of Mn^{4+} being responsible for the green colour. Unfortunately, no structural information is provided to support the purported deformation of the M2 site, and the article overlooks the relationship with Fe pointed out by Bosshart *et al.* (2011).

Thus, curently we can only be sure that the photochromism of kunzite is related somehow to Mn, but the specific origin of the green colour remains the subject of debate.

DIOPSIDE

Diopside ($CaMgSi_2O_6$) belongs to the pyroxene group, like spodumene, with related crystallographic structures and possibly a related photochromism mechanism. It is rarely considered a gem material. The first and possibly only published note on photochromic diopside was by Hyršl (2016) on non-gem-quality material from Bazenovskoe, Russia. It was initially yellow or dark yellow, but turned brownish green after UV irradiation. It returned to its initial colour when exposed to visible light. The phenomenon can be repeated at least over months without any observable fatigue.

We obtained an opaque, non-gem diopside sample (also from Bazenovskoe) for which we recorded reflectance spectra of its greenish yellow and yellowish green colour states (Figure 10). The difference spectrum is characterised by a very broad band peaking at around 700 nm, or possibly showing a change in the absorption continuum. We have as yet no hypothesis for the origin of this absorption change. Additional work and samples are obviously needed. By analogy with the absorption spectra of other pyroxenes (e.g. hedenbergite, jadeite and

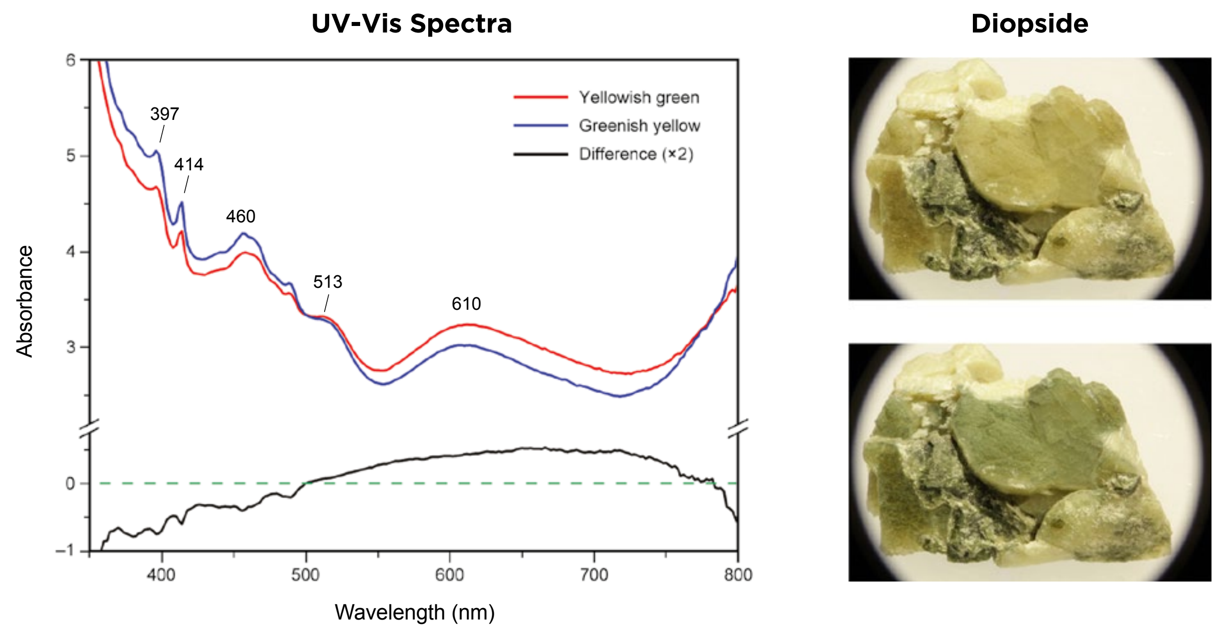

Figure 10: Photos and absorption spectra of an 8.37 g photochromic diopside from Russia are shown before (greenish yellow) and after (yellowish green) short-wave UV illumination. The absorbance was calculated from reflectance spectra using the Kubelka-Munk approximation. The difference spectrum is multiplied by a factor of 2 for clarity. Photos by F. Blumentritt.

spodumene; http://minerals.gps.caltech.edu), it does not seem that bands related to Fe^{2+} or Cr^{3+} are involved in the photochromism.

ZIRCON

In 1904, Max Bauer published probably the first account of photochromic zircon (Bauer 1904, p. 342):

> The color and lustre of some hyacinths is liable to change even at ordinary temperatures if the stones are exposed to light, especially to the direct rays of the sun. In some cases the color becomes pale, while in a few stones it changes to a brownish-red which gradually becomes more decidedly brown.

He also indicated that the initial colour returns when samples are stored in the dark for a few hours, and that the time necessary for this reversal differs among stones. So from the start, several different photochromic behaviours were observed in zircon. However, it is difficult from this short description to understand if the modification is due to 'white visible light' (sunlight) or to the action of natural UV irradiation (also in sunlight). Recent discussions with a gem dealer familiar with zircon (Michael Gray, pers. comm. 2019) are consistent with Bauer's observations and also provide more detail. Three behaviours stand out, as described below.

Behaviour 1. When exposed to visible light, the brown-to-orange colour fades to a stable near-colourless state (Figure 11). Then, the brown colour can be produced by exposure to long-wave UV radiation or by keeping a sample in the dark (McClure 2011). Such zircon is often sold as colourless or, if presented in its coloured state, as 'chameleon zircon'—a trade term with no precise definition. According to several rare-stone and mineral dealers, this behaviour appears to be the most common for photochromic zircon. Figure 11 shows that the absorption of those brown zircons is a continuum with superimposed broad features at about 510 and 800 nm. The few sharp peaks (at 654 and 691 nm) are due to uranium (U^{4+}). The 510 nm feature has been attributed to a complex colour centre related to yttrium (Y^{3+}) trapping an oxygen hole centre (Zeug *et al.* 2018). The difference spectrum reveals that actually all features change together, which complicates the interpretation of the photochromism.

Behaviour 1 could also apply to heat-treated blue zircon for which a brownish component appears upon exposure to UV radiation and then fades under artificial light (Koivula & Misiorowski 1986; Renfro 2016; Zeug *et al.* 2018).

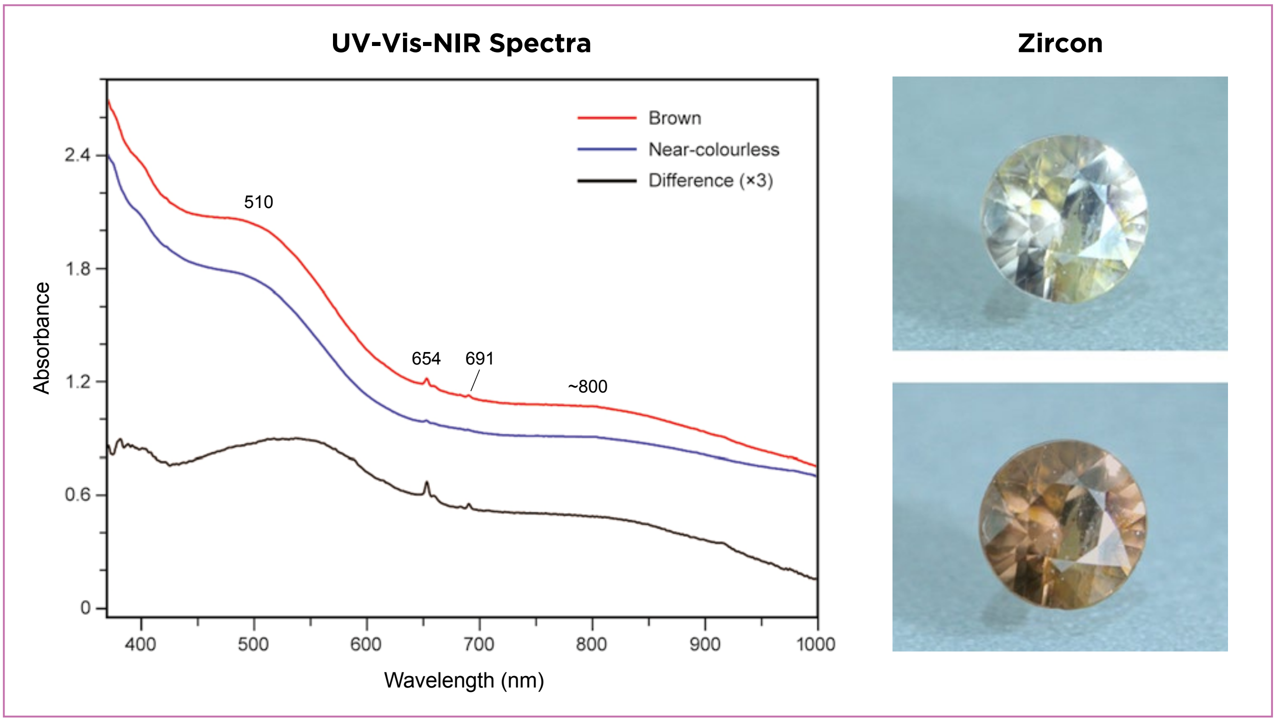

Figure 11: These photos and absorption spectra of a 0.43 ct photochromic zircon were taken before (near-colourless) and after (brown) long-wave UV exposure. This photochromism corresponds to behaviour 1 (see text). The path length of the beam was approximately 1.8 mm, and the difference spectrum is multiplied by a factor of 3 for clarity. Photos by F. Blumentritt.

Figure 12: This 62 ct light brown photochromic zircon of unknown locality (left) shows an impressive change, becoming dark brown after exposure to long-wave UV radiation (centre). It returned to lighter brown with exposure to visible light. Interestingly, after heating at about 400°C it became bright yellow-orange (right), but that colour was not stable. Photos courtesy of Thomas Hainschwang.

It has been pointed out to us (Thomas Hainschwang, pers. comm. 2021) that at least in some cases, brown zircon becomes orange after heating, but not permanently (Figure 12). The blue colour of zircon is typically not a natural colour but the result of heat treatment of certain brown zircons in a reducing atmosphere (Smith & Balmer 2009). One wonders if a brown zircon used to produce a photochromic blue zircon would itself be photochromic.

Behaviour 2. This behaviour refers to dark reddish brown zircon that changes to a stable orangey red colour (Figure 13) when slightly heated (about 100°C) or kept in the dark for several days. The dark brown colour returns upon exposure to daylight for several minutes (Smith & Balmer 2009), but this change is faster (a few seconds) under long-wave UV radiation. This is an alternative to behaviour 1 described above because the brown photogenerated

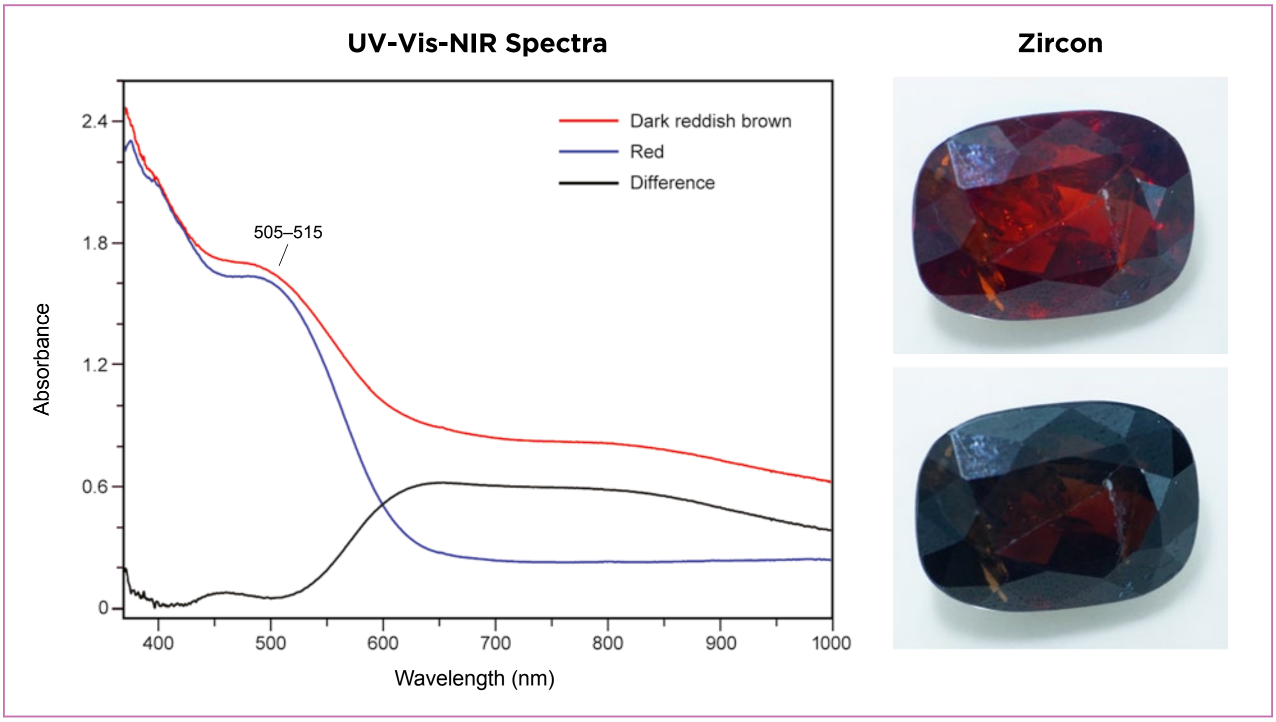

Figure 13: Photos and absorption spectra of an exceptional 21.3 ct photochromic zircon from Cambodia show its stable orangey red colour (top photo, shown after heating the sample at about 100°C) and its dark reddish brown appearance induced by brief exposure to long-wave UV radiation (bottom photo). This photochromism corresponds to behaviour 2 (see text). The path length of the beam was approximately 6.2 mm. Photos by F. Blumentritt.

colour is removed with heat (a non-radiative process), rather than with visible radiation, corresponding to type T photochromism (see Definitions section). Note that the UV-Vis-NIR spectrum of the brown zircon in Figure 11 is similar to that of the dark reddish brown gem in Figure 13. So far this behaviour has been observed in brown zircon from Ratanakiri, Cambodia (Smith & Balmer 2009), Dong Nai, Vietnam (Le & Pham 2021) and Jemaa, Nigeria (Michael Gray, pers. comm. 2021).

As shown in Figure 13, this photochromic effect is mainly due to a decrease in the absorption continuum (of unknown origin), thus removing the brown component, and an increase in the band around 505–515 nm (related to Y^{3+} trapping an oxygen hole centre; Zeug *et al.* 2018), which removes the green and reinforces the red appearance.

Behaviour 3. In some colourless to light brown zircon (reportedly from Australia), exposure to long- or short-wave UV radiation for a few minutes causes the colour to turn brown to brownish yellow. The stable colouration can be returned by heating in an alcohol flame, which causes the zircon to fade to an unstable orange (which always disappears upon cooling) before turning colourless or light brown. This is reversible by exposure to UV radiation, although the brown colour does not always return to the same intensity (Michael Gray, pers. comm. 2019).

Regarding the possible origin of zircon photochromism, McClure (2011) indicated that LA-ICP-MS analysis did not reveal any clear differences between the chemical composition of photochromic and non-photochromic stones. Energy-dispersive X-ray fluorescence analysis by Suthiyuth (2014) also did not show any chemical evidence for photochromism, only normal impurity elements. The lack of correlation of photochromism with any particular impurity or trace element (such as a rare earth), and its occurrence in zircon from various geographical origins, suggest that the phenomenon involves an intrinsic defect (as in corundum; see part 2 of this article). However, little is known about colour centres in zircons, especially brown colour centres. The work of Kempe *et al.* (2017) suggests that the brown colour originates from either hole or electron centres. A hole represents the lack of an electron, with a charge of +1. If Kempe *et al.* are correct, an electron transfer from one centre to another could explain some of the photochromic behaviours in zircon.

CONCLUSION

Photochromism in silicates is quite varied. However, there may be a consistent explanation for the change in colour shown by the three aluminosilicates with cage structure (sodalite, marialite and tugtupite), in which the optical phenomenon is principally related to chlorine vacancies, possibly induced by the presence of sulphur polyanions (e.g. Figure 14).

In other silicates, we are at best limited to conjectures involving possible electron movement. For spodumene this electron is associated, at least in part, with the Mn impurity ion. The absence of any detailed description and interpretation of photochromic zircon behaviours points to a need for further studies.

In general, this review illustrates the need for fundamental knowledge about photochromism in inorganic materials. In the second part of this article, we will explore photochromism in diamond, corundum and barite. Not surprisingly, the large amount of research on diamond results in greater understanding of the phenomenon.

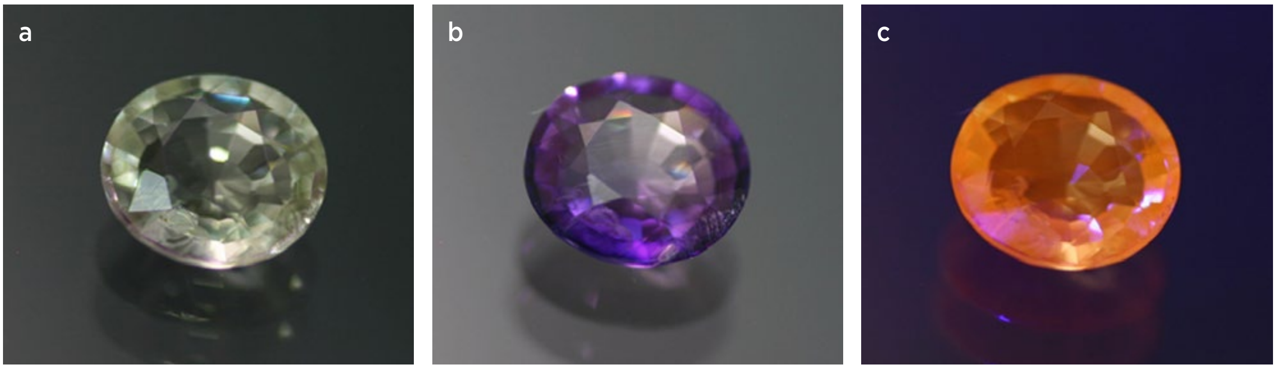

Figure 14: The photochromism of aluminosilicates with cage structure—sodalite, marialite and tugtupite—is thought to be related to chlorine vacancies, possibly induced by the presence of sulphur polyanions. One such polyanion, S_2^-, is also responsible for the yellow-orange luminescence of sodalite and scapolite. This 0.47 ct faceted hackmanite from Myanmar provides a nice example of this photochromism (**a**, **b**) and luminescence (**c**). Photos by Brad Payne (The Gem Trader, Cave Creek, Arizona, USA).

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