Assessing the Stability of Mineralogical Collections in Museums

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Abstract

At least 10% of currently identified mineral species are susceptible to deterioration within the museum setting. The significance of this, however, is largely unknown, as there is a substantial lack of quantitative information pertaining to mineral susceptibility within the heritage literature. Findings from other scientific fields—such as the geosciences and materials science—rarely enter the heritage sector, as relevant research outputs are not easily accessible or transferable. The doctoral research outlined in this thesis was designed as a response to these challenges, with the aim of developing of an efficacious methodology for facilitating the determination of mineral susceptibility. This was achieved via database, survey, and colorimetric methods. The Mineral Susceptibility Database (MSD) was produced as a single, openly accessible repository of currently published research relevant for mineral preservation, and contains 957 entries for 596 mineral species. The Deterioration Phenomena (DP) State Survey Method was designed to mitigate current shortcomings of collection surveying and provide quantitative data pertaining to the state of mineral specimens. The DP Method was used to survey 13,716 specimens from Oxford University Museum of Natural History's (OUMNH) systematic mineral collection, and to characterise the types of deterioration prevalent within similar collections. The survey results corroborate that the types of reactions recorded in the MSD are indeed found within museum collections. Experiments validating the use of colorimetry on mineral specimens were performed and confirmed application to opaque and metallic species. Colorimetry was then used in conjunction with the DP Method to survey 1,273 pyrite specimens held at OUMNH, National Museum Cardiff, National Museums Liverpool, and the Sedgwick Museum of Earth Sciences. The results of this cross-museum survey elucidated the nature of pyrite deterioration within the museum environment, as summarised by the impurity hypothesis: the concentration of impurities within pyrite is the primary factor influencing the pyrite decay reaction. The formulation of this hypothesis demonstrates that the aim of this thesis was achieved, and that the aforementioned methods can produce robust data from which the deterioration of other mineral species can be characterised.

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Author Contribution Statement

Much of Chapters 2 and 3 was published as an article in Studies in Conservation (Royce et al. 2023), which was co-authored with the candidate's supervisors Prof. Viles and Dr. Baars.

Kathryn Royce Schronk is the primary author of the paper in question. The vast majority of the content is the result of her own conceptualisation and desk-research. She drafted and revised the manuscript, compiled and reviewed references for the Mineral Susceptibility Database (MSD), and created the MSD.

Dr. Baars participated in the conceptualisation of the paper. Both he and Prof. Viles provided a critical review of and substantive feedback on the various drafts of the manuscript.

By signing the Statement of Authorship, you are certifying that the candidate, Kathryn Royce Schronk, made a substantial contribution to the publication in question, and that the description above is accurate.





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Glossary of Key Terminology

The following definitions are either a.) taken directly from the Mindat Glossary (the Hudson Institute of Mineralogy 2023a) (1), Berns 2019 (2), or Kuehni 2003 (3), or b.) are this author's explanation based on the aforementioned sources and or those found in the References (4).

Terms defined in the glossary are italicized upon first instance within the text.

Geological Materials

Fossil: any remains, trace, or imprint of a plant or animal that has been preserved in the geological record. (4)

Gemstone: a mineral of sufficient beauty and durability that is used for personal ornamentation. (4)

↳ **Facet:** one of the polished plane surfaces of a gemstone. (1)

Habit: a general term for the outward appearance of a mineral or rock. (1)

Locality: the location of a geological specimen's formation and or extraction. (4)

Matrix: the rock material in which a fossil, crystal, or mineral is embedded. (1)

Mineral: a homogeneous, naturally occurring solid with a defined and unique chemical composition and crystalline structure. (4)

↳ **Species:** a mineral distinguished from others by its unique chemical and physical properties. (1)

↳ **Variety:** a mineral showing differences in colour, habit, or other external physical characteristics, or minor variations in composition from the material considered typical of the species. (1)

Ore body: a continuous, well-defined mass of material of sufficient ore content to make extraction economically feasible. (4)

Rock: a naturally-occurring solid aggregate of one or more minerals or mineraloids. (1)

Mineral Chemistry

Crystal: a solid that has a regularly repeating internal arrangement of its atoms; especially, a solid that has natural external plane faces as a result of the internal structure. (4)

Phase: a homogeneous, physically distinct portion of matter in a heterogeneous system. (1)

Polymorph: a chemical compound which crystallises in a different crystal class to another compound of identical chemical composition; e.g., quartz, tridymite, cristobalite, coesite, and stishovite. (1)

Pseudomorph: a mineral sample with the external crystal form of one mineral and the internal chemistry of another; e.g., cubes of goethite after pyrite resulting from oxidation of the ferrous sulfide to ferric oxyhydroxide. (1)

> ↳ **Paramorph:** a pseudomorph with the same composition as the original crystal, caused by a phase transformation; e.g., calcite with aragonite morphology. (1)

Stability Field: the conditions at which a mineral is stable. Conditions are classically defined as temperature, pressure, and the composition of compounds present in the surrounding environment. May be depicted in a stability (or phase) diagram. (4)

> ↳ **Stable:** a material that does not readily change under a given set of conditions. (4)
>
> ↳ **Metastable:** a material which appears stable under a given set of conditions but is capable of slow reaction or phase change over extended time periods (from weeks to millions of years); e.g., torbernite will dehydrate to metatorbernite, and aragonite can invert to calcite. (1)
>
> ↳ **Unstable:** a material that readily changes at a measurable rate under a given set of conditions. (4)

Mineral Reactions

Corrosion: the (electro-)chemical oxidation of metallic compounds within a mineral. (4)

Dehydration: the loss of a mineral's structural or interstitial water. (4)

Deliquescence: the dissolution of a mineral through the absorption of atmospheric moisture. (4)

Dissociation: the splitting of a hydrated compound into smaller units. (4)

Efflorescence: the crystallisation of soluble products at or near a mineral's surface. (4)

Hydration: the addition of water molecules to a mineral. (4)

Hydrolysis: a reaction between a mineral and water that produces new compounds. (4)

Hygroscopicity: the tendency for a material to absorb or adsorb atmospheric moisture. (4)

Oxidation: a change in the oxidation state of elements within a mineral, resulting in new compounds or mineral species. (4)

Key Heritage Conservation Concepts

Agents of Change: a.k.a. *Agents of Deterioration*; the ten currently-identified hazards that cause change to heritage objects: 1.) physical forces; 2.) thieves & vandals; 3.) fire; 4.) water; 5.) pests; 6.) pollutants; 7.) radiation: visible light, ultraviolet (UV), & infrared (IR); 8.) incorrect temperature; 9. incorrect relative humidity (RH); and 10.) dissociation (i.e., loss of information). (4)

Condition: an individual's subjective perception of an object and its history under specified contexts. (4)

Damage: a material change which is perceived to have negatively affected an item's value-defining aspects. (4)

State: the information inherent to an object; an object's material properties and any changes undergone by the object throughout its lifetime. (4)

Susceptibility: factors inherent to an object that make it prone to change. (4)

Colorimetry

Colour Attributes

Achromatic (Colour): a perceived color without hue: i.e., white, grey, black. (3)

Chroma: the degree of departure of the color from a neutral color of the same lightness. (2)

Chromatic Intensity: when the color of an area appears to be more or less chromatic. (2)

Hue: when an area appears to be similar to one of the colors red, yellow, green, or blue, or to a combination of adjacent pairs (when considered as the color wheel). (3)

Lightness: the brightness of an area judged relative to the brightness of a similarly illuminated area that appears to be white or highly transmitting. (2)

Primary: a.k.a. *unique hues*; the four hues of the color wheel that can not be matched with colors other than themselves: yellow, red, blue, and green. Unique red is a hue that is neither yellowish nor blueish. (3)

Pseudo-object Colour: colours which represent measured colour data. They are produced by converting tristimulus values (XYZ) into sRGB values. (4)

Visual Properties of Objects

Lustre: the character of the light reflected by a material. There are several kinds of lustre in mineralogy:

- Metallic - the lustre of metals
- Adamantine - the lustre of diamonds
- Vitreous - the lustre of broken glass
- Resinous - the lustre of yellow resin
- Pearly - the lustre of pearls
- Silky - the lustre of silk

These lustres have different degrees of intensity being either splendent, shining, glistening, or glimmering. When there is a total absence of lustre, the mineral is characterized as being dull. (1)

Opacity: the measure of impenetrability of visible light through a material. (4)

Opaque: a material that is impervious to visible light. (1)

Specular Reflection: the mirror-like reflection of light off a surface. This produces the reflections and highlights seen on shiny objects. (4)

Translucent: a material that transmits light without objects being visible through it. (1)

Transparent: a material that transmits light with objects being visible through it (e.g., a lens or a window). (4)

Colorimetric Devices and Standard Parameters

Colorimeter: an instrument designed to measure color without the intermediate step of measuring spectra. (2)

Spectrophotometer: an instrument that measures reflectance from or the transmittance through materials as a function of wavelength. (2) An instrument for measuring the relative intensities of light in different spectral regions. (3)

Standard Illuminant: standardized tabulated data that are based on physical measurements of a given illuminant (i.e., light source). They are defined as relative spectral power distributions. Most light sources have equivalent illuminants, but not all illuminants have equivalent sources (e.g., the CIE daylight series). (2)

> ↳ **D65**: CIE Standard Illuminant equivalent to average daylight—both direct sunlight and light diffused by a clear sky— in the northern hemisphere. This is ~6500°K CCT. Experiments (Judd *et al.* 1964) were conducted in Rochester, NY, USA; Ottawa, Canada; and Enfield, England (41° - 51° N lat.). (2)

Standard Observer: primaries (i.e., maxima of spectral peaks) used in colorimetric calculations that represent the average spectral sensitivities of the color-normal population. (2) The respective field of view corresponds to the size of the retinal image expressed in solid angle. (3)

↳ **2°**: a.k.a. *1931 Standard Observed*; primaries identified by experiments conducted between 1928 and 1931 that used only the fovea (the central part of the retina that only contains cones), whereby the participant only had a 2° field of view surrounded by darkness. This observer is recommended for use during small-field color matching. (2)

↳ **10°**: a.k.a. *1964 Standard Observed*; primaries identified by experiments in 1959 whereby the participant only had 10° field of view surrounded by darkness. This observer is recommended for use during large-field color matching (whenever conditions exceed 4° field of view). (2)

Aspects of Optical Geometry

Normal Angle: *n*; the angle perpendicular to the tangent of a surface. (2)

45°:**0°**: an instrument or accessory which illuminates a sample at 45° from the normal angle, and which reflectance is viewed along normal angle. This enables one to directly measure diffuse reflection, as this geometry excludes specular reflection. (4)

d:8°: an instrument or accessory which offsets the normal angle by 8° to enable the use of a specular port. (2)

- di: 8° = diffuse illumination & 8° efflux with SCI
- de: 8° = diffuse illumination & 8° efflux with SCE

Integrating Sphere: a hollow metal sphere coated with a highly reflecting diffuse material, such as barium sulfate or polytetrafluoroethylene (PTFE). The coating enables the sphere to collect all light reflected from or transmitted through a sample and direct it towards the instrument's sensor. (2)

Specular Port: a hole in the integrating sphere against which a material identical to the sphere's interior (in order to include specular reflectance) or a black trap (to exclude specular reflectance) is placed. (2)

Colour Space

Color Space: a three-dimensional geometrical space with axes appropriately defined so that symbols for all possible color perceptions of humans fit into it in an order corresponding to the psychological order. In this space, each color perception is represented as a point. Color spaces are indicative of the variation of color experiences of the average color normal observer under the limitations of the system, as each space is related to a highly specific set of viewing and general experimental conditions. (3)

Color-Mixing Spaces: a type of color space that exemplifies the relationship between color primaries and their intermixtures. Each unique color is defined by the amount of each primary. (2)

> ↳ **CMYK**: a color space used for mixing colorant (e.g., pigments, ink) based on the subtractive primaries of four-color printing: cyan (C), magenta (M), yellow (Y), black (K). In printing processes, the primary colors are defined in terms of standard printing inks. For digital rendering, CMYK is defined in terms of individual percentages of the four components. The gamut of CMYK is usually smaller than the gamut for RGB because of the limited chroma of printing primaries. (3)

> ↳ **RGB**: a regular, but not uniform, color space used for mixing colored light (e.g., digital screens) with the additive color primaries red (R), green (G), and blue (B). Colors can be identified in terms of R, G, B units of activation. Values for these units range from 0 to 255. (3)

CIELAB: a simple version of a zone model color space, recommended by CIE in 1976, and is at best a rough approximation of a large difference uniform color space. This space uses a Cartesian coordinate view of Euclidean space. Colors are identified by chromatic coordinates a* and b* and lightness coordinate L*. (3)

XYZ: a.k.a. *CIEXYZ, CIE tristimulus space*; a non-uniform color space, taken to be Euclidean, relating measured reflectance of a sample viewed in a standard light to a specific point in the space. It allows for the determination of quantitative relationships between colors in a linear system, but without consideration of surrounds. It also implicitly accounts for the reappearance of red at the shortwave length end of the spectrum and recognizes luminance and chromaticness as important color attributes. Its coordinates are the tristimulus values: X, Y, and Z. (3)

> ↳ **Tristimulus Values**: in the case of object colors, are the normalized sums of the reflectance function weighted by the spectral power distribution of the light source and the three color-matching functions: $\bar{x}, \bar{y}, \& \ \bar{z}$. Y represents luminance, and X and Z represent in some fashion the chromatic components from which hue and chroma are derived. (3)

Colour Difference

Color Difference Formula: a mathematical expression resulting in numbers proportional to perceived difference between points in the space. Formulae tend to only reflect one set of test conditions: normally daylight illumination and a singular, achromatic surround. Thus, resultant numbers are not comparable to those produced under different test conditions. (3)

ΔE: the notation used to indicate the total colour difference between a pair of colour measurements as plotted in a three-dimensional colour space. (4)

ΔE*$_{ab}$: the colour difference formula published by CIE in 1976 to be used with CIELAB colour space. It has been found that this equation has poor correlation with perceived colour differences between 0.5 and 5 ΔE*$_{ab}$. (4)

$$\Delta E^*_{ab} = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$$

ΔE*$_{00}$: a.k.a. *CIEDE2000*; series of colour difference formulae published by the CIE in 2001 to correct the errors in the CIELAB formula in order for it to better reflect human colour perception. These corrections include weighting functions, an interactive term between chroma and hue that improves the performance for blue colours, and a scaling factor of the a* axis to improve the performance of neutral greys. See Luo *et al.* 2001 and Sharma *et al.* 2005 for further details and formulae. (4)

Chapter 1. Introduction

"*While the proportion of unstable to stable minerals is comparatively small, it should be borne in the mind that, in terms of numbers of geological specimens, the proportion in many collections is very much larger. This is because a small number of unstable minerals occur commonly in a wide variety of fossils, rocks and mineral assemblages*." — Howie 1984: 308

This project is part of the Science and Engineering in Arts, Heritage, and Archaeology Centre for Doctoral Training (SEAHA CDT), and is funded by the Engineering and Physical Sciences Research Council (EPSRC), the Pilgrim Trust, the Barbara Whatmore Charitable Trust, and the National Conservation Service (NCS).

Each SEAHA project is a collaborative initiative between academia, heritage, and industry, and has at least one partner from each sector. Projects are co-created by the partners to answer specific questions and problems currently faced by members of the heritage sector. This project in particular is formed of five partners: the University of Oxford; Amgueddfa Cymru – Museum Wales, particularly National Museum Cardiff (NMC); National Museums Liverpool (NML); OR3D; and BSRIA Ltd. The project remit stems from a lack of knowledge of the behaviour of geological materials in museum environments. It was proposed as a means of rectifying this lack by beginning the scientific studies required in order to bring current understanding up to par with that for other heritage material types, such as paintings, ceramics, paper, and archaeological finds.

1.1. Project Context and Scope

"Detailed data on their stability fields within collections is poorly known;" — Howie 1984: 309

This doctoral research focuses on *minerals*, as they are the primary constituents of other geological materials. As of September 2023, 5,975 unique *mineral species* have been approved by the International Mineralogical Association (IMA). However, not all of these species will ever be present within museum collections due to their rarity.

Over half of known mineral species are considered rare (Hazen & Ausubel 2016). These are minerals that are documented to occur in five or fewer localities, and comprise of those which:

- form under uncommon, extreme, or very specific conditions,
- incorporate uncommon groupings of elements or include rare earth elements,
- are unable to persist outside their formation conditions or at Earth's surface,
- only form at the micro- or nano-scale, or
- are found in geological settings and locations which are not commonly studied.

Mineral rarity directly affects the cost to acquire specimens of these species. Given the current economic situation for the majority of museums, if any funds are granted for specimen acquisition, it is usually explicitly for purchasing new display specimens. Unfortunately, most rare mineral species are not large or aesthetically pleasing enough to warrant display.

Rare mineral species would thus be considered specimens that fill gaps within the systematic collection, which is generally off-display. Currently, these specimens are normally acquired via donations from academic or research institutions or from private collectors. So whilst it is not impossible for museums to hold a few rare mineral specimens, it would be rather uncommon and largely restricted to larger or university-affiliated museums.

The Oxford University Museum of Natural History has approximately 1,230 unique mineral species (plus 30 organic 'minerals' like amber and coal). Using Oxford's figure as a reference point, one could surmise that up to 1,500 unique species could be presently found in museum collections. These same species will also be found in various other collections types—including petrology, palaeontology, archaeology, ethnography, fine art, and social history—as minerals are a common and long used raw material for many human-made objects.

Whilst most museums will only have up to a quarter of all currently known mineral species, this still requires a sufficient understanding of favourable storage conditions for these species. A non-substantial fraction of these will require unique, species-specific environmental conditions. Obtaining the relevant data for these species ranges from difficult to nearly impossible, depending on a museum professional's accessibility to information.

Perhaps one would first turn to PAS 198:2012 (British Standards Institution 2012; withdrawn on publication of BS EN 16892:2018), a well known and referenced standards document for museum collection care guidance. It provides wide-ranging recommendations for the environmental and pollution-related requirements of many different cultural heritage materials. However, PAS 198 provides insufficient advice on the appropriate storage conditions for geological collections (ibid. Tables E.1 and G.2). Table E.1, meant to outline the effects of temperature and relative humidity on materials, only covers pyrite and marcasite deterioration and does so briefly. Other humidity-sensitive minerals are grouped together in one sentence that makes no reference to which minerals are affected by humidity and under which conditions. Whereas in Table G.2, 'Pollutant-material interaction in enclosures', only broad mineral groups are mentioned—"carbonate, borate, phosphate and similar soluble minerals of weak acids" (British Standards Institution 2012: 40)—and are stated to only be susceptible to formic and acetic acids.

Realising that this information is insufficient for their needs, one may then search for guidance documents written specifically for geological collections, such as those developed by the British Museums and Galleries Commission in 1993—updated in 2004 by the Museums, Libraries and Archives Council (MLA) (Stanley 2004)—or by the Geological Curators Group (GCG) (Brunton *et al.* 1984). However, one would come to find that these do not offer much additional information.

Appendix E of the MLA Standards (Stanley 2004) provides relative humidity and temperature recommendations for the display and storage of geological specimens. However, only four categories of specimen type are suggested: 'general', 'sensitive', 'pyrites and marcasites', and 'sub-fossil bone, tusks, teeth, fossils with shale or clay

matrix'. This crude delineation inadequately reflects the diversity of mineral collections, even though the diversity is clearly discussed in the texts cited by Stanley (e.g., Howie 1992a, Nassau 1992, Waller 1992). Similar oversimplifications also occur in the GCG Guidelines (Brunton *et al.* 1984). In this text, the authors mentioned several minerals which will change at a given moisture content or under humidity fluctuations. These changes include the likelihood of hydration state changes of sulfates and some zeolites, the vulnerability of halides to deliquesce, and the hygroscopicity of clay minerals. Yet the authors still recommended a blanket approach of 50±5% RH; the *de facto* standard which likely arose due to titular prestige rather than any technical or scientific evidence (see Henderson 2018). A sole, unspecific caveat was provided for vulnerable materials: "Specialized collections or specimens may require high or low regimes of humidity" (Brunton *et al.* 1984: C16). This statement is echoed in the MLA Standards: "Sensitive minerals and other materials: depends on mineral or material" (Stanley 2004: 64). Yet neither document provides the detail necessary for determining which minerals are 'sensitive' nor the appropriate storage conditions for them.

For this, one would have to turn the original sources referenced in these three guidance documents. One such source is Howie's 1992 publication, *The Care and Conservation of Geological Material*. It is the most comprehensive text on mineral instability to date, providing some degree of information for more than 300 mineral species and devoting a whole chapter to pyrite and marcasite. However, the publication is very much of its time. It was written as "a 'state of the art' text […. to] encourage others to tackle many areas where problems continue to cause loss and decay" (Howie 1992a: xi). Whilst the data may have been accurate at time of publication, 30 years have elapsed without revision or addition. It would be unsurprising then for one to find this source lacking too. Thus one would have to turn to other fields to find the information necessary to fill in the remaining knowledge gaps.

As explored in Chapter 2 of this thesis, most current knowledge on mineral stability comes from other fields, such as the geosciences, chemistry, and materials science. However, much of this literature is inaccessible to a majority of heritage

professionals both physically (due to the lack of open access publications) and in terms of the lexicon used.

It can be argued that literature from scientific fields may appear to outsiders as laden with specific and technical jargon, strange graphs, and terrifying equations. This can overwhelm and confuse even the most scientifically inclined if they are unfamiliar with the subject being presented (Hoyles 2020). Thus, the lack of easily accessible and digestible information tailored for a museum professional's understanding significantly hampers knowledge transfer into the heritage sector.

But perhaps the largest barrier to knowledge exchange stems from a lack of awareness and effective communication (Tennent 1994, Viñas 2002, Henderson 2018). Many heritage professionals are unaware that relevant knowledge is indeed available from other sectors. And many researchers from other sectors are equally unaware of their findings' implications for museums and heritage. Those who do acknowledge such uses fail to effectively communicate across disciplines, as their work is rarely advertised or published within heritage literature.

1.2. Thesis Aim and Structure

To tackle these challenges, the doctoral research outlined in this thesis aims to develop an efficacious methodology for facilitating the determination of mineral susceptibility to conditions found within the museum environment. This is achieved through the following objectives:

1. Identify which minerals are not stable within the museum context and the parameters which induce instability.
2. Develop and test low cost, easy-to-use techniques that can detect changes in mineral specimens.
3. Apply these methods to a single mineral species (pyrite) to confirm efficacy.

Figure 1.1 demonstrates how the following chapters address each objective.

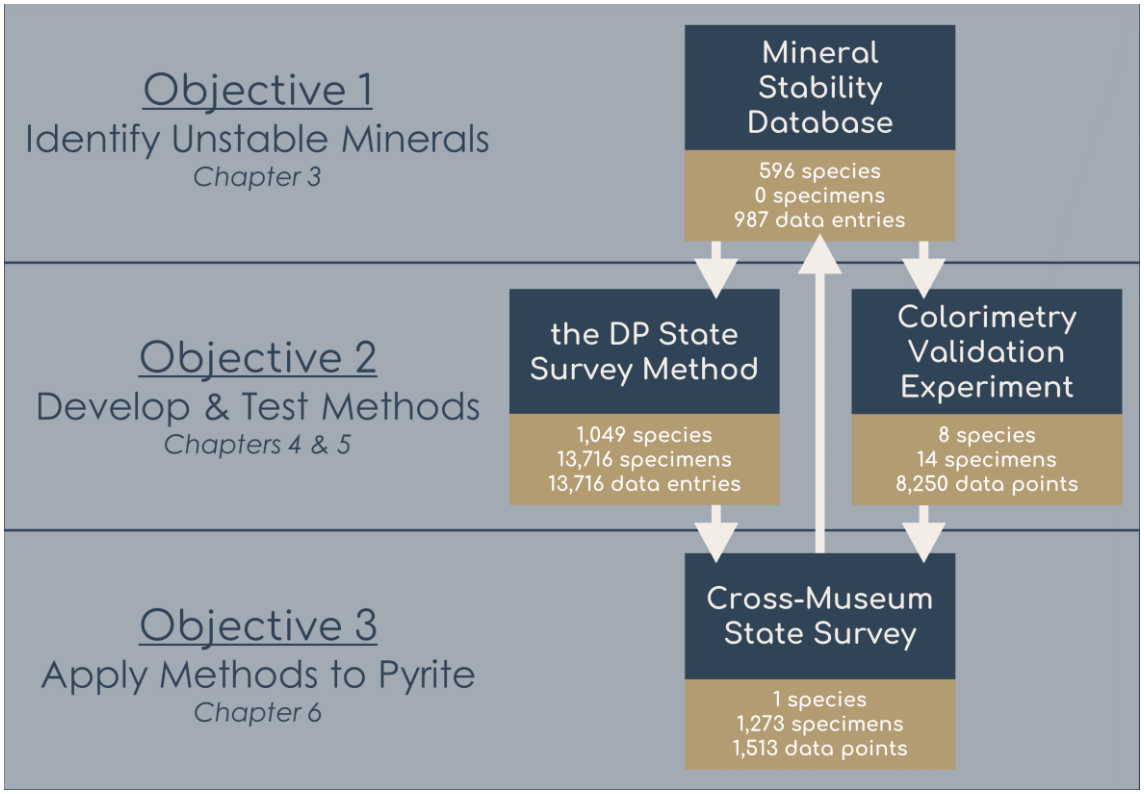


Figure 1.1. Map of the thesis chapters and objectives.

Chapter 2. Minerals as Collection Items is the primary literature review. Here, minerals and their values and uses are introduced. The concepts of *damage* and *susceptibility* are then defined and applied to mineral collections. Historic conservation treatments are subsequently outlined, and the state-of-the-art is summarised.

Chapter 3. The Mineral Susceptibility Database introduces this database and discusses how the data within it was acquired. A brief examination of its contents and a comparison to the OUMNH systematic mineral collection is made. The Database itself can be found in Appendix 4 or accessed via https://doi.org/10.5287/bodleian:r17kVJb7d.

Much of Chapters 2 and 3 was published as an article in *Studies in Conservation* (available online from January 2021, published in-print in volume 68, 3). For the full citation, see Royce *et al.* 2023 in the References.

Chapter 4. The Deterioration Phenomena (DP) State Survey Method introduces the collection surveying method created and employed by the author during this research. Building upon the literature and ideas presented in Chapter 2, a novel framework for characterising object *condition* is put forth, followed by a review of common challenges encountered whilst performing condition assessments. The DP State Survey Method is then proposed as a means of mitigating these challenges. How the Method is employed and its results analysed are then explained.

This chapter will be published as a proceeding to the NatSCA 2023 conference in the *Journal of Natural Science Collections*. The manuscript has been submitted and is currently in press.

Chapter 5. The Colorimetry Validation Experiment examines the application of colorimetry to mineral specimens. Key colorimetric concepts are explained and current applications are reviewed prior to the presentation of the experimental methodology and findings.

Chapter 6. The Cross-Museum State Survey of Pyrite covers the application of the methods developed in Chapters 4 and 5 to pyrite specimens held within four mineralogy collections. The justification as to why pyrite was selected is first presented followed by the survey's method and findings. A hypothesis for pyrite deterioration within a museum setting is subsequently proposed.

Chapter 7. Discussion and Conclusions addresses how the work presented in this thesis advances the state-of-the art, affects practice, and encourages shifts in perspective. Actions that are currently underway and areas for future research are also outlined.

Chapter 2.
Minerals as Collection Items

A mineral is currently defined as “a naturally occurring solid with a specific chemical composition and a distinctive internal crystal structure” (Bonewitz 2008). Minerals can be classified as individual species. What distinguishes one mineral species from another is its unique chemical and physical properties (the Hudson Institute of Mineralogy 2023b). To date, 5,975 mineral species have been approved by the International Mineralogical Association (IMA) (2023).

Minerals are the essential building blocks of *rocks* and *fossils*, and are the raw products for a variety of objects common to daily life (Fig. 2.1). Minerals have been used since prehistory (Whittle 1996, Renfrew 2013) to create a wealth of objects, such as pigments, pottery, metalwork, and jewellery. As such, minerals are ubiquitous throughout museums and heritage sites and possess a variety of values and uses beyond display.



Figure 2.1. The Economic Minerals display at the Field Museum (Chicago, IL, USA), exhibiting various minerals and their resultant products. These include currency, medication, nails, and toothpaste.

2.1. Value and Use of Mineral Collections

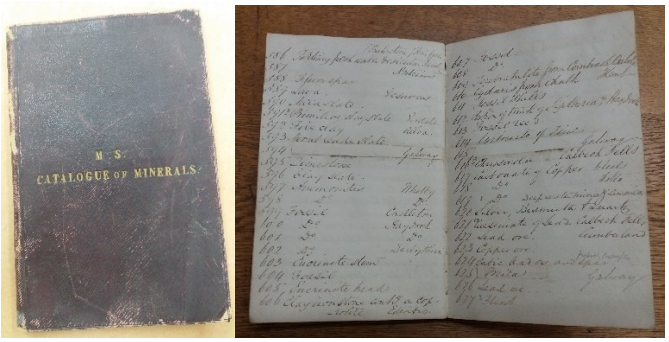
Beyond their scientific and industrial uses, minerals are predominantly valued and collected for their beauty and rarity, which is directly reflected in a collector's specimens (Fig. 2.2). Usually when presented with an array of similar specimens, it is the most aesthetically pleasing of them that is chosen. Of course, what is considered to be aesthetically pleasing will vary between individuals (for reasons akin to those outlined in Ch. 4, Section 4.2). Collectors with greater mineralogical knowledge (such as museum curators) may be more inclined to acquire raw specimens that demonstrate how the minerals formed *in situ*. However, even in such circumstances, there is arguably an aspect of composition—an artistic arrangement of elements (e.g., specimen 3 in Fig. 2.2)—that affects specimen acquisition and display. This leads to the practice of specimen preparation (Pezzotta 2021) or development (King 1983: 54): "the removal [… of undesired] associated minerals of a mineral paragenesis […. to] expose the more desirable underlying minerals." Specimens available through mineral dealers are more likely to have undergone such processing pre-sale to enhance and broaden its appeal to prospective buyers. Thus, if museum specimens are predominantly acquired in this way—either directly through a dealer or from a private collector—there is already an imposed aesthetic. Particularly one which reflects what is consensually agreed upon by collectors of a certain time period (Pezzotta 2021). Effectively, the more middlemen between specimen *locality* and museum, the greater the likelihood of specimen processing and the more general the aesthetic appeal.



Figure 2.2. Some of the author's personal specimens: 1.) baryte; 2.) rubellite, lepidolite, mica, & quartz; 3.) aragonite & calcite; 4.) atacamite; 5.) hemimorphite; and 6.) malachite in gypsum.

Raw, unprocessed, old, 'unattractive', or 'worthless' specimens still hold a great deal of value and use. This includes educational and research potential as well as historical and cultural significance. These values are largely determined by the nature and extent of any associated materials (Table 2.1) and publications which provide context to the specimen (Knell & Taylor 1989, Robb *et al.* 2013). As such, both the specimens and their associated materials hold information relevant to both the sciences and the humanities (Robb *et al.* 2013).

Table 2.1. Examples of different types of associated materials. Images used with permission courtesy Oxford University Museum of Natural History and the Sedgwick Museum of Earth Sciences.

Category	Material	Example
Museum Records	- catalogues - indexes - labels - registers	the original, handwritten catalogue for Oxford University Museum of Natural History's mineral collection, listing specimen number, locality, and species name 
Housing & Storage Material	- boxes - cabinetry - trays - wrappings	the items within Dr. John Woodward's study at the Sedgwick Museum of Earth Sciences, including the collection's original custom-built cabinets, Woodward's notebooks and his college gown 
Belongs of the Collector or Previous Owner	- correspondences - equipment - maps - notebooks - personal effects - photographs	

2.1.1. Scientific Value

"*Even after the arrival of new technology, progress in geology is still dependant on specimens, especially those in museum collections*" —Knell & Taylor 1989: 2

Minerals evidence a wealth of past and present planetary and environmental processes. As documents of the history of life, they are used to determine and interpret the past, present, and future (Allmon 1994, Rickard 2015), and help tackle society's biggest questions and challenges, such as climate change, resource management, evolution, the origins of life, the potential for extra-terrestrial life, and

planetary formation (Putirka 2015, Hazen & Ausubel 2016, The Geological Society 2016). The isotopic composition of inclusions and impurities within ancient minerals has been used to examine Earth's previous environments. In particular, analysis of ancient pyrites has been used to determine the presence of liquid water at Earth's surface and the formation of an oxygenated atmosphere (Rickard 2015). These pyrites have also been used to develop the 'Iron-Sulfur World Hypothesis', an explanation for how life began on Earth (ibid.)

Museum mineralogical collections are particularly useful, as they are local, accessible, and cost-effective repositories of primary documents and evidence (Allmon 1994, Rumsey 2021). They facilitate research and identification without the need of purchasing material or going into the field and collecting new specimens, which is crucial as many specimens are actually quite rare. As mentioned in Chapter 1 (Section 1.1) rarity in minerals may be due to physical circumstances, such as uncommon or restricted formation conditions and the incorporation of rare elements, resulting in the mineral only being known to occur in a handful of localities (Hazen & Ausubel 2016, Rumsey 2021). Rarity can also be the result of land use change, whereby collection localities become either inaccessible or no longer exist due to human or natural processes (Allmon 1994, Chalk 2009, Baars 2010, Rumsey 2021), making museum specimens the only remaining tangible evidence.

2.1.2. Historical and Cultural Value

Any object, including minerals, can be a link between a material and its people. Specimens can be associated with a particular culture (jades to Chinese culture) or person (Mary Anning's fossils), or have an interesting story and provenance (Robb *et al.* 2013). The specimens carry on the legacies of the people and traditions with which they are associated (Baars 2010, Robb *et al.* 2013, The Geological Society 2016). Many view these legacies as tremendously valuable and powerful, especially when the specimen embodies contextual information. This usually occurs when the specimen is housed in its original case (Table 2.1) or with original labels (Robb *et al.* 2013).

Even better if this associated material is created by the famous person themselves, as with Darwin's microscope slides (Baars 2010).

Specimens can also act as time machines for the history of science. Records and associated material can be informative of what was state-of-the-art and how the specimens were perceived at the time of accession (Baars 2010, The Geological Society 2016). An example is Dr. John Woodward's (1665-1728) collection, now housed at the Sedgwick Museum of Earth Sciences in Cambridge (see Table 2.1). Woodward and his contemporary at the Ashmolean, Edward Lhwyd, considered mineral specimens as "facts from which the earth would eventually be understood" (Cook 2003: 95), resulting in collections that "were wholly uncharacteristic" (Embrey & Symes 1987: 63) for the period. Woodward intentionally acquired specimens of all kinds (not just the rare or unusual) in order "to get as compleat and satisfactory Information of the whole Mineral Kingdom[1] as I could possibly obtain" (Woodward 1723: 4). His prolific collecting in turn initiated the first attempt at systematic mineral organisation and curation. In addition to labelling each individual specimen, Woodward created collection catalogues within which he described the specimens and their collection localities (particularly the mines) in "meticulous detail" (Embrey & Symes 1987: 63). Woodward's specimens and their entries provide a clear glimpse into 17th century mining practices, scientific understanding and advancement.

2.1.3. Educational and Outreach Value

Mineralogical collections also have value as teaching materials for students and the general public (Allmon 1994, Robb *et al.* 2013, The Geological Society 2016). A number of specimens are often set aside by a museum for use as a handling collection, allowing for visual and tactile learning and engagement. As concrete sources of evidence, these collections are used for teaching about specific minerals and their properties, and to exemplify complex concepts, such as climate change and

[1] At the time, the Mineral Kingdom included both minerals and fossils. Woodward's collection and observations were subsequently used to devise early geological theory, in particular the origin of fossils (Cook 2003).

plate tectonics. They are also used to create an appreciation of science and the natural world (The Geological Society 2016).

2.1.4. Potential Value

Values change over time, as does technology, context, and perception. This means that a specimen which has little apparent value now could become valuable in the future (Ashley-Smith 1995, Baars 2010). This is especially true for collections which have not received rigorous research and examination. Some specimens have been unknowingly mislabelled or misdescribed, or just forgotten, and require reinterpretation based on current understanding and analytical methods (Knell & Taylor 1989, Allmon 1994, Chalk 2009, Rumsey 2021). Thus, there is the potential for new information and discoveries upon further study.

A recent example is the discovery of kernowite. Mike Rumsey—Principal Curator of Minerals at the Natural History Museum, London—was investigating the cause of coloration in liroconite ($Cu_2Al(AsO_4)(OH)_4 \cdot 4H_2O$). Normally, liroconite is "teal to deep sky blue" (Rumsey 2021: 2) but can be found in various shades of green. Analysis was performed on an emerald green liroconite (NHMUK BM.1964,R8908). The results confirmed previous claims that the green liroconites are iron-rich (the Hudson Institute of Mineralogy 2023c). However, Rumsey and co-investigators found that there was sufficient replacement of aluminium by ferric iron to warrant classification as a new mineral species. Kernowite ($Cu_2Fe(AsO_4)(OH)_4 \cdot 4H_2O$) was approved by the IMA in November 2020 (Rumsey *et al.* 2020).

2.2. But Minerals are not Stable

"A problem which frequently confronts a museum curator is the proper preservation of certain choice specimens of minerals." — Parsons 1922: 59

The prevalence of preserved mineral-derived objects has fed into the popular assumption that minerals are inherently stable (Howie 1979a, 1992a; Chalk 2009). Whilst indeed, minerals and the objects made from them are relatively more stable than those derived from many organic materials (especially if focusing on a human timescale), minerals are not immune to entropy and will eventually be subject to deterioration.

The first publications discussing mineral instability within the museum context appeared in the first half of the 20th century (Parsons 1922, 1926; Bannister 1933, 1937). Yet as Parsons' (1922) opening line (above) suggests, mineral instability has been a long-standing and bemoaned issue. Parsons hoped that by discussing the occurrence of unstable minerals, he could "stimulate a study" (Parsons 1922: 62) of mineral stability parameters within the museum context. Fortunately, interest and examination of mineral instability grew within the sector throughout the 20th century, culminating in an intensive period of research from the mid-1970s through to 2000 (e.g., Howie 1979a, 1984, 1992a; King 1985; Waller *et al.* 2000). Whilst the quantity of information and discussion on the topic has greatly increased throughout the past century, many questions regarding best practice for mineral collection care have remained unanswered to this day (Waller *et al.* 2000, Baars & Horak 2018). In order to address these questions though, we must first clarify and define certain terminology, specifically 'damage' and 'susceptibility'.

2.3. What is Damage?

The cornerstone of heritage preservation is the mitigation of damage to collections to improve their longevity and continued access and use (Ashley-Smith 1999, Appelbaum 2007, Baars 2019). The basis of damage mitigation must be a thorough and unambiguous understanding of what damage actually means

for a specific material. What one considers 'damage' may be seen by another as part of an object's history. Thus, a shared definition of damage enables a consensus on how to best monitor, detect, and assess changes within collections, and defines when treatments are considered necessary. Therefore, it is critical to have an established definition of damage to carry out this work as effectively as possible.

But this is easier said than done. Damage is a complex and highly subjective concept because it implies not only a detrimental change in *state* but also a negative change in value (Strlič *et al.* 2013) and use. This is reflected in damage's common definition: "Injure (a thing) so as to diminish its value or usefulness" (Trumble & Stevenson 2002: 596).

Changes in state involve changes to the intrinsic, material properties of an object (Ashley-Smith 1995), whilst changes in value—and subsequently use—entail alterations in extrinsic, human-assigned concepts (Ashley-Smith 1999, Appelbaum 2007). Yet not all change in an object's state results in a change of value. Nor is all change negative (Fig. 2.3). In some cases, change may even be beneficial to the object's value (e.g., evidence of wear or use). Hence, whilst damage is usually associated with a change in state, change does not always equate to damage (Ashley-Smith 1999, Meul 2008) as it may not necessarily affect value.

Change may be accumulated rapidly or gradually, and certain types of change may be considered acceptable, or indeed inevitable (Michalski 1994, Rose & Hawks 1995, Waller 1995). Yet at some point, a threshold is reached where the amount of change accrued is perceived as unacceptable and negatively affects the object's values and uses (Appelbaum 2007, Robb *et al*. 2013, Strlič *et al.* 2013). The decision whether a type or amount of change is classified as unacceptable—and hence considered damage—is dependent on the clarity of the object's values and uses (see Allmon 1994, Appelbaum 2007, Baars 2010), many of which rely heavily on associated contextual information (Robb *et al.* 2013). This emphasises that damage is an observer- and context-dependent concept (Ashley-Smith 1999, Appelbaum 2007).

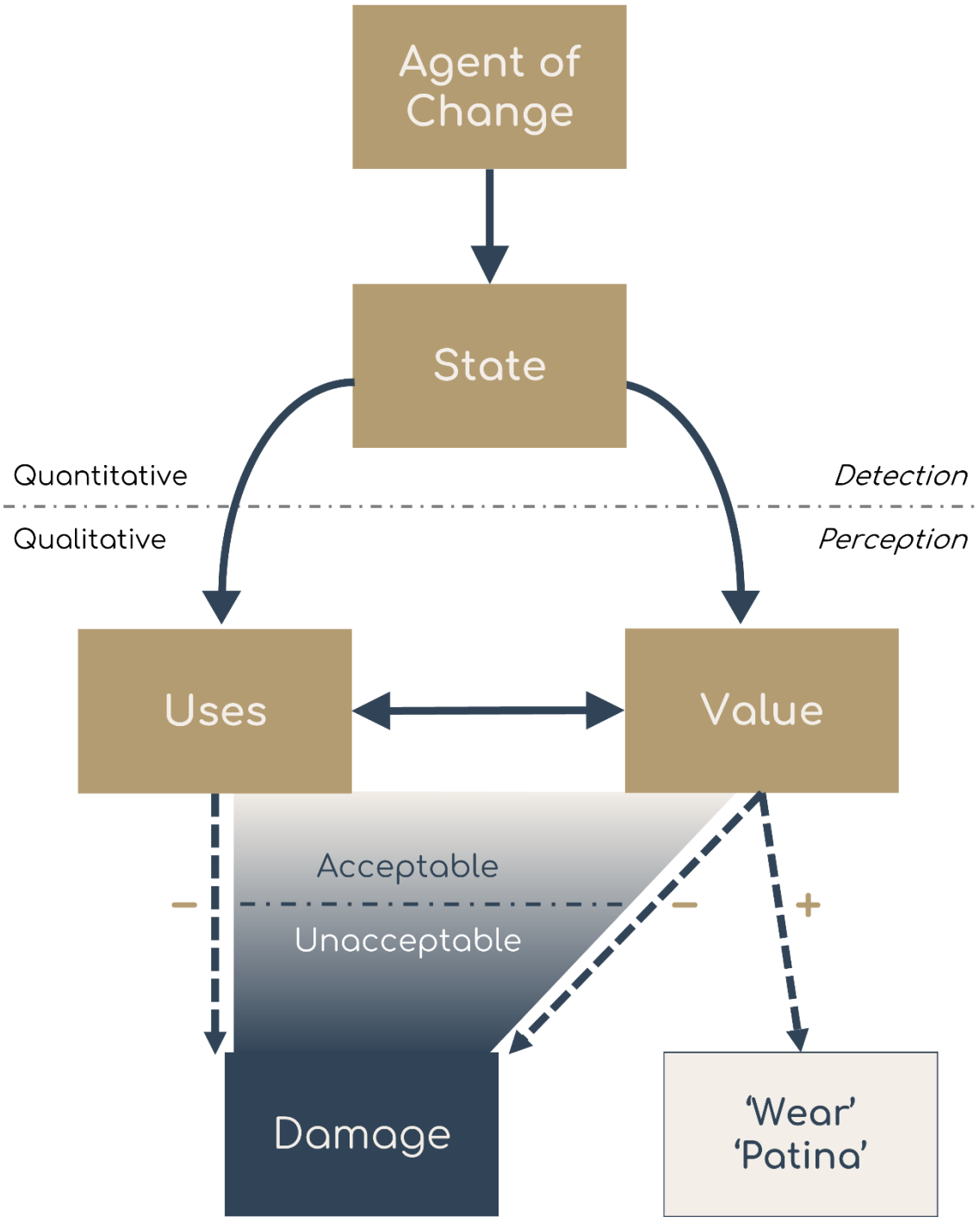


Figure 2.3. A schematic representation of how an agent of change produces damage (author's own). Damage is not a straightforward process of cause and effect. Rather, it is the result of a perception that an object's value and or use has decreased due to changes in state caused by exposure to a given agent of change. A change in state resulting in a positive change in value is often termed 'wear' or 'patina'. If however it results in a negative change in value and or use, it is termed 'damage'. Yet as change is inevitable, there may exist a threshold where a certain degree of change in state is deemed acceptable as it has little impact on the object's value or use.

Many pre-existing definitions of damage—including those presented in European standards (British Standards Institution 2019)—inadequately characterise damage due to omitting phrasing reflective of its subjective nature. Thus, the author proposes the following definition: *Damage is a material change which is perceived to have negatively affected an item's value-defining aspects.*

2.4. Determining Unacceptable Change

It is important to demarcate the threshold between acceptable and unacceptable change (the dashed line within the shaded region of Fig. 2.3) in order to define an appropriate response and to suggest when intervention and treatment are necessary (Howie 1979a, Strlič *et al.* 2013). But how is this possible when damage and value are subjective and variable? While some may hold the view that defining damage objectively is "an illusion" (Viñas 2002:26), Strlič *et al*. (2013) have suggested this can be achieved through decoupling 'value' from 'change'.

The decision to focus on material change, rather than change in value, is largely due to the complexity of the latter. Value is a multifaceted and subjective concept, which varies with the object being assessed, the assessor, and the context (Ashley-Smith 1995, Baars 2010, Robb *et al.* 2013, Strlič *et al.* 2013). Thus, the interpretation of value and its terminology will also vary from person to person. Each individual will apply their own frame of reference to determine what the terms mean for a given context (Taylor 2013), often introducing interpretational bias (Taylor & Stevenson 1999, Taylor 2013). This is demonstrated most notably during condition assessments when subjective and imprecise terminology—such as 'good', 'bad', 'stable', or 'degrading' (Ashley-Smith 1995, Taylor 2013, Gioventù 2018, Kosek & Barry 2019)—are used for ranking condition. The inherent subjectivity of value and value terminology makes it difficult to measure value consistently, let alone to define, and compare across institutions, regions, cultures, and eras.

Material change, on the other hand, is often consistently quantifiable using scientific methods. The use of measurements generated by instrumentation, rather than human observation, is advantageous in minimising subjectivity and error

(Ashley-Smith 1995, Baars & Horak 2018), although neither can be completely removed (e.g., sampling and confirmation biases). The resultant data may be recorded objectively in a standardised manner, allowing for communication and comparison across time and space.

2.5. Vulnerability and Susceptibility

Conservation as a discipline exists because many objects are vulnerable to damage and require careful management to ensure preservation. Unsurprisingly, there is much reference in conservation literature to vulnerability (e.g., Sabbioni *et al.* 2009, Ortiz & Ortiz 2016), yet the term itself is rarely defined.

Vulnerability is commonly defined as: “Able to be wounded; […] liable to damage or harm, esp. from aggression or attack, assailable” (Trumble & Stevenson 2002: 3562). Like damage, the definition of vulnerability embodies an inherent intrinsic–extrinsic duality. The object’s properties are again the intrinsic factor. Yet this time the extrinsic factor is the external conditions (rather than human-assigned concepts). However, unlike damage, the intrinsic and extrinsic factors of vulnerability are mutually dependent. Without either the propensity or the circumstances for vulnerability, one cannot claim an object to be vulnerable. This is emphasised by the need to state the context when discussing vulnerability (in example, ‘vulnerable to wear and tear’).

These same concepts apply to susceptibility; the “capacity to undergo or be affected by something” (Trumble & Stevenson 2002: 3127). While vulnerability and susceptibility have similar definitions and are often used interchangeably, vulnerability has a more emotional connotation than susceptibility due to societal implications; where those most vulnerable within society are often defined as children, the elderly, and those whom are disabled or immunocompromised. The conservation implications of vulnerability and susceptibility, however, are the same and the choice of terminology is a matter of preference. The author prefers ‘susceptibility’, which will be used henceforth.

2.6. Conservation Implications of Susceptibility

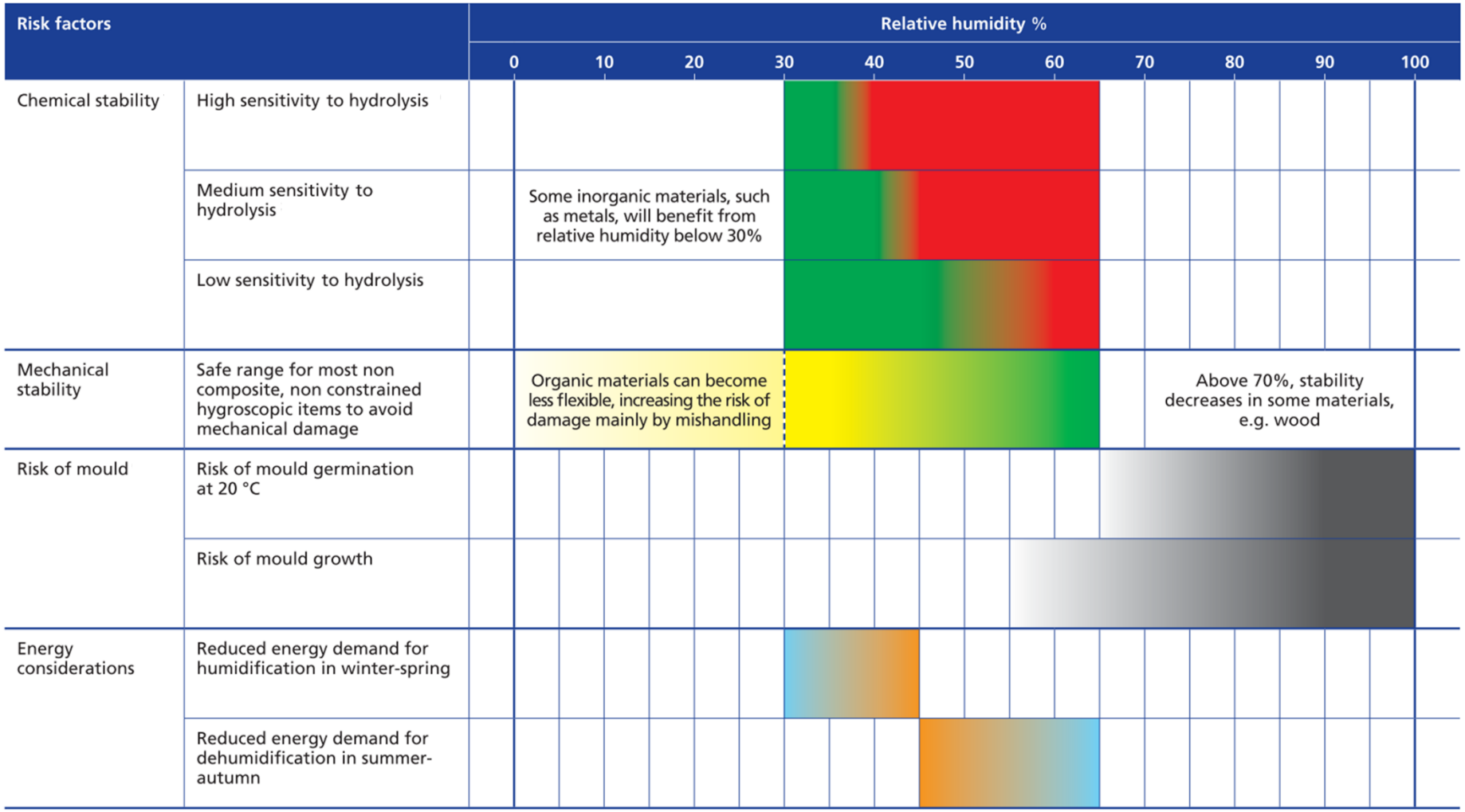
Susceptibility is governed by two interrelated factors: 1.) an object's physical and chemical properties, and 2.) the ambient environmental conditions.

Object properties determine which conditions are favourable for stability (or metastability; Waller 1991) and the object's response to unfavourable conditions (i.e., *agents of change*). As the object's physical and chemical properties are inherent and will not spontaneously change without reason, one could say that susceptibility is an inherent, secondary property of an object. Susceptibility may be acquired or altered through the addition of new material or a previous change. For example, a repair undertaken using a chemical consolidant can make an item susceptible to further physical change if the consolidant subsequently fails (Chiantore & Lazzari 2001).

Whether an object's susceptibility is expressed, however, is dependent on the probability of exposure to unfavourable conditions. For example, a pigment's photosensitivity is not expressed until the pigment is exposed to visible or ultraviolet light. It is only after some degree of exposure that the pigment will respond through colour and or chemical changes.

As a result of being context-dependent, an object's susceptibility is relative compared to those of other objects. Not only can the objects' responses vary widely, but so can the sets of conditions required to evoke these responses. Within museums, this is exemplified by the contrasting relative humidity (RH) requirements (Fig. 2.4) for different material and collection types (Erhardt & Mecklenburg 1994).

Figure 2.4. Relative risk of deterioration due to relative humidity, from BSI 2012: 22.



Additionally, some objects may be susceptible to conditions that rarely or never occur within a given context. The museum environment encompasses a rather narrow range of conditions compared to those possible on, in, and beyond Earth (see Section 2.8). Some minerals cannot persist within the museum environment, as they require high temperatures and or pressures to exist. One such example is β-quartz (SiO_2). Above 573°C at 1 bar (~1atm) pressure, the hexagonal *crystal* structure of β-quartz is thermodynamically preferred. When cooled below 573°C, the β-quartz unit cell structure immediately collapses into the denser, trigonal cell structure of α-quartz (Heaney 1994) through bond bending and kinking (Heaney & Veblen 1991). This structural adjustment is reversible, but requires heating to the transition temperature. Thus, while α-quartz specimens will not structurally rearrange into β-quartz under typical museum conditions, all β-quartz specimens in collections are actually α-quartz *paramorphs* displaying a β-quartz *habit* (the Hudson Institute of Mineralogy 2023d). This example emphasises that not all susceptibilities are relevant within the museum context.

Thus, the degree of susceptibility an object has towards unfavourable conditions can be considered the product of both the probability and the effects of exposure. It is important to understand the material and how it responds to potential environmental parameters in order to identify susceptibility and determine which pose as deterioration risks within the museum setting. This process includes the accurate identification of an object's composition, as knowledge of its material properties is imperative for the determination of appropriate storage conditions (Baars *et al.* 2021).

2.7. Why Minerals are Susceptible to Change

As each mineral species has a unique chemical composition and crystalline structure, each requires unique conditions to form. It is at these formation conditions that the mineral is stable and can persist indefinitely until a significant change in conditions occurs.

Conditions at which a mineral is stable are termed its *stability field*, which may be depicted in a stability (or *phase*) diagram (Fig. 2.5). Stability fields are classically defined by temperature, pressure, and the composition of compounds present in the surrounding environment (Hazen & Ausubel 2016). Other conditions relevant to phase stability include acidity and alkalinity (pH), bioactivity, and the presence of energy sources such as light or radiation.

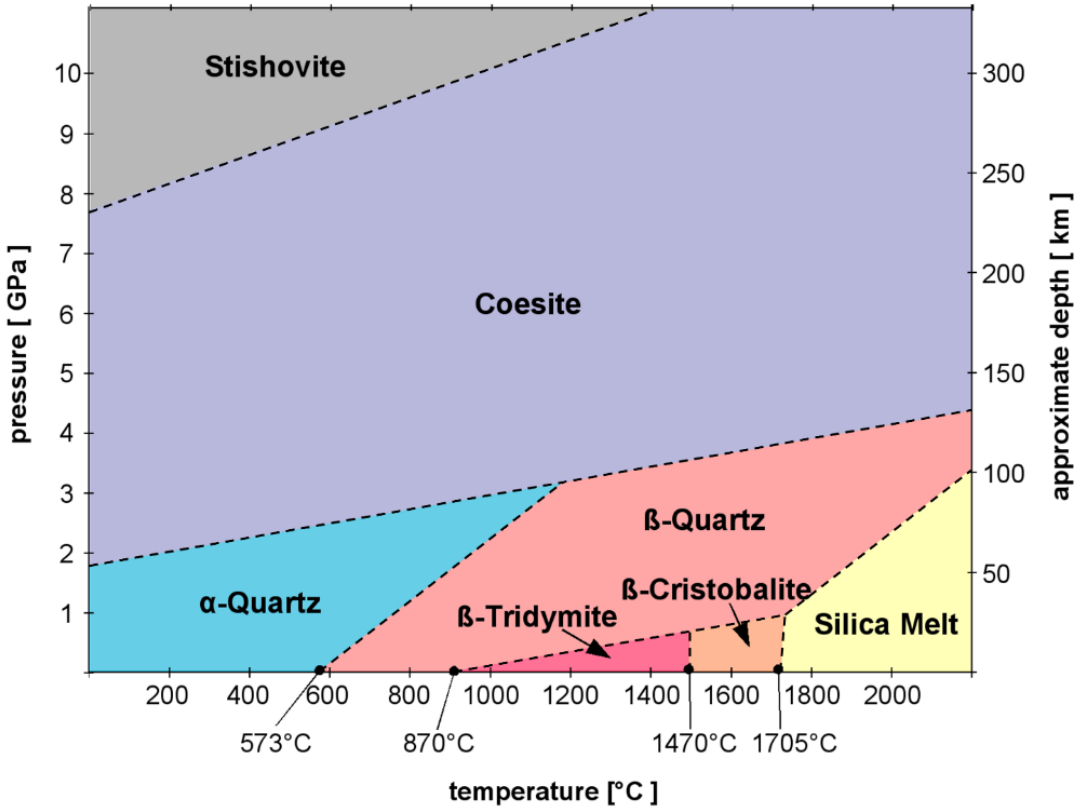


Figure 2.5. Phase diagram of SiO_2 polymorphs*. While coesite has the largest stability field of the silica polymorphs, it cannot exist at the surface, as the structure of α-quartz is energetically preferred. Image used with permission courtesy Akhavan* (2014).

A mineral's stability field is governed by both the chemical composition and crystal structure of a mineral. Minerals with greater stability can withstand greater variations in environmental conditions. For example, coesite's (SiO_2) monoclinic structure is stable over a wider range of temperatures and pressures compared to those of the other silica species (Fig. 2.5).

A narrow stability field, on the other hand, means that a mineral can only exist under tight, well-defined conditions. Even slight variations in conditions—be it the presence of other elements, variation in cation ratios, or the pH of the formation

solution—can mean the formation of, or alteration to, a different mineral species (Hazen & Ausubel 2016).

When conditions are beyond a mineral's stability field, the mineral is either *metastable* or *unstable*, given the amount of energy in the system. When metastable—such as aragonite ($CaCO_3$) or the allotropes of tin (Sn)—minerals may persist beyond their stability field, but have insufficient energy to change into the compound that is energetically stable at those conditions (Nesse 2012). This means that the reaction will not occur until the ambient conditions change so that there is a sufficiently great difference in free energy between the current metastable phase and the energetically preferred phase (e.g., significant undercooling is required for tin's structural rearrangement to occur; Ojima *et al.* 1993, Zeng *et al.* 2014). Or the reaction does occur but at such a slow rate that it may take a very long time (in some cases, thousands of years) to completely alter to a different phase (Putnis 1992), for example aragonite's structural transformation to calcite ($CaCO_3$) (Crawford & Hoersch 1972). This differs from instability, which occurs when there is sufficient energy available to initiate a reaction that causes the mineral to alter into an energetically more stable phase (Putnis 1992, Nesse 2012) at a rate noticeable within a human time frame. For many mineral reactions, this results in the formation of a new mineral species, yet other chemical compounds may also be produced, including gases, liquids, and non-crystalline solids.

2.8. How Minerals Change within the Museum Environment

Approximately 10% of mineral species are susceptible to change under the conditions present in indoor environments (see Ch. 3 and Appendix 4). Here, the indoor museum setting is defined to be approximately 1 bar pressure, -20-50°C, 1-99% RH, and exposure to light and common indoor pollutants (see Grzywacz 2006: Appendix 1). While this range does include some values that may be considered 'extremes', it covers conditions which may occur in buildings without insulation or

HVAC, or during rare events, such as equipment failure, unusual weather conditions, flooding, and localised heating by spotlights.

Means of mitigating damage to mineral specimens induced by physical forces—such as shock, vibration, and abrasion—have been discussed in other texts (Brunton *et al.* 1984, Howie 1984, King 1986, Stanley 2004) and are thus not covered here. Therefore, we focus on four agents of change: temperature, moisture, light, and atmospheric pollutants. At present, nearly 600 minerals have been identified (see Ch. 3 and Appendix 4) as being susceptible to these agents under museum conditions. Furthermore, many of these species are widely represented in collections, whilst others are considered to be rare and difficult to acquire (Howie 1979a, 1984; Hazen and Ausubel 2016).

2.8.1. Temperature

Temperature and humidity are intimately related, however there are a handful of minerals that are affected by changes in temperature, regardless of a change in or maintenance of RH. One such example is lansfordite ($MgCO_3 \cdot 5H_2O$), which will *dehydrate* into nesquehonite ($MgCO_3 \cdot 3H_2O$) if temperatures are above approximately 10°C (Waller 1992), despite maintaining 100% RH. Nesquehonite can subsequently lose additional water and CO_2 when kept under ambient conditions (Robie & Hemingway 1972).

While lansfordite's transition to nesquehonite is from one solid state to another, dissolution into a liquid phase is possible for some species. Nitrocalcite ($Ca(NO_3)_2 \cdot 4H_2O$) will enter solution as a result of *dissociation* into the highly soluble trihydrate ($Ca(NO_3)_2 \cdot 3H_2O$) and liquid water when exposed to ~30°C at a fairly low (20-30%) RH (Waller 1992). Similarly, hydrated sodium metasilicates ($Na_2SiO_3 \cdot nH_2O$) can melt into a liquid phase at temperatures greater than 47.85°C (Baker *et al.* 1933).

Rapid changes in temperature can also lead to fracture, depending on the species' thermal properties. Differential temperatures between a specimen's interior and exterior result in increasing stresses, which are consequently released through

cracking or spalling (Waller 1992, Horak 1994). Native sulfur (S_8) is a well-known example (Howie 1984, Nassau 1992, Waller 1992) that shatters with handling and localised heating from lighting. Waller (1992) lists a number of characteristics that increase the likelihood of a mineral to fracture, including easy cleavage and high brittleness.

Temperature variation can also produce less dramatic, but equally significant changes in some minerals. Trögerite ($(H_3O)(UO_2)(AsO_4) \cdot 3H_2O$) undergoes a reversible structural rearrangement over 18-28°C (de Benyacar and de Abeledo 1974). Above this range, trögerite exhibits a tetragonal structure, but below 18°C the mineral displays a low symmetry, pseudo-tetragonal form. Similar structural transformations are believed to occur to the other minerals in the metatorbernite group (de Benyacar & de Abeledo 1974).

2.8.2. Moisture

The effects of inappropriate levels or fluctuations in relative humidity are varied and complex, as they are dependent on material type (see Erhardt and Mecklenburg 1994). Relative humidity is involved in numerous reactions including phase changes (i.e., *hydration*, *deliquescence*, *efflorescence*) and *oxidation*. As a result, more than 400 minerals are susceptible to humidity, most of which have different stability ranges which often do not overlap (Appendix 4).

Hygroscopic materials respond to RH fluctuations by absorbing or desorbing moisture (Howie 1979a) to maintain equilibrium with the environment. Yet this process is not instantaneous and may induce stresses throughout the specimen with large RH fluctuations (Erhardt and Mecklenburg 1994). These stresses may result in dimensional changes, cracking, and delamination (Howie 1984, Erhardt and Mecklenburg 1994). Changes in hydration state are also frequent, leading to an altered composition. The loss of structural water can lead to shrinkage, fractures, and even disintegration (Howie 1984, Waller 1992).

Water-soluble minerals will also absorb moisture from the atmosphere and deliquesce. Halite (NaCl) is a prime example, entering solution when the RH is above 75.3% at 20°C (Feldman 2011). If deliquescent conditions are temporary, the specimen can slump, round, or flatten when in a semi-liquid phase (Waller 1992). When conditions persist for prolonged periods of time, the *transparency* and *lustre* of a specimen can be affected (Fig. 2.6), resulting in a *translucent* or *opaque*, matte surface finish. Deliquescent minerals can also be affected by *hydrolysis* or oxidation when in solution (Waller 1992).



Figure 2.6. A specimen of halite (OUMNH-MIN.26782) featuring the characteristic rounding of corners and edges, and an opaque matte surface due to deliquescence.
Image used with permission courtesy Oxford University Museum of Natural History.

Similarly, water-soluble minerals can migrate through a porous medium given a sufficiently high RH, the exact value of which is species-specific. This process occurs with cycles of fluctuating humidity, where the salts enter solution when the RH is above the deliquescence point and recrystalise when the RH drops below it (Howie 1979b, Erhardt & Mecklenburg 1994). Crystallisation at the surface (efflorescence) often results in surface disfiguration (Howie 1979b). Recrystallisation can also occur within the material matrix, causing mechanical stress and damage. The presence of

soluble salts can facilitate oxidation reactions and increase susceptibility to pollutants (Erhardt and Mecklenburg 1994).

Example: Pyrite (FeS_2)

Pyrite has long been a bane to all who have encountered it (see Torrens 1977, Lowson 1982). Its decay is the most frequently documented form of mineral deterioration in geological collections (Howie 1992b; Blount 1993; Rouchon *et al.* 2012; Odin *et al.* 2014, 2018; Miles 2019) due to the mineral's ubiquitous nature. Pyrite is often quoted as the most abundant metal sulfide on Earth's surface (Kullerud & Yoder 1959, Lowson 1982, Eggleston *et al.* 1996, Rimstidt & Vaughan 2003, Miles 2019). This is because pyrite is formed in a variety of environments and occurs in all major rock types (Kullerud & Yoder 1959, Guevremont *et al.* 1998a, Rickard & Luther 2006).

The deterioration mechanisms and pathways of pyrite are complex and variable, and are heavily dependent on the conditions present, such as: water and oxygen concentration, pH, and the availability of catalytic ions, compounds, and biological agents (Lowson 1982). For abiotic oxidation pathways, the presence of oxygen or water, or both, is required for oxidation to occur (Guevremont *et al.* 1998b, Rosso *et al.* 1999a).

When only molecular oxygen (O_2) is available, oxidation is slow, forming discrete oxide patches around defects (Rosso *et al.* 1999a). These defects are non-stoichiometric, sulfur-deficient sites (Guevremont *et al.* 1998a, 1998b; Rosso *et al.* 1999a; Dos Santos *et al.* 2016) which expose iron to the atmosphere. Iron has a higher affinity for molecular oxygen than sulfur (Guevremont *et al.* 1998b, Rosso *et al.* 1999a), resulting in the preferential adsorption of oxygen at iron sites and the formation of Fe-O groups (Rosso *et al.* 1999a).

Pyrite oxidises similarly when exposed to only water, albeit at a faster rate than when exposed to only molecular oxygen (Guevremont *et al.* 1998b). Water is also preferentially adsorbed onto defects (Guevremont *et al.* 1998b, Rosso *et al.* 1999a;

also see Yalcin *et al.* 2020), producing Fe-O and Fe-OH bonds. The formation of these bonds causes nearby sulfur sites to become slightly more electropositive, increasing their susceptibility to water. Water can then react with these sulfur sites to produce S-O bonds, the precursors to sulfate formation (Rosso *et al.* 1999a).

Yet when pyrite is exposed to *both* water and molecular oxygen, the rate of oxidation is significantly greater than the sum of O_2-only and H_2O-only oxidation, indicating a synergy between O_2 and H_2O (Guevremont *et al.* 1998b). Oxidation is most aggressive when equal quantities of O_2 and H_2O are present (Rosso *et al.* 1999a). Additionally, Usher and co-authors (2004) established that the oxygen from the water, rather than molecular oxygen, is the primary source of oxygen in the resulting sulfate products.

The products of abiotic pyrite oxidation are ferrous sulfate and sulfuric acid (Eq. 2.1). Both of these products are hygroscopic and often may react further with atmospheric moisture (Howie 1992b, Jerz & Rimstidt 2004). Sulfuric acid may scorch labels (Fig. 2.7) and housing materials (Howie 1992b, Larkin 2011, Miles 2019), and is capable of dissolving or altering other mineral species (Howie 1992b, Waller *et al.* 2000, Jerz & Rimstidt 2004, Rickard 2015).

$$FeS_2 + \frac{7}{2}O_2 + H_2O = FeSO_4 + H_2SO_4 \quad (2.1)$$

The composition and hydration state of the sulfates varies with the ambient RH and the composition of the specimen undergoing oxidation (Jerz & Rimstidt 2004, Odin *et al*. 2014). Ferrous sulfate also frequently undergoes an additional series of reactions. It may hydrate, dehydrate, hydrolyse, or oxidise depending on the ambient conditions. These reactions produce ferroso-ferric sulfates, basic sulfate-hydrates, and ferric sulfates (Howie 1979a, 1992b; Blount 1993; Jambor *et al.* 2000; Jerz & Rimstidt 2004), which may also react even further to form a complex series of products.

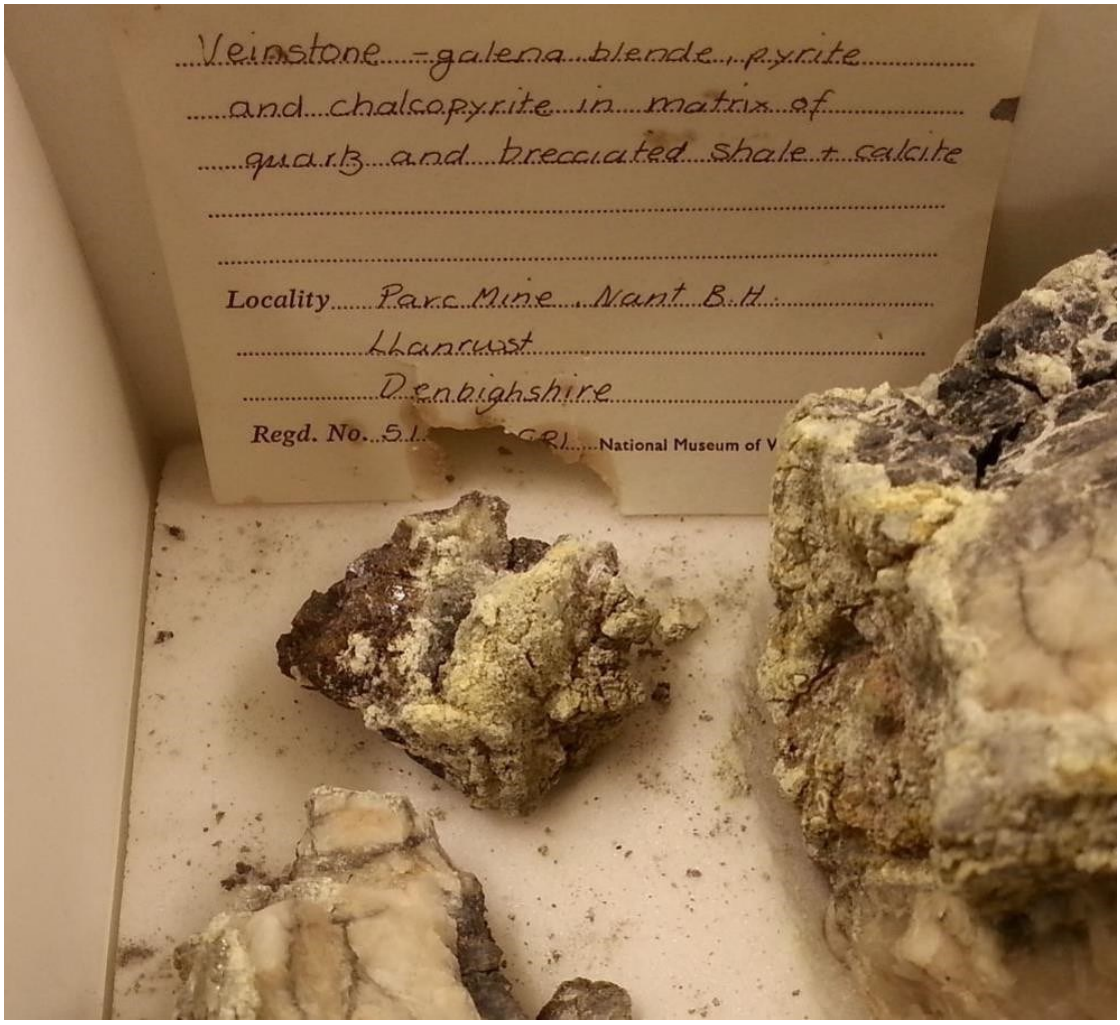


Figure 2.7. A veinstone specimen affected by pyrite decay. A section has spalled off the body; both feature characteristic yellow and white sulfate efflorescence. Also note the 'scorching' of the label, caused by sulfuric acid, which has defaced the accession number.
Image courtesy National Museum Cardiff.

The molar volumes of product sulfates are much larger than those of the initial pyrite (Table 2.2), resulting in volumetric expansion (Wiese *et al.* 1987, Howie 1992b, Jerz & Rimstidt 2004). If formed within a specimen, the expansion produces stresses that frequently result in the specimen cracking, spalling (Fig. 2.7), and eventually disintegrating (Wiese *et al.* 1987, Howie 1992b, Blount 1993, Jerz & Rimstidt 2004, Larkin 2011, Miles 2019).

Table 2.2. Molar volumes of pyrite and some common iron sulfate reaction products, illustrating the increases in molar volume during pyrite oxidation reactions.

Mineral Name	**Chemical Formula**	**Molar volume** (mol/cm^3)	**Difference in molar volume compared to pyrite** (mol/cm^3)	**Increase in molar volume compared to pyrite** (%)
Pyrite	FeS_2	23.94*	-	-
Melanterite	$FeSO_4 \cdot 7H_2O$	146.50*	122.56	512
Szomolnokite	$FeSO_4 \cdot H_2O$	55.90*	31.96	134
Mikasaite	$Fe_2(SO_4)_3$	130.80*	106.86	446
Jarosite	$Kfe^{3+}{}_3(SO_4)_2(OH)_6$	159.26†	135.32	565

* data from Robie & Hemingway 1995 † data from Alpers *et al.* 1989

2.8.3. Light

Light absorbed by specimens may cause phase transitions as well as colour change or loss. Light can also activate or accelerate reactions with other decay agents (Nassau 1992, Child 1994a). Many photosensitive minerals only undergo colour change (Nassau 1992). A limited number of these display reversible colour change upon the removal of the light source or through irradiation (Howie 1984, Nassau 1992, Horak 1994), as only the electronic states within these minerals have been altered. This is demonstrated in many coloured α-quartz (SiO_2) varieties, including amethyst. Its purple colouration is attributed to ferric iron (Fe^{3+}) which can either be a substitution for silicon or interstitially included in the quartz structure (Rossman 1994). When exposed to ionising radiation, Fe^{3+} is oxidised to Fe^{4+} and produces the violet colour (Rossman 1994). Amethyst's colour may be lost upon heating (Nassau 1992, Rossman 1994) or exposure to ultraviolet radiation (Currier 1985, Kane 1985), as non-ionising radiation reduces the iron back to Fe^{3+}. However, colour "may be restored by ionizing radiation, if the heating is not excessive" (Rossman 1994: 442).

Light may induce chemical reactions—such as oxidation (Howie 1984) and elemental liberation (Howie 1992c, Nassau 1992)—that may result in the formation of a different mineral species and irreversible colour change. Photosensitivity can be

inherent to the mineral (due to its structure and or chemical composition) or produced by impurities, which often act as colourants. The degree of photosensitivity may also vary with the specimen's origin (Nassau 1992), formation conditions, and associated mineralogy.

It is likely that many minerals are susceptible to only specific wavelengths within the visible, infrared, and ultraviolet regions of the electromagnetic spectrum, and that the reaction rates are intensity- and wavelength-dependent (Villmann & Weickhardt 2018). Research into realgar's (As_4S_4) photo-induced alteration to pararealgar (As_4S_4) has evidenced this (Douglass *et al.* 1992, Kyono 2007, Jovanovski & Makreski 2020), but comparable research for other photosensitive minerals is lacking. Relatedly, there has been no investigation of how a photosensitive mineral's reactions differ across types of illuminants (e.g., sunlight, LED, halogen) and under varying illuminance.

Example: Cinnabar (a-HgS)

Cinnabar is a notoriously photosensitive mineral, irreversibly blackening upon light exposure. Several localities have been identified that produce photosensitive specimens (Dreyer 1939, McCormack 2000). At these locations, cinnabar is associated with various mercury halide minerals (McCormack 2000, Neiman *et al.* 2015) and often contains trace amounts (~1 wt%) of alkali halogens, usually chlorides (Dreyer 1939, McCormack 2000, Keune & Boon 2005). At these concentrations, halogens are integral catalysts for the photochemical redox reaction which produces the blackening (Keune & Boon 2005, Anaf *et al.* 2013, Neiman *et al.* 2015). Moisture also plays a key role in the reaction (Saunders & Kirby 2004, Neiman *et al.* 2015); increasing RH results in a greater colour change from red to black.

This surficial blackening of cinnabar (Fig. 2.8) is attributed to the formation of colloidal metallic mercury nanoparticles (Dreyer 1939, Keune & Boon 2005, Anaf *et al.* 2013, Da Pieve *et al.* 2013, Neiman *et al.* 2015), rather than the long assumed metacinnabar (βHgS) (Gettens *et al.* 1972), calomel ($[Hg_2]^{2+}Cl_2$), or corderoite

($Hg^{2+}{}_3S_2Cl_2$) (Da Pieve *et al.* 2013, Neiman *et al.* 2015), although the latter two minerals are produced during the reaction process.



Figure 2.8. A cinnabar specimen (OUMNH-MIN.15474) displaying a dark, silvery appearance, attributable to the surficial formation of metallic mercury.
Image used with permission courtesy Oxford University Museum of Natural History.

Whilst the exact reaction pathway is still uncertain, the general pathway for mineral specimens is believed to be as follows. Cinnabar first transforms into corderoite and or kenhsuite (both $Hg^{2+}{}_3S_2Cl_2$) upon exposure to light, moisture, and chloride ions (Keune and Boon 2005, Radepont *et al.* 2011) (Eq. 2.2).

$$3HgS + 2Cl \rightarrow Hg_3S_2Cl_2 + S \qquad (2.2)$$

However, corderoite is structurally unstable when exposed to light and oxygen (Da Pieve *et al.* 2013), and will degrade into calomel, metallic mercury, and sulfur

(Keune & Boon 2005) (Eq. 2.3). Kenhsuite, an even less stable polymorph of corderoite (Radepont *et al.* 2011), is also photosensitive and will likewise decompose; first structurally into corderoite and then into the subsequent products of calomel, metallic mercury, and sulfur.

$$Hg_3S_2Cl_2 \rightarrow Hg + 2S + Hg_2Cl_2 \quad (2.3)$$

Calomel may be subsequently reduced (Neiman *et al.* 2015) to mercuric chloride and metallic mercury (Eq. 2.4).

$$Hg_2Cl_2 \rightarrow Hg + HgCl_2 \quad (2.4)$$

Additional reactions may occur and produce several other chlorine- and sulfur-containing species (Keune & Boon 2005, Anaf *et al.* 2013), which may or may not contain mercury (Radepont *et al.* 2011).

2.8.4. Atmospheric Pollutants

Museum pollutants are unwanted gases or particulates that cause or accelerate deterioration. Indoor sources of pollutants include human activity, display and storage materials, and sometimes the collection objects themselves (Waller *et al.* 2000, Eggert *et al.* 2004, Stanley 2004, Grzywacz 2006). Gaseous pollutants (e.g., carboxylic acids, sulfur dioxide, mercury vapour, hydrogen sulfide) may be more concentrated inside tightly sealed storage or display cabinets (Tétreault *et al.* 1998, Waller *et al.* 2000, Schieweck *et al.* 2005). Indoor pollutants are known to cause damage to limestone, metals, glass, and ceramics, but few studies have investigated the effects of indoor pollutants on geological collections.

Significant sulfur gases include hydrogen sulfide (Howie 1979b), carbonyl sulfide, elemental sulfur, and sulfur dioxide (Waller *et al.* 2000, Eggert *et al.* 2004). These reduced sulfur gases may be emitted from geological specimens or housing materials (Waller *et al.* 2000, Eggert *et al.* 2004, Lussier & Smith 2007), and damage adjacent minerals, paper labels, trays, and even wooden drawers. For example,

these gases produce copper sulfide and sulfate efflorescence on copper-containing materials (Fig. 2.9) and cause pitting to the substrate (Eggert *et al.* 2004). The formation and composition of the efflorescence is dependent on the ambient temperature, relative humidity, and pollutant type and concentration. Reduced sulfur gases also tarnish metallic minerals, such as those containing silver (Waller *et al.* 2000).

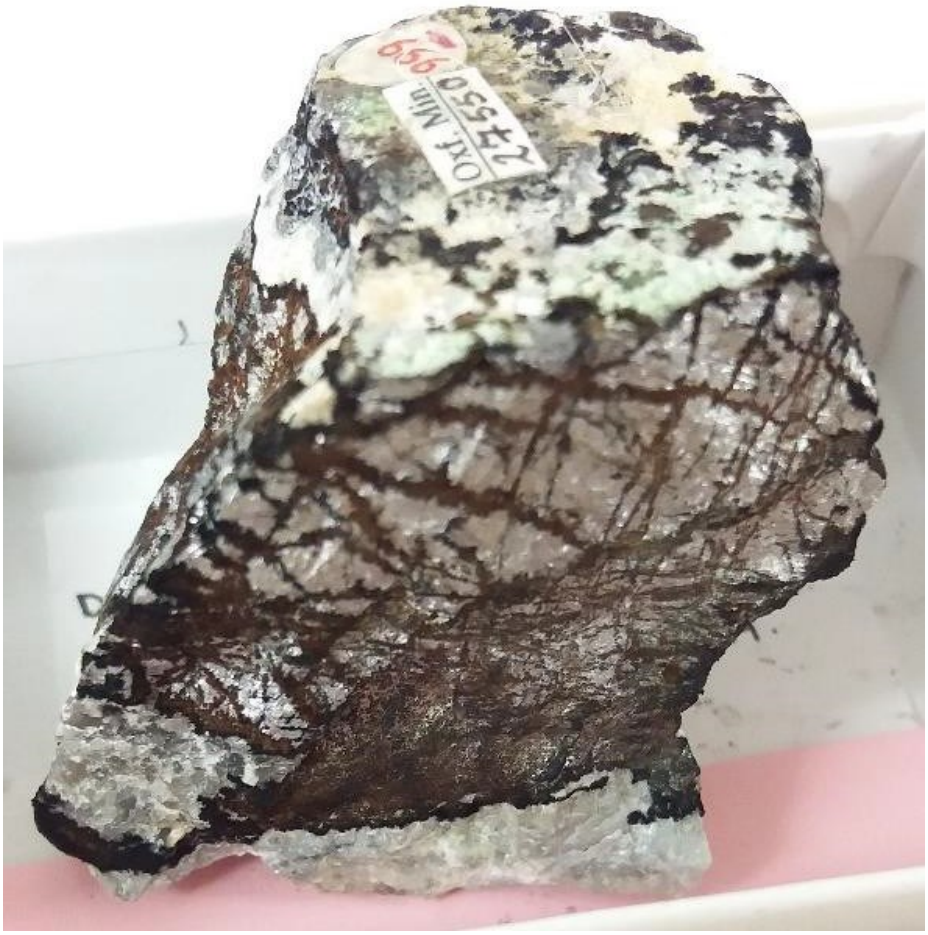


Figure 2.9. A specimen of domeykite (Cu_3As; OUMNH-MIN.27550) displaying patches of a dark navy-blue efflorescence and lines of a cocoa brown efflorescence, which have likely formed by the off-gassing of storage materials or the deterioration of neighbouring specimens.
Image used with permission courtesy Oxford University Museum of Natural History.

Carboxylic acids (formic and acetic acids, formaldehyde, and acetaldehyde) generally originate from wooden housing materials (e.g., oak, chestnut, cherry, MDF), adhesives, sealants, varnishes, and plastics (Grzywacz 1992, Child 1994b, Gibson & Watt 2010). These acids corrode limestone, egg- and other calcareous shells, and metals including lead, copper, zinc, tin, and iron (Tétreault *et al.* 1998, 2003; Raychaudhuri & Brimblecombe 2000; Waller *et al.* 2000). Reaction rates accelerate with increasing acid concentration and RH (Tétreault *et al.* 1998, 2003).

Example: Calcite ($CaCO_3$)

Calcareous material—including shell (Tennent & Baird 1985, Caracanhas Cavallari *et al.* 2014), limestone, and marble (Stipp *et al*. 1996)—is particularly susceptible to acids. Frequently discussed in museum literature is Byne's Disease, a disfiguring white or grey efflorescence occurring on shells and other calcareous material exposed to carboxylic acids (Tennent & Baird 1985, Caracanhas Cavallari *et al.* 2014). Yet less discussed are the effects of sulfur dioxide and nitric acid on calcareous materials, even though they are equally damaging.

When calcite is exposed to ambient conditions, its surfaces react with atmospheric water to produce a hydrated layer of strongly chemisorbed hydroxyl (-OH) groups, altering the surface composition to $Ca(OH)(CO_3H)$ (Stipp *et al.* 1996; Al-Hosney & Grassian 2004, 2005; Usher *et al.* 2007) (Eq. 2.5). This hydrolysis species can even form at low (~10%) RH (Al-Hosney *et al.* 2005), as the formation satisfies any dangling bonds that may be on the mineral surface (Stipp *et al.* 1996, Usher *et al.* 2007).

$$CaCO_3 + H_2O \rightarrow Ca(OH)(CO_3H) \quad (2.5)$$

The $Ca(OH)(CO_3H)$ layer readily adsorbs water (Al-Hosney & Grassian 2005), and forms a water film as the RH increases. A monolayer is formed at 20% RH (Baltrusaitis & Grassian 2009), the multilayer gains a liquid-like structure above 50% RH (Al-Hosney & Grassian 2005) and bulk-like properties above 90% RH (Usher *et al.* 2007).

This adsorbed water plays a major role in the uptake of atmospheric pollutants (Al-Hosney & Grassian 2005). Surface reactivity and reaction rates are significantly enhanced by the presence of a water film (Krueger 2003, Al-Hosney & Grassian 2005, Al-Hosney *et al.* 2005, Prince *et al.* 2008, Baltrusaitis & Grassian 2009) and increase with increasing RH. Additionally, surface adsorbed water enhances further pollutant uptake on the mineral surface and aids in mobilising surface ions (Stipp *et al.* 1996, Tétreault *et al.* 1998, Al-Hosney & Grassian 2005, Prince *et al.* 2008). This increases the solution's acidity and exposes fresh $CaCO_3$ for reaction (Al-Hosney & Grassian 2005,

Al-Hosney *et al.* 2005, Usher *et al.* 2007), allowing for greater $CaCO_3$ dissolution. The reaction can then extend into the mineral bulk and produce pitting and etching (Chiarello *et al.* 1993, Usher *et al.* 2007).

Under ambient conditions, a pollutant species—such as sulfur dioxide, nitric acid, acetic acid, or formic acid—reacts with hydrated calcite surfaces to form the respective product through an ephemeral intermediate, carbonic acid (H_2CO_3) (Al-Hosney & Grassian 2004). Surface material is incorporated in the formation of the reaction product, resulting in significant erosion and disfigurement of surface features (Usher *et al.* 2007). Products may be amorphous or crystalline (Al-Hosney *et al.* 2005, Usher *et al.* 2007) and appear as patches or a contiguous layer. However, when exposed to nitric acid, an aqueous electrolyte ultimately forms on calcite surfaces, as calcium nitrate is unstable at ambient RH; its deliquescence point is between 7 and 18% RH. (Al-Abadleh *et al.* 2003, Krueger 2003).

2.9. Historic Treatments for Mineral Collections

As with any museum collection, there are two potential approaches for managing and mitigating the deterioration of mineral collections: interventive treatment and preventive practices. While the approaches differ in terms of what actions are taken and when, both interventive and preventive conservation practices are designed to ensure object longevity and to retain as much information, value, and use as possible.

Interventive treatments are actions that are made directly to the object and that actively change the object's state, such as cleaning, repair, and restoration. The general rule of thumb within heritage conservation is to avoid interventive treatments unless they are absolutely necessary, "either for [the object's] own good or to enable its better use in study and display" (Horie 1988: 49).

Preventive practices, on the other hand, are actions made to the object's environment in order to avoid or mitigate changes in the object's state (British Standards Institution 2019). Preventive conservation practices include environmental

control, physical arrangements (i.e., improving housing materials or location), and ensuring that the object is appropriately supported. In short, these actions "should involve no change in the specimen and are designed to prevent any change" (Horie 1988: 49), either before the onset or after the treatment of deterioration.

Many interventive treatments historically used for mineralogical collections (Table 2.3) were designed to treat pyrite deterioration. Most are no longer used due to chemical toxicity, methodological inefficacy, or treatment failure. Those that are still in use—chiefly ammonia or ethanolamine thioglycolate treatments and the occasional use of coatings and consolidants (Larkin 2011)—are limited almost exclusively to larger institutions, as these methods are time and resource intensive and require specialist knowledge and equipment (Howie 1984, Larkin 2019).

Table 2.3. List of interventive treatments applied to mineral collections and their intended purposes.

Interventive Treatment	**Purpose of Treatment**	**Reference**
Dry brush cleaning	remove loose efflorescent salts & other deterioration products	Howie 1979b; King 1985; Larkin 2011; Caracanhas Cavallari *et al.* 2014
Spot cleaning with or rinsing in solutions of: - (deionised) water - (ethyl) alcohol - detergent - morpholine - organic solvents - oxalic acid	remove efflorescent salts, tarnishes, & other deterioration products	Howie 1979a, 1979b; King 1985; Tennent and Baird 1985; Caracanhas Cavallari *et al.* 2014; Fenlon & Petrera 2019
Application of paste or poultices using: - (deionised) water - acetone - ethanolamine thioglycolate - industrial methylated spirt - isopropanol - morpholine	neutralise & remove deterioration products &/or previously applied chemical treatments	Howie 1979b; Larkin 2011; Caracanhas Cavallari *et al.* 2014; Fenlon & Petrera 2019
Boiling in water	remove soluble salts; treat pyrite decay	Tennent and Baird 1985; Fenlon & Petrera 2019

Suspension over or immersion in a solution of: - ammonia - ammonium thioglycolate - ethanolamine thioglycolate - hot caustic alkali - morpholine	neutralise & remove pyrite deterioration products	Howie 1979a, 1979b; King 1985; Larkin 2011; Caracanhas Cavallari *et al.* 2014; Fenlon & Petrera 2019; Irving & Hadland 2019
Refrigeration	maintain hydration state	King 1985
Liquid storage in: - alcohol - carbon tetrachloride - glycerol - linseed oil - liquid paraffin - mineral oils - silicone fluids or oil - water	prevent further reactions; maintain hydration state	Parsons 1922; Howie 1979a, 1979b; King 1982; Fenlon & Petrera 2019
Coating and consolidation with: - collodion - linseed oil - nitrocellulose - paraffin wax - polybutyl methacrylate - polyethylene glycol - polymethyl methacrylate - (poly)vinyl acetate - polyvinyl butyral - shellac - vaseline	improve structural stability; reduce porosity; protect from pollutants, moisture, &/or oxygen	Parsons 1926; Howie 1979a, 1979b, 1984; King 1985; Tennent and Baird 1985; Larkin 2011; Fenlon & Petrera 2019; Irving & Hadland 2019
Anti-bacterial treatments and fumigants	treat once believed biotic causes of pyrite decay	Howie 1979a; Howie 1984; Fenlon & Petrera 2019; Irving & Hadland 2019

2.10. Conclusions

Given the lack of accessible, efficacious treatment options, improving preventive practices and collections care is and has been the preferable route for preserving mineral specimens (Parsons 1922, Howie 1984, King 1985). However, this requires an understanding of ideal storage conditions for each mineral species. Obtaining the relevant data for these minerals was previously difficult and tedious at best because no single resource existed that would allow conservators and curators

to access the information they require. Thus, there was a need for a resource which outlines the species that are prone to deterioration and the conditions at which deterioration occurs. From such a foundation, it would then be possible to determine effective means of monitoring change and any interventive or preventive actions to mitigate further change.

Chapter 3.
The Mineral Susceptibility Database

The Mineral Susceptibility Database (MSD) was produced as a response to the aforementioned lack of (accessible) information pertinent to mineral stability within the museum environment (see Ch. 2), and to fulfil Objective 1 of the thesis (Ch. 1, Section 1.2). The MSD consolidates current relevant research from various fields (including heritage, the geosciences, chemistry, and materials science) into a single location. By being a repository of interdisciplinary research, the Database facilitates the identification of 1.) species that are susceptible to museum conditions, and 2.) current knowledge gaps which require further investigation.

The MSD was identified as a valuable resource for the heritage sector, and thus was made freely and openly available. The Database acts as a comprehensive reference—and a starting point for further research—to facilitate identifying the conditions required by mineral collections and objects. Further, the MSD addresses some of the aforementioned challenges (see Ch. 1 and 2) through:

- increasing awareness of which disciplines and institutions are performing relevant research,
- exposing additional research opportunities, and
- advocating cross-disciplinary research and communication.

3.1. Literature Acquisition

The MSD began as a project to pool data from various publications (Parsons 1922; Bannister 1937; King 1982, 1983, 1985; O'Donoghue 1983; Howie 1984, 1992a; Hazen & Ausubel 2016) into a single spreadsheet to facilitate personal consultation. Upon the realisation of the database's utility, a conscious effort was made to systematically locate and examine mineral stability literature to add to the MSD. Hundreds of scientific publications were reviewed to create as comprehensive a database as possible. Specifically, resources which addressed the following questions were sought:

- Which mineral species change under the range of conditions possible within a museum?
- How do these changes manifest in specimens?
- Under what conditions do these changes occur?

The following four-step process was used for identifying such literature.

Step 1. Identify Publication Sources

Over a dozen journals and the publication series *Reviews in Mineralogy and Geochemistry* were initially identified as containing information relevant to mineral alteration under surface conditions. Five of these journals—*American Mineralogist, Australian Journal of Mineralogy, Journal of the Russell Society, Minerals*, and *Studies in Conservation*—were selected as the first to review.

Step 2. Scan through Titles

For the five journals selected, all issues from volume 1 through to the current publication (as of summer 2020) were scoured for titles which suggested a study of minerals at surface conditions. Additional articles were amassed through citations found within—or via the 'Recommended' or 'Related' sidebars on *ResearchGate*, *Academia*, and publisher websites of—publications which had met the search requirements.

The use of academic search engines (e.g., *Google Scholar*, *Web of Science*) or even publisher search features was considered unsuitable for the following reasons. Firstly, different disciplines were being examined—the geosciences and heritage—within which differing degrees of technicality were being probed. The usage of keywords also varies considerably within these disciplines, and many publications do not have them at all. Secondly, mineral instability covers a whole gamut of reaction types induced by various agents. Due to the sheer breadth of the English vocabulary, there are multiple ways to phrase these reactions. This variety is most clearly and easily evidenced by the selection of titles outlined in Table 3.1. None of the examples

share similar words or phases, and the whole title is needed to make sense of the content. This is because three crucial elements are being sought in order to make an assessment of the paper's potential relevance:

1. mineral name or group,
2. reaction, and
3. conditions.

Each of these elements can be replaced with hundreds (if not thousands) of unique terms or phrases, resulting in a nearly infinite series of permutations. Whilst some phrasings are more preferable to others, there are no standardised conventions within or across disciplines. Thus, it was deemed more effective to review pre-existing titles than to use keyword searches.

Table 3.1. Example of titles for articles which are cited in the MSD, and a summary of their contents.

Title	**Content**	**Reference**
Water, sulfur dioxide and nitric acid adsorption on calcium carbonate: A transmission and ATR-FTIR study	The hydration of calcium carbonate (calcite) and how the hydrated layer affects the surface-pollutant reaction	Al-Hosney & Grassian 2005
Red lead darkening in wall paintings: natural ageing of experimental wall paintings versus artificial ageing tests	How water and sulfuric acid affect lead oxides (massicot & minimum)	Aze *et al.* 2007
Nature of the alterations which form on pyrite and marcasite during collection storage	Oxidation of iron disulfides (pyrite & marcasite) and what affects the hydration state of these products	Blount 1993
Acquisition and evaluation of thermodynamic data for bieberite-moorhouseite equilibria at 0.1 MPa.	How moisture availability (humidity) affects the hydration state of hydrated zinc sulfates	Chou & Seal 2005
Natural fading of amethyst	Light-induced colour loss of amethyst (purple *variety* of quartz)	Currier 1985
A method for removing iron oxide coatings from minerals	Iron oxide (hematite & goethite) dissolution by sulfuric acid	Drosdoff & Truog 1935

Step 3. Scan through Abstracts, Experimental Details, & Figures

Upon identifying articles by their titles, publications were then progressively weeded out by examining the abstract and experimental design. As with the titles, the three aforementioned elements were sought, with particular emphasis on the conditions. If the experiment was performed under atmospheric conditions, the rest of the paper was then scrutinised.

Step 4. Scrutinise the Contents

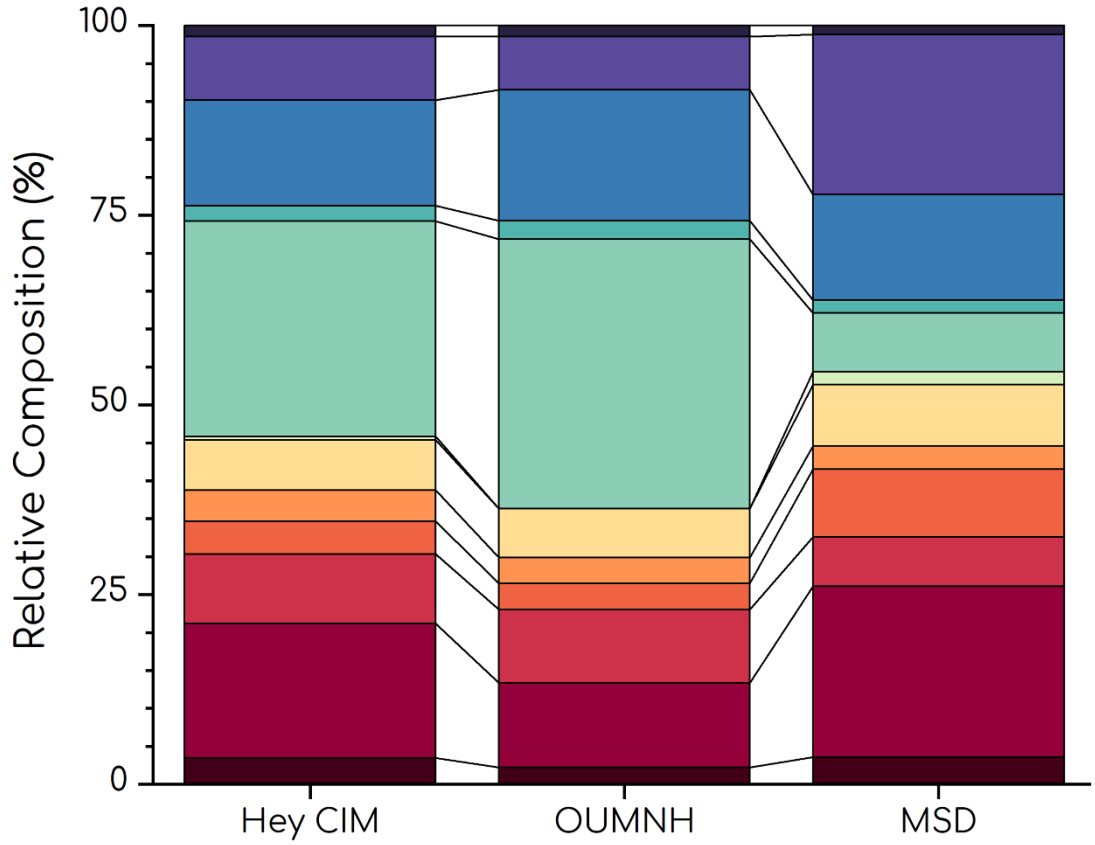
Due to the nature of the literature search methodology, it is difficult to determine how many publications were rejected in the first three phases. However, about 500 publications were selected for further scrutinization, which involved a closer reading of the paper. Experimental design and means for analysis were evaluated for statistical robustness, rigour, and representation. Other aspects relating to the quality of the paper—including scientific claims and reference use—were also considered. About half of the publications were rejected at this stage. The other half met all requirements, and key data, quotes, and reaction processes were then inserted into the Database.

3.2. Database Organisation and Contents

The current version of the Database (Appendix 4) is a Microsoft Excel spreadsheet, which has been exported as a pdf and uploaded to ORA-Data (the University of Oxford's data repository) where it is freely accessible. See Chapter 1 (Section 1.2) for the DOI.

The MSD contains 987 entries for 596 mineral species, which represents 17% of total species listed in the 3rd edition of Hey's Chemical Index of Minerals (CIM) (Fig. 3.1) and 10% of total IMA accredited species. Additionally, the MSD includes four 'precious' non-minerals (amber, pearl, obsidian, and coral) and four discredited mineral species (bromian chlorargyrite, zinnwaldite, betafite, and uranpyrochlore), as

examples of the latter may still be present and catalogued in museum collections under their old, now discredited name.



	Hey CIM	OUMNH	MSD
Elements & Alloys	97	23	21
Sulfides & Sulfosalts	499	116	131
Oxides & Hydroxides	258	101	38
Halides	121	36	52
Borates	115	35	18
Carbonates	187	67	47
Nitrates	12	0	10
Silicates	800	370	45
Niobates & Tantalates	57	25	10
Phosphates, Arsenates, & Vanadates	391	180	81
Sulfates	236	73	123
Chromates, Molybdates, & Tungstates	41	15	7

Figure 3.1. Comparative distribution of species according to the major mineral groups in the Hey CIM 3rd ed., the OUMNH systematic collection, and the MSD.

Minerals are ordered by their Hey Index number (Fig. 3.2), rather than alphabetically, to facilitate an understanding of how chemically related minerals may be similarly affected by a given agent of change. The effects of temperature, moisture, light, and pollutants are presented together—rather than separately, as seen in previous publications (Parsons 1922; O'Donoghue 1983; Howie 1984, 1992a; Horak 1994; Hazen & Ausubel 2016)—to increase clarity of a species' total susceptibility: the various ways a mineral can change depending on the agents present. Susceptibility is outlined in four fields:

1.) **Conditions:** the environmental parameters that induce a change
2.) **Response:** the type of reaction that occurs
3.) **Appearance:** visual changes to the mineral
4.) **Alterations:** physical and chemical changes to the mineral.

Using cuprite (Cu_2O) as an example, when it is exposed to chlorides (Conditions), cuprite will oxidise and hydrolyse (Response) to form a pale green crust (Appearance) composed of copper trihydrochlorides (Alterations) such as atacamite, paratacamite, or clinoatacamite (all $Cu_2(OH)_3Cl$).

Hey Number	Mineral Name	Chemical Formula	Conditions	Response	Appearance	Alterations	References
7	Oxides & Hydroxides						
7.3.1	cuprite	Cu_2O	light	photodecomposition	darkens	copper liberated	Nassau 1992
			light	surficial photo-oxidation	tarnish		Nassau 1992; O'Donoghue 1983; Howie 1984
			chlorides	oxidation & hydrolysis	colour change: pale green encrustation	to copper trihydroxychloride species	Sharkey & Lewin 1971; Scott 1990, 2000
7.4.7	periclase	MgO	moisture	tarnish	dull		O'Donoghue 1983
7.5.12	montroydite	HgO	light	surfical photo-oxidation	darkens		Nassau 1992
7.6.1	corundum	Al_2O_3	high light levels	colour change	yellow: fades		Nassau 1992
7.8.1	quartz	SiO_2	light, inc. sunlight	colour change (var. agate, amethyst, chrysoprase, citrine, morion, rose (crystalline), smokey)	fades		Currier 1985; Kane 1985; King 1985; Nassau 1992
7.8.8	opal	$SiO_2 \cdot nH_2O$	moist air	hydration			Howie 1984
			dry air &/or mild heating	dehydration	may show signs of shrinkage; cracks and loss of opalescence		Schumann 1977; King 1985
7.9.2	rutile	TiO_2	light	colour change	darkens		Nassau 1992
7.11.20	massicot	β-PbO	high RH	carbonation		to (hydro)cerussite	Aze et al. 2007
			sulfuric acid	sulfidation	yellow: black	to galena	Smith & Clark 2002
7.11.21	litharge	PbO	sulfuric acid	sulfidation	red: black	to galena	Smith & Clark 2002
7.11.22	minium	Pb_3O_4	sulfuric acid	sulfidation	red: black	to galena &/or other lead oxides	Smith & Clark 2002
			sulfuric acid	sulfidation		to platternerite & anglesite	Aze et al. 2007
7.11.23	plattnerite	PbO_2	acids				O'Donoghue 1983

Figure 3.2. An example of MSD Susceptibility entries for some oxide minerals.

3.3. Common Reactions

The Response fields for all entries were reviewed to better understand how a mineral collection as a whole may undergo change within the museum setting. Nearly 80% of change to mineral species (Fig. 3.3) can be classified as one of three types:

1.) 33% - changes to hydration state,

2.) 25% - soluble in water and or acids,

3.) 21% - changes in oxidation state.

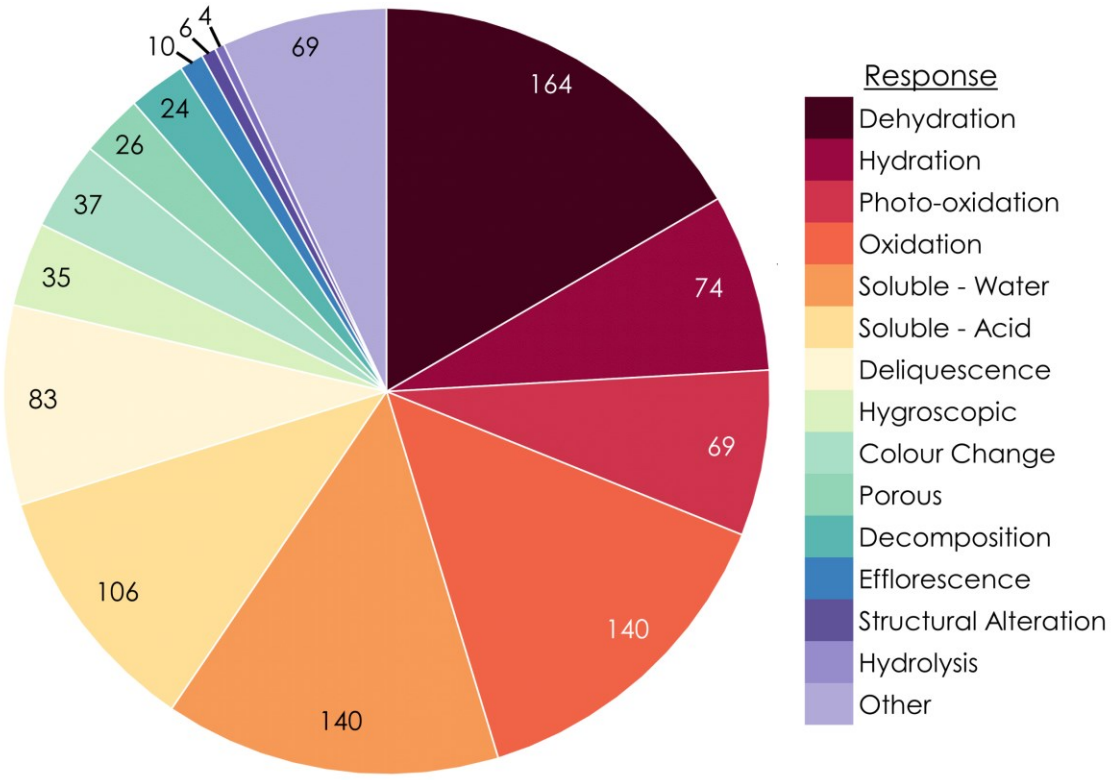


Figure 3.3. Distribution of MSD entries grouped by response to an agent of change.

There is a question, however, of whether these three response types are overrepresented within the MSD. Much of the literature relating to these changes came from the geo- and materials sciences, where the data was produced via robust, quantitative experiments. For example, details of hydration state changes in sulfates are now well characterised due to recent investigations into Martian mineralogy (see Wang *et al.* 2017 for the full list of Chou and Seal's work). Data for other reaction types, especially light-induced ones, are far fewer and generally more qualitative. As mentioned in Chapter 2 (Section 2.8.3), research investigating light intensity- and or

wavelength-dependent reactions for photosensitive minerals is lacking. Exact details—in terms of the length of exposure to a specific illuminant at a set distance and illuminance—are missing, effectively making the reports little more than anecdotal.

Physical examinations of mineralogical specimens held within museum collections were thus deemed necessary to determine:

1. whether there is agreement between the material changes experimentally reported and what occurs in the museum environment, and
2. whether there are any species seen to change in collections but not yet represented in the MSD.

This resulted in the survey of the Oxford University Museum of Natural History's (OUMNH) systematic mineral collection. 13,716 specimens belonging to 1,049 species from all mineral groups, including the silicates (Fig. 3.1), were surveyed. These specimens were those housed in the main sequence of cabinets (No. 1–58) of the upper Miers Room. Further aspects of data collection and analysis are addressed in Chapter 4 (Section 4.5).

Half (51%) of the species recorded in the MSD were found to be in the OUMNH collection. These 301 species (Table 3.2), however, only account for 29% of the species held by OUMNH. The majority of the 295 species in the MSD which were not found in OUMNH were hydrated and or rare species (e.g., sulfates, nitrates).

Of the species found in the OUMNH collection but not in the MSD, 634 species were primarily represented by only one or two specimens, thus any changes seen may not be characteristic of that species' deterioration. The remaining 115 species were present in sufficient numbers (i.e., 10+ specimens) to be used for analysis (Appendix 5).

Table 3.2. Number of species found per mineral group in the MSD and the OUMNH collection.

Mineral Group	Species Found in		
	MSD only	both MSD & OUMNH	OUMNH only
Elements & Alloys	6	15	8
Sulfides & Sulfosalts	52	79	37
Oxides & Hydroxides	9	29	73
Halides	33	19	17
Iodates & Borates	8	10	25
Carbonates	25	22	45
Nitrates	10	0	0
Silicates	9	36	334
Niobates & Tantalates	2	8	17
Phosphates, Arsenates, & Vanadates	43	38	142
Sulfates	82	41	32
Sulphites, Chromates, Molybdates, & Tungstates	3	4	11
Total Number Species	284	301	749

Only palladium (62 specimens) showed no signs of change. 28 silicate species showed minor signs of change (i.e., appeared in less than 25% of specimens surveyed). These, along with the remaining 51 silicate species, were predominately affected by physical forces, such as poor handling and or movement within the drawers. 21 of the 36 non-silicate species were also affected by physical forces. Two other potential reaction types were seen. Signs of oxidation were found in 13 species (elements, sulfides, and oxides), and those of moisture-induced changes in 11 species (carbonates, sulfates, and arsenates).

Also of note were visible signs of pollutant deposition—in particular, a dark, soot-like product (Fig. 3.4)—found on older specimens across all mineral groups. Some indication of this deposition can been seen in the survey data (Appendix 5). The composition of the sooty deposit is presently unknown, but is likely a combination of previously common outdoor pollutants (key sources being automotive exhaust and coal), cigarette smoke, and dust. Whilst it is unknown where the mineral collection was kept prior to being moved into the Miers Room in the 1980s, exposure to outdoor

pollutants would be likely due to the draughty nature of OUMNH. Smoking indoors was also common until fairly recently, and one of the previous curators was known to smoke whilst around the specimens (M. Price 2021, personal communication, 30 November). Specimens without this sooty deposit are those accessioned after the 1980s, which correlates to the reduction of both outdoor pollutants and indoor smoking, hence why the deposit is likely more than just dust. The sooty deposit could be affecting specimen deterioration, but cleaning is required to assess the impact.

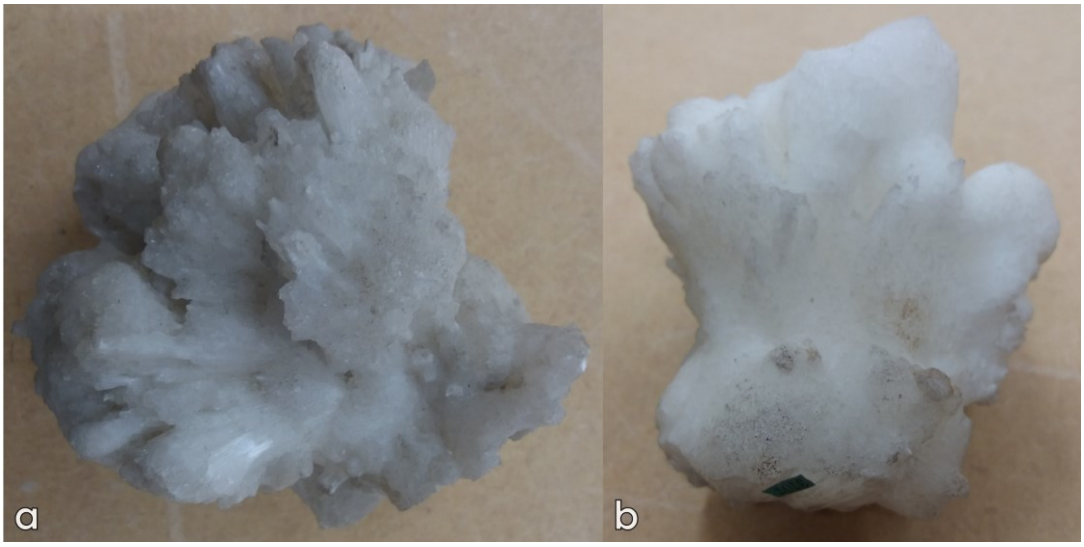


Figure 3.4. Two views of aragonite specimen OUMNH-MIN.13707: a.) the side that has been facing upwards displays a dark, grey soot-like deposit, whilst b.) the side upon which the specimen was resting has no sooty deposit and is much lighter.
Image used with permission courtesy Oxford University Museum of Natural History.

The results of the OUMNH survey suggest that the three aforementioned reaction types—solubility and changes in hydration or oxidation state—are indeed prevalent in museum collections and that these reaction types are not overrepresented in the MSD. However, museum collections may also contain more species susceptible to other reaction types, particularly photo-induced ones, than recorded in the MSD. The nature of museum storage (i.e., stored for extended periods in the dark in furniture with low air exchange rates) however, would make these species difficult to identify, especially without repeated surveying. Yet of foremost importance from the OUMNH survey results is the susceptibility of minerals to physical forces. These survey results act as a reminder that—whilst it is indeed important to identify a species' susceptibility to temperature, moisture, light, and pollutants—one cannot ignore physical forces altogether.

Chapter 4.
The Deterioration Phenomena State Survey Method

"It requires a very unusual mind to undertake the analysis of the obvious."
- Alfred North Whitehead

The Mineral Stability Database summarises the current understanding of mineral deterioration within the indoor environment and reveals current knowledge gaps which require further investigation. Ideally, quantifiable scientific methods would be employed during such investigations to measure material changes in an objective and standardised way (see Ch. 2, Section 2.4). Within heritage, various imaging and spectroscopic techniques (Royce 2019a, Royce *et al.* 2023) have been used to:

- record an object's appearance and properties at a given moment in time,
- identify and characterise an object's composition and decay products, and
- determine and quantify changes due to deterioration or treatment.

Whilst there are many factors one must take into consideration when deciding which technique(s) to use, methods are largely chosen because they are suitable for the object being analysed, affordable, and accommodate the schedules and skill sets of those involved.

However, analytical techniques are usually only applied to relatively small numbers of objects to answer specific research questions or to identify the state of high value or priority specimens. It is currently very difficult and impractical to scale up these techniques to examine an entire collection. The main limiting factor, other than resource availability, is the sheer size of collections. A high throughput method is required for completing analysis within a reasonable timeframe. Thus many turn to surveying, usually in the form of a condition assessment, as it is deemed most suitable for systematic examinations of museum collections. This chapter addresses the rationale and approach for performing a rigorous yet efficient semi-quantitative collection survey.

4.1. Surveys and the Perception Problem

"*One must understand perception before confirming that it is a solid means of knowledge acquisition and whether one can and should trust information gained by one's senses*."
– Cardinal *et al.* 2007: 85

As often discussed in philosophy, psychology and psychophysics, vision—and perception more generally—varies significantly across the human population, inherently making observations and other sensory data qualitative in nature. Does that in turn mean that methods which rely upon sensory data, such as condition surveys, are not valid ways for collecting meaningful and usable data?

Whilst the human senses are not standardised—in that no one truly senses the same thing in the exact same way—sensory data are arguably the "true foundation of human knowledge" (Cardinal *et al.* 2007: 53). For it is through our senses that we experience and come to know that which is outside of ourselves. Even if the experiences are at times variable or wrong (e.g., hallucinations), we cannot discredit that our senses provide sufficiently useful data most of the time.

Of the five traditional senses, vision is perhaps collectively the most reliable. Vision is the only sense that we have established a formalised means of improving. Corrective lenses (e.g., glasses and contact lenses) allow for an individual to see with more clarity and adjusts their focusing power to be within range of the population average (Palanker 2013). As such, there is arguably more similarity and better agreement between individuals' visual experiences than those of any other sense. Subsequently, visual survey criteria provide more consistent results than those reliant upon other senses (e.g., smell) or upon abstract concepts.

4.2. What is Condition?

"*What might be considered poor condition in one context, such as fine art, might be acceptable in another, such as social history which, in turn, could be regarded as in excellent condition in a third context, such as archaeology*." – Taylor & Watkinson 2003: 14

Condition is probably the most nebulous of the subjective "catch-all term[s]" (Taylor 2013: 99) commonly used in heritage. Like damage, condition reflects the intrinsic–extrinsic duality of an object's state and various human-ascribed uses and values (see Ch. 2, Section 2.3). Condition can encompass the concepts of stability, usability, acceptability, fitness, intactness, appearance, and even the urgency or extent of conservation treatment required (Taylor 2013). As with other terms that have a subjective, value-based element, the precise definition of an object's condition is highly variable. Person, place, time, and the object itself will all affect how condition is defined and evaluated.

Despite its central place in heritage research and conservation, there has hitherto been no formalised exploration of what governs condition. Many have touched upon factors influencing condition—usually when discussing an individual object or material type—but such reports have effectively remained anecdotal. There has yet been no standardisation into a framework that can be used to characterise condition for all object and material types. This section summarises the work this author has done to address this gap.

The relative, circumstantial nature of condition reveals that it is primarily determined by information that is external to the object and acts as context of object state. Such contextual information is comprised of three aspects:

1.) object history and environment,

2.) the observer's experiences and perceptions, and

3.) the observer's position within spacetime.

To illustrate how these aspects relate to each other and object state, the author has developed a visualisation in the form of concentric circles resembling an eye (Fig. 4.1).

The ‘Eye of Condition’ thus becomes an apt metaphor, as condition—like beauty—is in the eye of the beholder.

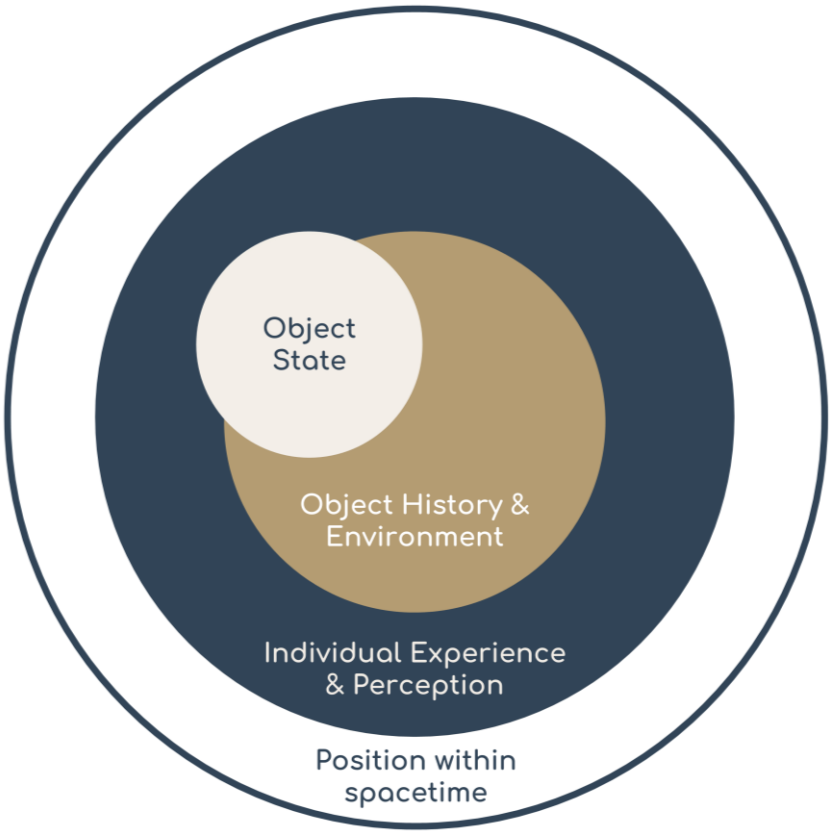


Figure 4.1. The Eye of Condition demonstrates the relationship between the four aspects that are used to determine an object’s condition. 1.) reflection of light: object state, 2.) pupil: object history and environment, 3.) iris: the observer’s experiences and perceptions, 4.) sclera, or whites of the eye: the observer’s position within spacetime.

Object state comprises information inherent to an object; its material properties and any changes it has undergone throughout its lifetime. As depicted in Figure 4.1, object state is not central to its condition. In fact, it is not truly part of the eye at all! It is merely a reflection of something out in the world which we may be able to sense but can never truly know. For even the most quantifiable and empirical evidence is subject to interpretation by one’s perception; we “can only understand and imagine the world of our experience” (Cardinal *et al.* 2007: 104). This degree of separation between the object’s true nature and the observer’s perception of it is thus reflected in Figure 4.1 by state’s position overlapping the pupil and iris.

The iris of condition addresses the observer themselves and their frame of reference. This is defined by physical and psychological factors—including one’s

biochemistry, anatomy, past experiences, knowledge, and expertise—that influence an individual's perception of the world and its contents. As with our anatomical eyes, condition's iris dilates to compensate for one's accessibility to knowledge pertaining to the object's history and environment. The less Information available, the more one has to rely on one's expertise and past experiences.

Condition's pupil, the innermost of the contextual circles, is the object's history and environment. Whilst object state is intimately related to its history and environment, the latter are still aspects outside of the object itself. They are the circumstances to which the object has been subjected, even if they produced no meaningful material change to the object. This type of contextual information is perhaps the most obvious of the three. It is frequently included in statements of object condition (e.g., 'That looks pretty good for being left out in the rain for 100 years!') and it is often asked for if not already known, as demonstrated in Taylor and Stevenson's experiment (1999: 37):

> Factors not entirely related to the task were occasionally asked by the surveyors. In particular requests [were made] for information regarding the environment in which the collection has been housed […. as well as] the hypothetical purpose of the survey—what it was expected to achieve.

The authors rightly mentioned that this information would be known prior to conducting an actual survey. However, the requests evidence that contextual information plays a fundamental role in determining condition and any subsequent actions to be taken (Baars 2019). Be it known or unknown, conscious or unconscious, a judgement cannot be made without contextual information, as the context is what gives condition meaning.

The latter of the two requests recorded by Taylor and Stevenson (1999)—that of purpose—relates to the final of the contextual circles: one's positioning. Here, positioning pertains to the where and the when; to one's exact placement before the object in four dimensional spacetime (Table 4.1). Position can be mundane: the difference between viewing a painting whilst standing up close versus seated a ways

away, or between viewing it at 10 am versus 4 pm. But position also encompasses more political aspects. An example would be the difference of viewing the Elgin Marbles in the British Museum today versus when they first went on display in 1817, versus seeing them *in situ* at the Parthenon in 430 BCE. The viewer in each of these three scenarios would experience the same Marbles in very different ways due to the politics of the time dictating the context within which they are to be viewed.

Given the number of variables which are involved in the determination of condition, we must acknowledge that condition is best considered as a short-hand for multiple factors rather than a singular concept. It is a suggestion—put forth by an individual for how others could view an object's state given its present context—rather than concrete fact. As such, the author proposes the following definition for condition: *an individual's subjective perception of an object and its history under specified contexts*.

Table 4.1. Select aspects of our position within space and time that influence perception.

	Aspect	Specifics

Space	*Viewability*	- Ease of obtaining an unimpeded view of the object.
		- Includes the following aspects:
		  - proximity: the distance between oneself and the object
		  - viewing angle: the ability to see multiple angles of an object (can be achieved by adjusting one's position or manipulating the object)
		  - obstruction: the presence of any obstructions between oneself and the object (e.g., display case, people, another object)
		  - lighting: whether there is sufficient lighting for observation and or the presence of shadow or glare

	Tangibility	- Whether one can touch and pick up the object. - Handling provides more information due to employing more senses.
	Institution	- One's place within the institution currently caring for the object. - Relates to 1.) the degree of information known about the institution's history and policies, and 2.) the ability to make decisions or take actions that affect the object. - Institutional history and policies also shape object use and value.
	Geography	- The city, country, and continent where one is observing the object. - Geographic location informs the values, laws, history, and privileges affecting both the observer and the object.
Time	*Time of Day*	- Natural lighting varies in colour and intensity throughout the day, leading to various results in object perception. - One's energy levels also fluctuate throughout the day, which in turn can affect one's mood and perception.
	Sequence of Events	- What occurred throughout the day prior to one viewing the object can also affect mood, energy, and perception.
	Historical Period	- Related to geography. - The societal values held at the time of viewing will affect both the observer and the object.

4.3. Condition Assessments: Approaches and Challenges

"Current survey techniques lack the rigour that would come from applying a more scientific method. The interpretational possibilities mean that it is difficult to tell, or prove, that a collection's condition is accurately characterized." – Taylor & Watkinson 2003: 16

A condition assessment is a non-invasive survey conducted to systematically examine the immediate condition of a collection (Taylor 2005). Whilst there are various reasons for performing a condition assessment (see Taylor & Stevenson 1999: 20), they are most commonly employed to aid collection management, improve decision-making, and garner additional resources (Taylor & Watkinson 2003, Norris 2015, Forleo & Francaviglia 2018, Kosek & Barry 2019). Condition assessments must be employed with care, however. As they occur fairly infrequently—perhaps every ten years or so—a well-designed assessment method is required to capture as much relevant and useful data as possible without being too complex and time demanding.

Putting the inherent complexities of condition as a concept to the side, its assessment is further complicated by numerous variables which introduce variation into the results and their interpretation. Be it the object, environment, surveyor, or means of documentation, each affects the reliability of the data being produced if not adequately controlled or mitigated (Taylor & Watkinson 2007, Taylor 2013).

Previously developed methods used generic forms (Fig. 4.2) with often ambiguous terminology in order to be applicable to multiple or mixed-media collections. However, such terminology introduces interpretational bias (Taylor & Stevenson 1999, Taylor & Watkinson 2003, Taylor 2013). If criteria are broad, overlap, or are not well defined, their interpretation will vary as each person applies their own frame of reference to determine what the terms mean for a given context (Taylor 2013). Terms such as 'good' and 'bad'—which are commonly used for ranking condition (Ashley-Smith 1995, Taylor 2013, Gioventù 2018, Kosek & Barry 2019)—are qualitative and subjective. Most may know what contributes towards 'good' or 'bad', but as there is no standardised definition for either term, each person will define them

differently according to their past experiences and knowledge of the material being assessed (Taylor 2013).

a

National Museum Condition Survey										
Dept.		Location								
Date		Sub-location								
Identity no.	Description	Complete-ness	Integrity	General condition	Stability	Damage	Disfigure-ment	Cons. urgency	Storage conditions	Curatorial assess.

b

COLLECTIONS CONDITION AUDIT

Survey code: 2002-C Initials: SG Date: 7.7.2002
Collection: COSTUME
Sub-collection: ACCESSORIES
Store: BH-Top
Location: SC3 S4

Condition grades:
1: GOOD: Good conservation condition, stable
2: FAIR: Disfigured or damaged, no immediate action
3: POOR: Probably unstable, needs remedial work
4: UNACCEPTABLE: Actively deteriorating

Damage categories:
MAJor structural damage
MINor structural-cracked, bent, loose
SURFace flakes, crazing, lifting
DISFigurement - stains, scratches
CHEMical - acid paper, corrosion, rubber breakdown
BIOlogical - mould, insect, rodent
OLD - sub-standard repairs
ACCretions of dirt, grease, deposits

			Tick								1-4	
Inventory no.	Object name	Materials	MAJ	MIN	SURF	DISF	CHEM	BIO	OLD	ACC	COND	Remarks
1294-36	Hat	straw, silk	✓								3	
A5434	Hat	silk		✓							1	
A21052	Hat	Wool						✓			4	live moth
A5549	Hat	Wool						✓			4	" "
A1890-154	Gloves	Leather		✓	✓						1	
1995-55	Gloves	Wool									1	

Figure 4.2. Examples of forms used for condition assessments (from Taylor and Watkinson 2003, and Taylor 2013, respectively). One form (a.) uses subjective, value-based terminology, whilst another (b.) uses terms more aligned with possible types of change, but there is still some uncertainty and overlap between the categories.

As exhibited in Fig. 4.2b, commonly used criteria do not directly convey what forms of material change can be seen in the object, but rather focus on the potential causes of the change (e.g. chemical or biological agents). This approach introduces interpretational bias (Taylor & Stevenson 1999), as one is not just recording what is seen, but rather determining what caused the effects and then translating it into the categories of the form. Causes are often difficult to determine as they necessitate inferences and assumptions. This multi-step thought process introduces variability by requiring additional information—such as knowledge of environmental conditions, housing materials, and how these react with objects—that is often not readily available (Taylor & Stevenson 1999, Taylor & Watkinson 2003) or is only known to a select group. The surveyor may not fully or correctly understand the potential causes

of damage or may only search for the specific causes that confirm their suspicions (Taylor & Stevens on 1999, Taylor & Watkinson 2003), resulting in attribution error and false data.

Even if the cause of material change is obvious when looking at the object, others may interpret it differently at a later stage if the cause is not accurately reflected in the form (Taylor & Stevenson 1999). An example seen both in Fig. 4.2b (the two wool hats) and Keene (2002) is biological deterioration: "combined with condition grade 4 [it] implies pest infestation or active mould growth" (ibid. 148). Keene here admits that there are two possible ways to interpret the same results. In the case of the two hats, we only know that they are being affected by an active pest infestation because of the note, "live moth". These notes can easily be divorced from the main data (that of condition grade and damage type) during bulk analysis of one or more collections. Thus the urgency of an active infestation becomes invisible beyond the form.

This example evidences that there should be no implied meaning in the survey form, and that specific types of material change need to be clearly differentiated. Thus, the selected criteria should allow for the surveyor to clearly record what they see in order to avoid false impressions and misunderstandings in subsequent review of the results.

Perhaps the simplest way to ensure clarity is to record the effects of material change, rather than the causes, as effects are easier to identify and document (Taylor 2013). This can be done by selecting phenomenological criteria applicable for the collection being surveyed (for examples, see Sully & Suenson-Taylor 1996, Kosek & Barry 2019). Although the exact number and terms used may vary between collection or material types, criteria should be specific, mutually exclusive, comprehensive, and well-defined to minimise subjectivity and accurately record condition without collecting redundant information (Sully & Suenson-Taylor 1996, Taylor & Stevenson 1999, Taylor 2013, DeMouthe 2017, Kosek & Barry 2019).

4.4. A Different Approach

"Although one can never expect to find the perfect representation of a collection the current process can be made less subjective." – Taylor & Stevenson 1999: 39

One may wonder whether it is truly possible to objectively evaluate condition, given the difficulty in constructing and performing assessments. However, as the problem of condition is akin to that of damage (see Ch. 2, Sections 2.3 and 2.4)—due to the difficulty in quantifying the subjective—arguably the solution is the same: decouple the tangible from the intangible and focus solely on material changes. This is achievable through approaching collection assessments as a bottom-up process (Fig. 4.3), and introducing a state survey as the initial step within the process in order to more holistically understand a collection.

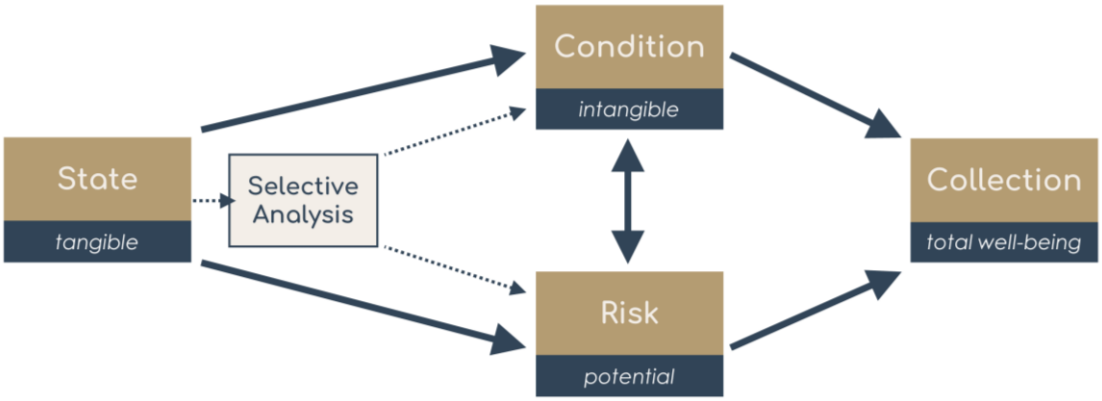


Figure 4.3. Flow chart illustrating a collection assessment approach.

The first step is a state survey, which collects information about the collection's current state via a physical examination. This can be supplemented with analytical tests and imaging, and or a review of surrounding infrastructure (including environmental conditions and housing materials) if any concerns are raised during examination. As Figure 4.3 illustrates, this survey is the foundation upon which the rest of the assessment is built. It is during this stage that one collects arguably the most critical information, as lacking a clear understanding of the collection's present situation will fail to provide any effective actions. For example, if one sees evidence of a pest problem, but does not investigate whether it is active, what pest species are involved, and what parts of the collection are being attacked, any actions taken could result in a misestimation or waste of resources, all at the collection's expense. Thus it

is critical to know collection state to move forward into the other parts of the assessment.

Separating state from condition not only addresses many concerns regarding subjectivity, but also facilitates data analysis. Whilst data relevant to object state can be recorded in previous assessment methods, the state data may not be extractable or statistically assessable. Having an analysable data set at this stage helps to identify key areas of concern and deploy immediate actions to address urgent hazards (like a pest infestation) and stabilise the collection, if necessary.

Whilst the state survey deals with the physical aspects of a collection, the condition assessment addresses the intangible. This is where the aforementioned aspects of the Eye of Condition (i.e., object history and environment, and stakeholders' experiences, perceptions, and positions) are used to contextualise the collection's state and identify its current values and uses. Information acquired during this phase would be derived from collection documentation (e.g., collection registries, environmental data), institutional documents (e.g., policies, mission statement, exhibition plans), and stakeholder opinions (collected via polls, interviews, social media, etc.).

Whilst state and condition are useful in assessing the current status of a collection, they cannot predict potential future changes. As such, it is critical to include a risk assessment, which uses both the tangible and intangible to make evidence-based predictions of what would happen to the collection were varying scenarios to occur. The data from the state survey is used to identify probable agents of change, likely exposure and outcomes, and any potential synergies between agents. This is again contextualised by the information from the condition assessment, which is used to accurately characterise the magnitude of risk and loss. The results of the risk assessment can then be fed back into the condition assessment—hence the two-way arrow in Figure 4.3—to determine how values and uses would change if damage were to occur.

This approach in and of itself is not truly novel; previous collection assessment methods all include the determination of state, condition, and risk to some degree.

However, by consciously dividing a collection assessment into these three discrete parts (Fig. 4.3), one can collect the correct information at the right time, and each part can be allocated to different individuals or teams (if the resources are available). When the information from the three parts is united, a holistic understanding of the collection emerges, which facilitates identifying efficacious targeted actions that address priority concerns, be they major revisions to infrastructure or maintenance of current procedures. As this new approach contains a relatively novel element (the state survey), an equally novel method needed to be developed.

4.5. The Deterioration Phenomena (DP) State Survey Method

The Deterioration Phenomena (DP) State Survey Method was intentionally designed to collect semi-quantitative and statistically robust data pertaining to the state of collection items whilst avoiding or mitigating the aforementioned biases and shortcomings of pre-existing methods. This was achieved chiefly through its signature feature: the use of phenomenological criteria, named ‘Deterioration Phenomena’.

4.5.1. Deterioration Phenomena

Deterioration Phenomena (DP) are criteria that are visual indicators of material change and are specific to the collection being examined. By selecting DP that are applicable for the items being surveyed, the DP Method can easily be adopted to other collection types, even those beyond natural history.

Some general examples of DP found on a wide range of materials are ‘cracking’ and ‘colour change’. These are important visual changes that one could anticipate to find in most, if not all, collection types. More specific examples include ‘dimpled’ for minerals, or ‘foxing’ for paper. Be they specific or general, it is critical that the chosen DP are simply and explicitly defined both verbally and pictorially (Fig. 4.4). This ensures that all parties involved, both in the present and future, have as similar of an understanding of the criteria as possible.

	
Dimpled Shallow divots in the mineral surface	**Foxing** Orange to brown discolouration of paper, usually away from foredges and present as discrete spots or blotches

Figure 4.4. Example DP definitions, each with an image that visualises how the change is exhibited within the select material type.
Image used with permission courtesy Oxford University Museum of Natural History.

Only the presence (1) or absence (0) of DP is noted. There is no grading, scaling, or determination of the extent or severity of a given DP. This is a very deliberate part of the method's design, first and foremost to maintain one's focus on state, rather than condition. It also essentially simplifies the process to a series of yes or no questions (i.e., Is this DP present; yes or no?), thus avoiding the variability inherent to categorisation. This is because categorisation it is a two-step thought process (Taylor 2013). It necessitates drawing upon external information to classify the observed changes, be in abstract terms (e.g., good, poor, unacceptable) or numerical ('on a scale from 1 to 5').

Categorisation also takes substantially more time than spotting the changes themselves because of the degree of thinking involved. This results in spending more time per object, which significantly increases both the total time required to complete the survey and the data's accuracy due to the increased likelihood of questioning one's perceptions and judgements.

Even if the extent or severity of criteria were measured quantitatively, collecting these measurements would still take a significant amount of time and arguably provides too much information. Whilst such information may be important to know for an individual object, it would be superfluous at a collection-scale, bogging down both data collection and analysis. Further information regarding specific material changes can be collected at a later date for selected objects which have been determined to be of concern.

Simplifying the surveying process also allows for it to be completed by non-experts, including volunteers, who may never have seen specific types of objects before and lack the contextual information necessary to determine condition. Thus lack of personal familiarity would not necessarily hamper data collection.

4.5.2. Applications and DP Used

The DP State Survey Method was employed on the mineral collections held at four UK museums (Table 4.2): Oxford University Museum of Natural History (OUMNH), National Museum Cardiff (NMC), National Museums Liverpool (NML), and the Sedgwick Museum of Earth Science.

Table 4.2. Summary of the studies conducted, including details of the collections and the length of the surveys.

Study Number	**Specimen Type**	**Museum**	**Number of Specimens**	**Percent of Collection**	**Time Taken** (hr)	**Average Rate** (spec./hr)
P	sulfide ore bodies	NMC	22	0.7–1.2%	—	—
1	systematic collection	OUMNH	13,716	40%	181	79
2	pyrite	OUMNH	358	63%	6	61
		NMC	482	72%	11	54
		NML	135	52%	3	45
		Sedgwick	298	82%	8	44

A pilot was first performed on 22 pyritic Minescan Reserve specimens at NMC to confirm that the chosen DP were applicable and sufficiently defined. The specimens surveyed—and those of the Minescan project more generally—are *ore body* samples of from mines across Wales, and were collected as physical records of the local geology. In addition to pyrite, the Minescan specimens are largely comprised of various ore (e.g., arsenopyrite, chalcopyrite, sphalerite) and gangue minerals (e.g., quartz, calcite).

Study 1 was then conducted with the systematic mineral collection held at OUMNH with the purpose of corroborating the Mineral Susceptibility Database to a museum collection, as described in Chapter 3. Study 2 was then performed on the pyrite specimens held at the four aforementioned museums in order to elucidate how pyrite oxidises in the museum context. This study is covered in more detail in Chapter 6.

During the pilot, a preliminary set of 13 DP were trialled (Table 4.3). Four DP—wet, abrasion, delamination, and porosity—were then discarded as they were not frequently seen in specimens or were difficult to define or identify. This however resulted in no DP to capture specimens which are hygroscopic or prone to deliquescence. Wet was then redefined as slumped (which was later rephrased as rounded) and dimpled to capture these specimens. Whist pitting was maintained from the pilot, it was eventually dropped as pits were very rarely seen.

The main difference between the sets of DP used for the pilot and the subsequent surveys is the addition of colour criteria. Although colour is perhaps the most variable and qualitative of an object's properties, it plays a significant role in our visual experience. Changes in colour also often correlate with other changes in an object, especially in minerals (as seen in Ch. 2, Section 2.8). Thus, it was determined that colour-based criteria would be included, but greater focus would be placed on changes in *lightness* ('dark', 'pale', and even 'dull') than in *hue* ('colour change'). This is because lightness is a universally recognised attribute of colour (Kuehni 2003), and changes in lightness are easier to identify and describe than those in hue (or *chroma*) regardless of one's chromatic vision (i.e., whether one is colour blind or not).

Table 4.3. The evolution of DP applied to subsequent studies.

Pilot		**Study 1**		**Study 2**
Wet	X →	Dimpled	→	Dimpled
		Slumped	→	Rounded
Corrosion	→	Corrosion	→	Corrosion
Tarnish	→	Tarnish	→	Tarnish
Efflorescence	→	Efflorescence	→	Efflorescence
Powdery	→	Powder	→	Powder
Crumbling	→	Crumbling	→	Crumbling
Flaking	→	Flaking	→	Flaking
Pitting	→	Pits	X	
Breakages	→	Breakages	→	Breakages
Cracking	→	Cracking	→	Cracking
Abrasion	X			
Delamination	X			
Porosity	X			
		Dull	→	Dull
		Dark	→	Dark
		Pale	→	Pale
		Opacity	→	Opacity
		Colour Change	→	Colour Change

X = Discarded; X → = Redefined; → = Retained

4.5.3. Pre-Survey

The three parts to the DP Method are pre-survey, surveying, and post-survey (Fig. 4.5).

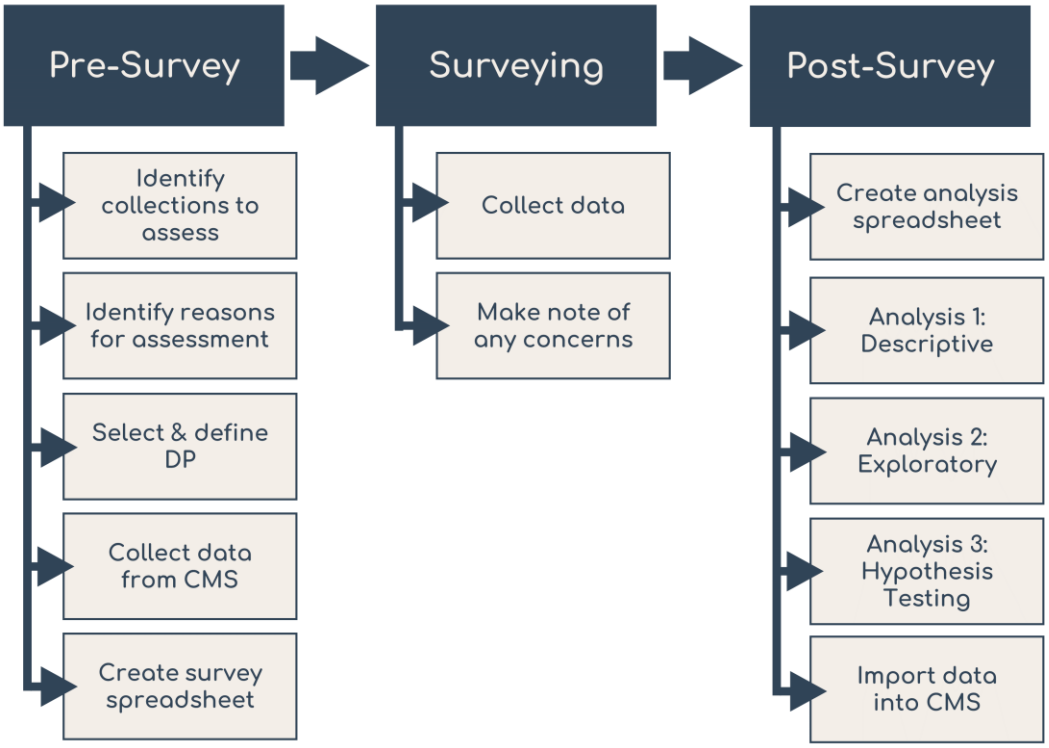


Figure 4.5. The three phases of surveying and the actions taken during each.

The pre-survey is crucial. It is a time of preparation: of identifying aims and objectives and collecting any pre-existing information in order for surveying to go as quickly and smoothly as possible. The first step is to identify what collections are to be surveyed and why, as these decisions shape how one approaches data collection and analysis. Using Study 2 as an example, pyrite specimens at OUMNH, NMC, NML, and the Sedgwick were surveyed to identify:

1. the state of the specimens,
2. any museum-specific deterioration patterns, and
3. any trends in deterioration which may elucidate how pyrite deteriorates in the museum environment.

Included in this first step is identifying which parts of a collection will **not** be surveyed. For Study 2, only specimens that were recorded to be primarily or exclusively composed of pyrite were surveyed. Specimens which contained pyrite as a secondary

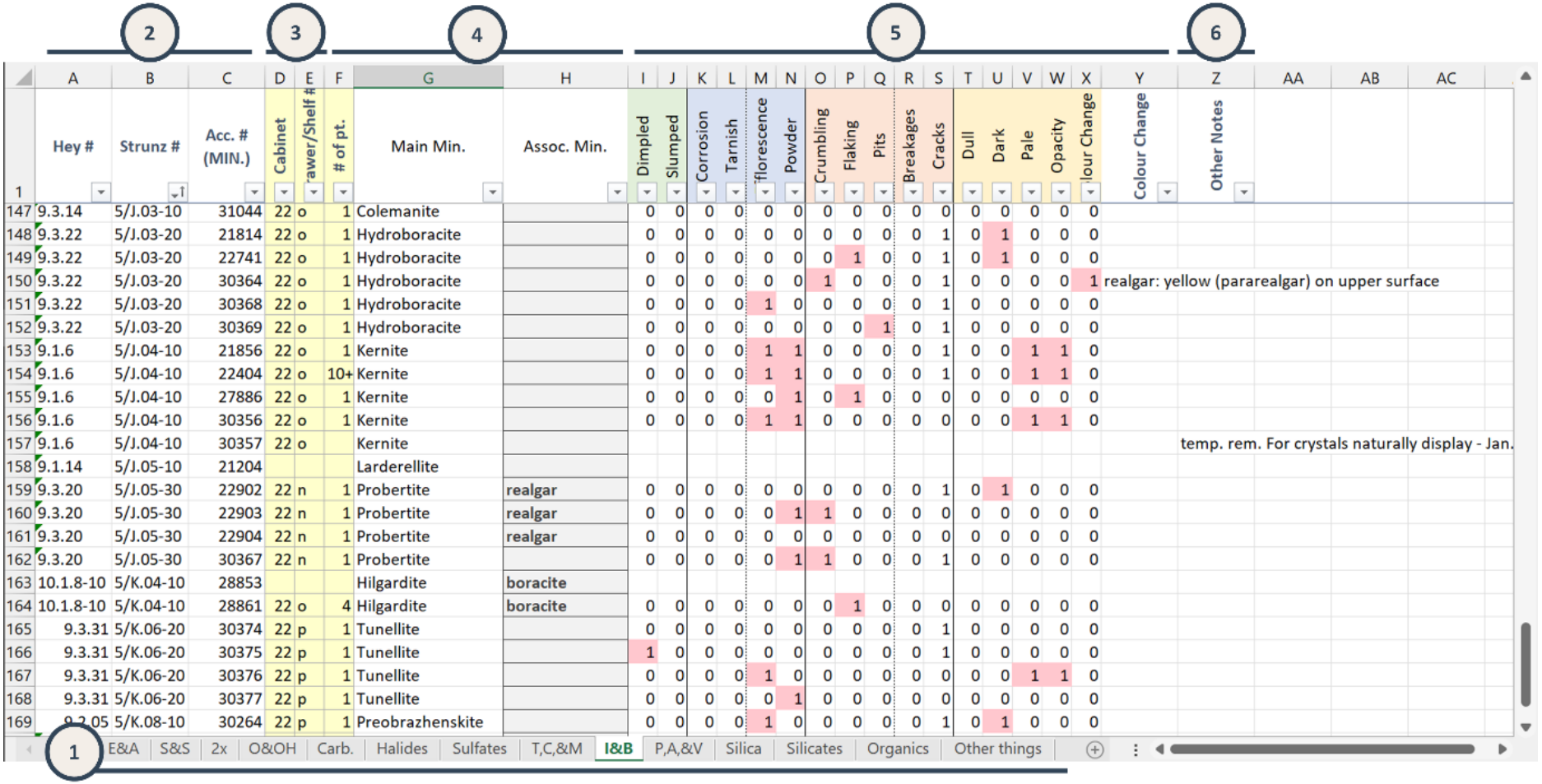
or associated mineral (be it with fossils, rocks, or other mineral specimens) were excluded. Additionally, only the specimens housed within the main sequence of drawers were surveyed; (extra)large and prepared specimens (e.g., slides, micro-mounts) were excluded. These choices were made primarily because excluded specimens were often stored elsewhere and would require significantly more time and effort to access.

Once the targeted collections are determined, DP are selected to reflect how the component objects deteriorate. A glossary of the chosen DP (Appendix 1) is then made, consisting of definitions and images like those seen in Figure 4.4. After this, relevant pre-existing information pertaining to each collection is retrieved from the institution's collection management system (CMS). What is deemed relevant depends on the overall purpose of the collection assessment, but should always include 1.) accession or object numbers, and 2.) the basic name or identifier of the targeted objects (e.g., pyrite, pheasant, platter). These two bits of information are key to ensuring that all subsequent information, including the survey data, is attached to the correct object. For both Studies 1 and 2, the following information was requested:

- accession/object number,
- primary mineral,
- associated mineralogy,
- locality, and
- accession/collection date.

The CMS data is then used to structure and populate the survey spreadsheet, which is divided into 6 main components (Fig. 4.6).

1. **Worksheets** are used to divide the collection into its component groups (e.g., main mineral groups). This avoids having tens of thousands of objects in one worksheet.



	Hey #	Strunz #	Acc. # (MIN.)	Cabinet	Drawer/Shelf #	# of pt.	Main Min.	Assoc. Min.	Dimpled	Slumped	Corrosion	Tarnish	Efflorescence	Powder	Crumbling	Flaking	Pits	Breakages	Cracks	Dull	Dark	Pale	Opacity	Colour Change	Colour Change	Other Notes
147	9.3.14	5/J.03-10	31044	22	o	1	Colemanite		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0		
148	9.3.22	5/J.03-20	21814	22	o	1	Hydroboracite		0	0	0	0	0	0	0	0	0	0	1	0	1	0	0	0		
149	9.3.22	5/J.03-20	22741	22	o	1	Hydroboracite		0	0	0	0	0	0	0	1	0	0	1	0	1	0	0	0		
150	9.3.22	5/J.03-20	30364	22	o	1	Hydroboracite		0	0	0	0	0	0	1	0	0	0	1	0	0	0	0	1		realgar: yellow (pararealgar) on upper surface
151	9.3.22	5/J.03-20	30368	22	o	1	Hydroboracite		0	0	0	0	1	0	0	0	0	0	1	0	0	0	0	0		
152	9.3.22	5/J.03-20	30369	22	o	1	Hydroboracite		0	0	0	0	0	0	0	0	1	0	1	0	0	0	0	0		
153	9.1.6	5/J.04-10	21856	22	o	1	Kernite		0	0	0	0	1	1	0	0	0	0	1	0	0	1	1	0		
154	9.1.6	5/J.04-10	22404	22	o	10+	Kernite		0	0	0	0	1	1	0	0	0	0	1	0	0	1	1	0		
155	9.1.6	5/J.04-10	27886	22	o	1	Kernite		0	0	0	0	0	1	0	1	0	0	0	0	0	0	0	0		
156	9.1.6	5/J.04-10	30356	22	o	1	Kernite		0	0	0	0	1	1	0	0	0	0	0	0	0	1	1	0		
157	9.1.6	5/J.04-10	30357	22	o		Kernite																			temp. rem. For crystals naturally display - Jan.
158	9.1.14	5/J.05-10	21204				Larderellite																			
159	9.3.20	5/J.05-30	22902	22	n	1	Probertite	realgar	0	0	0	0	0	0	0	0	0	0	1	0	1	0	0	0		
160	9.3.20	5/J.05-30	22903	22	n	1	Probertite	realgar	0	0	0	0	0	1	1	0	0	0	0	0	0	0	0	0		
161	9.3.20	5/J.05-30	22904	22	n	1	Probertite	realgar	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0		
162	9.3.20	5/J.05-30	30367	22	n	1	Probertite		0	0	0	0	0	1	1	0	0	0	1	0	0	0	0	0		
163	10.1.8-10	5/K.04-10	28853				Hilgardite	boracite																		
164	10.1.8-10	5/K.04-10	28861	22	o	4	Hilgardite	boracite	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0		
165	9.3.31	5/K.06-20	30374	22	p	1	Tunellite		0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0		
166	9.3.31	5/K.06-20	30375	22	p	1	Tunellite		1	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0		
167	9.3.31	5/K.06-20	30376	22	p	1	Tunellite		0	0	0	0	1	0	0	0	0	0	0	0	0	1	1	0		
168	9.3.31	5/K.06-20	30377	22	p	1	Tunellite		0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0		
169	9.3.05	5/K.08-10	30264	22	p	1	Preobrazhenskite		0	0	0	0	1	0	0	0	0	0	1	0	1	0	0	0		

Figure 4.6. The six components of a (completed) DP survey spreadsheet.

2. The **Organisational columns** act as a means of sorting items by how they are found in the store and within the component groups. This allows for one to anticipate what is coming next.
   For example, minerals are often arranged by an organisational system (i.e., Hey, Dana, Strunz), which functions similarly to the Dewey Decimal System used in libraries. In these organisational systems, the main mineral groups are subdivided, either according to chemistry or crystal structure, and each mineral species is assigned a (alpha)numeric identifier. If a collection is arranged by such a system, one can sort the survey spreadsheet by the species identifier and then accession/object number. This allows for specimens that are stored together in the drawer to appear together in the spreadsheet, speeding up data entry.

3. The **Location columns** contain information pertaining to the objects' exact location in the store (i.e., cabinet, drawer, and or shelf).
   If this information is not already known, collecting it during the survey will prove beneficial and time-saving when searching for a specific object in the future. Recording the exact location may also be required for hazardous objects (i.e. asbestiform, radioactive).

4. The **Identification columns** correlate to immediately obvious visual characteristics (i.e., species, associated materials, colour). These aid surveying by providing visual clues that ensure one is attributing data to the correct object in case of a mix-up in the accession/object number.

5. The **DP columns** are the main data collection fields. Here one enters either a 0 or 1 depending on whether the DP is absent or present.

6. **Additional notes columns** can be included to document any curatorial or conservation actions that may need to occur. This may include missing labels, specimens, or parts; need for repair or treatment; temporary removal; and the presence of hazardous material.
   An example column one may wish to included is a 'To Action' or 'Priority' column; a field for the rapid identification of objects needing immediate

actioning. Ideally, this should be a binary (0/1) field like the DP columns, but institutional gradings can be applied for consistency. These notes columns can be used to identify key areas of concern within the collection and later facilitate resource allocation for collection care and development.

4.5.4. Surveying

Surveying itself is fairly straightforward: examine the object for the presence/absence of the chosen DP then type in the corresponding series of 1s and 0s. It took the author on average about a minute to examine and enter the data for each specimen. Whilst there are no true time restrictions for examining an object, one should spend only as much time as necessary to identify DP in order to mitigate questioning one's perceptions.

Whilst the DP Method was designed so that one could survey every specimen in a collection, doing so is not always feasible or necessary. For both Studies 1 and 2, certain specimens were not examined. Microenvironments were not disturbed in order to maintain their climate, assuming they were still as conditioned. Asbestiform specimens and those in anoxia were often double bagged and difficult to examine. The bags often reflected the overhead lights or were not entirely transparent, obscuring detail. The anoxic bags were also only transparent on one side, limiting how much of the specimen could be viewed.

4.5.5. Post Survey: Analysis

The primary purpose of analysis is the identification of deterioration; chiefly, what types of deterioration are occurring and to which specimens. This is achieved through examining the deterioration phenomena that are recorded as being present. Whether the deterioration is active, however, cannot be determined by visual observations alone and is out of the scope for the survey.

4.5.5.1. Analysis 1: Descriptive

Analysis begins by identifying how to collapse the data into meaningful subsets in order to identify trends. Subsets can be defined in various ways, but perhaps the most useful for initial analysis is defining the subsets by 1.) species, 2.) object type, or 3.) component group. For both Studies 1 and 2, subsets were defined by the primary mineral species, for which five descriptive statistics were calculated (Table 4.4). The 20 entries of Table 4.5 will be used as a worked example to explain this phase of analysis.

Table 4.4. The five descriptive statistics and how they are calculated in Excel.

How Data is Being Examined	**Descriptive Statistic**	**Abbreviation**	**What it is**	**How to Calculate**
Individually	Total DP	TDP	Sum of DP seen in 1 object *Row Summary*	Formula: SUM
Collection-wide OR *Grouped into Subsets*	Average DP	ADP	Average DP seen in all objects *Column Summary*	Formula: AVERAGE or Pivot Table, 'Values' *Value Field: Average*
	Number of specimens	# of sp.	Number of objects in a (sub)set *Column Summary*	Pivot Table, 'Values' *Value Field: Count*
	Percent DP	%DP	Percentage of objects displaying each DP *Column Summaries*	Pivot Table, 'Values' *Value Field: Average*
	%DP Patterning	—	Colour coding of %DP to facilitate data examination	Conditional Formatting *Highlight Cell Rules: 'Greater Than' &/or 'Between'*

Table 4.5. Survey and descriptive analysis results for 20 select specimens (ten each for sulfur and galena). Five DP (Dimpled, Rounded, Pits, Opacity, and Colour Change) were omitted here as they were absent from these specimens.

Mineral	Accession # (OUMNH-MIN.)	Corrosion	Tarnish	Efflorescence	Powder	Crumbling	Flaking	Breakages	Cracks	Dull	Dark	Pale	Total (TDP)
Sulfur	00201	0	0	0	1	0	0	0	1	0	0	0	2
	00202	0	0	0	0	0	0	0	0	0	0	0	0
	04533	0	0	0	0	0	0	0	0	0	0	0	0
	04549	0	0	0	1	0	0	0	0	0	0	0	1
	04591	0	0	1	0	0	0	0	0	0	0	0	1
	04594	0	0	1	0	1	0	1	1	0	0	0	4
	08345	0	0	1	0	1	0	1	1	0	1	0	5
	10284	0	0	0	0	1	0	1	0	0	0	0	2
	10285	0	0	0	1	0	0	0	0	0	0	0	1
	10286	0	0	0	0	0	0	0	0	0	0	0	0
	%DP	**0%**	**0%**	**30%**	**30%**	**30%**	**0%**	**30%**	**30%**	**0%**	**10%**	**0%**	**ADP: 2**
Galena	04965	0	0	0	0	0	0	0	0	1	0	0	1
	11059	0	1	0	0	1	0	0	0	1	1	0	4
	11071	0	1	0	0	0	0	0	1	1	1	0	4
	12827	0	1	1	0	1	0	1	1	1	1	1	8
	15289	0	1	0	0	0	1	0	1	1	1	0	5
	15427	0	1	0	0	0	0	0	0	1	0	0	2
	18712	0	1	0	0	0	0	0	1	1	0	0	3
	18922	0	1	1	0	0	0	0	0	1	1	0	4
	19281	0	1	0	0	0	0	0	0	1	0	0	2
	21516	1	1	0	0	1	0	0	1	1	0	0	5
	%DP	**10%**	**90%**	**20%**	**0%**	**30%**	**10%**	**10%**	**50%**	**100%**	**50%**	**10%**	**ADP: 4**
Colour Code		0–24%	25–49%	50–74%	75–100%								

After importing the survey data into a new workbook for analysis, the first metric to be calculated is the Total DP (TDP). The TDP is the sum of all DP observed in a singular object (i.e., the sum of all the 1s and 0s in a given row). For example, specimen 201 (sulfur; Table 4.5) has a TDP of 2 because two DP (powder and cracks) were observed.

The TDP are then used to calculate the Average DP (ADP): the average TDP of all the specimens being examined. In other words, the ADP represents the average number of DP seen in a (sub)set of specimens. The ADP for the ten sulfur specimens listed in Table 4.5 is 2.

TDP and ADP are useful in summarising the state of specimens, but they must be used with caution, for they are **NOT** indicators of the extent or severity of deterioration. A higher TDP or ADP does not always correlate with concerning deterioration.

Both specimens shown in Figure 4.7 have a TDP of 5, but display different DP. The DP seen in the sulfur specimen (Fig. 4.7a) largely correspond to the siliceous sinter *matrix* in which the sulfur crystals are imbedded, and indicate the matrix's friable nature and susceptibility to physical forces (e.g., poor handling, vibration). The DP of the galena specimen (Fig. 4.7b & c), however, are much more concerning as they are suggestive of surficial oxidation. This oxidation occurs when the relative humidity is greater than 65% (at 20°C) and may potentially lead to efflorescence as the mineral alters to the lead sulfate, anglesite ($PbSO_4$) (Swartzlow 1933, Howie 1992c). Thus the nature of one's response to change is not governed by a single value but by the "patterns of change" (Kosek & Barry 2019: 202) formed by the DP.

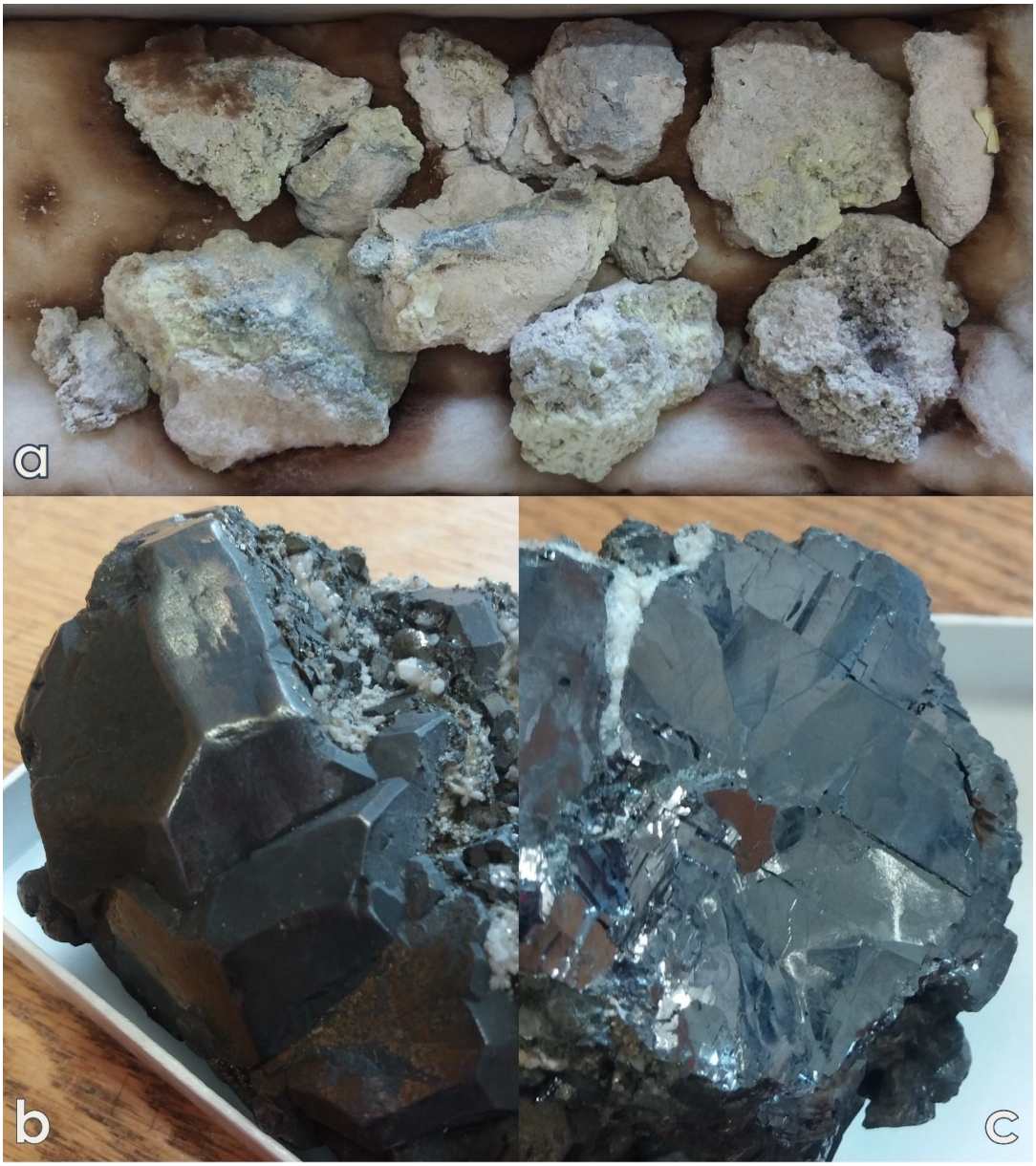


Figure 4.7. Two specimens with a TDP of 5. a.) Sulfur specimen OUMHN-MIN.08345 is in multiple parts and displays noticeable cracks and crumbs. Efflorescence and a dark soot-like coating is also visible upon close examination. Galena specimen OUMNH-MIN.15289 exhibits b.) a distinct dull and dark tarnish on all crystal faces, as well as c.) cracking and flaking on the bottom of one large crystal. Images used with permission courtesy Oxford University Museum of Natural History.

When reviewing multiple objects of the same type, one determines areas of concern by examining the patterns formed by the Percent DP (%DP). Each %DP is the percent average of the DP's occurrence within the subset being studied; it is the sum of the 1s and 0s of a given DP column (e.g., 'cracks') divided by the total number of specimens being examined, and displayed as a percentage. Three of the ten sulfur specimens in Table 4.5 were recorded to have displayed a crack of some kind, thus the %DP for 'cracks' would be 30%.

%DP patterning is produced by colour coding the %DP and is used to determine potential reaction types based on the DP observed. For mineral specimens, reaction types may include surficial oxidation, oxidation at depth, pollutant-induced oxidation, efflorescence, surface wetting, and physical forces. These reaction types are then categorised as first or second order depending on the percentage of specimens that exhibit these patterns. First order is a reaction that affects greater than 50% of specimens, whilst second order is that which affects less than 50%.

Determining which reaction types may be affecting the collection does require some knowledge of the material's deterioration, but one need not be an expert. The literature review required to identify which deterioration phenomena to use for the survey may often provide sufficient understanding for correlating signs of change to potential causes of that change. Yet even simply categorising potential reaction types into 'physical forces' and 'other' is extremely useful and can result in targeted action to address sources of the former.

4.5.5.2. Analysis 2: Exploratory

During the second round of analysis, supplemental information is included to contextualise the survey data by determining how the peculiarities of an object are related to its present state. Supplemental information may include additional object data (e.g., locality, habit, age), environmental data, results from analytical techniques (e.g., colorimetry), and details of the housing materials. Numerical data can be studied alongside the DP columns, and categorical data can be used to categorise or filter further subsets.

This round of analysis can be classified into two categories: 1.) mapping, and 2.) comparison and correlation (Table 4.6). The latter can manifest in a variety of ways due to the type of additional information used. Yet both can be considered as preliminary bivariate analysis; the relationship between object state and another variable—such as location—is being explored.

Table 4.6. Types of exploratory analysis conducted post-survey.

Category of Analysis	**Descriptive Statistic**	**Types Additional Information**	**Purpose**
Mapping	ADP	Drawer & cabinet numbers	- ADP are mapped onto the room's cabinets and drawers - Used to reveal hot spots that may indicate sources of deterioration (e.g., leaks, pests)
Comparison & Correlation	- ADP - %DP Patterning	- Locality - Habit - Housing material - Associated material - Collection or accession date - Analytical data - etc.	- Comparison of %DP patterns according to additional data - Examination of relationship between ADP/%DP & additional data - Used to determine difference in stability &/or reaction types

4.5.5.3. Analysis 3: Hypothesis Testing

The data produced by the DP Method is amenable to statistical methods used to examine intervariable relationships and to test hypotheses. Such examination is beneficial for better understanding how and why deterioration is occurring.

In order to test the hypothesis of whether situational variables (e.g. museum, habit, locality) affect specimen state, data from Study 2 was analysed in SPSS Statistics (IBM, ver. 28) with the following methods (scripts can be found in Appendix 2). Pearson's correlation coefficient was calculated to investigate the type and strength of the linear correlation between the variables examined (Table 4.7). Principal Component Analysis (PCA) was then performed to examine the overall association structure of the variables. In particular, the values produced in the pattern and structure matrices were used to determine which variables may be highly associated, the potential reaction type being characterised by said variables, and whether to explore the association further. When three or more variables strongly contributed to the formation of a given principal component, the reliability statistic Cronbach's Alpha (α) was calculated to numerically confirm the strength of the multi-variate association (i.e., whether the 3+ variables are significantly related). For all tests, a strong association or contribution was considered to be values ≥ |0.70|, and the significance

level was set to 95% ($\alpha = 0.05$). The results of this analysis are covered in Chapter 6 (Section 6.2.2).

Table 4.7. Example of variables from Study 2 that were examined in SPSS and how they were coded for analysis.

Museum	**Habit**	**Locality (Country)**	**DP**
1: NMC	1: aggregate	1.: Algeria	0: absent
2: NML	2: cubic	2: Aotearoa	1: present
3: OUMNH	3: massive	3: Australia	
4: Sedgwick	4: micro	4: Austria	
	etc.	etc.	

4.6. Discussion

Many have asserted that—given the lack of staff and other resources—the best way to extract meaningful condition data from large collections is by randomly sampling and surveying no more than 10% of its objects (Drott 1969, Glud & Johnsen 2002, Xavier-Rowe & Fry 2011). Yet often forgotten is the fact that sampling is "a compromise measure" (Drott 1969: 119) that provides at best an approximation, and that it is critical for a sample "to be as representative as possible of the entire population" (ibid. 120). Even though the number of objects surveyed are often in the hundreds when following this approach (Table 4.8), there remains the question of whether the results are truly representative of what is occurring in the collection, especially when the collection in question is highly heterogenous or mixed-media (e.g., social history and anthropology). Also often omitted from reports is the substantial planning and effort required to not only determine an adequate sample size but also to randomly select and then find the objects to survey (Drott 1969).

Table 4.8. Examples of surveys and the percentage of the collections covered.

Collection Type	Number of Objects	Percentage of Collection	Citation
Freeze-dried Leather	660	17%	Sully & Suenson-Taylor 1996
Still Photographs	656	< 10% *	Glud & Johnsen 2002
Homogeneous Objects/Materials	*	2%	Xavier-Rowe & Fry 2011
Mixed Materials	*	5%	
Iron Gall Ink Drawings	100	~ 0.09 – 0.13% †	Kosek & Barry 2019

* (Exact) values not provided by authors

† Calculated estimation based on values provided by Kosek & Barry 2019 and the British Museum 2023. The reported survey was a pilot study; assumedly subsequent work will survey a greater proportion.

The DP State Survey Method foregoes the need for such "tedious" (Drott 1969: 125) sampling procedures due its ability to quickly provide data for large proportions of a collection, regardless of size and variability. As Table 4.2 demonstrated, 40% or more of a collection can be surveyed in a reasonable timeframe utilising this approach. The DP Method thus ensures greater sample representation and provides a firm, rigorous statistical foundation for any subsequent decisions and actions.

The use of phenomenological criteria is what allows the surveyor to cover more ground. Newey and co-authors (1993) found that surveyors required about a minute to determine and record the condition score of an object (a single criterion). With the DP Method, one can capture the presence/absence of sixteen criteria in the same amount of time (Table 4.2). This shows that it is possible to collect more data by forgoing the time-intensive thought processes required to determine condition.

The data produced by the DP Method is more descriptive and quantitative than a condition score as well. As discussed in Section 4.3, condition scores are highly subjective and can imply multiple types of material changes. The DP Method results are far less ambiguous; the string of 1s and 0s convey exactly what is and is not present, allowing one to visualise an object's appearance. This greater clarity of object state facilitates:

- analysis of change over time,
- interpersonal review and communication of results, and
- locating the object at a later date.

This does not mean, however, that subjectivity is completely removed. All survey methods will contain some degree of subjectivity and variability, as survey data is primarily collected via human observation (see Section 4.1). While using the presence/absence binary with visual criteria does mitigate variation induced by categorisation, variability may still occur depending on whether surveyors can see the selected criteria on a given object. Many factors influence vision; having adequate lighting and an unobstructed view can aid observation, but cannot compensate for physiological variation (e.g., colour blindness, astigmatism; see Sections 4.1 and 4.2). Increasing the number of objects surveyed is a means of accounting for this variation; the larger the dataset, the less of an affect an individual observation has. Thus, surveying large portions of a collection has an additional benefit of reducing variability.

Further investigations and developments are still necessary to confirm that the DP Method is indeed more efficacious and advantageous than pre-existing collection surveying methods. In particular, work addressing reproducibility and inter-surveyor variability ought to be conducted (Table 4.9). Potential studies may include:

- a multivariate analysis of results conducted by multiple surveyors to examine the effects of knowledge, training, or even visual perception, and
- the determination of a minimal percentage required for surveying to adequately characterise collection state.

From such research, suitable means for the routine usage of the DP Method for collection monitoring could be established.

Table 4.9. Currently identified areas requiring further development and suggestions for addressing them.

Areas for Development	**Suggestions for Future Work**
Surveyor Variability and Subjectivity	Comparison of results produced by multiple surveyors with different levels of: - knowledge of the collection (i.e., conditions, history) - knowledge of object/material and its deterioration - training - vision (i.e., focusing powers, colour normal v. colour blind)
Confirming Adequate Characterisation of Collection State	Test of sampling procedures, comparing results for: - different percentages of a collection surveyed (e.g., 10% v. 25%) - variations in what is decided to be omitted from surveying
Reproducibility and Efficacy in Monitoring Changes over Time	Comparison of results produced: - by multiple surveyors - at various intervals in time (e.g., 6 months, 1 year, 5 years)

4.7. Conclusion

As discussed in this chapter, condition is a complex, multi-faceted concept fundamental to heritage and its preservation. The Eye of Condition framework was proposed to facilitate identifying influencing factors, such as object context and surveyor bias. A different approach to collection assessment was subsequently suggested based on the concept of decoupling the tangible and intangible aspects of condition, whereby changes to the tangible are recorded more quantifiably via a state survey.

The DP State Survey Method was developed to produce semi-quantitative, statistically robust data pertaining to object state via the use of phenomenological criteria. The presence or absence of these visual criteria, and the patterns that are produced, are used to characterise collection condition and determine any potential reactions occurring within it. By simplifying the process to a series of ‘yes or no’ questions, greater portions of collections can be surveyed in same amount of time as other methods. This benefits the data in three ways—improved collection representation, increased statistical rigor, and decreased variability—resulting in a better characterisation of collection state.

The DP Method can thus provide greater familiarity of a collection and an improved understanding of a collection's composition, inherent properties, and most common forms of material change. Such insights contextualise survey data, facilitate analysis, and ultimately lead to more informed decisions, such as whether any further investigation using analytical methods is required.

Chapter 5.
The Colorimetry Validation Experiment

"*Our inability to define color experiences from an object verbally or by some other subjective means with a high degree of accuracy and precision makes it desirable to use objective means of defining the color samples*." – Kuehni 2003: 6

An analytical method commonly used in heritage is colorimetry, due to being an easy to use, increasingly affordable, portable, and non-destructive means of quantifying change over time. Colorimetry has been applied to various material and object types (Table 5.1), and has been used alongside other common analytical methods (Royce 2019, Royce *et al.* 2023) to further characterise and monitor changes induced by light, pollutants, weathering, and or conservation treatments.

5.1. Introduction to Colour Science

Colorimetry is the science of colour measurement. Quantitative colorimetric methods numerically specify unique colours (Berns 2019), enabling one to plot all possible perceivable colours onto a three-dimensional geometric shape. These shapes are called *colour spaces* and are ordered according to human psychological colour order (usually that of the colour wheel) (Kuehni 2003). There are a variety of colour spaces with different scales (ordinal v. interval) and purposes (colorant mixing v. plot of total human perception). A type of colour space is uniform colour space, whereby "the distance between any two points can be taken as a measure of the magnitude of the difference between the two colour perceptions that are represented by the two given points" (Wyszecki 1981: 53). Such spaces are advantageous as they enable quantification of colour difference, but are difficult to achieve with a simple geometric model (e.g., Munsell, OSA-UCS). Thus, many uniform colour spaces are rather approximations of a compromised universal colour space (Kuehni 2003); they are close to—but not 1:1—representations of human colour perception under highly specified viewing and general experimental conditions.

Table 5.1. An inexhaustive list of materials to which colorimetry has been applied, focusing on geological materials and objects with irregular and or uneven surfaces. The purposes of application vary but largely involve the determination of total colour change between a before and after state.

	Material	**Purpose**	**Colorimetric Equipment & Parameters Employed†**	**Citation**
Archaeology	*skin of the Lindow Man (bog body)*	Quantification of light-induced colour changes	spectrophotometer - Perkin Elmer 551S - Konica Minolta 2600D **ΔE:** CIEDE2000	Bradley *et al.* 2008
	floor mosaics	Comparison of cleaning methods' efficacy in removing dust & other atmospheric pollutants	photometer - Konica Minolta LumiCam 1300 **ΔE:** CIEDE2000	Cabello-Briones & Mayorga Pinilla 2020
	papyrus	Evaluation of the suitability of laser cleaning to remove soils	spectrodensitometer - X-Rite 530	Elnaggar *et al.* 2015
	porcelain sherds	Exploration of the coloration mechanisms in Chinese white porcelain	spectrophotometer - Nippon Denshoku NF333 **SI:** D65	Wu *et al.* 2014
Textiles	*range of textiles from Southeast Asia and India*	Examination of the feasibility of monitoring colour change to dyed textiles on temporary exhibition	chroma meter - Konica Minolta CR-200 **SI:** C; **ΔE:** ΔE^*_{ab}	Ford 1992
	Islamic carpet	Microfading testing to determine 1.) dye light-fastness & 2.) lighting & display regimes	spectrophotometer - Hitachi U4000 **ΔE:** CIEDE2000	Pretzel 2008

† SI = standard illuminant, SO = standard observer

	Material	Purpose	Colorimetric Equipment & Parameters Employed	Citation
Building Stone	*marbles & limestones*	Evaluation of changes in colour & surface roughness caused by acid weathering	telespectroradiometer - Photo Research PR-650	Benavente *et al.* 2003
	ornamental granite	Evaluation of colour change after 1.) treatment with a consolidant &/or hydrofugant, & 2.) accelerated aging	colorimeter - Konica Minolta CR-310 **ΔE:** ΔE^*_{ab}	Iñigo *et al.* 2004
	ornamental terracotta & calcareous stone	Evaluation of colour change after 1.) application of hydrophobic solution & 2.) UV exposure	spectrophotometer - Lovibond RT 300 **ΔE:** ΔE^*_{ab}	Pelin *et al.* 2016
	limestone	Evaluation of colour change after consolidant application	**SI:** D65; **SO:** 10°; **ΔE:** ΔE^*_{ab}	Pinto & Rodrigues 2014
	ornamental granite	Establishing a methodology for characterising the colour of heterogeneous materials	spectrophotometer - X-Rite CE-XTH colorimeter - Konica Minolta CR-300 & CR-310 **SI:** D65; **SO:** 2° **ΔE:** ΔE^*_{ab} , CIE94, CIEDE2000	Prieto *et al.* 2010
	bricks	Comparison of colorimetric data to human preferences to select replacement bricks	spectrophotometer - Konica Minolta CM-2600d **SI:** D65; **SO:** 10°	Sammartino *et al.* 2020

	Material	Purpose	Colorimetric Equipment & Parameters Employed	Citation
Wall Paintings	*mineral pigments on lime plaster*	Evaluation of colour change after 1.) consolidant application & 2.) accelerated aging	spectrophotometer - Konica Minolta CM-700d **SI:** D65	Catenazzi 2017
	mineral pigments on gypsum plaster	Evaluation of colour change after 1.) consolidant application & 2.) outdoor weathering	spectrophotometer - Konica Minolta CM-2600d **SI:** D65; **SO:** 10°; **ΔE:** ΔE^*_{ab}	Collado-Montero *et al.* 2019
	limewashes coloured with mineral pigments	Evaluation of colour & surface appearance 1.) during limewash preparation & 2.) after lime carbonation	spectrophotometer - Data Color Mercury 3000 colorimeter - HunterLab MiniScanXE Plus **SI:** D65; **SO:** 10°	Gil *et al.* 2011
Other	*pastels on paper*	Microfading testing to establish pigment light-fastness	spectrophotometer - Ocean Optics Jaz miniature **SI:** D65; **SO:** 2°; **ΔE:** ΔE^*_{ab} , CIEDE2000	del Hoyo-Meléndez *et al.* 2018
	outdoor bronze statue	Evaluation of the suitability of laser cleaning to remove corrosion products	spectrophotometer - Konica Minolta CM-700d **SI:** D65	Sansonetti *et al.* 2015
	backplates of historic string instruments	Evaluation of applying colorimetry (& other non-destructive methods) to monitor changes to instruments that are played regularly	spectrophotometer - Konica Minolta CM-2600d	Valentina Fichera *et al.* 2018
	herbaria (pressed plants)	Evaluation of modifying colorimetric equipment to facilitate environmental field monitoring	spectrophotometer - Konica Minolta CM-700d **SI:** D65; **SO:** 2° ; **ΔE:** ΔE^*_{ab}	Sanmartin *et al.* 2020

5.1.1. CIELAB and ΔE

CIELAB is one such attempt at a uniform colour space, and has become the standard space for colorimetry in various industries, including heritage. This colour space was created by the International Commission on Illumination (CIE, after the French name: Commission Internationale de l'Éclairage) in 1976, and utilises rectangular coordinates L*, a*, and b*.

L* is the lightness axis, and is scaled from 0 to 100: 0 being absolute black and 100 being absolute white. The a* and b* axes are chromatic axes; both are centred at zero to enable positive and negative values. Manufacturers such as Konica Minolta (2007) often explain that a* is the red-green axis, and b* is the yellow-blue axis. This statement is likely used to simplify the already complex process of colorimetry, however, this correlation of *primary* colours to chromatic axes is not entirely accurate. These unique hues do not actually fall on the chromatic axes (Fig. 5.1). Therefore colour scientists largely consider the axes to "not [be truly] psychologically meaningful" (Kuehni 2003: 191) and deem it is best practice to not associate the axes with the unique hues (Berns 2019: 75).

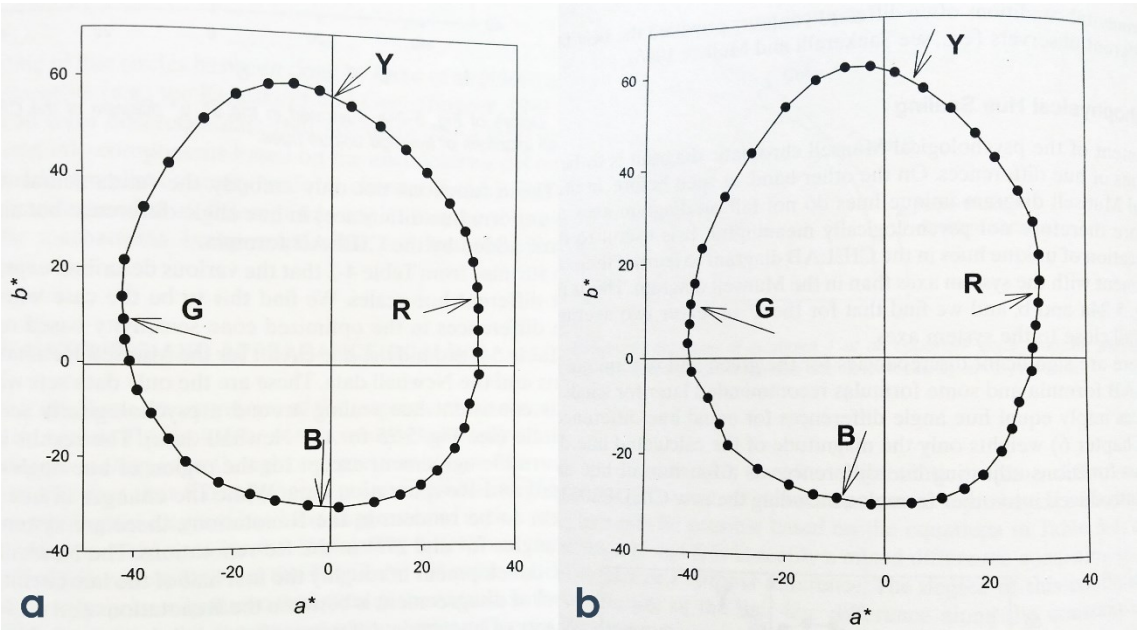


Figure 5.1. Plots depicting where the average unique hues—red (r), green (g), yellow (y), and blue (b)—are positioned relative to the CIELAB a and b* axes for both a.) the 2° and b.) 10° CIE standard observer. (After Kuehni 2003 Fig. 5-24a & b, pp. 191-192)*

As aforementioned, the advantage to uniform colour spaces is the ability to calculate the distance between any two points within them. This distance, referred to as *ΔE*, is a Euclidean distance (i.e., that which is the shortest and most direct) and represents the total difference in colour between the two points (Berns 2019). As ΔE represents a line, its length can be expressed as a single value. The lower the ΔE value, the closer the two points are to each other.

Colour difference formulae are used to calculate ΔE, and each colour space has different formulae to do so. The initial formula for CIELAB, ΔE^*_{ab} (Eq. 5.1), was published by the CIE in 1976 and is still commonly used, especially in heritage, likely due to its relative ease of calculation. However, it has been found that this equation has poor correlation with perceived colour differences between 0.5 and 5 ΔE^*_{ab} (Berns 2019). This is a problem because the threshold between an unobservable difference and a just-noticeable difference (JND) often occurs within these values. ΔE^*_{ab} also performs very poorly in the blue region of the CIELAB colour space (Kuehni 2003). A series of updates and corrections have been made to the CIELAB formula to produce more meaningful comparisons that better reflect human colour perception.

$$\Delta E^*_{ab} = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (5.1)$$

The most recent update was published by the CIE in 2001. Named the CIEDE2000 (notation: ΔE^*_{00}), this series of formulae attempts to correct the errors inherent to the CIELAB system and improve the correlation between calculated and visual colour differences (Kuehni 2003). These corrections include weighting functions, an interactive term between chroma and hue that improves the performance for blue colours, and a scaling factor of the a* axis to improve the performance of neutral greys (Luo *et al.* 2001, Wang *et al.* 2012). Research has demonstrated that the CIEDE2000 produces far more accurate colour difference predictions across all regions of CIELAB colour space, especially within the blue region (Luo *et al.* 2001, Wang *et al*. 2012, Berns 2019), and significantly outperforms ΔE^*_{ab} in determining threshold and small colour differences (i.e., those from 0.2–7 ΔE^*_{ab}) (Wang *et al.* 2012). Beyond these values, there is no significant difference between the 1976 and 2000 equations. However, Wang and co-authors (2012: 325) suggest using the CIEDE2000 "for predicting colour

differences involving different magnitudes, [as it] gave quite reasonable performance […] and should have no problem in applications involving a large range of colour differences."

There are various reasons one would want to examine and quantify (total) colour differences. For much of colour technology, colour differences are used to make decisions regarding quality, consistency, and acceptability (Berns 2019). They may be used to compare a reproduction to an original or to ensure that a manufactured product has acceptably consistent colouring across all individuals. In these cases, colour difference is used to examine colour variation within a given population. There is one set of data, from which outliers are identified and deviations are quantified. When used during experimentation, however, colour difference is most commonly employed to examine a change in colour due to some variable, be it time, an agent of change, or a treatment. There would thus be two sets of data, a before and an after, and comparisons are made between them.

5.1.2. CIE Standard Illuminants and Observers

The conditions which define a colour space, and subsequently colour measurements, are numerous (Kuehni 2003). However the illumination and field of view one uses to observe an object are perhaps of the foremost importance, as both have been standardised by the CIE (as *standard illuminants* and *standard observers*, respectively).

Standard illuminants are tabulated data that are based on physical measurements of a given illuminant (i.e., light source), and are defined as relative spectral power distributions (Berns 2019). Most light sources have equivalent CIE illuminants, but not all CIE illuminants have equivalent sources. This is the case for the CIE daylight series. The most commonly used—and recommended (Carter *et al.* 2004)—illuminant of this series is *D65*. This illuminant is equivalent to average daylight—both direct sunlight and light diffused by a clear sky—in the northern hemisphere, and has a correlated colour temperature (CCT) of approximately 6500°K. Data used to define D65 was collected by Judd and co-authors (1964) in Rochester, NY,

USA; Ottawa, Canada; and Enfield, England (41°–51°N latitude), hence it being explicitly defined as representing daylight in the northern hemisphere.

The CIE have defined two standard observers, the *2°* and the *10°*. Both observers are composed of three colour-matching functions: $\bar{x}, \bar{y}$, and $\bar{z}$ (Fig. 5.2). The 2° and 10° notation indicates the respective field of view (which corresponds to the size of the retinal image) and is expressed as a solid angle (Kuehni 2003). The 2° (1931) standard observer is recommended for use during small-field colour matching (i.e., the colour being examined subtends between 1° and ~4° at the eye of the observer), whilst the 10° (1964) is recommended for large-field (> ~4° field of view) colour matching (Carter *et al.* 2004).

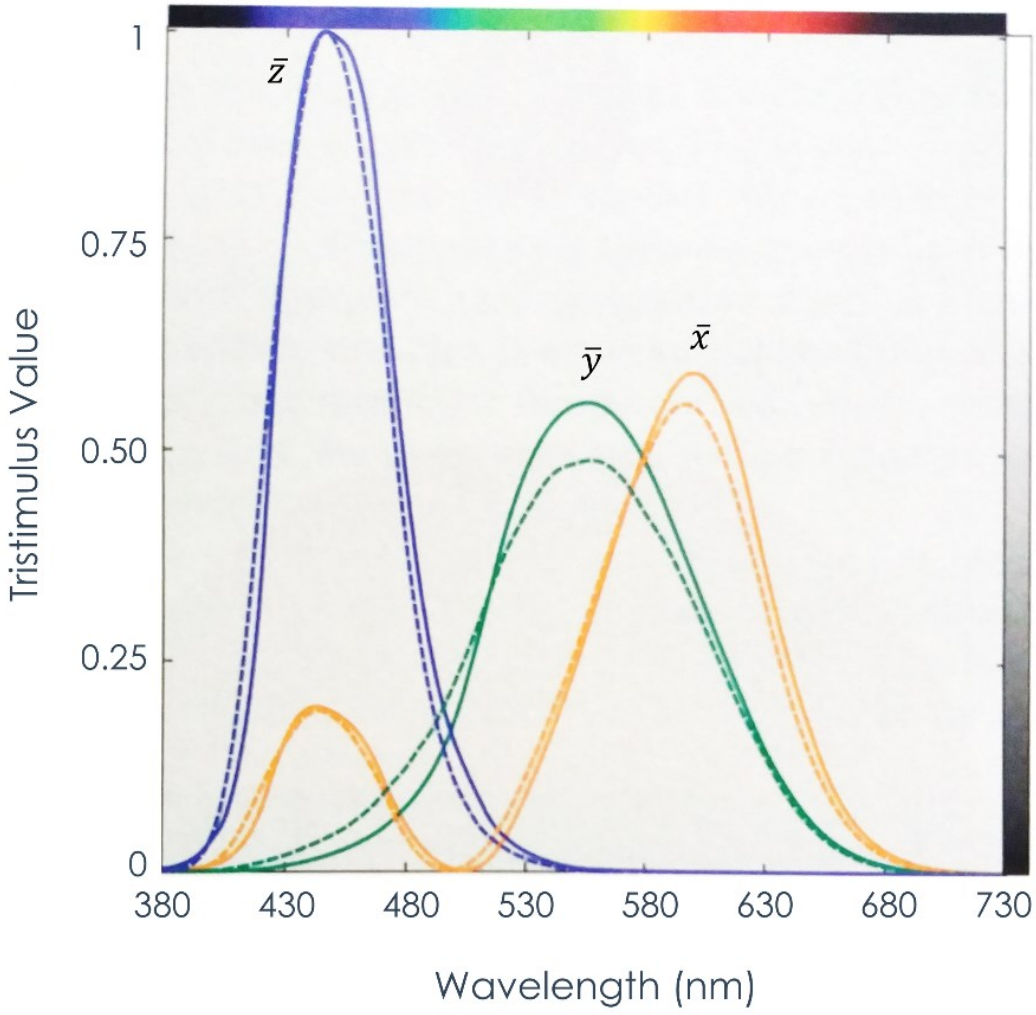


Figure 5.2. Plot comparing the colour-matching functions for the 2° (solid lines) and 10° (dashed lines) CIE standard observers. (After Berns 2019 Fig. 4-21, p. 62)

5.1.3. Colorimetric Devices

One can collect colorimetric data in a number of ways (see Table 5.1, 'Colorimetric Equipment'). The method used will depend on the data one wishes to collect. Two of the most common types of instruments available to collect colour data for a specific area of a physical object are *spectrophotometers* and *colorimeters*. A spectrophotometer measures the light reflected from or transmitted through the object of interest as a function of wavelength (Berns 2019). It collects the relative intensities of the reflected/transmitted light at consistent intervals across the visible light spectrum (usually at 10nm intervals between 400–700 mm). These result in reflectance/transmittance spectra (Fig. 5.3) which are then used to calculate CIE *tristimulus values* (X, Y, Z) based on the selected CIE standard observer and illuminant. From the tristimulus values, one can then calculate the colour's coordinates for any given colour space, such as CIELAB or *RGB*.

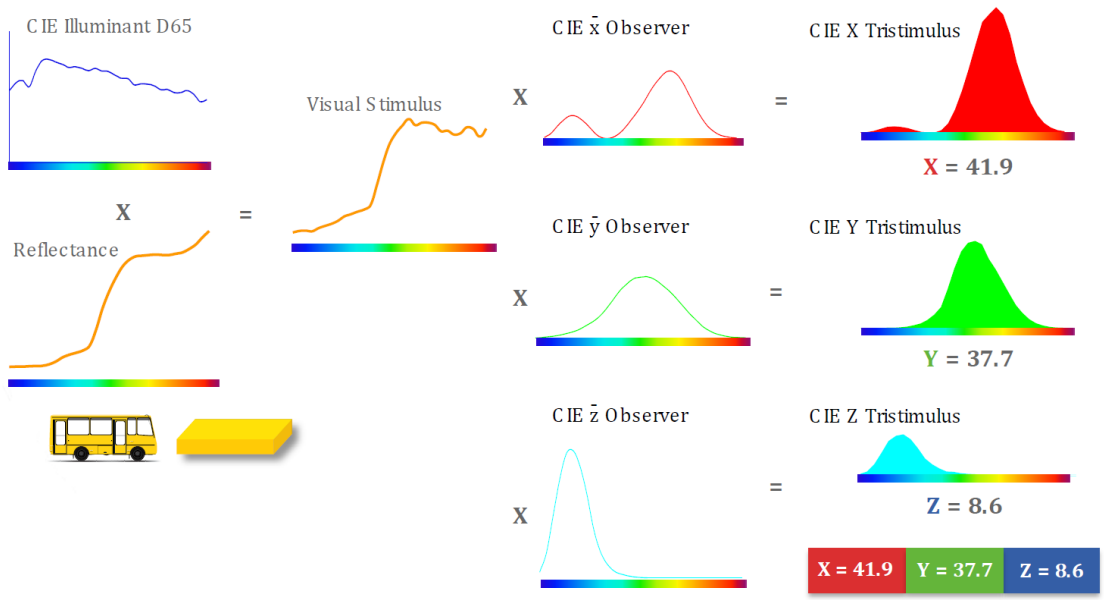


Figure 5.3. How tristimulus values are calculated from reflectance spectra, after HunterLab 2015.

Modern colorimeters will perform the same series of steps as a spectrophotometer but the initial means of collecting data differs. Rather than collecting data across the whole visible light spectrum, colorimeters simulate the human optical system by performing 'tristimulus' colour measurements (Konica Minolta 2023). The light that has been reflected from (or transmitted through) an object passes through three primary filters akin to the CIE standard observer primaries,

and it is only the relative intensities of the wavelengths encompassed by these filters that are used to calculate the tristimulus values.

This difference in data collection affects the complexity of the device's sensors and computational parts (and in turn its price and size), as well as the applications for which each is used. Spectrophotometers are primarily used by industries where detailed analysis for quality control and colour formulation is necessary (Konica Minolta 2023). Where such rigour is not needed, a colorimeter will often suffice.

5.2. Application of Colorimetry to Minerals

Colorimetry has been applied to a vast array of heritage objects and materials (Table 5.1), including herbaria specimens (Sanmartin *et al.* 2020), but remains underutilized for other natural (history) materials. Presently, colorimetric analysis of minerals appears in a limited number of applications despite minerals being a common raw material for industrial, technological, and artistic products since pre-history (see Ch. 2). Most papers focus on the industrial use of minerals, largely examining small quantities processed into pressed powder disks (Soriano *et al.* 1998, 2002; Bouzidi *et al.* 2014) or applied as thin films on wafer disks (Chappé *et al.* 2008). In heritage contexts, colorimetry of minerals has been exclusively applied thus far to swatches of mineral pigments to examine their lightfastness or changes in visual properties due to treatment and weathering (Table 5.1, 'Wall Paintings'). For non-ground samples, investigators at the Gemological Institute of America (GIA) (Liu *et al.* 1994, 1995, 2013) reported using benchtop spectrophotometers to quantify the colour of *gemstones*—such as ruby (Al_2O_3), alexandrite ($BeAl_2O_4$), and tanzanite ($Ca_2Al_3(Si_2O_7)(SiO_4)O(OH)$)—in order to investigate how mineral colours are produced.

There has yet been no documented colorimetric application to minerals beyond ground samples and selected *faceted* gemstones, both of which are highly processed to produce a uniform appearance. However, colorimetry has potential to be applied to minerals in other contexts, be it in their raw form as museum specimens, or even *in situ* in the field. Focusing on the former, colorimetry could facilitate the identification

of deterioration in mineral specimens and objects, as many forms of deterioration are correlated with a visual change. As mentioned previously in Chapter 2 (Section 2.8), changes such as the fading of amethyst and the blackening of cinnabar noticeably affect specimen appearance, which may be detected and monitored most simply with colorimetry. This information, in turn, may aid conservation decision making, including how the material will be treated and stored. With this in mind, the following experiment was designed to test the feasibility of colorimetry for the analysis of raw mineral specimens and to confirm whether results are adequately representative of specimen colour.

5.3. Experimental Methodology

5.3.1. Equipment

Two colorimetric instruments were used for this experiment: the Konica Minolta CM-700d spectrophotometer and the Nix Pro 2 colorimeter (reported specifications outlined in Table 5.2). The former is amongst the most commonly used in heritage research. Other commonly reported spectrophotometers are other portable devices made by Konica Minolta and those manufactured by X-Rite. The prevalence of portable equipment is likely due to both their lower cost and increased utility relative to their benchtop counterparts (i.e., the kit can be brought to static or difficult to remove objects, thus sampling is not required). To the author's knowledge, the Nix Pro colorimeter has not yet been used for heritage applications. This device was found via the company's online colour code converter (Nix Sensor Ltd. 2023a), and was deemed by the author to have great potential application for the heritage sector given its low cost, no maintenance, and ease of use.

Table 5.2. Reported specifications for the two colorimetric instruments used during the experiment.

Model	**Konica Minolta CM-700d**	**Nix Pro 2**
Measurement Type	Reflectance	Reflectance
Dimensions	73 x 211.5 x 107 mm	60 x 60 x 42 mm
Weight	~550 g	43 g
Spectral Range & Interval	330-740 nm; 10 nm	–
Geometry	di:8°, de:8°	45°:0°
Specular Component	SCI & SCE	SCE
Measurement Area	SAV: 3 mm; MAV: 8 mm	14 mm
Aperture Diameter	SAV: 6 mm; MAV: 11 mm	14.5 mm
Mask Diameter	23 mm	20 mm
Repeatability	Spectral reflectance: Standard deviation within 0.1% Chromaticity value: Standard deviation within ΔE^*_{ab} 0.04	<0.1 ΔE^*_{00} on white (D50, 2° observer)
Inter-Instrument Agreement	Within ΔE^*_{ab} 0.2 (MAV/SCI)	<0.4 ΔE^*_{00}
Initial Purchasing Cost	£7,995†	£280
Need for Manufacturer Calibration & Maintenance	Yes, annually	No
Cost of Calibration & Maintenance	£775†	–
Data Collection Software	SpectraMagic NX	Nix Toolkit‡
Software Compatibility	Microsoft Windows: 10 (2015) & 11 (2021)	Android: 5.0 (2014) & later Apple iOS: 15.0 (2021) & later

† Prices as of July 2022, costs have increased for 2023.

‡ Nix Toolkit is a unified software, in that the same software is compatible with all of their devices. Previously, each device had its own associated software. The program *Nix Pro* was used to collect data during the experiment; it was removed from the Google Play app store upon release of *Nix Toolkit* in 2023.

For the experiment, both instruments were used in reflectance mode (i.e., colour measurements were derived from light that was reflected from the sample). Data was collected with the meters' associated software (SpectraMagic NX and Nix Pro, respectively) using CIE standard illuminant D65 and the CIE 10° standard observer. Both the small aperture view (SAV) and medium aperture view (MAV) masks (as described in Table 5.2) were used for the Konica Minolta CM-700d. The Nix Pro 2's fixed aperture is between the standard medium (11 mm) and large (~20 mm) apertures, thus was abbreviated as MLAV for medium-large aperture view.

5.3.2. Samples

Two *CMYK* greyscale cards (greywhitebalancecolourcard.co.uk 2023), fifteen mineral samples (representing eight mineral species), and two rock samples (Fig. 5.4) were chosen for this experiment. The colour cards acted like controls, as they are flat, uniformly coloured samples. Any observed differences between the colour cards and the minerals would thus be attributable to the minerals rather than the device, etc.

For both colour cards, eight 15 mm^2 squares were selected: three *achromatics* (white, 50% grey, and black) and five primaries (red, yellow, green, cyan, and indigo). These primary colours were chosen as they represent unique areas of colour space and reflect colours found in minerals. The mineral samples used (Table 5.3) varied in colour, *opacity*, lustre, and surface texture. Baryte ($BaSO_4$) and the mudstone were chosen to act as opaque analogues to calcite ($CaCO_3$) and aventurine (SiO_2), respectively. Two metallic minerals of different colours (pyrite (FeS_2): golden; hematite (Fe_2O_3): steely grey) were included to evaluate the application of colorimetry to metallic minerals.



Figure 5.4. Annotated image of the samples used during the experiment. The colour squares used in this experiment are indicated by the dashed white lines. Calcite 10 White and Mudstone Reverse not shown; both on reverse of respective sample. T: tumbled, R: rough.

Table 5.3. Sample name, species, and attributes for the mineral samples.

Sample Name	Mineral Species	Naming Attribute(s), including pre-existing number*	Colour	Opacity†
m.1.r	Aventurine	rough	green	T
m.1.t		tumbled	green	T
m.2.8	Calcite	8	white	T
m.2.10o		10, orange	orange	T
m.2.10w		10, white	white	T
m.3.19	Chalcanthite	19	blue	T
m.3.20		20	blue	T
m.4.a	Pyrite	aggregate	golden	O
m.4.c		cubic	golden	O
m.4.t		tarnished	brown	O
m.5.r	Rose Quartz	rough	pink	T
m.5.t		tumbled	pink	T
m.6.o	Mudstone	obverse	green	O
m.6.r		reverse	green	O
m.7	Baryte	–	white	O
m.8	Hematite	–	grey	O
m.9	Onyx	–	black	O

*Numbers are from previous experiments by the author (Royce 2019a, 2019b)

†T = translucent, O = opaque

5.3.3. Experimental procedure

The Konica Minolta spectrophotometer was calibrated with its factory-provided black and white standards each day prior to colour measurements. According to the manufacturer's guidance, the Nix Pro 2 does not require calibration (Nix Sensor Ltd. 2023b).

A total of 8,250 measurements were collected. A set of fifty measurements were collected per sample for each of the five setting combinations listed in Table 5.4, producing 1,650 measurements per setting combination. The devices were lifted and repositioned between each measurement. Samples were measured in the same order: first the colour cards (card 1 then 2) followed by the minerals in the order shown in Table 5.3.

Table 5.4. The setting combinations tested.

Device	**Setting Combination**	
	Aperture	**Specular Component**
Konica Minolta CM-700d	SAV	SCI
		SCE
	MAV	SCI
		SCE
Nix Pro 2	MLAV	SCE

To ensure that all measurements occurred under the same conditions, the meter's position and operator grip were maintained as similarly as possible throughout the experiment, and the same measuring surface—a sheet of Plastizote (a white polyethylene closed-cell foam)—was used for all samples (Fig. 5.5). Additionally, all mineral samples—save for pyrite tarnished, calcite 10, and the mudstone—were placed in a Plastizote support (Fig. 5.5b) to aid measurement on the mineral's 'plane' surface (i.e., the surface which could be considered the most even or flattest).



Figure 5.5. The instruments used, with a sample on the Plastizote sheet: a.) the Konica Minolta CM-700d spectrophotometer with one of the colour cards, and b.) the Nix Pro 2 colorimeter with the rough rose quartz sample nestled into one of the holes in the Plastizote support.

Light levels within the room where measurements were being conducted were also qualitatively recorded. Overhead lights were recorded as 'on' or 'off', and the amount of sunlight entering through the windows was determined using the categories seen in Table 5.5.

Table 5.5. List of the explanatory variables examined, their abbreviations, and how they were coded for analysis in SPSS.

Aperture Size (AV)	**Specular Component** (SC)	**Overhead Lighting** (OL)	**Sunlight** (Sun)
1: SAV	0: Excluded (SCE)	0: Off	0: [not recorded]
2: MAV	1: Included (SCI)	1: On	1: overcast / rain
3: MLAV			2: mostly cloudy, occasional sun
			3: mostly sunny
			4: sunny

5.3.4. Data analysis

Data was examined using CIELAB colour coordinates. As per the aforementioned suggestion made by Wang and co-authors (2012) (see Section 5.1.1), total colour differences were calculated with the CIEDE2000 in Microsoft Excel by using the add-in *Colour Tools* created by Edgardo García (2022). These colour differences were used as a measure of variability within each set of 50 measurements by quantifying the difference between each measurement and the set's mean CIELAB values. An average of the 50 ΔE^*_{00} was then calculated. This value—known as a 'mean colour difference from the mean set of means', or MCDM—is similar to a standard deviation and describes the variability within the data set as a single value.

Further statistical analysis was performed in SPSS to examine the association between the colour coordinates and the explanatory variables examined (Table 5.5). Analysis was performed per sample. Firstly, Pearson's correlation coefficients were calculated to examine the linear correlation between variables. Principal Component Analysis (PCA) was then performed to examine the multi-variate association. When three or more variables strongly contributed to the formation of a given principal component, Cronbach's Alpha (α) was calculated to numerically confirm the strength of the association. For all tests, a strong association or contribution was considered to be values ≥ |0.70|, and the significance level was set to 95% (α = 0.05). Scripts for these analyses can be found in Appendix 2.

As the two meters use different optical geometries (Table 5.2), their results are not directly comparable in terms of CIELAB values. Thus, a set of standard scores (a.k.a. z-scores) was also produced for each set of measurements using Equation 5.2. This allows for comparisons to be made across devices and regions of colour space.

$$z = \frac{x - \overline{x}}{s} \tag{5.2}$$

where,

z: standard score
x: value of a single measurement
$\overline{x}$: mean of the set's measurements
s: standard deviation of the set's measurements

The standardised data was used to determine whether the devices produced statistically similar results via paired t-tests and one-way analysis of variance (ANOVA). The former was performed with the SCI standardised data and the latter for the SCE data, due to the number of populations being examined (Table 5.6). Pearson's correlation coefficients were also calculated for the standardised data. Again, an α of 0.05 was set for all tests.

Table 5.6. The hypotheses and setting combinations tested for comparing the two colorimetric devices.

Specular Component	**Apertures**	**Test**	**Hypotheses**
SCI	SAV, MAV	paired t-test	H_0: $\mu_S = \mu_M$ H_1: $\mu_S \neq \mu_M$
SCE	SAV, MAV, MLAV	one way ANOVA	H_0: $\mu_S = \mu_M = \mu_{ML}$ H_1: $\mu_S \neq \mu_M \neq \mu_{ML}$

The hypothesis test results were visualised through confidence ellipsoids. These ellipsoids are used in colour science to visualise confidence regions for perceptibility and acceptability judgements. They provide a graphical means of identifying variability and statistical difference within and between datasets (Tzeng & Berns 2005), and thus facilitate defining colour tolerance limits and instrumental precision (Berns 2019). For this experiment, ellipsoids were produced to compare the three-dimensional nature of the examined populations (Table 5.6).

The samples' average pseudo-object colours were also assessed. A *pseudo-object colour* is produced by converting the tristimulus values into sRGB values (R. Berns 2022, personal communication, 25 May), and is a digital visualisation of the colour represented by a given set of colour coordinates. Despite being largely ignored in both the colour science and heritage literature, pseudo-object colours are incredibly useful (especially for the non-expert) in determining the acceptability of the measured numeric values in representing the object's perceived colour.

The average pseudo-object colour was derived from each set's average CIELAB values. These were converted into HEX values by using Nix's (2023a) online colour

converter. Pseudo-object colours and photographs[2] of the samples' measurement area were viewed as 36 mm squares against a 50% grey background (RGB: 127, 127, 127), with no gaps or lines between the colours and the images, in a PowerPoint file on the author's computer (average CCT of screen at full brightness: 6655 K). The author compared the pseudo-object colours to both the images and the physical samples, and the colour that was the closest match to the image or sample was identified.

Overall colorimetric performance for the five setting combinations was determined by evaluating the MCDM (ΔE^*_{00}) and pseudo-object colours. For each sample, one point was awarded to the setting combination that:

1. produced the lowest MCDM value,
2. the author visually determined to be the closest match to the sample, and
3. the author visually determined to be the closest match to the photograph.

The best performer would be the one with the greatest total points. A maximum total score could be 48 for the colour cards (8 colour squares x 2 cards x 3 assessment categories) and 51 for the mineral samples (17 samples x 3 assessment categories).

5.4. Results

The full list of statistical results can be found in Appendix 6, *Colorimetry Stats Summary*.

5.4.1. Descriptive Statistics

Colour card measurements across the three colour coordinates display low variation (Table 5.7); all setting combinations produced small standard deviation and MCDM values (< 0.25 units). These values were much greater for the mineral samples; however, the chromatic axes a* and b* had notably lower standard deviations than L*. These differences are likely attributable to the increased complexity of the minerals

[2] Photographs were taken with a Canon PowerShot SX40 HS (camera settings: f/4, ISO 100) outdoors around 11:30am in indirect sunlight (weather: partly cloudy, average CCT = 5625 K, lux = 4825).

relative to the colour cards. The greater variation in surface colour accounts for much of the variation in a* and b* values. Likewise, dimensionality and surface texture are accountable for the variation in L* values due to compromised contact between the device and the samples (see Section 5.4.4).

Table 5.7. Standard deviations and MCDMs produced from the standardised data for the five setting combinations tested.

Setting Combination	Colour Cards				Minerals			
	Standard Deviation			MCDM	Standard Deviation			MCDM
	L*	a*	b*	ΔE^*_{00}	L*	a*	b*	ΔE^*_{00}
SAV SCI	0.08	0.09	0.15	0.12	1.97	0.42	0.91	1.68
SAV SCE	0.17	0.17	0.26	0.20	2.65	0.51	1.03	2.03
MAV SCI	0.22	0.25	0.39	0.20	1.01	0.26	0.49	0.84
MAV SCE	0.21	0.25	0.37	0.20	1.33	0.27	0.50	1.01
MLAV SCE	0.18	0.17	0.28	0.22	2.09	1.61	1.48	2.52

5.4.2. SPSS Analysis

5.4.2.1. Pearson's Correlation Coefficient

Of the four explanatory variables examined (Table 5.5), those for the external light sources (overhead and sunlight) appear to have little to no strong correlation with the colour coordinates for both the colour card and mineral samples (Appendix 6).

For the colour cards, aperture size (AV) is the only variable that is strongly and significantly correlated with the three colour coordinates across all colour squares (Table 5.8). The predominance of negative *r* values for L* suggests that lightness is inversely correlated with AV. This would mean that measured values generally decrease with increasing aperture size, and vice versa. Whether *r* is negative for the chromatic axes (a* and b*), however, appears to be related to the colour being measured. Negative *r* values for a* are seen for the greener (or less red) squares, and those for b* are seen for the bluer (or less yellow) ones.

Table 5.8. The correlation between aperture view and each of the three colour coordinates for the different colour squares. Highlighted values are those ≥ |0.70|.

Colour Square	L*	a*	b*
white	-0.47	-0.63	0.83
50% grey	-0.60	0.77	0.57
black	-0.73	0.79	-0.81
red	0.62	0.78	0.75
yellow	0.71	-0.82	0.57
green	-0.70	-0.75	0.10
cyan	-0.81	0.81	-0.76
indigo	-0.75	0.79	-0.77

Fewer strong correlations occur between the variables examined and the colour coordinates of the mineral samples. However, the most frequent is that between L* and specular component (SC). The five mineral samples that display this correlation (Table 5.9) are those with a high lustre, suggesting that the data one collects from lustrous specimens will vary depending on whether one includes or excludes specular reflectance.

Table 5.9. The correlation between specular component and each of the three colour coordinates for the different mineral samples. Highlighted values are those ≥ |0.70|.

Mineral Species	Sample Number	L*	a*	b*
Aventurine	m.1.t	0.72	0.21	0.10
Chalcanthite	m.3.19	0.79	-0.65	0.56
Pyrite	m.4.c	0.98	0.10	0.94
Hematite	m.8	0.86	0.04	0.37
Onyx	m.9	0.98	-0.26	0.59

Correlations between the variables and the colour coordinates were also calculated for the standardised data. However, no strong correlations emerged for either the colour card or mineral samples. This suggests that the variations exhibited in the non-standardised data is attributable to the samples rather than the devices.

5.4.2.2. PCA

For the colour cards, PCA was performed for each colour square. Dimensionality was reduced from seven (the four explanatory variables plus the three colour coordinates) to two. Greater than 70% of variance was captured in these two components for all colour squares save for white (Fig. 5.6). The colour coordinates and the two device variables (AV and SC) were predominantly described by the first principal component, whilst external light variables (overhead and sunlight) were described in the second component (Appendix 6).

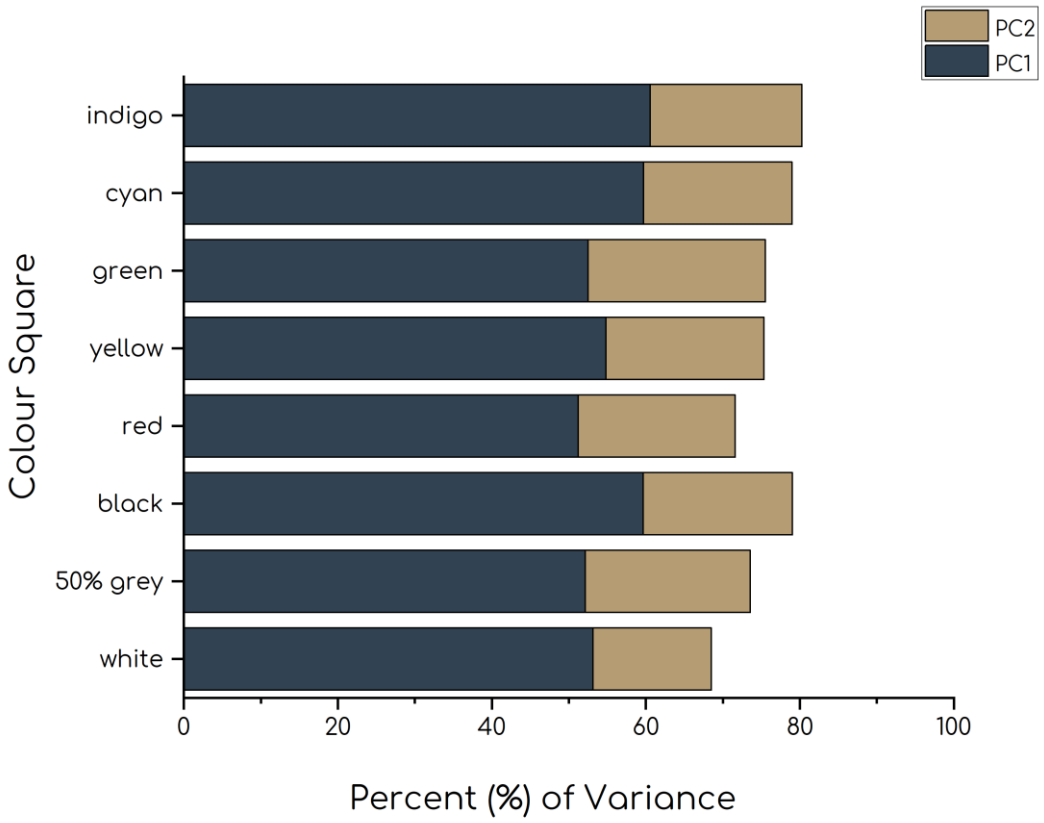


Figure 5.6. Percent of variance captured within two principal components for the eight colour squares.

Specular component was most often associated with L*, suggesting that including or excluding specular reflectance affects the value of that coordinate. Aperture size, on the other hand, was predominately associated with the chromatic coordinates (Table 5.10). Three of the four times that a* and AV were associated together, they contributed to defining the negative end of the first principal component and were counterposed by L* and b* at the positive end (Fig. 5.7). This occurred for black, cyan, and indigo, suggesting that aperture size plays a role in determining the secondary colour component (i.e., whether the colour is a greenish- or reddish-blue) for at least this area of colour space.

Table 5.10. Frequency of association between the colour coordinates and the device variables.

Colour Coordinate	*L**	*a**	*b**
Specular Component	5	2	3
Aperture Size	2	4	3

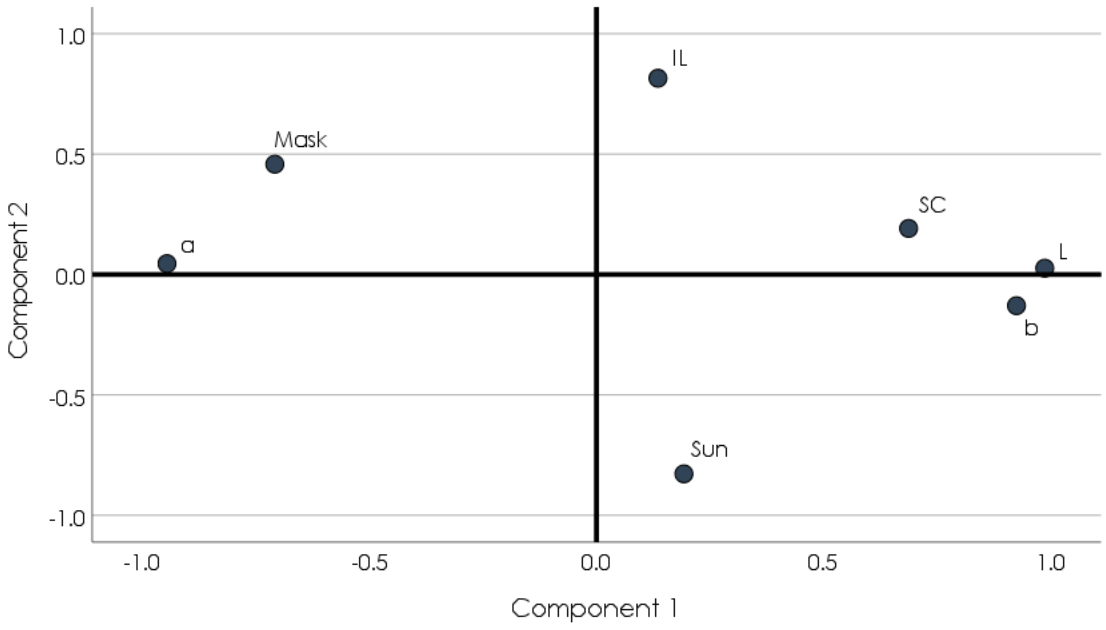


Figure 5.7. Component plot in rotated space for the black colour card data.

Dimensionality was reduced from seven to three for most of the mineral samples. Six samples, however, were able to be reduced to two dimensions (Fig. 5.8), but it is uncertain as to why exactly this is the case. Over half of the variance was captured in the first two components for all samples, and the average total percent of variance captured was 73%. However, there was no clear connection between the variables and the components to which they contributed, nor was there a distinguishable trend of commonly associated variables. This indicates that each mineral sample uniquely governs the data produced, rather than the explanatory variables.

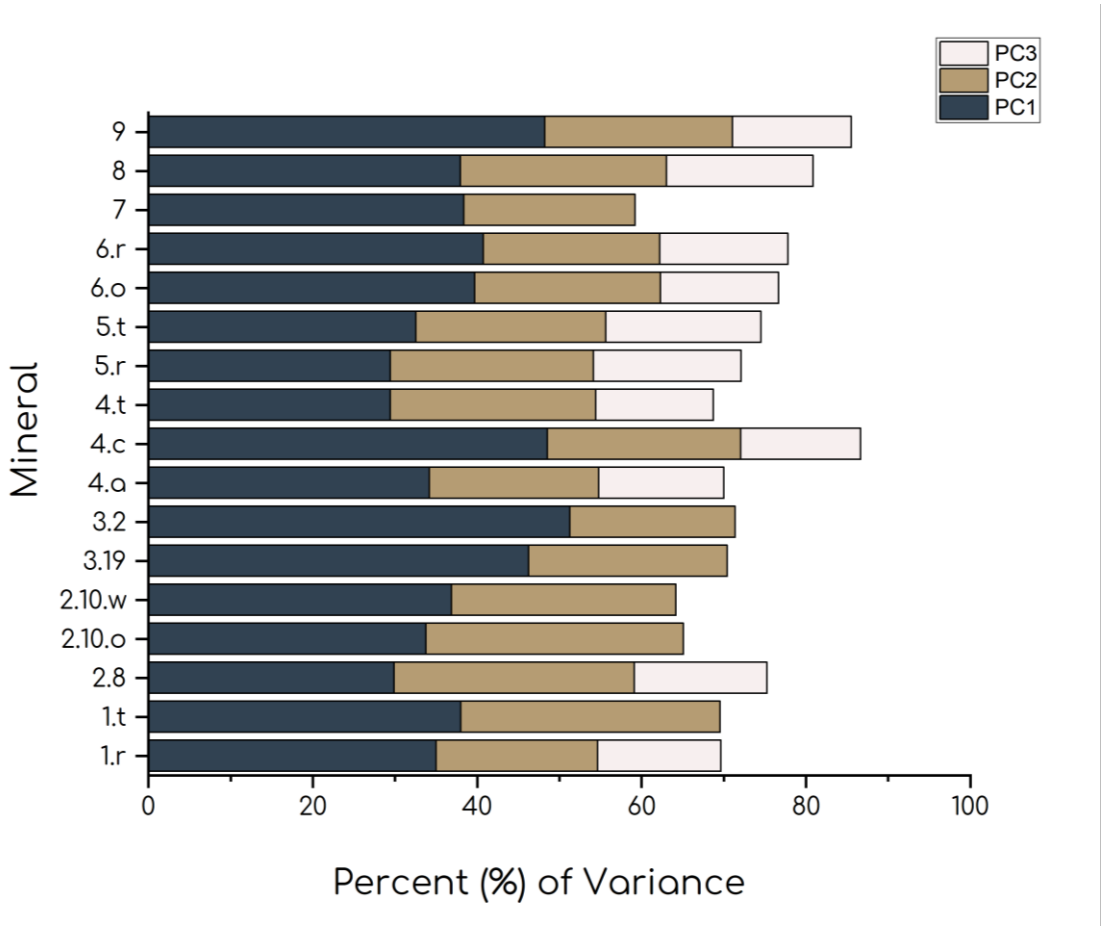


Figure 5.8. Percent of variance captured within three principal components for the 17 mineral samples.

5.4.2.3. Cronbach's Alpha

Based on the PCA results, Cronbach's Alpha (α) was calculated for seven of the colour squares and four of the mineral samples (Table 5.11). The association between three variables was examined for each sample: two of the colour coordinates and one of explanatory variables. None of the mineral samples produced significant α values, which suggests that the explanatory variables do not significantly affect colour measurements. Five of the colour squares produced α values ≥ 0.70, revealing that there is a significantly strong relationship between the variables examined in these areas of colour space. This indicates that there is a statistically significant difference in measurements between 1.) the aperture sizes for 50% grey, red, and yellow, and 2.) SCE and SCI for green and indigo. In other word, one's choice of device parameters can significantly affect the data collected within these regions of colour space.

Table 5.11. The samples and variables for which Cronbach's Alpha was calculated. Highlighted values are those ≥ |0.70|.

Sample	**Variables Tested**	**Cronbach's Alpha**
White	L, a, Sun	0.57
50% Grey	a, b, AV	0.83
Black	L, b, SC	0.56
Red	a, b, AV	0.81
Yellow	L, b, AV	0.71
Green	L, a, SC	0.70
Indigo	L, b, SC	0.84
4.a	L, b, OL	0.56
4.c	L, b, SC	0.40
8	L, b, SC	0.17
9	L, b, SC	0.36

5.4.3. Hypothesis Testing

As mentioned in Section 5.3.4, the hypothesis of whether the two devices produced statistically similar results was tested by comparing population means via paired t-tests and one-way ANOVA (Table 5.6). The result for all tests performed (Table 5.12) was to not reject the null hypothesis; i.e., at a 95% confidence level, the population means were determined to be statistically similar. This can be best visualised through the use of confidence ellipsoids.

Table 5.12. Statistics from hypothesis tests comparing the two colorimetric devices.

Colour Coordinate	**Test Statistic**	**Colour Card**		**Mineral**	
		t-Test (SCI)	**ANOVA** (SCE)	**t-Test** (SCI)	**ANOVA** (SCE)
L*	t // F	0.11	1.68 E-24	5.24 E-14	7.81 E-28
	p	0.92	1	1	1
a*	t // F	-0.04	5.32 E-25	1.22 E-15	0.001
	p	0.97	1	1	0.99
b*	t // F	0.05	2.08 E-25	-3.17 E-14	1.77 E-4
	p	0.96	1	1	0.99

For all four test groups (Fig. 5.9), there is a great similarity in the size and shape of the ellipsoids and a high degree of overlap between them. The Konica Minolta apertures show highly similar overlap, alignment, and volume (Table 5.13), confirming that this spectrophotometer produces highly consistent data, regardless of the aperture chosen. The Nix Pro ellipsoids display some minor differences. Most notably they are pointing in slightly different directions than the Konica Minolta ellipsoids. The Nix Pro ellipsoid for the mineral data is also approximately 14% larger than its comparators. Even so, there is still great overlap across all ellipsoids, confirming that there is generally good agreement between the Nix Pro and the Konica Minolta data. Additionally, the outer boundaries of all ellipsoids are plotted to two to three standard deviations from the mean (i.e., the plots' origins), suggesting that only ~5% or fewer of all data points will fall outside of this range, regardless of the aperture used.

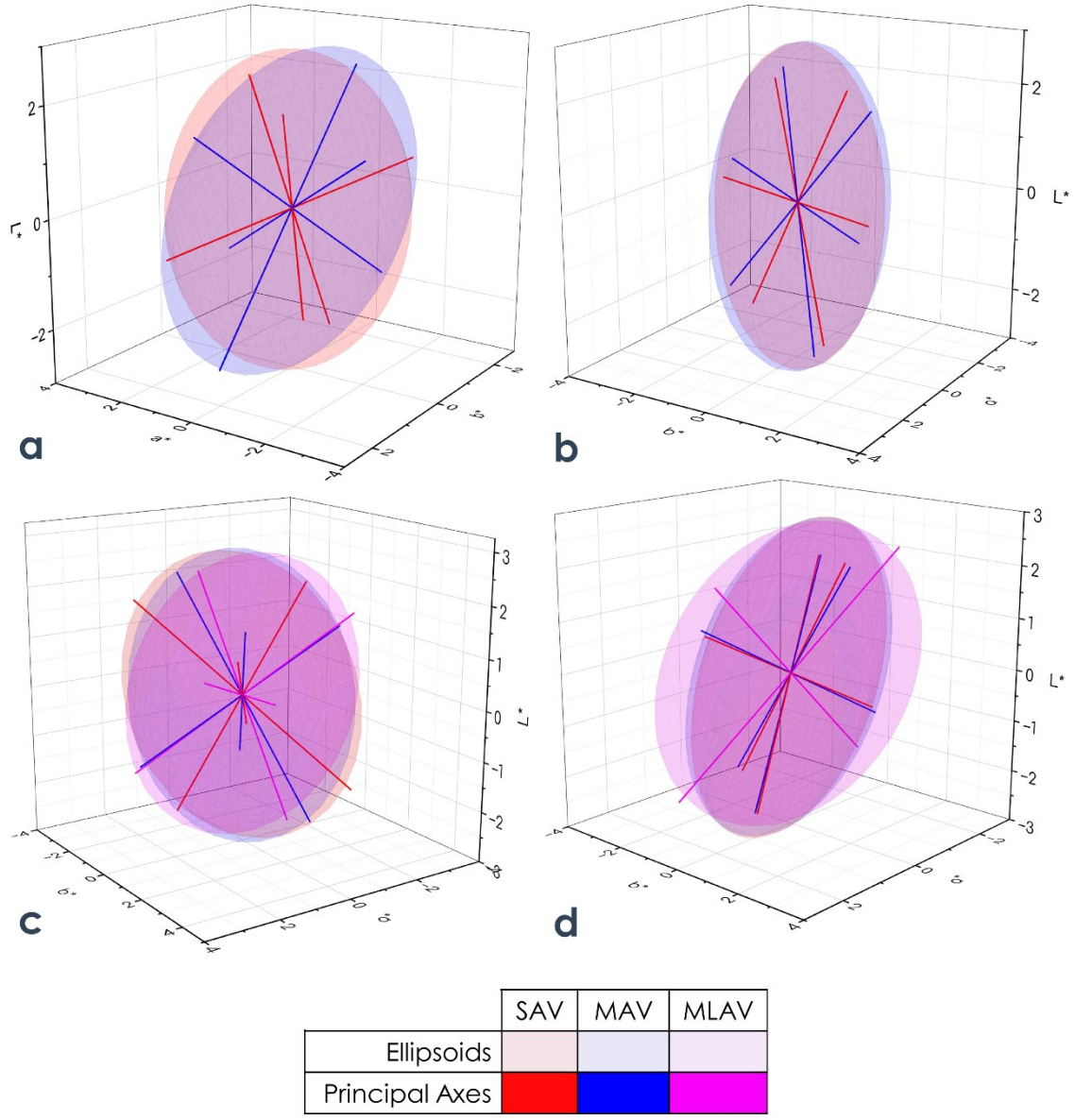


Figure 5.9. 95% Confidence ellipsoids for the four hypothesis test groups: a.) colour card SCI, b.) mineral SCI, c.) colour card SCE, and d.) mineral SCE

Table 5.13. Properties of the calculated ellipsoids.

Sample	Specular Component	Aperture	Length of Semi-Axis			Volume
			a	*b*	*c*	
Colour Cards	SCI	SAV	3.06	2.77	2.48	88.05
		MAV	3.07	2.91	2.31	86.44
	SCE	SAV	3.27	2.67	2.32	84.85
		MAV	3.11	2.84	2.33	86.20
		MLAV	3.13	2.67	2.51	87.87
Minerals	SCI	SAV	3.63	2.55	1.86	72.12
		MAV	3.62	2.56	1.89	73.37
	SCE	SAV	3.50	2.73	1.87	74.84
		MAV	3.42	2.75	1.98	78.00
		MLAV	3.09	2.74	2.48	86.89

5.4.4. Pseudo-object Colours

The average pseudo-object colours (Appendix 3) for the colour cards were deemed as a whole by the author to be a decent representation of the printed colours. For the colour cards, the Nix Pro pseudo-object colours were deemed to be the most representative. This is due to these pseudo-object colours appearing more vibrant than the Konica Minolta's. There was a noticeable difference in chroma—and potentially lightness—for all colour squares. The most notable of these differences is the yellowish tinge seen in white and 50% grey. A similar, but less noticeable, yellowing appears in the Konica Minolta MAV pseudo-object colours for colour card 2's white square, suggesting that it may indeed be yellower than colour card 1's.

The average pseudo-object colours (Appendix 3) for the mineral samples, on the other hand, vary considerably across the setting combinations. The Nix Pro and the Konica Minolta SAV pseudo-object colours largely appear darker than the mineral's colour and the other pseudo-object colours for that mineral.

The opaque minerals as a whole have more similar and representative pseudo-object colours than those of the translucent minerals. The greater variation in the translucent minerals' pseudo-object colours is likely attributable to the amount of light that escaped through the mineral. Due to the samples' translucency, the light emitted from the meters was not just reflected from the mineral's surface. Some light also diffused throughout the entire sample. This was confirmed by the observation of flashes of coloured light during measurements using both devices. This was most notable for the chalcanthite specimens where the escaped light was a distinct vivid blue. Aperture and mask size seemed to affect the amount of escaped light that was visible. This effect was most obvious with the Nix Pro colorimeter, followed by the Konica Minolta MAV then SAV measurements. However, the pseudo-object colours suggest that the larger apertures also allow for more of the diffused light to return into the meter than the smaller apertures.

Whilst all of the pseudo-object colours for the translucent samples were considered unrepresentative, those resulting from the Konica Minolta MAV data were deemed closer to the minerals' colours. The Konica Minolta MAV pseudo-object colours were also the most chromatic of the opaque mineral pseudo-object colours and were considered a near perfect match.

The SCE pseudo-object colours of the metallic minerals—pyrite cubic and hematite—were deemed poorly representative of the minerals' colours due to being far too dark. The SCI pseudo-object colours, on the other hand, were considered to be representative of the minerals' colour, given the translation of a metallic to a non-metallic colour.

The author determined that the Konica Minolta MAV SCI pseudo-object colours were most comparable with the minerals' colours as shown in photos and the specimens themselves. The only exception was for onyx, where the Konica Minolta MAV SCE pseudo-object colour appeared most representative of its corresponding sample.

5.5. Discussion

5.5.1. Device Comparison

The best colorimetric performer differed with the type of sample measured (Table 5.14). For the colour cards, the Nix Pro 2 had the highest total score (22), primarily due its pseudo-object colours being the best match to the physical cards. For the minerals, the Konica Minolta spectrophotometer using MAV and SCI proved best across all assessment categories.

Table 5.14. Scores of colorimetric performance for all setting combinations. The best overall performer for each sample type is highlighted.

Setting Combination	Colour Cards				Minerals			
	MCDM ΔE^*_{00}	Sample	Photo	Total	MCDM ΔE^*_{00}	Sample	Photo	Total
SAV SCI	8	–	–	8	1	1	3	5
SAV SCE	2	2	4	8	–	–	1	1
MAV SCI	3	–	3	6	11	9	5	25
MAV SCE	1	2	1	4	3	4	5	12
MLAV SCE	2	14	6	22	–	3	3	6

Whilst it did not produce the lowest MCDM values, the Nix Pro 2 proved to be statistically comparable to the Konica Minolta CM-700d. The Nix Pro standard deviations and MCDMs generally fell within the range of the other setting combinations examined (Appendix 6). This, in addition to the hypothesis test results (Section 5.4.3), indicates that the Nix Pro colorimeter produces consistent and repeatable values that are largely statistically comparable to the Konica Minolta spectrophotometer. Given its colorimetric performance (Table 5.14), the Nix Pro should be sufficient for most heritage applications, but requires further investigation to ensure applicability for general heritage use. Extrapolating this experiment's results, it is likely that the Nix Pro would do well measuring the colour of artworks and printed materials, finely woven textiles, building materials, and opaque plastics.

5.5.2. Selecting Devices and Settings

Experimental results have indicated that one's choice of colorimetric device and measurement settings is highly dependant on the sample's material properties. Figure 5.10 summarises the decision making process.

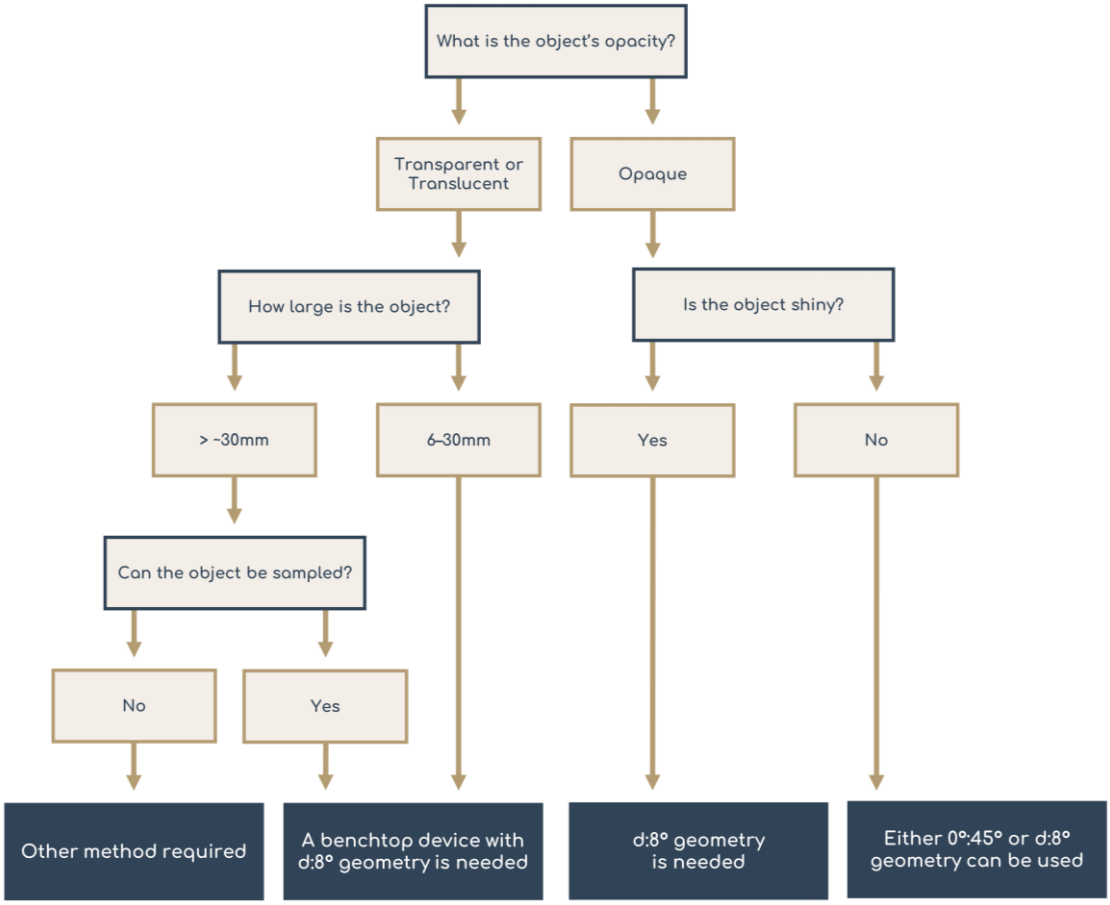


Figure 5.10. Summary of the decision making process when selecting a colorimetric device.

Portable equipment is currently limited to measuring opaque samples, as device design restricts one to reflection measurements. To quantify the colour of transparent or translucent samples, light needs to be transmitted through the samples, which can only be presently achieved with a benchtop instrument (like those used at the Gemological Institute of America). There is very little reason for a heritage institution to invest in this type of benchtop spectrophotometer unless there is a wealth of non-opaque objects and a demand to examine them colorimetrically.

This experiment has evidenced that opaque objects can be measured with a portable colorimetric device. As the pseudo-object colours revealed (Appendix 3), specular reflection plays a key role in perceiving the colour of high lustre objects. Thus meters with a d:8° optical geometry, like the Konica Minolta CM-700d, are needed when measuring metallic or lustrous materials. Many heritage objects and materials have lustres similar to minerals due either to the object's inherent optical properties or the application of protective varnishes, glazes, lacquers, enamels, and coatings. In these instances, SCI would be a requisite parameter.

If the aim of one's data collection is to capture the average colour of a sample, one should use the largest aperture available for the sample's size (Table 5.15). As this experiment demonstrated, larger apertures performed better—both statistically and in terms of acceptability—simply because they "spatially average the largest [surface] area" (Berns 2019: 107). Thus, to collect as representative data as possible, one ought to choose the aperture most suited for the object in question.

Table 5.15. Recommended aperture size based on sample size.

Sample Size (width/diameter; mm)	**Ideal Aperture Size to Use**
$6 \leq x < 8$	SAV
$8 \leq x < 20$	MAV
$x \geq 20$	LAV

5.6. Conclusion

A series of experiments were undertaken to critically evaluate the application of colorimetry to mineral specimens within heritage collections. The performance of the Konica Minolta CM-700d and the Nix Pro 2 was assessed statistically and by resultant pseudo-object colours for colour card and mineral samples. Both devices proved to produce consistent and statistically comparable results. The Nix Pro 2 colorimeter was determined to have the best overall colorimetric performance for

the colour cards, and the Konica Minolta spectrophotometer using MAV and SCI was best for the mineral samples.

Whilst there are some limitations in applying colorimetry to minerals, currently available portable spectrophotometers can be used to measure the colour of opaque and metallic specimens. Devices employing the d:8° optical geometry—like the Konica Minolta CM-700d—are necessary to allow for specular reflection to be included. This is especially critical for high lustre samples, as specular reflection significantly affects how one perceives the colour of lustrous objects. Further, mineral samples should have an approximately plane surface in order to enable sufficient contact between the aperture mask and the sample, and the sample must be large enough to cover the entire aperture.

Chapter 6.
The Cross-Museum Pyrite State Survey

"But if I let on that I research pyrite, my interlocutors look at me as though I am one of those wonderful beings who haunt the bowels of natural history museums as world experts on a rare species of toad. As with toads, most people in the world have heard of pyrite. They know it is a mineral or stone, and most know that it is also called fool's gold, a familiar theme of moral tales and nursery stories. So the idea of someone studying pyrite is not altogether the stuff of IgNobel prizes. Within the time limit imposed by decent conversation I cannot explain that pyrite is the mineral that made the modern world." – Rickard 2015: 1

Pyrite's ubiquity and noxious deterioration (Ch. 2, Section 2.8.2) has long made it the bane of collectors and museum professionals alike. Much to the chagrin of these caretakers, pyrite has also accrued millennia's worth of scientific and cultural value, allowing for it to appear in any collection, not just mineralogy.

Despite how it behaves at the surface, pyrite is "relatively resistant to the ravages of geological time" (Rickard 2015: 222). Some of the oldest pyrite is 3.8 billion years old, and have been used in conjunction with other ancient pyrite crystals to examine Earth's previous environments and develop the 'Iron-Sulfur World Hypothesis' (as mentioned in Ch. 2, Section 2.1.1). These specimens are incredibly important to preserve. The likelihood of finding more examples of similar age and typology are ever decreasing due to the nature of plate tectonics. As a plate is subducted and brought deeper into the Earth, the temperature and pressure rises, causing the rock and its composite minerals to alter into other compounds. This process essentially erases all information—including isotopic and other chemical signatures—pertaining to the rock's time at the (near) surface. Thus, the older the specimen, the more finite and unique, warranting sufficient preservation in order to corroborate previous research and facilitate future study.

There are also human-made pyritic objects that warrant preservation. The oldest are Palaeolithic fire starters; examples from central Europe date to c. 40,000–35,000 BCE (Stapert & Johansen 1999). Pyrite nodules were struck with flint to "produce hot and relatively long-lived sparks" (Stapert & Johansen 1999: 766) which would set alight tinder (often the fungus *Fomes fomentarius* in Europe).

The archaeological record evidences that pyrite fire starters were used in various locations throughout prehistory. Stapert & Johansen (1999) list key European occurrences, including the kit found on Ötzi the Iceman's person (dated to the central European Chalcolithic, c. 3230 BCE). Although the use of pyrite as a fire starter petered out during historical times, the same concept was later applied to wheellock pistols (Bonewitz 2005, Rickard 2015). Pyrite has also been used in personal adornment throughout recorded history and reached peak popularity during the Victorian period for its use in mourning jewellery (Rickard 2015). Thus, it is likely that pyrite can be found in decorative art, archaeological, and various other collection types.

In order to preserve pyrite, both as scientific specimens and as cultural objects, we must first understand how pyrite deteriorates in current collection environments. Despite over a century of study, the details of pyrite's deterioration are still poorly understood and those that are known are often over-simplified to the point of misunderstanding. Most reports remain effectively anecdotal; sample numbers are limited and do not truly represent pyrite's diverse nature. Further, no known substantial longitudinal studies have been conducted. Thus, the rationale to conduct this cross-museum study, employing the DP State Survey Method in conjunction with colorimetry, is to provide quantitative evidence of pyrite's long-term behaviour within the museum setting and infer the main causal factors that govern specimen deterioration.

6.1. Methodology

Much of the survey methodology employed for this cross-museum examination has already been covered at length in Chapter 4 (Section 4.5). Key aspects have been provided below for the reader's convenience. Based on the results of the previous chapter (Ch. 5), colorimetry was also implemented to further characterise pyrite tarnish and explore how tarnish relates to pyrite deterioration.

6.1.1. Specimens

Pyrite specimens from the mineralogical collections of four UK museums—Oxford University Museum of Natural History (OUMNH), National Museum Cardiff (NMC), National Museums Liverpool (NML), and the Sedgwick Museum of Earth Science (Sedgwick)—were surveyed. These collections were surveyed because they 1.) were within reasonable proximity via train to Oxford, and 2.) could easily be surveyed within 5 or fewer days. Access to OUMNH, NMC, and NML was also readily provided due to affiliation with the project.

Only specimens that were recorded to be primarily or exclusively composed of pyrite were surveyed. Specimens which contained pyrite as a secondary or associated mineral (be it with fossils, rocks, or other mineral specimens) were excluded. Additionally, only the specimens housed within the main sequence of drawers were surveyed; (extra)large and prepared specimens (e.g., slides, micro-mounts) were excluded. Those stored in sealed microenvironments were also excluded.

Selected specimens were chosen for colorimetry. These were specimens which:

1.) had at least one fairly plane face that could be used as the measurement location,
2.) fit under both the aperture and the mask of the spectrophotometer (see Section 6.1.3), and
3.) made sufficient contact with the mask.

These criteria were necessary to reduce light from escaping the spectrophotometer and producing unrepresentative results (as demonstrated in Ch. 5, Section 5.4.4). Thus, any specimens smaller than the small aperture view mask (SAV; 6mm diameter), lacked a plane face, or had any protrusions within the vicinity of an ideal measurement location were excluded. Secondary criteria also excluded specimens which:

1.) had an iron oxide alteration crust, as these crusts differ significantly both chemically and physically from a tarnishing pyrite surface, and

2.) those which were highly friable, as these specimens would not be able to withstand the gentle pressure required to ensure sufficient contact during measurement.

6.1.2. Survey

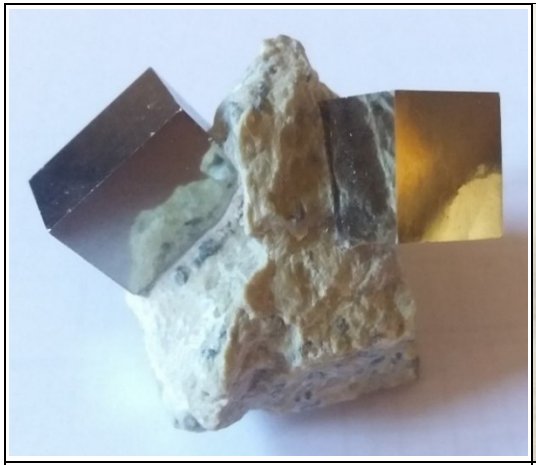
Specimens were surveyed for fifteen deterioration phenomena (DP), as listed in Chapter 4, Table 4.3. Information on the habit (i.e., macroscopic morphology) of the pyrite crystals was also captured during surveying.

There are numerous pyrite habits (the Hudson Institute of Mineralogy 2023e). Single crystals may be cubic, pyritohedral (pentagonal dodecahedral), or octahedral. Intergrown and twinned crystals are also possible. Other habits include massive, granular, radiating, reniform, discoidal or globular.

All observed habits were recorded during the survey, but only the primary habit and any secondary descriptors were used for analysis. The primary habit refers the main morphology displayed in the specimen. Generally, this would be discernible shape of the individual crystals (cubic, pyritohedral, or octahedral), even if the specimen was constituted of multiple crystals (an aggregate) or the crystals were just barely observable (micro[3]; $\lesssim$ 2mm). If no clear crystal faces were present, other habits were used as applicable (Table 6.1).

[3] The term 'micro' is being used—as a synonym of 'mini'—to refer to miniscule (but still visible) crystals rather than those on the micron scale (which are traditional referred to as microcrystals).

Table 6.1. Examples of pyrite habits observed during the survey.

			
Cubic	Pyritohedral	Octahedral	Nodule
			
Aggregate	Massive	Radial Disc	Micro

The entirety of the data was first examined before being defined by progressively narrower subsets, as shown in Figure 6.1, to determine what situational variables (e.g. museum, habit, locality) affect specimen state.

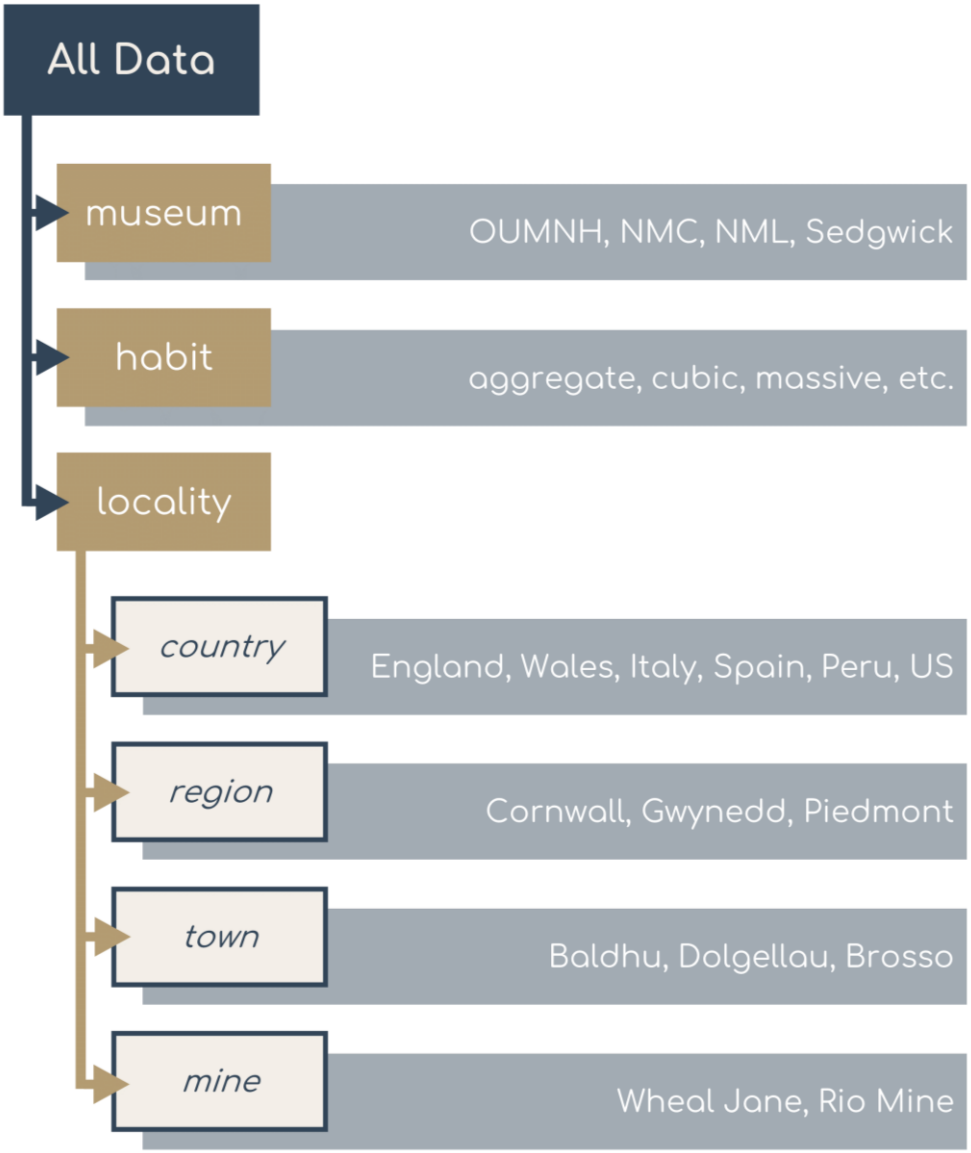


Figure 6.1. Flow of subsets explored during data analysis with examples.

Initial descriptive and exploratory analysis (as outlined in Ch. 4, Section 4.5.5) was performed in Excel for the main data set and all subsets. Total DP (TDP), Average DP (ADP), and Percent DP (%DP) were calculated, and the %DP were colour-coded to produce the %DP Patterning. First and second order reaction types were then determined from the %DP Patterning.

The main data set and all subsets (save the mine level) were examined in SPSS Statistics, primarily:

1.) to identify any highly associated variables amongst those examined (the DP, habit, and associated museum), and
2.) to confirm whether the results mirrored those produced by the %DP patterning.

The first goal was addressed by calculating Pearson's correlation coefficient for all investigated variables and Cronbach's Alpha (α) for select variables which were observed to strongly contribute to the formation of a given principal component. The second goal was addressed with Principal Component Analysis (PCA), where the values produced in the pattern and structure matrices were used to determine potential reactions. Component plots were not used for analysis as the reduced dimensionality was still greater than three. Thus, the visualisation would change depending on the PCs chosen as axes.

For all tests, a strong association or contribution was considered to be values ≥ |0.70|, and the significance level was set to 95% (α = 0.05). Oblimin rotation with Kaiser Normalization was selected for PCA. Scripts for these analyses can be found in Appendix2.

6.1.3. Colorimetry

Colour data was collected with a Konica Minolta CM-700d spectrophotometer using CIE standard illuminant D65 and the 10° standard observer. The specular component was included (SCI), in accord with the findings from the colorimetry experiment discussed in Chapter 5. The SAV mask was used as crystal faces averaged between 10 and 20 mm across. For consistency and comparability, the SAV mask was also used on larger crystal faces.

The spectrophotometer was calibrated with its factory-provided black and white standards each day prior to colour measurements. The associated software, SpectraMagic NX, was used to collect the data. Ten colour readings were collected per

specimen, lifting and repositioning the spectrophotometer between each reading. Colour measurements were visually examined in CIELAB colour space.

6.2. Results

Nearly 1,300 specimens were surveyed, of which 240 were used for colorimetry (Table 6.2) following the rationale explained in Section 6.1.1. Seven primary habits were found to be the most common (i.e., displayed in 25 or more specimens): aggregate, cubic, massive, micro, nodular, octahedral, and pyritohedral. The surveyed specimens were sourced from 38 countries across the globe, most of which were within Europe. Only six countries were represented by 25 or more specimens: England, Italy, Peru, Spain, the US, and Wales. Within these six countries, seven regions and five towns were represented by 20 or more specimens, and six mines by 10 or more specimens.

Four DP—dimpled, rounded, pale, and opacity—were either 1.) absent from all surveyed specimens or 2.) seen in only a few specimens but were directly attributable to associated species. These DP were thus omitted from analysis.

Table 6.2. Details of the pyrite surveyed from the four museum collections.

Museum	Approximate Age of Specimens	Environmental Conditions*	Number of Specimens		Percent of Collection	
			Surveyed	Used for Colorimetry	Surveyed	Used for Colorimetry
NMC	c.1850 – present	controlled T: 24°C; RH: 34%	482	60	72%	9%
NML	c.1950 – present	controlled T: 23°C; RH: 55%	135	33	52%	13%
OUMNH	c.1650 – present	uncontrolled T: 16–29°C RH: 33–65%	358	90	71%	18%
Sedgwick	c.1650 – c.1900	controlled T: 20°C; RH: 50%	298	57	82%	16%
		Total:	1,273	240	71%	13%

* Values were recorded during surveying and are assumed to representative of condition targets.

T = temperature; RH = relative humidity

6.2.1. Survey Results

Tarnish, dull, and dark were the most commonly seen DP in the surveyed specimens (Table 6.3), indicating a first order reaction type of surficial oxidation. The next most common DP was cracking, which was seen in over half of the specimens. The remaining DP were all seen in less than half of the specimens. Of note is efflorescence, which was observed in about a quarter of specimens. Efflorescence, in conjunction with cracking, crumbling, and powder indicates the secondary reaction type of oxidation at depth (i.e., oxidation which is not limited to the mineral surface and is occurring deeper within the specimen). Colour change was also seen in about a third of specimens, indicating the presence of a coloured, rather than dark, tarnish.

Table 6.3. %DP patterning for the four museums and the main pyrite data set (Total).

DP	NMC	NML	OUMNH	Sedgwick	Total
Corrosion	2%	7%	14%	23%	11%
Tarnish	91%	92%	70%	94%	86%
Efflorescence	25%	38%	3%	37%	23%
Powder	3%	11%	0%	19%	7%
Crumbling	22%	16%	16%	29%	21%
Flaking	3%	4%	2%	11%	5%
Breakages	4%	4%	7%	22%	9%
Cracks	63%	59%	51%	50%	56%
Dull	80%	89%	53%	99%	78%
Dark	57%	75%	16%	98%	57%
Colour Change	25%	44%	34%	40%	33%
ADP	4	4	3	5	4
# of specimens	482	135	359	298	1274
Key:	0–24%	25–49%	50–74%	75–100%	

As Table 6.3 demonstrates, pyrite as a whole appears to behave similarly, regardless of museum, age, or storage conditions. Variations in %DP are attributable to differences in collection size and composition; the NML specimens evidence the former, the Sedgwick pyrites the latter.

The higher %DP values at the Sedgwick (relative to those of NMC and OUMNH) suggest a greater number of deteriorating specimens, which is to be expected given their age (Table 6.2). The %DP for corrosion is also significantly higher for the Sedgwick pyrites; this is directly attributable to the Woodwardian collection. Most of the Woodwardian pyrite specimens are limonitised pyrite nodules (Fig. 6.2), and the presence of a limonite crust was indicated through the corrosion and colour change DP. The percentages for these two DP drop to 11% and 36%, respectively, if the 92 Woodwardian specimens are excluded. The other %DP values remain very similar (Appendix 7).



Figure 6.2. Drawer A.21 from the Woodwardian collection contains mostly pyrite nodules with a limonite crust. Image used with permission courtesy the Sedgwick Museum of Earth Sciences.

The Oxford collection, however, stands apart with generally lower %DP and ADP. This could be attributable to the curatorial work undertaken by former collections staff. The former curator, Monica Price, provided active stewardship of the

mineral collection for 40 years. Her dedicated attention to the collection and its needs—in addition to her mineralogical knowledge and expertise—may have resulted in more critical (de)accessioning policies and treatment programs relative to other museums. Since the 1990s, she and Joy Irving were actively identifying and treating specimens for pyrite decay (Irving & Hadland 2019), and many unsalvageable specimens were likely deaccessioned and discarded at this time. Had Price been less involved with the collection, the Oxford's %DP may have been significantly higher.

Positive curatorial practices are likely to be found at the other three museums, but were not brought to the author's attention within their brief visits to each institution. However, the author is aware that Tom Cotterell (mineralogy curator at NMC) has faced challenges with building infrastructure and administrative permission to achieve his desired management of the collection (T. Cotterell & J. Carter 2023, personal communication, 18 August).

Similar ADP and %DP patterning is seen across the most common pyrite habits (Appendix 7), and likewise reflects a first order reaction of surficial oxidation and a second order reaction of oxidation at depth. The three single crystal habits—cubic, pyritohedral, and octahedral—show similar %DP and indicate that individual crystals are generally more stable than the other pyrite habits. Aggregates and nodules are particularly most likely to undergo pyrite decay, whilst massive specimens are most prone to colour change (90%).

Differentiation within the %DP patterning begins to occur when examining the locality subsets (Appendix 7), especially at the regional level. Here, physical forces emerges as the secondary reaction type at three localities. For pyrite specifically, this reaction type is characterised by:

1.) significant cracking (> 50%),
2.) greater %DP values for crumbling than efflorescence, and
3.) greater %DP values for flaking and or breakages than powder.

At the town and mine level, physical forces becomes more common than oxidation at depth. Only four localities have %DP patterning that suggests the latter: Brosso and Rio de La Marina in Italy, and Llandovery and Dolgellau in Wales.

6.2.2. Principal Component Analysis of Survey Data

Thirteen variables were examined for the main pyrite survey dataset: the 11 observed DP, the associated museum, and the primary habit. Whilst many of the variables are significantly correlated, none appear to be strongly correlated; *r* values were between -0.14 and 0.56. Using PCA, dimensionality was reduced from 13 to five. These five principal components (PCs) describe a total of 57% of variance. In conjunction with the lack of strong correlations, this highlights the diverse nature of the specimens, and suggests that, at this level, pyrite's variability cannot be adequately characterised using these 13 variables.

Examination of the structure matrix (Table 6.4) revealed that the variables that strongly determined the composition of each PC correspond to those defining certain reactions, and each PC described a different reaction. These reactions are: pyrite decay, limonitisation, tarnish, physical forces, and flaking.

Flaking is associated with primary habit, suggesting that habit informs whether the specimen—or more specifically, the associated mineralogy—is prone to flaking. This is discussed further in Section 6.3.2. Museum is moderately associated with the variables indicating pyrite decay and limonitisation, and inversely related to those indicating physical forces. These associations likely describe the collection composition, in that a given museum is more likely to have specimens exhibiting these types of deterioration. Whilst it is possible that this association is indicating that museum conditions play some role in these reactions, it is unlikely given the values seen the structure matrix (Table 6.4) and exploratory analysis (Section 6.2.1). This alternative explanation would be more likely were the museum values closer to those of the other variables or to ±1.

Cronbach's Alpha was calculated for the three strongly associated variables seen in PC3: dull, dark, and tarnish. A value of 0.70 was produced, confirming that these three variables are indeed highly related.

Table 6.4. PCA structure matrix for the main pyrite data set.
Highlighted are variables that are strongly associated with each other.

DP	Component				
	1	**2**	**3**	**4**	**5**
Powder	0.75				
Efflorescence	0.63		-0.26	0.34	
Breakages	0.62			0.31	
Corrosion		0.83			
Colour Change		0.71			
Museum	0.46	0.48		-0.40	0.29
Dull			-0.84		
Dark	0.30		-0.76		
Tarnish			-0.75		
Cracks				0.81	
Crumbling	0.46			0.65	
Flaking					0.81
Primary Habit					0.59
Percent of Variance	19%	12%	12%	9%	8%
Reaction Described	Pyrite Decay	Limonitisation	Tarnish	Physical Forces	Flaking

6.2.2.1. Museums

Each collection was individually reviewed to 1.) confirm whether there was any difference between the museums, and 2.) to further characterise the reaction types hinted at in the %DP patterning. Additionally, the Sedgwick results were analysed including and excluding the Woodwardian specimens to examine how these primarily nodular specimens affected the data.

Twelve variables were examined: the 11 observed DP and the specimen habit. Again, none appeared to be strongly correlated (Appendix 7); all *r* values were less than |0.65|. Four or five principal components were extracted, which described on average 59% of the total variance (Fig. 6.3). No new information was obtained from the PCA results. The reactions described by the pattern matrices were similar to those

of the main pyrite data set (Table 6.4). Further, the results of the two Sedgwick datasets proved to be effectively the same. This corroborates the earlier findings;

1.) pyrite specimens are highly diverse and variable, and
2.) at the museum level, pyrite specimens look and behave similarly regardless of the where they are held.

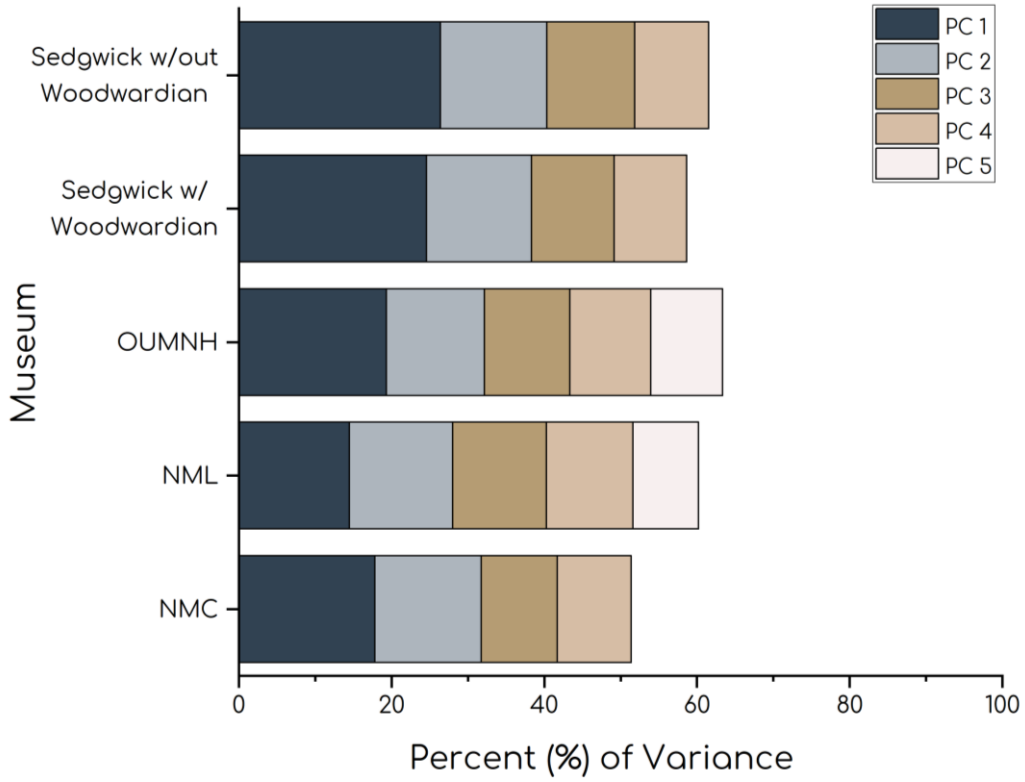


Figure 6.3. Percent of variance captured within five principal components for the museum collections.

Only three groups of 3+ variables were found to strongly contribute to the formation of the first PC:

1.) breakages, crumbling, and efflorescence (Sedgwick with Woodward)
2.) breakages, crumbling, efflorescence, and powder (Sedgwick without Woodward), and
3.) dull, dark, and tarnished (NMC).

These produced α values of 0.72, 0.79, and 0.70, respectively, confirming that these variables are highly associated within the given subsets. This suggests that:

1.) pyrite decay is a (if not *the*) prominent reaction occurring at the Sedgwick, and

2.) grey (dull and dark) tarnishes are commonly found on NMC specimens.

6.2.2.2. Habits

Twelve variables were examined for the seven habit subsets: the 11 observed DP and the associated museum. Only three pairs of variables were strongly correlated:

- aggregate: tarnish and dull = 0.90,
- massive: tarnish and dull = 0.71, and
- nodule: corrosion and colour change = 0.71.

These values suggest that it is highly likely for dull tarnishes to occur on aggregate and massive specimens, and nodules to often exhibit a limonite crust (as depicted in Fig. 6.2).

PCA reduced dimensionality to four or five principal components, which described on average approximately 60% of the variance (Fig. 6.4a). Tarnish was predominately explained by the first PC (Fig. 6.4b), and pyrite decay by the fourth. Physical forces was generally described by earlier PCs than limonitisation, and flaking was always described by the last PC. This pattern suggests that these reactions are not dependant on specimen habit, and that the relative occurrences of these reactions across the museums is largely the same.

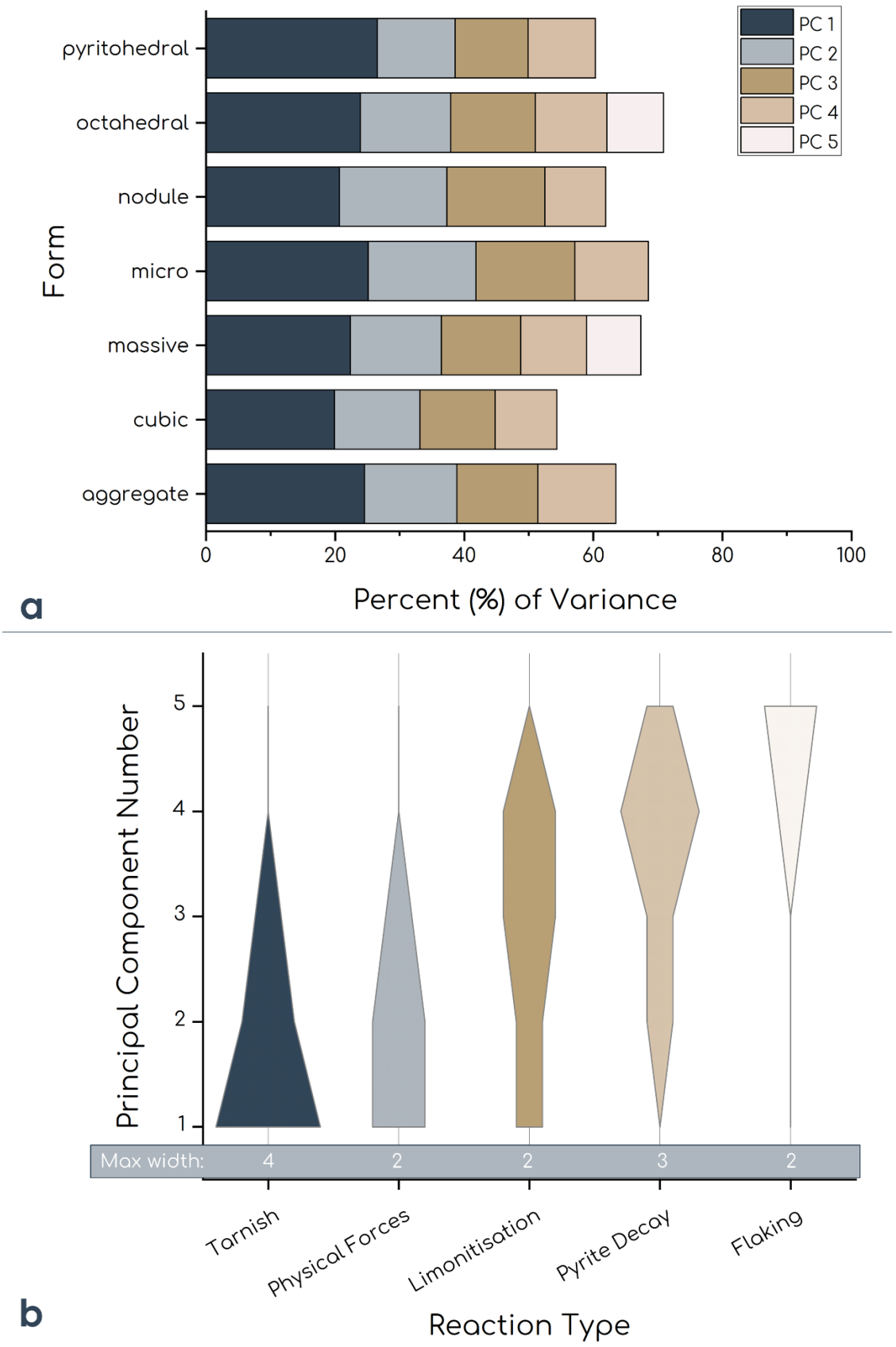


Figure 6.4. Visual summary of the habit PCA results; a.) the percent of variance each principal component describes, and b.) kite graphs depicting the reactions described by each principal component.

Reviewing the inverse relationships of the DP within the PCA structure matrixes indicates that pyrite decay and limonitisation are separate pathways. Corrosion and colour change were inversely associated with powder and or efflorescence for the aggregate, cubic, micro, and pyritohedral habits (Table 6.5). Other inverse relationships present in the structure matrixes did not conclusively indicate further counterposed reactions.

Table 6.5. DP and their values in the PCA structure matrices for select habits which demonstrate counterposed DP.

Habit	**PC #**	**+ DP**		**- DP**	
Aggregate	2	Cracks	0.56	Powder	-0.61
		Corrosion	0.54		
		Colour Change	0.47		
	4	Flaking	0.59	Efflorescence	-0.64
				Powder	-0.51
				Dark	-0.51
				Corrosion	-0.45
				Crumbling	-0.43
Cubic	2	Corrosion	0.73	Tarnish	-0.34
		Breakages	0.52		
		Dark	0.31		
	4	Colour Change	0.62	Powder	-0.62
		Corrosion	0.34	Efflorescence	-0.60
				Breakages	-0.28
Micro	1	Tarnish	0.87	Powder	-0.28
		Dull	0.83		
		Dark	0.79		
	3	Corrosion	0.81	Efflorescence	-0.28
		Breakages	0.60		
Nodule	2	Tarnish	0.80	Crumbling	-0.26
		Dull	0.70		
		Dark	0.64		
		Efflorescence	0.45		
	3	Cracking	0.77	Dull	-0.34
		Efflorescence	0.41		

Octahedral	3	Powder	0.76	Breakages	-0.35
		Efflorescence	0.75		
		Cracking	0.35		
		Flaking	0.31		
Pyritohedral	3	Corrosion	0.79	Powder	-0.34
		Colour Change	0.75	Efflorescence	-0.33
	4	Tarnish	0.32	Powder	-0.62
				Breakages	-0.52
				Flaking	-0.46
				Efflorescence	-0.36
				Dark	-0.33

Dull, dark, and tarnished strongly contributed to the formation of the first PC for the massive, micro, and octahedral data, and the third PC for the cubic data. However, only the massive and octahedral sets produced α values ≥ 0.70 (0.78 and 0.76, respectively).

6.2.2.3. Locality

Only the 11 DP were examined for the locality subsets. Primary habit was excluded as most localities produced specimens with the same morphology. Museums were also excluded because the specimens for all localities examined (save Elba, Italy) were housed at only one or two of the museums.

Fourteen pairs of variables produced strong *r* values (Table 6.6). There were two *r* values of 1.00:

1.) tarnish and dull for the Carmarthenshire data, and

2.) powder and break for the Cumbria data.

This indicates that these DP were always seen together for the specimens surveyed. Conversely, the Brosso data produced an *r* value of -1.00 for tarnish and corrosion, indicating that these DP were never seen together.

Table 6.6. Correlation coefficients for the locality subsets.

Locality Type	Locality Name	DP 1	DP 2	Correlation Coefficient I
Country	Spain	tarnish	dull	0.86
Region	Carmarthenshire	tarnish	dull	1.00
		tarnish	dark	0.80
		dull	dark	0.80
		efflorescence	cracking	0.71
	Cumbria	powder	break	1.00
	Piedmont	dull	dark	0.71
		efflorescence	powder	0.80
Town	Brosso	tarnish	corrosion	-1.00
		efflorescence	powder	0.91
		efflorescence	colour change	-0.73
		crumbling	breakages	0.75
	Dolgellau	tarnish	dull	0.71
		dull	dark	0.76

Three to five principal components were extracted across all locality subsets (Table 6.7). The average percent of total variance increased as localities became more specified (i.e., moved towards the town-level). This suggests that mines from the same town produce more similar specimens than mines from the same region, and indicates a type of 'fingerprinting' dependent on the local geology.

Table 6.7. Number of principal components and percent of total variance for the locality subsets.

Locality Type	Locality Name	Number of Principal Components	Percent of Total Variance	Number of Specimens included in Analysis
Country	England	5	69%	265
	Italy	4	66%	112
	Peru	2	55%	25
	Spain	3	72%	28
	US	3	60%	52
	Wales	5	67%	219
Region	Cornwall	5	71%	96
	Cumbria	4	80%	33
	Devon	5	75%	29
	Piedmont	4	73%	49
	Tuscany	4	69%	57
	Carmarthenshire	4	82%	26
	Gwynedd	4	58%	102
Town	Baldhu	4	79%	28
	Brosso	3	82%	21
	Traversella	4	71%	26
	Elba	4	69%	55
	Dolgellau	4	72%	33

At both the country- and region-level, the first three PCs primarily described tarnish, physical forces, and limonitisation, respectively (Fig. 6.5). At the country-level, pyrite decay was only seen in two PCs: PC1 for Italy, and PC2 for Wales. Pyrite decay was described by a PC for all regions examined, save Tuscany. When flaking was described by a PC, it was always described by the last PC (Appendix 7).

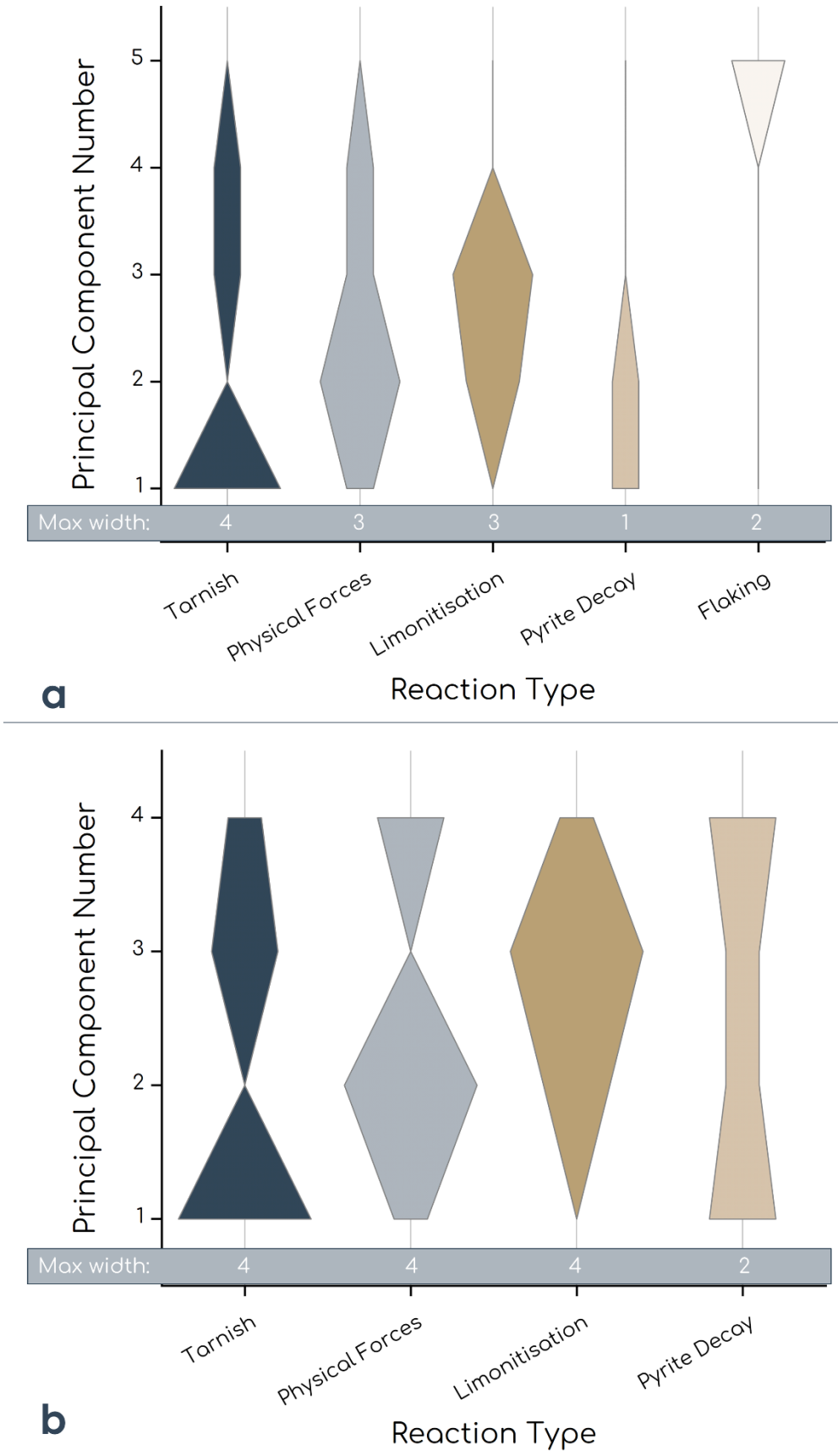


Figure 6.5. Kite graphs depicting the reactions described by each principal component at the a.) country- and b.) region-level

The structure matrixes for the Welsh regions begin to describe two counterposed reactions within the same principal component. This is defined by a more balanced number of positive and negative DP contributing to the component's construction; whereas in previous subsets, most DP were either negative or positive and only one or two DP were of the opposite sign (see Table 6.5 for examples). Nearly all of these counterposed reactions are limonitisation on one end and pyrite decay on the other (Table 6.8).

Table 6.8. DP and their values in the PCA structure matrices indicating counterposed reactions.

Region/Town	**PC #**	**+ DP**		**- DP**	
Carmarthenshire	1	Dull	0.97	Corrosion	-0.39
		Tarnish	0.97		
		Dark	0.92		
		Colour Change	0.38		
	2	Crumbling	0.86	Colour Change	-0.28
		Efflorescence	0.83	Dull	-0.28
		Cracking	0.77	Tarnish	-0.28
	3	Corrosion	0.64	Breakages	-0.78
		Colour Change	0.63	Efflorescence	-0.49
		Corrosion	0.38	Cracking	-0.45
	4	Flaking	0.82	Colour Change	-0.62
		Cracking	0.49	Corrosion	-0.29
Gwynedd	2	Colour Change	0.72	Efflorescence	-0.43
		Corrosion	0.67	Cracking	-0.41
				Dull	-0.27
	4	Powder	0.46	Flaking	-0.66
		Corrosion	0.29	Colour Change	-0.41
		Dark	0.27	Cracking	-0.31
Baldhu	3	Efflorescence	0.51	Colour Change	-0.91
				Crumbling	-0.46
				Tarnish	-0.27

Brosso	1	Efflorescence	0.96	Colour Change	-0.80
		Powder	0.92	Corrosion	-0.32
		Cracking	0.71		
		Breakages	0.56		
		Crumbling	0.41		
		Tarnish	0.32		
	2	Crumbling	0.86	Flaking	-0.81
		Breakages	0.78		
	3	Corrosion	0.99	Tarnish	-0.99
		Colour Change	0.37	Cracking	-0.56
				Crumbling	-0.28
				Efflorescence	-0.27
Traversella	4	Breakages	0.61	Flaking	-0.62
		Crumbling	0.58	Colour Change	-0.28
		Cracking	0.49		
		Tarnish	0.25		
Elba	2	Crumbling	0.81	Flaking	-0.53
		Cracking	0.65	Dark	-0.32
		Colour Change	0.51		
		Efflorescence	0.32		
	3	Corrosion	0.86	Tarnish	-0.85
		Colour Change	0.44		

Cronbach's Alpha was calculated for fifteen sets of variables across all locality subsets (Table 6.9). Dull, dark, and tarnish accounted for six of these sets, and five sets of variables were DP indicative of pyrite decay (efflorescence and or powder in combination with breakages, cracking, and or crumbling). Only five sets produced α values less than 0.70, four of which were at the country-level. The average value for α increased as localities became more specified.

Table 6.9. The localities and DP for which Cronbach's Alpha was calculated.

Locality Type	Locality Name	DP	Cronbach's Alpha (α)
Country	England	dark, dull, tarnish	0.67
		breakages, cracking, crumbling	0.58
	Italy	breakages, efflorescence, powder	0.76
	Peru	dark, dull, tarnish	0.72
	Spain	crumbling, dull, efflorescence, tarnish	0.83
	US	breakages, cracking, crumbling	0.61
	Wales	dark, dull, tarnish	0.79
		cracking, crumbling, efflorescence	0.56
Region	Cumbria	breakages, crumbling, powder	0.90
	Carmarthenshire	dark, dull, tarnish	0.95
		cracking, crumbling, efflorescence	0.83
	Gwynedd	dark, dull, tarnish	0.77
Town	Brosso	cracking, efflorescence, powder	0.86
	Elba	dark, dull, efflorescence	0.69
	Dolgellau	dark, dull, tarnish	0.88

6.2.3. Colorimetry

The majority of specimens used for colorimetry (Table 6.2) were pyritohedral (85) and cubic (84), and were generally single crystals without a matrix. Various other habits constituted the remaining specimens.

Specimen colour coordinates formed a triangle when plotted three-dimensionally in CIELAB (Fig. 6.6). The triangle is formed of two parts: 1.) the main column, and 2.) the apron. Most specimens fall within the main column. Colour values vary predominantly in lightness (76.52–30.49 L*), but also considerably along the b* axis (5.59–24.92). The smaller b* values (i.e., those closer to 0) are at the bottom of the column, producing a slight angle. The main column also shows a dense cluster of specimens in its upper half, and this is where the majority of low TDP (0–1) specimens are situated.

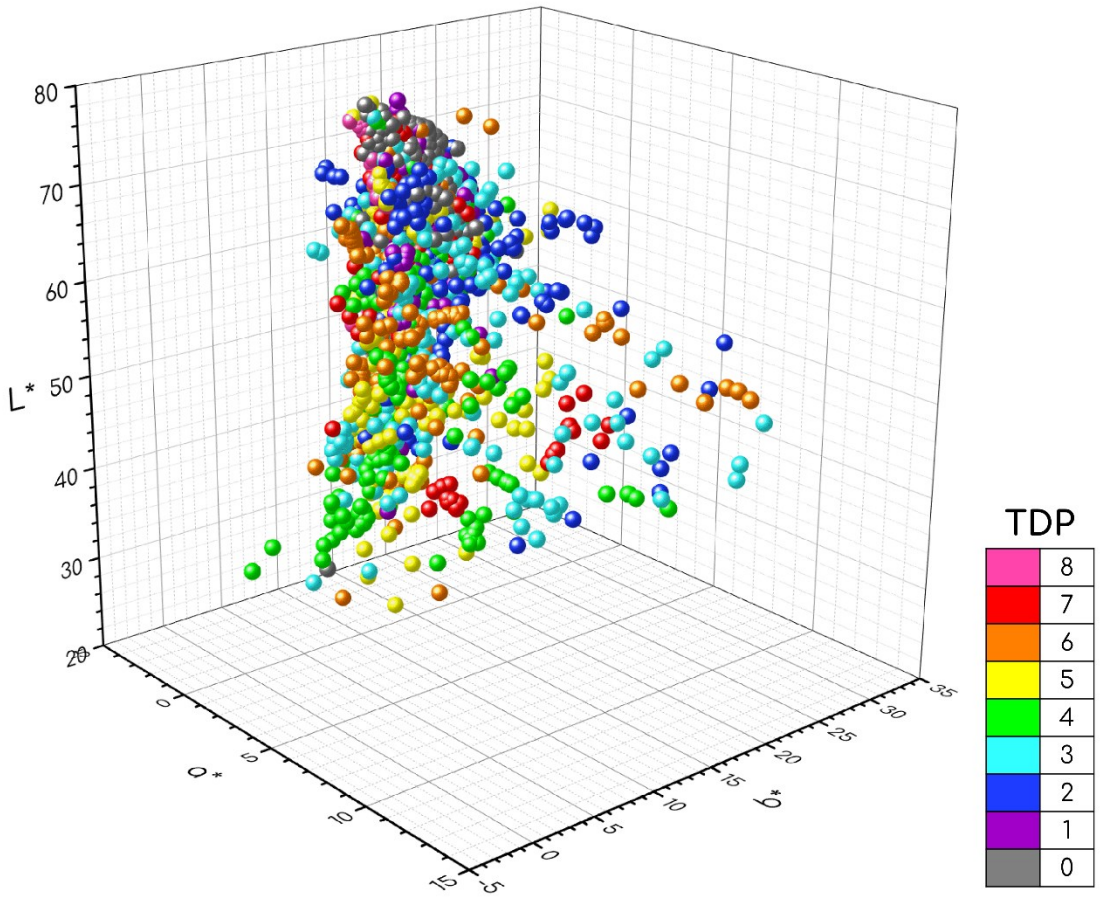


Figure 6.6. Average CIELAB colour coordinates for the pyrite specimens, colour coded according to that specimen's TDP.

After segmentation, it can be seen that the apron is indeed composed solely of specimens which displayed a visual change in colour (Fig. 6.7). However, specimens exhibiting colour change also plotted within the main column, and the majority fell within the dense cluster at the top of the column (Fig. 6.7c). Examining the individual colour axes (Fig. 6.8) further confirmed the similarities between the two groups of specimens. Both groups show a dense cluster centred at approximately 60 L*, 0 a*, and 15 b*. The primary difference between the two groups is the a* range:

- colour change absent: -2.13–5.46 a*
- colour change present: -3.11–11.66 a*.

This further supports visual observations. The majority of colour change specimens appeared red or orange, which colorimetrically corresponds to increases in a*.

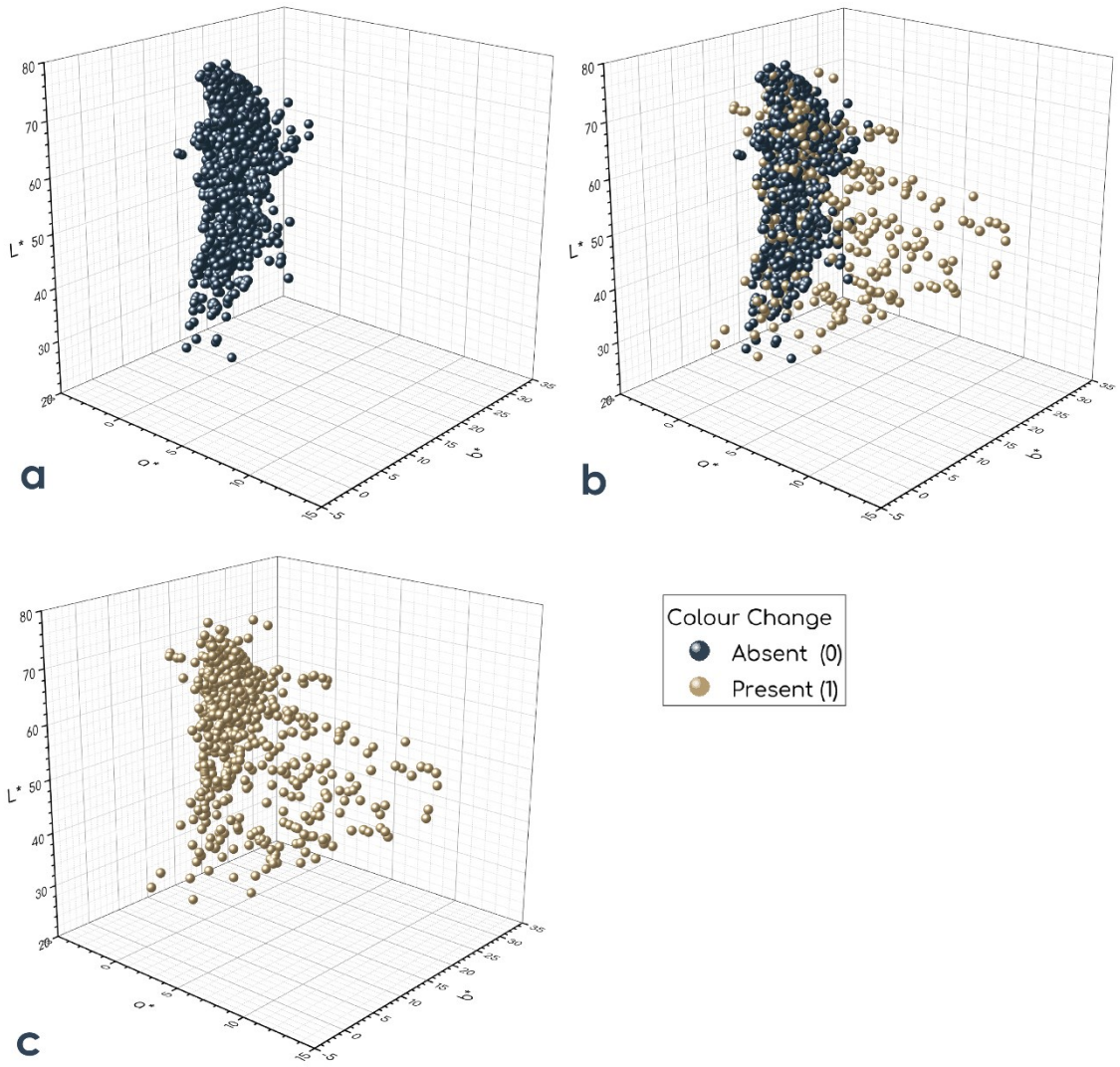


Figure 6.7. Average CIELAB colour coordinates, colour coded according to the presence or absence of colour change.

The colour change specimens that are within the main column likely have at least one red/orange face, yet another face was used for colorimetry. At the time of data collection, the importance of colour change in indicating a secondary reaction pathway was not recognised. The primary focus was on the development of dull and dark tarnishes, which was thought to be correlated with pyrite decay. Thus many coloured specimens were excluded, and faces exhibiting a colour change were not measured.

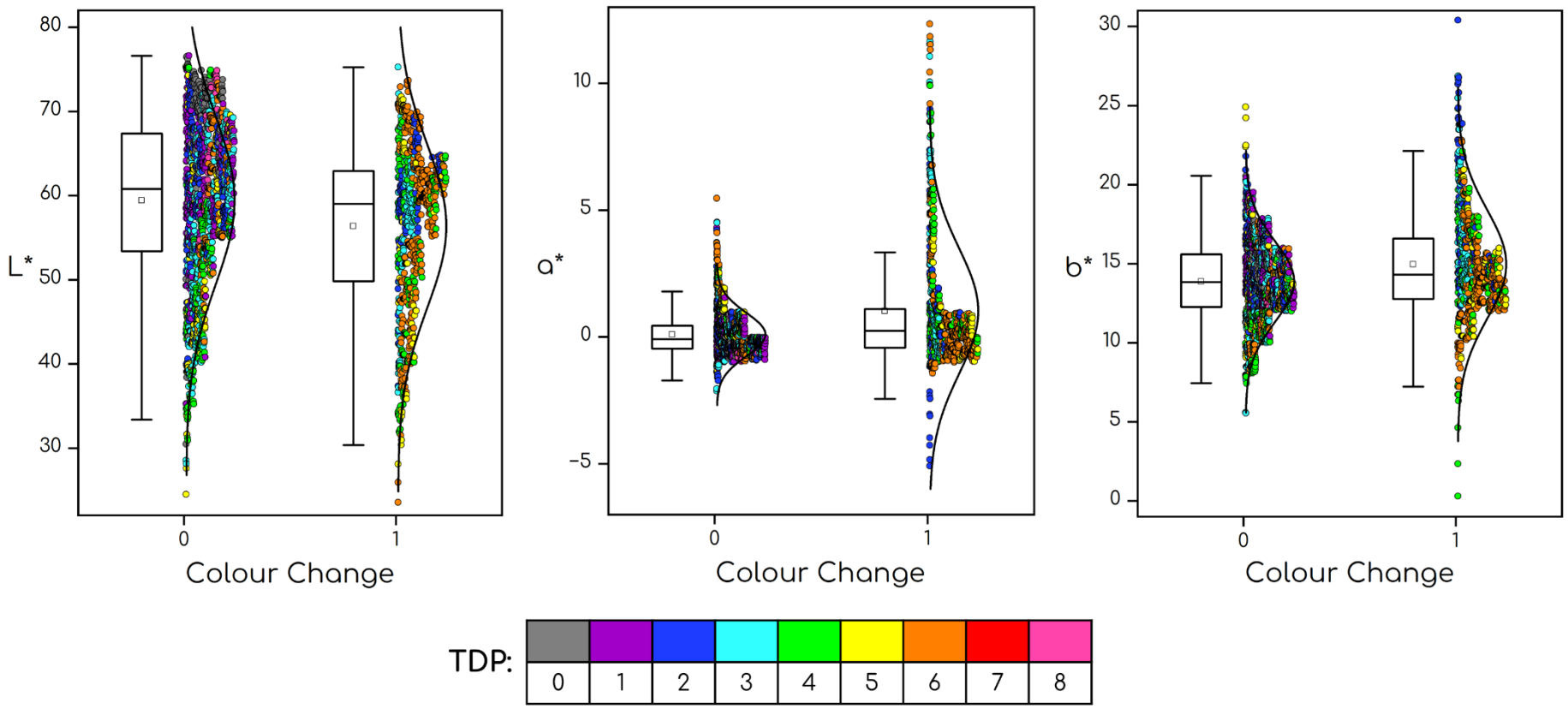


Figure 6.8. Distribution of average CIELAB colour coordinates; colour coded according to specimen TDP, and grouped according the presence or absence of colour change. Both groups exhibit a cluster of points about the same colour coordinates (approx. 60 L, 0 a*, and 15 b*). The primary difference is the larger ranges for the colour change group (1), especially for the a* axis.*

6.3. Discussion

"The problem is that all minerals contain impurities. In fact, all chemical compounds are impure —it is the level of impurities that is interesting." – Rickard 2015: 79

The survey and colorimetric results provided ample information to develop the impurity hypothesis: the concentration of impurities within pyrite is the primary factor controlling the pyrite decay reaction (that outlined in Ch. 2, Section 2.8.2) within the museum setting. What impurities are, how they are introduced to pyrite, and the visual indications and effects of impurities are outlined in the following sections.

6.3.1. Locality

The PCA results (Section 6.2.2) clearly suggest that of the three situational variables examined, locality is the one which has the greatest effect upon—and largely governs—specimen stability. Each locality has unique formation conditions (temperature, pressure, and elemental availability) which directly affect specimen habit and composition. As shown in Section 6.2.2.2, there are some inherent differences in stability across the various habits, assumedly due to energetic differences of the crystallographic faces (see Section 6.3.2). Yet the remaining variation is readily accounted for by deviations in specimen composition, such as:

- elemental substitutions,
- interstitial inclusion of compounds,
- inclusion of other geomaterials within the crystal,
- associated material abutting crystal faces, and
- matrix composition and properties.

The presence of any of these will affect the energy available within the system and may alter which reactions are more likely to occur. The former three compositional deviations will be referred to as impurities thus forth.

6.3.1.1. Hydrothermal Deposits

The survey results suggest that significant levels of impurities may be more likely to occur within specimens that formed in hydrothermal systems than those which were the product of sedimentary or metamorphic mineralisation. In hydrothermal systems, a liquid mineral solution (often containing a great variety of elements and compounds) is injected into faults and fissures in the county rock. As the solution cools, minerals crystalise along the fracture walls, forming veins deposits (Rickard 2015). Changes in solution temperature and composition dictate which minerals form (Dines 1956). Such changes may be sudden, leading to abrupt switches between species and great variation in vein mineralogy.

The vast majority of the museum specimens surveyed with known localities formed under hydrothermal systems. Of these, ten mines were represented by six or more specimens. Survey results were used to create the following three segmentations (Table 6.10).

Group 1 specimens generally only displayed a tarnish; this tarnish was coloured for 16 specimens. Cracks were also seen in the Quiruvilca and Llanharry specimens. Group 2 exhibited greater signs of deterioration; cracking, crumbling, breakages, and efflorescence were more prevalent. Specimens from both Groups 1 and 2 were generally accessioned, and likely collected, between the 1950s and 80s. The Ogofau specimens, however, were accessioned in 1937 (save one that was accessioned in 1917). Were these specimens contemporaneous with the rest, Ogofau may have been assigned to Group 1 instead of 2, as they appear to be like specimens from Llanharry or Parc Mine, just more deteriorated.

The majority of Group 3 specimens were accessioned between the late 1800s and the 1930s, although some were accessioned by OUMNH and NMC in the 1970s and 80s. The group is predominately characterised by specimens undergoing pyrite decay, which appears to be most severe within the Brosso specimens (ADP = 8). The younger Elban pyrites (c. 1950-90) are generally in a noticeably better state (ADP = 3) than the older ones (ADP = 5). This is in agreement with anecdotal reports that Elban

specimens appear to be fine for decades only to suddenly deteriorate (T. Cotterell 2023, personal communication, 18 August).

Table 6.10. %DP patterns for specimens within the three hydrothermal groups devised by the author.

Group	**1**	**2**	**3**
Corrosion	0%	20%	7%
Tarnish	82%	89%	94%
Efflorescence	9%	25%	30%
Powder	0%	0%	17%
Crumbling	3%	41%	39%
Flaking	0%	2%	13%
Breakages	0%	18%	22%
Cracks	32%	75%	72%
Dull	76%	82%	66%
Dark	56%	57%	47%
Colour Change	47%	27%	43%
ADP	3	4	4
Number of Specimens	34	44	102
Mines	- Cwmgwili Collery - Llanharry Iron Ore Mine - Parc Mine - Quiruvilca Mining District	- Ogofau Mines - Virtuous Lady Mine - Wheal Jane	- Brosso Mine - Rio la Marina, Elba - Traversella Magnetite Mine

Key:			
0–24%	25–49%	50–74%	75–100%

Whilst differences in specimen age can account for some of the variations seen between these three hydrothermal groups, Groups 1 and 2 suggest that there are additional variables at play. One-way ANOVA was performed using specimen TDP to confirm whether the groups indeed represent three separate populations

(H_0: $\mu_1 = \mu_2 = \mu_3$; H_1: $\mu_1 \neq \mu_2 \neq \mu_3$). At the 95% confidence level ($\alpha = 0.05$), these groups were determined to be significantly different (F test statistic = 6.82, P-value = 0.001). Figure 6.9 visualises the differences between the three hydrothermal groups.

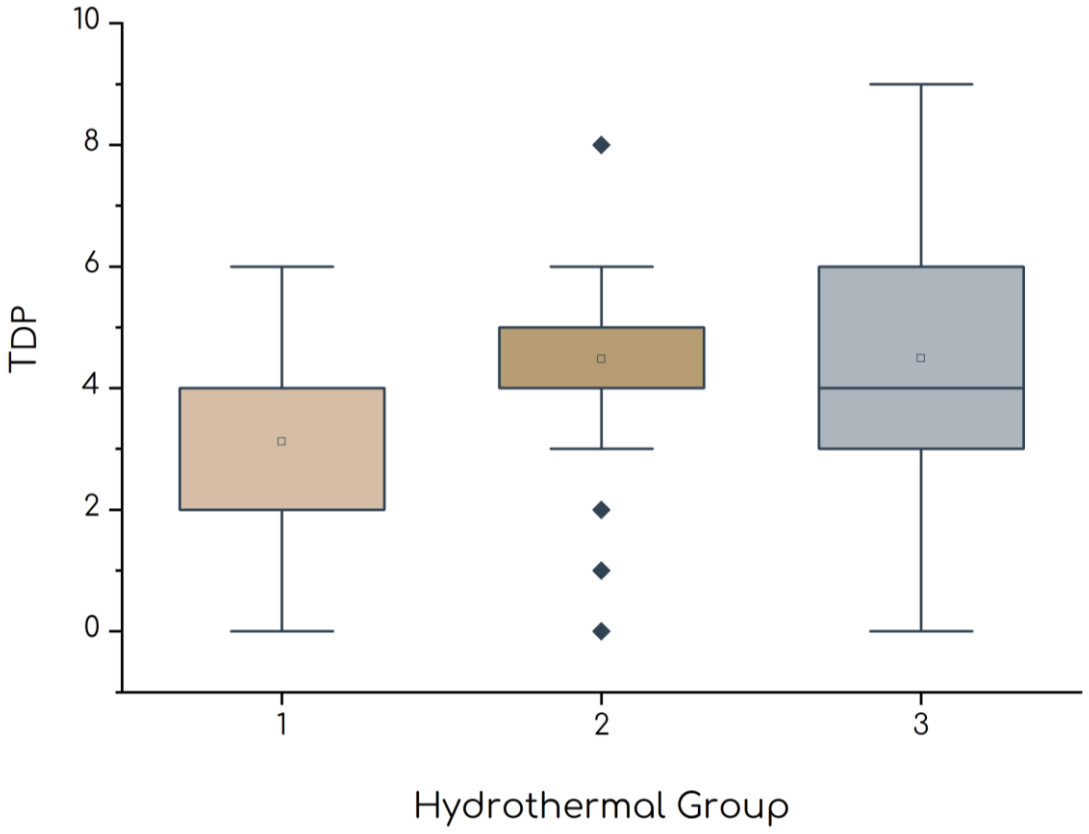


Figure 6.9. Distribution of specimen TDP according to hydrothermal group.

Differentiation is believed to be due to mineralisation temperature and, relatedly, the associated mineralogy. Specimens from the three Welsh mines in Group 1 mineralised at relatively low temperatures (100-150°C), whereas specimens from the mines of Groups 2 and 3 formed at significantly higher temperatures (300-500°C; Embrey & Symes 1987). What differentiates Group 3 from 2 is the presence of tungsten-bearing minerals, suggesting that mineralisation at the Group 3 localities likely occurred at the upper end of the 300-500°C range. The associated mineralogy of the Italian mines (the Hudson Institute of Mineralogy 2023f, 2023g, 2023h) is also significantly greater than that of the British mines (Dines 1956, Embrey & Symes 1987). This "complex and rich mineralogy reflect[s] many degrees of geochemical evolution" (Pezzotta 2021: 673) undergone by this region of Italy, including "significant tectonic movement and collision causing pressure (and heat) related metamorphism"

(T. Cotterell 2023, personal communication, 30 August). Thus, the composition and temperature, as well as the heat source, of the mineral solution significantly affects the stability of hydrothermally formed pyrite.

Example: Quiruvilca Mining District, Peru

Based on the survey data, the Quiruvilca Mining District in Peru would appear to fall between Groups 1 and 2. This is related to the district's size and nature; it is comprised of over 100 known veins across four different mineralisation zones (Table 6.11). These veins can be characterised as one of the following (Bartos 1987):

1.) **pyritic**: ≥ 50% volume of pyrite
2.) **sphalerite-galena**: sulfides ≥ non-sulfides;
    < 50% volume pyrite, ≥ 15% volume sphalerite
3.) **gangue**: sulfides < non-sulfides

Table 6.11. Predominant mineralogy of the four mineralogic zone within the Quiruvilca Mining District, adapted from Bartos 1987.

Mineralogic Zone	**Enargite**	**Transition**	**Lead-Zinc**	**Stibnite**
Mineralogy	alabandite barite calcite chalcopyrite enargite galena hutchinsonite orpiment pyrite quartz sphalerite tetrahedrite-tennantite	calcite chalcopyrite dolomite galena manganocalcite pyrite quartz sphalerite tetrahedrite-tennantite	arsenopyrite calcite chalcopyrite clinozosite dolomite galena manganaxinite manganocalcite marcasite pyrite quartz rhodochrosite sphalerite stibnite tetrahedrite-tennantite	arsenopyrite calcite chalcopyrite galena manganocalcite pyrite quartz rhodochrosite sphalerite stibnite tetrahedrite-tennantite
Common Vein Types	pyritic	pyritic, sphalerite-galena	sphalerite-galena, gangue	sphalerite-galena, gangue

The varying proportions of the three veins types within the mineralogical zones (Table 6.11) suggest that mineralisation began with the innermost zone and progressed outwards (Bartos 1987). Temperature also decreased with each progressive depositional phase. Both pyrite and sphalerite-galena veins are believed to have formed during the initial sulfide ore deposition, which occurred at approximately 300-350°C (Bartos 1987). Gangue dominant veins generally formed later at lower temperatures (230-300°C).

The locality data for the eight specimens surveyed do not indicate the mineralogic zone or vein type from which the specimens were extracted. Two specimens (OUMNH-MIN.26296 and 86.99G.M.5) are attributed to the Quiruvilca Mine, which appears to be in the transition zone. Based on the DP patterning and specimen habit, it is probable that four other specimens (OUMNH-MIN.22642 and 26813; 78.46G.M.3; and 83.41G.M.1326) were extracted from similar veins in any of the outer three mineralogic zones. Of the remaining two specimens, NMC's 83.41G.M.1335 is associated with enargite, clearly indicating that it was extracted from pyritic veins in the enargite zone. The DP patterning for 78.46G.M.10 is very similar, therefore it is probable that it was also extracted from a pyritic vein. These latter two specimens may have formed at higher temperatures than the former six. In conjunction with a greater potential associated mineralogy, this would explain the differences in observed DP and why this locality straddles hydrothermal Groups 1 and 2. Quiruvilca thus demonstrates that specimen stability can vary significantly within the same locality due to conditional variations that occurred during mineralisation.

6.3.1.2. Metamorphic Deposits

Only a few of the museum specimens surveyed were produced through metamorphic mineralisation. Relative to hydrothermal systems, metamorphic mineralisation generally occurs in more stable environments. Any compositional or temperature changes occur more gradually, and the sum of elements and compounds present can be far fewer. Thus, there is generally less variability within these systems.

The primary example of metamorphic pyrite are specimens from Ampliación a Victoria Mine, Navajún, Spain. The associated mineralogy is highly limited: "green chamosite in nodules; chloritoid as inclusions in pyrite; cookeite as white coatings on [pyrite] faces; manganese minerals; and calcite-lined vugs inside fractured pyrite" (Greene 2015: 31). This confirms that the range of elements present during mineral formation was limited.

The Navajún pyrites are almost exclusively cubic, and appear to be practically perfect in nature (see the cubic specimen in Table 6.1). This suggests a relatively slow crystallisation process under moderate temperatures (c. 350°C; Rickard 2015) and an equal (i.e., nondirectional) pressure distribution. Higher temperatures and uneven pressure would encourage more rapid crystallisation, producing striated faces or preferential growth along one axis (i.e., the formation of rectangular prisms) (Greene 2015, Rickard 2015). The perfect cubes and their clear impressions left within the matrix have led both Carl Francis (Greene 2015) and Tom Cotterell (2023, personal communication, 18 August) to believe that the Navajún pyrites formed metamorphically in a manner similar to garnets in schist. The pressure within the sedimentary deposits gradually increased as they became buried. After a critical point, the pyrite crystallisation began, locally displacing the soft host rock. Cotterell (ibid.) supposes that the rigid physical constraints imposed by the host rock led to a more densely packed crystal structure compared to pyrites from hydrothermal deposits.

Together, the limited mineralogy and dense, near perfect cubic morphology likely contribute to the Navajún pyrites' reported (Calvo & Sevillano 1989, Greene 2015) and observed stability. Of the ten specimens surveyed, only two displayed DP. The two DP (cracking and efflorescence) associated with this pair of specimens were seen within the host rock itself and were observed to not be exclusively in proximity to the pyrite (Fig. 6.10). Thus, it was deemed unlikely that pyrite decay was the cause of these DP. The author subsequently acquired two specimens from the same locality and observed the same phenomena occur within a few months of purchase.

The host rock has been defined as a "marl, which is composed of more than 50% clay and at least 15% calcium carbonate" (Lodders *et al.* 1998: 138). It is highly

likely that the clay is drying out within the indoor environment, causing cracking and soluble salt efflorescence. Powder x-ray diffraction (XRD) was performed on efflorescence sampled from one of the author's personal specimens (Fig. 6.10) to confirm this hypothesis. A PANalytical Xpert-Pro diffractometer with a Cu anode was used to continuously scan the rotating powdered sample. Spectra were acquired at 40kV and 30mA over the range of 5-70°2Θ, with each step (0.02°) being scanned for 15 seconds. Spectral analysis was performed by Tom Cotterell.



Figure 6.10. One of the author's personal specimens of Navajún pyrite within the marl matrix. White spots of efflorescence cover the exhibited face, and are concentrated in some areas towards the bottom of the image. A distinct crack is seen in the middle of the specimen running horizontally from the pyrite cube to the rock's edge.

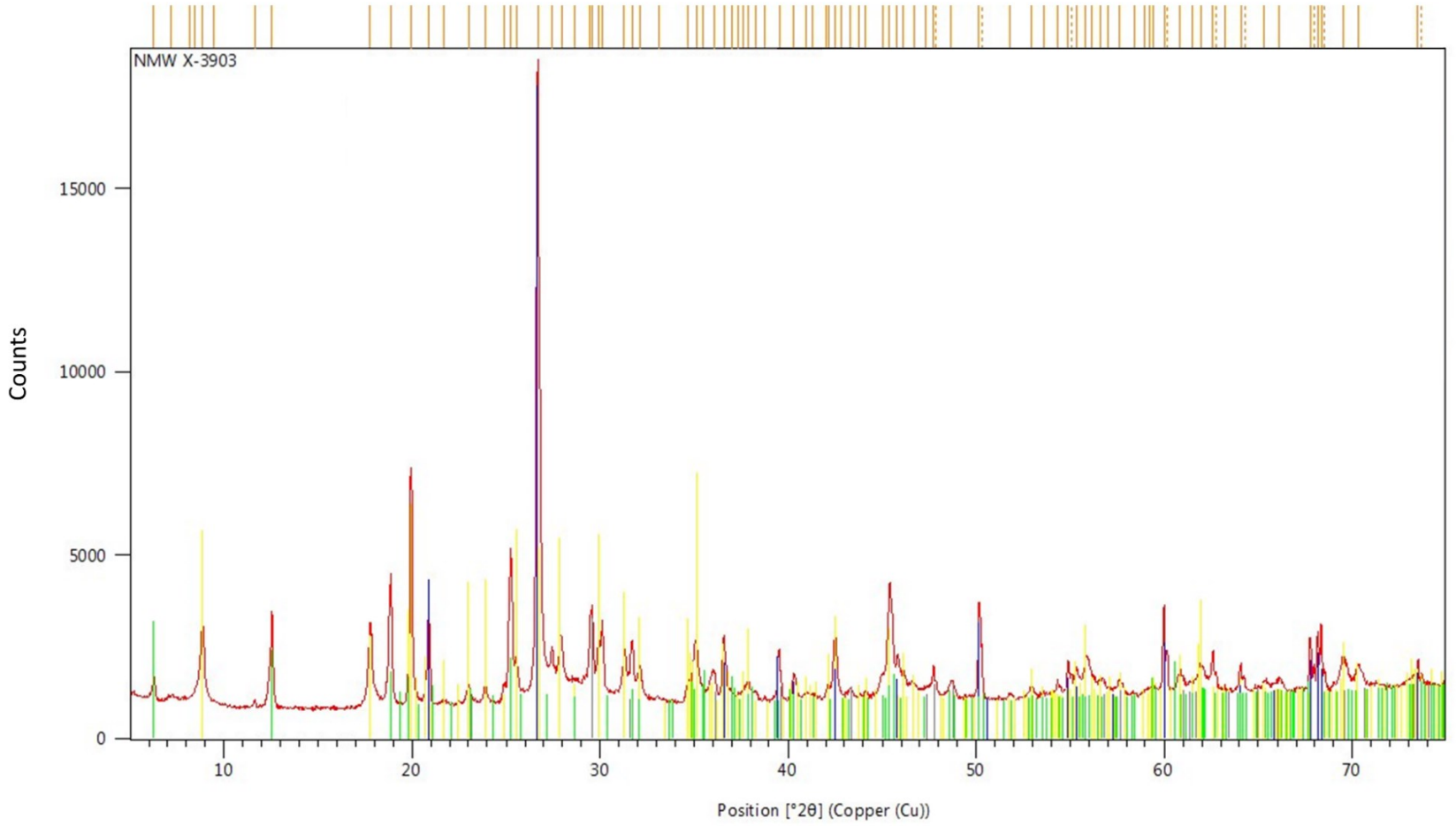


Figure 6.11. X-ray diffraction spectrum for the efflorescence sampled from the author's personal specimen of Navajún pyrite. The coloured lines correspond to peak positions of muscovite (yellow), quartz (blue), chlorite (green), and magnesium-bearing calcite (grey).

XRD patterns for four minerals were identified in the spectrum (Fig. 6.11). Muscovite was identified to be the primary constituent (> 66%), followed by quartz (~20%), chlorite (~10%), and magnesium-bearing calcite (3%). Chloritoid may also have been present (~20%), but Cotterell expressed some uncertainty. These results are in agreement with Lodders *et al.*'s (1998) analysis of the host rock, and confirm that the efflorescence is not a product of pyrite oxidation.

6.3.2. Tarnish

Tarnish (surficial oxidation) is the first reaction to occur during pyrite's deterioration. The vast majority of specimens recorded as exhibiting DP indicative of pyrite decay also had tarnish present. Only a handful of tarnish-less specimens were observed to have efflorescence. These were all specimens for which alternative causes of efflorescence are highly likely, such as:

1.) previous conservation treatment,
2.) associated minerals prone to efflorescence due to variations in relative humidity, and
3.) matrixes that could contain soluble salts.

An example of the latter are the Navajún specimens that are still embedded within the host rock (see Section 6.3.1.2).

The first visual indication of tarnish formation is a change in lustre. This was recorded as dull in the survey and colorimetrically responds to a decrease in L* values. The differentiation between grey and coloured tarnishes begins at approximately 60 L*. It is likely that specimen crystallography controls this differentiation. As multiple investigators have demonstrated (Eggleston *et al.* 1996, Guevremont *et al.* 1998a, Rosso *et al.* 1999b), the crystal's termination structure varies for each crystal face, leading to differing availabilities of sulfur and iron (Fig. 6.12). In addition, any crystallisation defects and sulfur-deficient sites present at the surface will affect the rate of oxidation and the composition of resultant products (Eggleston *et al.* 1996; Guevremont *et al.* 1998a). Combined, these produce "a variety of reactive site,

introducing the interesting possibility that distinctly different oxidation mechanisms may be proceeding across the pyrite surface" (Rosso *et al.* 1999b: 1535). Although these investigations of pyrite's surface structure do not mention the colour of the oxidised surfaces (presumably due to the nature of the experiments), it is highly likely that the colours observed in the surveyed museum specimens correlate to the primary oxidation product (i.e., a red/orange tarnish correlates to limonite; Moses & Herman 1991).

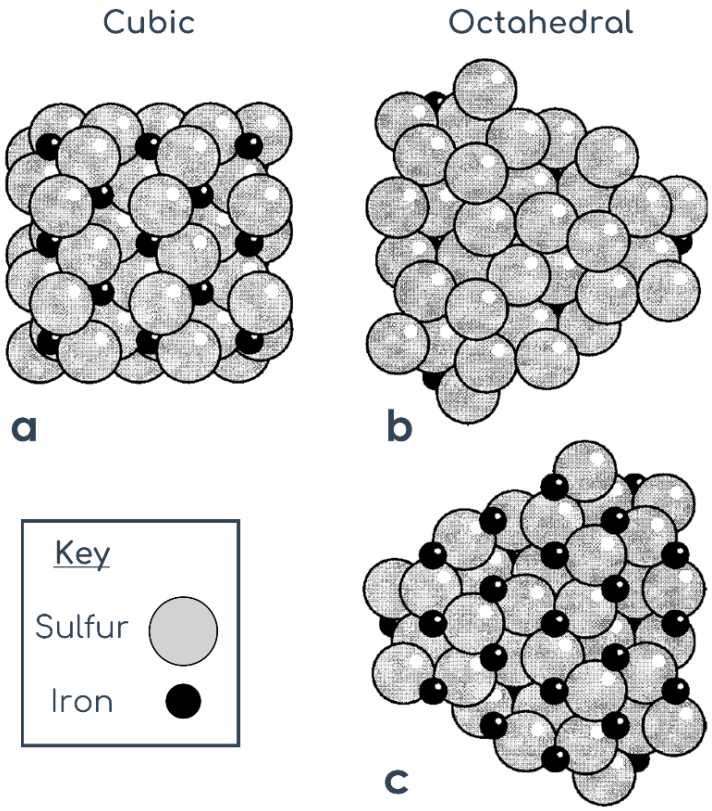


Figure 6.12. Ideal pyrite crystallographic planes after Guevremont et al. *1998a; a.) sulfur-terminated (100), b.) sulfur-terminated (111), and c.) iron-terminated (111).*

Tarnish colour also appears to signify later occurring reactions. The survey results demonstrate that grey tarnishes correspond with specimens which undergo pyrite decay, whilst coloured tarnishes largely do not (only 15 specimens with coloured tarnishes also exhibited signs of pyrite decay). The speed at which pyrite decay occurs in specimens is probably dictated by the quantity of inclusions and impurities (Fig. 6.13) within the specimen, which in turn affect the types of reactive sites present and the potential energy of the system.

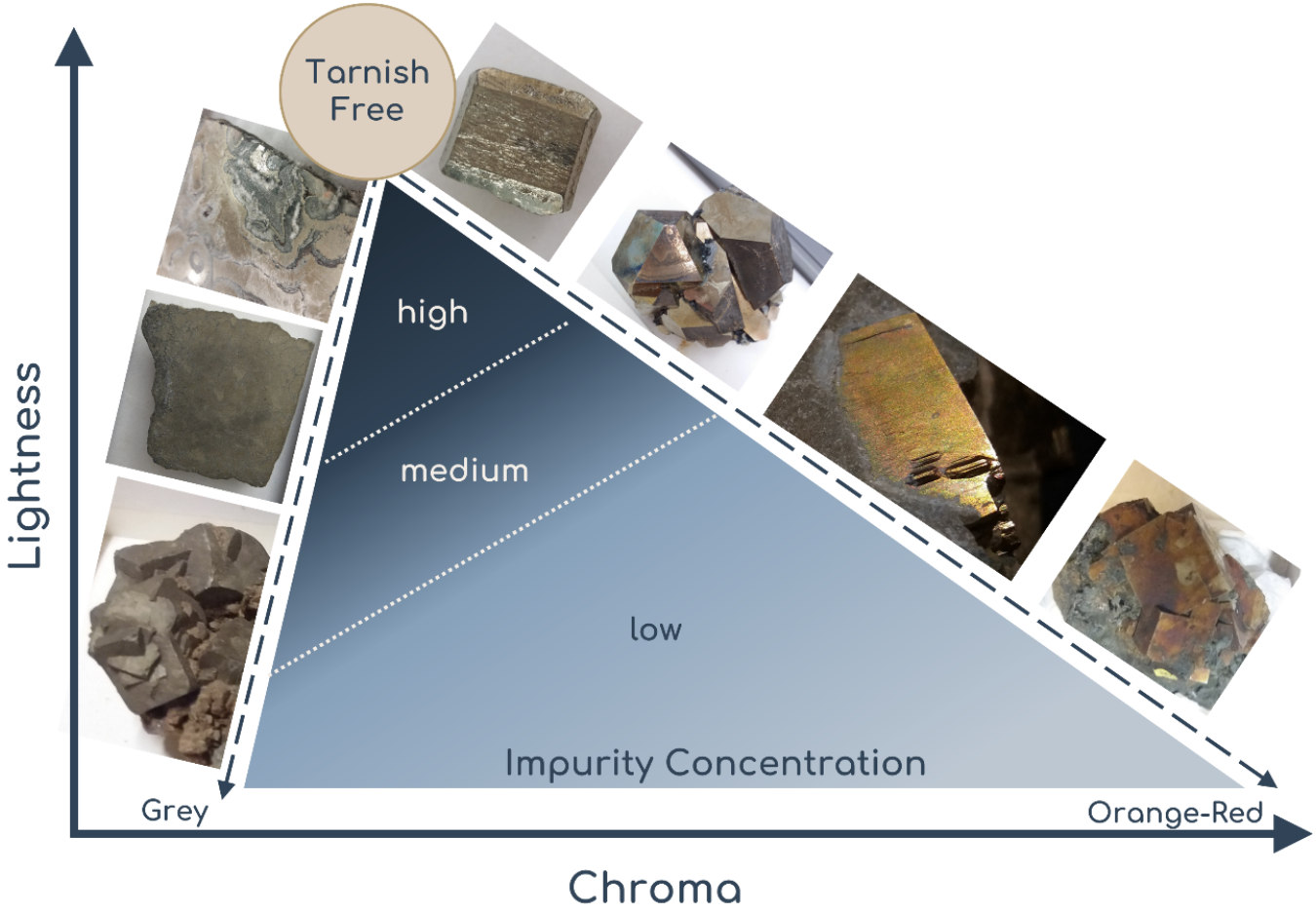


Figure 6.13. Graphic summary of this work's findings. Colour data can be reduced to two axes: lightness (L) and chroma (a* and b*). The very lightest of specimens have not yet tarnished. The higher the concentration of impurities, the faster the specimen deteriorates. The darkest of specimens are likely those with low impurity levels and are thus more stable. The colour of the tarnish likely correlates to the primary oxidation product, which will be that into which the specimen ultimately morphs (i.e., orange-red specimens will become limonite* pseudomorphous *after pyrite).*

Specimen images used with permission courtesy Oxford University Museum of Natural History, National Museum Wales, and the Sedgwick Museum of Earth Sciences.

Specimens with high concentrations of impurities are assumedly the ones which deteriorate extremely rapidly (i.e., will be little more than powder within a few years). In addition to various other DP indicative of pyrite decay, these specimens (TDP ≥ 7) generally have tarnishes which are very difficult to spot, even for the trained observer (i.e., very slight dulling and darkening relative to an untarnished specimen). These specimens are predominately situated within the dense cluster of points at the top of the main column (Fig. 6.6. & 6.8), with fairly high L* values (50–75). Thus, these highly reactive specimens are difficult to identify prior to the emergence of other DP.

Specimens with mid-level impurity concentrations likely correlate to those which suddenly deteriorate decades after extraction. In these circumstances, the potential energy in the system was building up over the years alongside a more readily noticeable tarnish. The suddenness of deterioration corresponds to finally achieving sufficient energy for the pyrite decay reactions to occur.

Low impurity grey-tarnish pyrites appear to be relatively rare; the only example seen during this survey were the nine specimens from French Creek Mines, Pennsylvania, US. Of these, pyrite decay was only observed in one aggregated specimen accessioned by the Sedgwick in 1899. The remaining specimens (single crystals, also accessioned about the turn of the 20th century) only exhibited tarnishes and cracking along crystal faces. It is uncertain what produces these cracks as no additional signs of pyrite decay are visible and no further analysis was conducted at this time. However, the oxidation reaction occurring within these specimens is probably unrelated to those typical of pyrite decay. This reaction appears to be akin to that which produces coloured pyrite tarnishes in terms of speed and the production of a passivating oxidation layer.

Example: Traversella and Elba, Italy

The hematite (Fe_2O_3) variety specularite—an aggregate of "silvery, metallic, specular ("mirror-like") hematite flakes" (the Hudson Institute of Mineralogy 2023i)—is often intimately associated with pyrite at Traversella and Elba. The micaceous nature of the hematite induces its friability (flaking was commonly observed in these specimens), and directly affects the stability of the adjoining pyrite.

At these localities, the hematite crystallised prior to the pyrite, as evidenced by the notches left within the pyrite when the hematite flakes away (Fig. 6.14). Pyrite crystallisation likely proceeded from the hematite interface outwards. Nucleation would begin at various sites between the hematite flakes. It is reasonable to believe that the crystallographic orientation of the nascent pyrite would differ at each site relative to the others. Thus, once the pyrite crystallisation fronts emerged from the hematite interstices, the fronts would have converge into the dominant orientation. Subsequent crystallisation would proceed accordingly and produce well-defined crystal faces (as exhibited on the specimens) upon depletion of the mineral solution (Rickard 2015).

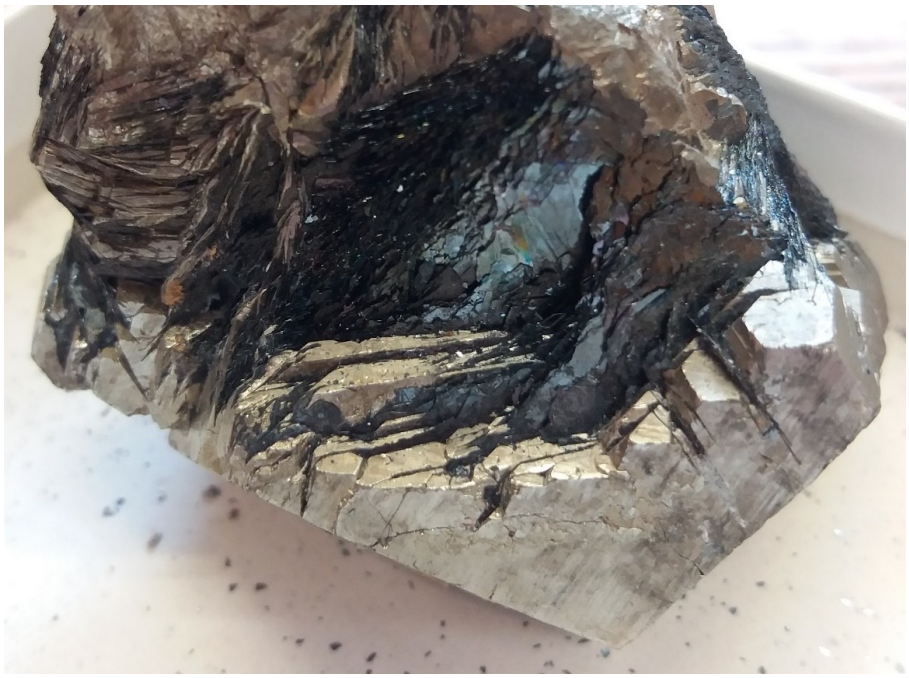


Figure 6.14. Pyrite specimen OUMNH-MIN.23575; notches in the pyrite indicate crystallisation after the formation of the micaceous hematite.
Image used with permission courtesy Oxford University Museum of Natural History.

Subsequently, the pyrite–hematite interface introduces greater reactive potential relative to the other pyrite faces. Firstly, the pyrite at the hematite interface has a far greater surface area due to the intergrown nature. Secondly, various crystallisation defects would be localised at the transition between the pyrite within the hematite interstices and the bulk pyrite crystal to compensate for orientational differences between the two. Together, this would greatly increase the number of reactive sites available for oxidation. Lastly, hematite is composed of ferric iron, a known oxidant often involved in pyrite decay reactions (Lowson 1982, Moses & Herman 1991, Rickard 2015). Ferric ions from the hematite would be immediately available to the reactive sites at the pyrite–hematite interface, allowing for pyrite oxidation to begin here well before it would commence at the other faces.
This is in agreement with both the previously stated anecdote that Elban pyrites appear to suddenly deteriorate decades after extraction and observations made during the survey; most signs of pyrite decay were found at the pyrite–hematite interface or along cracks that propagated from it.

Whilst the micaceous hematite of Elban pyrite is not considered an impurity, it demonstrates a similar effect. The presence of both impurities and intimately associated mineral species—which is dictated by formation conditions—can produce greater reaction potential in pyrite through the introduction of site defects and oxidants.

6.4. Conclusion

Pyrite specimens from four UK museums were examined using the DP State Survey Method and colorimetry. The state of these specimens appeared largely similar across all collections. Whilst some variations in state were observed for the different pyrite habits, specimen locality was determined to be the predominant indicator of pyrite stability.

The formation conditions occurring at a given locality—temperature, pressure, elemental availability, heat sources, and even geological activity—dictate which

minerals form and the speed of their formation. This directly affects specimen habit and composition, including the presence of elemental substitution and (interstitial) inclusion of compounds and other geomaterials. These aspects, in conjunction with the presence and properties of associated materials, influence specimen stability and possible reaction pathways. This is directly supported by the data collected during this survey, and led to the development of the pyrite impurity hypothesis: the concentration of impurities within pyrite is the primary factor influencing pyrite deterioration within the museum environment.

High impurity levels likely induce rapid deterioration, as indicated by the emergence of DP suggestive of pyrite decay prior to the formation of a visible tarnish. Thus, noticeable tarnishes would correlate with lower impurity concentrations. Tarnish colour appears related to the primary oxidation product at the pyrite surface, which is most likely determined by the specimen's crystallographic orientation. Grey-tarnished pyrite in particular appears to oxidise more aggressively within the museum environment relative to those with coloured tarnishes, as dark grey stable pyrites were rarely observed.

The results of this survey suggest that locality can be used as a indicator of specimen stability, which can facilitate the determination of any curatorial actions, be it treatment or storage modification.

Chapter 7.
Discussion and Conclusions

As outlined in Chapter 1 (Section 1.2), the aim of the doctoral research presented in this thesis was the development of an efficacious methodology for facilitating the determination of mineral susceptibility. This was successfully achieved via the concepts and methods discussed in the previous chapters. The Mineral Susceptibility Database (MSD; Ch. 3), the DP State Survey Method (Ch. 4), and colorimetry (Ch. 5) can be used in conjunction to identify specimen state and determine susceptibility to conditions present within the museum context. The data produced by these means in turn provides sufficient evidence for the development of hypotheses of specimen deterioration, as indicated by the formulation of the impurity hypothesis for pyrite decay (Ch. 6, Section 6.3). By being capable of untangling and clarifying the complexities of specimen deterioration, the methods presented in this thesis further advance the state-of-the-art within the heritage sector and support necessary shifts in perspective.

7.1. Advancing the State-of-the-Art

Advancements have been made on three fronts: 1.) philosophy, 2.) methods, and 3.) knowledge of mineral susceptibility. Philosophically, the concepts of damage and condition were explored and defined (Ch. 2 and 4) in order for these terms to be applied with greater consistency, regardless of the material or object type in question. Clarifying and documenting that these two concepts involve an intrinsic–extrinsic duality—that of object state and its human-ascribed uses and values (see Ch. 2, Section 2.3 and Ch. 4, Section 4.2)—was critical for establishing frameworks for the robust characterisation of state, use, and value. In particular, the Eye of Condition framework (developed in Ch. 4, Section 4.2) was proposed as a means for surveyors to assess object context and consciously identify any personal predilections they might hold.

Identifying methods for the robust characterisation of state built upon the suggestion of Strlič *et al.* (2013) of decoupling changes in state from those in value. This led to the appraisal of readily available techniques (surveying and colorimetry) and the development of quantitative and statistically rigorous methodologies. The DP State Survey Method (Ch. 4, Section 4.5), in particular, improved upon pre-existing survey methods through the removal of the primary complicating factor (condition) and simplifying the process to a series of yes-or-no questions. The DP Method has proven to be adept at characterising deterioration through the examination of visual indicators of change (Ch. 3, Section 3.3), yet becomes extremely powerful when used in conjunction with other analytical methods and associated object information (as demonstrated in Ch. 6).

Knowledge of mineral collection susceptibility has been advanced as well. As seen in Chapter 3, the MSD and the state survey of the Oxford University Museum of Natural History's (OUMNH) mineralogy collection have identified key agents of concern and the extent to which they affect mineral collections. Also detected are the current knowledge gaps, both in terms of what has yet to be adequately characterised and that which is completely unknown. But perhaps the project's most noteworthy achievement is the determination of impurities as the primary factor controlling the pyrite decay reaction within the museum setting (Ch. 6, Section 6.3). Sufficient quantitative evidence was produced to resolve the century-long pyrite problem and to make impactful suggestions for the future care of pyritic specimens and objects.

7.2. Shifting Perspectives

This project's findings have evidenced that necessary shifts in perspective must occur in order to effectively and sustainably preserve heritage collections. Common impasses stem not from an impossible task, but from using the wrong question as a foundation. The evaluation of damage and condition is a choice example. Many ask the question: "how can we measure damage/condition?" But as demonstrated in Chapters 2 and 4 (Sections 2.3 and 4.2), these concepts cannot be measured because the subjective cannot be quantified. The decoupling approach is critical for it rephrases

the question to: “which changes negatively affect the object?” This in turn allows for material changes to be quantified and for changes in value and use to be appropriately assessed.

The decoupling approach also allows for a more critical appraisal of any observed material changes. For example, cracking and efflorescence are often signs of concern, yet in certain contexts—like that of the Navajún specimens (Ch. 6, Section 6.3.1.2)—these changes could be viewed positively. Although the cracks and efflorescence observed indicate that some degree of physical change is indeed occurring to the specimen matrix, the overall reduction of moisture and salt content—both contributors to pyrite decay reactions—within the specimen will aid its longevity.

7.2.1. Specimen Storage

Perhaps related to the assumption that minerals are inherently stable (Ch. 2, Section 2.2) is the assumption that mineral specimens are generally robust. This may have led to the knock-on effect of ‘minimalistic’ storage; placing the specimens in trays with no further padding. But as found during the OUMNH survey (Ch. 3, Section 3.3), physical forces is by and large the primary agent of change affecting mineral specimens due to inadequate support. Previously at OUMNH, the practice was to place specimens in larger trays than perhaps necessary to 1.) facilitate handling and 2.) mitigate any damage to potentially present micro-minerals whilst picking up a specimen (M. Price 2022, personal communication, 22 November), as most newly identified species are not visible to the naked eye (Hazen & Ausubel 2016). However reasonable the intention, the act of storing specimens in trays too large for them without further support causes the specimens to rock and roll about as the drawer is opened. This is likely the primary cause of the cracks, breakages, crumbling, and even flaking observed across the entirety of the OUMNH systematic collection. It is also plausible that such specimen movement damages any microminerals present. Thus, the author suggests ensuring that mineral specimens are stored so they do not move when the drawer is opened. This can be most easily achieved through resting the specimen on the face

that produces the least movement (if possible), and the use of appropriately-sized trays and acid-free tissue for further support.

Related is the matter of storage conditions, in particular microenvironments. As demonstrated in the MSD (Appendix 4), minerals are susceptible to a variety of environmental conditions, many of which occur at common indoor temperatures and humidity levels. Various types of microenvironments have been employed over the centuries (Ch. 2, Table 2.3) to preserve these specimens; the most recent methods are 'Tupperware' boxes (often the *Stewart* brand) containing silica gel, and sealed bags made from barrier film containing silica gel and sometimes an oxygen scavenger (Fig. 7.1). Whilst the efficacy, practicality, and sustainability of such microenvironments are currently under debate, many fail to question whether the use of microenvironments actually solves the problem initially posed.



Figure 7.1. The two microenvironments most commonly used in mineral collections: a.) 'Tupperware' boxes, and b.) sealed bags made with barrier film. Although both require considerable space, boxes are considered more efficient as they can hold multiple specimens and more readily fit into trayed out drawers.

In the case of pyrite, the use of oxygen-free microenvironments (i.e., anoxia) is considered a means of mitigating (further) pyrite oxidation by removing moisture and oxygen from the system (Fenlon & Petrera 2019, Irving & Hadland 2019, Allington-Jones *et al.* 2020). Some consider this a worthwhile venture—despite the laundry list of drawbacks (ibid.)—for this method presently appears to be the only way to ensure specimen preservation. However, research uncovered by the author during the literature review suggests that anoxia may cause more harm than good.

Currently, the heritage sector is aware of three pyrite oxidation pathways (Howie 1992b, Newman 1998, Miles 2019):

1.) chemical (or 'molecular' due to Newman's (1998) use of the term),
2.) electro-chemical, and
3.) biotic, particularly bacterial.

In heritage literature, the first two pathways are not generally differentiated. This is reasonable given the complex nature of pyrite oxidation (Rickard 2015), and that it is very unlikely for there to be no electro-chemical component (D. Rickard 2020, personal communication, 9 March) given pyrite's electrical conductivity (Rosso *et al.* 1999b). This is the oxic pathway outlined in Chapter 2 (Section 2.8.2, Eq. 2.1). The bacterial pathway, whilst still often mentioned, has been generally ignored since the 1980s due to failed treatment attempts (see Ch. 2, Table 2.3) and the inability to produce cultures from specimens (Howie 1979a, 1992b). There is, however, another pathway that is still unknown to the heritage sector: pyrite's anoxic oxidation pathway. This is the strongest argument against storing pyrite specimens in anoxia.

Molecular oxygen—from any air, water, and or humidity present in the system—are the primary oxidants in the oxic pathway (Ch. 2, Section 2.8.2), whilst ferric iron is the primary oxidant in the anoxic pathway (Moses & Herman 1991). Ferric iron can easily be in close contact with pyrite as impurities or associated minerals (Ch. 6, Section 6.3.2) and or pre-existing surficial oxidation products (Eggleston *et al.* 1996; Guevremont *et al.* 1998a). Thus, placing any pyrite specimen in anoxia, regardless of previously known oxidation, will almost inevitably subject the specimen to oxidation by ferric iron. To make matters worse, the anoxic reaction pathway is significantly faster (Moses & Herman 1991) and more aggressive than the oxic pathway (Rickard 2015: 178):

> The production of acid from the oxidation of pyrite is quite dramatic. For every two molecules of pyrite oxidized, twice as many molecules of sulfuric acid are produced by the oxygen reaction. The oxidation of pyrite by ferric iron is even

more efficient as an acid producer. The equivalent of sixteen molecules of acid are produced for each molecule of pyrite oxidized.

Thus, having four times as much sulfuric acid in a sealed microenvironment would likely:

1.) accelerate pyrite oxidation by providing a means of ion transportation if the acid is present as a liquid on the mineral surface,

2.) oxidise and or dissolve any associated minerals, potentially "releasing other, more toxic elements like mercury and arsenic into the environment" (Rickard 2015: 178),

3.) cause dissociation via damage to labels, and

4.) compromise the barrier film, potentially increasing permeability and introducing sulfuric acid to the drawer/cabinet within which the microenvironment is being stored.

These effects have yet to be observed in pyrite specimens stored in anoxia, so it is unknown if or when they would manifest. However, the anoxic oxidation pathway and its effects pose a sufficient enough risk to warrant discontinuing the use of anoxia for pyrite preservation.

Given that microenvironments are not the cure-all they once were made out to be, perhaps it is time to change our perspective of them. Rather than solely being used to protect an object from the surrounding environment, (unconditioned) microenvironments could be implemented as a means of protecting the rest of the collection from an object. Effectively, a quarantine. This is already standard practice for radioactive specimens; they are being stored apart from the main collection because they can negatively affect the collection and its users. Anecdotal evidence further suggests that when deteriorating pyrite is removed or stored in sealed containers, change to neighbouring specimens becomes more gradual. Thus it is completely justifiable to apply such practices to particularly noxious objects, like pyrite, that pose substantial risk to other objects in the collection.

7.2.2. Accession and Deaccession

In conjunction with viewing microenvironments as object quarantines is a secondary perspective shift: foregoing an object-based approach in preference of a collection-based one.

Here, an object-based approach refers to feeling the need to preserve every single object in a collection for an indefinite period of time, regardless of the cost. Such an approach is a constant fight against entropy, and one that we will always fail to win. This is something the sector has increasingly been coming to terms with since the early 1990s, particularly in reference to the fact that an object cannot be persevered in a singular state forever (Krumbein *et al.* 1994, Appelbaum 2007). This movement away from viewing objects (and collections) as static, however, has not yet translated into viewing them as dynamic, probably because the sector is so fundamentally against the notion of change.

The dynamic approach views a collection as a system composed of objects and their surrounding environment, both in terms of materials and conditions. The individual objects and the particulars of the storage environment change with time, context, and knowledge (Ch. 4, Section 4.2). It is the caretaker's job to monitor and make any necessary adjustments to "the ecology of the collection", as Julian Carter wisely phrased it (2023, personal communication, 18 August). These adjustment include those currently practiced—such as modifying the storeroom's temperature and humidity, updating housing materials, and regular building maintenance—but also allowing objects to be more readily deaccessioned and being more selective of which are accessioned in the first place. This dynamic approach would allow for more effective use of already limited resources by prioritising the collection as a whole, and conservation treatments and strategies would be targeted for ensuring general collection preservation.

Pyrite is a particularly potent example of an object that should be more readily disposed if found to be actively deteriorating. As addressed above, once pyrite decay begins, there is not much one can do to save the specimen. Current treatments may be largely effective (Larkin 2019), but there is still the possibility that a latent reaction is

occurring. Storing the specimen in microenvironments, whilst protecting its neighbours from the decay products, only 'kicks the can down the road'. Storage in anoxia will probably make the situation even worse. In situations like these, the best question to ask would be: "how can I best use available resources to preserve the greatest number of objects?" The answer, in regards to pyrite at least, would be to dispose the deteriorating specimens because they pose more risks than benefits to the collection.

This is easier said than done for high value specimens—such as those in the Woodwardian collection—but most pyrites are only valued aesthetically and scientifically. Both of these values are usually lost once the specimen is significantly decayed. What prevents these specimens—and other unsalvageable objects—from being disposed are deaccessioning policies and paperwork. As Christian Baars confided (2023, personal communication, 14 July), it is not a matter of being hesitant of disposal, but rather a lack of time.

Due to the impurity hypothesis (Ch. 6, Section 6.3), pyrite is also an excellent example of an object that requires critical evaluation prior to accession. If a specimen from a known unstable locality enters a museum, and it holds no exceptional value (e.g., it is not from a now inaccessible locality), it would be better to not accession the specimen. It can still become a display, handling, or teaching specimen. But by being accessioned, one is imposing a level of commitment to care for an object that will ultimately produce a net loss for the museum (i.e., little is gained from accessioning the specimen, and much is lost via the resources used). Conversely, if one does decide to accession a specimen that may be a risk to the collection, or is known to require specific conditions (Baars *et al.* 2021), action can be taken immediately to mitigate any negative affects. Treatments and storage accommodations will thus be proactive rather than reactive.

7.3. Actions Currently Underway

Actions using the findings of this thesis as evidence are already underway. At NMC, plans are being made for moving parts of the mineral collection into different storerooms (J. Carter & T. Cotterell 2023, personal communication, 18 August). Firstly, species requiring moist conditions (≳ 65% relative humidity) will be moved into a pre-existing 'cave-like' (cool and damp) room in the NMC basement. Not only is this beneficial for specimens, it is also a sustainable approach to building management. Utilising such rooms for storing collections that require atypical conditions (i.e., those beyond ~20°C, 40-60% RH) would allow for space to be used more effectively and could reduce energy costs (see Ch. 2, Fig. 2.4), as these rooms would need little conditioning. Secondly, pyrites will be moved to another location and distributed about the room in a manner similar to that in place for radioactive minerals. Specimens would be spaced at a reasonable distance from each other, and there would be significant gaps between drawers in all directions. This would, in theory, facilitate air flow about the room and prevent hotspots of high sulfuric acid concentration, in turn mitigating specimen deterioration.

The colorimetric data collected during the cross-museum pyrite survey has been used by the author in collaboration with OR3D to develop PyrΔTE: an AI-based web application piloting whether AI can be used to help identify change in museum specimens. OR3D trained the algorithm with the colour and tarnish data. Two separate regressive AI were developed in Python: firstly, a linear regression model was established using the TensorFlow package, and secondly, the Keras module within TensorFlow created the neural network layers. The graphic user interface (GUI) was also created in Python using the Tkinter package. The application was then made available through this research project's website, *Reference for Mineral Care* (https://mineralcare.web.ox.ac.uk/).

PyrΔTE uses CIELAB colour data to predict the likelihood of an untrained eye to detect tarnish and to calculate the overall colour difference (ΔE*). This is especially useful for high-impurity pyrite (Ch. 6, Section 6.3.2); being able to identify tarnish prior to the emergence of visual indicators of pyrite decay is critical for swift and effective

curatorial action. PyrΔTE thus demonstrates that, with further development, similar AI tools could be created to aid identifying and treating visual and material changes to museum objects.

Lastly, the DP State Survey Method has also been applied to pyritic fossils held within two palaeontological collections in Canada, namely those at the Royal Alberta Museum and the Royal Tyrrell Museum. These surveys were performed by Alessandra Hood during her student internship, employing the same 15 DP as those used for the cross-museum pyrite survey (Ch. 4, Table 4.3 and Appendix 1). The results from these surveys are being used to determine specimen treatment and care.

7.4. Areas for Future Research

As conveyed by the language used in the above discussion, much of this project's work is generally applicable. The methods were developed with mineralogical collections, but are not confined to them. Surveys similar to the ones conducted (Ch. 3, Section 3.3 and Ch. 6) could be implemented to elucidate the reaction pathways for other minerals and materials, and to identify means of effective monitoring. As currently available portable spectrophotometers are capable of measuring the colour of opaque and metallic minerals (Ch. 5, Section 5.5), colorimetry will likely prove to be capable of monitoring light-induced colour changes and tarnish formation in a wealth of materials, including minerals, photosensitive pigments, meteorites, and metals. AI-based applications, like PyrΔTE, could also be developed to facilitate the detection of unobservable or just-noticeable changes.

For minerals specifically, research is required to address the identified gaps within the MSD. This can be achieved through adding further pre-existing literature as well as conducting experiments to quantify reaction conditions and products. The results of the cross-museum pyrite state survey (Ch. 6) and the discussion of its practical applications (Section 7.2) may lead to work:

- confirming the pyrite impurity hypothesis via imaging and chemical analysis,
- examining whether the sulfuric acid produced by pyrite decay does indeed act as a catalyst in the deterioration of neighbouring mineral specimens, and
- monitoring pyrite oxidation by ferric iron within anoxia to confirm and quantify reaction occurrence.

7.5. Conclusions

Whilst it is largely known that the information latent within museum collections can be of use to many other parties and sectors (Allmon 1994, Robb *et al.* 2013), the means of effectively extracting this information has been a significant challenge. The research presented in this thesis has demonstrated that, with the right methods, the examination of a substantive proportion of a collection is indeed feasible and does not have to be resource-intensive. Further, longstanding quandaries can readily be resolved if sufficient data is collected. It is hoped that the deterioration mechanisms of other minerals, especially photo-sensitive ones, undergo further examination, and that the resources, methods, and frameworks developed over the course of this doctoral project are readily implemented and built upon by the heritage sector at large.

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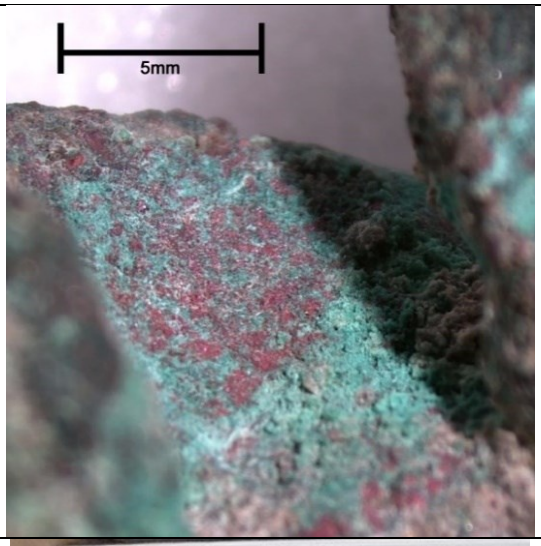
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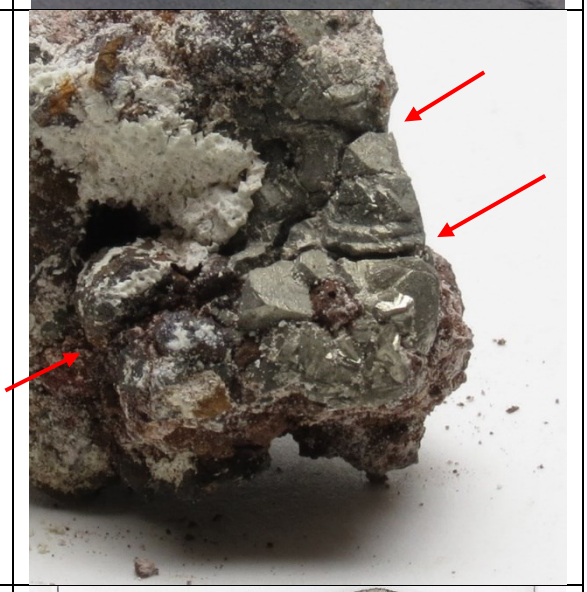
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Appendix 1.
Glossary of Deterioration Phenomena

Criteria Definition	**Example Images**
Dimpled Shallow divots in the mineral surface	
Rounded Mineral appears 'melted' with smooth edges	

<u>Corrosion</u> Voluminous amorphous products on mineral surface • May be localised or extend across a wide surface area	
<u>Tarnish</u> A coating on the mineral surface • Coating may be darker, metallic, iridescent, or different colour than the original colour of mineral	
<u>Efflorescence</u> Crystalline growth on surface and or within cracks of the mineral	

<u>Powder</u> Amorphous grit covering the mineral surface • Often comes away upon touch	
<u>Crumbling</u> Mineral falling apart into many round, distinct pieces, usually of various sizes	
<u>Flaking</u> Mineral surface removed in distinct, angular pieces • Denotes flakes free from or loosely attached to the mineral body	

<u>Breaks</u> Distinct pieces have come away from the main body • Differs from *flaking* in that the pieces are thicker and more three-dimensional • Differs from *crumbling* in that the breaks are usually clean and sharp	
<u>Cracks</u> Splits in the mineral surface • Can be of various length, widths, and depths, but does not go completely through the specimen (depth-wise)	
<u>Dull</u> Lustre of a mineral has changed or become absent (i.e., no shine) • e.g., the finish of a metallic mineral has become sub-metallic or is no longer shiny	

Dark Coloured mineral is a darker shade of that colour or black	
Pale Coloured mineral is a lighter shade of that colour or white/colourless	
Opacity Mineral has become 'clouded', translucent, or opaque	

<u>Colour Change</u> Mineral colour altered from one distinct colour to another distinct colour that is not white or black (e.g., blue to yellow), or has developed an iridescence	

Appendix 2.
SPSS Scripts

The following four scripts were used to analyse the data presented in Chapters 5 and 6. The relevant variable names were inserted into the variables fields (which have been left blank here).

Pearson's Correlation Coefficient

```
CORRELATIONS
  /VARIABLES=
  /PRINT=TWOTAIL NOSIG LNODIAG
  /MISSING=PAIRWISE.
```

Highlighting Correlation Table

```
OUTPUT MODIFY
  /REPORT PRINTREPORT=NO
  /SELECT TABLES
  /IF COMMANDS=[LAST] SUBTYPES="Correlations"
  /TABLECELLS SELECT=[CORRELATION] SELECTDIMENSION=ROWS
SELECTCONDITION="Abs(x)>=0.7"
    BACKGROUNDCOLOR=RGB(255, 255, 0) APPLYTO=CELL
  /SELECT TABLES
  /IF COMMANDS=[LAST] SUBTYPES="Correlations"
  /TABLECELLS SELECT=[SIGNIFICANCE] SELECTDIMENSION=ROWS
SELECTCONDITION="x<=0.05"
    BACKGROUNDCOLOR=RGB(255, 255, 0) APPLYTO=CELL.
```

PCA

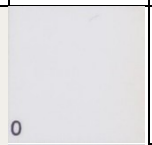
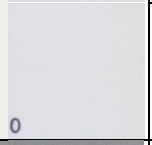
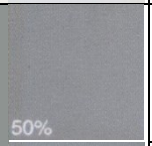
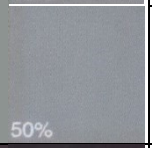
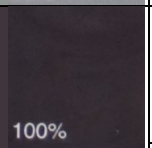
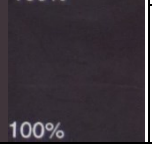
```
FACTOR
  /VARIABLES
  /MISSING LISTWISE
  /ANALYSIS
  /PRINT CORRELATION EXTRACTION ROTATION
  /FORMAT SORT BLANK(.25)
  /PLOT EIGEN ROTATION
  /CRITERIA MINEIGEN(1) ITERATE(100)
  /EXTRACTION PC
  /CRITERIA ITERATE(100) DELTA(0)
  /ROTATION OBLIMIN
  /METHOD=CORRELATION.
```

Cronbach's Alpha

```
RELIABILITY
  /VARIABLES=
  /SCALE('x') ALL
  /MODEL=ALPHA
  /STATISTICS=SCALE CORR
  /SUMMARY=TOTAL.
```

Appendix 3.
Average Sample Pseudo-object Colours

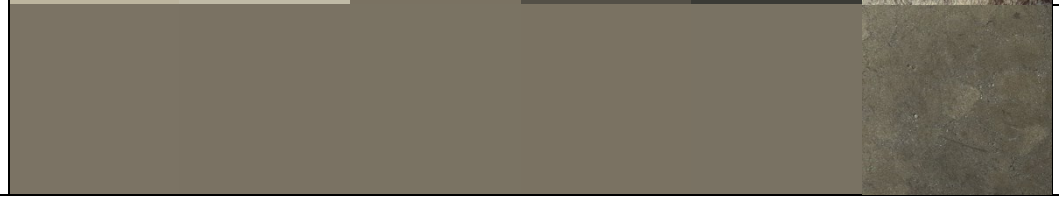
The tables below compare the average pseudo-object colours of each sample to the respective image of the sample area. All sample images were taken outdoors around 11:30 am in indirect sunlight (weather: partly cloudy, average CCT = 5625K, lux = 4825). Results of the visual assessments are also provided.

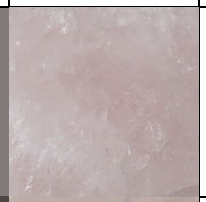
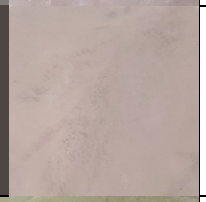
Device	Konica Minolta				Nix Pro	Image of Sample Area	Results of Visual Assessment		
Specular Component	SCI		SCE						
Aperture	SAV	MAV	SAV	MAV	MLAV		Sample	Photo	Notes
cc.1.a							Nix Pro: MLAV SCE	Konica Minolta: MAV SCE	
cc.2.a							Nix Pro: MLAV SCE	Konica Minolta: SAV SCE	
cc.1.b							Konica Minolta: MAV SCE	Nix Pro: MLAV SCE	MLAV is closer in tone to the photo
cc.2.b							Konica Minolta: MAV SCE	Nix Pro: MLAV SCE	
cc.1.c							Nix Pro: MLAV SCE	Nix Pro: MLAV SCE	
cc.2.c							Nix Pro: MLAV SCE	Nix Pro: MLAV SCE	

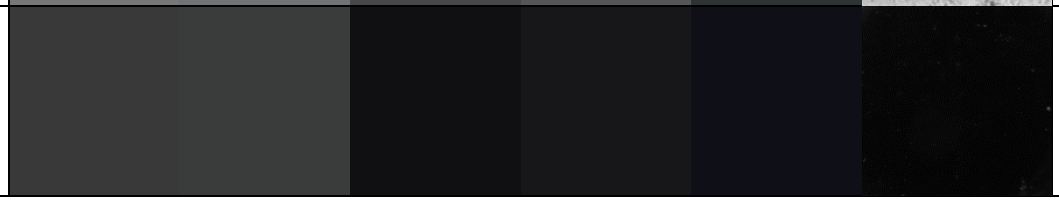
Device	Konica Minolta				Nix Pro	Image of Sample Area	Results of Visual Assessment		
Specular Component	SCI		SCE						
Aperture	SAV	MAV	SAV	MAV	MLAV		Sample	Photo	Notes
cc.1.d							Nix Pro: MLAV SCE	Konica Minolta: SAV SCE	
cc.2.d							Nix Pro: MLAV SCE	Konica Minolta: SAV SCE	
cc.1.e							Nix Pro: MLAV SCE	–	Photos very greenish; Konica Minolta colors seem more golden (reddish)
cc.2.e							Nix Pro: MLAV SCE	–	
cc.1.f							Nix Pro: MLAV SCE	Konica Minolta: MAV SCI	Pseudo-object colors & photos lack vibrancy, seem yellow-tinted
cc.2.f							Nix Pro: MLAV SCE	Konica Minolta: MAV SCI	

Device	Konica Minolta				Nix Pro	Image of Sample Area	Results of Visual Assessment		
Specular Component	SCI		SCE						
Aperture	SAV	MAV	SAV	MAV	MLAV		Sample	Photo	Notes
cc.1.g							Konica Minolta: SAV SCE	Konica Minolta: MAV SCI	Pseudo-object colors & photos lack vibrancy
cc.2.g							Konica Minolta: SAV SCE	Konica Minolta: SAV SCE	
cc.1.h							Nix Pro: MLAV SCE	Nix Pro: MLAV SCE	Near perfect match: photo, card, & MLAV color
cc.2.h							Nix Pro: MLAV SCE	Nix Pro: MLAV SCE	

Device	Konica Minolta				Nix Pro	Image of Sample Area	Results of Visual Assessment		
Specular Component	SCI		SCE						
Aperture	SAV	MAV	SAV	MAV	MLAV		Sample	Photo	Notes
m.1.r							Konica Minolta: MAV SCE	Konica Minolta: SAV SCI	Pseudo-object colours too grey, but MAV better match in lightness
m.1.t							Konica Minolta: MAV SCI	Konica Minolta: MAV SCE	MAV closer in lightness & chroma
m.2.8							Konica Minolta: MAV SCI	Konica Minolta: MAV SCI	All pseudo-object colours very off
m.2.10o							Konica Minolta: MAV SCI	Konica Minolta: MAV SCI	MAV matches better in lightness; SCI slightly better for chroma
m.2.10w							Konica Minolta: MAV SCI	Konica Minolta: MAV SCI	

Device	Konica Minolta				Nix Pro	Image of Sample Area	Results of Visual Assessment		
Specular Component	SCI		SCE						
Aperture	SAV	MAV	SAV	MAV	MLAV		Sample	Photo	Notes
m.3.19							Nix Pro: MLAV SCE	Konica Minolta: MAV SCE	Nix Pro chosen for vividness
m.3.20							Konica Minolta: MAV SCE	Konica Minolta: MAV SCE	
m.4.a							Konica Minolta: MAV SCI	Konica Minolta: MAV SCI	MAV SCI best for tone & lightness
m.4.c							Konica Minolta: SAV SCI	Konica Minolta: SAV SCI	SAV SCI closest to specular tone, & SCE MLAV best for aspecular tone
m.4.t							Konica Minolta: MAV SCI	Konica Minolta: MAV SCE	All are very close matches & are acceptable

Device	Konica Minolta				Nix Pro	Image of Sample Area	Results of Visual Assessment		
Specular Component	SCI		SCE						
Aperture	SAV	MAV	SAV	MAV	MLAV		Sample	Photo	Notes
m.5.r							Konica Minolta: MAV SCI	Konica Minolta: MAV SCE	SCI MAV has same undertones as specimen
m.5.t							Konica Minolta: MAV SCI	Konica Minolta: MAV SCI	
m.6.o							Nix Pro: MLAV SCE	Nix Pro: MLAV SCE	All are very close matches & are acceptable
m.6.r							Konica Minolta: MAV SCI	Nix Pro: MLAV SCE	
m.7							Konica Minolta: MAV SCE	Nix Pro: MLAV SCE	

Device	Konica Minolta				Nix Pro	Image of Sample Area	Results of Visual Assessment		
Specular Component	SCI		SCE						
Aperture	SAV	MAV	SAV	MAV	MLAV		Sample	Photo	Notes
m.8							Konica Minolta: MAV SCE	Konica Minolta: SAV SCI	MAV SCE for aspecular tone, SAV SCI for specular tone
m.9							Nix Pro: MLAV SCE	Konica Minolta: SAV SCE	