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## Caring for geological collections: unresolved questions

Kathryn Royce<sup>1\*</sup> and Christian Baars<sup>2</sup>

<sup>1</sup>*School of Geography and the Environment, University of Oxford, South Parks Road, Oxford OX1 3QY, UK*

<sup>2</sup>*National Museums Liverpool, Conservation Centre, Midland Railway Building, 1 Peter Street, Liverpool L1 6BL, UK; previous address: National Museum Cardiff, Cathays Park, Cardiff CF10 3NP*

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\*Corresponding author: [kathryn.royce@ouce.ox.ac.uk](mailto:kathryn.royce@ouce.ox.ac.uk)

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### Abstract

Caring for geological collections is neither as simple nor as straightforward as widely perceived. Several hundred mineral species are vulnerable to the effects of moisture, temperature, air pollutants, and light. Some species undergo significant changes when exposed to minor deviations from their stability limits. One example—well documented by geochemists, engineers, and conservators alike—is iron sulfide oxidation; whilst reaction products and pathways are well characterised, the precise causes of deterioration of iron sulfide species within museum collections remain largely elusive. There is even less knowledge about the stability of many other susceptible mineral species—such as realgar or lansfordite—within the museum sector. Published guidelines for managing geological materials are often contradictory and evidence the lack of applicable information on optimal storage conditions and suitable conservation actions. In addition, currently available condition assessment methodologies are not always appropriate for the routine monitoring of large collections, and the results of such surveys are not necessarily reproducible. A new approach is required to answer the numerous questions regarding the care of geological collections, and to establish evidence-based conservation guidance, both of which requires substantial research. This paper introduces a framework for a research agenda that would underpin a robust approach to establish satisfactory conservation practices. This includes defining the extent at which material change constitutes damage, categorising damage, developing a protocol for routine condition assessments, determining adequate storage environments, and rigorously testing the suitability of conservation treatments presently available.

**Keywords:** geological collections, stability limits, minerals, environmental conditions, conservation

### Introduction

The chemical and physical properties of each species of rock, mineral, and fossil are unique and determine the material's stability under various environmental conditions. Under typical museum storage and display environments many specimens in geological collections may be unstable.

Unsuitable storage conditions may have a number of deleterious effects (Table 1), which can result in damage, dissociation from contextual information (for example, damaged or corroded labels), or even complete specimen loss.



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Agent of Deterioration	Potential Impact on Specimens	Mineral Examples	Citation
Temperature	Decrepitation	Sulfur	O'Donoghue, 1983
	Dissociation	Nesquehonite	Robie and Hemingway, 1972
	Phase Change	Tin	Ojima <i>et al.</i> , 1993; Zeng <i>et al.</i> , 2004
Relative Humidity	Carbonation	Massicot	Aze <i>et al.</i> , 2007
	Corrosion/Oxidation	Pyrite	Howie, 1992b; Guevremont <i>et al.</i> , 1998a; Rosso <i>et al.</i> , 1999; Jerz and Rimstidt, 2004
	Dehydration	Sulfates such as chalcantite & melanterite	Waller, 1992; Chou <i>et al.</i> , 2002
	Deliquescence		
	Efflorescence		
	Hydration	Clay minerals such as montmorillonite & sepiolite	Howie, 1984
Water film formation	Calcite	Stipp <i>et al.</i> , 1996; Al-Hosney and Grassian 2004, 2005; Usher <i>et al.</i> , 2007	
Light	Darkening	Rutile	Nassau, 1992
	Fading	Quartz varieties, including amethyst	Currier, 1985; Kane, 1985; King, 1985; Nassau, 1992; Rossman, 1994
	Loss of colour/fluorescence	Fluorite	Nassau, 1992; King, 1985
	Photodecomposition	Silver halides, including chlorargyrite, bromargyrite, iodargyrite, & miersite	Nassau, 1992
	Photo-oxidation	Proustite	Howie, 1992c; Nassau, 1992; King, 1983; King, 1985
	Structural Alteration	Realgar	Dougllass <i>et al.</i> , 1992; Kyono <i>et al.</i> , 2005; Kyono, 2007; Jovanovski and Makreski, 2020
Pollutants	Alteration	Hematite & goethite	Drosdoff and Truog, 1935
	Corrosion	Metals such as lead & copper	Scott, 1990; Tétreault <i>et al.</i> , 1998; Raychaudhuri and Brimblecombe, 2000; Scott, 2000; Tétreault <i>et al.</i> , 2003
	Efflorescence	Calcite	Krueger, 2003; Al-Hosney and Grassian, 2004, 2005; Al-Hosney <i>et al.</i> , 2005; Usher <i>et al.</i> , 2007; Prince <i>et al.</i> , 2008

Table 1. Some effects of different agents of deterioration on mineral specimens. For further effects, please see Howie 1992a and Child, 1994a.

This paper provides a brief overview of the current knowledge available regarding the susceptibilities of geological materials, chiefly minerals, and introduces a research agenda devised to address some current knowledge gaps. Further thoughts on the topical unresolved issues surrounding the conservation of geological collections were published by Baars and Horak (2018).

### Vulnerability and instability

Of the 5,673 known mineral species (International Mineralogical Association, 2021), at least 10% are susceptible to damage under museum conditions (Howie, 1984; Walker, 1992). Deterioration may present itself as physical change, yet chemical changes are equally possible. Additionally, some specimens may seem unaffected, but closer inspection and analysis may reveal that unwanted changes have taken place.

## Temperature

A number of polyhydrated mineral species dissociate into a lower-hydrate mineral and water vapour, regardless of the relative humidity (RH) level, if exposed to sufficiently high temperatures. This process results in an irreversible change to the crystalline structure. One such example (Figure 1) is lansfordite ( $\text{MgCO}_3 \cdot 5\text{H}_2\text{O}$ ) which dehydrates to nesquehonite ( $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ ) if temperatures are above approximately  $10^\circ\text{C}$ , even under 100% RH (Waller, 1992). Other examples of minerals with temperature-dependant changes into lower hydrates include epsomite, natron, and nitrocalcite (Waller, 1992).

Rapid changes in temperature can also lead to fracture within specimens (Child, 1994a; Stanley, 2004). Differential temperatures between a specimen's interior and exterior result in stresses which may be released through cracking or spalling (Walker, 1992; Horak, 1994). Waller (1992) lists further physical characteristics that increase the likelihood of fracture, including easy cleavage and high brittleness. Some brittle minerals include carrollite, polybasite, sartorite, colemanite, and gaylussite.

## Relative humidity

The effects of low, high, or fluctuating relative humidity may produce a variety of unwanted changes in minerals, such as alterations in hydration state, efflorescence, deliquescence, and oxidation. Some polyhydrated mineral species, such as melanterite and other sulfates, may Dehydrate - that is, move from a higher hydration

state to a lower one - often producing a powdery efflorescence on the mineral surface (Waller, 1992). Not only can dehydration change a specimen's chemical composition, but the loss of structural water can lead to shrinkage, fracture, and even disintegration (Child, 1994b).

The migration of soluble salts from the interior of a porous object to its surface is also a form of efflorescence. This type of efflorescence has been documented to affect archaeological material (Wheeler and Wypyski, 1993) and building stone (Franzen and Mirwald, 2009), yet can also affect porous minerals such as turquoise, chalcedony, agate, and clay minerals. Salt migration occurs during cycles of fluctuating RH. When the humidity is above the salt deliquescence point, it absorbs atmospheric moisture and enters solution. During this liquid phase, the salt migrates to areas of lower salt concentration, such as the object's (near) surface. Once the RH drops below the salt's deliquescence point, the salt recrystallises (Howie, 1979; Walker, 1992).

Deliquescence occurs when a substance absorbs water from the atmosphere and subsequently dissolves into a solution (Brunton *et al.*, 1984; Erhardt and Mecklenburg, 1994). Halite ( $\text{NaCl}$ ) is a prime example, entering solution at approximately 75% RH (Erhardt and Mecklenburg, 1994). When deliquescent conditions are temporary, the specimen may slump, round (Figure 2), or flatten whilst in a semi-liquid phase (Waller, 1992). But if permanent, the deliquescent mineral will cease to exist and adopt a liquid form.

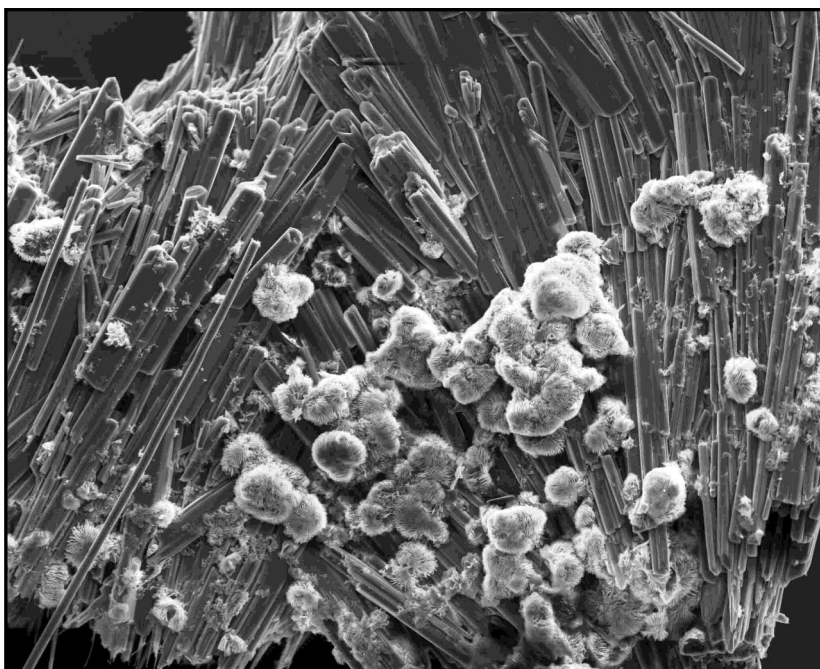


Figure 1. Electron micrograph of prismatic nesquehonite pseudomorphs after lansfordite (needles) and feathery hydromagnesite (globules). Image courtesy of Tom Cotterell, National Museum Cardiff.



Figure 2. Halite specimen which was subject to repeated cycles of high and low relative humidity, consequently partly deliquesced and now with rounded edges. Length of specimen: ca. 65mm. Image National Museum Cardiff.

### Example: Pyrite

Pyrite is found in many rock types (Kullerud and Yoder, 1959; Howie, 1992b; Larkin, 2011) and is the most abundant metal sulfide on earth's surface (Kullerud and Yoder, 1959; Lowson, 1982; Eggleston *et al.*, 1996; Guevremont *et al.*, 1998; Rimstidt and Vaughan, 2003; Dos Santos *et al.*, 2016; Miles, 2019). Due to its abundance, pyrite is ubiquitous in geological collections as mineral specimens and as inclusions in rocks and fossils. In its various forms, pyrite is notoriously unstable, and its oxidation is the most commonly documented mineral deterioration process in museum collections.

A simplified description of the pyrite decay reaction is the oxidation of sulfide to sulfate in the presence of water and oxygen (Lowson, 1982; Guevremont *et al.*, 1998; Rosso *et al.*, 1999; Rimstidt and Vaughan, 2003). Oxidation rates may accelerate

with increasing RH and surface area (Howie, 1992b; Larkin, 2011; Caracanhas Cavallari *et al.*, 2014). Various sulfates may be formed (melanterite, copiapite, jarosite, gypsum, etc.) depending on specimen composition and moisture availability (Howie, 1992b; Jerz and Rimstidt, 2004; Rouchon *et al.*, 2004). The formation of these oxidation products is frequently associated with a volume expansion (q.v. Wiesse *et al.*, 1987; Howie, 1992b; Jerz and Rimstidt, 2004), inducing significant stresses within the surrounding material. These stresses are released through cracking and spalling (Figure 3), and may result in disintegration if deterioration is sufficiently severe (Wiese *et al.*, 1987; Howie, 1992b; Blount, 1993; Jerz and Rimstidt, 2004; Larkin, 2011; Miles, 2019). In addition, pyrite deterioration also produces sulfuric acid, which may damage other minerals, labels (Figure 3), and storage or display materials (Howie, 1992b; Larkin, 2011; Miles, 2019).

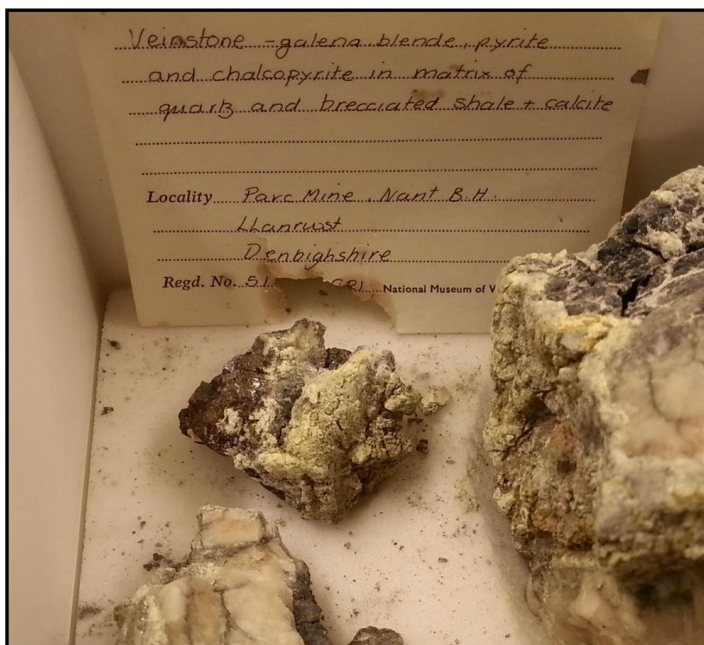


Figure 3. Image of a veinstone specimen affected by pyrite decay. Part of the specimen has spalled off. All parts feature characteristic yellow and white sulfate efflorescence. Also note the 'scorching' of the label caused by sulfuric acid, which has defaced the accession number, potentially resulting in dissociation of specimen and contextual information. Image National Museum Cardiff.

## Light

Exposure of some mineral species to light may cause colour change or loss, or activate and accelerate reactions with other decay agents (Nassau, 1992). This sensitivity can be inherent to the mineral or be caused by the presence of elemental impurities or substitutions (e.g. cinnabar). Some colour changes may be reversible upon removal of the light source or through irradiation (Nassau, 1992; Horak, 1994), and usually do not alter the physical or chemical properties of the specimen. This is true for a number of quartz varieties (Rossmann, 1994). However, light may cause chemical decomposition via the transition of one mineral into another - for example, realgar to pararealgar (Brunton *et al.*, 1984; Nassau, 1992) - or liberation of volatile elements, such as silver or mercury (Howie, 1992a; Nassau, 1992).

## Pollutants

Atmospheric pollutants are unwanted gases or particulates that cause or accelerate deterioration. Internal sources of these pollutants include human activity, display and storage materials, and sometimes even geological specimens (Waller *et al.*, 2000; Eggert *et al.*, 2004; Stanley, 2004; Grzywacz, 2006). Some minerals may release sulfur, silver, copper, or mercury as volatile decay products (Howie, 1992a; Waller *et al.*, 2000). A well-known example of this is sulfide minerals, such as pyrite, which may release volatile sulfur acids upon oxidation (Howie, 1979b; Waller *et al.*, 2000; Lussier and Smith, 2007) that may damage adjacent minerals and materials (Waller *et al.*, 2000).

### Example: Carboxylic Acids

Carboxylic acids (formic and acetic acids, formaldehyde, and acetaldehyde) are emitted from all wood and wood products, some adhesives, and common housing materials used for the display and storage of collections (Waller *et al.*, 2000; Grzywacz, 2006). These acids affect some metals (Tétreault *et al.*, 1998; Raychaudhuri and Brimblecombe, 2000; Tétreault *et al.*, 2003), and are documented to react with calcareous materials, such as ceramics, shells, and stone (Tennent and Baird, 1985; Child, 1994b; Waller *et al.*, 2000; Caracanhas Caallari *et al.*, 2014). This reaction, known as 'Byne's disease', occurs when calcareous material reacts with acetic or formic acid to produce white or grey efflorescent calcium acetate or formate salts (Fig. 4) on the specimen's surface (Tennent and Baird, 1985; Waller *et al.*, 2000; Caracanhas Cavallari *et al.*, 2014). As the relative humidity increases, atmospheric moisture

can condense to form a layer of liquid water on the object's surface and penetrate porous materials, allowing for reactions to occur within the matrix. Salt crystallization within the specimen may cause volumetric expansion (Caracanhas Cavallari *et al.*, 2014), often resulting in the fracture (Figure 4) and decrepitation of the specimen.

## Research agenda

Pyrite decay has been recorded as a problem for more than one hundred years (Parsons, 1922; Bannister, 1937; Torrens, 1977; Lowson, 1982). Its reputation stems not just from damaged museum specimens and collections, but also environmental effects through its role in acid mine drainage (Bonnissel-Gissingner *et al.*, 1998, Bigham and Nordstrom, 2000, Frost *et al.*, 2006, Qian *et al.*, 2017). Yet despite numerous - mainly observational - studies on pyrite decay, few publications address the initial catalyst and subsequent decay mechanisms in non-aqueous, relatively cool and dry environments such as those within museums.

Despite these gaps in knowledge, pyrite remains the best studied mineral. Many other environmentally susceptible mineral species have not been studied at all in relation to museum storage. It may be possible to glean potential conservation insights from the results of some stone, metal, and pigment deterioration studies (such as Scott, 1990; Scott, 2000; Cole *et al.*, 2004;

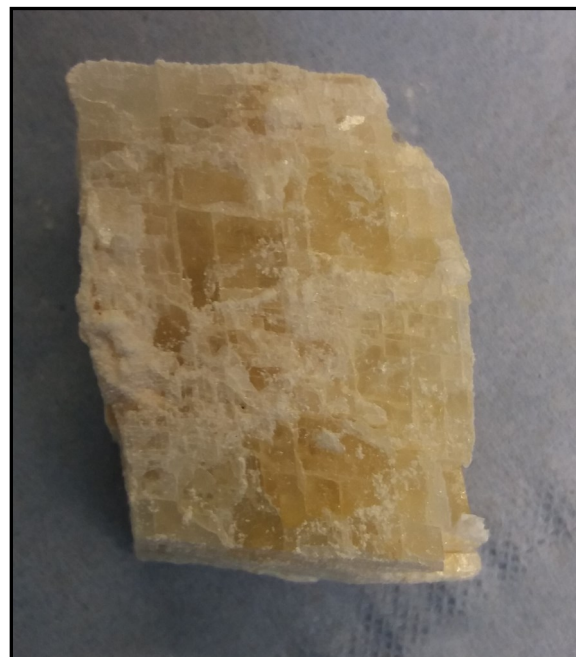


Figure 4. A calcite ( $\text{CaCO}_3$ ) sample displaying spalling, cracking, and efflorescence following exposure to acetic acid within severe accelerated aging conditions.

Lussier and Smith, 2007), but such research is insufficient to fully resolve the difficulties posed by unstable geological specimens. The lack of published studies regarding the instability of geological materials reflects the state of knowledge concerning the care of geological collections more generally and has hindered the development of appropriate collection care strategies.

It is evident that we require a better understanding of the collection care needs of geological collections. As such, we have begun a four-year research project with the aim of addressing current knowledge gaps through identifying:

- which minerals are vulnerable to museum environments,
- the stability parameters for these mineral species, and
- potential preventive measures to ensure mineral longevity in museum collections.

To achieve this, it is important that we first define what is meant by ‘damage’. Without a clear definition, it is impossible to draw the line between acceptable and unacceptable change. Consequently, it would be impossible to meaningfully measure whether change has indeed occurred without first determining what constitutes a significant change. Secondly, the efficacy of both interventive and preventive treatments require assessment. Are current methods effective and appropriate? Thirdly, condition and risk assessments are to be re-evaluated, along with current collection care standards, in order to better fulfil the needs of

the collections and their caretakers.

### Defining damage

‘Damage’ is a complex term in heritage and museum conservation. This is because it encompasses two aspects: the material and the intangible. The former is change to intrinsic properties - or the physical state - of an object (Ashley-Smith, 1995), which is often quantitatively perceptible and measurable. The latter regards perceived changes in value and use; extrinsic concepts applied to an object by its stakeholders (Ashley-Smith, 1999; Appelbaum, 2007).

To best embrace these two aspects, ‘damage’ may be defined as unacceptable degradation. The inclusion of the word ‘unacceptable’ (or ‘undesirable’; Ashley-Smith 1995) acknowledges that there could be an acceptable amount of change that can occur before value is negatively affected (Appelbaum, 2007; Strlič *et al.*, 2013). It is important to determine what constitutes unacceptable change in order to define appropriate conditions and suggest when intervention and treatment becomes necessary (cf. Baars and Horak, 2018). One way to address this is a proposed ‘plot of total damage’ (Figure 5); a hypothetical solution requiring future exploration. Reflecting the above definition of damage, the ‘plot of total damage’ embraces both the quantitative and qualitative aspects of damage, graphically depicting the magnitude and perception of change that has occurred with 0-100 scales for each axis.

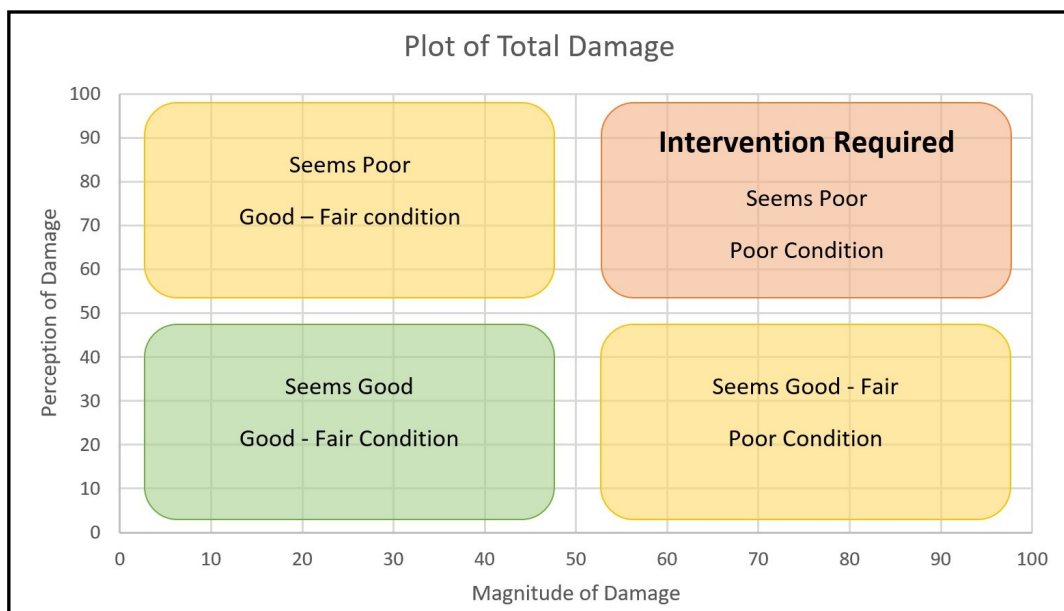


Figure 5. The ‘Plot of Total Damage’ - a graphic depiction of the proposed relationship between perceived and measured damage. Categories are roughly assigned to quadrants, but the actual thresholds have yet to be determined and may lie elsewhere on the plane.

The magnitude of change would be determined by the extent of change that has occurred to a specimen, identified by the qualitative, analytical study of the specimen's chemical, physical, and optical properties. Potential analytical techniques include:

- X-ray diffraction (XRD)
- Fourier transform infrared spectroscopy (FT-IR)
- Scanning electron microscopy (SEM) with energy dispersive x-ray analysis (EDX)
- Raman spectroscopy
- 3D imaging and reconstruction
- X-ray absorption near edge structure (XANES)

Of course, it is unrealistic to assume that all, if any, of the techniques listed above are available to the majority of museums. Even if they were, capacity limitations may preclude each new specimen being examined in detail. This is a very practical problem for the majority of museums and potentially affects the accuracy of species identification, which is crucial to determine the most appropriate storage conditions.

As for the other axis, damage perception may be defined more closely through discussion of common uses of geological collections, identifying how they are valued by different users, and at what degree of change a specimen become unusable. User involvement is crucial to determine intervention thresholds, as the value of a specimen may be considered to lie in contextual information (i.e. collector, locality, collection date) rather than the specimen itself (Allmon, 1994, Baars, 2010, Robb *et al.*, 2013). This is an area which requires further investigation, perhaps at a larger scale than previously studied (cf. Robb *et al.*, 2013).

With the two axes of the damage plot defined, it should then be possible to map the total damage of specimens or collections. If the total damage plot lies above the threshold of acceptability, intervention would be required. The current thinking is that this graph could assist in decision making and may lead to objective choices on intervention and prioritisation of treatments.

### **Condition surveys and risk assessments**

A condition survey is an important collection management tool used to develop strategies and measures to preserve collections. It acts as the basis for recommending preventive conservation, maintenance, and immediate repairs. Routine surveys of collections for damage can only be undertaken if a consensus exists on observable damage indicators. Pyrite decay, for example,

appears to manifest itself in tarnish, cracking, sulfurous odour, and efflorescence. If it can be proven that pyrite decay follows a sequence of changes that always starts with tarnish, followed by cracking and later by efflorescence, it would be possible to establish 'tarnish' as an early indicator of change. The certainty of tarnish being followed by further signs of damage would then trigger a response by the conservator or curator to intervene and undertake steps to prevent any further changes to the specimen. This relationship is currently not established for most minerals (Baars and Horak, 2018).

At present, condition surveys of geological collections rely heavily on non-objective methods, such as the visual examination of specimens by an experienced curator or conservator. The results of such assessments are subjective and therefore not necessarily comparable in time nor reproducible, even if undertaken by the same person, and less so across collections and museums if undertaken by different people (cf. 'intersurveyor differences' in Taylor, 2005). Focussing on chemical, physical, and optical changes to specimens - such as the presence and or absence of oxidation, hydration, or dehydration products that could be analysed non-invasively and in situ – would result in more objective determination of changes. Naturally, the technologies that enable such analyses would need to be affordable and easy to use, and accessible even to museums with limited specialist technical expertise.

It is, of course, impossible to determine retrospectively whether a particular specimen is damaged because it reacted in a linear fashion over a period of time to something, such as conditions of permanently elevated RH, or whether it responded catastrophically to a single short-term incident, such as a sudden and large fluctuation in RH. Therefore, a more nuanced approach is required to condition checking which would include the assessment of past storage conditions, where such data exist. Risk assessments can help categorise the vulnerability of parts of a collection and help target conservation resources most effectively. Whilst condition surveys provide information on a collection's current condition, risk assessments add predictive aspects regarding the collection's potential for deterioration. Probable causes of damage identified by a condition survey can be linked to the agents of deterioration identified by a risk assessment. Combining these two complementary assessments is a powerful tool to clarify priorities for the collection's management goals (Taylor, 2005; Fry *et al.*, 2007).



## Conservation treatments

Whilst recommendations exist for strategies of how to protect vulnerable materials including minerals (Larkin, 2011), a systematic evaluation of the long-term success of packaging these materials in microenvironments is still outstanding. There is presently only circumstantial evidence (Fenlon and Petrera, 2019, Irving and Hadland, 2019) that the use of microenvironments in geological collections has brought about improvements in their long-term preservation. Contrastingly, there is some evidence that specimens sealed in microenvironments using barrier films with low gas permeability may suffer accelerated, sometimes catastrophic, damage compared to similar specimens stored in the same store but under ambient conditions (Tom Cotterell pers. comm. 2016).

## Guidelines and standards

The aim of researching mineral deterioration is to establish standards that best reflect the needs of geological collections to increase their longevity and aid conservation measures. This is achieved through clear and specific recommended conditions that are tailored to each species. Guidelines for the care of museum objects almost always include recommended conditions specific to material type, such as paper, metals, or photographs (PASI98: 2012). Just as various types of photographs are stated to have their own ideal conditions, so do geological materials. This has been acknowledged to an extent in Appendix E of the 'Standards in the Museum Care of Geological Collections' (Stanley, 2004), dividing the RH and temperature recommendations by material type. While the table references some notable works (i.e. Waller, 1992, Shelton and Johnson, 1995), its brevity amplifies the lack of research. Only four categories of specimens are suggested: 'general', 'sensitive', 'pyrites and marcasites', and 'sub-fossil bone, tusks, teeth, fossils with shale or clay matrix'. These categories do not account for the complexity of geological materials and their requirements, as highlighted throughout 'The Care and Conservation of Geological Material' (Howie, 1992b), and are therefore insufficient. Additional guidelines were reviewed by Baars & Horak (2018) who concluded that addressing open questions in relation to the conservation of geological questions must result in updated sector guidance.

## Conclusions

Caring for geological collections is neither as simple nor as straightforward as widely perceived. Geological materials are by no means collectively stable under typical museum storage and display

conditions. At least 10% of known mineral species are vulnerable to environmental conditions (Howie, 1984, Waller, 1992), some even undergoing significant changes if conditions deviate from their stability limits. While pyrite and other sulfur mineral deterioration have been described in multiple case studies, the empirical research is still limited in scope and little published work can be directly applied to museum specimens. Many other vulnerable mineral species have yet to receive quantitative assessment of their stability parameters in the context of museum collections. Published guidelines for the management of geological materials are sparse and insufficient. Experimental investigations of decay mechanisms and environmental thresholds are needed to rectify this. This involves defining damage and how to assess and measure it, and evaluating conservation treatments. Lastly, conservation guidelines and standards need to be updated to reflect best practice based on comprehensive research. This is an undertaking that is likely to take a considerable amount of time and resources, but is necessary to ensure important improvements in the care and conservation of geological collections.

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