Patinated glass from Cossack, Western Australia

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Abstract

The weathering of anthropogenic glass buried in a refuse site for 70–100 years in calcareous quartz sand at Cossack, Western Australia, in a tropical arid climate, has produced a patina (a thinly-laminated encrustation on the glass), some 6–100 μm thick. The patina was studied by Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS), and X-Ray Diffractometry (XRD) to ascertain its structure and chemistry. In contrast to the structureless glass, SEM shows the patina to be comprised of micro-structures of planar to undulating lamination, micro-unconformities, and micro-cavities. The relationship of patina to parent glass shows it to be invasive (corrosive) into the glass, producing pitting along its contact, indicating dissolution, with the patina accreting at the expense of the (metastable) glass. The flatness of the upper surface of one sample of patina suggests little upward accretion. The locally-undulating upper surface of the other samples of patina, and the mosaic nature of the crust suggest there has been at least some outward (upwards) accretion. EDS shows the glass to be mainly Si, Ca, and Na, and the patina to be dominated by Si and generally depleted of Na. The patina is enriched in Ca, and this is interpreted to be exogenically derived from the surrounding calcareous quartz sand. There also appears to be enrichment of Fe, Al, and K in the patina, derived exogenically from the surrounding sand and dust. XRD shows calcite and aragonite in the patina. The patina on the glass from Cossack appears to involve solution and precipitation, vadose-zone illuviation, and accretion. There is solution of the parent glass, precipitation of silica as laminae in the patina, solution and precipitation of carbonate minerals, and solution of earlier-formed patina. In an environment where the pellicular water alternates between carbonate dissolving (and silica precipitating) and carbonate precipitating (and silica dissolving), carbonate minerals within the laminae of the patina, precipitated during the evaporation phase of any remaining pellicular water during the hot summer, is dissolved during the wet season to leave intra-patina cavities. Glass elsewhere in different environments globally show differences in style of weathering in terms of structures and lamination compared to the Cossack samples, indicating that it is probable that the environment of weathering influences the weathering micro-processes and hence result in different types of micro-structures and mineralogy in the weathering of glass and formation of patina.

Keywords: patina, glass, weathering, corrosion, Cossack, Western Australia.

Introduction

The weathering of glass is a phenomenon which has attracted the attention of industrial chemists, conservators, museum conservators, and archaeologists. It has been the subject of a number of studies into the effects that humid atmosphere (Newton 1976; Schreiner *et al.* 1999; Garcia-Valles *et al.* 2003; Fearn *et al.* 2004), seawater and sea-bed sediments (Weier 1973; Cox & Ford 1989; Brzezinski *et al.* 2003), soil (Brewster 1863; Brill 1961; Brill & Hood 1961), and groundwater (Cox & Ford 1993) have on glass.

The weathering of glass is dependent upon the composition of the glass itself, the nature of the surface of the glass, the surface area exposed (Frank 1982), and aspects of the environment (*e.g.,* the pH of the attacking solution, and temperature which act upon the glass: Newton 1971; Cox & Ford 1993). Weathering effects and products include: iridescence (Brewster 1863; Guillot

1934; Vader & Murray 1975; Pollard & Heron 1996); crusts (Newton 1971); leached layers (Schreiner *et al.* 1999); pits [surface pitting, this paper] (Maloney 1968; Garcia-Valles *et al.* 2003; Watkinson *et al.* 2005), plugs (Watkinson *et al.* 2005); crizells and dulling (Frank 1982; Fearn *et al.* 2004); and patinas (Garcia-Valles *et al.* 2003; this study). Weathered glass may be found in a variety of locations and environments: *in situ* (*e.g.,* medieval window glass in monasteries and cathedrals in Europe); in the marine environment (*e.g.,* glass artefacts from shipwrecks); in historic refuse sites in humid climates (*e.g.,* glass from the cullet heap at Bagot's Park, Staffordshire, England [Newton 1976]); and in historic refuse sites in arid climates (*e.g.,* flat glass and bottle glass from Cossack, Western Australia, this study).

The study of the weathering of glass is important for a number of reasons. Firstly, with the prolific use of glass in architecture in many polluted cities, its weathering is of concern as it affects the clarity and integrity of the glass. Secondly, glass has many applications in industry, one of the most important being the confining or storing of toxic waste products, including nuclear waste, in

silicate glass matrices (Sterpenich & Libourel 2001), and how glass responds hydrochemically to fluids with which it is in contact is important in waste management. Thirdly, characterising glass decay that affects the stained-glass windows of centuries-old monasteries and cathedrals assists conservators whose aim it is to understand the processes of glass decay, and to restore and preserve such windows. Lastly, in the archaeological context, researchers have noted weathered surfaces on glass artefacts which, for instance, have been found in burial sites and in the remains of ancient cities, and have suggested its use for dating. In a field where absolute dating of glass artefacts at present is not possible, some researchers believe that weathering of glass could prove to be a dating method for some ancient glass (*e.g.,* the number of layers often found in any patina on glass being used in much the same way that tree rings are used to date wood [Brill 1961; Brill & Hood 1961]).

One of the products of weathering is patina, which is any fine layer or encrustation, usually laminated, on the surface of rock or other material (Bates & Jackson 1987). The term is also used with reference to the oxidation of metals such as bronze or copper, as well as for the layer on rock surfaces in arid regions (*e.g.,* "desert varnish", *cf.* Bates & Jackson 1987; Jackson 1997). While various terms have been applied to the products of weathering or corrosion products on the surface of glass (*e.g.,* "crust" [Newton 1971; Cox & Ford 1993]; "weathered crust", or "weathering crust" [Brill 1961; Brill & Hood 1961; Newton 1976; Cox & Ford 1993; Schreiner *et al.* 1996]; "corrosion crust" [Brill & Hood 1961; Cox & Ford 1989]; encrustations), the term patina was first applied to the weathering crust on glass by Garcia-Valles *et al.* (2003).

Definitions of the term "patina" vary, but there is a general consensus that it is any fine layer or encrustation on a given surface (Fowler & Fowler 1969; Wilkes & Krebs 1982).

Use of the term "weathering" or "weathered" for the altered surface of glass, for any crusts developed on glass, and for the development of the patina on glass at Cossack is only justified if the encrustations can be shown to be (at least in part) an alteration product of the parent glass and not merely a micro-sedimentary feature wholly accretionary on its surface (such as for desert varnish as suggested by Garvie *et al.* 2008; or similar to diagenetic or pedogenic accretionary features such as the laminae of calcrete ooids, other soil ooids, or ironstone pisolites; see Figure 7 in Read 1974, and Plates 73 and 81 in Brewer & Sleeman 1988). As will be shown later, that while there has been accretion of laminae in the "encrustations" on the glass from Cossack, there also has been corrosion and alteration of the parent glass, with remobilisation of Si and Na from the parent glass, which warrants the use of the terms "weathering" or "weathered". However, the "encrustations", as will be interpreted later, may be a complex product involving *in situ* alteration as well as accretion of laminae deriving from endogenic and exogenic sources. For this reason, for the glass from Cossack, the term "weathering" alone does not describe the processes that produce exogenic accretionary laminae, and the term "micro-sedimentation", if it were to be applied, also does not describe the processes that involve corrosion and the

invasive alteration of the parent glass. Both processes are occurring, and therefore the term "patina" is used to refer to both the weathering products and micro-accretionary products developed on the glass from Cossack, Western Australia. Also, given the literature review above, use of the term "patina" in this study to refer to the laminated crust formed by weathering of glass at Cossack in Western Australia is appropriate, since it is both an encrustation and a product of weathering.

This study examines the patina on flat and bottle glass from Cossack, to ascertain the nature of the patina, and the potential source of the components of the patina (that is, whether it derives from the corrosion and reprecipitation of the primary material, and hence is endogenic, or has formed from an external source, *i.e.,* it is exogenic). To date, as noted earlier, much of the research into the weathering of glass has been undertaken in Europe and the United States of America and, in fact, much of the research in the last twenty to thirty years has focussed on the industrial applications of glass and the problems caused by corrosion of glass in that context. This study of the weathering of glass from Cossack is the first of its kind in Australia, and it contrasts with the weathering of glass described elsewhere (in submarine environments, buried in submarine sediments, buried in fresh groundwater environments, or exposed to humid atmosphere) because it is buried in a calcareous quartz sand located in a tropical arid environment.

The glass used in this study, which was exposed to seasonal precipitation as the main agent of weathering, was retrieved from a refuse site near the town of Cossack. Using Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS), and X-Ray Diffractometry (XRD), the patina on the glass was analysed to ascertain its structure and chemistry, and to determine the effects of short-term burial (70–100 years) on the primary glass material in a tropical arid coastal environment in a carbonate quartz sand, and its exposure to seasonal precipitation.

Review of previous research on weathered glass

There has been a focus by other researchers on the depletion of the principal constituents of glass as a result of weathering, and on the species of minerals in the patina which are of exogenic origin. In this review, the various types of weathered glass are described in terms of type of glass, the setting of the weathered glass (*viz.,* whether in groundwater, sea water, or exposed to air), and weathering products.

The corrosion of glass has been documented since the 17th Century especially in Europe and the United States of America (Fearn *et al.* 2004). Some of the earliest research was carried out by Brewster who, in 1863, studied the diffraction effects (iridescence) arising from thin layers in a weathered crust on glass from the ancient city of Ninevah, located on the eastern bank of the Tigris River in Iraq (formerly Assyria). Newton (1971) cites Brewster's contemporary, Hausmann who, in 1856, conducted quantitative analyses of weathered crusts of

the original glass from Ninevah and concluded that the crust was hydrated and that the alkalis, which had been essential ingredients in the glass, had been replaced by water, and that other metals such as iron, calcium and magnesium had been picked up from the environment.

A century later, Brill (1961) also focussed on the layers (laminae) in weathering crusts on ancient glass from Sardis, Turkey (buried sometime between the late 3rd century and the early 7th century), postulating that the laminae reflected periodic or cyclic change (such as seasonal variations in temperature or alternating wet and dry seasons) which were imposed during the long time of exposure (Brill 1961; Brill & Hood 1961). Brill (1961) also proposed that dating of glass artefacts could be achieved by counting the laminae of the weathering crusts on glass buried for many centuries. Though not accepted by some (*e.g.,* Newton 1966; Pollard & Heron 1996), this notion nonetheless had the potential to provide a chronometric method for archaeologists for whom the dating of glass artefacts was problematic.

Newton (1976), in a study of the weathering of medieval glass, noted that "conditions of burial seem much more exacting than even the worst ravages of atmospheric weathering". Newton (1976) recorded that weathering seemed to cause some fundamental changes to glass, and that buried glass not infrequently had a multi-laminated crust on its surface. In a study of hundreds of pieces of medieval stained glass by Newton (1976), provided they had not been buried, no weathering crust was found with the exception of some Austrian stained glass, the crust on which was quite thick compared with the laminae on archaeological [*sic*] glass. Newton (1976) also described the anomaly of the weathering crust on 300 kg of glass excavated from a cullet heap at the glassworks site at Bagot's Park in Staffordshire, England (dated to about 1535 AD); one half of the glass showed a heavy, opaque weathering crust whilst the other half was transparent and uncrusted.

More recently, Cox & Ford (1989), using SEM, electron-probe analysis, X-Ray and electron diffraction, described the nature of glass decay processes from alkali-lime-silicate glasses which had corroded on the sea bed for approximately 240 years. The samples (fragments of glass containers) were retrieved from two in-shore shipwrecks, the first, the *Drottengin af Sverige,* which was wrecked off Lerwick Harbour (Shetland Islands) in 1745, and the second, the *Amsterdam,* which foundered off Hastings in 1749. The samples exhibited opaque corrosion crusts which were between 0.2 mm and 0.5 mm thick, had become coloured, and were extremely fragile. Cox & Ford (1989) found that leaching and dissolution of glass networks had occurred. Corrosion crusts comprising regular discrete layers (or laminae) were formed through reprecipitation, and were depleted of calcium and magnesium, while aluminium was concentrated through the crusts and silicon was enriched at the glass-corrosion interface (Cox & Ford 1989).

Cox & Ford (1993) also examined the long-term corrosion of glass by groundwater. The samples of glass used in that study were excavated from several sites in the United Kingdom, (*viz.,* Eltham Palace, Kent; Rievaulx Abbey, North Yorkshire; Stamford Castle, Lincolnshire; and Wroxeter, Shropshire). The samples were corroded soda glass and potash glass which had been exposed to groundwater for between 350 years up to 1650 years. The corrosion crusts varied in thickness, colour, and uniformity of corrosion within and between samples. Cox & Ford's (1993) research showed that the surface layers on all samples had been depleted (to varying extents) of their principal constituents, with the exception of Si, Al and Fe. They identified deposits of calcite, calcium phosphate and manganese-rich minerals occurring within the crusts which were largely of exogenic origin, and that the geochemistry of the local groundwater played an important role in determining the chemistry of the weathering crusts.

Garcia-Valles *et al.* (2003) examined medieval stained glass from three restoration works to characterise glass decay. The medieval stained glass (from the 13th to 15th centuries) was from the Santa Maria del Mar and the Pedralbes Monastery church in Barcelona, and the Tarragon Cathedral in the northwestern Mediterranean area. The glasses were of two types: an Na-rich type and a K-Ca-rich type. Their research showed that Na-rich type glass did not weather (due to high silica content around 60% by weight), but the K-Ca-rich type of glass exhibited decay in the form of destructive (micro- and meso-pitting), and constructive (patina and microcrust) glass surfaces (Garcia-Valles 2003). The stained glass used in the study of Garcia-Valles *et al.* (2003) adds a level of chemical complication to the decay processes and the decay products that are not present in simple clear glass, therefore their results may not be directly comparable to this study. However, the results of Garcia-Valles *et al.* (2003) are useful in that they identify some of the chemical processes in the weathering of glass.

To date there have been no studies of the weathering of glass buried in calcareous quartz coastal dune sand in a tropical arid climate.

A summary of the features of weathered glass is presented in Table 1.

Current ideas of patina-forming processes

Patination occurs as a result of weathering processes acting on the surface of natural materials which include volcanic glass (obsidian) and rocks, and on glass artefacts. Maloney (1968) notes that pure silica is attacked by alkaline solutions, also noting that common glasses of soda-lime-silica composition "contain the seeds of their own chemical destruction" and, when it is exposed to water, a silica-rich surface layer [patina] develops on the surface of the glass.

Jackson (1997) notes that with obsidian (a volcanic glass, usually of rhyolitic composition), hydration rims are sometimes present in obsidian artefacts or Holocene volcanic glass.

Desert varnish (synonyms: desert crust; desert lacquer; desert patina; desert rind; rock varnish) is a possible type of patina less than 500 µm thick, often characterized by ultra-thin laminae. Desert varnish is found most frequently on rocks (sedimentary, igneous, or metamorphic rocks) with stable surfaces, in arid environments (Jackson 1997; Krinsley *et al.* 1998). It is composed of a thin coating of ferromanganese oxides, clay minerals, and trace elements (Krinsley *et al.* 1998). The mechanisms leading to desert varnish formation are

Table 1

Summary of types of glass, setting, and weathering products

Type of glass	Setting	Weathering products
ancient glass (Brewster 1863; Newton 1971 citing Hausmann (1856); typically high soda glass (Newton 1876)	excavated from Ninevah (Iraq), located on the eastern bank of the Tigris River	thin layers of weathered crust; diffraction effects (iridescence) noted
ancient glass (Brill 1961; Brill & Hood 1961); composition not described	excavated from Sardis, Turkey; glass buried for about 1600 years	weathering crust comprised of 1582 laminae
waste glass (Newton 1976); composition not described	excavated from a cullet heap at a glassworks site in Bagot's Park, Staffordshire, United Kingdom; exposed to groundwater for about 430 years	heavy, opaque weathering crust only on one half of the sample; the other half of the sample was transparent and uncrusted
medieval stained glass, typically high potash, high lime, and high magnesia (Newton 1976)	*in situ* stained glass in cathedrals and monasteries; exposed to humid atmosphere	no weathering crusts
alkali-lime-silicate glass (Cox & Ford 1989)	excavated from two shipwrecks (one located off Lerwick Harbour, Shetland Islands, the other off Hastings, United Kingdom); shipwrecks dated to 1745 and 1749 AD respectively	fragile opaque corrosion crusts between 0.2 mm and 0.5 mm thick arranged in regular, discrete layers;
soda and potash glass (Cox & Ford 1993)	excavated from several sites in the United Kingdom; various samples exposed to ground water for 350 up to 1650 years	corrosion crusts varying in thickness, colour, and uniformity of corrosion within and between samples
Na-rich and K-Ca-rich glass (Garcia-Valles *et al.* 2003)	*in situ* stained glass (13th–15th centuries) at Santa Maria del Mar and the Pedralbes Monastery church, Barcelona, and Tarragona Cathedral, north-western Mediterranean area.	glass decay in the form of destructive (micro- and meso-pitting) and constructive (patina and microcrust) glass surfaces. In the case of the Mediterranean medieval stained glasses, development of generalised corrosion and associated thick crusts are absent.

not completely understood, but it is postulated by some researchers to be the product of both abiotic and biotic processes (Krumbein & Jens 1981; Krinsley *et al.* 1998). Jackson (1997) cites that it is caused by exudation of mineralized solutions from within and deposition by evaporation on the surface [of the rock]. Garvie *et al.* (2008), on the other hand, disagree, describing desert varnish as neither a weathering rind, nor patina, but a unique subaerial authigenic sediment that forms under continuing adjustment to changing environmental conditions. As such, Garvie *et al.* (2008) would consider desert varnish not to be alteration *in situ*, but addition of microlayers of sediment and authigenic material.

Glass as the parent material to weathering crusts and patina

The composition of glass, particularly common, present-day commercial glasses, varies depending on the application for which the glass is intended. For example, fused silica, which is quite shock resistant, is > 99.5% SiO_2. Borosilicate, a glass that is thermally shock- and chemically-resistant, is composed of 81% SiO_2, 3.5% Na_2O, 2.5% Al_2O_3 and 13% B_2O_3. Soda-lime glasses, which are durable and are used for containers, have a composition of 74% SiO_2, 16% Na_2O, 5% CaO, 1% Al_2O_3,

with 4MgO (Callister 1991). Most commercial glasses are referred to as silica-soda-lime glasses because the main constituents are silica (in the manufacturing of glass, derived from quartz sand), soda ash (Na_2CO_3) and limestone ($CaCO_3$) [Callister 1991]. The main difference between current industrial glass and historic glass is the relative greater proportion of flux in historic glass which was made at the expense of silica but which enhances chemical weakness of the glass with respect to corrosion (Garcia-Valles *et al.* 2003).

The composition of ancient glass varies markedly from present-day glass. Newton (1976) reports that ancient glass (*e.g.*, Roman glass) was typically high soda (11.99–23.73% Na_2O), low potash (0.15–3.29% K_2O), moderate lime (4.83–9.14% CaO), and low magnesia (0.08–2.20% MgO). By the 12th to 14th centuries, the composition of glass had changed quite considerably being low soda, high potash, high lime, and high magnesia; the high lime content gave the glass greater durability (Newton 1976).

Materials and methods – this study

In 2005, Alistair Paterson from the Centre for Archaeology at The University of Western Australia provided three pieces of glass from an historical archaeological site at Cossack, collected either from the

surface, or from within the upper 5 cm of the soil, as part of an archaeological surface survey (Paterson 2003). These glass fragments form the basis for this study, however, to obtain supplementary information, I visited the Cossack archaeological site to ascertain the nature of the environmental setting where the glass was found. The historic glass from the Cossack refuse site, comprising two pieces of flat glass and one piece of medicine bottle glass, are soda-lime-silica glasses.

Field work

The refuse site where the glass was found was visited to determine the nature of the terrain, the type of sand or soil that the glass was buried in, and the proximity of the water table to the ground surface (to determine whether the weathering of the glass was a subaerial, vadose zone, or phreatic zone process), and to determine the types of natural processes that are operating in the area (*e.g.*, aeolian activity, rain infiltration, faunal and vegetation bioturbation). Three randomly-located samples of sand were collected for laboratory processing.

Laboratory studies

In the laboratory, the glass with patina was washed with distilled water to free it of any dust (derived from its period of burial in the sand), that may have been adhering to its surface. When dry it was examined under stereoscopic binocular microscope to describe its appearance, extent of patina coverage, and relative thickness. To determine whether the patina was calcareous, a fragment of each of the three glass samples was tested for calcium carbonate by placing a drop of 10% HCl on a portion of the patina while examining it under a stereoscopic binocular microscope.

The glass from Cossack was also examined and analysed using SEM and EDS at the CSIRO facilities at Kensington, Western Australia. A fragment of each of the glass samples, broken transversely to expose the glass-to-patina contact, was coated with carbon. The edge of the broken glass, transverse to the plane of the glass, was examined under high resolution by SEM to obtain images 10–200 μm in size. Image fields of view 100–200 μm in size also were obtained using back-scattered electron emissions (BSE) in order, firstly, to map the distribution of average atomic number which was used as a surrogate to determine the consistency of element distribution, and hence consistency of the distribution of micro-structure types, and secondly, to map the distribution of selected elements (specifically Ca, Mg, Al, and Si). During the SEM, within each SEM field of view some 10–50 μm across, the sample was also analysed by EDS to quantitatively determine elemental composition; routine spot analyses of areas 1–3 μm in size were carried out, with selection of the area of analysis based on the heterogeneity of the SEM image, or heterogeneity of the BSE field, on micro-structural and/or textural contrast, and on micro-topography.

Where Ca or Al was present in abundance in the patina compared to the parent glass, with the implication that calcium carbonate or a clay mineral was present, some of the patina was scraped off and the sample analysed by XRD.

The glass samples from Cossack, each comprised of the essential ingredients soda-lime-silica, used in this study were:

- Sample A1 = flat glass 1.4 mm thick
- Sample A2 = flat glass 1.4 mm thick
- Sample A3 = bottle glass (medicine flat) ~ 3.6 mm thick

The EDS results are presented in two forms: as raw data of the main constituent elements of Si, Ca, Na, K, Al, and Fe (as cps, *i.e.*, counts per second) [Table 2], and as transformed data of the same elements against a normalised Si content (Table 3). The latter method highlights the relative depletion or enrichment of a given element against Si as a standard (*i.e.*, the relative proportion of the other elements compared to Si since Si is by far the most abundant element in the parent glass and the patina), and highlights the exogenic origin of some specific elements.

The sand in which the glass samples were buried is a calcareous quartz sand. The sand also was examined under stereoscopic binocular microscope to ascertain the nature of the surface of the carbonate grains. Shell grit from a modern nearby mid-tidal flat also was similarly examined for comparative purposes. Subsamples of the three randomly-collected sand samples were dry-sieved at 1 ϕ intervals to characterise their grainsize. The < 63 μm fraction, derived from the sieving, was analyzed by XRD to determine its mineral composition. Subsamples of the three randomly-collected sand samples also were subjected to acid digestion with dilute HCl to determine the % carbonate in the sediment.

The study area

Cossack is located 20° 40' 43" S 117° 11' 20" E in the Pilbara region of Western Australia on the shore of Butcher Inlet near the mouth of the Harding River (Fig. 1A). The town was founded in 1863 (Lorblanchet & Jones 1979), and was a colonial town in Western Australia in the middle to late 19th century. Cossack was the first port in Western Australia, and between 1866 and the early 1890s it was the centre of the pearling industry (De La Rue 1979) in the State. The former Cossack settlement was located on a narrow spine or peninsula, underlain by Precambrian rock, elevated above the surrounding tidal flats, mangrove-vegetated flats, and salt marshes (Geological Survey of Western Australia 1979), or salt flats of Semeniuk (1986), and mantled by and flanked by calcareous quartz sand dunes, supratidal sand flats, and spits (Figs 1A, 1B and 1C). In this context, the refuse site is located partly on a calcareous quartz sand dune, and on a terrain of calcareous quartz supratidal sand flat and sand spit.

During its short history, Cossack was a small town with a population of only several hundred permanent residents at its peak in the 1890s, though the population fluctuated with the seasonal arrival and departure of the pearling boats at the beginning and end of the pearl-fishing season. The town went into decline when the pearling fleet moved to Broome in the early 1890s. In 1910 the prominence of the port further declined with the opening of the tram line to Port Samson, the new port for the region (De La Rue 1979). Cossack was a "ghost" town by the mid-1940s.
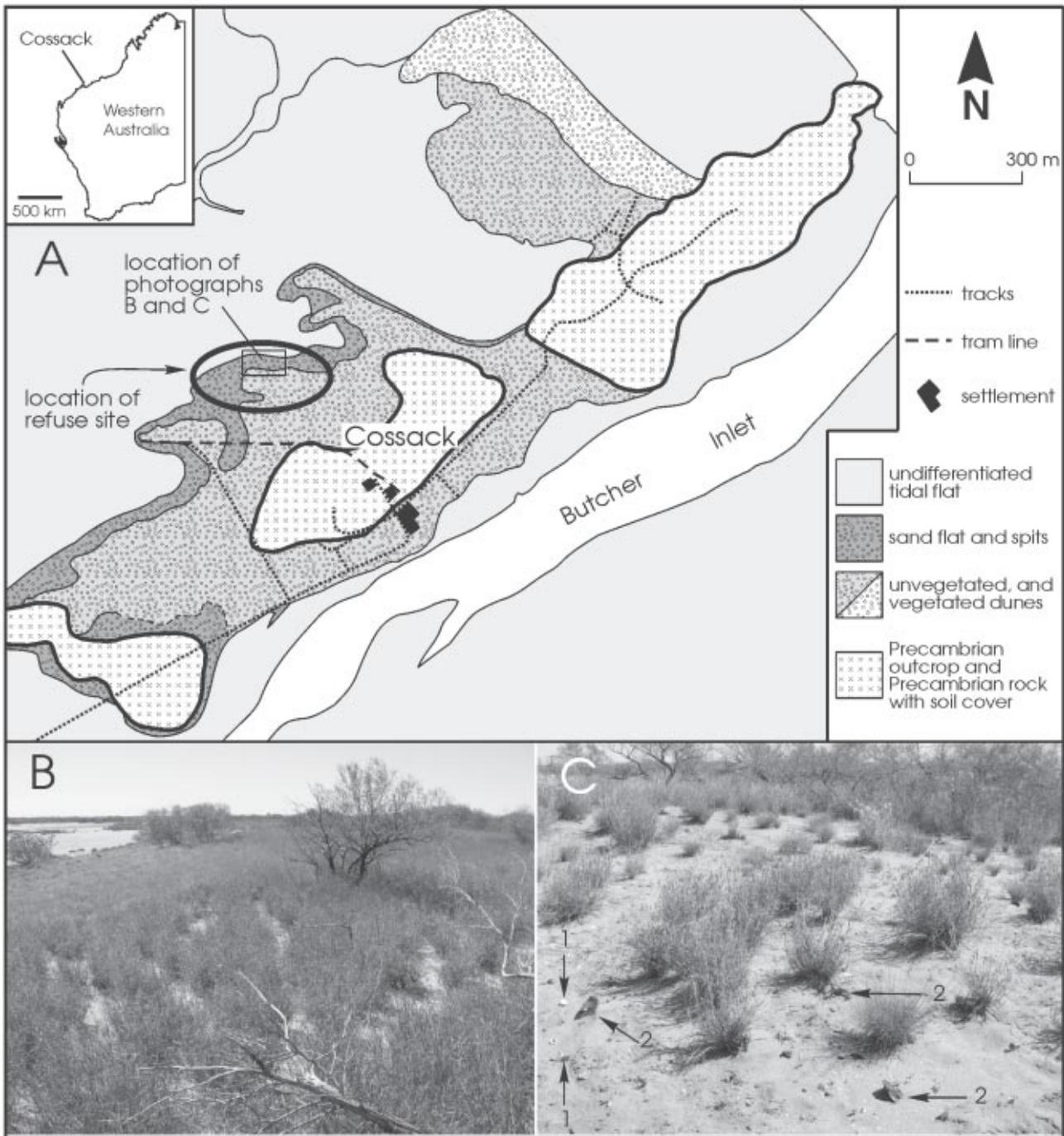
Figure 1. Location of site. A. Map of the Cossack area showing landscape units, the location of the refuse site (as noted on Figure 4 of Paterson [2003]), and the location of photographs. B. Photograph of the sand flat adjoining the dune; tidal flat visible to left of photograph. C. Close-up of the surface of the sand flat that functioned as a midden site and then as a refuse site, showing shell (middens) scattered on the surface (arrow 1), and partly buried bottle fragments (arrow 2).

The climate of the Cossack area is tropical arid, with an annual average rainfall of 315 mm (Bureau of Meteorology 1973, 1975). Average summer temperatures range from a maximum of 36.5 °C and a minimum of 24.5 °C, with average winter temperatures ranging from a maximum of 25.5 °C and a minimum of 14.1 °C (Bureau of Meteorology 1973, 1975). Annual evaporation is ~ 3200 mm/pa (Bureau of Meteorology 1988). Cossack experiences summer rain with the highest rainfall

occurring between January and March. The area also experiences strong, sand-shifting winds throughout the year (Semeniuk & Wurm 1987).

The refuse site is located 750 m north of Cossack town, and is located on a sand dune, supratidal sand-flat, and sand spit complex bordering a muddy tidal flat that occurs to the north of the spine or peninsula of Precambrian rock (Fig. 1A). The refuse site is composed of historic material comprising broken bottle glass,

broken ceramic crockery, metal utensils, other domestic metal objects, and corrugated iron and other building materials, as well as Indigenous artefacts such as bottle-base fragments exhibiting flake scars, and accumulations of *Anadara granosa* (Lamprell & Healy 1998), broken *Telescopium telescopium* and *Terebralia palustris* (Abbot & Dance 2000) [all three species being a food source in that area], and *Melo amphora* (Wilson & Gillett 1974). As a sand dune and sand spit complex, the surface of the terrain of the refuse site is well above the water table (> 1 m above the water table); thus the deposits of broken glass are not located in the phreatic zone but in the subaerial and vadose zones. The surface of the refuse site is subject to strong winds such that the assemblage of historic glass has been variably covered and uncovered by ephemeral sand veneers, and additionally there is evidence that burrowing macrofauna have exhumed and buried the glass artefacts. As such, through the agencies of wind and fauna, the glass artefacts have been alternately covered in sand and exhumed, *i.e.*, they have been alternately in the vadose zone and subaerial zone.

A broken cylindrical bottle, *in situ* in the field, partly buried by sand, shows the relationship between patina and its burial in sand (Fig. 2B). The curved sand-to-glass interface has resulted in a curved margin to the developing patina, and progressive exposure of the bottle by wind erosion has resulted in curving parallel bands of the edges of the patina as it accreted and at the same time the bottle was progressively exposed.

From their setting, all three samples of glass from the refuse site at Cossack are estimated to have been buried for between 70–100 years.

Results

Field results

In the field, the historic glass fragments are strewn across the surface of, or buried to shallow depth in the sub-surface of the sand dune, sand flat, and sand spit (Figs 1C and 2A). Evidence of burial and exhumation of historic glass by wind (as noted above) is shown by lines of patina on wind-exposed glass. (Fig. 2B).

Laboratory results

The sediments and soils on which the refuse site is located are comprised of medium and fine calcareous quartz sand in which the carbonate component is shell, mainly as fragments. The carbonate content in the sand varies between 10% and 15%. Coarse sand-sized shell fragments and shell gravel in the sediment and soils had surfaces that were predominantly corroded in comparison to shell grit from modern tidal flats.

Viewed under a stereoscopic binocular microscope, each of the samples of glass showed the patina to be present on both sides of the glass fragments, however, the patina was of a different thickness on one side of the glass compared with the other; the patina also coated the old broken edges. The upper surface of the patina generally appeared flat, though locally there were surface, low-amplitude undulations. The patina appeared relatively uniform in thickness on a given surface, and although it generally covered the glass, it was not
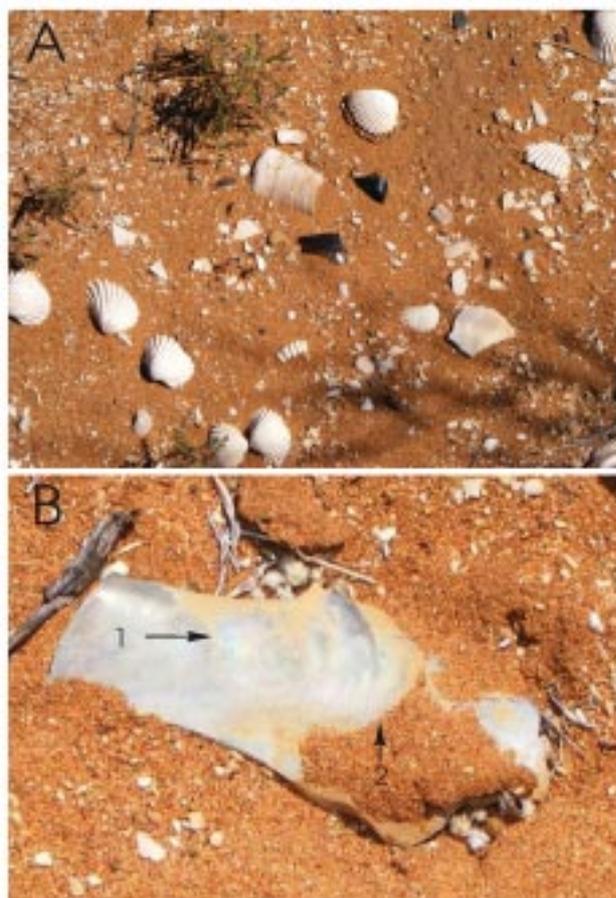
Figure 2. Photographs of the surface of the refuse site. Both photographs show the nature of the orange sand that is typical of coastal sands in this arid environment. A. Surface littered with *Anadara granosa*, partly buried, broken *Telescopium telescopium*, and partly buried dark bottle fragments. B. Close-up of a bottle fragment, *in situ* in the field, partly buried by sand. Edges of patina, in curving parallel bands, are evident on this bottle surface. Arrow 1 shows the limit of patination on the bottle. Arrow 2 shows a curved interface of sand on glass, where the cylindrically curved body of the bottle was buried. The curved sand-to-glass interface has resulted in a curved margin to the patina, and progressive exposure of the bottle has resulted in curving parallel bands of the edges of the accreting patina.

uniform in extent – while dominantly covering the glass surface, there were patches where it was absent, or patches where it was more thinly developed. Where the patina was thin, the pitting on the parent glass surface was evident. The patina appeared to be a mosaic of overlapping plates or flakes, and the surface of the patina locally was undulating. There also were patches of closely-spaced "micro-vesicles" (see later) on the surface.

Wetting the surface of the patina with a drop of water showed that it was porous and permeable, with the water dispersing rapidly throughout the patina by capillary action along lamination interfaces and micro-cavities (this observation will have implications for pellicular water interactions with the patina and the parent glass). The patina was milky white (with local iridescence) appearing as an encrustation on the glass surface.

The testing of patina by dilute HCl showed effervescence in all samples, and hence the presence of calcium carbonate. However, the treatment of the patina with dilute HCl did not remove all of the encrustation – the residue remaining on the glass surface was a transparent to translucent, very finely-laminated crust (presumably of insoluble silica). The species of calcium carbonate within the patina (determined by XRD) are calcite and aragonite.

XRD results of the < 63 μm fraction show it to be composed of the following: the clay mineral kaolinite; micas biotite and clinochlore; feldspars as ordered calcian albite, disordered calcian albite, disordered anorthoclase, sodian anorthite, anorthite, and orthoclase; carbonates as aragonite, calcite, and dolomite; and other minerals such as quartz, geothite, haematite, talc, cordierite, ferroan cordierite, and rutile. Notwithstanding that these minerals have variable rates of weathering, and therefore different potential rates of availability of the metals as cations, the list provides an indication of the cations that may be mobilised during weathering. It also provides a list of the specific minerals (with their diagnostic cation signatures) that potentially can be incorporated into the patina. From a consideration of the chemistry of these minerals (Sinkankas 1964; Deer *et al.* 1966), the metals that can therefore be expected to occur in the patina, either as part of the minerals incorporated into the patina, or as remobilised elements, are: Al, Ca, Fe, K, Mg, and Na.

Description of SEM images and EDS results

The images obtained by Scanning Electron Microscopy are presented in Figures 3–8, which show a variety of micro-structural features, and glass to patina relationships.

The SEM images and EDS of all samples show the parent glass to be structureless (massive) and compositionally uniform. EDS of the samples shows it to be a soda-lime-silica glass, with Ca and Na in moderate proportions relative to the silica which is dominant (Table 2).

Table 2

Results of selected element content by EDS of glass and patina for the 3 samples

Sample A1

Element	Glass (cps)	Patina (cps)
Si	56.0	62.0
Ca	13.0	11.0
Na	6.0	1.0
K	0.5	1.0
Al	1.0	4.0
Fe	0.2	0.5

Sample A2

Element	Glass (cps)	Patina (cps)
Si	175.0	105.0
Ca	35.0	55.0
Na	30.0	0.2
K	–	–
Al	–	0.6
Fe	–	0.1

Sample A3

Element	Glass (cps)	Patina (cps)
Si	160.0	106.0
Ca	30.0	20.0
Na	23.0	18.0
K	0.5	1.0
Al	–	trace to 6.0
Fe	–	trace
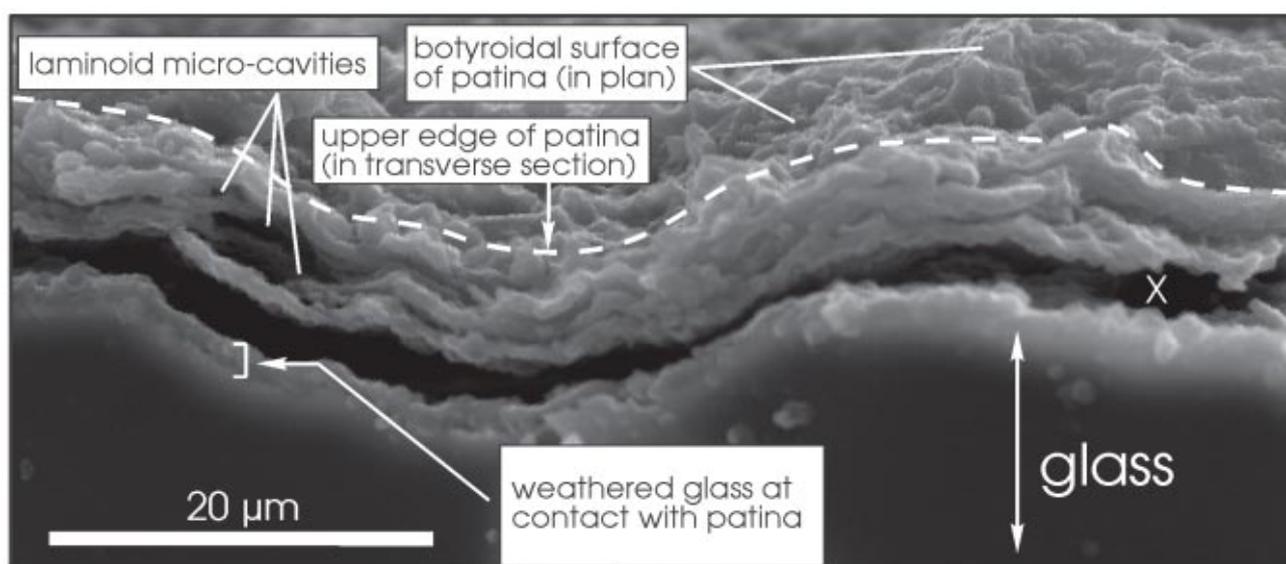
Figure 3. SEM image of a cross-sectional view of patina on glass (sample A1) showing undulating lamination and laminoid micro-cavities. The surface of the patina is botryoidal. The black zone (marked X) between the glass and the patina is a separation crack formed during sample preparation.
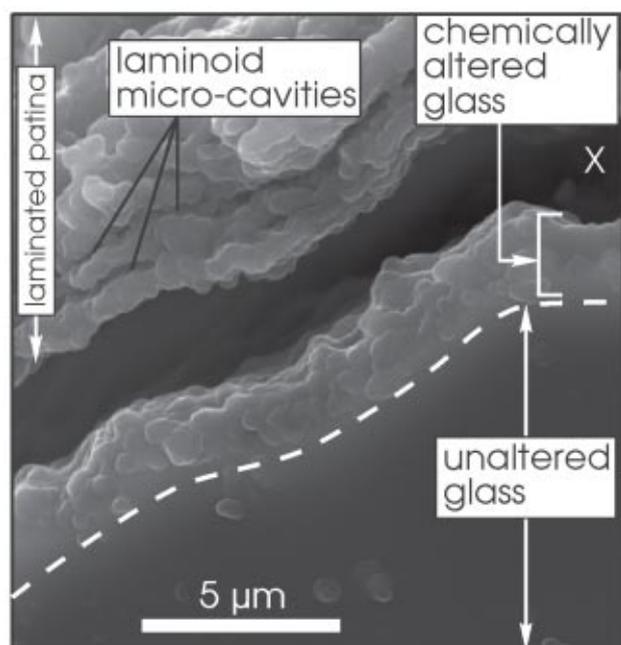
Figure 4. SEM image of a cross-sectional view of patina on glass (sample A1) showing details of features across the glass-to-patina interface. The image also shows a close-up of laminoid micro-cavities within the patina lamination. The black zone (marked X) between the glass and the patina is a separation crack formed during sample preparation.

The SEM images of the samples in transverse section show the patina to be a thinly-laminated crust (6–100 μm thick) on the glass surface. Depending on the glass sample examined, there are 5–12 laminae within the patina. The upper surface of the patina generally is botryoidal to undulating (Fig. 3). The lower contact of the laminated patina with the parent glass generally is sharp and irregular to scalloped. Also, there may be a zone of transition (5–100 μm thick) where the parent glass grades into the base of the patina through chemical alteration.

As will be described in detail later for each of the glass samples, the patina on the Cossack glass commonly contains micro-cavities. Two types are recognised (Figs 3, 6C and 8): 1) a lamination-parallel form that is platy, termed here "laminoid micro-cavity", that produces a laminoid micro-cavernous structure throughout the patina; and 2) another form that is more equant in shape, termed here "micro-vesicle", that produces a micro-vesicular structure in the patina. The laminoid micro-cavities tend to vary in size but range from 3–25 μm in length and from 0.2–1 μm in width in cross-sectional shape. The micro-vesicles tend to be 1–3 μm in diameter and are equant in cross-sectional shape.

In all patinas there are micro-unconformities where an undulating set of laminae is truncated by a later set of laminae (Figs 6B and 6C).

In plan, the SEM images show the patina may be micro-vesicular (Fig. 5A), and where it has been flaked off to expose the parent glass, the parent glass exhibits micro-pitting (or micro-etching) with individual micro-

pits 1–20 μm in diameter and extending 5–10 μm into the glass (Figs 5A and 5B). Plan view images of the patina show a concentric pattern where the patina lamination follows the morphology of the pits (Fig. 5B). In transverse section, all samples show the contact between the parent glass and the patina to be a series of undulations, pits, and scallops where the glass has been corroded and there has been "invasion" by weathering products into the glass (Figs 5A, 5B, 6A, 6B, 6C, and 7). Figures 6A and 7 particularly well illustrate the corroded, pitted nature of the contact between parent glass and the overlying patina.

EDS results show that while the glass is dominated by the elements Si, Ca, and Na (typical soda-lime-silica glass), the patina is still dominated by Si but tends to be depleted of Na (though A3 is the exception). Ca may be depleted or enriched, though it is difficult to ascertain just from EDS results whether the Ca content is a residual from the parent glass, or exogenically derived. If present, K and Al are enriched in the patina relative to the parent glass.

All three glass samples provide good examples of the micro-structural, textural, and compositional characteristics of the patina, and the contact between it and the parent glass.

The patina in sample A1 is ~ 6 mm thick, and has 5 sub-parallel laminae (Fig. 3). There is minor compositional layering between laminae, with variation in content of Al, K, Fe and Na. The surface of the patina is botryoidal (Fig. 3). The lamination is undulating, with undulations subparallel to each other and parallel to the patina-glass contact. The parent glass along this contact is not flat, but appears pitted, and the undulations in the patina appear to perpetuate the micro-topography of the corroded parent glass. There are numerous laminoid micro-cavities varying between 3–11 μm in length and between 0.25–0.75 μm in thickness in cross-section, parallel to the lamination, and micro-vesicles averaging ~ 2 μm in diameter between and within the lamination (Figs 3 and 4). The EDS results for sample A1, that have been normalised with respect to Si, show that in the patina, Ca is relatively mildly depleted, Na is markedly depleted, K is relatively enriched, Al is markedly enriched, and that Fe also is enriched (Table 3). These EDS results show endogenic depletion and exogenic enrichment of the different elements, as will be discussed later.

The patina in sample A2 shows thick development on one side of the glass and thin development on the other. The thin side was examined by SEM. The thick side was analysed by XRD. The patina examined by SEM is up to ~ 30 μm thick, and has 10 sub-parallel laminae (Fig. 6), with minor inter-laminae compositional layering showing variation in Al. The lamination is undulating (Fig. 6C), similar to sample A1, but here the undulations do not always follow the irregularities of the topography of the parent glass. There also are numerous laminoid micro-cavities varying between 7–16 μm in length and between 0.4–1 μm in thickness, appearing in cross-section sub-parallel to the lamination, and micro-vesicles averaging ~ 3 μm in diameter between and within the lamination. The small micro-vesicles in fact dominate the structure of the patina (Fig. 6C). When the EDS results have been normalised with respect to Si, they show that
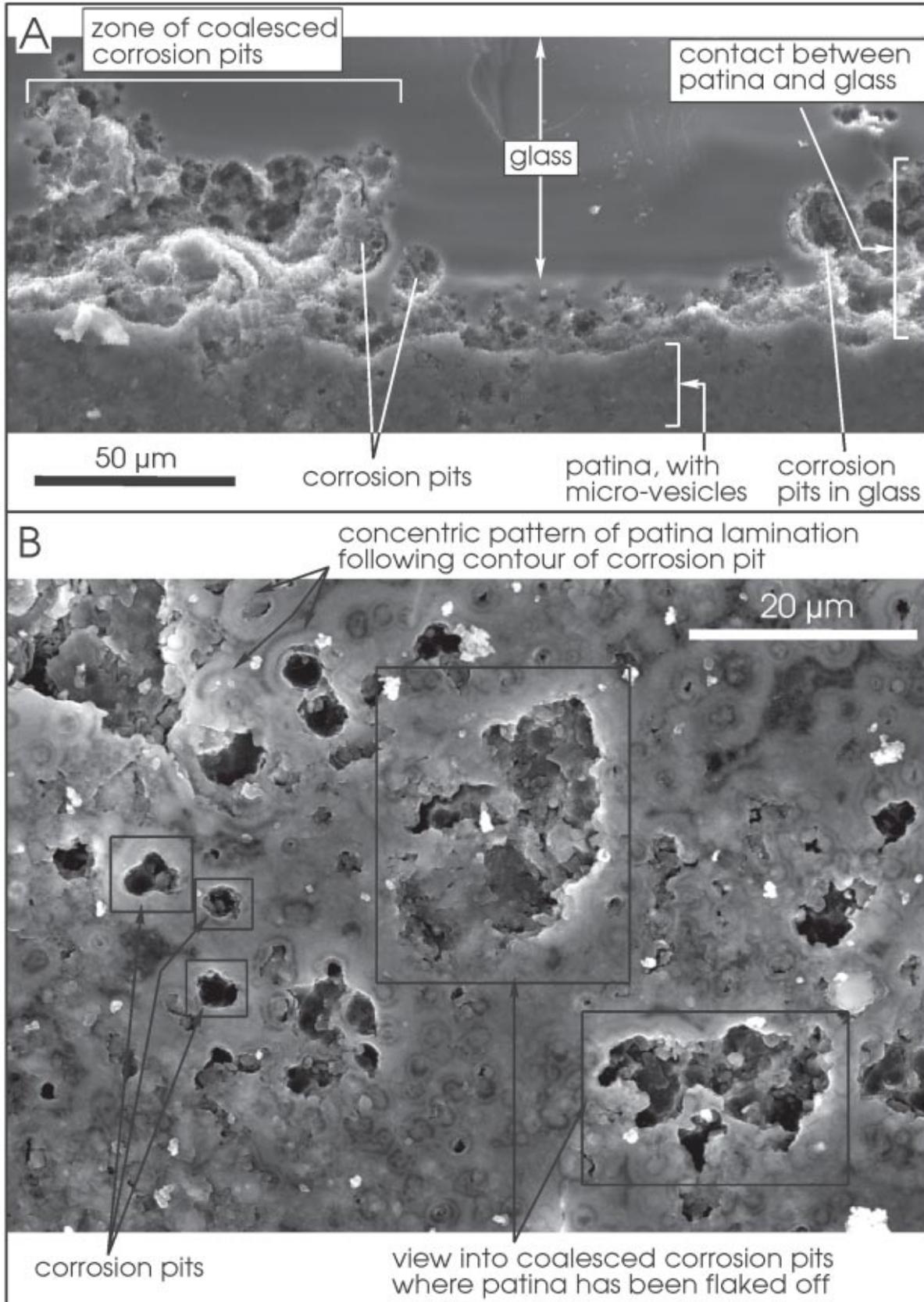
Figure 5. SEM images of a plan view of patina on glass (sample A1). A. Image shows details of features across the glass-to-patina interface at the edge of the patina crust, where it has been flaked off. The patina has micro-vesicles. The glass is structureless. The contact of the patina on glass is marked by a zone of corrosion pits and coalesced corrosion pits. B. Image shows abundance of corrosion pits and coalesced corrosion pits, and the concentric pattern of the laminated patina where it has followed the morphology of the pits.
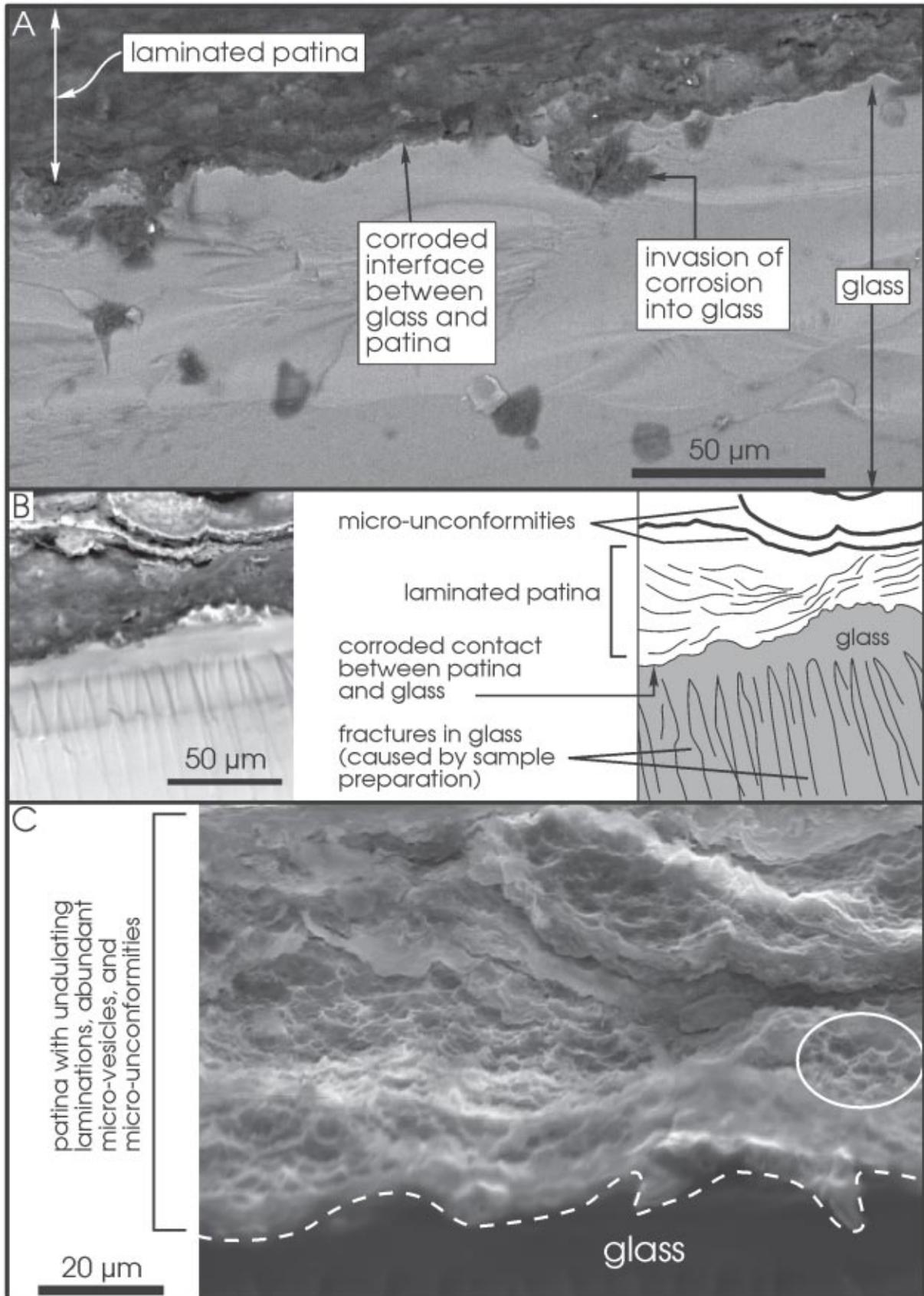
Figure 6. SEM images of a cross-sectional view of patina on glass (sample A2). A. Image shows structureless glass, the corroded interface with the patina, the invasion of corrosion into the glass, and the laminated patina. B. SEM image and annotated line diagram showing corroded contact between glass and patina, undulating lamination in the patina, and micro-unconformities. C. Undulating lamination in the patina, and an abundance of micro-vesicles (one set is circled).

Table 3

Results of selected element content by EDS normalised with respect to Si

Sample A1

Element	Glass	Patina	Comments
Si	100.00	100.00	
Ca	23.21	17.74	Ca relatively mildly depleted in patina
Na	10.71	1.61	Na markedly depleted in patina
K	0.89	1.61	K relatively enriched (because of imported clay minerals)
Al	1.79	6.45	Al markedly enriched (because of imported clay minerals)
Fe	0.36	0.81	Fe enriched (because of imported dust)

Sample A2

Element	Glass	Patina	Comments
Si	100.00	100.00	
Ca	20.00	52.38	Ca markedly enriched in patina
Na	17.14	0.19	Na markedly depleted in patina
K	–	–	
Al	–	0.57	Al markedly enriched (because of imported clay minerals)
Fe	–	0.10	Fe mildly enriched (because of imported dust)

Sample A3

Element	Glass	Patina	Comments
Si	100.00	100.00	
Ca	18.75	18.87	no change in relative Ca content
Na	14.38	16.98	more or less the same Na content
K	0.31	0.94	K relatively enriched in patina
Al	–	trace to 5.66	
Fe	–	trace	

in the patina Al is enriched, Ca is markedly enriched, Na is markedly depleted, and that Fe is mildly enriched (Table 3). Again, these EDS results show endogenic depletion and exogenic enrichment of the different elements, as will be discussed later. The EDS results also show that there is compositional layering of Al.

The patina in sample A3 is ~ 50 μm thick, and has 12 finely-spaced, sub-parallel (mainly planar) laminae (Fig. 8). There is minor compositional layering between laminae, with variation in content of Al, K Fe, and Na.
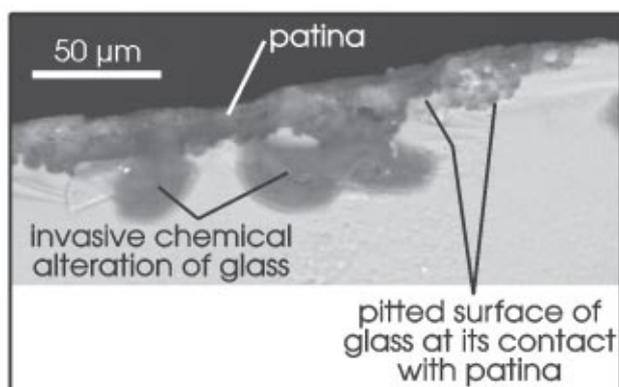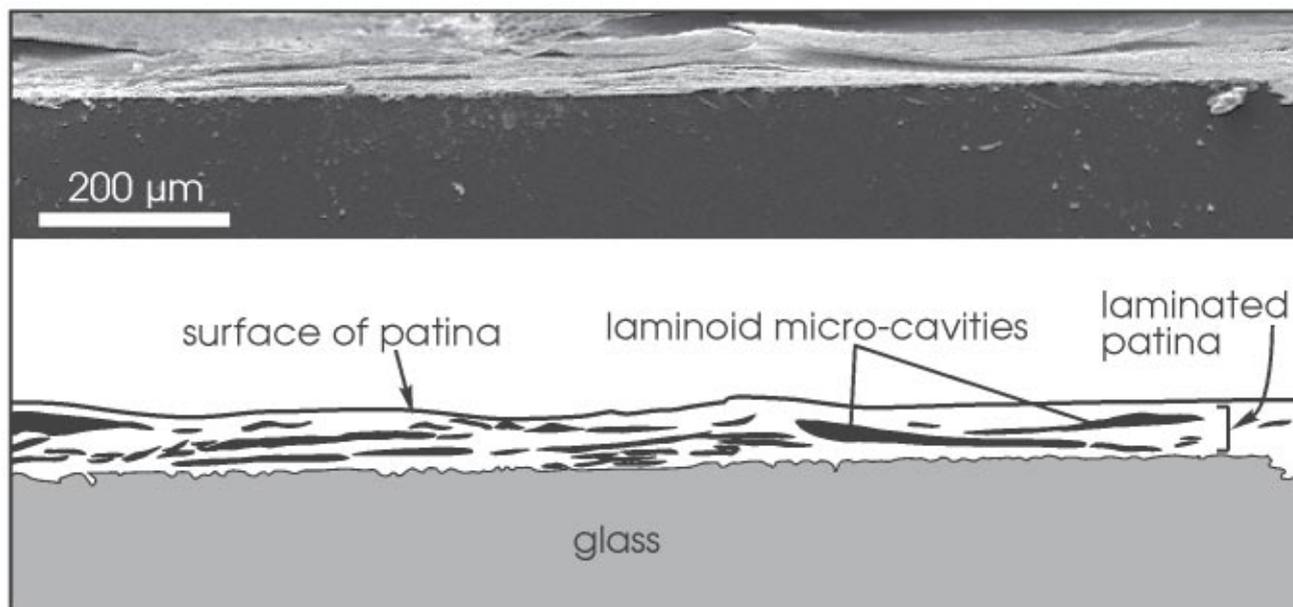

Figure 7. SEM image of a cross-sectional view of patina on glass (sample A2) showing invasive chemical alteration of the parent glass, and the pitted surface of glass at its contact with patina.

The lamination is generally parallel to the flat surface of the glass, *i.e.*, it is not undulating. There are numerous small cavities in the patina parallel to the lamination; these are laminoid micro-cavities varying between 6.5–24.5 μm in length and between 0.2–0.4 μm in thickness in cross-section (Fig. 8), and micro-vesicles averaging ~ 0.75 μm in diameter sub-parallel to the lamination. When the EDS results have been normalised with respect to Si, they show no change in relative Ca content, Na content remains more or less the same, and K is relatively enriched (Table 3). Trace amounts of Al and Fe appear in the patina. These EDS results show exogenic enrichment of K, Al and Fe, as will be discussed later.

Discussion and conclusions

The EDS results corroborate that chemically the parent glass is Na-Ca-Si. The elemental composition of the glass (and largely free or depauperate of Al and Fe) and its structureless (massive) nature provides a baseline to contrast the composition of the patina, and also an indication of what elements may be endogenic or exogenic in the patina.

Chemically, while the patina is dominated by silica, it shows both endogenic and exogenic elements. The definite endogenic element is Si. Although Na and some K are present in the glass and in the patina, it is not unequivocal that these latter elements have been derived endogenically from the weathering of the glass, or

Figure 8. SEM image and annotated line diagram of a cross-sectional view of patina on glass (sample A3) showing laminated patina, and laminoid micro-cavities.

whether they have been introduced exogenically as a part of the interaction of patina with the Na-rich and K-rich components in the < 63 μm mineral fraction in the sand, given that Na and K are present in the parent glass *and* in the exogenic minerals. Na also could have been contributed to the patina as precipitation of halite, as the sand (in which the glass was buried) is in a coastal environment where wind-fall can bring in sea salt; rain also can be charged with sea salt. The concentration in the patina of Al, Fe, some Ca (as $CaCO_3$), and some K, as compared to their occurrence in the parent glass, suggests exogenic enrichment. How these elements occur within the patina, whether as elements bonded within the silica network, or as infiltrated minerals incorporated into and between the layers of silica, is not known. The EDS element map of Al shows that this element is compositionally layered within the lamination of the patina, and therefore its incorporation into the patina was in phase with the accretion of the patina lamination.

Of the range of elements available as leachates from the < 63 μm mineral fraction, and the dust-sized minerals themselves available to be incorporated as particles in the patina, only Al and Fe appear in the patina to any significant extent, and K appears in the patina moderately enriched. Probably the Al and K reflect the clay minerals and feldspar grains that were delivered as dust to the site in the Pilbara coastal region, and washed in by vadose processes or involved in the wetting and drying of sand grains and glass by dew-related processes. Some of the Na may also be exogenic as it may have a source from the breakdown of feldspars. Fe appears in all samples of patina at Cossack, and is exogenic. This is not unexpected as Fe-rich dust, containing geothite and haematite, is the hallmark of red dust in the general Pilbara region.

The occurrence of Ca in the patina is problematic to interpret. Some may be endogenic (derived by weathering from the Ca in the parent glass), but some

may be exogenic deriving from dissolution of carbonate grains in the sand. Interestingly, while EDS shows Ca-enrichment in the patina which signals the potential presence of a carbonate species, laminae of carbonate were not evident in the EDS images. However, XRD shows calcite and aragonite in the patina, indicating that while the parent glass is free of aragonite and calcite, both these mineral species have been precipitated (or perhaps even illuviated) onto and within the patina. Some of the Ca which has been detected by EDS also may be present as trace amounts of (Ca-bearing) feldspars incorporated into the patina, though XRD did not detect these mineral species in the patina. It is more probable that the Ca presence in the patina is due to the occurrence of aragonite and calcite laminae. The removal of carbonate minerals by dilute HCl in the laboratory changes the appearance of the patina from laminated and milky white (*i.e.,* interlayered silica and carbonate) to laminated transparent/translucent (*i.e.,* laminated silica without carbonate), indicating that carbonate minerals are part of the patina structure.

The local iridescence of the weathered glass is the result of light interacting (diffracting) with a finely-laminated silica in which there are lamination-parallel micro-cavities.

While the EDS and XRD analyses provide useful chemical and mineralogic information on the element content and their possible endogenicity or exogenicity, micro-structural and textural data are required to more fully interpret the processes that produce patina and its internal structures.

In contrast to the structureless (massive) glass, the patina is rich in micro-structures: it is laminated; the laminations may be undulating; there are micro-unconformities; and the patina exhibits laminoid micro-cavities and micro-vesicles. These micro-structures provide information on processes that have operated in the formation of the patina, though a full investigation of

these processes and products is beyond the scope of this paper. However, in the first instance, the laminated micro-structure shows that patina is accretionary on (or into) the parent glass surface. With accretion, some of the exogenic cations (incorporated as elements into the silica of the patina, or incorporated as mineral particles) are interlayered with the lamination producing compositional layering.

The micro-structural relationship of patina to parent glass shows that the base of the patina is invasive (corrosive) downwards, producing pitting in its contact with the parent glass. This indicates dissolution along the contact, with the patina accreting at the expense of the parent glass. This invasive relationship downwards would imply that a major component of the accretion of laminae is directed inwards towards the parent glass. The flatness of the upper surface of one of the patinas suggests little upward accretion, however, the locally undulating upper surface of other patinas, and the mosaic nature of the crust suggest there has been at least some outward (upwards) accretion.

That the patina on the glass from Cossack is porous suggests that there is possibility of thorough wetting of material during the wet season, and the possibility that accretion is in fact in two directions: that towards the glass, and that outwards from the surface of the patina. However, with the interior surface of the patina interfacing with the metastable glass, it is more likely that the major part of the accretion is, in general, downwards into the glass.

Pellicular water has been documented as being asymmetrical on sand grains, forming "gravitational" structures (Muller 1971), or "pendant" structures (Blendinger 2004) on the lower surface of the grain. At Cossack, if the glass is not being rotated within the soil/sand profile (*e.g.,* by bioturbation), asymmetrical pellicular water interacting with metastable glass has the potential to form an asymmetric patina.

The micro-structures also suggest that accretion alternated with dissolution, resulting in micro-unconformities. Sets of laminae are truncated by solution, and then the solution-sculptured surface provided the foundation for later micro-accretionary processes. The undulations, as described earlier, appear to be accretionary perpetuation of the irregular contact of the parent glass with the patina. Other undulations are the accretionary perpetuation of laminae superimposed on a solution-corroded surface sculptured earlier on the patina. The micro-unconformities and diverse sets of undulating laminae suggest that the patina has been through alternate phases of surface dissolution and silica accretion.

As noted above, although EDS shows Ca-enrichment in the patina relative to the parent glass, which signals the possible presence of a carbonate species; distinct laminae of Ca layers (as calcium carbonate) were not evident in the EDS images. The lamination-parallel micro-cavities in the patina suggest that these cavities may represent former laminae of carbonate minerals, and that their dissolution created the lamination-parallel cavitation. That is, in an environment where the pellicular water alternates between carbonate dissolving (and silica precipitating) and carbonate precipitating (and

silica dissolving), the calcite and aragonite laminae within the patina, precipitated during the evaporation phase of any remaining pellicular water during the hot summer, is dissolved during the wet season to leave intra-patina cavities.

The processes of patination on the glass from Cossack appear to involve solution and precipitation, vadose-zone illuviation, and accretion. There is solution of the parent glass, precipitation of silica as laminae in the patina, solution of carbonate minerals, and solution of earlier-formed patina. There is precipitation of silica as laminated patina and precipitation of aragonite and calcite. There is probable vadose-zone illuviation of fine-grained mineral particles into the evolving patina, and incorporation of these particles into the accreting patina.

However, the weathering of glass at Cossack to form the patina did not involve just the parent glass in its interaction with pellicular water, but also complex interactions with the particles of the fine-grained mineral components and their weathering products (leachates and precipitates) of the sediment in which it was buried. Metastable anthropogenic glass is particularly prone to chemical weathering when it is exposed to water (Maloney 1968), and weathering can be expected to take place, but this weathering will be particularly accelerated if the water which the glass comes in contact with is alkaline. Weathering of metastable anthropogenic glass may have taken place at a slower rate, for instance, if it were to have been buried in a quartz sand with mildly or moderately acidic groundwater or pellicular water. At Cossack, dissolution of carbonate grains in the sand by rainwater resulted in a mildly alkaline pellicular water which could more actively chemically attack the glass (see below).

The relationship of silica dissolution and precipitation, and carbonate dissolution and precipitation, particularly where both materials co-exist in the same sediment or rock, and when pore waters are alkaline or acidic, or alternating alkaline to acidic, has long been a focus of sedimentary geochemistry (Walker 1962; Sharma 1965). Silica dissolution and precipitation can be complicated, and can be influenced by pH, lime, other metal salts, and electrochemical coagulation, amongst other factors (Fanning & Pilson 1971; Potapov *et al.* 2005). Also, according to the geochemical studies, precipitation of silica from sea water is almost impossible by inorganic means because of its low concentration, so organic agents have been invoked to precipitate the silica (Correns 1950; Siever 1957; Krauskopf 1959). These issues are important because the weathering of anthropogenic glass in the calcareous quartz sand at Cossack is in a silica/carbonate dissolving/precipitating environment, and the principles involved in the type of geochemistry outlined above are applicable to the weathering of glass at Cossack. However, notwithstanding that biomediation and other hydrochemical factors can reverse and influence some general patterns of silica solution/precipitation and silica and carbonate chemical relationships, there is a generally-held notion that acidic waters are carbonate dissolving, and silica precipitating, and alkaline waters are silica dissolving and carbonate precipitating (Walker 1962; Sharma 1965; Southwick 1984; Kendrick 2002). If silica, as quartz, is susceptible to dissolution under alkaline conditions, metastable anthropogenic glass can

be considered to be even more susceptible to dissolution under alkaline conditions.

In a setting such as the coastal sands at Cossack that receives annual rainfall in the summer, the pellicular water micro-environment, as discussed above, can be alternating in pH. The laboratory observations indicate that water disperses rapidly through the patina, suggesting that any solutes present in the pellicular water derived from the sand, from shell, from the < 63 μm fraction in the sand, from the patina, and from the glass itself, have the potential to be transferred to any location within the patina and could interact with laminations, inter-laminations, and micro-cavities in the patina.

The research carried out by Semeniuk (2007) on the coastal calcareous quartz sands and wetland calcilutites ($CaCO_3$ muds) in the Point Becher area provides information and insights into some of the rainwater-and-carbonate interactions that can occur in the vadose zone. Semeniuk (2007) found that while rainwater was weakly acidic, rain-derived pellicular water around calcareous sand grains in coastal dunes, de-ionised water used as pellicular water around calcareous sand grains in laboratory experiments, and rainwater infiltrating calcilutites, dissolved the calcium carbonate component of sediments. With dissolution of calcium carbonate, the pore waters became alkaline.

In the Cossack area, with the onset of rain, the pellicular water initially would be weakly acidic. In contact with carbonate grains, the pellicular water would corrode them (the corroded carbonate sand grains and shell in the sand enclosing the glass attest to this), and would become weakly alkaline. Once alkaline, the pellicular water would attack the glass, promoting dissolution and the other chemical processes involved in patination. When the pellicular water evaporates, it would leave behind a precipitate of carbonate minerals (either crusted on the patina, in the pore spaces of the patina, or along the contact of the patina and the parent glass). The next episode of rain would re-introduce weakly acidic meteoric water which would dissolve the carbonate grains in the sand (liberating more calcium carbonate in solution), *and* dissolve carbonate minerals within the patina. The formation, structures and chemistry of the patina reflects the history of the glass embedded in a calcareous quartz sand with an annually alternating hydrochemistry and acidity/alkalinity of pellicular water as outlined above. The pellicular water chemistry, however, is more complicated by virtue of the fact that the mineralogy of the < 63 μm fraction in the sand appears to play a part in the evolution of the patina through its dissolution and perhaps its illuviation.

All glasses elsewhere that have been studied to date have been weathered in different types of environments (under the sea, buried in soil in humid England, in groundwater-saturated soil, and exposed to a humid atmosphere in Europe). They have all shown differences in style of weathering in terms of structures and lamination compared to the Cossack samples. For example: 1. glass in groundwater-saturated soil resulted in the formation of morphological features such as parallel layers, hemispherical layers, zigzag banding, rotated bands, and plugs (Cox & Ford 1993); 2. glass buried in soil exhibited circular and parallel weathering layers, and plugs (Newton 1971); and 3. medieval stained glass exposed to atmospheric weathering contained such features as curved-branched, irregular micro-pitting (Garcia-Valles *et al.* 1993). In contrast, the glass buried in calcareous quartz sand at Cossack, in an arid environment, has weathered to form a patina that is laminated, with undulations in the laminae, and with micro-unconformities, micro-cavities and micro-vesicles, and calcite/aragonite in the structure. This indicates that it is probable that the environment of weathering can influence the micro-processes of weathering and hence result in different types of microstructures and mineralogy. Axiomatically, the results from one area, with its particular climate, soil, and hydrochemistry, cannot be transferred to other areas in terms of deducing processes, products, or age.

In the literature the main agent identified in the environment responsible for the weathering of glass is water (Brill 1961; Cox & Ford 1989, 1993), whether as groundwater, pellicular water, sea water or atmospheric water, and the geochemistry of that water in these different environments will determine which constituents will be depleted from the parent glass, the composition of the patina, and the rate of dissolution and accretion depending on the pH.

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