Applied Geochemistry 41 (2014) 107–114

Contents lists available at ScienceDirect

Applied Geochemistry

journal homepage: www.elsevier.com/locate/apgeochem

Characterization and modeling of the cemented sediment surrounding the *Iulia Felix* glass

Denis M. Strachan [a,*], Jarrod V. Crum [a], Joseph V. Ryan [a], Alberta Silvestri [b]

[a] *Pacific Northwest National Laboratory, Richland, WA 99354, USA*
[b] *Department of Geosciences, University of Padova, Padova, Italy*

ARTICLE INFO

Article history:
Received 7 June 2013
Accepted 2 December 2013
Available online 8 December 2013
Editorial handling by M. Kersten

ABSTRACT

About 1800 years ago a Roman Corbita sunk off the coast of Italy carrying a barrel of glass cullet to the floor of the Adriatic Sea. Samples of glass cullet and the cemented surrounding sediment have been characterized and the reaction between the glass and the sea water saturated with respect to calcite and dolomite has been modeled. Results from characterization and modeling show that the phase surrounding and cementing together the sediment grains is a high-Mg calcite. We find that the origin of this cementing phase is likely the reaction between the glass and the sea water to form a Mg–silicate, here modeled as sepiolite [$Mg_4Si_6O_{15}(OH)_2{\cdot}6(H_2O)$].

1. Introduction

About 1800 years ago, a Roman Corbita sank at the entrance of the Gulf of Trieste off the coast of Italy near the present town of Grado. When excavated, it was named the *Iulia Felix*. Among the artifacts found in this shipwreck was a barrel of glass cullet (Auriemma, 1999) that probably was being shipped to a melter to be recycled into useful articles (Fig. 1). The wooden barrel contained about 140 kg of glass consisting of some 11,000 pieces, about 6000 of which were colored (pale green, pale blue, green and blue-green) and the remainder colorless glass. Colorless glass represented about 30% of the total mass in the barrel (Toniolo, 2005, 2007, 2008). In this article, we attempt to use our knowledge of how nuclear waste glasses dissolve in water to interpret the results of the 1800-year 'test' on Roman glasses that was started when the *Iulia Felix* sank.

Silvestri and coworkers have characterized these glasses both with respect to composition and the degree of corrosion (Longinelli et al., 2004; Silvestri, 2008). Macroscopically, the *Iulia Felix* glasses show two textural morphologies of the alteration crusts. The colored samples are coated with many iridescent lamellae, imparting a rainbow-like effect. Instead, the surfaces of colorless samples are coated with an opaque white crust, extending more deeply into the bulk of the glass (Silvestri et al., 2005, 2011). There was not very much difference in composition between the two types, however. The main differences between the colored and colorless glasses were in the Al_2O_3, CaO, and Na_2O contents with the colored glass being 0.5 mass% richer in Al_2O_3, 2 mass% richer in CaO, and about 3 mass% richer in Na_2O than the colorless glass (at the expense of SiO_2). These composition differences could be the reason for the difference in behavior. However, glasses richer in alkali and poorer in silica are typically less durable (dissolve faster); the opposite of the observed trend in the *Iulia Felix* glass artifacts.

Pictures, taken during the recovery of the shipwreck, show divers removing the overlying sediment with vacuum hoses to expose the artifacts. For the most part, the sediment is loose. However, the sediment surrounding the glass cullet is extensively cemented (Fig. 2). Why the sediment surrounding the glass cullet should be cemented is important to understanding how the glass dissolved in water. This reaction is complex as witnessed by the periodic pattern of alteration products on the surface of the glass (see Fig. 3 from (Silvestri et al., 2011)).

Several studies of the sediment stratigraphy in the Gulf of Trieste have been made to understand anthropogenic and natural sources of organic carbon, phosphorus, mercury, etc. (Covelli et al., 2006; Emili et al., 2011; Orginc and Faganeli, 2006; Orginc et al., 2005). Most of the sediments are clay and sand with the first 0.8 m being clayey sand and more silt with increasing depth (Orginc and Faganeli, 2006). These deeper sediments are described as: "…olive grey silty clay, well hydrated at the top and more compact below that…" (Covelli et al., 2006) suggesting that the sediment surrounding the *Iulia Felix* artifacts should be loose and consistent with the description given Orginc and Faganeli (2006). The origin of these sediments is from the local rivers that drain primarily the Dolomite Mountains and Julian Alps. Thus, the sediment consists largely of calcite and dolomite that make up a large fraction of the regional mineralogy (McKenzie and Vasconcelos, 2009).

* Corresponding author. Address: PO Box 999 (K6 24), Richland, WA 99354, USA. Tel.: +1 541 593 4628.

E-mail addresses: denis.strachan@pnnl.gov (D.M. Strachan), jarrod.crum@pnnl.gov (J.V. Crum), joe.ryan@pnnl.gov (J.V. Ryan), alberta.silvestri@unipd.it (A. Silvestri).

0883-2927/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.apgeochem.2013.12.003

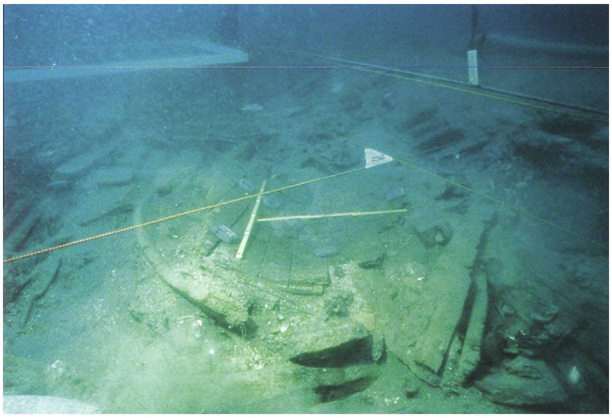

Fig. 1. A picture of the *Iulia Felix* shipwreck remains with a focus on the glass cullet barrel (staves at the intersection of the rulers).

Fig. 2. A photo showing the cemented sediment surrounding a piece of glass cullet, in this case colorless glass.

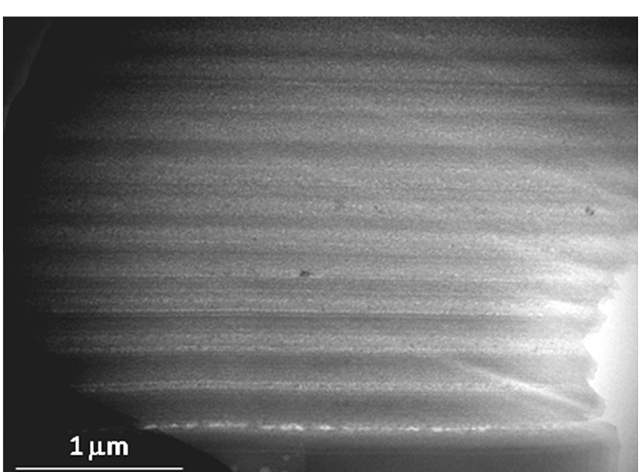

Fig. 3. A TEM photomicrograph of the alteration products on the surface of a colored glass specimen from the glass cullet on the *Iulia Felix*.

The presence of calcite and dolomite in these sediments prompted us to investigate if the precipitation of sepiolite [$Mg_4Si_6O_{15}(OH)_2{\cdot}6(H_2O)$] or similar Mg–silicate on the surface of the glass might be related to the cementing of the grains surrounding the glass artifacts from the *Iulia Felix*. There is precedence for this supposition. Grambow and Strachan (1984) modeled the dissolution of two nuclear waste glasses in 1 mmol/kg $MgCl_2$ and found that the resulting solution compositions matched a phase similar to sepiolite. Magnesium silicate precipitation was also found to have a major effect on high-level nuclear waste glass dissolution by Maeda et al. (2011). Magnesium silicates have been found in the sea water altered Embiez glass (Debure et al., 2012, 2013; Gin et al., 2006; Verney-Carron et al., 2010a, 2010b) and, while crystalline Mg–silicates were not found in the alteration layers of the *Iulia Felix* glasses, the presence of Mg throughout the samples and the glass alteration layers (Silvestri et al., 2005, 2011) does not rule out the possibility of amorphous or crypto-crystalline Mg-bearing alteration products. Silvestri et al. (2011) (see their Fig. 2) found poorly crystalline interlamellar material that yielded diffuse ring diffraction and ill-defined, bent lattice fringe structures in the transmission microscope, suggestive of a smectite-like material. Debure et al. (2012, 2013) and Verney-Carron et al. (2009, 2008, 2010b) have shown the presence and likely effect of Mg-minerals on the Embiez glass Geisler et al. (2009, 2010) and Scheiter et al. (2007), albeit dissolving glasses in acids, suggest an alteration process involving congruent dissolution of the glass followed by diffusion through a growing alteration layer. This leads to Liesegang-like banding structure to the alteration layer, similar to that observed in the *Iulia Felix* colored glass. However, the emphasis of our article is not the effect on the glass, but the source of the high-Mg calcite precipitate on the surfaces of the overlying sediments. This is a first step toward understanding the mechanism by which the glasses dissolved in the Adriatic Sea water. Since it is newly-formed on the surface of the grains and has cemented them together (Silvestri et al., 2005), our intent was to determine, at least qualitatively, the origin of the newly-formed high-magnesium calcite – glass reaction with sea water alone or glass reaction with a Mg alteration product (sepiolite in this case).

With respect to the Embiez glass, Mg–silicates were found when the glass was in contact with a sea water from the western Mediterranean Sea where the Mg concentrations are about 1.3 g/kg (Verney-Carron et al., 2010b). The *Iulia Felix* was found in the northern Adriatic Sea with different sediments and, presumably, different Mg concentrations, although the composition(s) of Adriatic Sea water was not found in the literature. Additionally, the Embiez glass was in contact with fresh sea water since the boat sank. In the case of the *Iulia Felix* glass, the glass was quickly covered with a dominantly calcite-dolomite sediment.

In this article, we provide supporting results from calculations of the interaction between a typical Roman glass and Adriatic Sea water to show that as the glass dissolves in sea water the grains of sediment might be expected to be cemented with a calcite phase.

2. Materials

A set of samples was graciously provided by the Dipartimento di Geoscienze, Universita' di Padova with permission from the Italian Minister of Cultural Heritage. Of particular interest for the study reported here is the cemented sediment that surrounds the glass cullet (Fig. 2). A portion of this sediment was ground to a powder for X-ray diffraction (XRD) analysis. Another portion was removed, potted in epoxy, sectioned, and polished for analysis in a scanning electron microscope (SEM). A sample of modern beach