SEM–EDS analysis of copper, glass and iron recovered from the 1st century AD shipwreck site off Godawaya, Southern Sri Lanka

Recent maritime archaeological explorations conducted at a shipwreck site in the offshore regions of Godawaya, a fishing village on the south coast of Sri Lanka led to the retrieval of several artefacts such as copper slag, glass ingots, iron concretions and wood pieces[1]. This ship wreck site, at a water depth of 33 m, is situated ~ 4 km offshore in the vicinity of river mouth of the Walawe Ganga on the southern coast of Sri Lanka (Figure 1). A carved inscription on a natural rock located to the north of the Stupa, states about the existence of a seaport at Godawaya during the historical period[2].

The explorations and excavations at Godawaya during the last two decades have unearthed several archaeological remains such as a temple, a harbour and also an important inscription[3]. Close to Godawaya, there are famous monasteries at Mahanavulupura and Ramba monastic complexes, which have been either excavated or thoroughly explored. Results of these studies indicate active maritime activity in the historical and medieval periods in the port area of Godawaya. The present study includes results from analysis of elemental oxides of the artefacts (copper, glass and iron) and ^{14}C dating of a wood piece recovered from the shipwreck site off Godawaya, Southern Sri Lanka.

SEM–EDS analysis: The clear specimens (size 2–4 mm) of these artefacts are placed on a carbon conductive tape stuck on a nylon stub. Each specimen is mounted on a separate stub in such way that the surface to be analysed faces upwards. These specimens are then sputter-coated with about 20-nanometre-thick gold coating using a gold sputter coater. Each coated specimen image was analysed by SEM (model JSM 5600) with an EDS attachment (model JOEL 5800 LV).

Extraneous material within the pores of the wood samples such as carbonate deposits were removed by treating the wood sample with dilute hydrochloric acid repeatedly followed by a thorough wash with deionized water. The wood sample was then dried and powdered, and combusted in presence of O_2 to yield CO_2. The CO_2 obtained was converted to benzene for ^{14}C measurement. The ^{14}C activities were assayed using a low background PACKARD 2250CA Liquid Scintillation Counter[4]. The calculated ^{14}C ages were calibrated using INTCAL09 (ref. 5).

In order to determine the abundance of elemental oxides and compositional variations of the copper slag, iron concretion and glass, SEM–EDS studies were

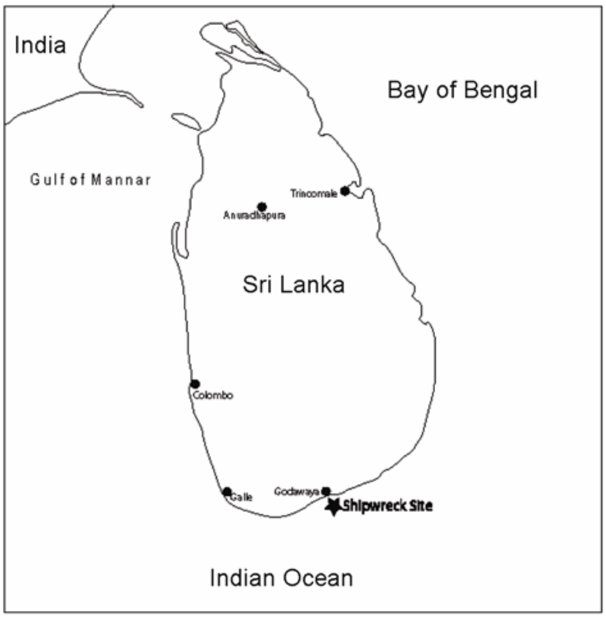

Figure 1. Location of shipwreck site off Godawaya.

Table 1. EDS results of minimum, maximum and average abundance (wt%) of elemental oxides of copper slag, glass ingot and iron concretion

Elemental oxide	Average	Minimum	Maximum	Number of spots
Copper slag				
SO_3	1.95	1.41	3	*N* = 9
FeO	0.29	0.24	0.36	*N* = 4
CuO	97.91	97	98.59	*N* = 9
Glass ingots				
Na_2O	12.85	5.17	21.49	*N* = 5
MgO	0.42	0.00	0.92	*N* = 3
Al_2O_3	8.10	7.08	9.29	*N* = 5
SiO_2	62.67	60.61	64.17	*N* = 5
K_2O	1.76	1.22	2.26	*N* = 5
CaO	8.07	4.61	11.91	*N* = 5
TiO_2	0.63	0.00	1.53	*N* = 3
FeO	3.33	1.26	5.87	*N* = 5
CuO	1.37	0.00	2.92	*N* = 4
Ag_2O				*N* = 1
Iron concretion				
MgO	1.39	1.11	1.26	*N* = 3
Al_2O_3	2.43	0.6	4.25	*N* = 2
SiO_2	7.06	0.88	17.76	*N* = 4
SO_3	16.48	13.74	18.25	*N* = 3
K_2O	0.37	0.37	0.37	*N* = 1
CaO	0.93	0.45	1.19	*N* = 3
FeO	77.54	66.58	83.96	*N* = 4

carried out on these artefact samples. To further understand the intra-granular compositional variation, measurements were also done at several spots across each specimen. Results are shown in Table 1.

Even though several antiquities such as pottery (Figure 2), a stone quern (Figure 3), a piece of wood, glass ingots, copper lump and iron concretion were recovered from the explored site, only copper lump, glass ingots and iron concretion were selected for SEM–EDS studies owing to their unaltered surfaces devoid of weathering and also absence of any foreign material on their surfaces (Table 1, Figure 4). A wood sample has been dated using radiocarbon (^{14}C).

EDS analysis was carried out on the copper slag at nine spots. The major elemental oxides distribution according to their abundance is CuO, SO_3 and FeO. The average weight (%) of CuO, SO_3 and FeO in the copper slag is 97.91, 1.95 and 0.29 respectively (Table 1). Interestingly, CuO wt% values range from 97.00 to 98.59 whereas FeO has an average wt% of 0.29 only at four spots.

The SEM–EDS studies were carried out at five spots in the glass ingot. These glass ingots weigh about 2–3 kg with a diameter of about 20 cm. Results show that major elemental oxides present in order of their abundance are SiO_2, Na_2O, Al_2O_3, CaO, FeO, K_2O, CuO, TiO_2 and MgO with average wt% of 62.67, 12.85, 8.10, 8.07. 3.33, 1.76, 1.37, 0.63 and 0.42 respectively. SiO_2 is the major component with an average value of 62.67% varying within a narrow range of 60.61–64.17%. TiO_2 is present in three spots with an average value of 0.63%.

The SEM–EDS results of four spots in iron concretion show that major elemental oxides present in order of their abundance are FeO, SO_3, SiO_2, Al_2O_3, MgO, CaO and K_2O with average wt% of 77.54, 16.48, 7.06, 2.43, 1.39, 0.93 and 0.37 respectively. FeO is the major component (Av. 77.54%) ranging from 66.58% to 83.96%.

Radiocarbon age obtained from the wood sample is 1910 ± 100 yrs BP. The calibrated age based on INTCAL09 is 1865 ± 100 yrs BP corresponding to 85 ± 100 yrs AD[5].

Discovery of copper smelting technology led to the emergence of early civilizations around the world as early as during the mid-Holocene (4000 yrs BC) and was used to make weapons and other household items. Copper continued to be an important element in the Indian culture until stainless steel replaced it in the recent times. The advanced smelting and refining techniques date back to the pre-Harappan times in the Indian subcontinent. As a result, a large number of copper and bronze artefacts have been reported from many sites in this region. The analysis of copper artefacts, from the Harappan sites at Lothal[6] and Kalibangan[7], revealed copper purity as high as 99.6% without any arsenic traces. However, copper objects discovered from Harappa are reported to contain arsenic contaminants[8], thus indicating different source materials. During the Harappan times, Khetri mines of Rajasthan, India, had been a major source of copper in addition to Oman and UAE in the Gulf region[9]. The copper alloy in the present study is composed of a mixture of copper oxide (CuO av. wt% 97.92), iron oxide (FeO av. wt% 0.29) and sulphite (SO_3 av. wt% 1.95). It suggests that the source mineral ore used to make this copper slag is probably a sulphide ore, chalcopyrite ($CuFeS_2$), a mineral that accounts for ~50% of the world copper deposits.

In India, glass has been known since the 2nd millennium BC[10]. Glass ingots recovered from the Uluburun wreck[11] were dated back to the late Bronze Age. The present finding attains significance because glass ingots are not so often reported in this part of the world. Glass ingots in the present study constitute SiO_2 as a major component with an average wt% of 62.67 and contain an average high Al_2O_3 of 8.10% in a narrow range of 7.08–9.29% and its Al/Si ratio varies between 0.125 and 0.173. K_2O contents range from 1.22 to 2.26 wt% with an average wt% of 1.76. Lime (CaO) content varies from 4.61 to 11.91 wt% with an average wt% of 8.07, whereas soda (Na_2O) ranges from 5.17 to 21.49 wt%

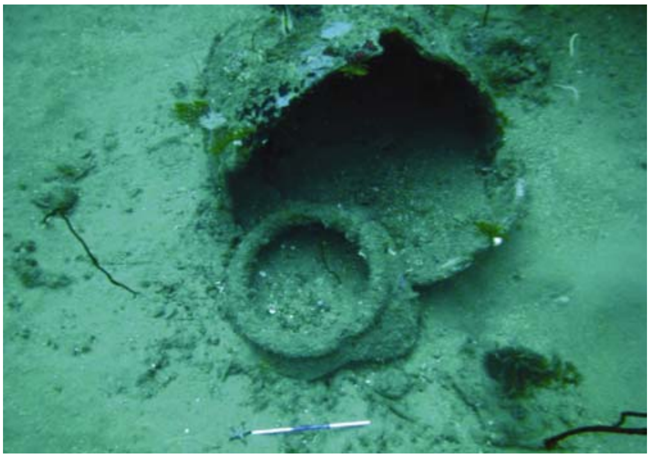

Figure 2. Large-sized jar noticed in the shipwreck.

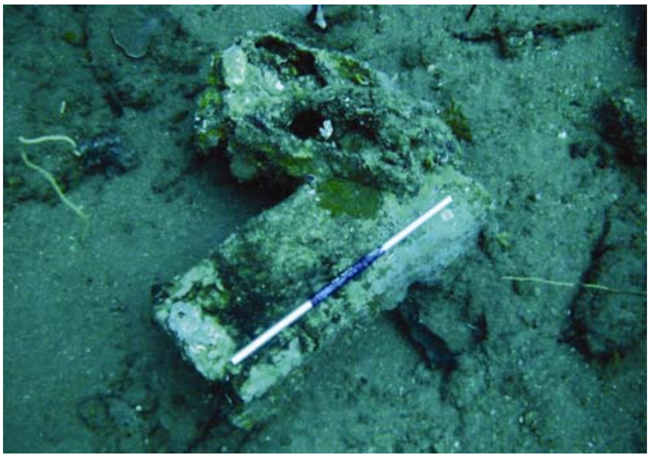

Figure 3. Four-legged stone quern in the shipwreck.

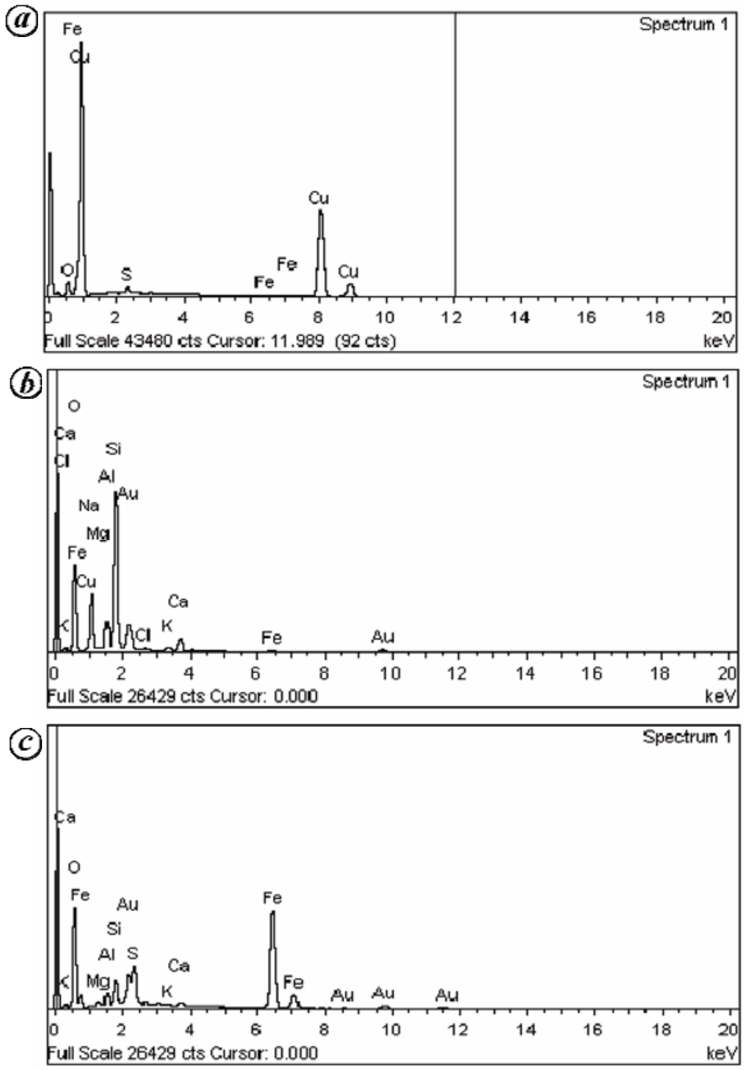

Figure 4. Representative SEM–EDS spectra of copper slag (***a***), glass ingot (***b***) and iron concretion (***c***).

with an average wt% of 12.85. These alkali contents affect the melting point of quartz sands during glass-making. Glass ingots from our study can be listed in the soda-lime category, as soda-lime glasses comprise low CaO and K_2O content around 10% and potash-lime glasses mostly have high K_2O content of about 10–20% with CaO content of more than 12% and less than 18%.

The earliest shipwreck studied in this part of the Indian Ocean was in the Belitung Island of Indonesia and is dated as 9th century AD[12]. Pottery such as Martaban, Khamer or Islamic glazes were exclusively traded overseas around the 9th century irrespective of the origin of the ship. Bass[13] reported that large-sized jars were used in the ships for cargo transportation since the Bronze Age until the late medieval period. The jars of Godawaya shipwreck showed a globular base, implying that they were placed over a suitable base. Other ceramics from the Godawaya shipwreck such as carinated dishes showed variation that existed both in prehistoric and historical periods, whereas the fabric of these ceramics/pots indicates a time-period older than Megalithic.

Stone querns reported earlier from various archaeological sites in India and Sri Lanka appear to be of the Mesolithic period (and continued till modern times in a different form). However, four-legged querns were dated between 4th century BC and 4th century AD in many archaeological sites in India. Its prolific appearance may be traced to the *Satavahana* period[14] (2nd century BC to 1st century BC). Thus, a possible time bracket for this wreck may be between 2nd century BC and 2nd century AD.

As expected, the results of radiocarbon (^{14}C) dating of the wood showed radiocarbon age of 1910 ± 100 yrs BP and calibrated age of 1865 ± 100 yrs BP based on ^{14}C half life of 5730 ± 40 years. The calibrated age of the sample thus obtained is 85 ± 100 yrs AD (1st century AD) after subtracting 1950 from the age.

^{14}C dating of the wooden piece and other archaeological studies on pottery and stone quern suggest a date bracket of 1st century AD for the shipwreck. This shipwreck could perhaps be the oldest reported so far in the southeast Asian region and likely to provide more evidence and deeper insights into the trade and commerce of the early historic period.

The EDS analysis of artefacts indicates existence of advanced metallurgic techniques with an ability to produce durable and high quality iron, copper and glass ingots till the historical period. Recovery of glass ingots from the wreck site point out that glass took a centre stage amongst the trade items during this period.

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ACKNOWLEDGEMENTS. We thank Prof. Nimal De Silva, Director General of Central Cultural Fund, Sri Lanka for supporting this programme. We also thank the funding agencies: UNESCO, Bangkok and The Cultural Heritage Agency of the Netherlands (through their Mutual Heritage Policy Programme). This is NIO contribution no. 5208.

Received 12 March 2012; revised accepted 9 July 2012

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