Bacterial corrosion of cast bronzes in anaerobic sea water

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Objective

Archaeological bronze statues discovered in both fresh and marine water often appear in an **excellent conservation state**, with little or no evident corrosion. The **black colour** and the **nature** of the **patina** formed seems to be related to the presence of superficial **copper sulphides**. Their formation could be connected to: 1) an **intentional patination**; 2) **bacterial corrosion**. Microorganisms can hence survive and thrive in **anaerobic conditions** and in presence of copper alloys **exploiting sulfur** (cathodic half reaction) and the **metallic matrix** (anodic reaction) as alternate sources of carbon promoting the precipitation of **copper** (I) and (II) **sulfides** [1].

Aim of the research

This study aims to characterize the effect of **anaerobic bacteria** on analogues of **ancient bronzes** reproducing those of **classical statuary** buried in **seawater**

Materials

Three different **Cu alloys** were produced by casting:

- **CuSn10**
- **CuSn10Pb5**
- **CuSn3Pb5Zn3**

Experimental set-up

Seawater was collected from the **Genoa harbour** and **two conditions** were set: :

- **Deoxygenated filtered Seawater** without living bacteria (**blank** condition - **SW**)
- **Deoxigenated Seawater + peptone** with **bacteria** (**SWB**)

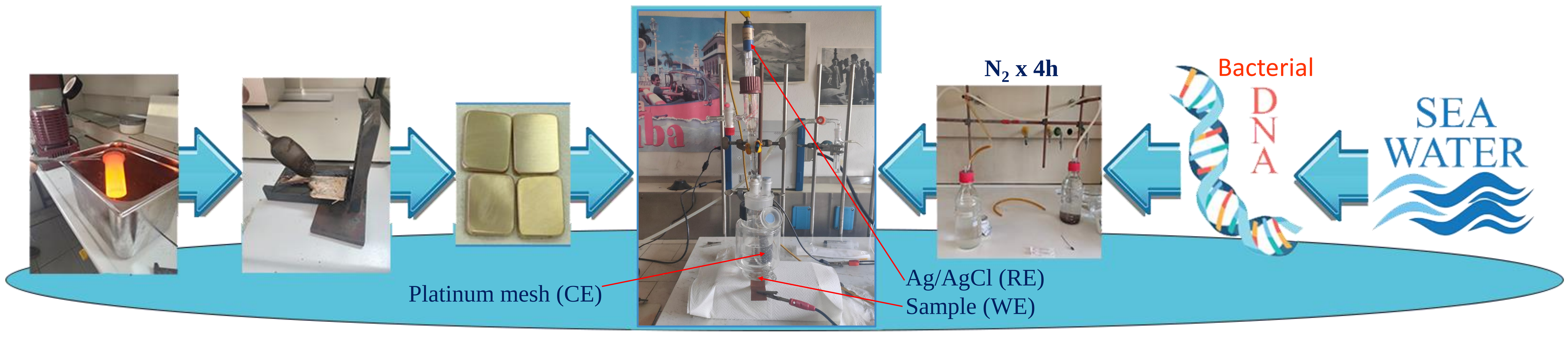
Methods

Electrochemical tests for ageing:

- Open circuit potential (**OCP**)
- Potentiodynamic polarization (**PDP**)

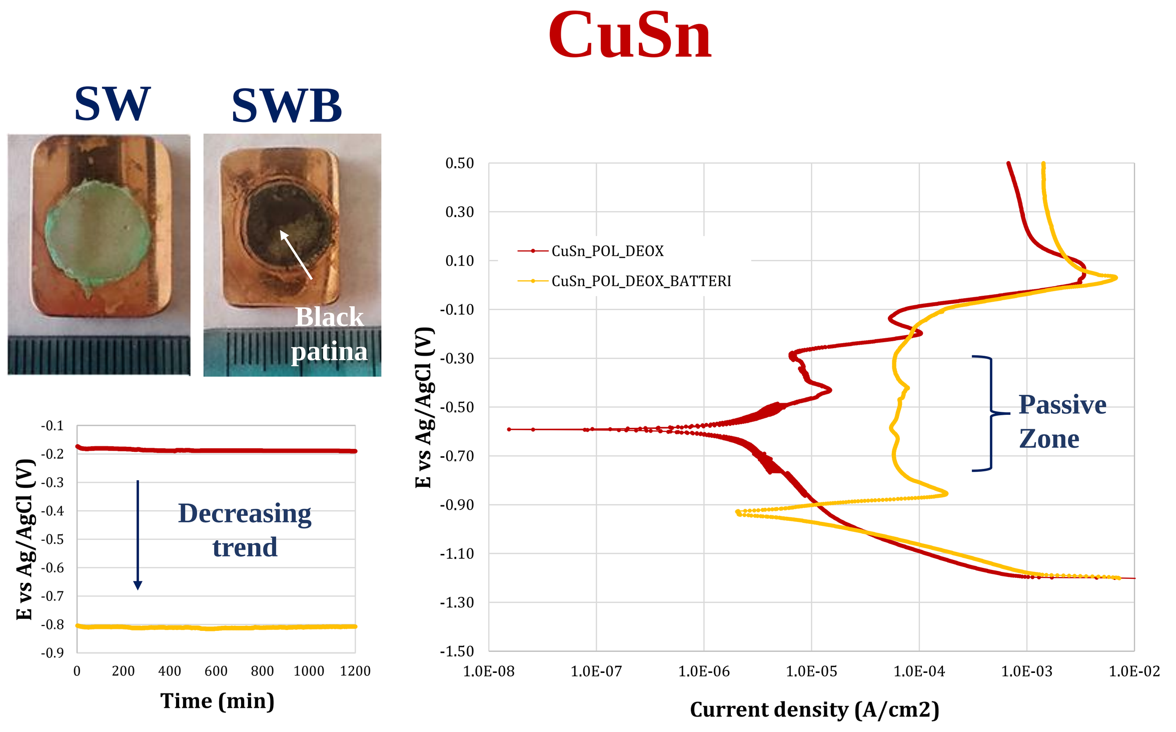
Post-experimental analyses:

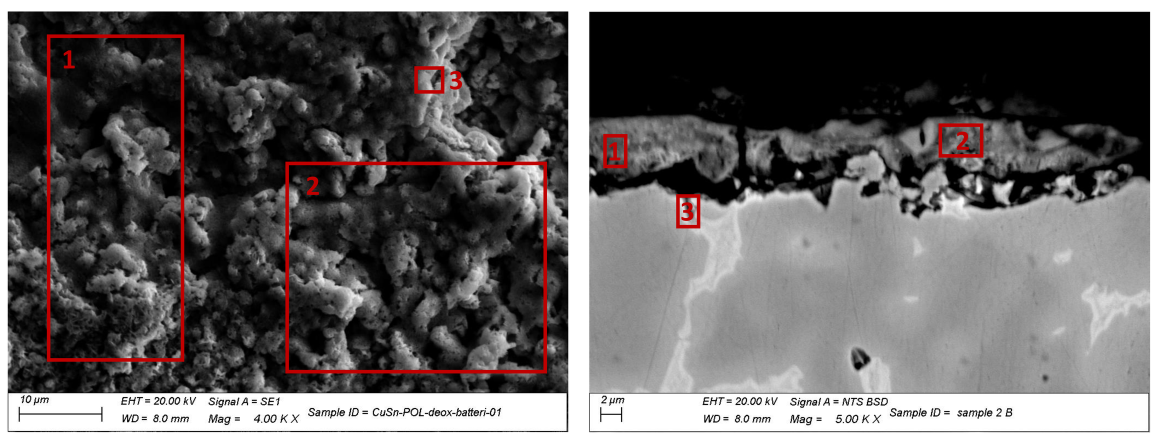
- Optical microscope (**LOM**)
- Scanning electron microscopy (**SEM-EDS**)
- X-ray photoelectron spectroscopy (**XPS**)



RESULTS

CuSn

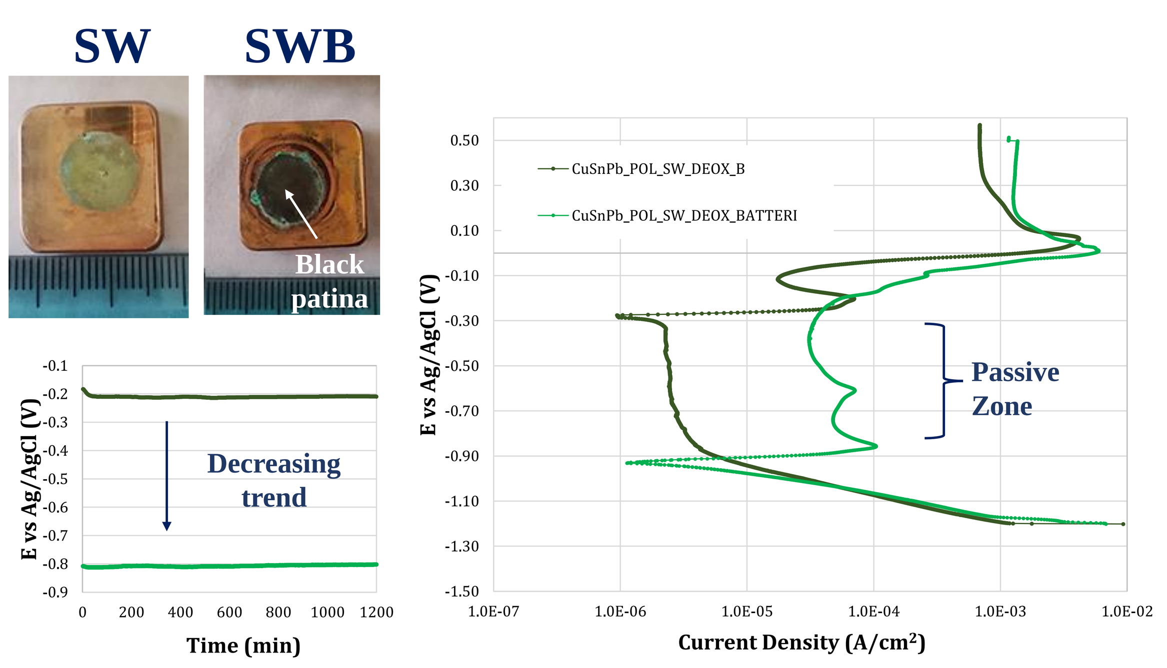


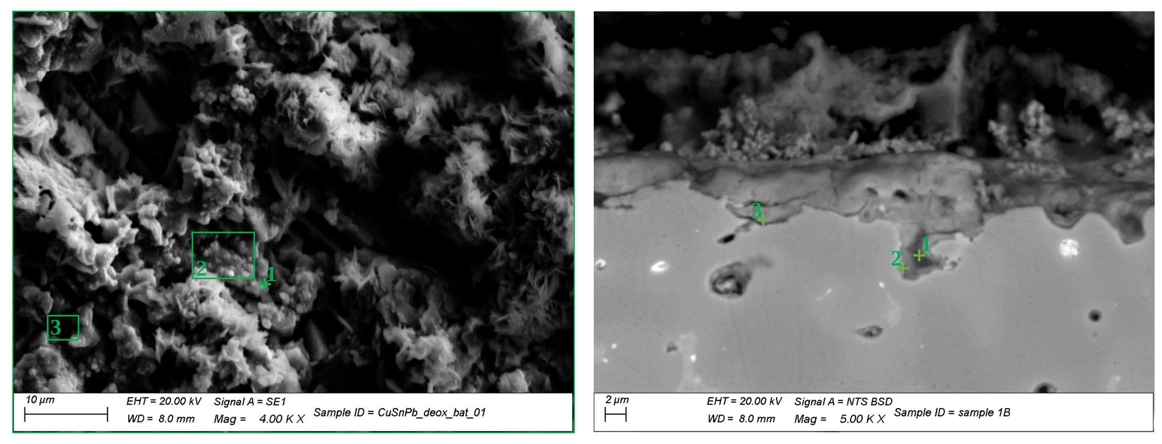


Spectrum	Atomic%			
	O	S	Cl	Cu
1	40.8	4.2	20.9	34
2	43.1	4.0	18.9	33.9
3	51.9	2.6	18.6	26.8

Spectrum	Atomic%				
	O	S	Cl	Cu	Sn
1	19.53	0.67	7.01	38.94	33.86
2	62	1.07	5.98	17.68	13.28
3	52.39	0.75	9.75	29.88	7.23

CuSnPb

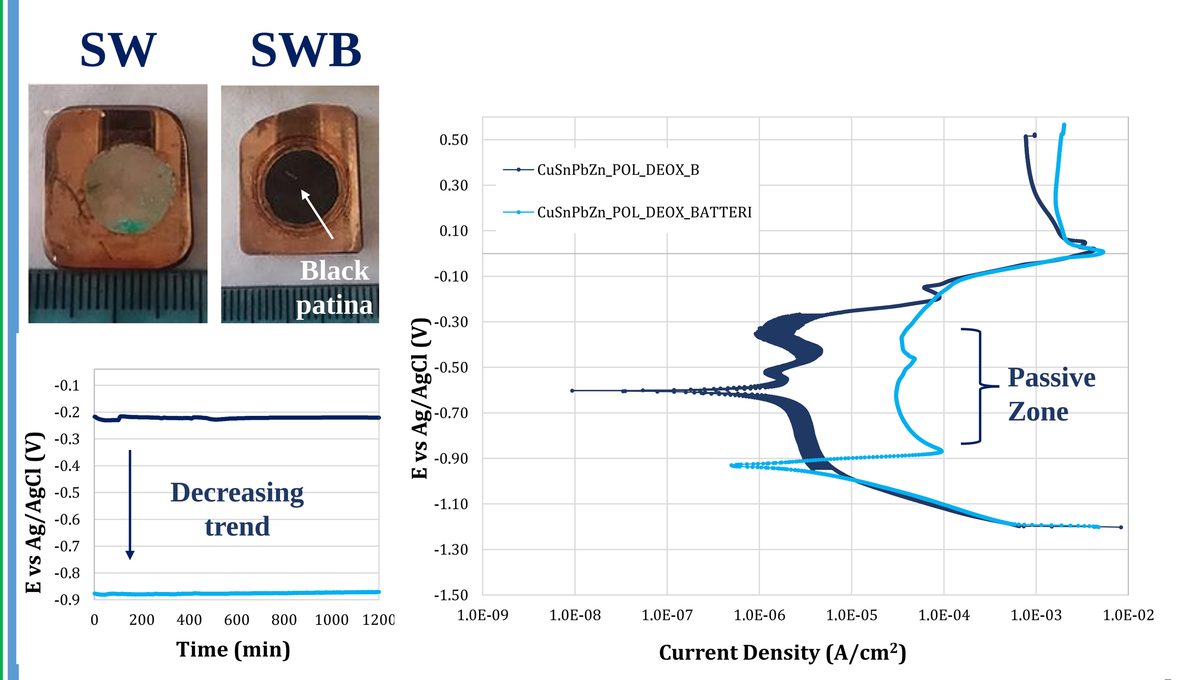


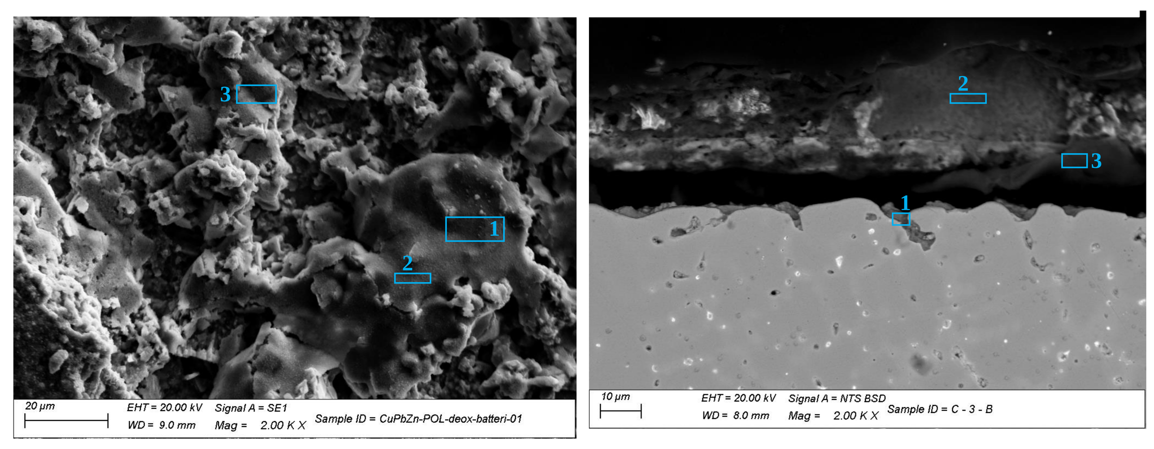


Spectrum	Atomic%				
	O	S	Cl	Cu	Sn
1	4.62		22.68	72.7	
2	28.64	1.29	20.68	49.03	0.36
3	40.8	2.71	18.06	36.05	2.37

Spectrum	Atomic%					
	O	S	Cl	Cu	Sn	Pb
1	39.29	0.3	8.36	43.69	6.84	1.51
2	49.04	1.43	2.91	29.17	17.44	
3	33.73	0.7	12.36	39.29	12.06	1.85

CuSnPbZn

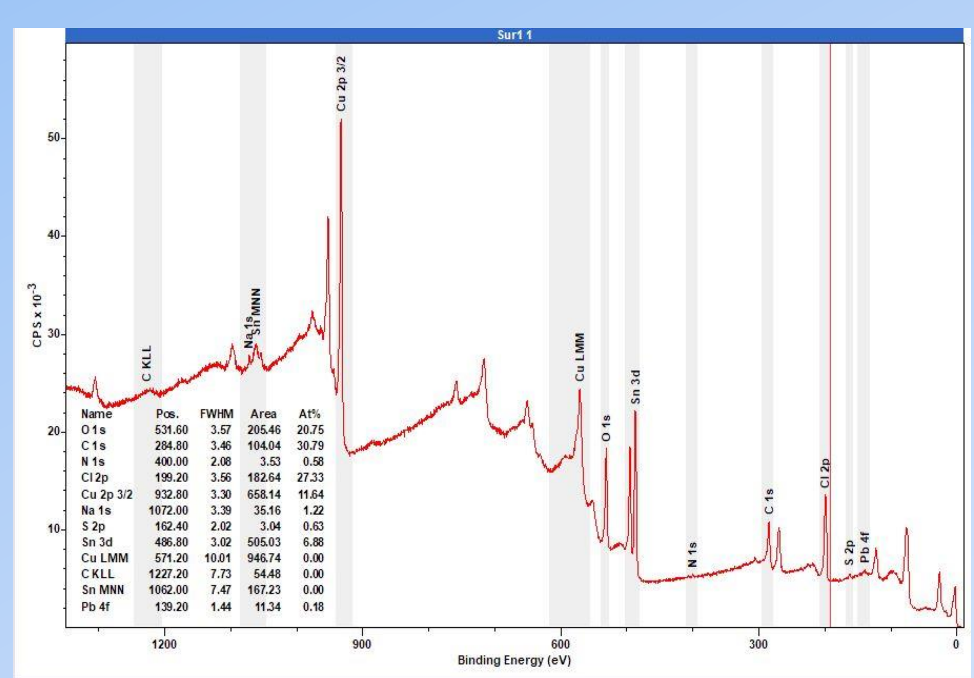




Spectrum	Atomic%			
	O	S	Cl	Cu
1	49	9.7	17.4	24
2	34.7	2.6	23	39.7
3	42.2	1.9	19.6	36.2

Spectrum	Atomic%					
	O	Si	S	Cl	Cu	Sn
1	36.6		6.58	2.53	54.29	
2	14.55	0.83	0.81	7.69	70.99	5.13
3	43.09	9.08		2.88	44.96	

XPS



Preliminary analyses on the **CuSn10Pb5-SWB** show a **layer** of **Cu_2O** and **SnO_2**. The corrosion area was **sputted** with Ar^+ to **remove** part of the **superficial carbon** and reach the **layers closest** to the **bulk**. Also **Cl** and **S** bound to the metal were detected. Furthermore, given the presence of **C** and **N** in **high quantities**, we can deduce a **biotic activity** due to the presence of **biofilm/sessile cells** attached to the **surface**

Conclusion

In presence of **bacteria**, the OCP measurements show a **decreasing trend** for each alloy (**CuSn10**, **CuSn10Pb5**, **CuSn3Pb5Zn3**), with a potential **variation** between **SW** and **SWB** of more than **600 mV**. The presence of **Zn** in the alloy **further lowers** the corrosion potential. The **corrosion phenomenon** in **presence** of **microorganisms** is very consistent and occurs as a **localized mechanism**. Hence, the **anodic curves** show **passive areas** with higher currents with production of a **passive** but **more conductive film** on the surface.

The **EDS results** show the **presence** of **S** on the surface of each alloy (**CuSn10**, **CuSn10Pb5**, **CuSn3Pb5Zn3**), coherently with a **corrosion mechanisms** that involves the **sulphate-reducing bacteria (SRBs)**. A **larger quantity** of **S** was detected in the **CuSn3Pb5Zn3**, probably due to the **dissolution** of **Zn** which **favors the metabolic action** of **bacteria**. It is hence hypothesized the precipitation of **Cu_2S**, **CuS** and **$CuSO_3$** that limit the kinetics of corrosion. Accordingly, the environment enriched in **SRBs** allows for the production of a **passive patina with** a **composition** and **appearance** very close to those analysed on submerged objects [4]**.**

References

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