

# Preliminary evaluation of antifouling properties of high temperature ceramic glaze coatings in marine environment

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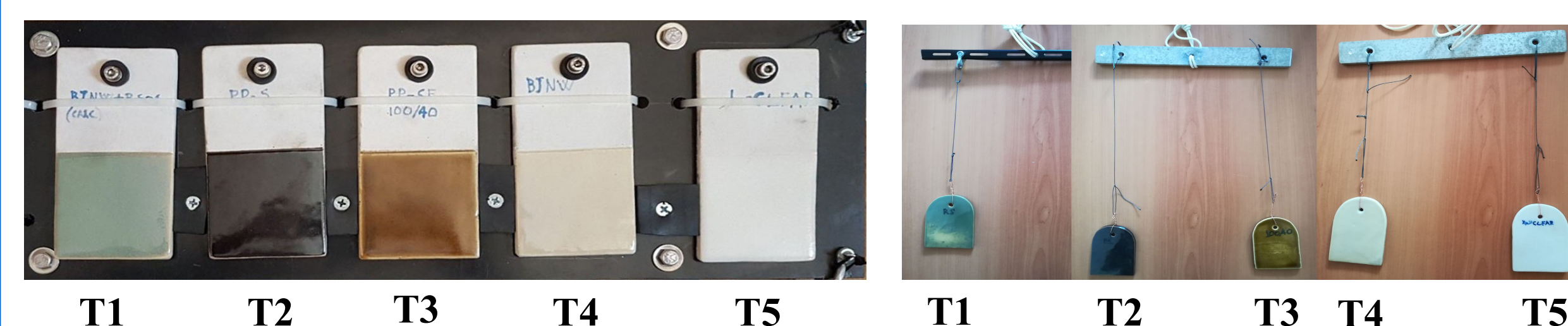
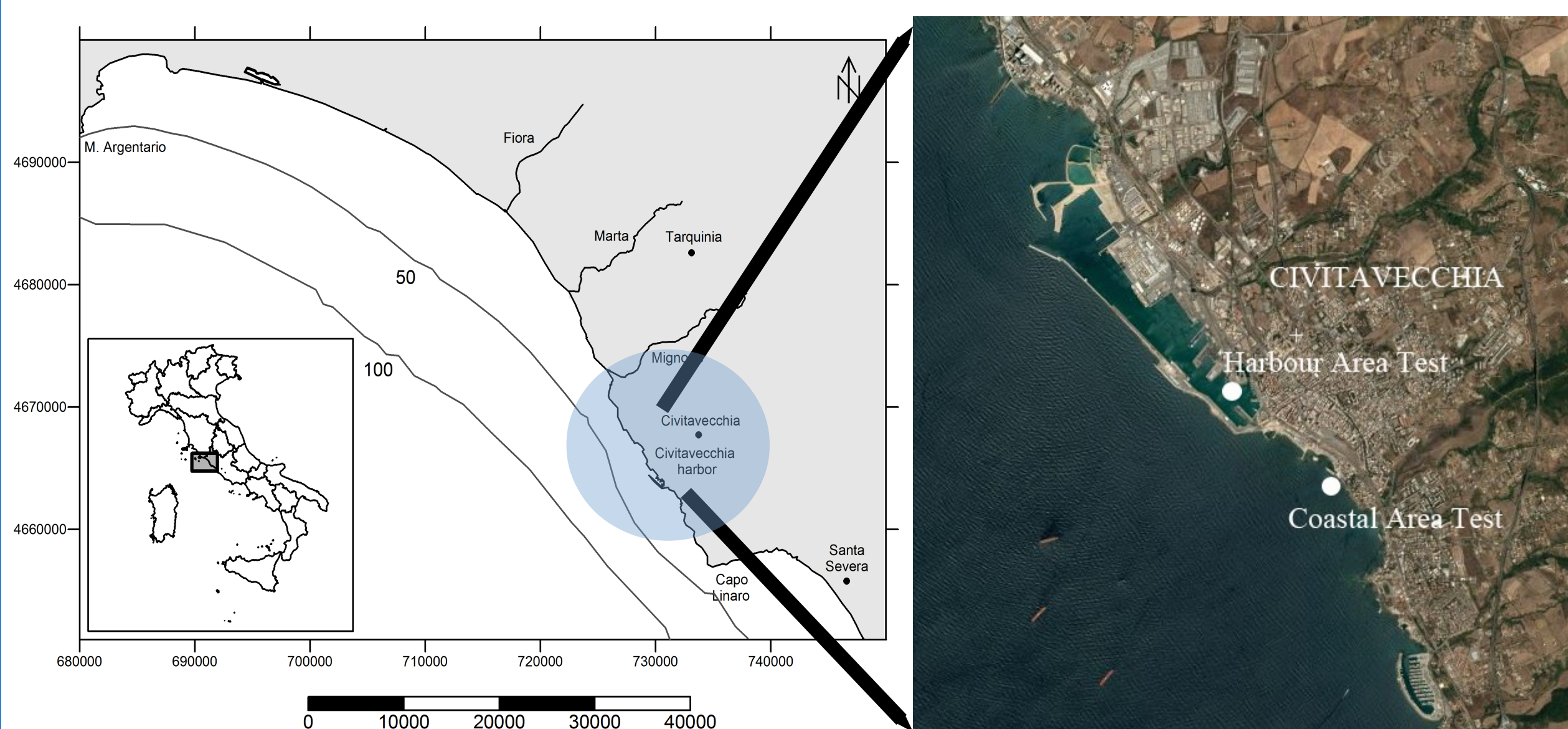


## INTRODUCTION

This work presents some preliminary results concerning the assessment of antifouling properties of high temperature ceramic glaze coatings in marine environment. As traditional antifouling measures, such as toxic coatings, are a threat to marine biodiversity because of the toxic releases that affects marine organisms and represents a direct source of marine pollution, the use of new materials and strategies to approach the problem is needed. High temperature ceramics presents some remarkable technical properties such as hydrophobicity and low roughness coefficient. These characteristics, combined with others such as the very high resistance to wear, the chemical inertia and the very low coefficient of electrical conductivity, have made ceramic a material widely used in various fields of technical and scientific application. The original idea for the current research comes from suggestions related to the historical-artistic-artisan aspect from which this material has had its origins with reference to deductive observations centered on the state of conservation of some artefacts found and recovered from ships wrecks, sunk in different eras and lying at different depths in the sea, along the trade routes connecting the far east with the west. Attention was focused on this last step; it has been noted how the artefacts have remained immersed in the sea for decades and, for the most part, for centuries, have been recovered to the original beauty with extreme ease, removing, without excessive difficulty, sediment and encrusting organisms.

## STUDY AREA

To perform a preliminary test of antifouling properties of high temperature glazes coatings, five tiles of 14 cm x 7 cm were placed in the coastal area of Civitavecchia (Northern Tyrrhenian Sea, Italy), at a depth of 1 m. Half of the surface of each tile is covered with glaze of different composition. The tiles were placed in a structure fixed with a buoy. Five tiles of the same composition were also placed at a depth of 1 m. in Civitavecchia Harbour using a fixed structure with tiles attached to supports. These tiles have been glazed on both sides and there are no unglazed parts. The tests were performed between October and December 2017.

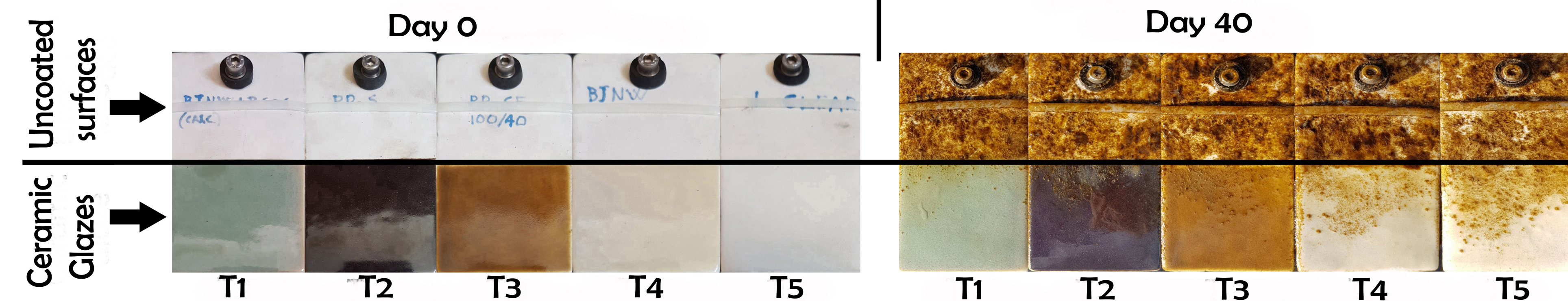


High Temperature Glaze characteristics:

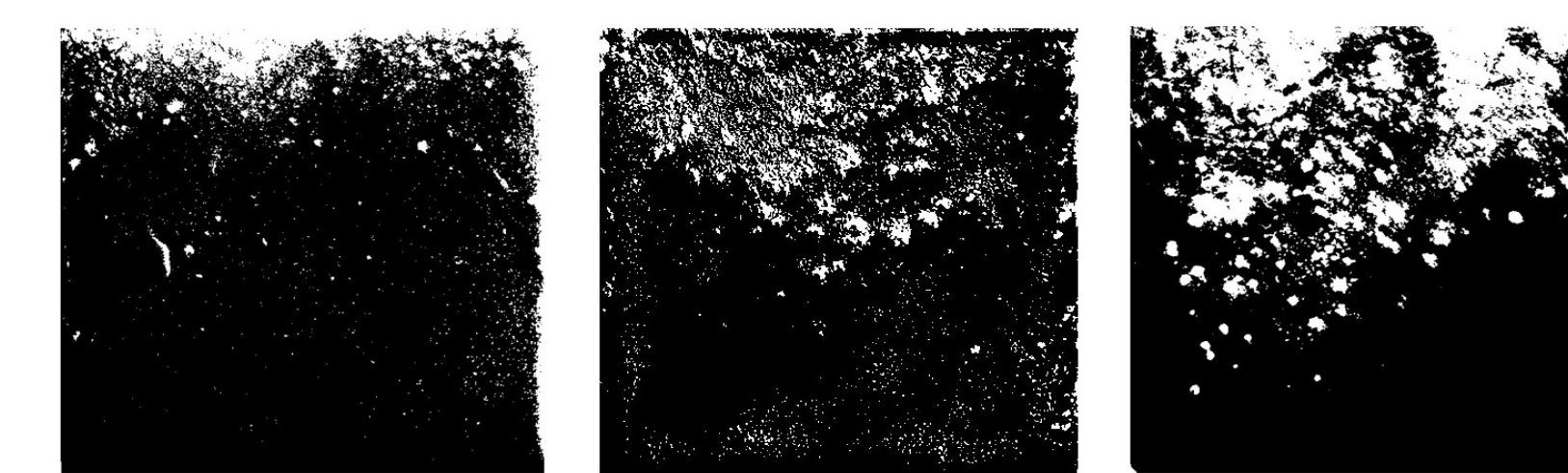
**Glaze T1:** Si/Al ratio  $\leq 10$ ; Ca  $\geq 10\%$ . Additions of Cu and Sn oxides ( $<3\%$ );  
**Glaze T2:** Glaze obtained from local volcanic rock (ignimbrite);  
**Glaze T3:** Ignimbrite + sandstone coating. Ratio between the component rocks: 100/40.  
**Glaze T4:** coating as "T1" without addition of Cu and Sn oxides;  
**Glaze T5:** High temperature eutectic coating (Al-Si; Ca; K).

All the glazes were fired at a temperature of about 1280 °C in an oxidizing atmosphere.

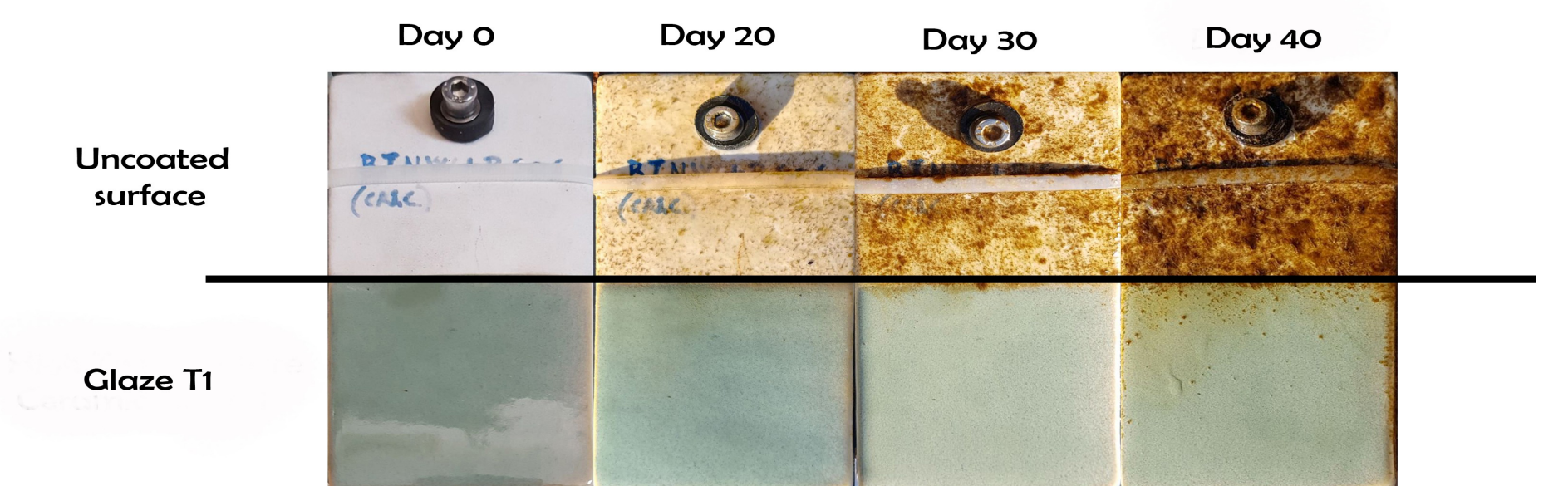
## HIGH TEMPERATURE GLAZE: COASTAL AREA RESULTS



The tiles should have been left in water for 50 days but after 42 days a storm destroyed the fixed buoy and the tiles were lost. However during the 40 days periodic photographic surveys were carried out to macroscopically evaluate the fouling progression. The surface occupied by fouling organism was quantified using a photographic technique as reported by Jarabek et al. 2016.

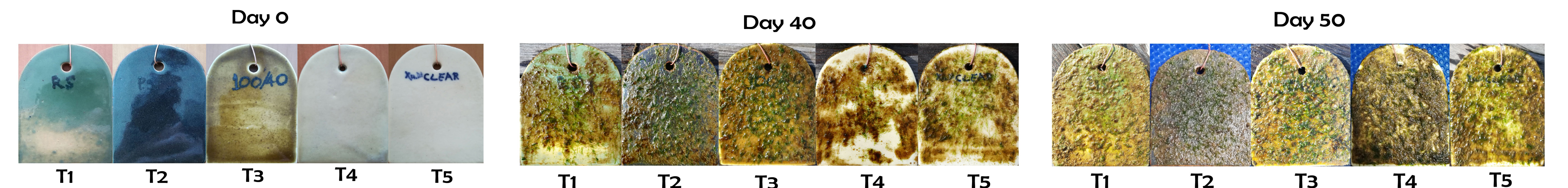


T1, T3 and T5 glaze surface analysis (day 40) performed through Imagej software

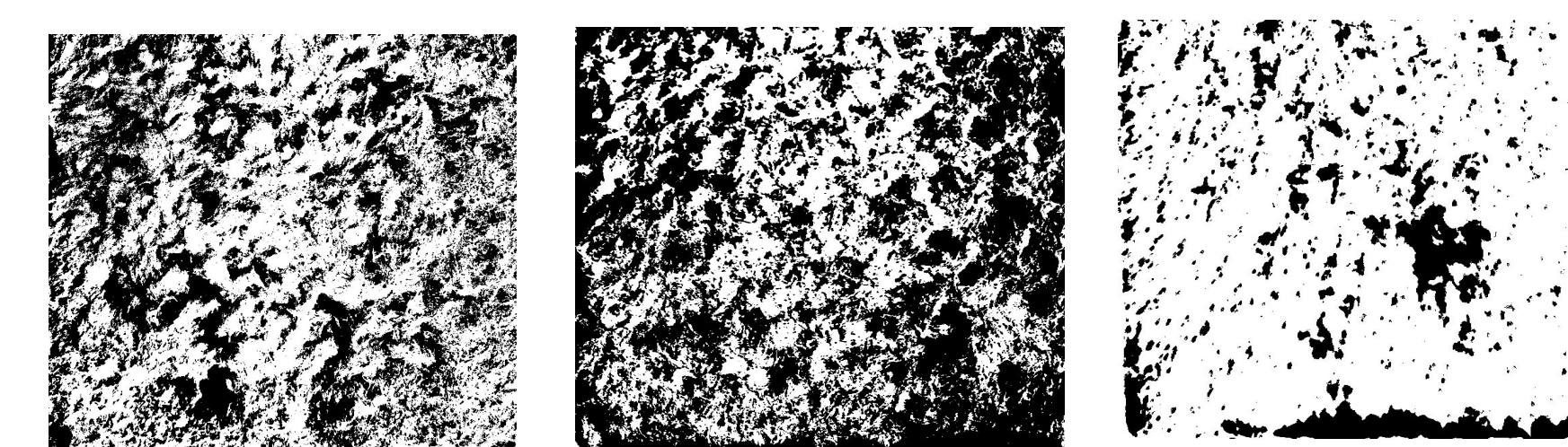


Fouling coverage measurements show that the best performance for the coastal area test was that of glaze T1 with a total coverage after 40 days of about 7%. Glaze T3 and T4 show similar results with a total coverage of about 13% while glaze T5 shows a coverage of about 22%.

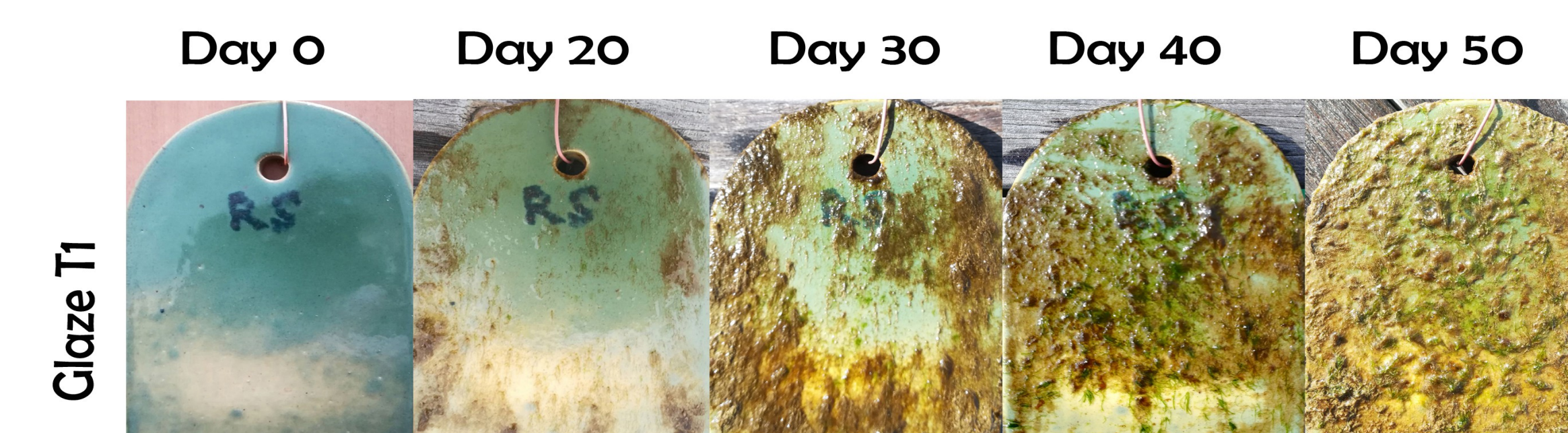
## HIGH TEMPERATURE GLAZE: HARBOUR AREA RESULTS



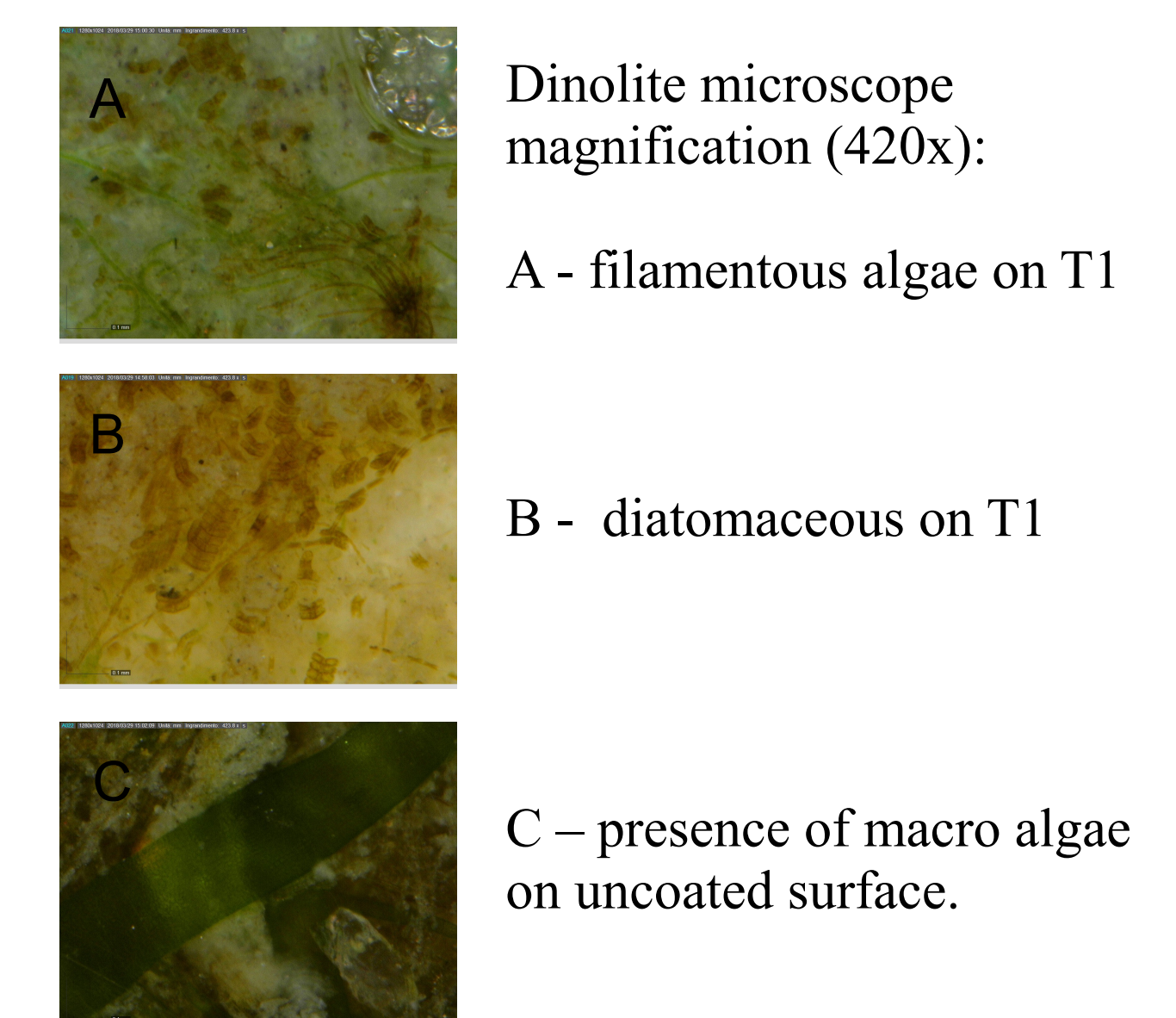
The tiles have been left in water for 50 days. Periodic photographic surveys were carried out to macroscopically evaluate the fouling progression. The surface occupied by fouling organism was quantified using the same technique as for the coastal area.



T1, T3 and T5 glaze surface analysis (day 50) performed through Imagej software for harbour area test.



Fouling coverage measurements show that all coatings have a worse performance in the harbour environment than the results obtained in the coastal environment. The coverage analysis confirms that the T1 glaze is the best (55% of colonized surface) compared to T2 and T3 (60%) and T4 and T5 (85%) coatings. Although the coatings are strongly colonized, none of the glazes show colonization of macro algae.



Dinolite microscope magnification (420x):  
A - filamentous algae on T1  
B - diatomaceous on T1  
C - presence of macro algae on uncoated surface.

## CONCLUSIONS

Preliminary results show that:

- in coastal area glaze T1 shows a significant fouling reduction compared to unglazed areas. Also different glaze chemical compositions seem to influence the fouling progression, suggesting a not only physical effect in the antifouling properties of the glazes used.
- in harbour area the results are much more modest suggesting the predominance of the influence of surface roughness on colonization. In the harbour environment, as the hydrodynamic effect is much lower than in the coastal area, colonization is much more aggressive on all coatings. However, T1 glaze is confirmed as the best among those used in tests.

The obtained results shows that the use of high temperature glazes could represent a promising approach for the study of new antifouling materials with short-term application possibilities in oceanographic measurements, contributing to the preservation of the marine environment.

## References

- Bonetta S., Bonetta S., Motta F., Strini A., Carraro E. Photocatalytic bacterial inactivation by TiO<sub>2</sub>-coated surfaces. *AMB Express* 2013, 3:59.
- Coutinho M.L., Miller A.Z., Macedo M.F. Biological colonization and biodeterioration of architectural ceramic materials: An overview. *Journal of Cultural Heritage* Volume 16, Issue 5, 2015, 759-777.
- Chambers L.D., Stokes K.R., Walsh F.C., Wood R.J.K. Modern approaches to marine antifouling coatings. *Surface & Coatings Technology* 201 (2006) 3642-3652.
- Durr S., Thomason J.C. Biofouling. 2010 Blackwell Publishing Ltd.
- Jarabek A.S., Wall W.R., Stallings C.D. A practical application of reduced-copper antifouling paint in marine biological research. *PeerJ*. 2016 Jul 14;4:e2213.
- Joonas E., Aruoja V., Olli K., Syvertsen-Wiig G., Vija H., Kahru A. Potency of (doped) rare earth oxide particles and their constituent metals to inhibit algal growth and induce direct toxic effects. *Science of the Total Environment* 593-594 (2017) 478-486.
- Maatta J., Piispanen M., Kuisma R., Kymalainen H.R., Uusi-Ruava A., Hurme K.R., Areva S., Sjöberg A.M., Hupa L. Effect of coating on cleanability of glazed surfaces. *Journal of European Ceramic Society* 27 (2007) 4555 - 4560.