Sunlight-enhanced calcareous deposition on cathodic stainless steel in natural seawater

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In replicate series of experiments in natural seawater, one in full darkness and the other in a 1:1 diurnal cycle with as little as ~5% of natural solar illumination, sunlight promoted calcareous deposition on cathodic stainless steel surfaces. As exemplified by scanning electron microscopy, the deposit that formed under the natural diurnal cycle, in the presence of photosynthetic biofilms, was composed of finer calcareous crystals that provided more compact and more uniform surface coverage than the one formed in the dark. The light-enhanced deposit also possessed better scale properties, as suggested by X-ray analysis and electrochemical measurements. Sunlight enhancement of calcareous deposition looked all the more conspicuous when day and night regimes were examined independently. These results not only bear important implications for cathodic protection in marine waters, but also provide an intriguing analogy to coral reef calcification.

Keywords: stainless steel in seawater; cathodic protection; calcareous deposits; biofilms; photosynthesis; coral calcification

Introduction

Practised throughout the world and particularly prevalent in seawater, cathodic protection (CP) uses the electrochemical principles of the corrosion process. Accordingly, an external current is applied to the metal to be protected, which balances the current produced from normal corrosion reactions (LaQue 1975). The application of CP generates a rise in pH at the cathode/seawater interface. The alkalinity thus generated decreases the solubility levels for calcium and magnesium dissolved in seawater, causing calcareous deposits to form on the cathode surface (Hartt et al. 1984; Johnsen 2006). The efficiency and economics of CP rely largely on the rate and chemistry of these deposits, and delivery of the protection currents that would otherwise be required would be improbable. The formation of calcareous deposits is influenced by a number of factors such as hydrodynamics (Mentel et al. 1992), water temperature (Kunjapur et al. 1987; Lin & Dexter 1988; Barchiche et al. 2003), pressure (Chen et al. 2003), salinity and alkalinity (Aromaa et al. 2006; Eashwar et al. 2009), and biological fouling (Eadyvean & Moss 1986; Mansfeld et al. 1990; Dexter & Lin 1992; Little & Wagner 1993; Eashwar et al. 2009).

An influence of sunlight on CP is now beginning to receive attention. Benedetti et al. (2009) made the first investigation of the influence of sunlight on the CP of carbon steel in seawater. These authors reported that irradiation by sunlight increased the currents required for CP, both in biologically inactivated natural seawater as well as in 3% NaCl solution. This study, however, was conducted for a very short duration (72 h) and under experimental conditions that were far from ambience. For instance, owing to the location of the test tanks under direct sunlight, the temperature of the seawater electrolyte fluctuated in daytime by as much as 10°C, with the possibility that other water quality parameters may have also changed. This observation led these investigators to deal separately with the possible effects of heat and light. To the present authors’ knowledge, there have been no other investigations on the effect of illumination on CP. Insights into the present theme of work was also provided by the authors’ recent work (Eashwar et al. 2011) in which as little as ~10% of full sunlight led to substantial inhibition of localized corrosion of stainless steel (SS) in natural seawater. The mechanism involved photoinhibition, in addition to a marked alteration in the biological effects on the cathodic kinetics. This provided an indication that sunlight can also possibly influence the process of CP. Thus, the objective of the present work was to investigate what effect sunlight can have on calcareous deposition during the CP of SS under marine conditions that support the concurrent accrual of natural biofilms.

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Methods

Study site, materials, and exposure methods

The present investigation was carried out in Mandapam on the southeast coast of India (9°16’N; 79°9’E) in February–March 2011. This particular period of the year is known to have the maximal hours of sunshine at this site and a very nearly 1:1 day/night period. The mean times of sunrise and sunset during the period of this study were 06:29 and 18:27 h, respectively (Indian Standard Time). Descriptions of the site and the major water characteristics relevant to marine corrosion have been presented previously (Eashwar et al. 2009, 2011).

Type 316 SS (UNS S31600) was the study material in this work, while carbon steel (CS) served as the sacrificial anode for effecting CP. The SS–CS combination was chosen on the basis of recent data (Eashwar et al. 2009) showing that a potential of −0.7 V (saturated calomel electrode [SCE]) is adequate for the CP of SS under tropical Indian conditions through the abundant formation of calcareous deposits. The metal sheets (1.1 mm thick and nominal compositions as in Table 1) were cut to 75 × 25 mm coupons. The coupons were pickled, polished on motor wheels with progressively finer grits and finally buffed to an approximate 2000-grit mirror finish, before degreasing in acetone and rinsing in ethanol prior to use. The top of each coupon had a 5 mm drill for fastening and a 1 mm drill for copper lead connections. The metal/lead junctions were insulated with marine epoxy.

A continuous, gravity-feed and overflow setup was used wherein freshly sampled coastal seawater flowed from a reservoir tank (100 l) into the test tank (40 l) at a rate of about 10 l h⁻¹. The influence of illumination was investigated by employing dark and diurnal (day/night) conditions of exposure as devised in earlier work (Eashwar et al. 2011). The dark exposures were made in a completely darkened portion of the laboratory, while the diurnal exposures were carried out outdoors, underneath an opaque roof, such as to allow only diffuse sunlight to pass through. Thus, the experimental method ensured very nearly identical conditions of seawater quality in the dark and diurnal exposures, in terms of physico-chemical parameters as well as the flow rate.

Coupons were fastened to wooden frames and placed across the test tank such that the cathode to anode separation was 7.5 cm and the coupons were aligned edge-on to the flow. Couples (1:1 area ratio) were established using alligator clip connections as soon as they were immersed in the test tanks. The SS cathodes were removed at periodic intervals over a period of 37 days. During the exposure tests, the water temperature was measured using a standard mercury thermometer (0–50°C; 0.1°C resolution), while pH was read on a DOT-461 model digital meter. These readings were taken in the natural sea (water sampling site) as well as in the experimental tanks three times a day, around 9:00, 13:00, and 18:00 h to ascertain the deviation in the laboratory values from the ambient. Other water quality parameters were also measured periodically following standard procedures (Strickland & Parsons 1978). Light measurements were made with a calibrated Li-COR model Li-250A Light Meter in conjunction with a Type Li-192 Quantum Sensor that permitted use in air as well as underwater. These measurements were made regularly to quantify the amount of full sunlight at the latitude of Mandapam, as well as the diffuse light within the experimental chamber and at the location of the coupons underwater.

Surface characterization

The calcareous deposits formed on the SS cathodes were examined by scanning electron microscopy (SEM) at various time periods during the seawater exposures. A simple drying procedure was followed in which the SS coupons were first gently rinsed in deionized water, cool-air-dried, and then dried in a CaCl₂·2H₂O atmosphere in a desiccator. The coupons were then observed on a Model S-3000 H, HITACHI SEM at an accelerating voltage of 20 kV. Although this procedure was not specific to biological examination of surfaces, it was very effective in capturing diatoms. It is believed that a combination of the drying technique and the siliceous nature of the diatom cells (the frustules) afforded explicit images of these photosynthetic micro-organisms. An aggregate of 47 images of the diurnal coupons and 35 of the dark coupons was analyzed, while the total field scanned and photographed was ~12.6 mm². The percentage cover data on calcareous deposition were obtained by importing the SEM images on to Corel PHOTO-PAINT 11 software, using gridlines to create 10³ squares, and by measuring the filled area relative to the overall area of the pixel. The mean percentage cover value was calculated by zooming in to quadruplicate images taken at 300X. This method also permitted size measurements of fully formed calcareous crystals. Data were also obtained on the densities of diatoms occurring with the calcareous deposits, calculated as the number of cells relative to a surface area of 1 mm². Diatoms were identified using keys pertinent to the study region (Santhanam et al. 1987).

The mass percentages of calcium (Ca) and magnesium (Mg) in the deposits were determined using X-ray

Table 1. Nominal compositions of the alloys used in the present work.

| Alloy        | Cr | Ni | Mo | Fe | C  | Mn | P  | S   |
|--------------|----|----|----|----|----|----|----|-----|
| 316 SS       | 17.0 | 7.0 | 2.1 | Bal. | 0.07 | –  | –  | –   |
| Carbon steel | –  | –  | –  | –  | Bal. | 0.1 | 0.46 | 0.07 | 0.03 |
fluorescence spectroscopy (XRF, Model HORIBA XGT 2700) at the end of the 37-day exposure period, after the calcareous deposits were removed, dried, and powdered with a mortar and pestle. Powder X-ray diffraction (XRD) patterns of the deposits were obtained on a JEOL Model JDX 8030 instrument at a step size of 0.017 (°2θ) and a step time of 16 s. The scans were made in the 2θ range of 20–70, and the compounds were characterized using the Joint Committee on Powder Diffraction Standards database. Samples were processed immediately after removal such that all surface characterization steps, including analyses, were completed within 48 h.

Electrochemical measurements

The mixed potentials of the SS–CS couples were measured on a daily basis using a high-impedance voltmeter (Tektronix, Model DMM155) in conjunction with type PE-77 SCE that was calibrated as previously described (Eashwar et al. 2009). The couples were disconnected at the end of the 37-day exposure periods. The potential variation trends for the disconnected SS coupons were monitored through periodic measurements of the open-circuit potentials (OCP) until they equilibrated. Potentiodynamic polarization tests of the SS coupons were then performed on an AUTOLAB Electrochemistry System (Model: PG STAT 30; Eco Chemie, Utrecht) at a scan rate 0.16 mV s⁻¹. A conventional three-electrode system was used with platinum as the counter electrode and SCE as reference. The electrochemical cell had a volume of 1 l, and freshly collected seawater was used as the electrolyte after 0.22 μm membrane filtration (Millipore). The SS coupons were polarized cathodically from their equilibrium potential to −0.75 V (SCE).

Calcareous deposition during day/night regimes

An additional experiment was conducted in February–March 2012 in which calcareous deposition was examined during daytimes and nighttimes, independently, under a diurnal cycle. This study used experimental methods including coupon arrangements, quiescent seawater exposure, and light conditions identical to those in the diurnal tests described earlier. However, the time duration to which the couples remained connected was only partial, thus setting up ‘day’ and ‘night’ regimes of calcareous deposition. Here, one series of the couples, designated ‘day’, remained connected from 30 min after sunrise to 30 min before sunset on each day of the experiment, i.e., the couples were connected 30 min after dawn and disconnected 30 min before dusk. The ‘night’ samples represented an opposite of the day exposures, with a reversal of the periods of connection and disconnection every day. Thus, these couples remained connected only in the night hours, from 30 min after sunset to 30 min before sunrise. The start of this experiment was timed in such a manner that the coupons remained coupled as soon as they were immersed in the test tanks. Thus, the day exposures commenced first, just after sunrise, while the night exposures also started on the same day, but a little after sunset. This experiment lasted 14 days, at the end of which the cathode surfaces were removed and examined by SEM as previously described. A combination of 28 images each of the day and night coupons was obtained, while the total field scanned and photographed was ~6.4 mm². The percentage cover and crystal size data on calcareous deposition were again computed as in the diurnal vs dark experiments.

Statistical analyses

One-way ANOVA was employed on Microcal ORIGIN software to evaluate the statistical significance of variance in respect of mixed potentials under diurnal and dark conditions of exposure. This statistical test was also used to evaluate the potential variation data pertaining to disconnected SS cathodes under diurnal and dark conditions. The significance of variation was calculated as statistical F and p values.

Results

Water characteristics and light levels

The mean ambient water temperature at the sampling site during the entire study was 29.4 ± 1.3°C. The mean readings in the diurnal and dark exposure tanks were 29.7 ± 1.4 and 30.3 ± 1.1°C, respectively. The pH of the seawater ranged from 8.23 to 8.44 under all conditions. The salinity and dissolved oxygen levels during the study period varied between 33.7 and 34.8 practical salinity units and 5.6 and 6.0 mg l⁻¹, respectively. The levels of other major seawater parameters relevant for marine corrosion have been presented earlier (Eashwar et al. 2009, 2011). Light measurements showed that the average intensity of full sunlight at local noon was 1640 ± 170 μmol photons m⁻² s⁻¹ during the study period. The light intensity was reduced to ~10% of this level under the opaque-roofed chamber, while it was further reduced to ~5% at the location of the coupons underwater. The amount of underwater illumination on the coupons ranged from ~12 μmol photons m⁻² s⁻¹ in the early morning and evening hours to ~80 μmol photons m⁻² s⁻¹ at noon on a typically cloud-free day. The light level in the dark exposure area was lower than the minimum threshold of the light meter at all times (<0.01 μmol photons m⁻² s⁻¹).

Diurnal vs dark test results

The progressions of calcareous deposition on cathodic SS during seawater immersion in the diurnal and dark exposures are explained below. Under both exposure conditions, calcareous deposits after exposure for 2 days were composed of individual crystals (Figure 1(a) and (b)). At this stage, the crystals that formed in the diurnal
cycle appeared finer and more tightly packed, providing larger surface area coverage than those in the dark. The percentage cover data showed values of 54.5 ± 7.2 and 32.3 ± 5.6 for the diurnal and dark test conditions, respectively. Measurements of the fully formed crystals from four replicate frames such as those in Figure 1(a) and (b) showed mean sizes of 21.41 ± 2.49 μm and 30.69 ± 3.38 μm under the diurnal and dark conditions, respectively. Further patterns of calcareous deposition are illustrated in Supplementary Figure 1(a)–(d). [Supplementary material is available via a multimedia link on the online article webpage.] Calcareous deposits after exposure for 4 days showed aggregation, where the crystals converged together. SEM images again revealed that the deposit under the diurnal cycle was tightly filled (Supplementary Figure 1(a)), while that in the dark was patchy and more voluminous with conspicuous hollow spaces (Supplementary Figure 1(b)). At this time, a complete 100% calcareous deposit cover was evident while an unfilled area of about 37.7 ± 6.8% still remained in the dark phase. By day 7, the deposits had transformed to a structured, cauliflower-type arrangement in the diurnal phase (Supplementary Figure 1(c)). In the dark, although the deposits transformed in shape during the corresponding exposure time, they remained more voluminous and still revealed unfilled spaces (Supplementary Figure 1(d)). In general, the crystalline particles under the diurnal exposure showed expansion on the x–y axis, while those in the dark appeared to be stacked primarily on the z-plane.

Table 2 summarizes the taxonomic list and the densities of diatoms associated with the calcareous deposits on the diurnal SS samples after exposure to natural seawater for 2 and 7 days. In quantitative terms, Amphora spp., Navicula spp., and Bacillaria paradoxa showed relatively higher densities than the other diatoms at 2 days, while Amphora spp. exclusively dominated the community at 7 days. The deposit in the dark was devoid of diatoms at any time.

XRD patterns for the calcareous deposits (Figure 2) revealed mostly the aragonite form of CaCO₃ (designated ‘A’) under both conditions of exposure, although some departures were readily apparent. The aragonite peaks in the diurnal exposure appeared stronger in intensity, and also there were five additional aragonite peaks here compared with the dark exposure. Furthermore, the three calcite peaks noted in the dark (designated ‘C’) were all missing in the diurnal exposure. The XRF data in Figure 3 show that the deposit in the diurnal cycle was almost exclusively Ca (with only 0.4% Mg), while that in the dark had a much higher content of Mg (6.1%).

The mixed potentials of the SS–CS couples depicted in Figure 4(a) are the means of 5 SS coupons for each category, and they show slightly more negative values for the diurnal couples than those for the dark couples at any given time. The difference became particularly obvious during the second half of the exposure period, being consistently ~10 mV. Although this difference would, at first glance, appear rather small, the statistical significance of the variance was enormous (F = 38.82;
Disconnection of the SS–CS couples led to the potential variation patterns shown in Figure 4 (b), where the data are again the means of five coupons for each category. The potentials in the dark increased to \(-0.25\) V (SCE), while those in the diurnal cycle did so more slowly and remained more negative, at values \(-0.25\) V (SCE), over several hours. Again, the statistical significance of the variation between the diurnal and dark data was very high (\(F = 75.44; p = 3.2 \times 10^{-8}\)). The potentiodynamic polarization curves obtained on the above coupons are illustrated in Figure 5. The scans show markedly smaller current densities in the diurnal cycle than those in the dark, particularly down to \(-0.5\) V (SCE). The variation in current density was very nearly two orders of magnitude, at \(-0.2\) V (SCE) and about one order of magnitude at \(-0.5\) V (SCE), as it gradually narrowed down to a certain extent at the more negative potentials.

\(\rho = 2.6 \times 10^{-8}\). Day vs night test results

The images in Figure 6(a)–(d) illustrate the influence of day/night regimes on calcareous deposition and...
associated diatom settlement after exposure to natural seawater for 14 days. Consistent with the results for diurnal vs. the dark phases, daytime deposits (Figure 6(a) and (c)) appeared finer and more tightly packed than those formed at night (Figure 6(b) and (d)). Thus, daytime deposits provided 69.8 ± 7.9% coverage of the cathodic SS surface, while nighttime deposits were substantially lower in percentage cover (14.7 ± 4.4). The mean sizes of fully formed calcareous crystals were 11.86 ± 1.81 μm in the day and 21.45 ± 2.44 μm at night, respectively.

By virtue of the outdoor exposure and a diurnal cycle employed in this experiment, diatoms were associated with calcareous deposition under day as well as night phases. Table 3 summarizes the taxonomic list and the densities of the diatoms after exposure for 14 days under the day and night regimes of calcareous deposition. The microfloral composition remained almost identical to that in the diurnal exposure (Table 2), barring the exclusion of the centric diatom Coscinodiscus sp. and the addition of the pennate diatom, Achnanthes longipes. The data in Table 3 reveal that the overall diatom density associated with nighttime calcareous deposits was threefold higher than that associated with daytime deposits.

Table 3. Taxonomic list and the densities of diatoms on cathodic SS samples after exposure for 14 days to natural seawater under day and night regimes of calcareous deposition.

| Diatom species         | Density (cells mm⁻²) |
|------------------------|----------------------|
|                        | Day  | Night |
| Achnanthes longipes    | 46   | 178   |
| Amphora spp.           | 120  | 340   |
| Bacillaria paradoxa    | 40   | 122   |
| Diploneis robustus     | 22   | 66    |
| Navicula henneydii     | 60   | 148   |
| Navicula longa         | 18   | 52    |
| Nitzschia sigma        | 6    | 68    |
| Pleurosigma sp.        | 2    | 24    |
| Thalassiothrix sp.     | 28   | 10    |
| Total cells            | 342  | 1008  |

Figure 6. Morphology of the calcareous deposits formed on cathodic SS surfaces after exposure to natural seawater for 14 days under day–night cycles. The images (a) and (c) show deposits formed in daytime, while (b) and (d) are images at corresponding magnifications of the nighttime deposits. Scale bars = 50 μm on images (a) and (b), and 5 μm on images (c) and (d).

Discussion

It becomes very clear from this study that sunlight has a promoting effect on the process of calcareous deposition on SS surfaces in seawater. As exemplified by SEM, the calcareous deposit under a natural diurnal cycle was composed of finer calcareous crystals that provided more compact and more uniform surface coverage than the deposit formed in the dark (Figure 1). Corresponding variations in deposit morphology were also evident when daytime and nighttime patterns were independently inspected (Figure 6). The deposit that formed in the presence of light also possessed better scale properties in
terms of the chemical composition (Figures 2 and 3). In general, aragonite is acknowledged to be more protective than calcite (Liu et al. 2011). Also, the Ca:Mg ratio has historically been considered to be a reasonable measure of the scale quality, with the lower amount of Mg in the deposit generally reflecting better protectiveness (Harrt et al. 1984; Okstad et al. 2007). It is possible that the higher amount of Mg in the deposit formed in the dark was calcite related as Mg is known to adsorb on the surface of calcites causing an increase in surface roughness and distortion of crystals (Chen et al. 2005). It is believed that the potential variation trends for the SS cathodes upon disconnection (Figure 4(b)) reflect the potency of cathodic polarization during the coupling and, consequently, the stability of the calcareous deposit. Thus, the propensity of the disconnected SS samples to sustain a more negative potential, which was stronger for the diurnal than for the dark samples, is believed to be an indicator of scale quality. Additionally, the cathodic polarization data (Figure 5) indicated that the current density requirements for cathodically protecting SS in seawater should be considerably lowered by sunlight. The overall results from this work are discussed below from the perspectives of possible mechanisms of sunlight-enhanced calcareous deposition and the implications of the present data.

There are two possible explanations for the observed results, the first involving the semiconducting property of the surface passive film on SS. It has been well established that illumination can enhance the passivity of SS in its open circuit and lead to a substantial reduction in localized corrosion initiation and propagation in neutral chloride media (MacDonald & Heaney 2000; Moussa & Hocking 2001; Fujimoto & Tsuchiya 2007). The phenomenon, known as photoinhibition, has been shown to occur under practical seawater situations also, through a significant alteration in both anodic and cathodic processes on SS (Eashwar et al. 2011). The passive film that forms on SS surfaces in seawater is generally an n-type, where the potential shift from illumination would be in the cathodic direction (Faimali et al. 2008; Eashwar et al. 2011). The consistently more negative mixed potentials for diurnal samples over those in the dark phase (Figure 4(a)), which was highly statistically significant, can be deemed to reflect a photoelectrochemical effect. For an n-type alloy, such as UNS S31600 in the present work, illumination can be envisioned to produce a change in the fermi level due to the promotion of electrons to the conduction band (MacDonald 1999). Consequently, it is possible that sunlight transformed the passive film to one that was more conductive, thus enhancing the cathodic reaction and hence calcareous deposition.

The second possibility is biologically enhanced calcification, through the photosynthetic activity of micro-organisms accrued on to the cathodic SS surfaces concomitantly with the calcareous deposits. The biologically assisted phenomenon proposed here is analogous to coral reef development (eg Gattuso et al. 1999; Cohen and McConnaughey 2003) where sunlight is known to promote aragonite calcification through an enhancement of the photosynthesis carried out by symbiotic organisms known as the zooxanthellae. Indeed, coral calcification is known to occur three to five times faster in daytime than at night (Moya et al. 2006). It is generally accepted that calcification and photosynthesis proceed according to the following equations (Gattuso et al. 1999):

\[
\text{Ca}^{2+} + 2\text{HCO}_3^- \rightarrow \text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \text{ (calcification)}
\]

\[
\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{CH}_2\text{O} + \text{O}_2 \text{ (photosynthesis)}
\]

where the \( \text{CO}_2 \) produced within the skeletal material is removed by photosynthesis. It is also acknowledged (Gattuso et al. 1999) that calcification may, in turn, stimulate photosynthesis by supplying \( \text{CO}_2 \). In the present work, the general presence of photosynthetic diatoms in association with the deposits (Table 2) provides adequate support for the inference that the biofilm in the diurnal phase was photosynthetically active while that in the dark was almost certainly not. Although larger numbers of diatoms were associated with the nighttime deposit rather than with the light-enhanced daytime deposit (Table 3), contrary to what might be expected, it must be taken into account that photosynthetic activity and the promotion of calcification may be controlled by the physiology of the algae rather than algal cell numbers (eg Abramovitch-Gottlib et al. 2005). Also, calcium (Geesey et al. 2000) and alkalinity (Nandakumar et al. 2003) can favor the physiology of certain species of diatoms. Indeed, the dominant presence of Amphora spp. on cathodic surfaces in this work (Tables 2 and 3) could possibly be attributed to the above-mentioned effects. It must additionally be considered that the surface preparation procedure adopted in this work compromised biological examination of surfaces to some extent. The simple drying procedure was preferred over conventional fixing and dehydration steps in order to retain the configuration of the deposits, which otherwise appeared deformed (Eashwar et al. 2009). Thus, the SEM technique employed in this work disregarded other micro-organisms such as bacteria and cyanobacteria that may also contribute to photosynthesis. The significance of the biological mechanism on light-enhanced calcareous deposition in the context of cathodic surfaces should form a very interesting research pursuit.

Regardless of the major mechanism, the present results suggest a substantial benefit from sunlight. Although most studies of calcareous deposition and improvements in the application of marine CP have
Conclusions

A marked influence of sunlight was noted in the present study where light levels as low as ~5% of full solar illumination promoted calcareous deposition during the CP of UNS 31600 in natural seawater. The light-enhanced calcareous deposit possessed improved scale properties over the deposit formed in the dark, as evaluated by SEM (morphology), XRF (Ca: Mg ratio), and potentiodynamic polarization (current densities). Sunlight enhancement of calcareous deposition was also marked when day and night phases were independently examined in diurnal exposures. The phenomenon of light-enhanced calcareous deposition appears strikingly similar to coral reef calcification. The present work has implications for marine CP as well as electrochemical stimulation of coral restoration.

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