

# CRAG CORROSION CHEMISTRY

Report 2017/2018

## Abstract

Over the last year, 46 samples from 8 different locations, representing 32 crags have been analyzed for 10 electrolytes. A major finding has been that, for maritime crags, the chemical environment differs markedly from that of the nearby ocean. In particular, it was noted that all limestone crags with a history of stress corrosion cracking of stainless steel anchors have elevated sulphate levels. It is postulated that the results are consistent with a role played by an external sulphur source such as volcanism. There are a number of ways in which high sulphate levels could accelerate the onset of stress corrosion cracking, but for now, we do no more than note this strong correlation.

Supported by UIAA Safety Commission

Views expressed in this report are those of the author and not those of the UIAA Safety Commission.

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The data for this project is publicly accessible at the following website.  
<http://bit.ly/WallWashDetail>

## Statement of the problem to be solved:

At many marine climbing locations, failure of stainless steel anchors through stress corrosion cracking (SCC) is a matter of serious concern. The role of elevated chloride levels in this process is not doubted. However, there are many marine locations where the SCC of anchors is unknown, and thus, there needs to be 'something additional' to the elevated chloride levels to explain what is happening at the highly corrosive crags.

Theories have been put forward, and some laboratory work points to potential vulnerabilities, but to date, the scarcity of field data means we are still guessing as to what that 'something additional' might be. The aim of the Crag Chemistry Project is to look for additional factors by examining the chemical environment of various crags across the world.

## Wall wash sampling process:

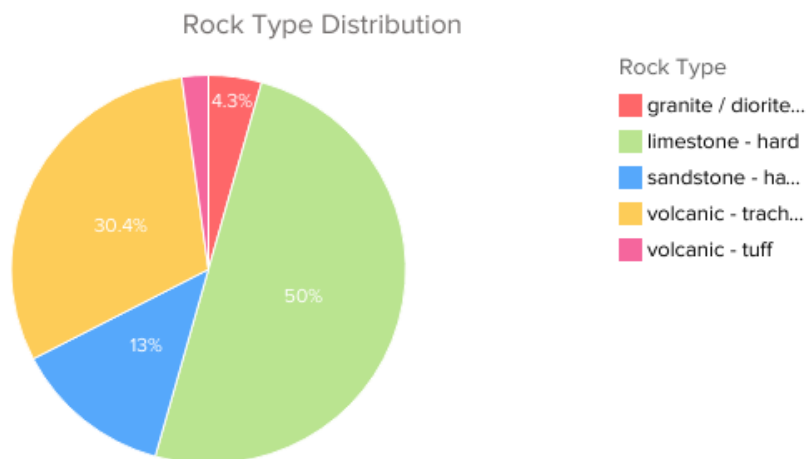
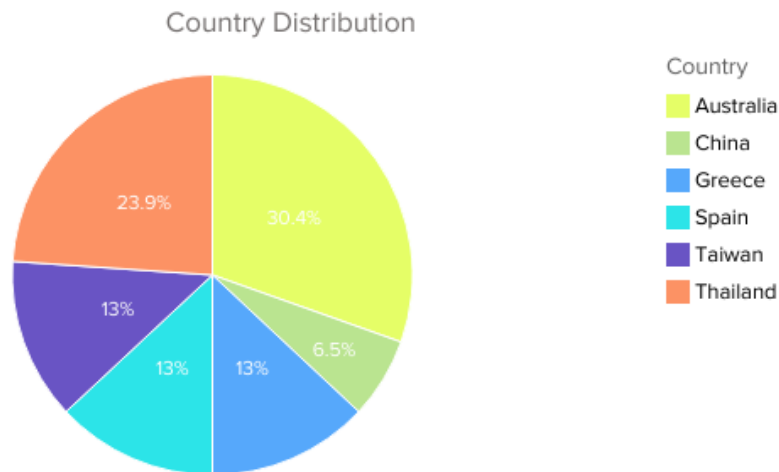
- Volunteers are sent a number of sample kits
- A 20 x 20cm area of the cliff is repetitively washed into 40ml of deionised water in a sample container
- The samples are returned to the laboratory
- The sample is analysed for free electrolytes as well as those easily released by mild acid digestion
- The number of electrolytes analysed has steadily increased over the year. We now routinely measure the cations,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Na}^+$ , and  $\text{K}^+$ , and the anions  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$  and  $\text{SiO}_4^{2-}$

## Total Number of Samples Analysed:

To date, 46 samples from 8 different locations representing 32 unique crags have been analysed.

## Areas Sampled:

Location	Country	Environment	Corrosion History
SE Queensland	Australia	Subtropical maritime	mild
Tonsai	Thailand	Tropical maritime	severe SCC
Chiang Mai	Thailand	Tropical inland	mild
Lopburi	Thailand	Tropical inland	mild
Long Dong	Taiwan	Subtropical maritime	severe SCC
Hong Kong	China	Tropical maritime	some mild, some SCC
Kalymnos	Greece	Temperate maritime	mostly mild, some SCC
Ibiza	Spain	Temperate maritime	severe SCC



## Major Findings:

### 1. Maritime crag electrolyte profiles are not dominated by sea salt:

It is widely assumed that the major electrolytes to be found on a sea cliff will be the same as those that comprise sea water. This has led to the belief that a 'marine' grade of stainless steel would be a suitable choice for rock anchors on sea cliffs.

However, almost every maritime crag we have sampled shows that the fixed hardware is exposed to a chemical environment quite different to the marine exposure one might expect for, say, a stainless steel fitting on a boat.

Figure 1 below shows typical results for 6 major electrolytes comprising wall-wash samples taken from a number of limestone crags.

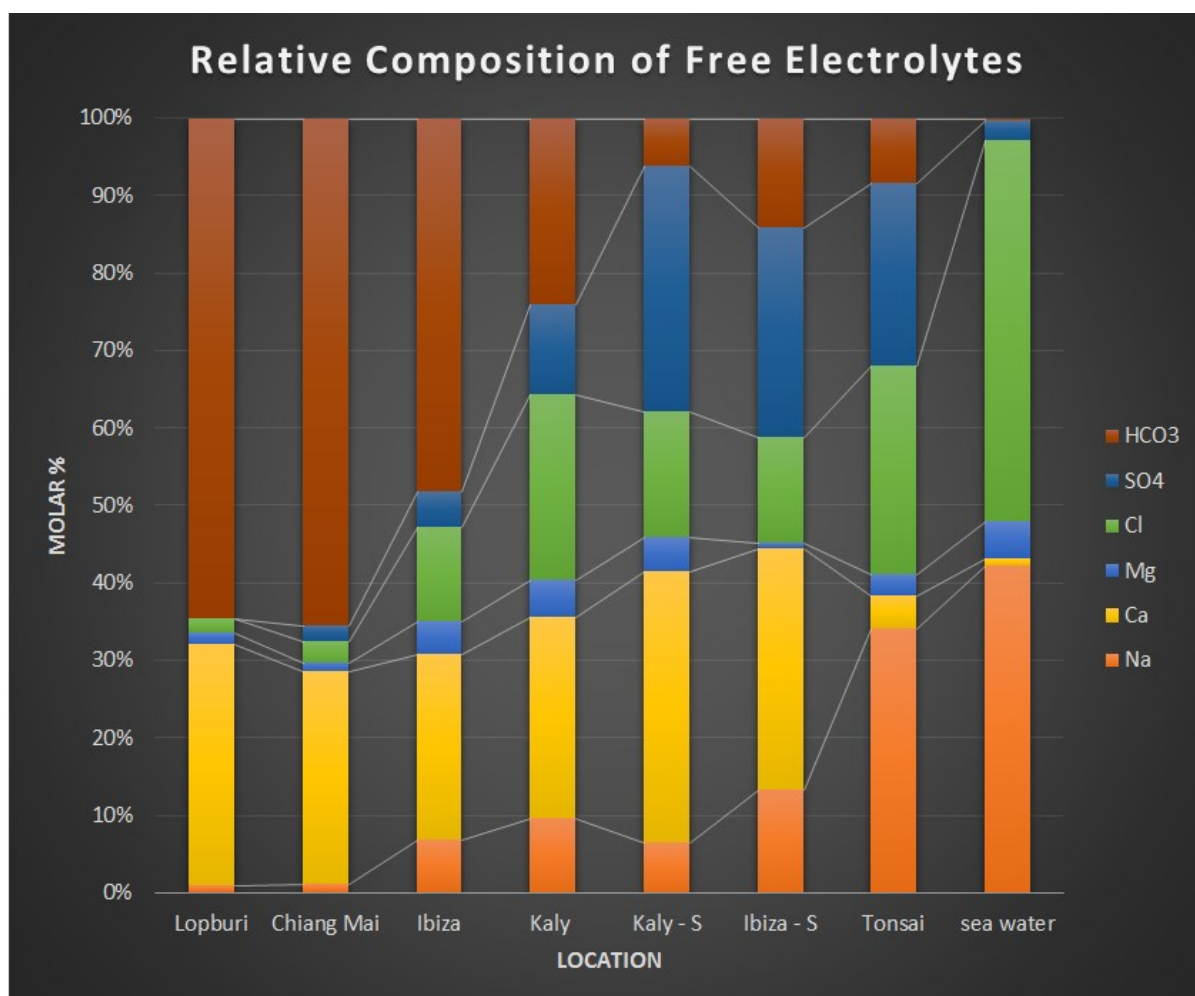


Figure 1: Free electrolyte ratios for a number of typical limestone crags

Starting on the left of the figure we have the two tropical inland crags, Lopburi and Chiang Mai that show the anticipated limestone equilibrium electrolyte pair, calcium and bicarbonate, as the dominant species. Note the maritime signature of sodium chloride is measurable even well inland. The next two crags are located on the Mediterranean islands of Ibiza and Kalymnos. Here we see an increase in the sodium chloride levels, but note that, despite proximity to the sea, the system is still dominated by the calcium bicarbonate electrolytes arising from the limestone.

The final three samples are from what we are beginning to understand as ‘sulphur’ crags. These samples were all taken from SCC prevalent crags on Kalymnos, Ibiza and Tonsai. Here we see the introduction of sulphate into the calcium bicarbonate system. This will be discussed in detail later.

On the very right is typical sea water composition. Samples taken directly from an active spray zone will match this, but, such samples are rare, and a crag situated only metres from the sea’s edge will show marked differentiation of the electrolyte balance.

The above differentiation of electrolytes is not restricted to limestone crags, and has been observed across all rock types studied thus far. Figure 2, below, gives an indication of the electrolyte composition of a number of non-limestone marine locations.

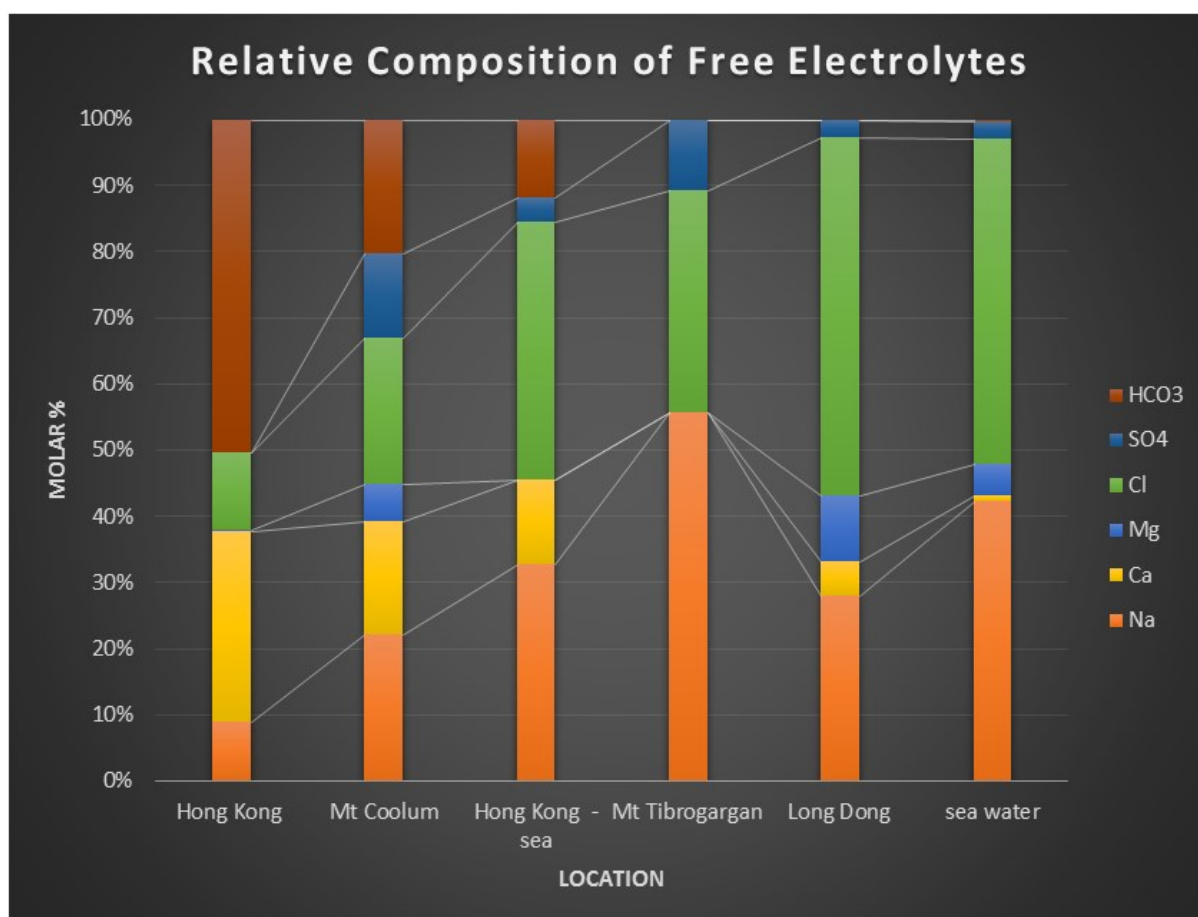


Figure 2: Free electrolyte ratios for a number of non-limestone crags

On the far left, we see a sample from Hong Kong, for a granite cliff situated just a few kilometres inland. The marine signature is suppressed by a dominant calcium bicarbonate system similar to that for a limestone crag. From a geochemical point of view this is quite unexpected. Again in Hong Kong, we find the presence of a calcium bicarbonate system persisting at a crag, volcanic tuff this time, just a few metres from the sea. A similar pattern occurs on the immediately coastal rhyolitic volcanic plug of Mt Coolum in South East Queensland.

By way of contrast, the coastal trachytic volcanic plug of Mt Tibrogargan in South East Queensland has very low electrolyte levels, and is carrying a predominantly maritime signal, with some elevation of sulphate, but no calcium bicarbonate system.

The sandstone sea cliffs of Long Dong in Taiwan are a case apart. This is an extreme 'sulphur' crag where groundwater seeping out of the porous rock deposits crystalline sodium aluminium sulphate mixed with sulphuric acid. Yet, the wash samples we have taken to date show little more than splash from the adjacent sea water. These samples were taken subsequent to several weeks of stormy weather, and it may be that the surface electrolyte balance will be more representative of the ground water at the end of the dry season.

The fact that the calcium bicarbonate system dominates limestone electrolyte chemistry comes as no surprise. However, it was surprising to observe its presence in the case of non-limestone crags as well. A solid conclusion that arises from this finding is that, for as long as calcium/bicarbonate equilibrium is maintained, the pH of the environment is buffered to the

range 7.5 – 8.5. Thus, on the macroscopic scale, it seems unlikely that rock anchors are ever exposed to acidic conditions.

## 2. The surface concentration of sodium and chloride falls steeply with distance from the sea:

We find that the areal chloride concentration in units of nmoles/sqcm falls steeply with distance from the sea. Although there is substantial variation between samples, the trend is clear when the median values are plotted.

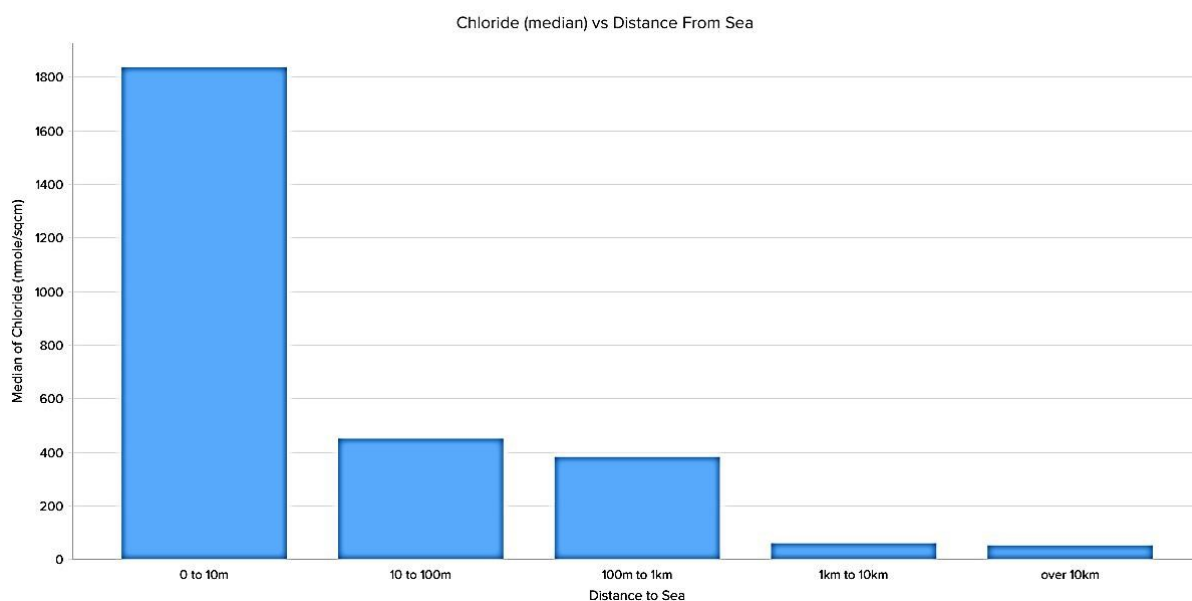


Figure 3: Median chloride levels for all 46 samples representing 32 different crags. The chloride levels fall rapidly within a short distance from the sea.

This observation is in keeping with a mechanism of transport via the coarse aerosol fraction (>10 $\mu$ m) where transport times are small (< 1hr), chemical differentiation during transport is insignificant, and the main depositional mechanism is gravitational settling rather than impaction or diffusion.

As would be anticipated, the areal sodium concentration in units of nmole/sqcm follows a similar pattern. However, the correlation with chloride is not perfect, and we observe that the sodium to chloride ratio falls below that of the initial sea water ratio for sites no more than tens of metres inland. There appears to be a chloride sparing mechanism operating at the

geochemical level. The significance of this finding is unknown at this stage.

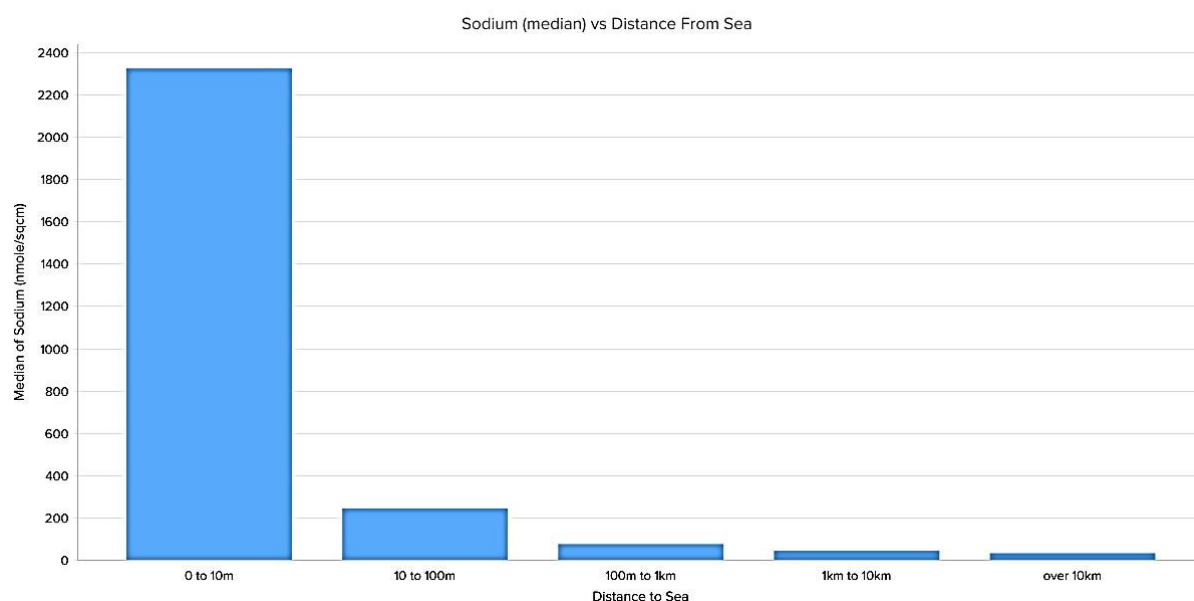


Figure 4: Median sodium levels for all 46 samples representing 32 different crags. The sodium levels fall rapidly within a short distance from the sea.

### 3. All rock surfaces are washed to some degree – overhangs less so:

It is reasonable to expect that marine salts would build-up on surfaces protected from rain. For example, one would reason that locations under steep overhangs would harbour high salt levels, thereby rendering such locations more corrosive. As shown by the plot below, the sum of all samples we have to date supports that general contention.

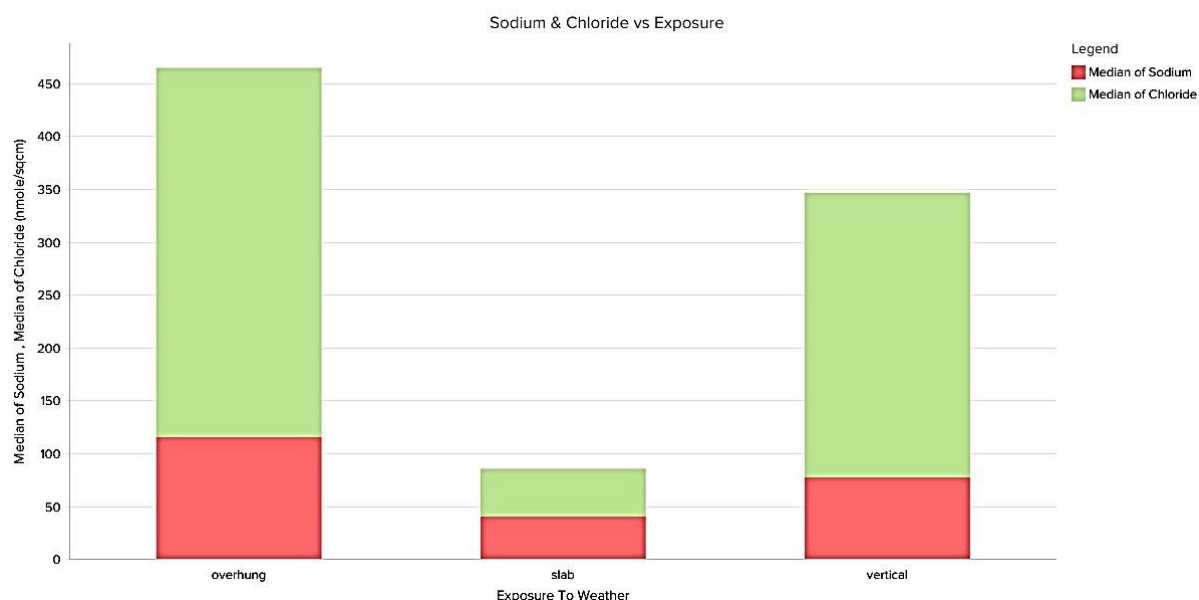


Figure 5: Median sodium and chloride levels for all 46 samples representing 32 different crags. The effect of exposure to rain is observable, but not particularly striking.

Two points can be made about the crag exposure plot above. Firstly, the sparing of chloride is



apparent for the steep walls, but not the slabs. This adds weight to the fact that a geo/biochemical process is involved, and is one that evolves over time.

The second point is that the overhanging crags, whilst definitely acting as accumulators of electrolytes, show surface concentrations not much more than four times that of slabs. Given the millennia over which such processes must run, one can only assume that even overhanging sections of rock must be washed by rainwater on a regular basis. The data plotted below, Figure 6, lends support to this idea.

Two quick-draw dog-bones that had been fixed for five years on the steeply overhanging coastal crag of Coolum Cave were taken down and analysed for free electrolytes. These results are compared with those from adjacent wall-wash samples.

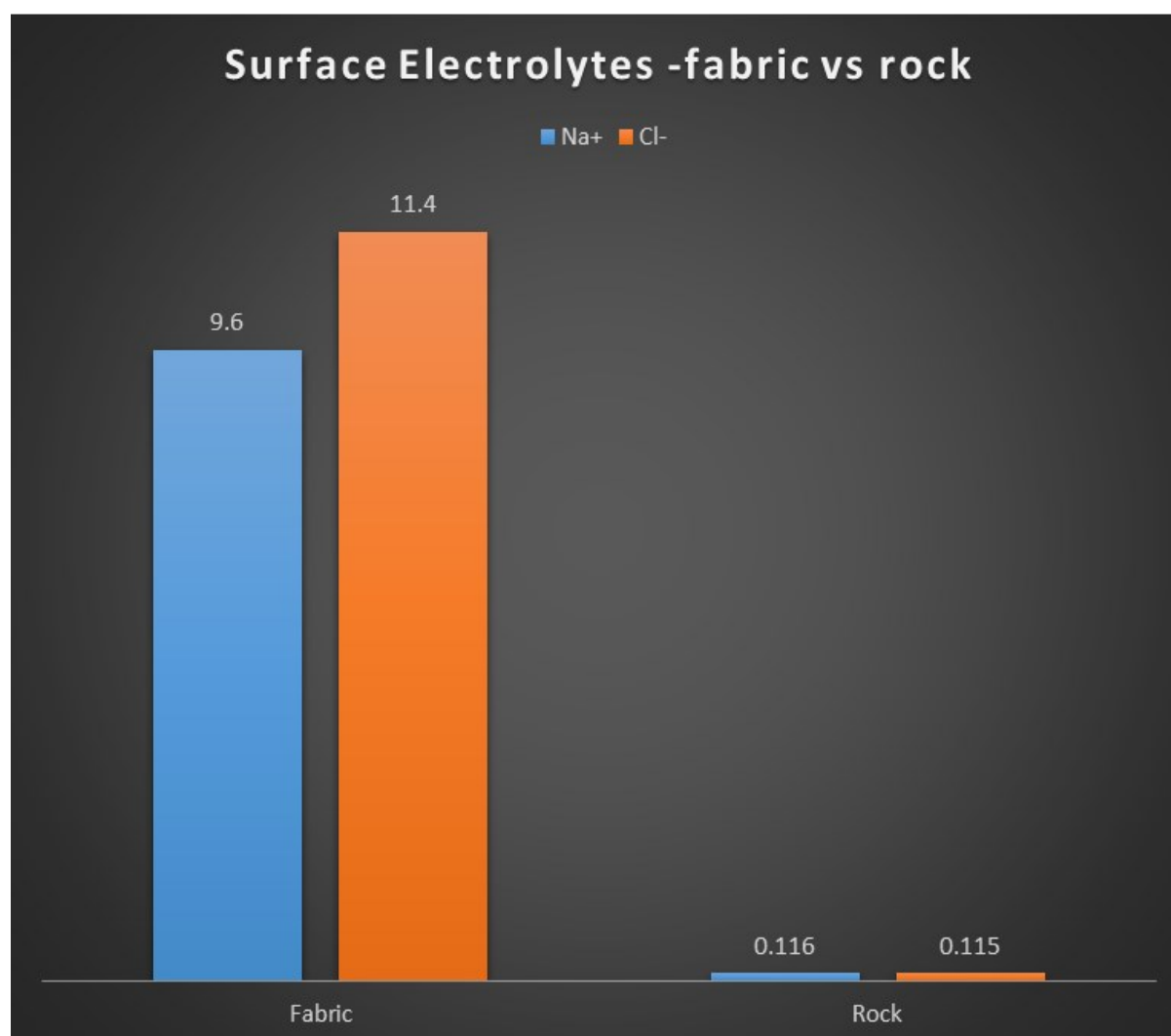


Figure 6: Sodium chloride accumulation at Coolum Cave. The rock surface must be washed more frequently than would be anticipated for such a sheltered location.

The fabric revealed electrolyte levels x100 higher than that of the adjacent walls. Given the quick-draws had been fixed for just 5 years, it is clear the rock surface, in spite of its location tens of metres within a large spacious cave, must be regularly washed by surface water.

#### 4. Corrosive limestone crags are associated with an active sulphur process:

One of our earliest findings was that calcium levels for wall-wash samples taken at Tonsai were unexpectedly high given the constraints of the basic calcium/carbonate/bicarbonate/CO<sub>2</sub> system. This led to the discovery of high sulphate levels in solution, and high levels of precipitated solid calcium sulphate on the surface. Analysis of the rock material itself showed it to be free from even traces of sulphate, and it became clear that sulphur was being introduced into the system via an external agency.

We have subsequently sampled many other locations, and have found that all crags with a history of SCC exhibit the signature of an active sulphur process. The figure below illustrates this signature.

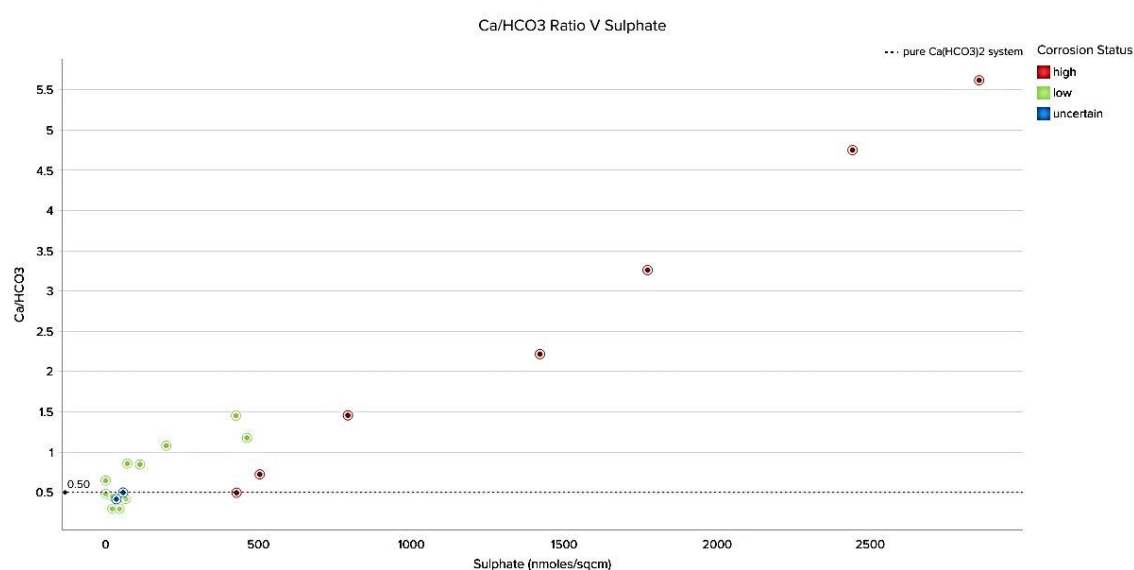
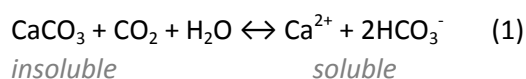


Figure 7: Data for all limestone crags illustrating the stoichiometric insertion of sulphate into the calcium bicarbonate system that occurs at those crags with a history of SCC

For a pure limestone rock surface, depending upon prevailing moisture levels, we would expect the calcium carbonate/bicarbonate equilibrium to dominate. Any wall-wash sample should reveal a calcium to bicarbonate ratio of 1:2, because only the soluble bicarbonate can be taken up into the sample.



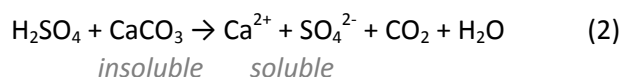
Note that, given the lack of an ion in common, even quite high concentrations of Na<sup>+</sup> and Cl<sup>-</sup> from sea spray have little effect on this equilibrium,

In the figure above we see a clustering of green sample points around Ca/HCO<sub>3</sub> = 0.5, a value in keeping with a system controlled by equation 1. The green circles indicate samples from non-corrosive<sup>1</sup> crags.

<sup>1</sup> By non-corrosive we mean a crag with a > 15 year history free of SCC.

Sulphur oxidizing bacteria are ubiquitous players in the terrestrial sulphur cycle. They oxidise elemental sulphur and sulphide to sulphuric acid. We currently don't know the source of the sulphur feeding the process we are observing, but it appears very likely that sulphuric acid is being released by biological processes operating within the thin cliff top soils.

Sulphuric acid immediately reacts with the solid carbonate of the limestone to release additional calcium ions plus sulphate ions.



Calcium sulphate is poorly soluble, and where sulphate levels are high enough, calcium sulphate precipitates out as a thin powdery film on the wall surface.

Thus when we take a wall-wash sample, it is to be expected that for a 'sulphur' cliff we will observe charge balance for the system  $\text{Ca}^{2+}/\text{HCO}_3^-/\text{SO}_4^{2-}$ , with the only other major species,  $\text{Na}^+$  and  $\text{Cl}^-$ , not playing a significant role. Looking at the figure above, we see the  $\text{Ca}/\text{HCO}_3$  ratio rising linearly with sulphate concentration in the manner expected.

Perhaps, it is not surprising to find this result, once we understand that the sample is a calcium/bicarbonate/sulphate solution. However, what is striking is the fact that, without fail, if the surface concentration of sulphate exceeds 500 nmoles/sqcm, we encounter SCC at that crag as indicated by the red sample points in Figure 7 above.

A second feature of corrosive sulphur crags is that elevated sulphate is nearly always associated with elevated chloride, although no close correlation is to be observed. There is no immediately obvious reason why this should be so. This loose relationship can be seen in Figure 8 below.

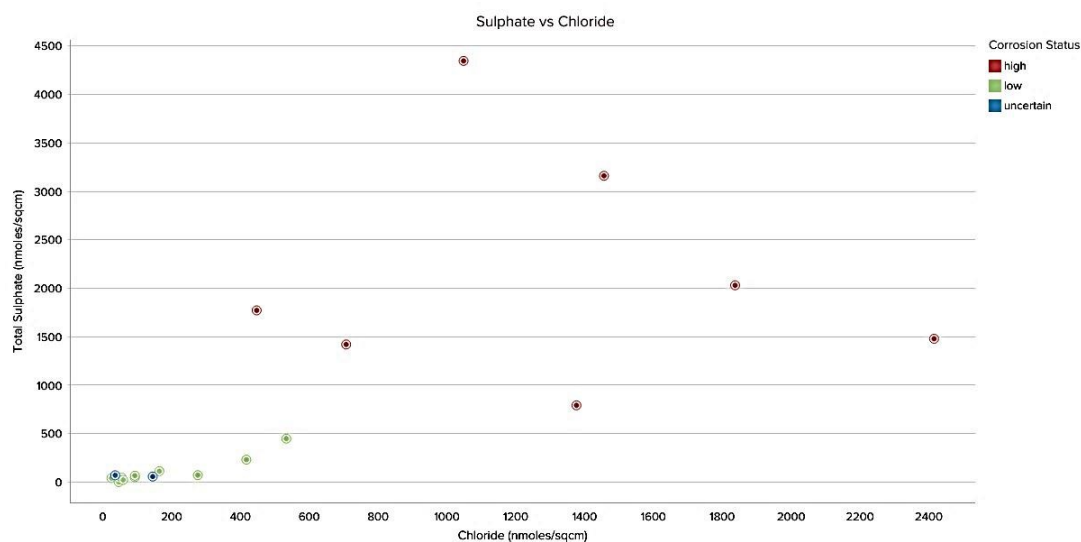


Figure 8: Data for all limestone crags illustrating the loose tendency for elevated chloride to be associated with elevated sulphate for those crags with a history of SCC

Further evidence for the operation of a geo/biochemical process operating at the rock

surface can found in the analysis of rope 'threads' taken from Monitor Wall at Tonsai. See Figure 9 below. We find that, for the 'threads', the sulphate to chloride ratio of the accumulated electrolytes tracks that of sea water, and we can conclude that they are doing little more than accumulating the coarse fraction of the marine aerosol. This finding contrasts with the sulphate to chloride ratio of electrolytes on the actual rock wall, where the sulphate level is greatly elevated compared with chloride. We also find that the surface concentrations of electrolytes built-up on the 'threads' is some ten times greater than that on the rock surface indicating the wall, although overhanging, must be subject to some degree of groundwater flow.

The evidence for sulphate being introduced at the top of the cliff as sulphuric acid is compelling.

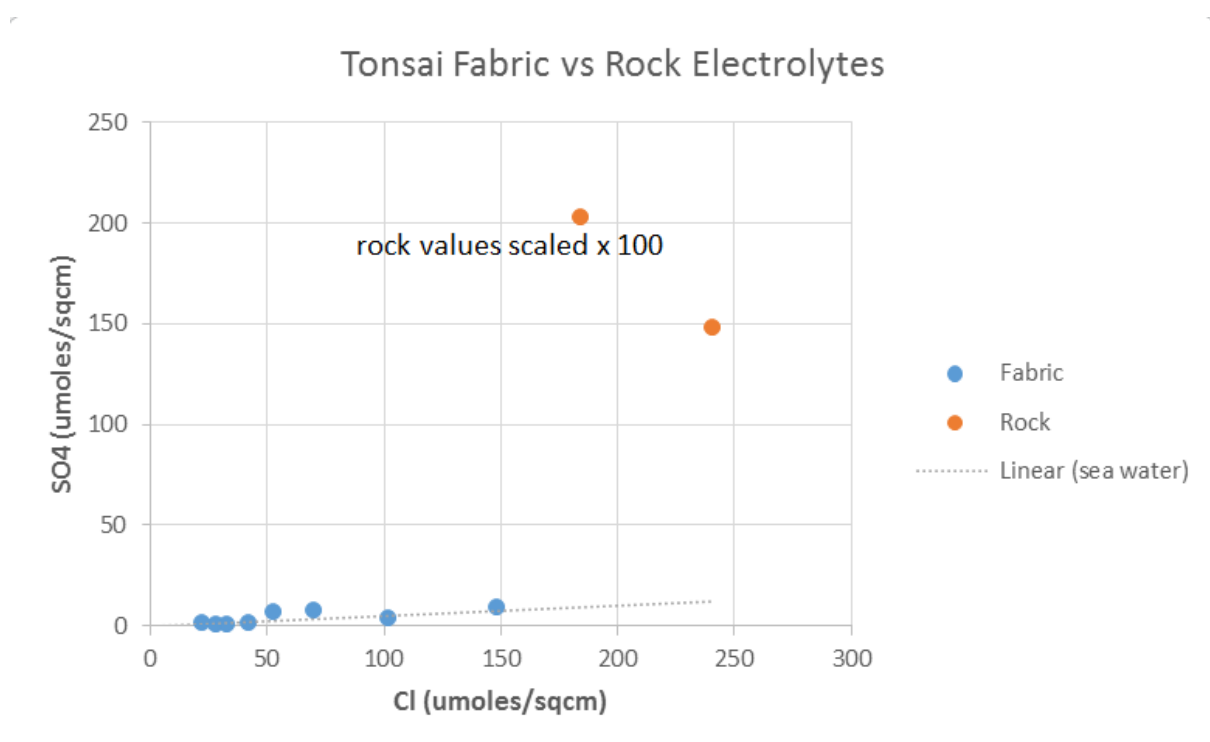


Figure 9: Multiple samples of 'threads' taken from Monitor Wall exhibits a sulphate/chloride ratio that is indicative of passive accumulation of sea aerosol. This is in striking contrast to wall wash samples where a geo/biochemical process is clearly biasing the electrolyte ratio.

Sulphate tends to be conserved within the environment by the tightly closed sulphur cycle, a process whereby sulphur is firstly released from decomposing vegetation as sulphide, then oxidised to sulphate by sulphur oxidising bacteria resident within the soil, to be taken-up again by new vegetation to complete the cycle. Thus the biological sulphur cycle is pretty much closed with little scope for releasing the large amounts of sulphate we see being introduced at the surface of 'sulphur' crags. This fact leaves us looking for an external source of sulphur.

The most attractive, and perhaps only, possibility for this source is active volcanism. We note that all locations where SCC is reported as being severe are located in regions of active volcanism. Furthermore, whilst there may exist 'sulphur' crags well inland, all those documented to date are within the reach of the coarse maritime aerosol fraction, a fact

which supports the idea that the source is elemental sulphur released from undersea fumaroles, and transported as part of the ocean surface biofilm.

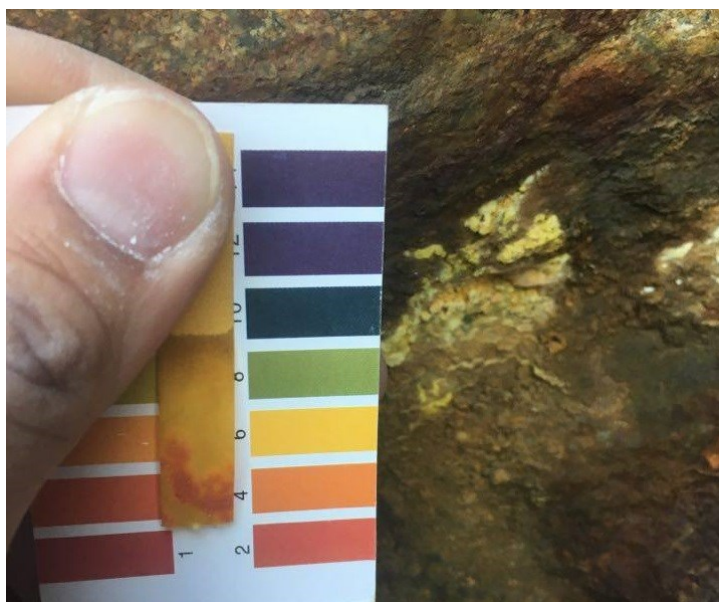
We have looked for elemental sulphur in wall-wash samples on a number of occasions but have never found any at levels above our detection limit of 1nmole/sqcm. However, given the hydrophobic nature of elemental sulphur, there are good reasons to suspect that the standard wall-wash sample is inadequate for this task, and another method is required.

From a practical point of view, the mechanism by which sulphur is introduced to the crag doesn't matter. The important thing is that, potentially, we have a chemical handle by which a problem crag can be identified before a financial outlay on hardware is made.

## 5. Are all corrosive crags associated with an active sulphur process?

Whilst it is certainly true that elevated sulphate is a hallmark of all the corrosive crags we have sampled, the majority have been limestone, and we need to diversify our sampling if we are to show this is generally true for other rock types.

We do know the extremely corrosive sandstone cliffs at Long Dong in Taiwan are subject to an active sulphur process. Analysis of the efflorescence around seepage points in the cliff provides clear evidence of sulphuric acid leaching the feldspar matrix from the sandstone to build high levels of aluminium sulphate.



*Figure 10: Acidic efflorescence forming at weepage points on Long Dong cliff line*

Calculating back from electrolyte levels to the putative crystalline components we get the mixture illustrated below.

## Efflorescent Material - Putative Composition of Water Soluble Components

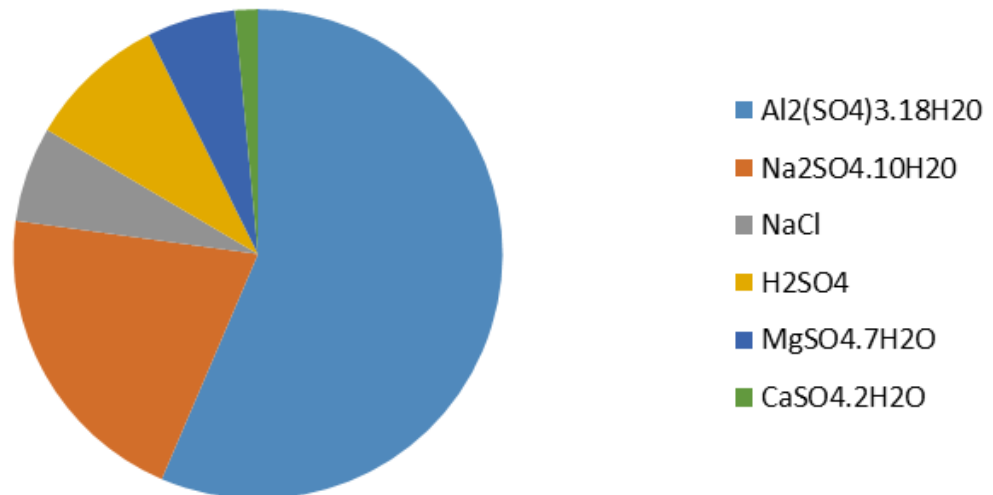


Figure 11: Analysis results for the efflorescence forming at weepage points on the Long Dong cliff line

This is a highly corrosive mix, and will provide challenges for adequate materials selection at this site. Interestingly, the only wall-wash samples we have taken from Long Dong don't reveal this underlying corrosion risk. It could be the rock surface was thoroughly washed with sea water at the time of sampling. Re-sampling after an extended dry period may tell a different story.

Based on the chemistry, we can predict that 'sulphur' limestone crags, with their surface film of poorly soluble calcium sulphate will preserve the sulphur fingerprint through mild washing episodes, whilst crags like Long Dong, where the sulphate component is present as freely soluble sodium and aluminium sulphates will be readily washed clean by sea spray and rain. Thus, it is clear that adequate sampling of non-limestone crags will be an issue.

The only corrosive, non-limestone crag we have sampled apart from Long Dong, is Technical Wall on Tung Lung Chau, Hong Kong. The limited sampling we have done shows no evidence for a sulphur process. However, sampling was limited, and we plan a more thorough investigation.

### 6. Are magnesium levels an issue?

Over the years, there has been circulating, that which is little more than urban myth to the effect that high magnesium levels, along with high tropical temperatures, are the villains when it comes to SCC of hardware installed on tropical karst. This popular idea can be traced back to two sources. Firstly, Angele Sjong in her analysis of a failed hanger from Tonsai showed a relatively high magnesium peak in the EDS spectrum taken from the fracture surface, and secondly, the standard test for SCC resistance, ASTM G36 utilises boiling magnesium chloride.

In our opinion, it is quite wrong to conflate these two facts. There are sound, physical-chemistry-based reasons why magnesium chloride is a suitable reagent for the accelerated SCC test. However, without going into detail here, the same reasons point to why it is unlikely to be a factor in the corrosion of crag hardware. Furthermore, we can show that magnesium levels are not high at any crag we have sampled, including the very corrosive ones. There seems no obvious reason for the fluctuations in magnesium levels that we do observe, except to note that, they are all comparable with sea water concentrations or lower.

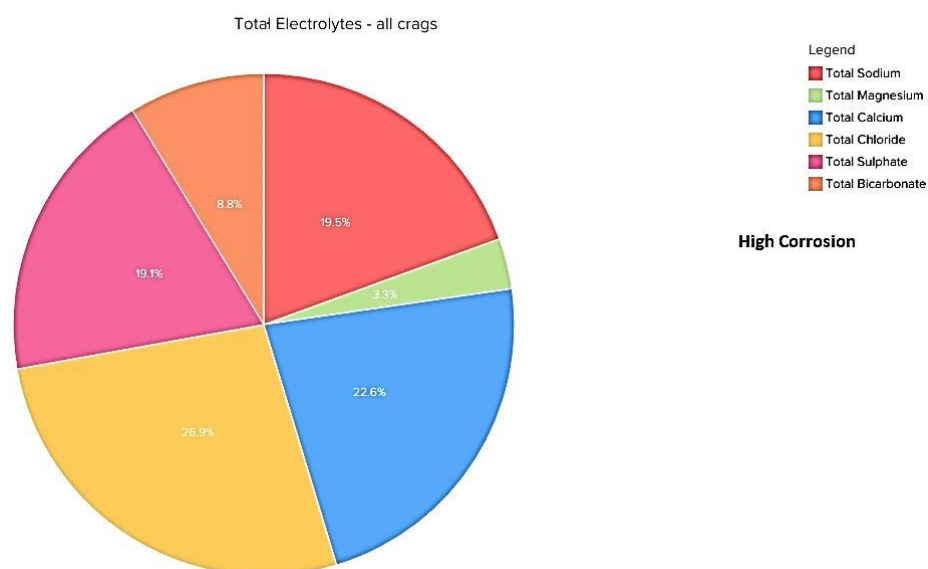


Figure 12: Electrolyte composition for all corrosive crags in database. Magnesium (green) is the minor component.

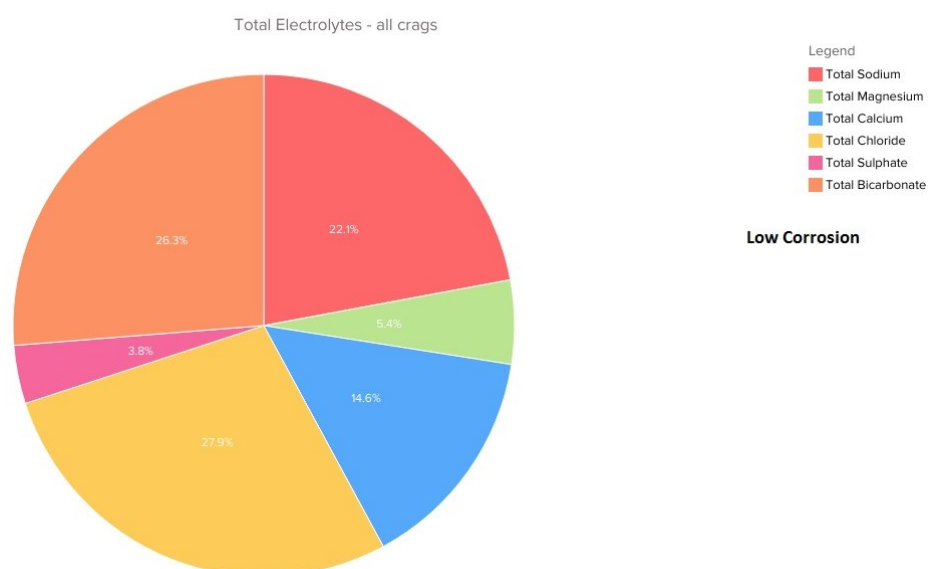


Figure 13: Electrolyte composition for all non-corrosive crags in database. Magnesium (green) is the second most minor component.

## Implications for Corrosion Resistance of Anchors:

It is premature to speculate on what these findings might imply for future choices of rock anchor materials. Although a general picture is emerging for high corrosion crags, we need to underpin this with a greater breadth of sampling.

However, we can make some broad assertions based on what we have found to date.

Firstly, the idea that sea water is corrosive at some crags and not others based on local differences in the humidity regime has always suffered from difficulties in explaining how the relative humidity can so vary. Given that the atmosphere at a sea crag is never far from equilibrium with an adjacent large body of sea water, it is unlikely that relative humidities lower than say 60% can persist for extended periods. Now we have the more plausible possibility that the differences in observed corrosiveness are due to differences in the chemical environment.

Secondly, the prevalence of sulphate at the corrosive crags almost certainly means that sulphur reducing bacteria (SRB) will be present in the various, anaerobic micro-environments created by the rock anchor, i.e. in the threads between nut and bolt, between hanger and rock, between glue and bolt at the rock interface etc. Based on the literature, we can anticipate such micro-environments will be very acidic, and that the potentially corrosive sulphide ion will be added to the mix. We have some evidence that this is the case, but it is by no means sufficient to support a general theory that somehow SRB are acting as initiators of chloride-based stress corrosion at the highly corrosive 'sulphur' crags. More work is necessary.

Thirdly, just because we know that corrosive crags differ in electrolyte composition, it doesn't follow that we are any the wiser in terms of making an informed materials choice. Undoubtedly there will be test regimes that might serve as proxy for different classes of sea cliff, but the clear role played by microenvironment cautions against taking a simplistic approach.

## Methodology:

The analytical methodology employed has evolved over the year, as interferences became better understood, and verification procedures pointed to inaccuracies. The current protocols are listed in abbreviated form below.

### Work Up:

*The sample, as received, is washed from the sample container, filtered and made up to 100ml. This is the soluble fraction which forms the basis of most of this report. The filtered portion was digested with HCL 1.0M for 2 hours at 90°C, filtered, and made up to 100ml. This is the acid soluble fraction (AS).*

### Chloride:

*A 25ml aliquot is titrated against standard silver nitrate using a chromate indicator – Mohr's method.*

*LOD = 5nmole/sqcm*



### Sulphate:

*A 25ml aliquot is treated with excess barium chloride and the precipitate is assayed for barium by indirect EDTA titration using magnesium nitrate and eriochrome black T as indicator at pH10*

*On sample LOD = 5nmole/sqcm*

### Bicarbonate:

*A 10ml aliquot is titrated against standard hydrochloric acid using a mixed methyl red, bromocresol green indicator.*

*LOD = 25nmole/sqcm*

### Sodium and Potassium:

*Analysis by dual channel flame photometer calibrated against multipoint standards for both sodium chloride and potassium chloride.*

*LOD Na = 0.3nmole/sqcm and LOD K = 0.04 nmole/sqcm*

### Calcium and Magnesium:

*Two 10ml aliquots are firstly freed of organic matter by oxidation with nitric acid, prior to a dehydrating with hydrochloric acid to precipitate silicate, and finally held at pH6 to precipitate aluminium and iron. Thus freed of potential interfering species, one aliquot is used to determine calcium and magnesium in combination by indirect EDTA titration against standard magnesium nitrate using an eriochrome T black indicator at pH10. The second aliquot is used to determine calcium alone by direct titration against EDTA using Paton and Reeder's indicator at pH13.*

*LOD Mg = 13nmoles/sqcm, LOD Ca = 13nmole/sqcm*

### Iron and Aluminium:

*One 10ml aliquot is used to determine combined iron and aluminium by indirect EDTA titration against standard lead nitrate using xylenol orange as the indicator at pH 5. An excess of sodium fluoride is then used to decomplex the aluminium, but not the iron, and titration continued to measure aluminium alone.*

*LOD Fe = 25umoles/sqcm, LOD Al =13umole/sqcm*

### Silicate:

*A 1ml aliquot was used in the analysis of low order silicate species by the standard reduced silicomolybdate method. A multipoint standard curve was used to calibrate spectrophotometric response at 820nm. LOD (as SiO<sub>2</sub>) = 1nmole/sqcm*