Measuring calcification in the field

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Common approaches to measuring benthic calcification

Organism scale

^{45}Ca incorporation method

- Assumes that Calcif=rate of incorporation of ^{45}Ca into the skeleton
- Advantages – extremely sensitive so small organisms can be used and measurement period can be minutes, only method for studying kinetics and pathways of Ca^{2+} transport, only method that truly measures gross calcification
- Disadvantages – organism must be killed to analyze, not easily scaled up for large organisms or communities
- Precision – RSD is 12% using latest protocols
- Accuracy – intercomparison with TA and Ca depletion methods finds that ^{45}Ca incorporation is highly correlated but underestimates the former by ~12%

Coral density banding

- Assumes that a historical record of the calcification rate of a long-lived coral colony can be obtained by taking a core from the colony and measuring the distance between annual bands and the density of the skeletal material laid down between the bands.
- Advantages – one of the only ways of obtaining historical rates of calcification for a species over months to 100s of years
- Disadvantages – records are generally very noisy and in practice many records must be averaged to obtain a statistically significant trend

Buoyant weighing method

- Assumes that any increase in mass is due to calcification, generally used to measure calcification over 1 week or longer although it has been used to measure daily rates
- Advantages – very simple, fast, non-destructive, can easily handle many replicates
- Disadvantages – assumption that changes in soft tissue mass do not contribute to buoyant weight may not always be good
- Precision – RSD is 10-50% (typically 20-25%)
- Accuracy – unknown, this method has not be rigorously compared with the TA or Ca^{2+} depletion methods

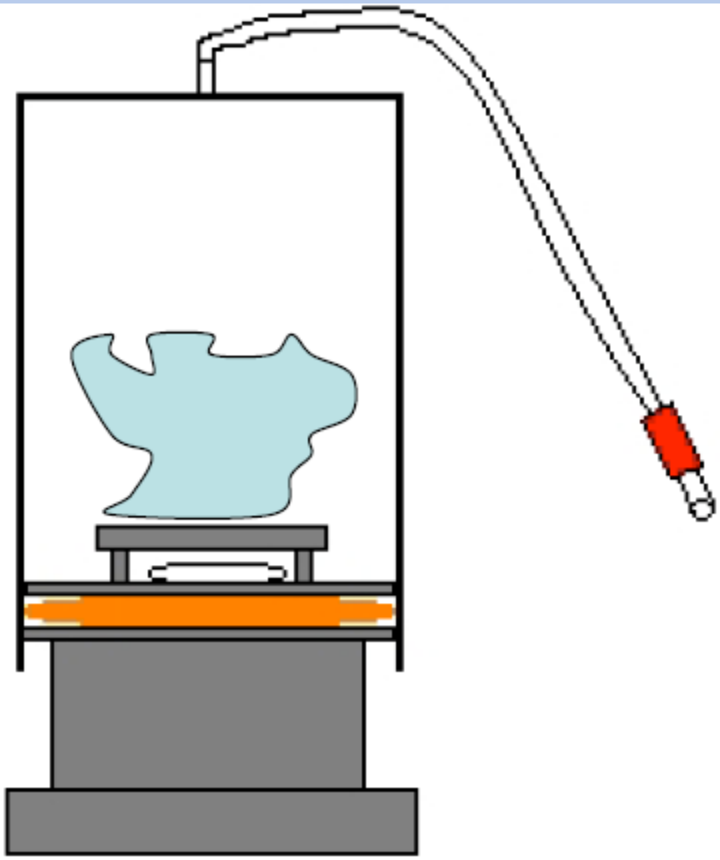
Alkalinity depletion or anomaly method

- Assumes that Calcif=-0.5ΔTA and NCP=ΔDIC-0.5ΔTA, measures net calcification
- Advantages – widely used and compared with other methods, non-destructive, broadly applicable to small (1L) and short (1-3h) or large (1000s m3) and long (days to months) experiments, also useful for dissolution studies
- Disadvantages – change in NH4, PO4, SiO3 concentration can invalidate the Calcif=-0.5ΔTA assumption if concentrations are high

Ca^{2+} change method

- Advantages – a direct measurement of the process of interest, all the other advantages are the same as the TA method
- Disadvantages – precision of the [Ca^{2+}] analysis is not quite as high as for TA, has not been as widely used as the TA method, does not yield a measurement of NCP

Examples of chambers that are being used for *in situ* OA work



2 L incubation chamber
Langdon

SHARQ 10 m^3, K. Yates, USGS

Problems

- All organism based studies face the problem of what to normalize the rate of calcification against (organism mass, surface area, protein)
- It is difficult to inter compare studies because rates have been reported on a different basis
- Variability between replicates is high because the methods we use leave a significant amount of organism to organism variability unexplained

Community scale

Slack water method

- Assumes that Calcif=-0.5ΔTAρh/Δt, where r is the density of seawater, h is average water depth and Δt is the duration of the observation period
- Advantages – fast and easy, only need to measure water depth and TA change
- Disadvantages – only possible to make measurements for a few hours out of the day making daily rates difficult to obtain, not applicable to forereef where much of reef calcification occurs, rates measured during slack water not be representative of rates during the rest of the day when currents are stronger

Lagrangian method

- Assumes that the change in TA as a parcel of water flows over the study area is related to the calcification by the expression $Calcif=-0.5(TA_2-TA_1)\rho h/(t_2-t_1)$, where TA_1 and TA_2 are the TA of the water parcel at time t_1 and t_2, r is seawater density and h is the average water depth.
- Advantages – measures calcification under completely natural conditions, relatively easy to implement (requires a means of collecting water samples and a drogue to follow water mass)
- Disadvantages - limited to shallow areas, laborious to obtain a daily rate, must repeat many short term drifts over the study site and there is no assurance that the drifter will always pass over the same part of the community or that the community under the drifter will be uniform

Eulerian method

- Similar to the Lagrangian method except that TA is measured simultaneously at an upstream and downstream location and calcification rate is computed as $Calcif=-0.5(TA_d-TA_u)\rho uh/L$, where TA_d and TA_u is the TA of the water at the up and down stream location,*u* is the current speed and L is the transect length.
- Advantages – measures calcification under completely natural conditions, greater potential for automation but requires greater investment in equipment
- Disadvantages – limited to shallow areas, and to areas where the current direction is predictable

TA depletion/water mass residence time method

- Assumes that temporally and spatially averaged calcification rate of region is proportional to the salinity-normalized difference in TA between a source region and region of interest and inversely proportional to the residence time of the water in the study area, $Calcif=-0.5(NTA_r-NTA_o)\rho h/\tau$, where NTA_r and NTA_o are the salinity-normalized TA of the study area and the source area, p is seawater density, h is average water depth and τ is the water residence time.
- Residence time can be estimated from a knowledge of the circulation, salt or water budget or geochemical tracer
- Advantages – method gives a temporally and spatially averaged rate for the study area
- Disadvantages – not suitable for areas where the water residence time is <1 day.

Standing crop and turnover or Calcimass method

- Involves making a census of the standing crop of all important $CaCO_3$ producing species in a study area and multiplying by the average turn over time (life time) characteristic of each species.
- Advantages – theoretically provides a way to validate estimates based on changes in water chemistry
- Disadvantages – very labor-intensive, probably will only provide a crude estimate but may be valuable for getting a rough idea of the calcification rate of a new study area

Promising new methods

Control volume method

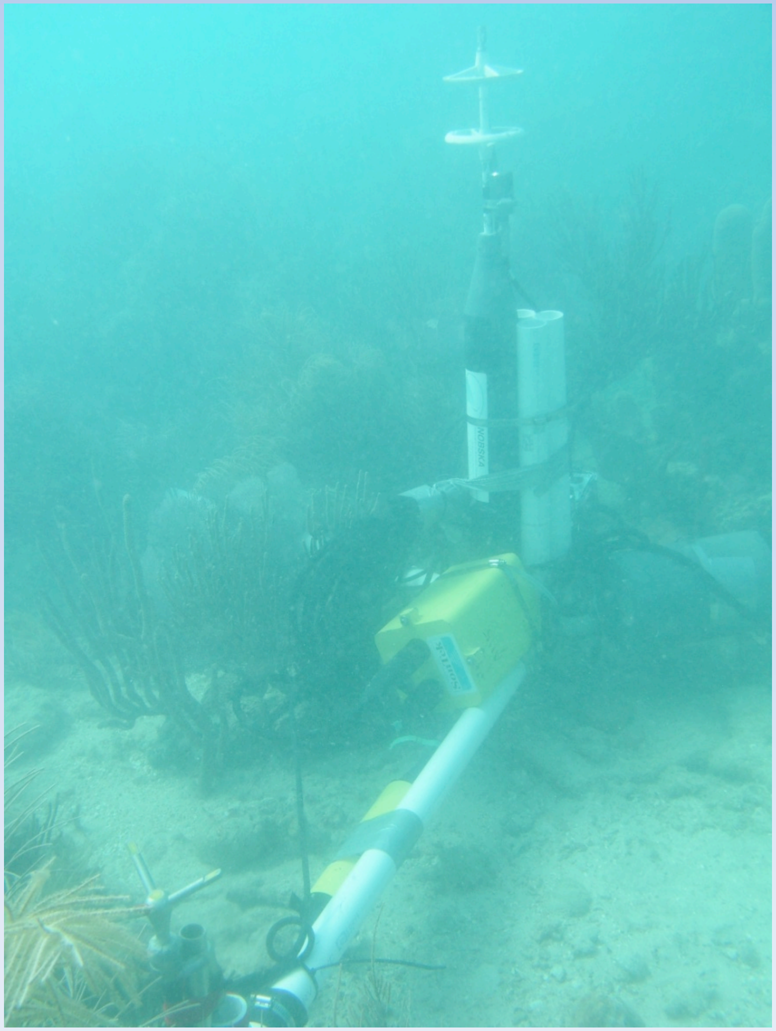
- The flux of water and material into and out of defined volume of water (control volume) overlying a study area is monitored continuously using current meters and chemical sensors.

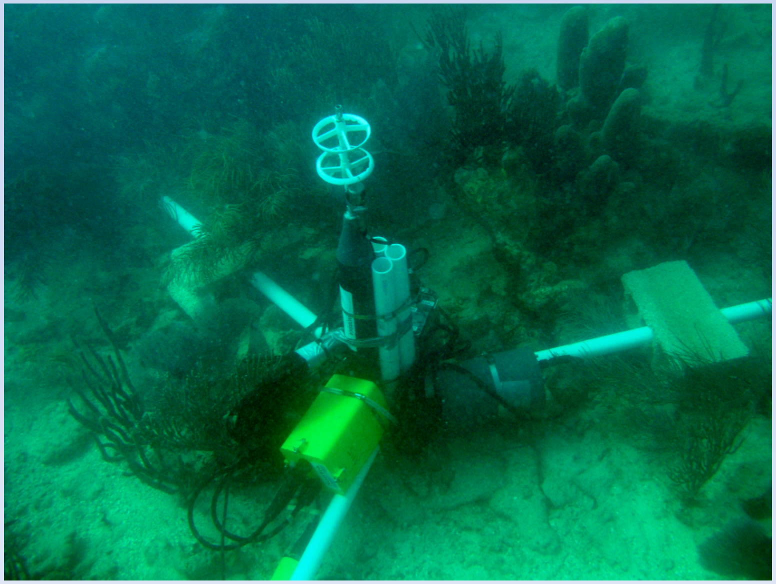
  J_{bio}=local accumulation-advection-$J_{gas\ exch}$
- Advantages – instantaneous rates measured under completely natural physical, chemical and biological conditions that can be integrated to obtain daily and weekly rates
- Disadvantages – O_2 is the only suitable sensor meaning that only NCP can be measured at this time, limited to shallow waters, very expensive in terms of equipment, biofouling limits accuracy

Boundary layer-gradient flux measurements

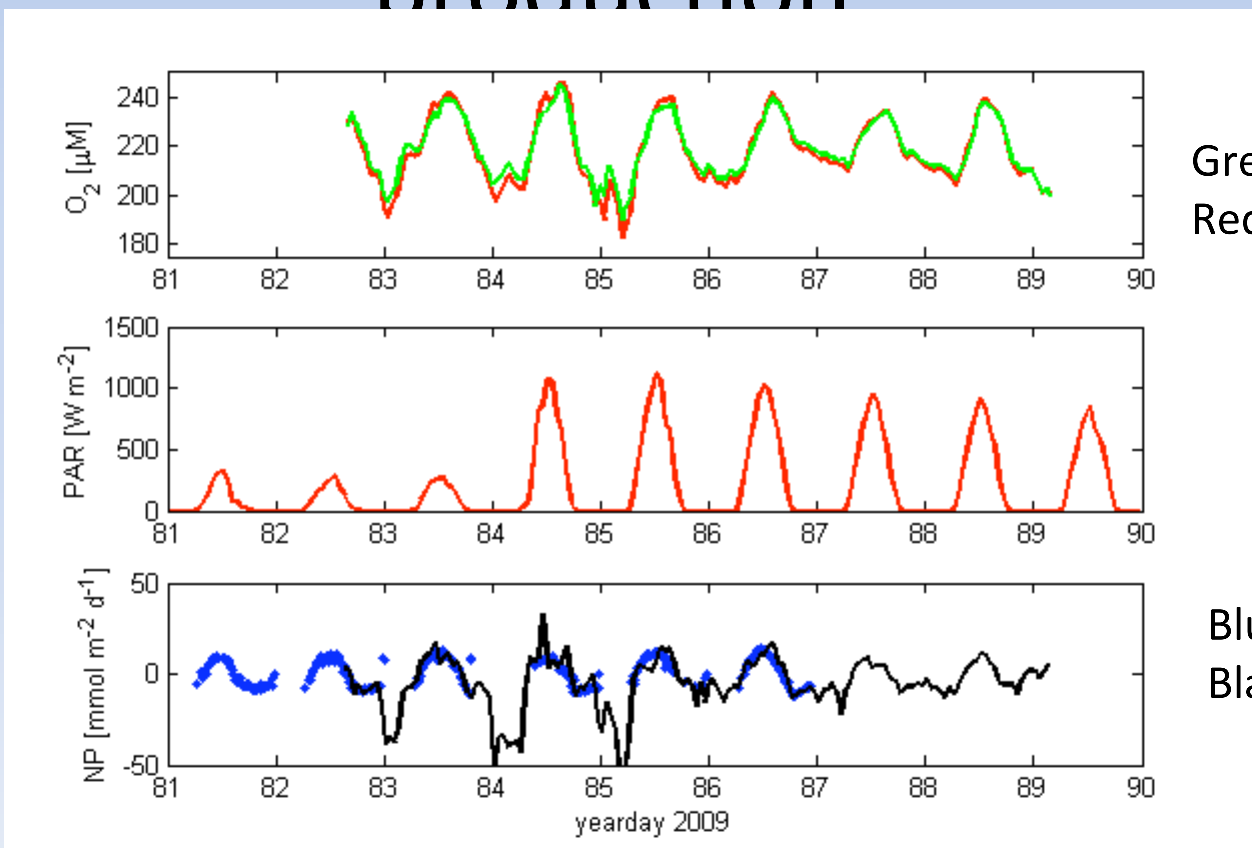
- Measurements of currents and concentration gradients in the boundary layer surrounding a benthic organism or community provides a new means of estimating rates of metabolism.
- Advantages – relatively simple, non-invasive, rates measured under completely natural physical, chemical and biological conditions, gives instantaneous rates that can be integrated to obtain daily, weekly and seasonal rates, can be employed at any depth because only the gradient in the boundary layer matters
- Disadvantages – requires stable and fast response chemical sensors, today only O_2 sensor meets this criteria. However, automated water samplers could solve this problem.

Boundary layer instrument deployed on coral reef in La Parguera, Puerto Rico





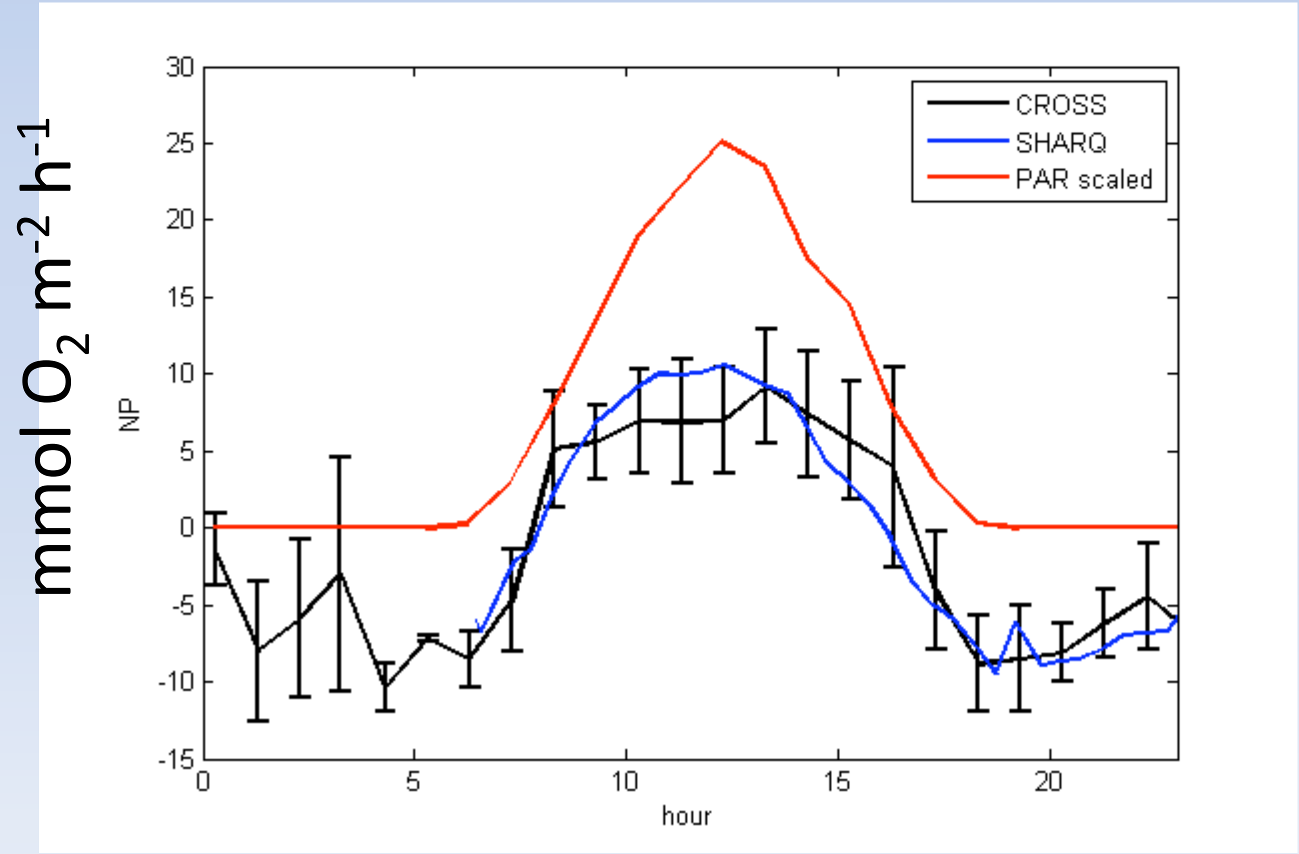
Comparison of boundary layer-gradient flux and SHARQ net primary production



Green shallow O_2
Red deep O_2

Blue SHARQ NP
Black Boundary Layer NP

Comparison of composite daily NP Boundary layer gradient flux vs SHARQ



Needed improvements to field methods

- Need to improve the ease with which daily, seasonal and annual rates of calcification/dissolution can be obtained. Only then do we stand a hope of observing global warming and ocean acidification signals in natural communities.
- Ideally we need sensors to measure TA and DIC with a precision and accuracy of ±2-4 μmol kg^{-1} at the seafloor-water boundary. A Ca^{2+} sensor of similar precision and accuracy would also be nice.