Measuring Elemental Ratios in Corals by LA-ICP-MS

Application

Environmental

Author

Stewart Fallon
The Australian National University
E-mail: Stewart.Fallon@anu.edu.au

Malcolm McCulloch
The Australian National University
E-mail: Malcolm.McCulloch@anu.edu.au

Michael Shelley
The Australian National University
E-mail: Mike.Shelley@anu.edu.au

Abstract

A rapid analytical technique of laser ablation inductively coupled plasma mass spectrometry was developed to measure trace element constituents in corals and hard sponges. This technique is illustrated by measuring B, Mg, Ca, Mn, Zn, Sr, Ba and U in a Porites coral collected from the Great Barrier Reef, Australia. The accuracy of laser ablation inductively coupled plasma mass spectrometry for the measurement of Sr/Ca and Ba/Ca in corals by comparison with solution isotope dilution inductively coupled plasma mass spectrometry is discussed. We demonstrate the significance of the Sr/Ca ratio by correlation with in situ sea surface temperature data to show that Sr/Ca in corals provides a means to retrospectively measure sea surface temperature prior to available instrumental records. Coral Ba/Ca ratios as an indicator of riverine sediment input during times of runoff into the Great Barrier Reef are also examined.

Introduction

General circulation models (GCM's) describe the time-evolving circulation and thermodynamics of the atmosphere and oceans, the two main components of the Earth's climate system. Understanding the processes that control the Earth's climate and making accurate predictions of future changes in climate requires computer models of the climate system that are more realistic then those currently available. One of the principal impediments to the development of better models is the lack of accurate reconstructions of paleoclimate records (e.g. sea surface temperature).

Reliable high-resolution paleoclimate records are needed to understand the patterns and mechanisms of natural climate variability. Tropical air-sea interactions that affect the global distribution of water vapor (the most potent greenhouse gas) are largely dependent on sea surface temperature (SST) and sea surface salinity. Therefore, understanding the sensitivity of tropical SST and salinity in response to major global climate change is of particular importance. Until a good understanding of natural climate variability is obtained, the impacts on climate attributable to anthropogenic causes (increases of CO_2, etc.) cannot be fully understood.

An organism capable of providing this information is reef-building coral (Figure 1). Corals provide a continuous "time series record" of the marine environment through chemical records preserved in their aragonite skeletal lattice. Elemental ratios

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(Sr/Ca) in corals have been shown to provide geochemical proxies for reconstructing the SST during the corals growth. Obtaining long time series by traditional methods (thermal ionization mass spectrometry, solution ICP-MS) is very time consuming and expensive. The development of rapid multi-element analysis by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) improves the quantity and quality of information that can be extracted from corals, an essential prerequisite for their practical application as environmental proxies.

Figure 1. **A diver drilling a Porites coral to obtain a core for geochemical analysis.**

LA-ICP-MS is gaining wide use as an analytical tool for the analysis of trace elements in a diverse range of sample materials. Semi-quantitative and quantitative elemental concentrations using LA-ICP-MS are being reported using chemically and matrix-matched standards as well as the NIST Standard Reference Material glass suite (NIST 610, 612, 614). Laser ablation has the technical advantage of analyzing elements in situ without time-consuming sample dissolution, thereby providing a rapid and relatively non-destructive technique. In this paper, we describe the LA-ICP-MS method used to measure the Sr/Ca ratio in corals as a monitor of sea surface temperature variations and the Ba/Ca ratio as an indicator of terrestrial runoff from the Great Barrier Reef.

Experimental

Coral Collection

The massive Porites coral can live for hundreds of years. To measure elemental ratios in corals, we take a core from the center of the coral colony using an underwater drilling system (Figure 1). The 5-cm diameter core is sliced into 7-mm thick slabs and X-rayed to show the growth bands (Figure 2). The coral is then cut into 45 × 25 mm pieces to fit into the laser-sampling chamber.

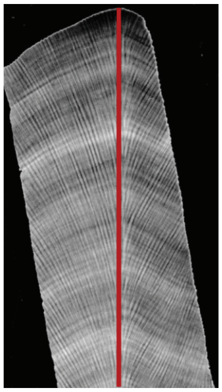

Figure 2. **X-Ray positive of a Porites coral core slab. Light and dark bands correspond to different coral skeletal densities and growth. The red line indicates the track the laser follows along a main growth axis.**

ICP-MS

Our LA-ICP-MS system uses an ArF excimer laser (193 nm wavelength) coupled to an Agilent 7500s. The operating parameters for the ICP-MS are listed in Table 1. The laser system consists of an in-house constructed sample chamber that holds a 45 × 25 mm coral piece for ablation. The laser illuminates a rectangular aperture which is imaged onto the flat surface of a coral slice and with each laser pulse ablates a rectangle 0.1 microns deep, 50 µm wide parallel to the growth axis, and 500 µm wide perpendicular to the growth axis (Figure 3). This rectangular laser beam is a crucial component of LA-ICP-MS of corals to ensure representative analysis across the interlocking branch-like structural elements of the corals. The long focal length (150 mm) of our excimer laser optical system and this large sampling window minimizes the depth related fractionation observed for material removed from the bottom of holes. The time resolution depends on the growth rate of the coral and the slit width, and we usually obtain sub-weekly resolution in corals (>100 samples year $^{-1}$). The fast mass switching (1 msec mass to mass, or 2 msec for large jumps) and high sensitivity of the 7500s allows us to measure many elements together without compromising this spatial resolution. A significant time interval between masses would result in noisy element ratios because a combination of the coral surface topography and the sample cell and carrier gas transport system gives signal intensity variations with about a 1-second time constant. The laser has a pulse length of 25 nsec and the power density on the sample surface is 0.32 GW/cm^2.

For coral analysis, the laser is pulsed at 5 Hz. The material is ablated in helium and entrained in argon for analysis by ICP-MS. A side view of the laser sample cell is shown in Figure 4. The isotopes ^{10}B, ^{25}Mg, ^{46}Ca, ^{55}Mn, ^{66}Zn, ^{84}Sr, ^{138}Ba and ^{238}U are measured with ^{46}Ca (0.004% abundance) as an internal standard to compensate for variations in ablation yield due to coral surface porosity. The data is standardized to a pressed powder disc prepared from a cleaned and finely crushed Porites coral from the Great Barrier Reef. Some other elements we routinely measure are lead and rare earth elements. They are standardized using the NIST 614 glass. The dual simultaneous detector system of the Agilent 7500s enables us to measure the low concentration elements (manganese and zinc) simultaneously with the more abundant elements (Figure 5).

Table 1. Agilent 7500s Operating Parameters

	Laser Mode
ICP-MS	Agilent 7500s
Forward power	1250 W
Reflected power	< 1 W
Gas flow rate:	
Cool gas	14 L min^{-1}
Carrier gas Ar	1.14 L min^{-1}
Optional gas He (into cell)	0.3 L min^{-1}
Cone composition	Nickel
Detector mode	Dual simultaneous
Acquisition mode	Time resolved
Isotope dwell time	25 to 60 ms
Points per peak	3
Time slice	~ 1 s

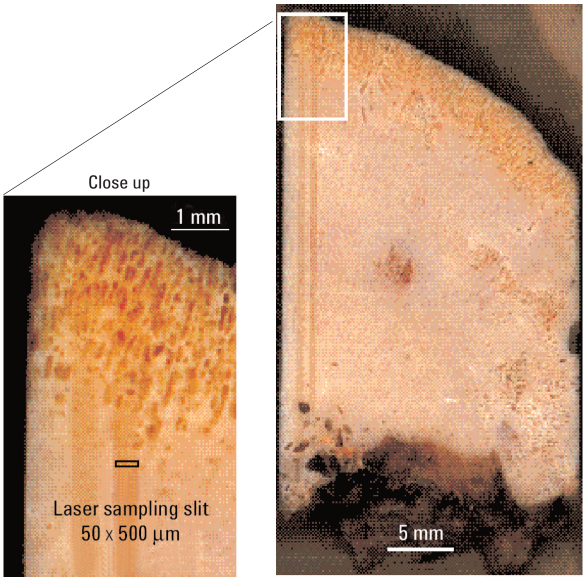

Figure 3. Laser sampling on a coralline sponge showing parallel tracks (right side) and close up of boxed section (left side) of the laser sampling slit. Laser tracks are not visible on corals due to surface porosity.

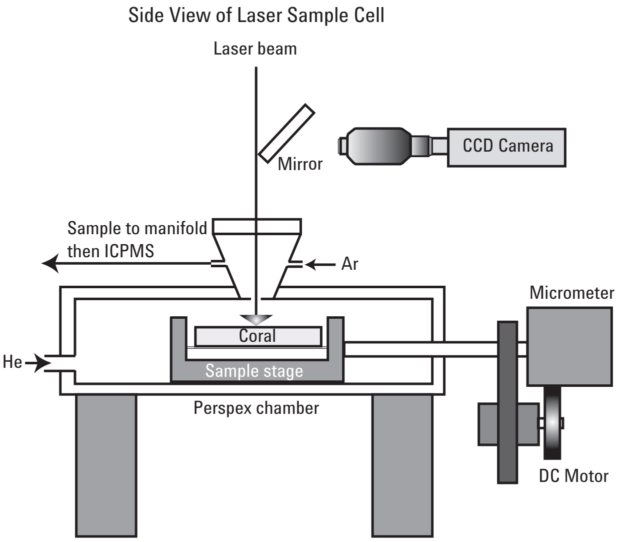

Figure 4. Side view of the laser sample cell. Coral is ablated in a sealed Perspex chamber under a helium atmosphere. The sample stream is entrained in argon and enters a smoothing manifold before entrance to the Agilent 7500s ICP-MS. The sample is viewed by CCD video camera. A DC motor with a high-ratio gearbox scans the sample beneath the laser, enabling continuous sampling.

The analytical procedure is shown in Figure 5. Background and standards are collected for 60 seconds each before and after the coral analysis, a motor scans the coral sample and standards beneath the laser at a speed of 0.03 mm s^{-1}. The entire protocol takes around 40 minutes for each piece of coral.

Results and Discussion

Accuracy: Comparison with Isotope Dilution Solution ICP-MS

One of the methods used to check the accuracy of LA-ICP-MS was analysis of three other calcium carbonate samples. A coral from the Huon Peninsula, Papua New Guinea, an aragonite coralline sponge and a calcite coralline sponge were finely crushed and pressed to form pellets. The Sr/Ca and Ba/Ca

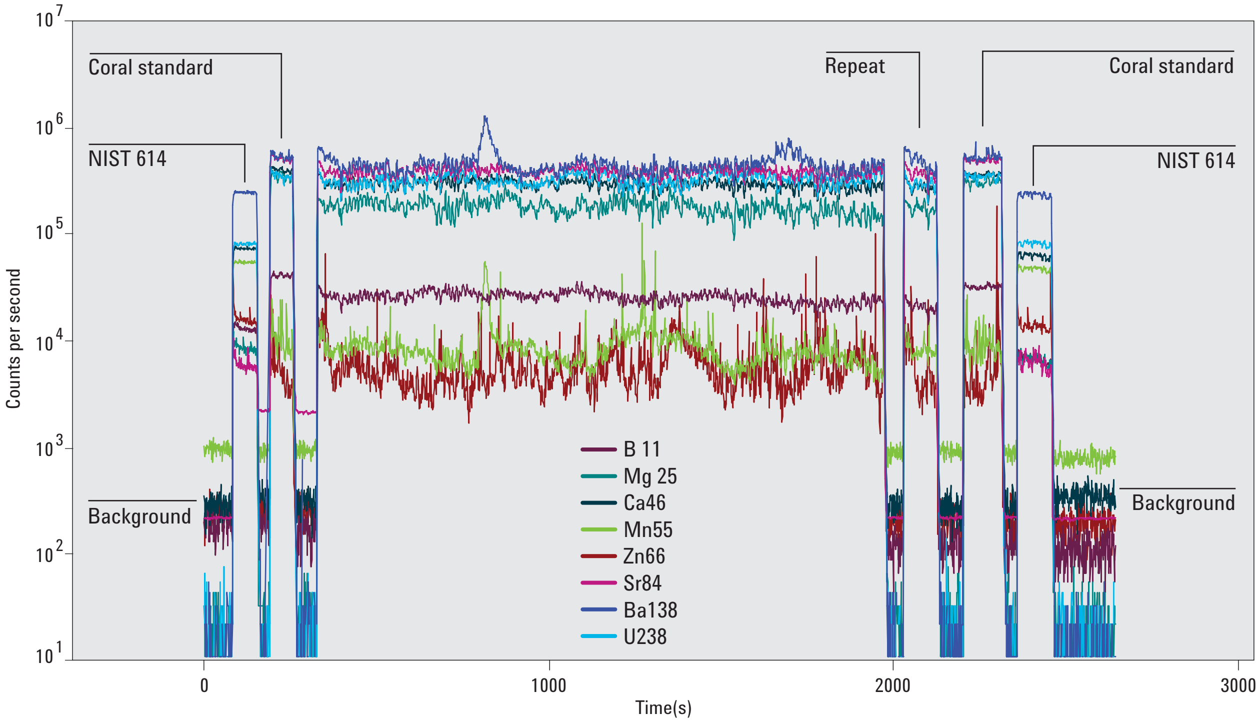

Figure 5. LA-ICP-MS protocol for coral analysis, in counts per second for each isotope.

concentration of the bulk powders was measured by isotope dilution solution ICP-MS. The pressed powder samples were also analyzed with LA-ICP-MS by scanning 2 to 3 mm long sections. The coral sample was measured 12 times over a 1-month period, the aragonite sponge sample 50 times over a 3-month period and the calcite sponge sample five times in 1 day. The LA-ICP-MS and solution measurements agree within the statistical error (Figure 6). Using a pressed powder standard constructed from a calibrated coral provides accurate fully quantitative LA-ICP-MS for $CaCO_3$ (corals and sponges) with differing concentrations.

Sea Surface Temperature Proxy: Sr/Ca

A Porites coral from the Great Barrier Reef was analysed with the LA-ICP-MS. The comparison between the coral Sr/Ca ratio and the known sea

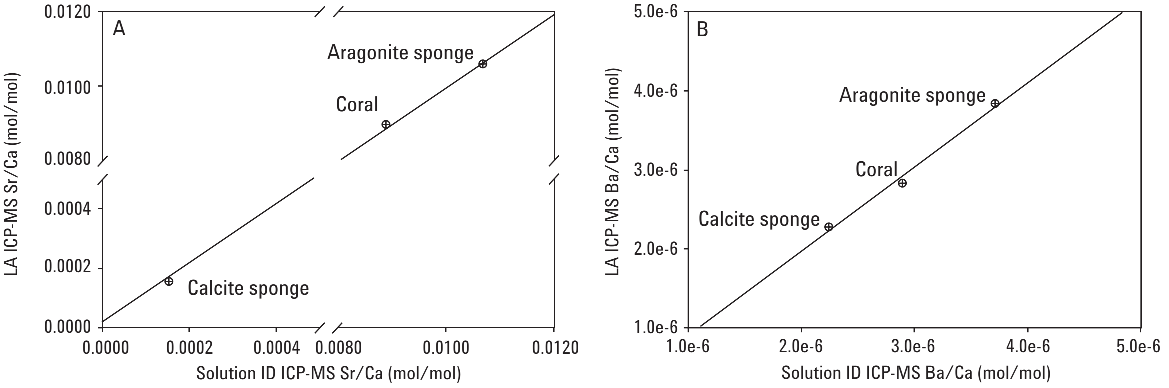

Figure 6. Accuracy of LA-ICP-MS method. Comparing solution ID ICP-MS (x axis) with LA ICP-MS (y axis) of three samples, a calcite sponge, a coral, and an aragonite sponge. Error bars and linear regression for the three samples are shown. A) Sr/Ca B) Ba/Ca.

surface temperature for about 90 mm of the core is shown in Figure 7. The correlation coefficient between the two data sets is r = - 0.93, or approximately 86% of the Sr/Ca variation is attributable to SST, indicating the value of coral Sr/Ca as a SST proxy. Sr/Ca has been measured by various labs and in many corals from different locations and it has been proven to be robust in terms of its ability to record SST. With such a calibration between Sr/Ca and SST, it is possible to reconstruct water temperatures before the advent of instrumental records from a particular reef.

Terrestrial Runoff: Ba/Ca

The Ba/Ca ratio in corals can be influenced by the upwelling of nutrient rich water, and in coastal corals by river runoff. This coral was collected from near shore on the Great Barrier Reef (GBR) near a major river system, the Burdekin. Sediment input to the GBR has elevated levels of barium, and heavy river flooding brings higher than normal barium into the surrounding seawater. The inshore corals of the Great Barrier Reef register floods by an increased Ba/Ca ratio. The influence of river runoff on GBR corals is also recorded as luminescent or fluorescent lines/bands in the coral skeletons. This coral records the floods of 1996, 1997 and 1998 (Figure 8). The relation between river discharge and coral Ba/Ca is not necessarily linear; with factors such as wind and ocean current conditions affecting the path of the flood plumes. Nevertheless the Ba/Ca runoff proxy in corals can be used as an indicator of sediment input into the GBR and for other areas around the globe.

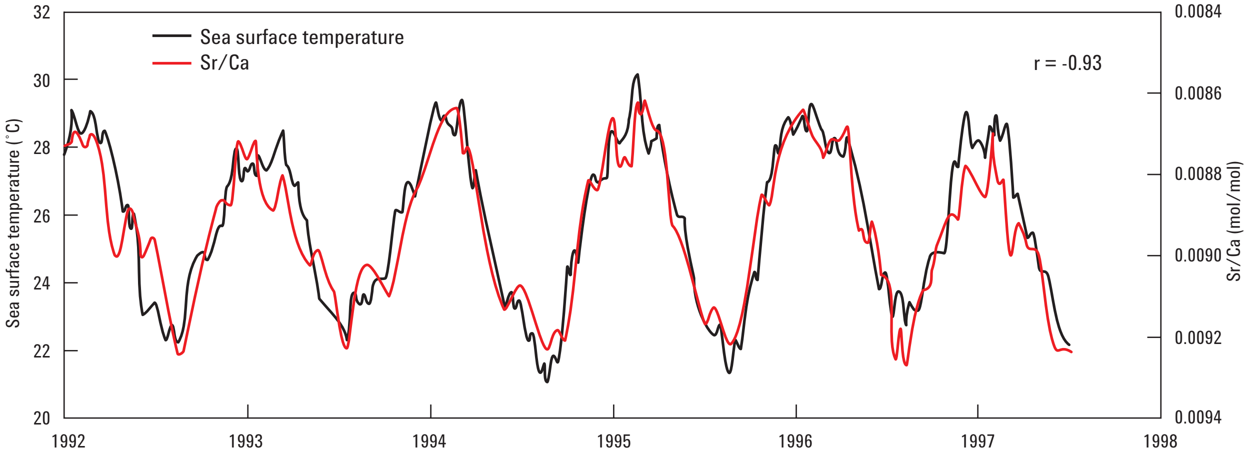

Figure 7. Measured coral Sr/Ca in red (right. axis) vs. in situ sea surface temperature record in black (left axis).

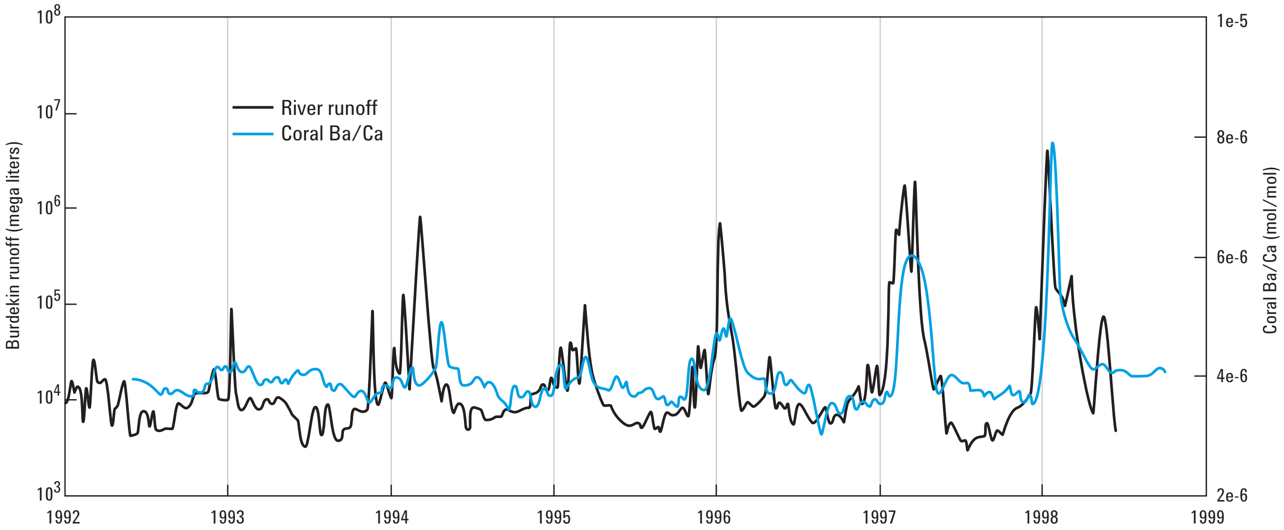

Figure 8. Comparison between terrestrial runoff (Burdekin River in mega liters, log scale) on the left axis and Coral Ba/Ca (mol/mol) on the right axis.

Conclusions

Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) provides a rapid analytical technique for measuring B, Mg, Ca, Mn, Zn, Sr, Ba and U concentrations in corals. The power of this technique lies in its ability to measure these elements simultaneously with appropriate spatial resolution regardless of coral growth rate. Researchers have collected long coral cores spanning several centuries from various locations throughout the globe but producing long time series at monthly or higher resolution has previously been very time consuming and prohibitively expensive. The LA-ICP-MS discussed here makes it practical to produce long high-resolution climate reconstructions from corals, to enable a greater understanding of the role of the oceans in the dynamics of the Earth's climate.

Further Reading

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Printed in the USA
November 13, 2001
5988-3742EN

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