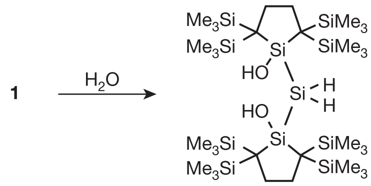
Information for the experimental details, spectral data and X-ray analysis for **5**).



5 (3)

The bent-allenic and conjugated structure with facile intramolecular rotation of the Si^2 atom around the Si^1–Si^3 axis found for the first stable trisilaallene is far from a reasonable extension of the bonding description for carbon allenes. Trisilaallene derivatives are expected to be useful synthetic reagents and building blocks for silicon functional materials in the future because of their unusual electronic structure. □

Methods

Synthesis of trisilaallene 1

When tetrachlorodisilane **3** (279 mg, 0.52 mmol) was treated with potassium graphite KC_8 (311 mg, 2.30 mmol) in THF (45 ml) at −40 °C for 24 h, the solution turned to dark green. Changing the solvent to hexane, elimination of insoluble materials by filtration, and then concentration of the solution to 1 ml produced crystals of trisilaallene **1** (117 mg, 0.15 mmol, 59%). Recrystallization from hexane afforded single crystals suitable for X-ray analysis.

Spectral data for 1

Dark-green crystals with a melting point of 198–200 °C. ^1H NMR spectrum (C_6D_6, chemical shift δ in p.p.m.): 0.39 (singlet, 72H), 2.00 (singlet, 8H). ^{13}C NMR spectrum (C_6D_6, δ): 3.3 ($SiMe_3$), 27.2 (C), 34.3 (CH_2). ^{29}Si NMR spectrum (C_6D_6, δ): 1.6 ($SiMe_3$), 157.0 (Si=*Si*=Si), 196.9 (*Si*=Si=*Si*). UV–vis spectrum (hexane): $\lambda_{max} = 390$ nm ($\varepsilon = 21300$), $\lambda_{max} = 584$ ($\varepsilon = 700$). Mass spectrometry (70 eV, electron impact ionization): $m/z = 772$ (molecular ion; relative intensity, 10%), $m/z = 373$ (41%), $m/z = 73$ (100%).

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Correspondence and requests for materials should be addressed to M.K. (e-mail: mkira@si.chem.tohoku.ac.jp).

Coral record of increased sediment flux to the inner Great Barrier Reef since European settlement

Malcolm McCulloch*, Stewart Fallon*†, Timothy Wyndham*, Erica Hendy*, Janice Lough‡ & David Barnes‡

* *Research School of Earth Sciences, Australian National University, Canberra 0200, Australia*
‡ *Australian Institute of Marine Science, Townsville, Queensland 4810, Australia*

The effect of European settlement on water quality in the Great Barrier Reef of Australia is a long-standing and controversial issue[1–6]. Erosion and sediment transport in river catchments in this region have increased substantially since European settlement[6–10], but the magnitude of these changes remains uncertain[1–10]. Here we report analyses of Ba/Ca ratios in long-lived *Porites* coral from Havannah Reef—a site on the inner Great Barrier Reef that is influenced by flood plumes from the Burdekin river—to establish a record of sediment fluxes from about 1750 to 1998. We find that, in the early part of the record, suspended sediment from river floods reached the inner reef area only occasionally, whereas after about 1870—following the beginning of European settlement—a five- to tenfold increase in the delivery of sediments is recorded with the highest fluxes occurring during the drought-breaking floods. We conclude that, since European settlement, land-use practices such as clearing and overstocking have led to major degradation of the semi-arid river catchments, resulting in substantially increased sediment loads entering the inner Great Barrier Reef.

Since European settlement, large-scale modification of the river catchments has occurred from grazing, agriculture, mining and associated activities such as land clearing. Their impact on the marine environment remains highly uncertain[1–6,11,12]. With few exceptions[13], it has been difficult conclusively to demonstrate a link between enhanced levels of terrestrial runoff and large-scale reductions in coral reef cover. This is due not only to the complex sequence of events that may ultimately lead to a shift from coral- to algae-dominated communities[11,12], but also because it has been difficult to quantify long-term changes in water quality regimes. Here we describe a new approach based on the application of *in situ* geochemical tracers in corals[14–16] that has the advantage of providing a direct quantitative measure of the long-term changes in sediment fluxes that are actually being delivered to the Great Barrier Reef (GBR).

Long-lived (300 to 400 years old) *Porites* corals from the Havannah and Pandora reefs, located on the inner GBR of northern Queensland, experience episodic discharges of freshwater flood plumes from the Burdekin river (Fig. 1). The Burdekin river is the largest single contributor of suspended sediment to the inner GBR lagoon, and often delivers more than 10^7 tonnes of suspended sediment during single runoff events[6–10]. During periods of flood, freshwater discharges form buoyant, low-salinity flood plumes that generally move northwards along the GBR coastline[17]. Occasionally flood plumes may also reach the mid-shelf region of the GBR and thus directly affect the more 'pristine' regions of the GBR[17,18]. Flood events are manifested in the coral as narrow fluorescent[19] or luminescent[20] bands, thought to be due to the incorporation of either humic acids or low-density zones in the coral skeleton. Here we show how Ba/Ca ratios in coral cores can provide high-fidelity records of suspended sediment loads entering the GBR. Barium is desorbed from fine-grained suspended particles (clays) in the low-

† Present address: Lawrence Livermore National Laboratory, California, USA.

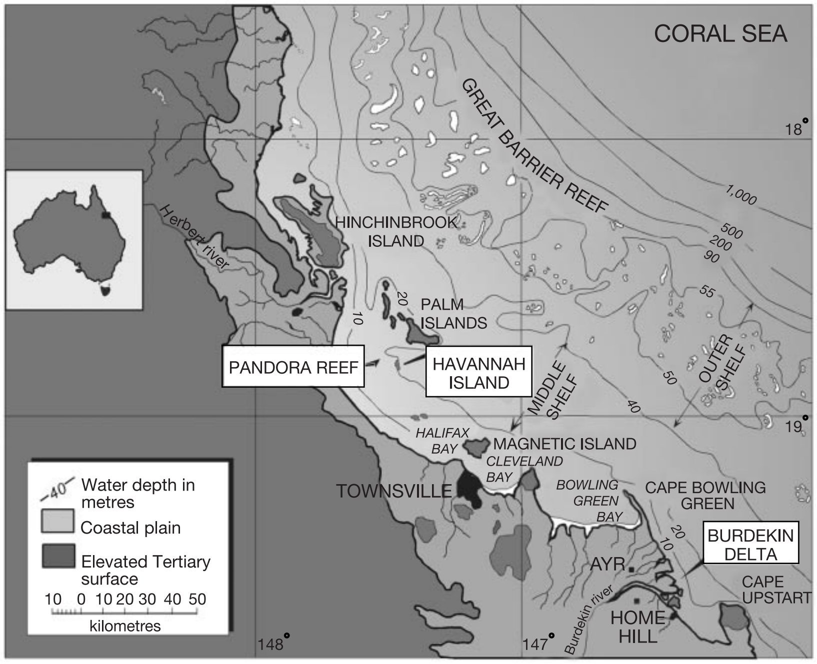

Figure 1 Map showing the location of the central Great Barrier Reef (after Belperio[7]). During flood events, low-salinity plumes are discharged from the Burdekin river and advected in a northwards direction within the inner-mid-shelf region of the GBR[17]. Coral cores were analysed from the inshore Havannah and nearby Pandora reefs, which are in the pathway of Burdekin river flood plumes.

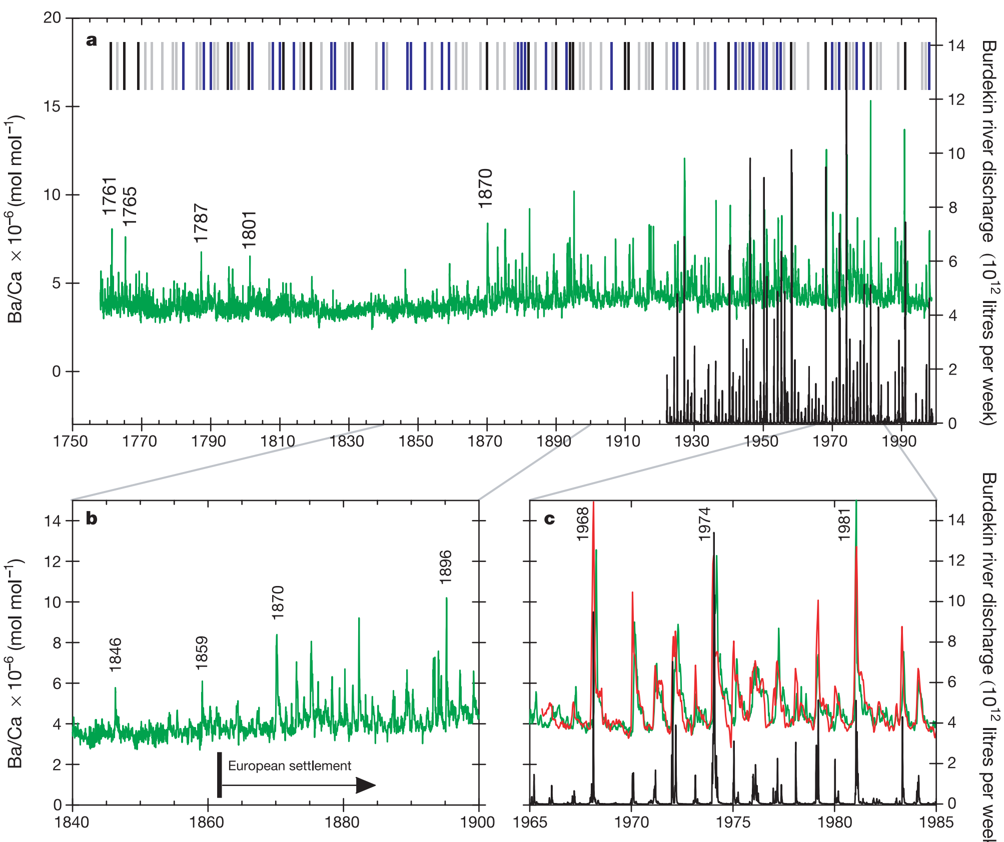

Figure 2 The coral Ba/Ca record of suspended sediment into the GBR by the Burdekin river over approximately the past 250 years. Barium provides a proxy for suspended sediments as it is desorbed from flood plume sediments[21] and quantitatively partitioned into the corals, calcium carbonate skeleton[22]. **a**, Coral record from Havannah Reef (green line) for the period from 1760 to 1998 with Ba/Ca peaks proportional to the sediment flux delivered by Burdekin flood plume events. The frequency and intensity of flood events is indicated by luminescent bands in the coral skeleton[19,20,28], represented here as major (black bar), average (blue bar) and small (grey bar) discharge events. The record of discharge for the Burdekin river, available from 1921, is also shown (black line). **b**, Coral record for the period from 1840 to 1990 showing the large increase in Ba/Ca that commences in 1870, the first major flood following European settlement. **c**, Coral records from Havannah (green line) and Pandora reefs (red line) for the period 1965 to 1985 show excellent agreement and a good correlation with the Burdekin river weekly discharge (black line).

salinity region (0–5 p.p.t.) of the estuarine mixing zone[21]. Thereafter Ba behaves as an essentially conservative dissolved tracer, being advected with the flood plume and partitioned into the coral carbonate skeleton in proportion to the ambient seawater concentration[22]. Ba/Ca ratios in corals[23] therefore provide a long-term record of changes in suspended sediment loads and hence in the nutrients that are entering the GBR.

Using the relatively new technique of laser ablation inductively coupled plasmas mass spectrometry (ICP-MS) specifically adapted for coral studies[14–16], it is now possible to investigate the detailed geochemical characteristics of entire coral cores, at approximately weekly resolution. A 5.3-m-long Havannah coral core was analysed for the period from about 1750 to 1985, supplemented by shorter cores collected in 1998 from Havannah and the nearby Pandora Reef. The Ba/Ca systematics in the coral core reveal two distinctive patterns (Fig. 2). Prior to European settlement there is surprisingly little evidence for flood-plume related activity from the coral Ba/Ca ratios. The only significant peaks that are present correspond to the major floods of 1761, 1765, 1787 and 1801 (Fig. 2a). From the early 1800s to 1860, which includes major flood events in the years 1811, 1817, 1819 and 1831, the coral does not exhibit any significant Ba peaks, despite the presence of major luminescent bands (Fig. 2a).

Soon after European settlement, which commenced in the Burdekin catchment in 1862 (ref. 24), there is a large change in the behaviour of Ba. The 1870 flood band (Fig. 2b), the first major flood following European settlement, has a large Ba/Ca peak, indicative of a significant increase in suspended load being delivered to the inner GBR. Large peaks also occurred soon after in 1875, followed by major peaks accompanying the floods in 1882 and 1896. The 1896 flood, from cyclone *Sigma*, produced a large Ba/Ca peak ($> 10 \times 10^{-6}$), despite a flood level of only 15.8 m, compared to the first recorded flood height of 20.9 m for the 1870 flood.

Another important feature of the Havannah coral record is the significant increase in the Ba/Ca baseline that also occurred from around 1870 onwards (Fig. 2a, b). Baseline ratios increase from the pre-European range of $(3–4) \times 10^{-6}$, to a present-day range of $(4–5) \times 10^{-6}$, an increase of about 30%. The sustained increase in the Ba/Ca baseline that commences after the 1870 flood is interpreted as indicating a finite but significant residence time of at least several years, for an enhanced flux of terrestrially derived Ba. Fluctuations in the Ba/Ca baseline and the apparent persistence after some large flood events (indicated by shoulders on the Ba peaks, Fig. 2c), suggests that processes such as biological recycling[21], continuing Ba supply from estuaries[16], and possibly groundwater inputs[25] to the GBR may also make second-order contributions to the inshore Ba budget. Upwelling of Ba-rich waters may also contribute to fluctuations in the Ba/Ca baseline[22,26], but these effects are relatively minor and mainly restricted to the outer reef. Together, these results indicate that within one to two decades after the arrival of European settlers in northern Queensland, there were already massive impacts on the river catchments that were being transmitted to the waters of the inner GBR. This is mainly attributed to the rapid expansion in numbers of (initially) sheep and, most importantly, cattle[24] (Table 1) and the resultant erosion that introduced hoofed animals would have had on the highly fragile riverbanks of the Burdekin.

The relationship between Ba/Ca in corals and the Burdekin river discharge is shown in Fig. 3, where Ba/Ca peak heights are plotted versus the maximum weekly river discharge using records that commence in 1921. Weekly discharge is used, as this is the time-frame for transport of flood plumes from the mouth of the Burdekin river to the Havannah reef site (Fig. 1). There is an approximately linear relationship between the maximum weekly discharge of the Burdekin river and the maximum coral Ba/Ca ratio ($r^2 = 0.68$), which is greatly improved if floods that follow periods of drought (peak Burdekin flow $<0.7 \times 10^{12}$ litres per week) are excluded (Fig. 3). The relationship for non-drought modern (1921 to 1998) floods is given by:

$$\mathrm{Ba}_{\mathrm{modern}} = 4.8 + 0.6 \times 10^{12} \text{ litres per week} \qquad (1)$$

where $\mathrm{Ba} = \mathrm{Ba/Ca} \times 10^{-6}$ (atomic ratios) and the intercept is 4.8×10^{-6}. If the floods of 1981 and 1991 are excluded (see later discussion), then a highly coherent array ($r^2 = 0.87$) is obtained. The observation that drought-breaking floods have much greater suspended sediment loads is not surprising considering the loss of groundcover and hence the enhanced erosion that occurs during periods of drought. Prominent examples are the runoff events of 1927, 1936, 1968, 1970 and 1988, which were all preceded by droughts. The higher Ba/Ca ratios in drought-breaking floods indicates that suspended sediment loads are approximately doubled, relative to the $\mathrm{Ba}_{\mathrm{modern}}$ reference line. The 1981 flood is highly anomalous, possibly reflecting expansion of landclearing[6,27] and the large increase in cattle stocking in the Burdekin catchment that occurred during the 1970s, with the introduction of more drought-resistant cattle breeds from India, such as *Bos indicus*[27]. The very large flood event of 1991 is also unusual, as it is a double-pulse flood event, and hence estimates of the weekly discharge maximum are more sensitive to the flood hydrograph.

The natural or pre-European influence of the Burdekin river on

Table 1 **Cattle and sheep numbers in the Townsville region[24,27]**

	1862	1868	1872	1889	1990
Sheep	0	176,956	1,284	2,983	-
Cattle	0	31,098	53,457	250,912	>1,000,000

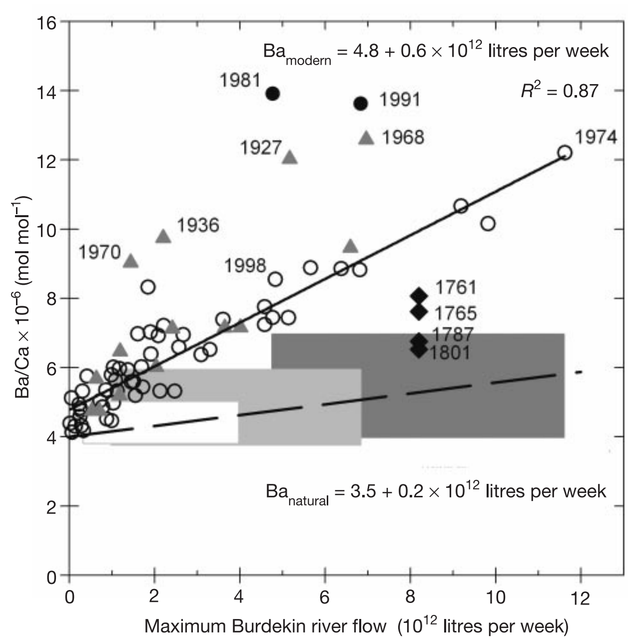

Figure 3 Plot of the maximum Ba/Ca flood peak height versus the maximum weekly Burdekin river discharge for flood events from 1921 to the present. Triangles correspond to floods that follow periods of drought (that is, peak Burdekin flow $<0.7 \times 10^{12}$ litres per week). If the events of 1981 and 1991 are also excluded (see text) then there is an excellent correlation ($r^2 = 0.87$) between Ba/Ca (that is, sediment flux) and maximum weekly discharge for flood events. The magnitude of pre-European floods is estimated using both luminescent bands[28] and Sr/Ca–δ^{18}O systematics[29] (see Supplementary Information for details). Luminescent bands for pre-European floods are shown for major floods (dark grey), average (light grey) and small discharge events (open rectangle). Solid diamonds show the magnitude of the largest pre-European floods.

the inner GBR can be determined using the same approach and is given by:

$$\mathrm{Ba}_{\mathrm{natural}} = 3.5 + 0.2 \times 10^{12} \text{ litres per week} \quad (2)$$

Where pre-historic Burdekin river flows (that is, before 1860) have been determined using the relative intensity of luminescent bands[19,20,28] as shown in Fig. 2, together with more limited δ^{18}O–Sr/Ca systematics[29] (see Supplementary Information). The increase in both the slope and baseline of the Ba/Ca versus river-discharge relationships—equations (1) and (2)—indicates a five- to tenfold increase in suspended sediment load following European settlement of the Burdekin river catchment. The most pronounced deviation from the pre-European reference line are the floods of 1761, 1765, 1787 and 1801, all of which occur after periods of drought. This shows that even in its 'natural' state the Burdekin river catchment was subjected to enhanced erosion due to drought, albeit at a reduced level. It is also noted that from 1850 to 1870 a shift in δ^{18}O in coral cores has been observed[30], indicating freshening of the waters of the inner GBR. Although this has been attributed[30] to a regional scale phenomenon marking the end of the Little Ice Age, there remains the possibility that land-use changes since European settlement have also increased freshwater discharges into the inner GBR. Regardless, it is clear that climate change (especially droughts), combined with the adoption of European-style land use has had a severe impact on river catchments and hence on the near-shore coral reefs of the GBR.

The impact of higher loads of sediment and nutrients from river runoff in the GBR is difficult to quantify, but past experience[11–13] suggests it should cause concern. It is clear, for example, that dissolved components such as inorganic P, organic P and N, nitrite and nitrate, are enriched in flood plumes[2,10] and often result in higher levels of biologic activity such as phytoplankton blooms[2]. Fortunately for the GBR, these effects are probably mainly limited to the duration of flood plumes, that is, from weeks to months. Arguably[1–6], of most concern are the direct (for example, increased turbidity) and indirect (for example, desorption of P from anoxic sediments) impacts of increased sediment loads in the GBR. Burdekin river flood plumes supply an average of $10^{10}\,\mathrm{m}^3$ of water and 10^7 tonnes per year of suspended sediment to the inner GBR[6–10]. Suspended sediment concentrations measured close to the river mouth are typically $500\,\mathrm{mg\,l^{-1}}$ to $1{,}500\,\mathrm{mg\,l^{-1}}$ (refs 2, 10), consistent with the range expected from estimates from erosion and soil loss in the catchment[6,8,9]. More distal from the river mouth (>10 km), suspended sediment concentrations generally decrease stepwise to levels of approximately $10\text{–}20\,\mathrm{mg\,l^{-1}}$, concomitant with increasing salinity[2]. This indicates that only about 5% to 10% of the sediment remains suspended in flood plumes. Nevertheless, flood plumes from the Burdekin river have the potential to disperse large amounts of sediment (10^5 to 10^6 tonnes) over a significant region (for example, 500 km $\times$ 20 km) of the inner and mid-GBR. The fate of the more than 10^9 tonnes of additional sediment deposited at the river mouth since European settlement commenced has not been considered in this budget, but depending on the tide- or wind-driven lateral transport processes is also likely to have significant impacts.

Fine-grained suspended sediments are likely to have the most deleterious effects on coral reefs. These sediments can be readily transported and dispersed throughout the inner to mid-shelf regions of the GBR, and are more chemically reactive, being the major source of terrestrial P and other important nutrient elements. Reducing sediment fluxes to coral reefs must be a high priority if corals are to survive the damaging combination of direct anthropogenic impact and rapid climate change. □

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Correspondence and requests for materials should be addressed to M.M. (e-mail: Malcom.McCulloch@anu.edu.au).