The contribution of organic-rich mudstones to the Mesoproterozoic silicon cycle: criticality of microbial life

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Article

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Abstract

The secular evolution of marine silicon, carbon and phosphorous cycles influences interpretation of Earth's life and climate histories. In today's ocean, planktic siliceous skeletons are deposited in sediments as particulate biogenic opal that transforms to authigenic quartz. Si biomineralizing organisms only radiated in the early Phanerozoic and in the absence of biosiliceous skeletal grains, the pathway for Si transfer from seawater into Pre-Cambrian sediments remains enigmatic.

Here we determine the abundance and stratigraphic distribution of authigenic quartz in the c. 1.38 Ga Velkerri Formation (Australia), a key archive of Mesoproterozoic ocean chemistry. Petrographic, geochemical and isotopic analyses demonstrate that a major fraction of quartz (up to 45 % of the rock volume) is not of extrabasinal, detrital origin but instead authigenic and concentrated in subunits rich in organic carbon and phosphorus, indicative of high primary productivity. We argue that this authigenic quartz results from recrystallization of amorphous silica sequestered from sea water due to the presence of cyanobacteria.

We probabilistically estimate that the Velkerri Formation contains several thousands cubic kilometres of authigenic quartz representing an important and previously unrecognised mineral record of silicification in Mesoproterozoic sedimentary basins, critically linked to bacterial blooms and organic carbon burial.

Introduction

The global Si-cycle is coupled to cycles of C\textsuperscript{1,2} and nutrient elements such as P and N\textsuperscript{3}, that are critical to interpretation of the histories of Earth's life and climate. Chert, and particularly chert replacement in Precambrian shallow platform and peritidal carbonate successions, has long been a key focus for understanding the nature and secular history of the silicon cycle through petrographic and geochemical characterization of microquartz\textsuperscript{4,5}. Quartz is also a major constituent of distal, marine siliciclastic sediments (mudstones) wherein its occurrence can be partitioned into i) extrabasinal quartz derived from weathering of continental crust and ii) intrabasinal authigenic quartz precipitated in-situ, post deposition\textsuperscript{6,7}. In Phanerozoic mudstones an authigenic quartz component in excess of the extrabasinal detrital quartz, reaching as much as 50-70 percent of the rock volume, has been reported widely, based on analysis of bulk rock chemistry\textsuperscript{8,9}. Abundant authigenic quartz is confirmed petrographically in such rocks, locally comprising 25-45% of rock volume as microcrystalline quartz in organic-rich siliceous mudstones (e.g. \textsuperscript{6}). This early-formed microquartz is interpreted as a reaction product of dissolving biogenic silica that was present as part of the primary grain assemblage\textsuperscript{10–13} as remnants of Si-biomineralizing organisms like sponges and radiolarians that radiated in the early Phanerozoic or diatoms in the Cenozoic that are considered the main sinks of dissolved silicon in modern oceans\textsuperscript{2}.

In the absence of biosiliceous skeletal grains, the primary pathway for Si transfer from seawater into sediments during the Precambrian is challenging to discern. The dominant paradigm postulates that removal of dissolved Si from sea water was largely driven by inorganic reactions\textsuperscript{14} due to the absence of
known biological sinks in the Precambrian rock record. Nevertheless, recent studies indicate that silicon uptake and accumulation by unicellular cyanobacteria like *Synechococcus* can also make a non-negligible contribution to marine biogenic silica production and silicon flux and levels of cyanobacterial silica accumulation may be comparable to or even exceed that of diatoms\(^{15}\), passing a huge volume of silica into the sediment via gravity settling of particulates (grains) onto the sea floor\(^{15-17}\). Recent work on microbial genetics\(^1\) and metabolism\(^{19}\) suggests that marine cyanobacteria have long possessed the ability to concentrate Si from sea water, perhaps extending to the Archean\(^{16,20,21}\). A volumetric assessment of this cyanobacterial contribution to the long-term marine Si-cycle has not yet been achieved.

Here we determine the abundance and stratigraphic distribution of authigenic quartz in the Mesoproterozoic Velkerri Formation (c. 1.38 Ga; McArthur Basin, Northern Territory, Australia). We note that other Mesoproterozoic, unmetamorphosed, siliciclastic-dominated, organic-rich mudstones are known worldwide\(^{22-24}\) and possibly share similar characteristics with the Velkerri Formation described here.

The organic-rich marine mudstones of the Velkerri Formation are globally recognised as an important archive of the Mesoproterozoic ocean chemistry\(^{25,26}\) and are rich in organic material derived from biomass dominated by cyanobacteria with minor input from archaea and eukaryotes\(^{27}\). The Velkerri mudstones contain large volumes of authigenic quartz over thick vertical intervals that also contain significant organic carbon (up to 10 wt %) and phosphorous (up to 0.5 wt %). We examine the origin and volumetrics of this authigenic quartz in the Velkerri Formation deep-water mudstones and speculate on its origin and contribution relative to the Proterozoic silica cycle. Importantly, a mechanism for post-depositional Si emplacement unrelated to opaline skeletal debris has implications for understanding and quantifying elemental budget and diagenetic evolution of Phanerozoic siliceous mudstones.

The Proterozoic McArthur Basin system extends over large parts of northern Australia (SI 1) and it is filled by a thick sedimentary succession deposited over a billion years between the Palaeoproterozoic to the Neoproterozoic\(^{28,29}\). The Velkerri Formation constitutes the upper part of the basin fill and of the Roper Group, a c. 1- to 5-km-thick package of regressive-transgressive cycles of siliciclastic rocks, it is a thick (up to 1480 m) fine-grained unit mostly constituted of siliceous mudstone, siltstone, and minor sandstone lithologies deposited in a marine environment below wave base, in a distal outer shelf setting\(^{29}\). It is rarely exposed and most of its characterization is based on drill cores which indicate laterally persistent facies across the basin. Since deposition, it has undergone limited deformation and is essentially unmetamorphosed excluding localised, contact metamorphism around igneous sills\(^{30}\).

The Velkerri Formation is subdivided into three members: Kalala, Amungee, and Wyworrie in ascending stratigraphic order, each several hundred of meters thick\(^{31}\). The Amungee Member is the focus of this study and represents the deepest and most distal depositional environment containing the highest proportion of fine-grained, organic-rich sediments. Geochemically, the base of the Amungee Member is
defined by a sharp increase in organic carbon content, phosphorous and base metals (e.g., copper, zinc, molybdenum, nickel, and vanadium) and decrease in clay and heavy mineral associated elements (e.g., Al, K, Sc, Nb, Th, Sn and Cr) reflecting an overall reduced detrital input with respect to Kalala and Wyworrie members\textsuperscript{31}. Total organic content (TOC) values can be higher than 10 wt\%, but generally ranges between of 4 to 6 \%. Organic-rich lithologies are characterised by high gamma ray counts in petrophysical logging, reflecting high uranium concentrations (Fig. 1A).

The Velkerri Formation is composed of quartz, illite, albite, and K-, chlorite, and minor amounts of kaolinite, pyrite, apatite and carbonates\textsuperscript{26,32}.

**Results**

**Whole-rock composition**

We used publicly available mineralogical and whole rock geochemical analyses from individual well completion reports to estimate vertical variations of authigenic silica in excess of the detrital, extrabasinal component \((\text{Si}_{\text{excess}})\), see methods. The vertical profiles analysed in this study return values of \(\text{Si}_{\text{excess}}\) within the Amungee Member of c. 20–30 wt\% (i.e., up to 60\% of the total Si) over continuous intervals as thick as 250 m (Fig. 1A and SI 1). These show a negative correlation between authigenic Si and extrabasinal clastic dilution (using Al as a proxy) and positive correlations between authigenic Si, total quartz, and primary productivity (using P as a proxy) (Fig. 1B and SI 1). Vertical co-variations of organic content and authigenic quartz abundance are regionally consistent. Organic rich intervals represent condensed sections associated with stratigraphic horizons interpreted as flooding surfaces\textsuperscript{31} and stratigraphic stacking patterns interpreted as fourth-order transgressive-regressive sequences\textsuperscript{32}.

**Quartz types**

Petrographic analyses of samples from several wells show that quartz in the Velkerri Formation occurs in detrital and authigenic varieties that can be distinguished using a combination of high-resolution electron microscopy analyses (see Methods and Supporting information).

Extrabasinal detrital quartz has features similar to equivalent quartz observed in Phanerozoic mudstones: coarse clay- to medium-silt size, angular shape (Fig. 2), and relatively bright and variable color in cathodoluminescence (CL) (SI 2). Visually, extrabasinal detrital quartz constitutes a lesser portion of the total quartz, as confirmed by the bulk measurements discussed above.

Particles of intrabasinal and early diagenetic origin are also present, including organic matter, pyrite, authigenic clays\textsuperscript{1} and phosphatic spherules measuring 2–10 micrometers in diameter occurring as individual objects and as clusters of spheroids in close spatial association with organic matter. The spherules are interpreted as being of organic origin and nucleated on partially degraded microbial cell
walls associated with decaying organic matter before significant compaction as described in other Mesoproterozoic carbonaceous shales\textsuperscript{34,35}.

Similar to diagenetic quartz in chert\textsuperscript{14}, the dominant quartz within the Amungee siliceous mudstones is post-depositional in origin. Authigenic quartz takes two main forms, discriminated petrographically from detrital quartz. The most abundant type occurs as tiny euhedral grains with diameter ranging from 200 nm to 1000 nm (Fig. 3). These quartz nanocrystals are dispersed through the clay-size matrix, along with clay-size extrabasinal detrital components and interstitial organic matter.

The authigenic character of the nanoquartz is indicated by the euhedral shape, indicating a pore-filling origin (Fig. 3). Subtle inclusion-rich internal boundaries suggest that the nanoquartz is subequally partitioned into a generally rounded inner core (a probable replacement of primary opal) overlain by a euhedral, pore-filling overgrowth visible via Transmission electron microscopy (TEM). TEM elemental analyses indicate a consistently high Al content in this quartz type (0.73 wt% ± 0.28; 1\textsigma, N = 31; SI 2). Volumetrically, nanoquartz dominates the clay-size component.

A second form of authigenic quartz occurs as localized masses of intergrown microquartz crystals (typically 1–10 µm; up to 20 µm) (Fig. 4). The masses are elongated in the plane of bedding (50 µm x 200 µm as seen in thin section). Intercrystalline spaces within the masses contain mostly organic matter and also blocky pyrite and phosphatic spherules. Individual quartz crystals can be rich in nanometric C-bearing inclusions and locally, engulf the phosphatic spherules (Fig. 4 C, D, E).

Notably, extrabasinal detrital grains such as quartz, feldspar, mica, and clay minerals are excluded from the microquartz masses, indicating that the masses were present and persisted as discrete bodies during sedimentation. CL images show that quartz crystals within the masses are zoned and display a relatively limited range of CL color. The quartz masses do not contain the angular and bright-luminescing extrabasinal detrital quartz and feldspar grains observed in detrital dominated strata of the sediment. Electron probe microanalyses show a significantly higher Al content (0.10–0.21 wt% SI 2) in this quartz type compared to the quartz grains identified as detrital with average Al content of 0.04 wt% ± 0.07 (1\textsigma, N = 78). Although these quartz masses are volumetrically exceeded by the nanoquartz, they are locally abundant and can represent up to 15% of representative microscopic areas (Fig. 4). In-situ oxygen isotopes analyses show that the $\delta^{18}$O\textsubscript{VSMOW} values of the crystals within the quartz masses are strongly positive: 20.8 ± 1.4‰ (1\textsigma, N = 23; SI 3).

\section*{Discussion}

\subsection*{Timing of Si introduction}

Pores in siliciclastic marine mud are generally one micrometer or less in the earliest stages of burial and total porosity reaches around 50\% at 100 m of burial and 25\% at 1.5 km\textsuperscript{36}. Thus, the large volume of authigenic quartz (up to 45\% of the rock volume) requires that the Si be introduced early in the burial
history. The sub-micron size portion of the authigenic quartz, being pore-filling, had to be introduced prior to compactional reduction of the intergranular space to values less than the cement volume. Furthermore, the authigenic nature of the micro-quartz masses is confirmed by the strongly positive $\delta^{18}O_{\text{VSMOW}}$ values, similar to those reported for Pre-Cambrian cherts$^{37}$, suggesting precipitation from a low-temperature pore fluid little-modified from seawater.

**How much authigenic quartz?**

We estimate the amount of authigenic quartz in the Velkerri formation using a probabilistic approach that accounts for uncertainties in: i) the areal extent of the Velkerri Formation; ii) variation in thickness of the Amungee Member; and iii) the amount and vertical distribution of $\text{Si}_{\text{excess}}$. The probabilistic estimations were performed using a Monte Carlo framework to account for parametric uncertainty (details in Methods). Results of the calculations are presented as a probability function (Fig. 5) of the volume (in km$^3$) of authigenic quartz. Our conservative estimate yields a volume of 7883 km$^3$ (P50). The results are consistent with the hypothesis of a large sink of marine silica in the organic-rich mudstone of the Velkerri Fm. The P50 volumetric estimates can be expressed as $\sim$ 347,000Tmol of quartz, thus, the Amungee Member of the Velkerri Formation contains approximately 23,000x the annual Si input to the modern ocean$^{38}$. Such an amount, while seemingly large, is plausible, and needs to be tested against the large uncertainties characterizing the depositional period of 10 Ma estimated for the Amungee Member$^{39}$. Additional numerical determinations of authigenic Si sequestration with the broader Velkerri Formation and within coeval units globally is needed. What is clear, however, is that Si emplacement within Mesoproterozoic organic-rich siliciclastic mudstones is significant relative to global Si reservoirs and must be accounted for to understand the secular history of the marine Si-cycle.

**Cyanobacterial role**

Evidence for microbial mineralization in the Velkerri includes the numerous phosphatized spherules displaying shape, internal structure and size similar to fossil coccoidal bacteria. Experimental studies demonstrating phosphatization of decaying soft tissues within two to four weeks after death$^{40}$ are consistent with the petrographic interpretation of the early authigenic timing of the spherules. Another likely microbial process is reflected in the euhedral pyrite crystals found in spatial association with organic laminae and interpreted as the results of authigenic precipitation resulting from in-situ bacterially mediated reduction of pore-water sulfate$^{41}$.

Positive correlation between $\text{Si}_{\text{excess}}$ and P (Fig. 1B) suggests feedback between primary productivity (availability of phosphorus) and authigenic silica and, indeed, phosphorus is considered the limiting nutrient for biological productivity and bacterial growth throughout the Proterozoic$^{26,42,43}$. 
The above observations are useful in sequentially linking an increase of primary productivity through delivery of phosphorus, bacterial bloom and a high rate of organic burial to the abundance of authigenic quartz. Active microbial Si concentration is petrographically inferred by the small sizes of the nano-quartz, and notably, their interior cores, consistent with primary particulate material of sizes reasonably postulated to have formed as Si-rich blebs on surfaces or within cyanobacteria\textsuperscript{17}.

Additionally, silicification of organic-rich intervals could have arisen by a passive mechanism. The shape and size of micro-quartz aggregates composed of pseudo-spherical bodies closely resembles that of individual cell-like units within a benthic colony similar to extant, mat forming benthic colonial coccoid cyanobacteria of the Chroococcales group that have also been reported in Mesoproterozoic cherts\textsuperscript{44} and Silurian organic-rich mudstones\textsuperscript{45}. As seen in Fig. 4, the cell – like units are embedded in organic matter that we interpret as the degraded remains of mucilage sheaths that isolated the aggregates from the detrital component of the sediment during early burial. We postulate a syn-depositional to early diagenetic silicification in a highly porous mud at the sediment water interface linked to decomposition of organic matter resulting in production of organic acid (typically acetate, CO\textsubscript{2}, and H\textsubscript{2}) and consequently a local reduction in the pH. At the high concentration expected in Proterozoic seawater, the nucleation of silica is governed by the pH of the solution\textsuperscript{46}, therefore, early phosphatization\textsuperscript{40} and the presence of organic acids contribute to a drop in pH in the pore water that could lead to nucleation of silica\textsuperscript{47}. Similar mechanisms of bacterially mediated silicification have been invoked to explain massive silicification of Neoproterozoic laminated siliceous shales in Oman\textsuperscript{48,49}.

The elevated Al content in both authigenic quartz types is assumed to reflect the composition of the porewater at the time of precipitation and further supports the presence of an acid source suitable for Al mobilization from reactive detritus\textsuperscript{50}.

**Conclusions**

Quartz in the Velkerri Formation is present as detrital and authigenic components. Authigenic nanoquartz is the dominant quartz type. Introduction of Si into the Velkerri mudstones as primary opal via a cyanobacterial pathway of Si concentration and particulate sedimentation is the most plausible explanation for the petrographic character and large volume of the authigenic quartz. The volume of authigenic quartz in the Velkerri (on the order of 7900 km\textsuperscript{3}) may rival that of chert-bearing units of similar age and represents a major and perhaps dominant mineral record of the Mesoproterozoic Si-cycle. Assessing the full implications of the massive authigenic quartz volume in the Velkerri Formation requires additional inquiry into the stratigraphic extent and mineral compositions of global Mesoproterozoic mudstones. Possible microbial influences in Phanerozoic mudrock silicification is also implicated and needs further study.

**Declarations**
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References


Methods

Petrography

Samples were embedded in 25 mm diameter epoxy resin mounts and mechanically polished to a 1 µm finish. A thin carbon coating was applied to the mounts prior to high-resolution imaging and elemental analysis using a Tescan TIMA for automated mineralogical maps at CSIRO’s X-ray and Electron Beam Laboratory in Kensington (Western Australia).

A Tescan Lyra 3 focused ion beam (FIB)–SEM with a Ga ion source hosted by the John de Laeter Centre, Curtin University was used to produce site specific cross-sections approximately 10 µm deep to enable high-resolution imaging of specific regions of the samples. The FIB-SEM was also used for site-specific lift out of lamellas, which were mounted onto copper grids and then thinned to approximately 100 nm, followed by a low voltage (2-kV) “clean up” routine to remove surface damage.

These electron transparent foils were used for visualization and chemical analysis of nano-grains with transmission electron microscopy (TEM) using a FEI Titan G2 TEM/scanning TEM (STEM) microscope.
operated at 200 kV at the John de Laeter Centre, Curtin University. High-angle annular dark-field (HAADF) STEM images were collected where the grey level in the images is proportional to the atomic number and thickness of the material. Additionally, a Super-X EDS detector system was used to collect elemental maps and spot analyses to verify the elemental distribution at the nanoscale.

Further surface preparation included broad ion beam polishing using an SEMPrep2 instrument from Technoorg Linda operated for 10–15 minutes at 2kV, 10 minutes at 1kV and 10 minutes at 400 V all done at 5 degrees slope that was used prior to hyperspectral cathodoluminescence (CL) and elemental mapping conducted on a JEOL 8530F-CL field emission gun electron probe micro-analyser (FEG-EPMA). Several maps of different size and spatial resolution were acquired using acceleration voltage of 20 kV, beam current of 50.1 nA and dwell time of 30 ms. Specific regions of interest were mapped at high resolution using 12 kV acceleration voltage, 40.1 nA beam current and 30 ms dwell time at CSIRO’s Micro Beam Laboratory in Clayton (Victoria).

At each pixel of the maps, elemental composition was measured by wavelength dispersive x-ray spectrometry (WDS) and energy dispersive x-ray spectrometry (EDS). Reference standards were used to calibrate the measurements of each element. In parallel to the EDS and WDS measurements, the backscattered electron (BSE) signal was measured, as well as the infrared, visible and ultraviolet cathodoluminescence (CL) spectra (wavelength between ca. 200 and 970 nm), collected using a ‘xCLent’ cathodoluminescence spectrometer system.

Once quartz grains were identified and mapped, quantitative microanalyses of the chemistry of detrital and diagenetic portions were acquired on a JEOL 8530F electron probe microanalyser using an accelerating voltage of 20 kV, beam current of 50 nA and defocussed beam of 2 µm, measuring Si, Na, Fe, and Al by wavelength dispersive spectrometry. Analytical points and transects were collected from the regions of interests identified in the hyperspectral maps. The analyses were quality checked by filtering out results with measurements below detection limits, with analytical total < 95% and points that landed at the interface between grains, pores and inclusions. Points that fell at the transition between grains and or diagenetic cements were also excluded. For analysis of detrital grains, we focused on a sample from the Marmbulligan 1 well (depth 122.25 m) in a silt-rich portion of the Velkerri Fm with where detrital grains of quartz and K-feldspar constitute the dominant mineralogical fraction (SI 2). For analysis of authigenic quartz, we focused on the micro-quartz masses identified in organic-rich sections of the Amungee Member in samples from wells Altree 2 (depth 671m), Marmbulligan 1 (depth 169 m) and Tanumbirini 1 (depth 3258 m) (SI 2).

**Estimation of Si_{excess}**

Whole rock geochemical analyses on the Velkerri Formation are available from laboratory studies on rock chips and continuous wireline logs collected from exploration wells that allow the assessment of vertical distribution of major and minor elements.
For the calculation, we used continuous logs (lithoscanner) acquired on wells Amungee NW1, Kalala South 1 and Beetaloo West 1 and the bulk rock geochemical data acquired on cuttings at the source via X-ray fluorescence (SI 1). The data was sourced from publicly available well completion reports accessible online from the Northern Territory Government Geoscience Exploration and Mining Information System (GEMIS) of the Northern Territory Geological Survey (https://geoscience.nt.gov.au/gemis/)

The amount of authigenic silica ($\text{Si}^{\text{excess}}$) in excess of the detrital extrabasinal component$^3$ is estimated as:

$$\text{Si}^{\text{excess}} = \text{Si}_{\text{total}} - (\text{Al}_{\text{total}} \times \text{Si/Al}_{\text{background}})$$

Where $\text{Si}_{\text{total}}$ and $\text{Al}_{\text{total}}$ are the measured whole rock Si and Al concentrations (wt%) and $\text{Si/Al}_{\text{background}}$ is the lowest measured value in the analyzed section representing the Si:Al ratio of terrigenous clastic material$^4$.

**Volumetric estimation of authigenic quartz**

The volume of authigenic quartz is calculated as the product $A \times T \times V_{\text{authqz}}$ where:

- $A =$ Areal extent of the Velkerri formation.
- $T =$ Thickness of the Amungee Member.
- $V_{\text{authqz}} =$ Volumetric fraction of authigenic quartz.

$V_{\text{authqz}}$ is calculated as total quartz – detrital quartz.

The probabilistic estimation of the volume of diagenetic quartz present in the Velkerri Formation is implemented using a Monte Carlo method. We set up the predictive model identifying the relation between a set of independent variables and the total volume of diagenetic quartz present in the studied formation.

Probability distributions of the independent variables are illustrated in Fig. 5 and limited by their minimum and maximum values (Fig. SI 3).

**Oxygen isotopes**

Oxygen isotope composition of authigenic quartz was determined in situ using the large geometry secondary ion mass spectrometer (SIMS) Cameca IMS 1280 hosted by the Centre for Microscopy, Characterisation and Analysis (CMCA), University of Western Australia (UWA).

For the analysis, the sample surface was sputtered with a focused 10 kV, Gaussian Cs + beam with intensity of ~ 500 pA and total impact energy of 20 keV. An electron gun is used to ensure charge
compensation during the analyses. Secondary ions were admitted in the double focusing mass spectrometer within a 90 µm entrance slit and focused in the centre of a 2500 µm field aperture (x 130 magnification). They are energy filtered using a 30 eV band pass with a 5 eV gap toward the high-energy side. $^{16}$O and $^{18}$O are collected simultaneously in a Faraday cup detector fitted with $10^{11}$ Ω (L1) resistors and an electron multiplier (H2), respectively at a mass resolution of ~ 2430.

Each analysis includes a pre-sputtering over a 3 x 3 µm area for 90 seconds and the automatic centering of the secondary ions in the field aperture. Each analysis then consists of 60 four-second cycles, which give an average internal precision of ~ 0.15‰ (2 SE). The analytical session was monitored in terms of drift using at least two bracketing standards every 5 sample analyses.

Uncertainty on each analytical spot has been calculated by propagating the errors on instrumental mass fractionation determination, which include the standard deviation of the mean oxygen isotope ratio measured on the primary standard during the session, and internal error on each sample data point. Analytical results are tabulated in SI 4.

Figures

Figure 1
Petrophysical and geochemical character of the Amungee Member of the Velkerri Formation. A) Wireline logs through the Amungee Member in well Amungee NW 1. Track 1: Gamma ray (GR). Track 2: total organic carbon (TOC) from elemental capture spectroscopy log (continuous gray line) and laboratory measurements (yellow filled circles). Track 3 Si$_{\text{Excess}}$ estimated from elemental capture spectroscopy log (continuous gray line) and X-ray fluorescence measurements on cuttings (yellow filled circles) illustrating the vertical variation in abundance of authigenic quartz, with values above 0 representing silica from non-detrital sources. Track 4: phosphorous content from X-ray fluorescence measurements on cuttings illustrating vertical variation in primary productivity. Stratigraphic surfaces from$^2$. B) Cross-plot of Si$_{\text{Excess}}$ and content of Al (as a proxy for detrital input); quartz and phosphorous. Wireline logs and geochemical data from wells in the Beetaloo Sub-basin discussed in this study are available through Northern Territory Geoscience Exploration and Mining Information System.

Figure 2

Petrographic appearance of detrital components in the Amungee Member of the Velkerri Formation as seen under scanning electron microscopy. Energy dispersive spectroscopy elemental maps (Si, Na, K, Ca, Mg and Fe) overlaid on back scattered electron images. Most detrital grains are in the 10-20 mm size range and include quartz (red), albite (aqua), K-rich mica occurring as highly elongate flakes (yellow arrows) (A and B) and chlorite (Chl) in pink (C). Outlined grains in A and B (dashed, white line) are lithic fragments (albite-quartz; K-feldspar-quartz). Other phases interpreted as authigenic are pyrite (Py) in bright yellow and euhedral and Ca-phosphate spherules (P) in blue. Organic material (OM) is black. Clay-size components, mostly K-rich detrital clay, nanoquartz and OM, cannot be separately resolved at this magnification and make up the matrix that uniformly surrounds the larger grains and crystals (red matrix in A, B and C). A) is from Tanumbirini 1 well (3258 m); B and C are from Walton 2 well (421 m).
Figure 3

Petrographic appearance of authigenic nano-quartz in the Velkerri Formation. A) Focused Ion Beam scanning electron microscopy section at the contact between an organic matter stringer (OM, in black) and fine-grained matrix composed of authigenic, euhedral quartz crystals of sub-micron size. Interstitial space between the quartz is filled by organic material (in black) and clay flakes (yellow arrows). Sample from well Lady Penhryn 2 (398.8 m). B) High-angle annular dark-field scanning transmission electron microscopy image providing detail of the quartz-rich matrix composed of euhedral quartz crystals joined along straight grain boundaries. Porous organic matter (OM) and clay flakes are found in the intergranular space. C and D) Scanning Transmission Electron microscopy images showing the
composite nature of authigenic nano-quartz composed of a vesicle-rich core (red-dashed line) surrounded by a euhedral rim (red lines). OM = organic matter; yellow arrows point to clay aggregates C) Bright field image of the red box in B. D) Dark field image. B, C and D) Sample from well Tarlee S3 (1347.7m).

Figure 4
Petrographic appearance of authigenic micro-quartz aggregates in the Velkerri Formation (interpreted as coccoidal cyanobacteria-like microfossils). A) Backscattered electron image of an area rich in elongate micro-aggregates (highlighted by a red overlay). B) Multichannel elemental map of the area marked by a white box in A, highlighting the spatial relationships between quartz (in red), organic material (green), other aluminosilicates (purple), pyrite and phosphatic spherules (black). Note how the aggregate is composed of almost pure quartz with no evident mixing of other detrital phases. C) Back scattered electron image of a micro-quartz aggregate with early diagenetic phosphatic spherules being overgrown by quartz. D) High-angle annular dark-field scanning transmission electron microscopy image of the cross-section along the x-x’ profile marked by the red line in C) showing quartz overgrowing the phosphatic spherule and intergrowing the organic material. E) Elemental map of the same region of interest shown in D highlighting the spatial relationships between quartz (in red), organic material (green) phosphatic spherules (blue). Note the C-rich inclusion within quartz grains, highlighted by the yellow circles. Sample from well Altree 2 (671 m).

**Figure 5**

Results of Monte Carlo probabilistic estimates of the volume of authigenic quartz in the Amungee Member of the Velkerri Formation. Values expressed in km$^3$ (lower horizontal axis) and Tmol x 10$^6$ (upper horizontal axis).

**Supplementary Files**

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