6. Sedimentary Carbon Isotopes From the 3.52 Ga Coonterunah Subgroup

1. Introduction

Despite much scientific effort, it is still unclear how long the Earth has been inhabited by living organisms. This uncertainty stems from two main problems: the scarcity of suitable low-grade metasedimentary facies in the early geological record, and the ambiguity of even the best-preserved relics of early life-forms. The first is partly due to the dearth of early Archean rocks in general (the older things are, the rarer they become) and partly because the vagaries of geologic history have subjected most very ancient rocks to considerable metamorphism and deformation, obliterating or obscuring any biological relics they might contain. The second results from the apparent simplicity of early organisms, rendering their physical remains and traces of their activities vulnerable, and difficult to distinguish from inorganic mimics. Hence, microfossils and stromatolites provide compelling evidence for life back to around 3.0 Ga (billion years) ago, but before that, all purported physical records of biological activity have been questioned, by one expert or another, on the grounds of syngenicity or biogenicity.

The carbon isotope record is somewhat more robust, but becomes controversial before about 3.45 Ga, the age of the oldest very low-grade sedimentary rocks in Australia's Warrawoona Group and South Africa's Onverwacht Group. Specifically, debate has focussed on the age and origin of carbonaceous matter in the Isua and Akilia areas of Greenland. These upper-amphibolite to granulite facies rocks are older than 3.7 Ga and contain massive carbonates and graphitic gneisses that show carbon isotopic fractionations not inconsistent with a biological origin followed by later metamorphic resetting (Schidlowski, 1988). However, the carbonates have recently been reinterpreted as metasomatic derivatives of ultramafic igneous rocks, not sediments (Rose *et al.*, 1996), and hence their isotopic values reflect abiotic processes only. Graphite yields a wide range of $\delta^{13}C_{org}$ values, from as heavy as -3‰ in ankerite-quartz-cummingtonite schist (Ueno *et al.*, 2002) to as light as -45‰ from minute inclusions in apatite crystals (Mojzsis *et al.*, 1996). To explain this spread, it has been

argued that the heavier values represent metamorphically reset biological ratios, whereas the lighter values are closer to an original autotrophic signature (Schidlowski *et al*., 1979; Ueno *et al.*, 2002). But it is now evident that much of the graphite thus far reported at Isua was produced abiotically (van Zuilen *et al*., 2002) and doubtful whether any graphite at all occurs at Akilia (Lepland *et al*., 2005; Moorbath, 2005). The most likely Isua graphite to be both biological and ancient (~3.8 Ga) is moderately abundant (TOC = 0.1-0.9 wt.%), resides in turbiditic metasediments that are not associated with metasomatic carbonate and ranges in $\delta^{13}C_{org}$ from –20 to -14‰ (Rosing, 1999). However, meteoritic organic carbon from carbonaceous chondrites and tarry residues from prebiotic synthesis experiments show a similar range of values. Moreover, the absence of a reliable sedimentary $\delta^{13}C_{carb}$ record makes it is impossible to prove that the total isotopic fractionation reflects biological autotrophy (Buick, 2001).

Here we present $\delta^{13}C$ analyses of organic and carbonate carbon from a recently discovered succession of slightly younger and better preserved sedimentary rocks from the Pilbara Craton in Australia. These yield much less equivocal data which extend the incontrovertible record of life on Earth back to the first billion years of this planet's history.

2. Geological Setting

The rocks examined here belong to the Coonterunah Group, the basal stratigraphic unit in Archean Pilbara Craton of northwestern Australia (Figure 1). The ~5.5 km thick succession, truncated at the base by slightly younger granitoid intrusions, is dominated by tholeiitic basalts with subordinate felsic volcanics and volcanogenic sediments, magnesian and komatiitic basalts, and synvolcanic gabbroic intrusions (Buick *et al*., 1995; Green *et al.*, 2000). From the widespread presence of pillows, sparse amygdales in basalts, rare breccias in dacites and paucity of clastic sediments, the depositional environment was apparently deep marine. Dacites and rhyolites from near the top of the succession have been dated by SHRIMP U-Pb in zircon techniques as 3515-3517 Ma old (Buick *et al.*, 1995). The metamorphic grade

varies along the exposed strike length of ~75 km from mid-greenschist facies to lower amphibolite facies (Green *et al*., 2000), with a tectonic fabric only developed in the higher-grade areas. In most areas, deformation has consisted of nothing more than early open folding, followed by block faulting and subsequent tilting to the present subvertical bedding planes. Following the erosional unconformity and subsequent deposition of the very low-grade and minimally deformed Warrawoona Group at ~3.4 Ga, very little has disturbed their repose (Buick *et al.*, 1995). Thus, they are the oldest known low-grade rocks on Earth and as such, are an excellent place to search for isotopic records of early life.

Ferruginous chert beds (Figure 2 (a)) form thin (~0.3m thick) layers between basalt flows and thick (10-30m) units between different volcanic lithologies. They have white and red or black banding on a centimeter scale and a poorly defined lamination on a millimeter scale. The layering is planar to undulating with diffuse boundaries, showing no evidence of clastic sedimentary structures or textures. However, the chert is clearly sedimentary and not secondary as the laminae drape topographic highs on underlying basalt flows, thickening into troughs and thinning over ridges (Figure 2 (b)). At a microscopic scale, all layers are predominantly composed of equigranular microquartz, with the colored bands and laminae containing varying amounts (up to 25%) of very fine-grained (~0.1 mm) hematite or magnetite. Laterally gradational contacts indicate that the hematitic layers are secondary modifications of originally magnetitic bands. Trace amounts of organic carbon exist in the magnetitic layers, but TOC is generally too low for successful extraction by acid digestion without risk of modern contamination. No detrital clastic grains have been observed in thin-sections. Thus, the cherts are best interpreted as interflow sediments resembling banded iron-formation that were deposited during times of volcanic quiescence under very low energy conditions with miniscule levels of clastic sedimentation. Their intimate association with surrounding volcanic rocks indicates that they formed in the same environmental setting; *i.e.* in deep marine conditions.

Associated with some of the chert beds are thin (5-30 cm) beds of massive to plane-laminated (2-5 mm) carbonate. In most places, these have been secondarily

silicified during Tertiary weathering, resulting in lenses and pods within layers of amorphous brown silcrete, with interfingering contacts and grain overgrowths showing that the carbonate was indeed the primary phase. The carbonate is now quite coarse grained (0.5-1 mm) and composed of equant grey-brown crystals, but this is almost certainly the result of metamorphic recrystallization and it was presumably finer originally. Along some contacts with adjacent siliceous beds, carbonate is interlayered with quartz-grunerite-magnetite laminae, gradually passing into quartz-magnetite chert. The present mineralogy of the carbonate layers is ferroan dolomite and calcite, identified through microprobe analysis. As in the cherts, no evidence of clastic sedimentary structures or textures has been observed, and on the microscopic scale, no detrital mineral grains have been found in thin-sections of the carbonate rocks. So, the depositional environment of the carbonates is best interpreted as similar to the interbedded cherts and volcanics; *i.e.* low energy chemical sediments formed in a deep-water submarine setting. Unlike the older Isua carbonates from Greenland, there are no cross-cutting carbonate veins and adjacent mafic igneous igneous rocks show only very limited carbonate alteration.

3. Methods

Surface samples were collected from minimally metamorphosed parts of the Coonterunah Group, as far as possible from igneous intrusions and cross-cutting faults. Exterior weathering was removed with a diamond saw and the rocks were then coarsely crushed. Fragments were etched in HCl and HF to remove any surface contamination and then finely crushed, in a steel puck mill for carbonates and by agate pestle and mortar for cherts. Kerogen was isolated from powders with higher TOC by demineralizing with HF and then removing secondary fluorides with H_3BO_3, a modification of the technique of Robl and Davis (1993). Some carbonates were reacted under vacuum with HPO_4 in sealed quartz-glass Y-tubes at 100°C for 24 hours, while others were reacted and analysed at 80 °C using a Kiel-III carbonate mass-spectrometer. Cherts were decarbonated with warm concentrated HCl. Some cherts and kerogen isolates were combusted under vacuum in sealed quartz-glass bombs with

CuO at 800°C for 4 hours, with the resulting CO_2 was purified cryogenically in a vacuum gas-distillation line and analysed on a Nuclide isotope-ratio mass-spectrometer. Others were analysed in a Thermo Finnigan MAT 253. Results are expressed in $\delta^{13}C$ or $\delta^{18}O$ notation as per mille (‰) values relative to the PDB standard. For oxygen isotopes in carbonates, values were calculated using a published calcite fractionation factor at the appropriate temperature.

4. Results

$\delta^{13}C_{org}$ values are tabulated in Table 1. It is evident that there is a major mode centered about -25‰ and a spread skewed towards heavier values from -20‰ to -5‰. The tight clustering of values around the major mode (-25.4‰, corrected for replicates) indicates that it is of primary significance, because low-grade metamorphism has inconsistent isotopic resetting effects depending on local conditions and tends to smear the distribution between original sedimentary and bulk earth values. Moreover, for high TOC samples where a $\delta^{13}C_{org}$ value could be obtained from isolated kerogen, all fall within the major modal population, suggesting that metamorphic resetting has only influenced kerogen-poor samples. Thus, the most reasonable interpretation is that the major mode represents mildly reset original values and therefore is an approximate indicator of the bulk $\delta^{13}C_{org}$ deposited during sedimentation. If so, it is roughly equivalent to the values observed in modern sediments where carbon isotopic fractionation is controlled by RuBisCO-modulated carbon-fixation. Though the spread in values around this particular mode gets as light as -31‰, it is unlikely that the original values were very much lighter than this, as maturational hydrocarbon expulsion probably did not shift values by much more than a couple of parts per mille, even given the extremely low TOC percentages (Buick *et al*., 1998). The minor light mode may highlight microbial remineralization of organic matter during diagenesis and the heavy outliers may represent metamorphic resetting (see Discussion).

Carbonates show a much narrower range of isotopic values than kerogen. $\delta^{13}C_{carb}$ ranges between -1‰ and -4‰, with a mean of 2.9‰ (Table 2). Values are strongly skewed towards lighter values. This tighter distribution probably reflects the

much higher amounts of carbonate in the samples compared with organic carbon. In such circumstances, metamorphic resetting is likely to have been minimal. Diagenetic alteration may have been significant, because the carbonate beds are thin and volumetrically minor within the stratigraphic succession. Interactions between sedimentary carbonates and diagenetic fluids can be monitored in very low-grade terrains by $\delta^{18}O$ values. In the Coonterunah carbonates, these range from -7‰ to -20‰ about a mean of -17.1‰. Though it is unknown exactly what marine Archean $\delta^{18}O$ values were, it seems likely that they became lighter back through time (Veizer *et al*., 1989). Diagenetic alteration in most sedimentary environments, excluding evaporitic basins, resets the marine signature to even lighter values. This would suggest that the closest Coonterunah $\delta^{18}O$ value to contemporary seawater was around -7‰ and that the lighter values represent diagenetic fluid-rock interaction. If so, then original $\delta^{13}C_{carb}$ values were probably not altered much during diagenesis, as lighter $\delta^{18}O$ values are not correlated with either extremity of the $\delta^{13}C_{carb}$ distribution (Figure 3, inset). So, while diagenetic and metamorphic fluid-rock interactions may have occurred, they do not appear to have substantially modified $\delta^{13}C_{carb}$.

$\Delta^{13}C$ ($\delta^{13}C_{carb}$ - $\delta^{13}C_{org}$) is an approximate measure of the fractionation between oxidized and reduced carbon species. Given the minor uncertainty about exact original isotopic compositions because of the effects of diagenesis and metamorphism, this is a more appropriate measure to use than the precise fractionation ε_{TOC}. As $\delta^{13}C_{carb}$ values form a single homogeneous population, their mean of -2.9‰ can be used in the calculation. For $\delta^{13}C_{org}$, the corrected mean of values clustered around the major mode (-25.6‰) is used, as this most closely represents the original material deposited. Hence, bulk $\Delta^{13}C$ is 22.7‰, very similar to the modern marine value of ~22‰. Though diagenesis and metamorphism have probably reduced the Coonterunah $\Delta^{13}C$ value, this was probably only by a few per mille. This is shown in the few kerogenous carbonates in which $\Delta^{13}C$ can be determined for individual samples (Table 3), where any re-equilibration between reduced and oxidized carbon species should be most pronounced. Collectively, these indicate a mean $\Delta^{13}C$ of 23.4‰, closely comparable to the bulk $\Delta^{13}C$ value. This confirms the validity of the latter value and demonstrates

that, for most samples, diagenetic and metamorphic isotopic homogenization has been limited.

5. Discussion

An integral problem in any paleobiological study of particularly ancient rocks is assessing whether the feature under examination, be it isotopes or organisms, is indigenous and syngenetic. Any rock with an extremely long geologic history has had ample opportunity for post-depositional contamination, and where contents of the material in question are extremely low, the chances of modern adulteration are high. Both of these problems have been encountered in previous organic and isotopic studies of the ~3.8 Ga gniesses of Greenland, with modern organic contaminants, once thought to be syngenetic, occurring abundantly in surface rocks, and massive carbonates, formerly believed to be sedimentary, forming metasomatically near ultramafic igneous rocks. In the case of the Coonterunah rocks, however, such difficulties were not encountered. The Coonterunah carbonates show sedimentary lamination, are interbedded with siliceous sedimentary facies and are kilometres removed from any source of ultramafic metasomatism. The kerogen in the Coonterunah cherts is clearly indigenous because it can be extracted by acid digestion, yielding similar isotopic values to *in situ* treatments that have been carefully manipulated to exclude the possibility of surface contamination. Moreover, carbonate samples also contain kerogen clearly embedded in metamorphosed ferroan dolomite and calcite crystals (Figure 2(c)), indicating its premetamorphic emplacement.

The spread of $\delta^{13}C_{org}$ values provides further evidence for the ancient origin of the Coonterunah organic matter, because if it were modern superficial contamination or ancient post-metamorphic adulteration, it should have a homogeneous isotopic composition. Instead, the isotopic diversity is best interpreted as representing either metamorphic resetting or metabolic disparity. As $\delta^{13}C_{org}$ ranges between -47‰ and -5‰ with a mode around -25‰, a purely biological explanation would have to invoke three distinct mechanisms of isotopic fractionation. The -25‰ mode could be the product of oxygenic photosynthesis by cyanobacteria using RuBisCO which imparts a

~25‰ total fractionation from dissolved CO_2, as seen here. Some of this primary production could then have been remineralized by methanogenic Archaea, which have a cellular biomass markedly lighter than the consumed organic matter, yielding the few values between -37‰ and -47‰. The heavy values between -15‰ and -5‰ could be the result of anoxygenic photosynthesis by green or purple sulphur bacteria, an autotrophic process with a smaller associated isotopic fractionation than its oxygenic equivalent. However, the range and extremity of heavy values observed make this rather unlikely as no form of photosynthesis yields organic matter heavier than dissolved CO_2, which would have been around -10‰ for carbonates near 0‰ (Des Marais, 1997). Instead, it is more plausible that differing degrees of maturational decarbonation of light hydrocarbons and metamorphic re-equilibration with heavy carbonates were responsible for the spread of heavy values. Though attempts were made to sample only lower grade rocks, the regional metamorphic grade, mid-greenschist to lower amphibolite facies, is right at the point where profound isotopic adjustments start to occur (Hayes *et al.*, 1983; Des Marais *et al.*, 1992; Des Marais, 1997). It is unlikely that the population around the mode of -25‰ also represents metamorphically reset kerogen that was originally very much lighter, of similar isotopic composition to the light subpopulation near -40‰, as the major modal cluster is large and distinct, without a skewed tail trailing towards the lighter mode.

The carbonates show a distinct similarity to younger Archean carbonates associated with BIFs. A trend in $\delta^{13}C_{carb}$ values from close to 0‰ to lighter values to -4‰ is evident in the Hamersley Group (Kaufman *et al.*, 1990), where it has been attributed to deposition in deeper water below a redox chemocline with increasing proportions of bicarbonate derived from recycled light organic matter. As the Coonterunah carbonates were apparently deposited in a similar environment and are associated with magnetite-grunerite cherts, a similar origin could be invoked. A metamorphic origin for the trend is unlikely, as the carbonates contain little kerogen and have many orders of magnitude more of the oxidized species than the reduced, providing a robust buffer to isotopic re-equilibration. If so, the initial oceanic $\delta^{13}C_{carb}$ ratio was probably around the heaviest $\delta^{13}C_{carb}$ value observed, about -1‰. This would

accord with estimates of near 0‰ obtained from somewhat younger Archaean shallow-marine carbonates (Veizer *et al*., 1989).

It is possible to erect a set of criteria for recognizing biogenic signatures in carbon isotopes very early in Earth's history when abiotic contributions may have been more significant than now. These are listed in order of increasing rigour, with only criterion 5, where both reduced and oxidized species are congruently preserved together, representing the highest likelihood of biogenicity. As most of the criteria are based on statistical parameters, sample numbers ($n > 10$) and sizes (CO_2 yield > 0.3 μmoles) have to be sufficiently large for robust analysis.

1. Organic negativity - because carbonaceous chondritic meteorites, mantle-derived diamonds and prebiotic organic syntheses all produce solid organic carbon with $\delta^{13}C_{org}$ values in the range -15‰ to 0‰, values should be lighter than this range (<-15‰), especially at low TOC (<0.1%);
2. Kerogen consistency - because abiogenic organic carbon tends to be broadly spread about a mean, the standard deviation should be low (<5) indicating high kurtosis;
3. Carbonate coherence - because biogenic fractionations over the past 800 Ma have ranged between 22‰ and 32‰ (Hayes *et al*., 1999) but inorganic carbonates and organics are generally fractionated less than this, the gross bulk fractionation between $\delta^{13}C_{org}$ and $\delta^{13}C_{carb}$ ($\Delta^{13}C$) from a single suite of rocks should be >20‰;
4. Complementary skewness - because metamorphic re-equilibration tends to skew the isotopic distribution to one side of the mean, if any skewness occurs, it should be positive around $\delta^{13}C_{org}$ modes and negative for $\delta^{13}C_{carb}$;
5. Fractionation congruency - because metamorphic resetting should be most evident in rocks with coexisting kerogen and carbonate, the standard deviation for the population of individual sample $\Delta^{13}C$ values should be low (<5).

The Coonterunah isotopic values satisfy all 5 of these criteria, so they evidently indicate biogenic carbon isotopic fractionation. It is thus reasonable to consider the

sorts of metabolic processes that might have been operative in early Archean ecosystems. The $\Delta^{13}C$ fractionation clearly represents autotrophic carbon-fixation which, given its magnitude and moderate metamorphic resetting, probably signifies the Calvin-Benson cycle using the enzyme ribulose-bisphosphate carboxylase-oxygenase (RuBisCO). This, however, need not have been oxygenic photosynthesis; indeed, it need not have been photosynthesis at all. Many forms of autotrophy employ this mechanism for carbon fixation, and so other geochemical evidence (*e.g.* Hayes, 1983; Buick, 1992; Brocks *et al*., 1999) is needed before oxygenic photosynthesis can be recognized. The minor modes in the $\delta^{13}C_{org}$ distribution may also represent distinct metabolic processes. The light mode possibly indicates methanogenesis, as values lighter than -40‰ are beyond the range of fractionation imparted by any form of photosynthesis but are characteristic of biogenic methane production. Given the sparse data, it is impossible to determine whether this methanogenesis relied on the heterotrophic breakdown of primary autotrophic production (organic recycling) or autotrophic redox reactions involving simple gas species (chemolithotrophy). It does not necessarily also imply oxidative methylotrophy as a means of fixing the light methane isotopic signature into biomass, because one class of methanogens, the methylotrophic methanogens which split methyl groups from simple methylated molecules to produce methane (Summons *et al.*, 1999). The heavy mode, as mentioned above, probably does not reflect the activities of green or purple sulfur bacteria metabolizing photosynthetically, which tend to produce organic matter lighter than -10‰. Given the broad spread of values and their extreme enrichment in ^{13}C, this mode is more likely to represent metamorphosed organic matter initially derived from other sources.

The secular distribution of sedimentary carbon isotope values for rocks older than 1 Ga is plotted in Figure 4. It can be seen that the Coonterunah kerogens and carbonates are not too dissimilar to those from other early Archaean successions. The carbonates are a bit lighter than those from shallow marine facies, such as the ~3.46 Ga Warrawoona Group, but are similar to those derived from deeper-water BIF successions. This difference is also manifest in mineralogy, with the shallow marine

carbonates dominatly composed of dolomite, whereas the deeper water facies, including the Coonterunah carbonates, are calcitic. The Coonterunah kerogens are a bit heavier than most comparable early Archaean organic carbon, though not markedly so. This may reflect their higher metamorphic grade than most, but as the coexisting kerogen-carbonate pairs show little sign of metamorphic re-equilibration, this may instead be a primary environmental or biological indicator. As there are several other deep-water successions represented in the early Archaean carbon isotope record, it seems unlikely to be a simple factor of depositional environment. It could possibly indicate lower levels of dissolved CO_2 in the water mass, as isotopic discrimination during microbial autotrophy diminishes with CO_2 availability (*e.g.* Calder & Parker, 1978; Des Marais *et al.*, 1989). It might also indicate a greater input of biomass from non-cyanobacterial microbial autotrophs (*e.g.* Ruby *et al.*, 1987; Des Marais *et al.*, 1989). Lastly, it may simply reflect lower levels of methanogenic recycling than in other Archaean successions (*e.g.* Hayes, 1983; 1994), though the presence of an apparently methanogenic light mode in the Coonterunah kerogen data would suggest otherwise. Regardless, a rather more refined instrument than carbon isotopes is needed to resolve the problem.

When comparing the Coonterunah with the ~3.8 Ga Itsaq data, it is striking that organic polymodality is a common feature. If the Itsaq data does indeed, in whole or in part, represent biological activity, then this perhaps reveals that early Archaean microbial ecosystems had more complex isotopic partitioning than occurs in younger settings. At present, carbon isotopic signatures are overwhelmingly dominated by biomass generated by oxygenic photosynthesis, producing unimodal isotopic signatures. As the secondary modes in Archaean isotopic distributions possibly represent diverse autotrophic and heterotrophic pathways, this suggests that biomass generation and recycling was not so simple. As many of these possible pathways are anaerobic or microaerophilic, this scenario would accord with the model of a less oxygenated early Earth that is widely, but not universally, upheld.

At present, it seems unlikely that older incontrovertible carbon isotope evidence for the existence of primordial life will be found in rocks that are currently known. All

more ancient successions lack coexisting sedimentary carbonates and kerogen, though they may have one or the other. Moreover, they have all suffered greater metamorphism and deformation, beyond the degree where substantial resetting of carbon isotopic values applies. Morphological evidence for life is very unlikely to survive such conditions. Though it is not inconceivable that older low-grade rocks will be discovered; indeed the Coonterunah Group was not recognized as being older and better preserved than other Pilbara greenstones until 1995; the co-occurrence of sedimentary carbonates and kerogens is not overly common in Archean successions generally. Though many Archean terrains are still poorly mapped and dated, it is likely that particularly ancient low-grade successions remain to be discovered only in cratons that are generally mildly metamorphosed and very old. Thus, this Coonterunah data might be as old as it gets. If so, it would be unfortunate for science, because most of the really interesting questions about the early evolution of life lie in the preceding billion years of Earth's history, when life itself began, diversified and developed the complex metabolic pathways already in evidence by the dawn of the biogeochemical record.

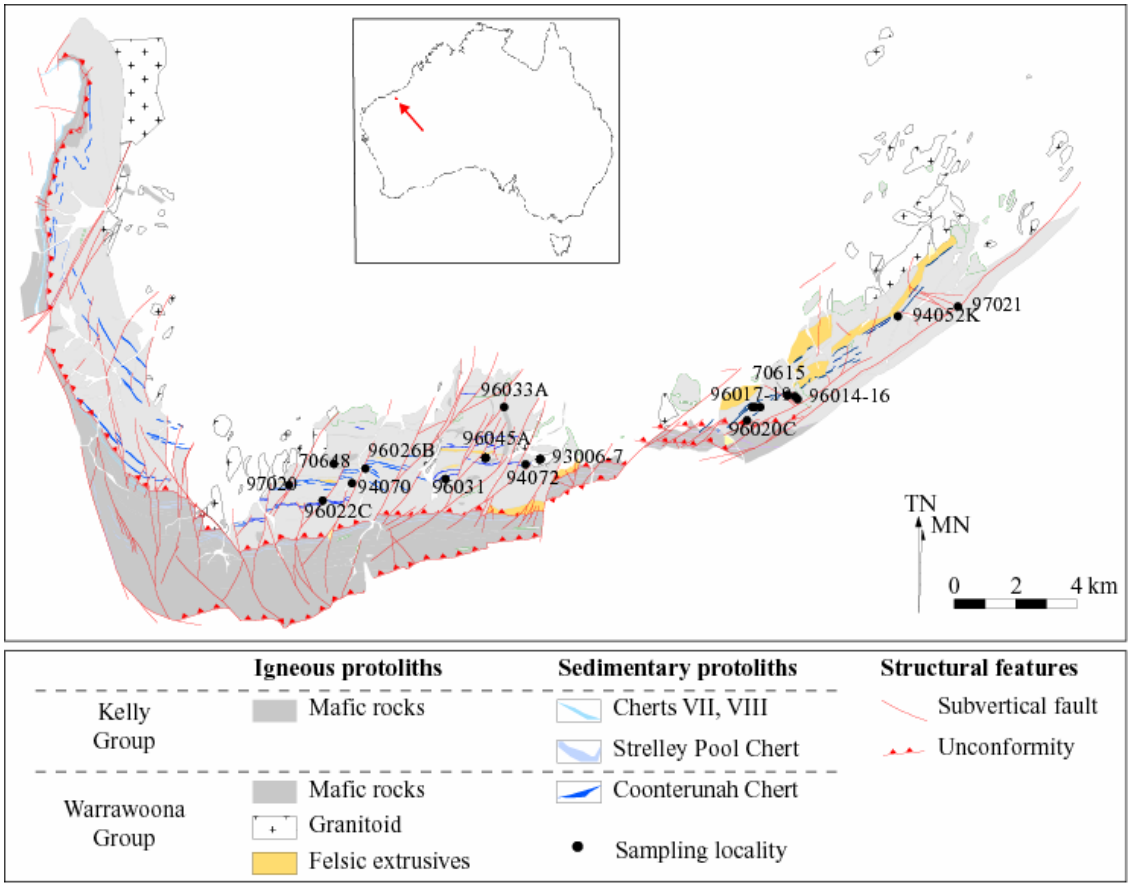

Figure 1: Geological map of the Pilgangoora Belt and Coonterunah Subgroup, showing sample sites.

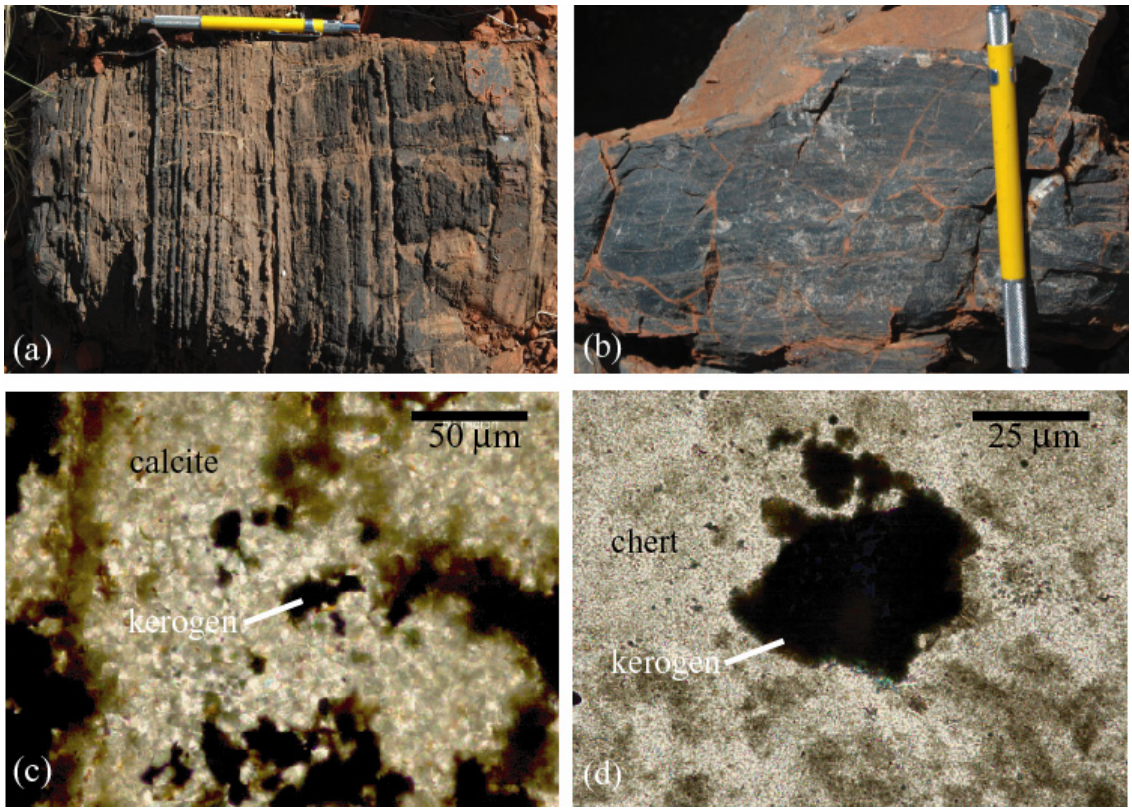

Figure 2: (a): Laminated carbonate in outcrop. (b): Banded chert in outcrop. (c): Thin-section of laminated carbonate. (d): Thin-section of chert-hosted kerogen**.**

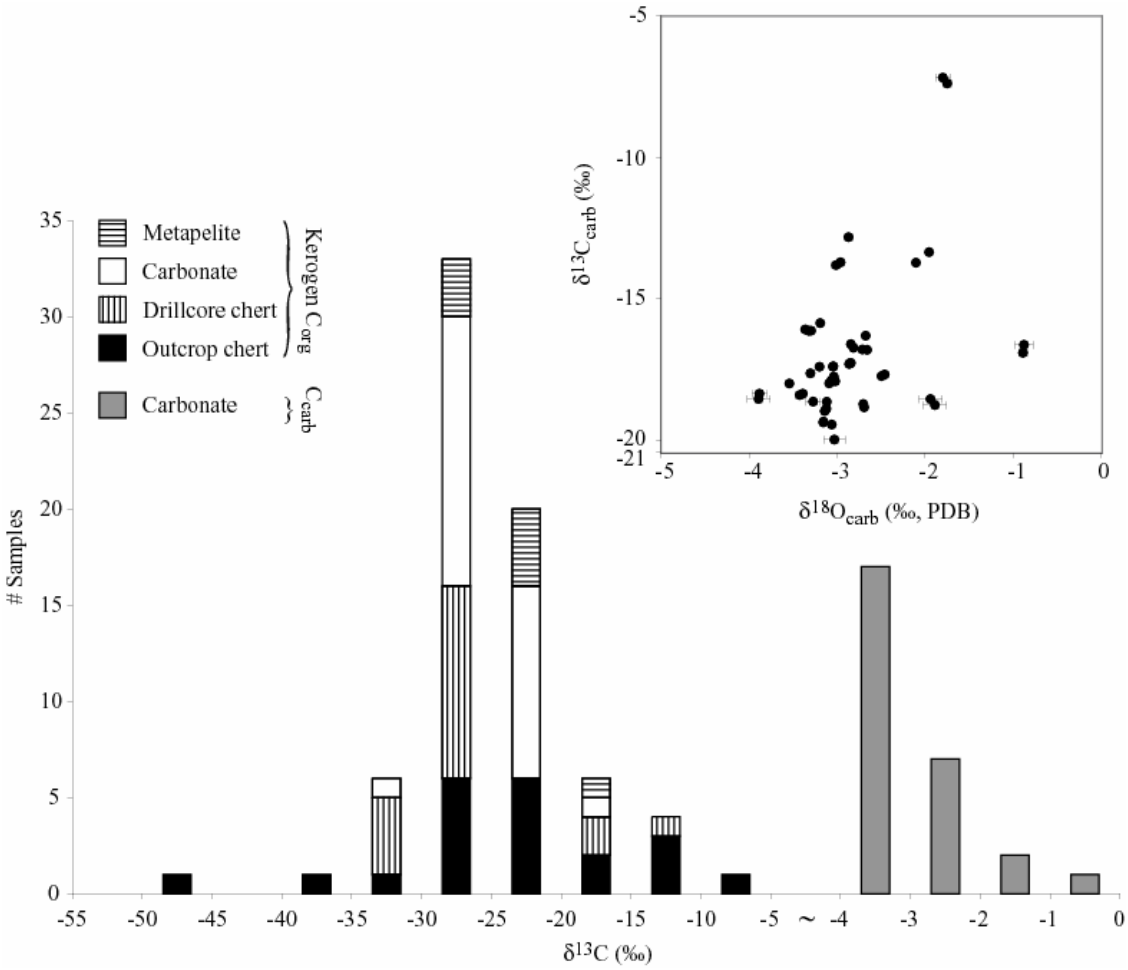

Figure 3: Carbon isotopic data from Coonterunah Subgoup. Inset shows cross-plot of $\delta^{18}O_{carb}$ vs. $\delta^{13}C_{carb}$.

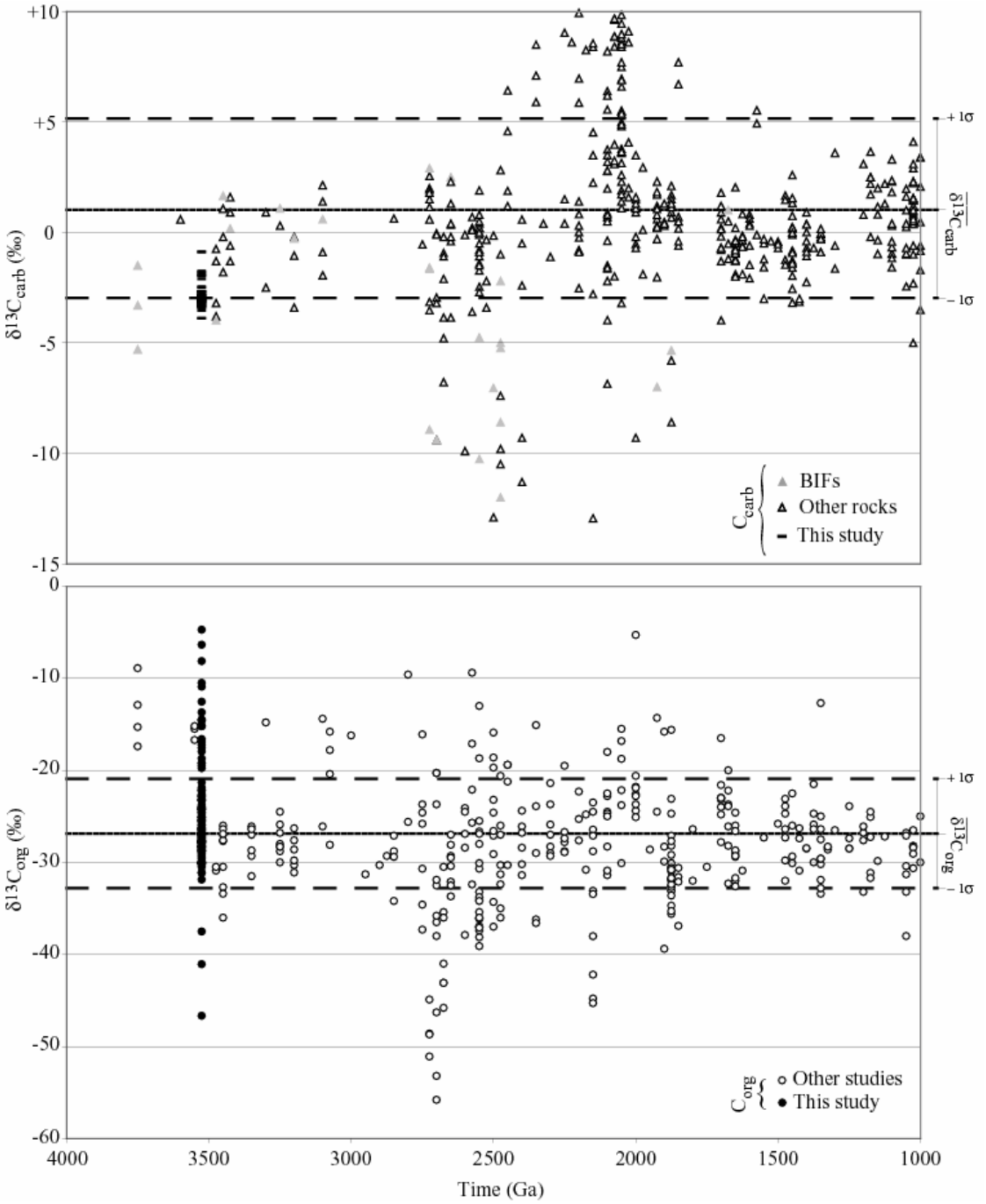

Figure 4: Secular trends in carbon isotopes before 1 Ga.

Table 1: Coonterunah kerogen $\delta^{13}C_{org}$ data. Suffix "K**"** in sample label indicates macerated kerogen, others are decarbonated whole-rock analyses, suffix "rep" indicates replicate analysis, suffix "lam" indicated microdremel laminar analysis. Laminar analyses are treated as distinct samples in calculation of averages.

Rock-type	Sample	Size (mg)	CO_2 yield (µmoles)	$\delta^{13}C_{org}$ (‰, VPDB)	± σ (‰)	Sample average (‰)
Chert-hosted kerogen	70615	249.6	2.9	-8.13	0.05	**-7.25**
	70615 rep1	196.3	1.11	-6.36	0.11	
	70615K	1.2	0.38	-22.76	0.11	**-22.76**
	70648	207	0.57	-27.52	0.11	**-27.52**
	70648K	0.4	0.58	-27.66	0.12	**-27.66**
	93007	200.5	0.36	-27.91	0.11	**-27.91**
	94052K	1.4	31.99	-28.87	0.08	**-28.87**
	94053 5sec	200.1	0.60	-30.50	0.09	**-30.56**
	94053 10sec	195.4	0.72	-31.11	0.07	
	94053 15sec	221.9	1.37	-31.86	0.08	
	94053 20sec	220.3	1.23	-29.06	0.08	
	94053 25sec	199.9	0.88	-30.29	0.07	
	96014	205.4	1.47	-22.8	0.06	**-22.80**
	96016	218.6	2.2	-14.48	0.11	**-14.48**
	96017B	208.3	14.87	-4.72	0.08	**-4.72**
	96018	197.3	1.27	-27.3	0.08	**-27.30**
	96019A	99.2	0.81	-12.55	0.08	**-11.53**
	96019A rep1	196.7	1.47	-10.5	0.07	
	96020C	105.7	0.49	-22.09	0.08	**-20.93**
	96020C rep1	201.7	0.82	-19.76	0.07	
	96022C	213.5	2.7	-10.92	0.08	**-10.92**
	96031	206	0.61	-25.42	0.11	
	96031 rep1	202.6	0.58	-24.31	0.16	**-24.87**
	97020A*	225.3	7.13	-46.66	0.08	**-46.66**
	97020B*	200.0	4.93	-41.07	0.04	**-39.29**
	97020B rep1	220.6	3.73	-37.50	0.07	
	97021*	204.5	9.78	-19.5	0.09	**-19.50**
	PC03-104	0.8	20.70	-23.78	0.38	**-23.78**
	PC03-119	2.8	0.20	-23.96	0.13	**-23.59**
	PC03-119 rep1	9.9	0.31	-23.22	0.13	
	PC04-005	13.1	1.77	-25.07	0.37	**-25.27**
	PC04-005 rep1	6.1	1.06	-26.01	0.37	
	PC04-005 rep2	10.0	0.94	-24.75	0.37	
	PC04-113	6.3	2.59	-17.95	0.38	**-17.16**
	PC04-113 rep1	19.4	6.95	-16.61	0.38	
	PC04-113 rep2	14.7	5.32	-16.91	0.38	
	Mean			***-23.33***	***9.21***	***-22.97***

Table 1 (cont'd).

Rock-type	Sample	Size (mg)	CO_2 yield (µmoles)	$\delta^{13}C_{org}$ (‰, VPDB)	± σ (‰)	Sample average (‰)
Carbonate-hosted kerogen	93006K	9.9	0.98	-26.65	0.08	**-24.88**
	93006K rep1	11.4	1.12	-23.1	0.04	
	96045AK	17.2	2.19	-24.27	0.09	**-23.57**
	96045AK rep1	12.4	4.72	-22.87	0.07	
	96045BK	4.2	7.24	-28.77	0.06	**-28.77**
	PC05-020A blk	5.0	3.90	-28.77	0.12	**-28.77**
	PC05-020B lam1	27.8	5.10	-25.34	0.12	**-25.34**
	PC05-020B lam2	24.1	5.17	-27.34	0.12	**-27.34**
	PC05-020B lam3	24.6	5.76	-26.49	0.65	**-26.49**
	PC05-020B lam4	15.2	4.22	-24.29	0.35	**-24.29**
	PC05-020B lam5	15.2	15.53	-29.63	0.35	**-29.63**
	PC05-020C lam1	32.0	5.57	-27.21	0.12	**-27.21**
	PC05-020C lam2	14.4	1.93	-27.67	0.12	**-27.67**
	PC05-020C lam3	21.0	2.08	-27.03	0.65	**-27.03**
	PC05-020C lam4	23.2	4.83	-26.26	0.35	**-26.26**
	PC05-020C lam5	22.5	4.37	-26.33	0.35	**-26.33**
	PC05-020C lam6	24.4	5.46	-27.11	0.35	**-27.11**
	PC05-020C lam7	8.0	0.68	-24.53	0.09	**-24.53**
	PC05-020C lam8	10.0	0.76	-23.24	0.09	**-23.24**
	PC05-021 lam1	5.7	2.29	-25.17	0.12	**-25.17**
	PC05-021 lam2	11.7	2.12	-31.13	0.12	**-31.13**
	PC05-021 lam3	5.5	2.28	-24.08	0.65	**-24.08**
	PC05-021 lam4	2.9	1.54	-24.20	0.35	**-24.20**
	PC05-021 lam5	0.6	0.31	-22.64	0.09	**-22.64**
	PC05-021 lam6	1.0	0.29	-21.32	0.09	**-21.32**
	PC06-031 lam1	8.3	0.62	-19.22	0.18	**-19.22**
	PC06-031 lam2	1.6	0.35	-23.28	0.18	**-23.28**
	PC06-041 blk	3.1	0.29	-25.53	0.18	**-26.16**
	PC06-041 blk rep1	1.1	0.29	-26.80	0.18	
	Mean			***-25.53***	***2.58***	***-25.60***

Table 1 (cont'd).

Rock-type	Sample	Size (mg)	CO_2 yield (µmoles)	$\delta^{13}C_{org}$ (‰, VPDB)	± σ (‰)	Sample average (‰)
	155.00m	9.2	0.26	-30.10	0.51	**-30.10**
	155.00m rep1	8.9	0.29	-30.10	0.51	
	157.60m	18.9	15.52	-28.29	0.51	**-28.03**
	157.60m rep1	18.2	16.05	-28.30	0.51	
	157.60m rep2	18.9	15.52	-27.80	0.51	
	157.60m rep3	18.2	16.05	-27.73	0.51	
	158.70m	21.0	12.41	-28.40	0.51	**-28.38**
	158.70m rep1	16.1	9.60	-28.14	0.51	
	158.70m rep2	21.0	12.41	-28.28	0.51	
	158.70m rep3	16.1	9.60	-28.70	0.51	
	160.40m	15.8	14.36	-28.54	0.51	**-28.29**
	160.40m rep1	17.5	14.86	-28.74	0.51	
	160.40m rep2	15.8	14.36	-27.98	0.51	
	160.40m rep3	17.5	14.86	-27.91	0.51	
	160.70m	23.5	24.59	-28.22	0.51	**-27.33**
	160.70m rep1	23.5	24.59	-26.45	0.51	
	162.40m	18.9	16.10	-27.80	0.51	**-27.76**
	162.40m rep1	18.9	16.10	-27.72	0.51	
	163.40m rep2	9.0	11.28	-27.62	0.51	
	163.40m rep3	18.3	20.06	-27.83	0.51	
	163.40m rep4	9.0	11.28	-28.45	0.51	
	163.40m rep5	18.3	20.06	-27.13	0.51	
	163.70m	17.2	15.77	-27.71	0.51	**-27.77**
	163.70m rep1	17.5	15.08	-27.72	0.51	
	163.70m rep2	17.2	15.77	-27.77	0.51	
	163.70m rep3	17.5	15.08	-27.88	0.51	
	169.45m	9.1	0.61	-27.43	0.51	**-28.36**
	169.45m rep1	10.8	4.88	-28.23	0.51	
	169.45m rep2	10.8	4.88	-29.41	0.51	
	170.75m	12.0	10.06	-29.25	0.51	**-28.59**
	170.75m rep1	11.2	1.58	-27.01	0.51	
	170.75m rep2	12.4	1.69	-26.84	0.51	
	170.75m rep3	12.0	10.06	-28.63	0.51	
	170.75m rep4	11.2	1.58	-29.90	0.51	
	170.75m rep5	12.4	1.69	-29.89	0.51	
	288.55m	7.7	0.40	-30.08	0.51	**-30.09**
	288.55m rep1	5.5	0.27	-30.10	0.51	
	310.53m	2.0	0.21	-30.11	0.51	**-30.09**
	310.53m rep1	3.4	0.53	-30.06	0.51	
	311.64m	3.6	0.56	-13.70	0.51	**-14.12**
	311.64m rep1	3.7	0.54	-14.55	0.51	
	312.32m	1.7	0.40	-17.56	0.51	**-16.39**
	312.32m rep1	2.8	0.52	-15.21	0.51	
	313.37m	2.4	0.36	-18.72	0.51	**-16.67**
	313.37m rep1	6.5	0.49	-14.62	0.51	
	Mean			***-26.78***	***4.30***	***-26.09***

Table 1 (cont'd).

Rock-type	Sample	Size (mg)	CO_2 yield (µmoles)	$\delta^{13}C_{org}$ (‰, VPDB)	± σ (‰)	Sample average (‰)
Metapelite-hosted kerogen	PC06-024B	37.3	0.93	-17.22	0.20	**-16.21**
	PC06-024B rep1	57.3	1.02	-15.21	0.20	
	PC06-024I	17.9	0.34	-21.88	0.20	**-22.03**
	PC06-024I rep1	17.9	0.35	-22.17	0.20	
	PC06-027	4.7	0.32	-24.05	0.20	**-23.14**
	PC06-027 rep1	20.4	0.32	-22.23	0.20	
	PC06-029	11.0	0.28	-25.74	0.20	**-25.58**
	PC06-029 rep1	12.8	0.30	-25.42	0.20	
	PC06-031	8.3	0.62	-19.22	0.13	**-21.25**
	PC06-031 rep1	1.6	0.35	-23.28	0.13	
	PC06-040	33.0	0.30	-24.58	0.13	**-24.37**
	PC06-040 rep1	42.1	0.35	-24.17	0.13	
	PC06-041	3.1	0.29	-25.53	0.13	**-26.16**
	PC06-041 rep1	1.1	0.29	-26.80	0.13	
	PC06-044	3.1	0.27	-25.97	0.13	**-26.14**
	PC06-044 rep1	3.2	0.27	-26.30	0.13	
	Mean			***-23.11***	***3.36***	***-23.11***

Table 2: Coonterunah carbonate $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$ data.

Sample	Size (mg)	CO_2 (μmoles)	$\delta^{13}C_{carb}$ (‰)	±1σ (‰)	$\delta^{18}O_{carb}$ (‰, PDB)	±1σ (‰)	Sample average (‰)	
							$\delta^{13}C_{carb}$	$\delta^{18}O_{carb}$
93006	2.90	10.36	-1.94	0.13	-18.55	0.11	-1.92	-18.66
93006 rep1	3.20	12.80	-1.89	0.13	-18.76	0.15		
94070	4.70	25.06	-3.03	0.12	-19.98	0.11	-3.03	-19.98
94072	2.90	15.95	-3.89	0.13	-18.54	0.14	-3.89	-18.54
94072 rep1	3.10	18.10	-3.88	0.08	-18.36	0.14	-3.89	-18.45
96026B	15.00	75.20	-1.75	0.05	-7.38	0.13	-1.78	-7.28
96026B rep1	13.10	62.83	-1.80	0.08	-7.18	0.09		
96033A	15.50	77.41	-3.27	0.08	-18.64	0.09	-3.27	-18.64
96033B	15.80	84.71	-2.96	0.04	-13.71	0.08		
96033B rep1	20.40	20.40	-2.87	0.04	-12.82	0.09	-2.92	-13.27
96045A	23.60	52.96	-0.88	0.10	-16.63	0.1	-0.89	-16.77
96045A rep1	28.40	28.40	-0.89	0.05	-16.91	0.13		
96045B	10.30	48.27	-3.01	0.05	-13.81	0.09	-3.01	-13.81
B55W	0.11	47.86	-3.12	0.03	-18.65	0.04	-3.12	-18.65
B63W	0.19	70.01	-3.09	0.03	-17.99	0.03	-3.08	-17.94
B63W rep1	0.19	64.47	-3.06	0.02	-17.89	0.04		
B75W	0.19	62.17	-3.54	0.03	-18.00	0.02	-3.54	-18.00
B79W	0.73	86.94	-3.05	0.03	-17.41	0.02	-3.04	-17.40
B79W rep1	0.54	84.79	-3.04	0.02	-17.39	0.03		
B80D	0.26	53.09	-3.30	0.04	-17.64	0.03	-3.25	-17.52
B80D rep1	0.31	59.24	-3.20	0.03	-17.41	0.04		
B82W	0.30	72.48	-2.81	0.02	-16.73	0.02	-2.78	-16.55
B82W rep1	0.17	49.24	-2.84	0.02	-16.60	0.03		
B82W rep2	1.27	86.63	-2.67	0.02	-16.30	0.02		
B87W	0.26	76.32	-2.66	0.02	-16.80	0.04	-2.69	-16.80
B87W rep1	0.14	55.70	-2.71	0.02	-16.80	0.03		
B89W	0.17	36.93	-3.39	0.02	-18.36	0.04	-3.41	-18.38
B89W rep1	0.12	23.39	-3.42	0.05	-18.41	0.05		
B90W	0.22	62.32	-2.85	0.01	-17.28	0.03	-2.85	-17.28
B90W rep1	0.14	55.24	-2.86	0.02	-17.31	0.04		
B90W rep2	0.30	68.17	-2.84	0.02	-17.27	0.01		
PC05-020C	0.40	64.45	-3.12	0.02	-18.89	0.04	-3.13	-18.93
PC05-020C rep1	0.58	69.99	-3.14	0.02	-18.98	0.03		
PC06-026	1.74	112.91	-3.29	0.04	-16.13	0.02	-3.24	-16.00
PC06-026 rep1	1.01	106.77	-3.19	0.03	-15.86	0.02		
PC06-028A	0.67	42.09	-3.06	0.02	-19.45	0.02	-3.06	-19.45
PC06-028B-i	0.71	74.74	-3.15	0.01	-19.35	0.04	-3.16	-19.36
PC06-028B-i rep1	0.43	68.96	-3.16	0.02	-19.38	0.03		
PC06-028B-ii	1.27	50.09	-3.04	0.01	-17.76	0.04	-3.03	-17.84
PC06-028B-ii rep1	1.28	47.12	-3.02	0.02	-17.92	0.04		
PC06-031	0.41	43.65	-2.49	0.04	-17.73	0.04	-2.48	-17.71
PC06-031 rep1	2.00	48.00	-2.46	0.04	-17.68	0.03		
PC06-041	2.31	67.17	-3.36	0.03	-16.08	0.01	-3.34	-16.11
PC06-041 rep1	1.69	67.52	-3.32	0.03	-16.13	0.03		
PC06-045	4.56	115.40	-1.96	0.01	-13.35	0.02	-2.03	-13.54
PC06-045 rep1	2.72	121.12	-2.10	0.02	-13.72	0.01		
PC06-053	0.51	72.85	-2.70	0.02	-18.73	0.03	-2.70	-18.78
PC06-053 rep1	0.30	70.28	-2.69	0.01	-18.84	0.03		

Table 3: Coonterunah $\Delta^{13}C$ data.

Sample	**$\delta^{13}C_{org}$** (‰)	**$\delta^{13}C_{carb}$** (‰)	**$\Delta^{13}C$** (‰)
96006K	-26.65	-1.89	24.76
96006K rep1	-23.1	-1.94	21.16
96045AK	-24.27	-0.88	23.39
96045AK rep1	-22.87	-0.89	21.98
96045BK	-28.77	-2.94	25.83
PC05-020 avg	-26.52	-3.13	23.39
Mean (n=5)	*-25.36*	*-1.94*	*23.42*
Bulk analyses	*-25.12*	*-2.91*	*22.75*

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