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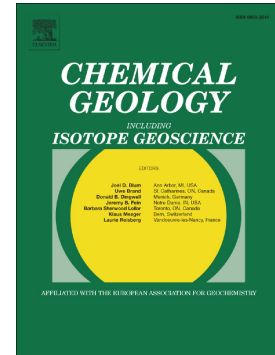
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The use of chromium reduction in the analysis of organic carbon and inorganic sulfur isotope compositions in Archean rocks.

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ABSTRACT:

One of the most serious issues with deciphering the evolution of organisms and their biogeochemical environments from the ancient rock record is the difficulty in obtaining well-preserved samples. Although not much can be done to avoid diagenetic and metamorphic alteration when they have occurred, alteration due to weathering can be avoided by working on drill core samples. This implies however that the amount of sample is limited, which may in turn restrain the number of possible chemical and isotopic analyses that can be performed. In order to save sample we show here that the chemical protocol used for the sulfur sulfide extraction (for later sulfur isotope analyses) is also suitable to decarbonate samples (for later organic carbon isotope analyses). In the case of carbonated rocks, both sulfur sulfide extraction and decarbonation require high amounts of sample so that coupling them may save a significant amount of sample and time. In addition it allows both organic carbon (TOC and $\delta^{13}\text{C}$) and sulfur isotope

composition measurements to be performed on the exact same powder, which is essential when trying to understand couplings between S and C cycles in heterogeneous samples. We thus tested the efficiency of the acidic chromium solution, commonly used to extract sulfur from sulfide, for sample decarbonation on various Archean rocks. Our results show that no significant carbon isotope fractionation is caused by this new decarbonation protocol, even for the samples with low organic carbon content. The chromium solution seems to be perfectly adapted for the analysis of organic matter in the ancient rock record, at least when the rock samples have experienced low greenschist facies metamorphism. Further tests will be needed to verify if this protocol can also be used for less mature organic matter.

Keywords: carbon isotopes, decarbonation, limited sample, Precambrian

HIGHLIGHTS:

- One chemistry for both sulfur sulfide extraction and rock sample decarbonation
- A new protocol that saves time and a significant amount of limited sample
- Organic carbon and sulfur isotope composition analysis on the exact same powder

1. INTRODUCTION

As shown by Lowe and Tice (2007), vanishingly few Archean rock units have survived to the present (less than 10 %; Garrels and Mackenzie, 1971) and outcrops have been affected by modern oxidative weathering. This surficial weathering can modify both the mineralogy and chemistry of the ancient rock record and thus represents an issue when investigating paleo-redox conditions and early traces of life (Hoashi et al., 2009, French et al., 2015). In order to recover relatively well-preserved rock samples from below the present weathering profile

(below the groundwater table ~10-50 m) and to obtain continuous rock cores that retain soft or friable units that outcrop poorly at the surface, several scientific drilling programs have been carried out in Archean terrains in the past decade (Kaufman et al., 2007, Yamaguchi et al., 2009, Philippot et al., 2009). The recovered cores have been extensively analyzed to investigate conditions at the surface of the Archean Earth: the composition, temperature, and redox state of the Archean ocean and atmosphere; the volcanic and sedimentary processes that operated early in Earth history; and above all, to search for pristine morphological or chemical traces of early life (Mojzsis et al., 1996, Philippot et al., 2007, Schopf et al., 2007, Thomazo et al., 2009b, Bontognali et al., 2012).

Since the first description of recognizable Archean microfossils a few decades ago (*e.g.* Dunlop et al., 1978, Buick et al., 1981), morphology-focused imaging techniques of fossil-like objects (Brasier et al., 2002, Schopf et al., 2002, Lepot et al., 2008, Wacey et al., 2011) have failed to absolutely confirm their biogenic origin. This is mainly because several abiogenic metamorphic and hydrothermal reactions have been identified that could produce kerogen-like polymers and graphite (*e.g.* Van Zuilen et al., 2002) and generate complex structures similar to microfossils (*e.g.* Garcia-Ruiz et al., 2003) and stromatolites (*e.g.* Grotzinger and Rothman, 1996). In view of these uncertainties and controversies, it is now recognized that studies of early life and associated environmental conditions depend on the multiplication of structural, isotopic and chemical tracers. Particularly, sulfur and carbon isotopes have been traditionally used to decipher ancient biogeochemical cycles (*e.g.*, review in Thomazo et al., 2009, Farquhar et al., 2010). Indeed, C and S isotopes retain records of microbial metabolisms where secondary processes such as metamorphism and weathering have obliterated or erased evidence for early life such as microfossils or other biogenic remains.

A prerequisite for measuring carbon isotopes of organic material in rocks (and sediments) is to eliminate carbonates which are widely occurring in various forms, *i.e.* mainly ankerite, dolomite and siderite in Archean rocks, since the isotopic value of the carbon atom of the carbonate would otherwise bias the isotopic signal. In the past, several methods dissolving carbonates by acid-treatment, thereby eliminating the carbonate carbon as carbon dioxide, have been described (Froehlich, 1980, Weliky et al., 1983, Hedges and Stern, 1984), the most commonly used being 10 % HCl followed by rinsing with deionized water (Schubert and Nielsen, 2000). In parallel, sulfur extraction for isotopic analysis of sulfides and sulfates is generally performed with a succession of different acidic attacks on sample powder. Therefore, sample preparation for either bulk C or S isotopic analyses is time consuming and requires important and independent quantities of sample, which are limited when working on drill core samples.

In this study, we tested the chemistry used for sulfur extraction and based on acidic chromium reduction for decarbonation of sample powders in order to save both time and sample and most importantly to perform bulk organic carbon and sulfur isotope measurements in the exact same samples. To our knowledge, this chemistry has never been used for simple decarbonation, and our objective here is thus to test if it is suitable for the determination of the Total Organic Carbon (TOC) content and carbon isotope compositions ($\delta^{13}\text{C}_{\text{org}}$). Ader et al. (2009) showed that the even standard decarbonation might lead to an increase by up to 1.4 ‰ in $\delta^{13}\text{C}_{\text{org}}$ values especially for samples with low amount of organic carbon and without changing significantly the TOC contents. Given the hotter (around 190 °C) conditions of the acidic chromium chemistry compared to a standard decarbonation procedure, one may be concerned by its effects on the TOC and $\delta^{13}\text{C}_{\text{org}}$ values. In order to investigate such effects we compared the results obtained after the acidic chromium chemistry and the standard

decarbonation on a selection of Precambrian rock samples with representatively low TOC contents (< 1 wt%).

2. SAMPLES

The samples studied here have been selected among some of the oldest best-preserved Archean rocks in the world. They stem from the Mapepe and Mendon formations on the Kaapvaal Craton (South Africa) and the Tumbiana and Kazput formations on the Pilbara Craton (Western Australia). These units, which have been deposited between 3.24 and 2.32 Ga, present various lithologies representative of the Archean eon. Geological details have been published in previous studies (Philippot et al., 2009, 2012, Thomazo et al., 2009, Martindale et al., 2015), and a short summary of pertinent information is given here. The selected rock samples present low TOC contents between 0.01 % and 0.40 % and a broad range of carbonate concentrations between 0.07 % and 63.80 %, which are representative of the Archean rock record.

2.1. Mapepe and Mendon Formations

Mendon and Mapepe formations belong to the Barberton Greenstone Belt (South Africa), which consists of a succession of Archean supracrustal rocks surrounded and intruded by granitoids (Viljoen and Viljoen, 1969). The Mendon Formation is mainly composed of ultramafic volcanics, interpreted to reflect large mantle plume magmatic activity (Lowe, 1994), alternated with bedded black cherts, probably recording deep-water sedimentation during times of magmatic quiescence (Hofmann and Harris, 2008). Radiometric age constraints on the tuffaceous band from the underlying Kromberg Formation provide a lower age limit of 3334 ± 3 Ma (Byerly et al., 1996). The unconformably overlying Mapepe Formation records shallow-water terrigenous and volcanoclastic sediments, interbedded with

bedded barite deposits. Zircon ages constrain the Mapepe Formation between 3259 ± 3 and 3226 ± 3 Ma (Kröner et al., 1991, Byerly et al., 1996). Both formations experienced only low greenschist facies regional metamorphism with a maximum temperature of $300\text{ }^{\circ}\text{C}$ (Knauth and Lowe, 2003, Tice et al., 2004) together with some deformation.

The samples analyzed in the present work were collected from a weathering-free drill core recovered by the Barberton Barite Drilling Project (BBDP; Philippot et al., 2009, 2012) at the so-called “barite syncline” locality. They have been selected as representative of the different lithologies forming the Mendon and Mapepe formations and include one basaltic komatiite and three carbonaceous black cherts from Mendon, together with two bedded barites, two ferruginous cherts, and four silicified terrigenous and volcanoclastic sediments from Mapepe (see Philippot et al., 2012 for more details). Except for black cherts, the other lithologies present low organic carbon content, as deduced from a petrographic observation. Quartz, green chlorite, Fe-Mg-carbonate, barite and pyrite represent the main mineral assemblage.

2.2. Tumbiana Formation

The Tumbiana Formation belongs to the Hamersley Basin (Western Australia), which presents a well-preserved succession of volcanic and sedimentary rocks deposited between 2.77 and 2.41 Ga on the granitoid-greenstone basement of the Pilbara Craton (Thorne and Trendall, 2001). This formation consists of large-scale cross-bedded calcareous sandstone, stromatolitic and fenestrate carbonate, and micaceous sandstone interlayered with volcanic siltstone (Thorne and Trendall, 2001, Thomazo et al., 2009). The Tumbiana Formation was deposited at 2724 ± 5 Ma, as indicated by zircon U-Pb dating (Blake et al., 2004), either in a shallow marine or lacustrine environment associated with influx of riverine freshwater derived from the continents (Buick, 1992, Thorne and Trendall, 2001, Bolhar and Van Kranendonk, 2007). The regional metamorphic temperature has been estimated $< 300\text{ }^{\circ}\text{C}$

using metamorphic mineral assemblages and the degree of organization of organic matter (Lepot et al., 2008).

The samples have been collected in the Pilbara Drilling Project (PDP1) diamond drill core, which recovered the upper section of the Tumbiana Formation at Meentheena. These include: one siltstone, one laminated mudstone and two homogeneous mudstones. In all samples, organic matter is homogeneously disseminated. Quartz, green chlorite, carbonate (mainly calcite) and pyrite represent the main mineral assemblage throughout the drill core. The $\delta^{13}\text{C}_{\text{org}}$ values of the Tumbiana samples studied here were previously determined by Thomazo et al. (2009).

2.3. Kazput Formation

The Kazput Formation consists of subtidal stromatolites, grainstones, and micrites deposited on a mixed carbonate-siliciclastic shelf and is lying within the upper part of Turee Creek Group in the southern Pilbara region of Western Australia (Martindale et al., 2015). The Turee Creek Group is thought to be a continuous stratigraphic sedimentary section hosting both the Great Oxidation Event and possibly two Huronian glaciations (Van Kranendonk et al., 2015, Van Kranendonk and Mazumder, 2015). Geochronological constraints for the Turee Creek Group are provided by the 2449 ± 3 Ma Woongarra Rhyolite at the top of the underlying Hamersley Group (Barley et al., 1997) and by the 2209 ± 15 Ma Cheela Spring Basalt of the unconformably overlying lower Wyloo Group (Martin et al., 1998).

The samples selected for this study come from the Turee Creek Drilling Project #3 (TCDP3) drill core and consist of four carbonated mudstones and one quartzite with low organic carbon content (as deduced from a petrographic observation) and mainly composed of quartz, carbonate, chlorite and pyrites.

3. METHODS

Twenty-one rock samples were powdered to $<100\ \mu\text{m}$ using a ring and puck mill. For fourteen samples, one single powder has been homogenized, processed using either the standard or the acid chromium method and analyzed for organic carbon content and isotope composition (**Table 1**). For seven additional samples, different initial powders have been used for the two different decarbonation techniques (**Table 2**).

3.1. Standard sample decarbonation

This method is a common procedure widely used to remove various carbonates such as calcite, andesite, dolomite and siderite (e.g. Bernasconi et al., 1997, Wu et al., 1999, Lorrain et al., 2003, Thomazo et al., 2009). Sample powders (about 200 mg) were reacted with excess HCl (6 N) at room temperature in glass beakers during one night. After removing the supernatant, samples were acidified again with HCl (6 N) at $80\ ^\circ\text{C}$ and agitated during two hours: this is to guarantee full sample decarbonation. After decantation, the residues were rinsed with deionized distilled water until neutral, centrifuged, and dried at $60\ ^\circ\text{C}$ overnight. During this step, acid-volatile sulfur (AVS) such as FeS or ZnS would react and release H_2S , some being potentially re-oxidized into insoluble elemental sulfur (Rice et al., 1993). Pyrite would however remain.

3.2. Combined sulfur sulfide extraction and sample decarbonation

The acidic CrCl_2 solution is extensively used for the extraction of reduced inorganic sulfur compounds in different types of geological samples, including modern sediments and ancient shales (Canfield et al., 1986, Fossing and Jorgensen, 1989), acid-sulfate soils (Sullivan et al., 2000, Burton et al., 2008), and basaltic glasses (Labidi et al., 2012). It was first designed by Traube and Passarge (1916) for the reduction of (non-sulfur bearing) complex organic

compounds (e.g. maleic, fumaric or cinnamic acids; Holmquist, 1969). This chemistry was first introduced to the geochemical community by Zhabina and Volkov (1978), and later improved by Canfield et al. (1986) and Gröger et al. (2009) for sulfur extraction. Gröger et al. (2009, p. 21) have shown that CrCl_2 solution typically yields 99 ± 1 % for both pyrite and elemental sulfur. In contrast, simple organic molecules are hardly reduced, with very low yields < 0.2 % (Gröger et al., 2009, p. 24). For more complex organic molecules, polysulfur bonds could be broken by the CrCl_2 solution. However, organic sulfur, to be quantitatively reduced, requires the use of Raney-nickel catalyst (e.g. Oduro et al., 2011).

Originally, the CrCl_2 solution was prepared and injected using a so-called Jones reductor, which is somewhat complex and time-consuming (i.e. a glass-column packed with granulated Zn amalgamated for a few minutes with an acidic 2 % mercuric nitrate solution and washed with three column volumes of 0.5 N HCl; Zhabina and Volkov, 1978, Canfield et al., 1986, Tuttle et al., 1986, Fossing and Jorgensen, 1989). As mostly done worldwide, we prepared our CrCl_2 solution daily using a much simpler procedure, where chromic chloride hexahydrate associated with granulated Zn is acidified with HCl 0.6 N under continuous flow of N_2 . On reduction, the chromium solution changes from green to blue, reflecting the valence change from chromic (III) to chromous (II) ion.

Sulfur extraction is undertaken adding 20 mL of freshly prepared CrCl_2 solution (2.1 N) and 10 mL of concentrated HCl (6 N) to ~1g of sample powder in the digestion flask at ~100 °C. As long as N_2 -gas bubbles through the solution, we did not face any sample powder aggregation that would prevent full decarbonation. In these hot, reducing and acidic conditions, reduced sulfur species (S^0 and S^{2-}) are quantitatively decomposed into H_2S (sulfate remains stable). Then, the released H_2S is transferred with a stream of N_2 from the reaction flask to the sulfide trap filled with AgNO_3 (0.3 M) where it reacts to precipitate Ag_2S (Trap 2 in **Figure 1**). A trap filled with distilled H_2O (Trap 1 in Figure 1) is intercalated in the

transfer between to reaction flask and the Trap 2 to clean the gas from any acid vapors that have not been stopped by the condenser. Approximately one hour is needed until completion of the H₂S transfer, as confirmed by the fact that no additional Ag₂S would precipitate if the AgNO₃ trap was changed. At the end of the reaction the sample powder residue, which has been decarbonated by the hot acidic CrCl₂ solution, is rinsed with deionized distilled water until neutral, centrifuged, and then dried at 60 °C overnight.

For sulfur isotope analysis, we generally estimate the sulfur content of the sample (with petrographic observations) to calculate the suitable quantity of initial powder needed to obtain ~ 4 mg of Ag₂S. However, for samples with low organic carbon content, at least 1 g of initial powder is necessary to analyze organic carbon compositions. This can be an issue for samples with high sulfur content, for which the chemical extraction with ~ 1g of powder releases large amounts of H₂S. In this case, the standard 10 mL of AgNO₃ quickly reaches the saturation and to prevent any H₂S loss, the volume of AgNO₃ has to be multiplied by 5. It produces large quantities of Ag₂S potentially heterogeneous that must be carefully homogenized before sulfur isotope analysis.

3.3. TOC and organic carbon isotope analysis

TOC content and $\delta^{13}\text{C}_{\text{org}}$ values were measured for carbonate-free residues obtained by both the standard and the new decarbonation method with a Flash EA1112 elemental analyzer coupled to a Thermo Finnigan DELTA plus XP isotope ratio mass spectrometer interfaced with a ConFlo IV interface at the stable isotope laboratory of the Institut de Physique du Globe de Paris (IPGP, Paris, France). Our results were normalized using three internal standards and an internal standard with 5 different amounts was used to estimate the concentration of C (wt%). Reproducibility of replicated standards is ± 0.1 ‰ for $\delta^{13}\text{C}$ (1σ). The $\delta^{13}\text{C}$ value of internal standards was determined using a classic sealed tube combustion

method (i.e. Dumas combustion) and isotope measurement on a Delta+XP mass spectrometer in Dual Inlet mode (see Ader et al., 1998 for a detailed description of the method). They are calibrated against the NBS-21 international standard and reported with the conventional δ notation relative to the V-PDB (Vienna Pee Dee Belemnite) standard. Reproducibility of the $\delta^{13}\text{C}_{\text{org}}$ and TOC measurements based on at least triplicate measurements of the samples is usually better than $\pm 0.4\text{ ‰}$ and $\pm 0.01\text{ wt\%}$, respectively (1σ ; **Tables 1 and 2**).

4. RESULTS & DISCUSSION

TOC content and organic carbon isotope compositions for the 21 decarbonated samples from BBDP (South Africa), TCDP3 and PDP1 (Western Australia) drill cores are reported in **Tables 1 and 2**. All the decarbonated samples present low TOC content between 0.008 ± 0.001 and $0.87\pm 0.04\text{ wt\%}$ and cover a large range of $\delta^{13}\text{C}_{\text{org}}$ between -57.3 ± 0.1 and $-15.8\pm 0.5\text{ ‰}$. Values measured by the two methods are in a range characteristic for organic material in Archean rocks ($\delta^{13}\text{C}_{\text{org}} = -26 \pm 7\text{ ‰}$ in average; e.g. Schidlowski, 2001 and reference therein). Average reproducibility (1σ), estimated from replicate measurements of TOC and $\delta^{13}\text{C}_{\text{org}}$ after the acidic chromium decarbonation, is similar to that obtained after the standard method with $\pm 0.014\text{ wt\%}$ and $\pm 0.41\text{ ‰}$ against 0.010 wt\% and 0.33 ‰ respectively, suggesting that no carbon addition (from reactant) or incomplete decarbonation occurred. In order to demonstrate that no carbon isotope fractionation is caused by the acidic chromium chemical protocol for decarbonation, we compared the results obtained after standard and acidic chromium decarbonation on the same powder and on different powders from the same samples (**Figure 2**).

First, starting from the same initial aliquot, we obtained similar results for both TOC and $\delta^{13}\text{C}_{\text{org}}$ values ($\delta^{13}\text{C}_{\text{Cr}}$ versus $\delta^{13}\text{C}_{\text{Std}}$ slope of 0.994 with $R^2=0.995$; **Figure 2**), suggesting that the new chemical protocol for decarbonation does not induce significant carbon isotope

fractionation (**Figures 2 and 3**). Carbon-richest samples ($\text{TOC} \geq 0.3 \text{ wt}\%$) show no significant difference in $\delta^{13}\text{C}_{\text{org}}$ with $\delta^{13}\text{C}_{\text{Cr}} - \delta^{13}\text{C}_{\text{Std}} \leq \pm 0.08 \text{ ‰}$, whereas carbon-poor samples ($\text{TOC} \leq 0.1 \text{ wt}\%$) sometimes display differences reaching $+1.2 \text{ ‰}$. No correlation between the carbonate content and the difference of carbon isotopic values has been observed (**Figure 3**), further confirming that decarbonation was complete. However, Ader et al. (2009) already observed similar deviations in $\delta^{13}\text{C}_{\text{org}}$ after successive standard decarbonation of samples with low TOC content $< 1 \text{ ‰}$ (i.e. $\delta^{13}\text{C}_{\text{org}}$ increased by $0.74 \pm 0.5 \text{ ‰}$). Even though these variations are very small compared to the range of $\delta^{13}\text{C}_{\text{org}}$ observed, they are still significant compared to the external reproducibility and should be taken into account in future studies regardless of the method used. We also duplicated one sample of mudstone from the Tumbiana Formation previously analyzed by Thomazo et al. (2009). The good reproducibility of $\pm 0.06 \text{ ‰}$ for $\delta^{13}\text{C}_{\text{org}}$ and $\pm 0.02 \text{ ‰}$ for TOC values estimated between the two studies (1σ ; **Figure 2**) allows us to validate the new protocol implemented.

Secondly, we observed less consistency between $\delta^{13}\text{C}_{\text{org}}$ and TOC measurements obtained on different powders from the same sample, with differences between $\delta^{13}\text{C}_{\text{Cr}}$ and $\delta^{13}\text{C}_{\text{Std}}$ varying from -7 to $+4 \text{ ‰}$ and differences in TOC from -0.01 to $+0.2 \text{ wt}\%$ (grey dots in **Figure 2**). These sometimes strong but non-systematic offsets are particularly striking when compared to the results obtained when the two procedures are undertaken on the same powder. These results point to rock sample heterogeneity at the centimeter scale and illustrate the importance of working on unique powder aliquots in particular when studying relations between different isotopic tracers. Therefore, our results demonstrate that the chromium reducing chemistry can be used for decarbonation without significant effects on TOC and $\delta^{13}\text{C}_{\text{org}}$ compared to the standard HCl decarbonation. This new protocol of decarbonation seems to be perfectly adapted for the analysis of organic matter in the ancient rock record that experienced at least low greenschist facies metamorphism.

For sedimentary rocks having been exposed to lower thermal conditions, it remains to be demonstrated if this protocol can also be safely used because the high temperatures of the acid attack might induce the breakdown of soluble organic molecules from the condensed organic matter, which may artificially decrease the TOC and modify $\delta^{13}\text{C}_{\text{org}}$. Likewise, modern sediments mostly contain immature organic matter and previous studies have already demonstrated that acidification, even at ambient temperature and lower acidity (down to 0.1 M HCl) might have a significant effect on their $\delta^{13}\text{C}_{\text{org}}$ values (from 0.12 to 1.77 ‰; Bunn et al., 1995, Jacob et al., 2005, Jaschinski et al., 2008, Brodie et al., 2011). In addition, it is highly unlikely that this chemistry, which is known to be a powerful reagent that can reduce some organic substrates, should be applicable for immature organic matter (see Hanson, 1974 for review).

5. CONCLUSIONS

Our results suggest that the acidic chromium solution can be used to eliminate inorganic carbon without significantly influencing the chemical composition of organic matter in rock samples of lower greenschist metamorphic grade or higher. This method is not only less sample consuming but also less time-consuming and ensures that bulk organic carbon and sulfur isotope measurements are performed on the exact same samples. Nevertheless, given the effects of simple HCl acidification on the $\delta^{13}\text{C}_{\text{org}}$ values of modern samples (Brodie et al., 2011) as well as Neoproterozoic samples (Ader et al., 2009), we recommend that this new method should be tested before being applied to lower maturity samples.

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FIGURE CAPTIONS

Figure 1: Experimental set-up for sulfide sulfur extraction and sample powder decarbonation. The acid attack consist in 20 mL of CrCl_2 solution and 10 mL of HCl (6 N). The solution with ground sample is kept at sub-boiling temperature (~ 100 °C) and a continuous flow of N_2 is bubbling through it. At the end of the reaction, we recovered the extracted sulfide sulfur as Ag_2S (in red) for sulfur isotope analyses and the residual decarbonated sample powder (in blue) for organic carbon analyses.

Figure 2: Comparison of $\delta^{13}\text{C}_{\text{org}}$ values (A) and TOC content (B) obtained after standard HCl decarbonation (Std) and reaction with acidic chromium solution for sulfur extraction (Cr). The black dots correspond to the analyses performed on the same initial aliquot whereas the grey dots correspond to the results obtained on different initial sample powders. The linear regression is associated with the black dots. Note the good agreement between the two techniques with $R^2 > 0.98$ for both $\delta^{13}\text{C}_{\text{org}}$ values and TOC contents.

Figure 3: Variations of $\delta^{13}\text{C}$ values (A) and TOC content (B) obtained by the two methods as a function of carbonate content of the samples. The analyses performed on the exact same aliquot (black dots) show small deviations for both TOC and $\delta^{13}\text{C}_{\text{org}}$ values suggesting that the new chemical protocol for decarbonation does not induce significant carbon isotope fractionation. $\delta^{13}\text{C}_{\text{org}}$ and TOC measurements are less consistent when obtained on different powders from the same sample (grey dots, $\delta^{13}\text{C}_{\text{Cr-Std}} > \pm 1\text{‰}$ and $\text{TOC}_{\text{Cr-Std}}$ up to 0.2 wt%).

Table 1: $\delta^{13}\text{C}_{\text{org}}$ and TOC measured after standard and new decarbonation of same initial sample powders. Carbonate content and $\delta^{13}\text{C}_{\text{carb}}$ have also been determined on the same samples. Underlined italic values are from Thomazo et al. (2009).

Formation	Lithology	Sample	Decarbonation by chromium solution				Standard decarbonation				Carbonate content			
			$\delta^{13}\text{C}_{\text{Cr}}$ (‰)	1 σ	TOC _{Cr} (wt%)	1 σ	$\delta^{13}\text{C}_{\text{Std}}$ (‰)	1 σ	TOC _{Std} (wt%)	1 σ	$\delta^{13}\text{C}_{\text{Carb}}$ (‰)	1 σ	%Carb	1 σ
Mapepe	Ferruginous chert	BBDP_52.72	-19.10	1.42	0.020	0.005	-19.31	0.78	0.019	0.001	0.65	0.02	33.10	1.65
Mapepe	Bedded barite	BBDP_67.95	-26.09	0.39	0.009	0.002	-26.88	0.72	0.008	0.001	-1.51	0.00	0.250	0.003
Mapepe	Felsic volcanics	BBDP_68.05	-23.66	0.22	0.015	0.001	-23.63	0.53	0.015	0.002	0.42	0.13	35.46	1.26
Mapepe	Felsic volcanics	BBDP_68.42	-26.75	0.37	0.023	0.001	-26.50	0.15	0.025	0.003	1.10	0.06	32.61	0.26
Mapepe	Bedded barite	BBDP_78.18	-27.56	0.05	0.031	0.002	-26.59	0.10	0.042	0.004	-6.01	0.16	0.070	0.001
Mendon	Laminated black chert	BBDP_95.41	-30.14	0.08	0.356	0.005	-30.22	0.08	0.398	0.002	-3.82	0.01	0.50	0.02
Mendon	Laminated black chert	BBDP_114.38	-31.26	0.17	0.85	0.02	-31.22	0.15	0.87	0.04	-7.03	0.04	8.13	0.02
Mendon	Laminated black chert	BBDP_139.8	-28.29	0.20	0.30	0.01	-28.43	0.10	0.249	0.005	-4.28	0.18	14.40	0.55
Turee Creek	Laminated mudstone	TCDP3_100.52	-27.49	0.70	0.095	0.029	-27.09	0.11	0.106	0.004	0.36	0.40	27.33	0.03
Turee Creek	Laminated mudstone	TCDP3_135.16	-27.87	0.67	0.16	0.06	-27.06	0.08	0.111	0.004	-0.10	0.40	19.68	0.03
Turee Creek	Mudstone	TCDP3_156.54	-29.04	0.51	0.136	0.036	-28.85	0.14	0.112	0.007	-5.55	0.40	9.56	0.03
Turee Creek	Mudstone	TCDP3_164.36	-29.83	0.48	0.130	0.062	-29.72	0.26	0.100	0.005				
Turee Creek	Quartzite	TCDP3_183.7	-28.89	0.71	0.042	0.015	-27.68	0.25	0.012	0.001	-6.08	0.40	4.19	0.03
Tumbiana	Homogeneous mudstone	PDP1_44.5	-55.82	0.24	0.433	0.006	<u>-55.9</u>	<u>0.4</u>	<u>0.40</u>	<u>0.03</u>	<u>-7.7</u>	<u>0.4</u>	<u>25.80</u>	<u>0.03</u>

Table 2: $\delta^{13}\text{C}_{\text{org}}$ and TOC measured after standard and new decarbonation of different initial sample aliquots. Carbonate content and $\delta^{13}\text{C}_{\text{carb}}$ have also been determined on the same samples.

Formation	Lithology	Sample	Decarbonation by chromium solution				Standard decarbonation				Carbonate content			
			$\delta^{13}\text{C}_{\text{Cr}}$ (‰)	1 σ	TOC _{Cr} (wt%)	1 σ	$\delta^{13}\text{C}_{\text{Std}}$ (‰)	1 σ	TOC _{Std} (wt%)	1 σ	$\delta^{13}\text{C}_{\text{Carb}}$ (‰)	1 σ	%Carb	1 σ
Tumbiana	Laminated mudstone	PDP1_88.2	-57.26	0.08	0.410	0.001	-52.70	0.40	0.21	0.03	-1.10	0.40	51.20	0.03
Tumbiana	Siltstone	PDP1_68.9C	-51.55	0.10	0.290	0.002	-44.90	0.40	0.09	0.03	0.40	0.40	63.80	0.03
Tumbiana	Homogeneous mudstone	PDP1_69.5	-49.84	0.27	0.135	0.002	-44.50	0.40	0.11	0.03	0.60	0.40	40.40	0.03
Mapepe	Ferruginous chert	BBDP_39.75	-15.78	0.43	0.034	0.001	-18.46	0.16	0.026	0.001	-0.59	0.01	9.94	0.05
Mapepe	Felsic volcanics	BBDP_45.99	-27.65	0.96	0.019	0.004	-31.53	0.31	0.015	0.000	-0.18	0.04	0.46	0.01
Mapepe	Felsic volcanics	BBDP_56.66	-25.94	0.33	0.028	0.004	-30.22	0.41	0.038	0.002	0.67	0.18	19.84	0.43
Mendon	Altered komatiite	BBDP_160.12	-28.50	0.31	0.077	0.024	-25.79	1.05	0.02	0.01	-1.06	0.06	15.64	0.54

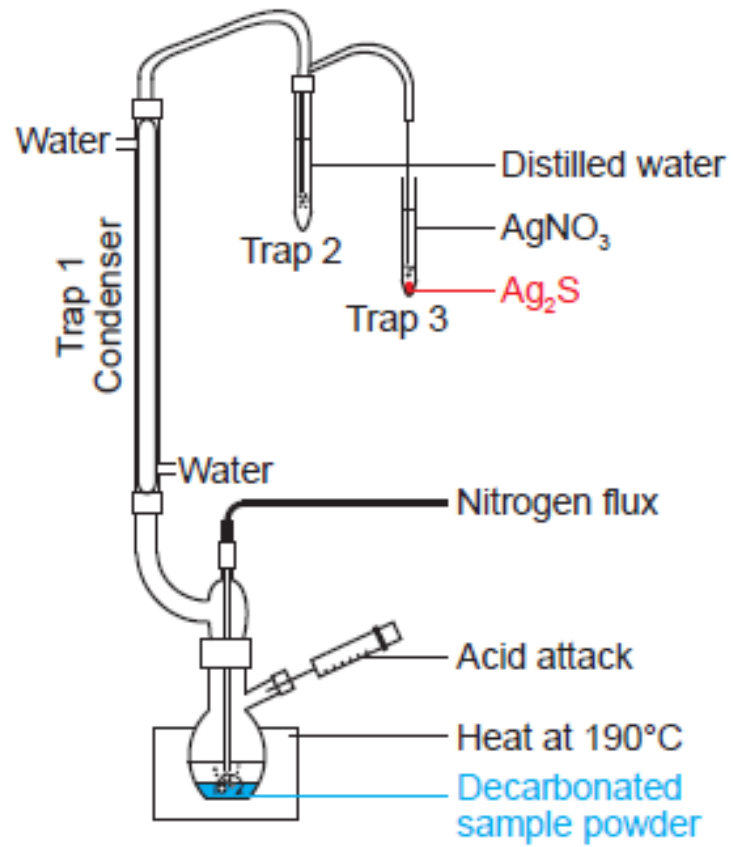


Fig. 1

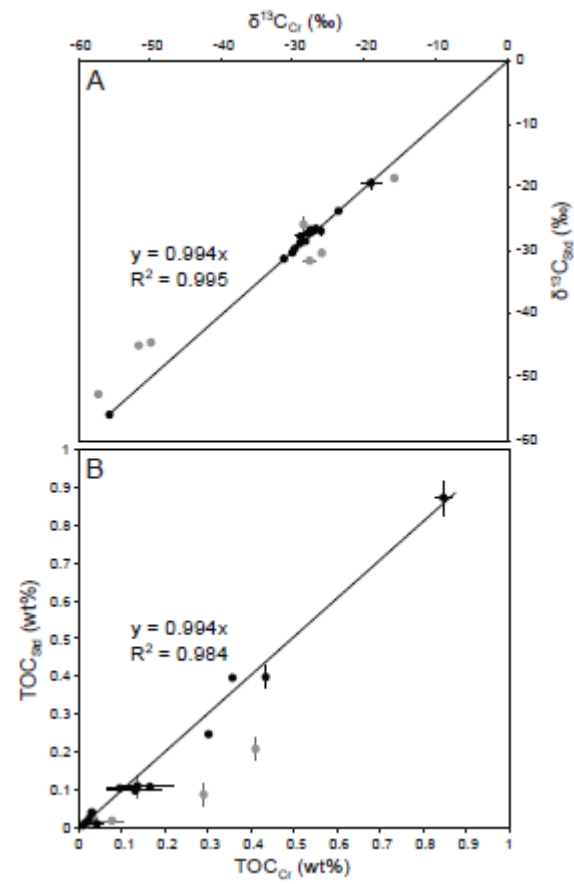


Fig. 2

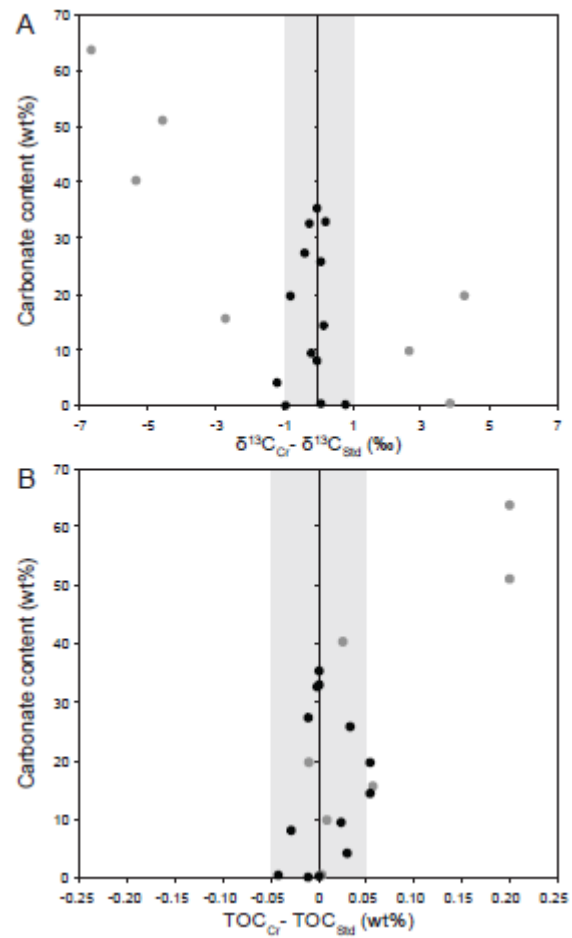


Fig. 3