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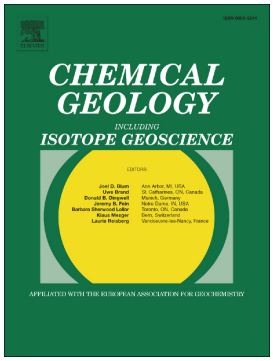

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Bias in carbon concentration and $\delta^{13}C$ measurements of organic matter due to cleaning treatments with organic solvents

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ABSTRACT:

Interpreting the organic carbon content (TOC) and stable carbon isotopic composition ($\delta^{13}C$) of organic matter in the sedimentary rock record depends on our capability to accurately measure them, while excluding sources of contamination. This however becomes increasingly problematic as we analyze samples with ever-lower organic carbon content. Accordingly, organic solvents are sometimes used to remove contaminating traces of modern organic matter from ancient rock samples. However, especially for very low TOC samples, traces of solvents or their impurities remaining in the sample may contribute a significant organic contamination that can impact the bulk measurements of both TOC and $\delta^{13}C$ values. This study, including three independent investigations performed in different laboratories, is the first detailed examination of the effect of cleaning treatments on the reliability of TOC and $\delta^{13}C$ values in a range of natural rock samples and synthetic materials with low TOC content from below detection limit to 3330 ppm. We investigated the four most common organic solvents used to remove modern organic matter: dichloromethane (DCM), *n*-hexane, methanol and ethanol, and evaluated the effect of grain size and mineralogy. We find that (i) cleaning treatments with methanol, *n*-hexane and dichloromethane contaminate rock samples when used directly on sample powder, regardless of the grain size; (ii) this pollution buffers the natural variability and homogenizes the $\delta^{13}C$ values of samples around the isotopic composition of the solvent, i.e. between -27 and -29 ‰; (iii) the extent of contamination depends on the solvent used, DCM being the most contaminating (up to 6000 ppm) and ethanol the only solvent that does not seem to contaminate rock samples above our detection limit; (iv) sample mineralogy also exerts an influence on the extent of contamination, clay minerals being more prone to adsorb contaminants. We conclude that the response of carbon concentrations and the stable

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carbon isotopic composition of organic matter in geological samples to cleaning treatments is neither negligible nor systematic when investigating samples with low carbon content.

Keywords: organic carbon, TOC, carbon isotope, contamination, solvents

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1. INTRODUCTION

The reliable determination of the carbon concentration (TOC) and isotopic composition ($\delta^{13}C_{org}$) of organic matter (OM) in the rock record have been regarded as key proxies for the interpretation of paleoenvironmental and paleoclimatic processes. They are widely used for instance, to identify OM provenance (e.g. aquatic versus terrestrial source; Meybeck, 1982; Hedges et al., 1986; Tyson, 1995; Meyers, 1997) and mineralization processes (e.g. Freudenthal et al., 2001; Leng and Marshall, 2004), and to inform about past atmospheric pCO_2 (e.g. Fischer et al., 1998), past primary productivity (e.g. Dumitrescu and Brassell, 2006; Adams et al., 2010) and changes in the global carbon cycle through time (e.g. Schidlowski and Aharon, 1992; Hayes et al., 1999). These interpretations depend on the assumption that we can accurately and reliably determine TOC and $\delta^{13}C_{org}$. Questioning this reliability may seem odd given that these parameters have now been routinely analyzed for decades in many laboratories. However, in the case of rock samples containing very low TOC abundances (<0.1 mg/g), possible contamination by modern OM compounds has not yet been systematically investigated. There are several potential sources of post-depositional OM contamination, notably associated with subsurface biological activity, groundwater penetration, sampling and storage (e.g. Brocks et al., 2003a; Brocks et al., 2003b; Gérard et al., 2009, Brocks, 2011). This contamination issue has been clearly illustrated by biomarker studies focusing on soluble organic matter (i.e. bitumen) of Precambrian rocks, which has been shown to be susceptible to a contaminating overprint (e.g. Brocks et al., 2008; Brocks, 2011; Illing et al., 2014). In contrast, the insoluble macromolecular OM (i.e. kerogen), characterized by covalent bonds, is generally accepted as unaffected by modern contamination and considered syngenetic to the host rock, thus representing a 'robust' indigenous organic fraction (Brocks et al., 2003a; Marshall et al., 2007). In order to clean rock samples from modern organic contaminations prior to analyses of TOC and $\delta^{13}C_{org}$, it is thus

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tempting to remove their soluble fraction – especially in the case of low TOC samples, where the modern contamination may represent a higher proportion of the total OM than indigenous kerogen. Different solvents such as dichloromethane–ethanol mixtures are frequently used before the decarbonation by acid treatment. In most cases, solvents are applied to small pieces of rock sample devoid of fractures and assuming that the modern contamination did not penetrate into the rocks' porosity (e.g. Wright et al., 1997; Beaumont and Robert, 1999; Derenne et al., 2008). Others prefer to wash rock powders with organic solvents, in order to ensure the complete decontamination of the sample (e.g. Thomazo et al., 2009). However, given the organic nature of the solvents themselves, as well as trace impurities therein, solvents have previously been suspected to contaminate very low TOC samples (Wright et al., 1997).

In this context, the aim of the present study is to establish in what circumstances solvent-cleaning treatments can be responsible for contamination, rather than decontamination, affecting the stable carbon isotopic composition of various samples with low carbon content. Solvents of varying polarity, such as methanol (MeOH), dichloromethane (DCM) and *n*-hexane can be used to clean rock samples from modern contaminations, but any potential pollution by these solvents has never been investigated. To examine the extent to which the cleaning procedures can modify the TOC and $\delta^{13}C_{org}$ in different types of samples, three independent series of tests were performed in three different laboratories. At the IPGP (Paris, France) and the Biogeosciences Laboratory (Dijon, France), we looked into the effect of DCM treatment, which is the most widely used solvent for rock cleaning, on TOC and $\delta^{13}C_{org}$ in Precambrian sedimentary rocks from the Turee Creek Drilling Project (TCDP) drill core (Philippot et al., in review). To do so, we compared TOC and $\delta^{13}C_{org}$ results obtained on DCM treated samples to those of untreated samples. At the Max-Planck-Institute for Biogeochemistry (Jena, Germany) and the MARUM (Bremen, Germany), the contamination

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effects of a variety of solvents (i.e. DCM, *n*-hexane and MeOH) were analyzed as a function of clay mineralogy. Additionally, we applied the technique to synthetic samples by comparing the $\delta^{13}C_{org}$ values measured in pure kaolinite and montmorillonite samples (heated at 500 °C) obtained after different cleaning treatments to those obtained on untreated materials. Finally, at the University of Washington (Seattle, USA), the effect of grain size on the extent of contamination was investigated using quartz sands devoid of OM. Our results are preliminary, but they demonstrate the occurrence of contamination by solvents and provide new guidelines for further investigations.

2. CARBON CONTAMINATION BY DCM IN ARCHEAN ROCK SAMPLES

2.1 SAMPLES

Investigated samples were collected from the Turee Creek Drilling Project drill core #3 (TCDP3) recovered from the Hamersley Basin, Western Australia. From bottom to top, TCDP3 intersects orthoquartzites of the Koolbye Formation, and shales and stromatolitic limestones of the Kazput Formation (Philippot et al., 2018), which both belong to the dominantly marine sedimentary succession of the Turee Creek Group (Trendall, 1981; Thorne and Tyler, 1996). Metamorphism of these deposits did not exceed ~300 °C (Smith et al., 1982; Rasmussen et al 2005). Geochronological constraints for the Turee Creek Group are provided by the 2,449 ± 3 Ma Woongarra Rhyolite at the top of the underlying Hamersley Group (Barley et al., 1997) and by the 2,209 ± 15 Ma Cheela Spring Basalt of the unconformably overlying lower Wyloo Group (Martin et al., 1998). These ages have been recently confirmed by new geochronological data at the base of the Meteorite Bore Member in the Turee Creek Group with a U-Pb detrital zircon maximum age of 2,340 ± 22 Ma (Caquineau et al., 2017) and a Re-Os age of 2,312.5 ± 6.2 Myr (Philippot et al., 2018). The ten samples studied here include 5 mudstones and 3 limestones from the Kazput Formation,

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and 2 orthoquartzites from the Koolbye Formation. Petrographically, the samples show a broad range of carbonate concentrations from 2 % to 68 %, mainly composed of calcite and ankerite according to XRD analyses (**Table 1**). They also contain differing proportions of quartz, chlorite, muscovite and albite.

2.2 METHODS

The rock samples were powdered to <100 µm using an agate ring and puck mill. The powder was homogenized and divided in several aliquots: one was treated with dichloromethane–ethanol before decarbonation and the other was directly decarbonated. Total organic carbon content (TOC) and organic carbon isotope composition ($\delta^{13}C_{org}$) were measured on carbonate-free residues (**Table 2, Supplementary Table 1**).

2.2.1 Combined DCM cleaning and acid attack

The first aliquot of the sample powders (~3 g) was loaded in 50 mL falcon tubes, mixed with 35 mL of a dichloromethane (CH_2Cl_2) and absolute ethanol (99.8 %) solution with a 9:1 ratio and continuously agitated for 30 min using an automatic digital rotator. The dichloromethane used in this study (RS Pestipur, n°442260) was manufactured by Carlo Erba Reagents, already stabilized with 0.3 % of ethanol, and certified for PAHs (Polycyclic Aromatic Hydrocarbons) ≤ 0.1 µg/L. After centrifugation, the residues were washed several times with deionized distilled water and dried at 50 °C in an oven. The residues were subsequently reacted with excess HCl 6 N at room temperature overnight, followed by 4 h at 80 °C to remove carbonate phases. After decanting, the residues were rinsed with deionized distilled water until neutral, centrifuged (3500 rpm for 5 minutes), and dried at 50 °C overnight.

Aliquots of dried decarbonated samples (~3–60 mg) were then weighed into tin capsules (Säntis Analytical AG). The TOC content and $\delta^{13}C_{org}$ values were determined at the

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Biogéosciences Laboratory of the Université de Bourgogne Franche-Comté, Dijon, France, on a Vario MICRO cube elemental analyzer (Elementar, Hanau, Germany) coupled in continuous flow mode to an IsoPrime stable isotope ratio mass spectrometer (Isoprime, Manchester, UK). USGS40 certified reference material (C = 40.8 wt. %; $\delta^{13}C_{VPDB}$ = -26.2 ‰) was used for calibration. The carbon isotopic composition is expressed in delta notation and reported in permil (‰) relative to the Vienna Pee Dee Belemnite (V-PDB) standard; external reproducibility based on triplicate analyses of samples was better than ± 0.2 ‰ (1σ; **Table 2**). From among these samples, four were selected for an additional decarbonation attack with $CrCl_2$ solution and re-analyzed at the Institut de Physique du Globe de Paris (IPGP, Paris, France; see description below). The results are presented in **Supplementary Table 1**.

2.2.2 Acid attack by chromium reduction

The second aliquot of the sample powders was reacted in a sub-boiling acidic $CrCl_2$ solution. The $CrCl_2$ solution was prepared by reducing $CrCl_3$ hexahydrate with granulated Zn in HCl 0.6 N. The decarbonation of the samples was performed under a N_2 atmosphere and acidified during the reaction with HCl 6 N (Zhabina and Volkov, 1978; Canfield et al., 1986). At the end of the reaction, the decarbonated sample residue was rinsed with deionized distilled water until neutral, centrifuged, and then dried at 60 °C overnight. This procedure, originally used for the extraction of reduced inorganic sulfur compounds in geological samples, has been validated by Muller et al., 2017 even for low TOC samples. In order to confirm the data, four of these samples were also decarbonated by the standard method with HCl 6 N. Results are reported in **Supplementary Table 1**.

The TOC content and $\delta^{13}C_{org}$ values were measured 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

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Globe de Paris (IPGP, Paris, France). Briefly, powdered samples were weighed into tin capsules (IVA Analysentechnik), inserted in the auto-sampler of the elemental analyzer and combusted with a pulse of O_2 gas. The $\delta^{13}C$ value of the resulting CO_2 gas was 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 $\delta^{13}C_{org}$ and TOC based on multiple measurements of the samples is usually better than ±0.5 ‰ and ±200 ppm (1σ; **Tables 2, Supplementary Table 1**).

2.3 RESULTS & DISCUSSION

Directly decarbonated samples exhibit low TOC values between 197 and 3330 ± 168 ppm, and $\delta^{13}C_{org}$ values between -29.5 ± 0.5 and -26.2 ± 0.3 ‰. The method of decarbonation used in this study (see section 2.2.2) has been previously validated on similar samples and gives reliable values for both TOC and $\delta^{13}C_{org}$ interpreted to reflect the indigenous kerogen (**Supplementary Table 1**; see Muller et al., 2017 for discussion on decarbonation methods). When treated with DCM, the same samples show a higher organic carbon content between 800 and 10100 ± 39 ppm (**Figure 1B**). The DCM treatment has thus added organic carbon to the samples and modified their $\delta^{13}C_{org}$ values (**Figure 1A**). The samples treated with DCM present more homogeneous $\delta^{13}C_{org}$ values, which cluster around an average value of -27.4 ± 0.5 ‰ (-28.4 > $\delta^{13}C_{org}$ > -26.6 ± 0.2 ‰).

The carbon contamination content (TOC_{cont}) can be estimated for each sample by mass balance, following Eq. (1):

$$TOC_{cont} = TOC_{DCMtreat} - TOC \quad (1)$$

with the associated error:

$$\sigma(TOC_{cont}) = [\sigma(TOC_{DCMtreat}) + \sigma(TOC)] / TOC_{cont}$$

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Here, the DCM treatment induced a significant contamination between 400 and 6700 ppm, in other words between 35 and 79 % of the total TOC in the DCM-treated samples (**Figure 1C**). This contribution is subsequently used in Eq. (2) to calculate the $\delta^{13}C$ of the contaminant ($\delta^{13}C_{cont}$) through isotope mass balance:

$$\delta^{13}C_{cont} = TOC_{DCMtreat} / TOC_{cont} * \delta^{13}C_{DCMtreat} - TOC / TOC_{cont} * \delta^{13}C_{org} \quad (2)$$

The $\delta^{13}C_{cont}$ varies between -25.5 and -28.0 ‰ with an average error of ±1.3 ‰ calculated through error propagation following (**Table 2**):

$$\frac{\sigma(\delta^{13}C_{cont})}{\delta^{13}C_{cont}} = \frac{\sigma(TOC_{DCMtreat})}{TOC_{DCMtreat}} + \frac{\sigma(TOC)}{TOC} + 2 * \frac{\sigma(TOC_{cont})}{TOC_{cont}} + \frac{\sigma(\delta^{13}C_{DCM})}{\delta^{13}C_{DCM}} + \frac{\sigma(\delta^{13}C_{org})}{\delta^{13}C_{org}}$$

Although the proportion of contamination varies widely between the samples, it presents a relatively constant $\delta^{13}C_{cont}$ value around -27.2 ± 0.8 ‰ (1σ, **Figure 2**). This value is similar to the average $\delta^{13}C_{org}$ value of the samples treated with DCM (-27.4 ± 0.5 ‰).

The observed variation of contamination proportions in TCDP3 samples (from 35 to 79 %) does not seem to be linked to differences in sample lithology. No correlation could be identified between the TOC_{cont} and the abundance of the main mineralogical phases in the samples (**Figure 3**). Considering the uniformly low TOC content of our samples, the absence of significant co-variation between the TOC_{cont} and the organic carbon content is not surprising. Therefore, we cannot draw firm conclusions about the precise contribution of the mineralogy and OM content to the fixation of the contaminants.

It could be interesting in the future to further investigate the effects of DCM treatment on natural samples of different mineralogy with more variable TOC and organic matter maturity in order to better characterize the absorption processes of contaminants depending on the matrix. These aspects are partially explored in the following section.

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3. CARBON CONTAMINATION BY SOLVENTS IN CLAYS

For this part, we investigated the intensity of contamination induced by DCM, methanol (MeOH) and *n*-hexane cleaning treatments as a function of two different mineral species: pure kaolinite and montmorillonite. These experiments were performed at the Max-Planck-Institute for Biogeochemistry (Jena, Germany) and the MARUM (Bremen, Germany).

3.1 MATERIAL AND METHODS

Powders were the same as those used in Leider et al. (2016). These were composed of kaolinite ($Al_2Si_2O_5(OH)_4$; Fluka Analyticals, Steinheim, Germany) or montmorillonite ($Al_2Si_4O_{10}(OH)_2$ x nH_2O, K10, pH 3-4, 250 $m^2.g^{-1}$; Sigma-Aldrich).

All glassware underwent combustion at 500 °C for 6 h before use. Spatula and tweezers were cleaned with organic solvents. Kaolinite and montmorillonite powders (ca. 5 g each) were transferred into glass beakers, covered with aluminum foil and combusted at 500 °C for 6 h. After cooling, the same amount of each powder (ca. 1 g) was distributed into three separate 40 mL 'ASE vials'. Each sample batch containing kaolinite and montmorillonite was extracted using 10 mL of MeOH (Merck, SupraSolv: max 3 ng/mL of residual *n*-$C_{11–40}$ alkanes), DCM (Merck, UniSolv: max 2 ng/mL of residual *n*-$C_{11–40}$ alkanes) or *n*-hexane (Merck, SupraSolv: max 3 ng/mL of residual *n*-$C_{11–40}$ alkanes) as organic solvents by ultrasonic agitation in a water bath for 5 minutes. After settling, supernatants were discarded and wet powders were dried under the fume hood covered with aluminum foil overnight, and subsequently on a heating plate at 80 °C for 2 h. Triplicates of 40 mg of extracted dry powders were weight into tin cups before bulk $\delta^{13}C$ analysis. Additional triplicates of powder blanks were directly weight into tin cups after combustion.

Samples in tin cups (Lüdiswiss Sn98) were analyzed after online combustion to CO_2 in an in-house refurbished and modified (MPI-BGC) Finnigan MAT Delta C prototype isotope ratio

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monitoring (irm) MS coupled to a Carlo Erba EA-11 via a ConFlo III interface. The stable carbon isotopic values are reported in the permil notation relative to V-PDB after calibration against NBS-22 ($\delta^{13}C$ = -30.031 ‰) reference material. The long-term instrumental precision is better than ±0.12 ‰, while the standard deviation for triplicate measurements of the samples reported here is given in **Table 3**.

3.2 RESULTS & DISCUSSION

For kaolinite, the measurements of carbon content in both treated and untreated samples are below the detection limit (**Table 3**). Therefore, the contamination by solvents can be considered as negligible in the kaolinite. In contrary, large variations in $\delta^{13}C$ values can be observed in treated montmorillonite, with a shift between 3.4 and 4.4 ‰ towards more negative values compared to triplicate measures of untreated sample (-24.3 ± 0.9 ‰; **Figure 4**). Moreover, the addition of carbon in these samples ranges between 500 and 1400 ppm on average compared to the untreated sample (which is below the detection limit) and suggests a large contamination by solvents. This range of contamination is similar to that observed in the TCDP3 samples (between 400 and 6700 ppm). The maximum contamination was induced by DCM treatment and is associated with the lowest $\delta^{13}C$ values (**Figures 4 and 5**). Montmorillonite is a clay mineral with a greater surface reactivity than kaolinite (Carroll and Starkey, 1971, Kowalska et al., 1994), which may explain why kaolinite was not contaminated by the solvent. However, both kaolinite and montmorillonite were combusted at 500 °C for 6 h. At this temperature, kaolinite loses its crystalline structure to become an amorphous "metakaolin", and montmorillonite loses molecular and hydroxyl water (Bradley and Grim, 1951; Glass, 1954). This thermal treatment thus changes dramatically the properties of these clay minerals compared to natural/original polymorphs clays. Amorphous metakaolin will likely have very different properties compared to its crystalline counterpart.

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The montmorillonite, having lost its water, may be much more prone to incorporate organic contaminants.

Otherwise, all samples contaminated by solvents display similar $\delta^{13}C$ values oscillating around -28.0 ± 0.4 ‰. This value is consistent with the $\delta^{13}C$ value previously calculated for DCM contamination in the previous section (-27.2 ± 0.8 ‰, **Figure 2**). It supports the idea that all the organic solvents including methanol, *n*-hexane and DCM tend to buffer the natural variability of the samples and homogenize the $\delta^{13}C$ values around -28 ± 1 ‰ (based on the results of Sections 2 and 3). In summary, this study suggests that the intensity of the contamination depends on both the solvent and the mineralogy of the samples considered. Based on the results on montmorillonite, DCM seems to be the solvent which introduced the most contamination into rock samples.

4. EFFECTS OF GRAIN SIZE ON CARBON CONTAMINATION BY SOLVENTS

In this third set of experiments, we focused our investigations on the effect of grain size on the contamination by solvents. This time, the experiments were performed at the Department of Earth and Space Sciences, University of Washington (Seattle, USA) on pure quartz samples.

4.1 MATERIAL AND METHODS

Pure silica sand (Fisher Scientific, mesh 40-100) was baked at 1000 °C to remove any initial contaminants. A sub-sample of the sand was then pulverized into a fine powder (< 63 µm) with an Al_2O_3 ceramic puck mill. The powder was baked again at 1000 °C to remove any contaminants that may have been added during the milling process.

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Several ~0.5 g aliquots of baked sand and powder were weighed into baked Pyrex tubes (500 °C overnight) and mixed with 10 mL of *n*-hexane (BDH, ACS-grade), reagent alcohol (BDH, 82 % ethanol, 5 % methanol, 5 % isopropanol, 9 % water), DCM (Fisher Scientific, ACS-grade) or HCl 6 N (BDH, ACS-grade) at room temperature overnight. The next day, the tubes were centrifuged and the solutions were decanted. The residue of the HCl treatment was washed three times with DI-H_2O (18 MΩ×cm); the residues treated with organic solvents were not washed. All residues were left to dry at 60 °C for three days in a closed oven with a light Al foil cover. For the analyses, aliquots of the treated and untreated materials were weighed into tin capsules (9x5mm, Costech) and flash-combusted with 20 mL of O_2 at 1000 °C in an elemental analyzer (Costech) coupled to a MAT253 Thermo-Finnigan isotope ratio mass spectrometer via a Conflo III. Organic carbon isotopes were calibrated by three-point calibration (Coplen et al. 2006) with in-house standards (glutamic acid-1: -28.3 ‰; glutamic acid-2: -13.7 ‰; dried salmon: -21.3 ‰) that had previously been calibrated against USGS-40 and USGS-41. Blanks resulting from carbon contained in the Costech tin capsules (0.95 ± 0.03 µg C/capsule, $\delta^{13}C$ = 28.55 ± 0.15 ‰, n = 10) were subtracted by mass balance. The analytical precision was ±0.15 ‰ (1 standard deviation of replicate standards). The peak area was calibrated for total organic carbon content with a relative error of 14 %.

4.2 RESULTS AND DISCUSSION

The presence of carbon in untreated sand (33.8 ppm), compared to untreated powder (2.5 ppm), as well as the difference in initial $\delta^{13}C$ values between the two, reflect the difficulty of removing all impurities in the sand solely by baking. HCl acid attack on quartz sand removed only a part of these impurities, as shown by the difference in $\delta^{13}C$ values between sand and powder (**Table 4** and **Figure 6**). The residual 2.5 ppm of carbon in powder likely represents background contamination introduced during handling and storage of the samples. This could

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include adsorption of airborne dust. The isotopic composition of the untreated powder can thus be considered as a blank value. Both quartz sand and powder record similar changes in TOC when treated with *n*-hexane compared to untreated samples (**Figure 6**). This suggests that solvents contaminate crushed samples independently of the grain size likely because a fixed residue of non-volatile contaminants remained in the centrifuge tubes after the bulk of the solvents had been decanted. The contamination was therefore independent from the surface area of the material. In both cases, this contamination is associated with a shift in $\delta^{13}C$ values toward negative values (**Figure 7**). In sand the $\delta^{13}C$ value reflects the contribution of impurities contained within the grains and the contamination by solvents, whereas in powder we can assume that impurities have been removed by baking so that $\delta^{13}C$ represents only the solvent contribution. With that assumption, we can estimate the expected isotopic composition of the hexane-treated sand. If the pure hexane adds 72 ppm carbon to the sand (106 ppm - 33.8 ppm, **Table 4**) with a composition of -29.5 ‰, then the expected isotopic composition of the mixture should be -25.9 ‰. This value is slightly more negative than the measured value of -22.5 ‰, which is most likely attributable to uncertainties in the abundance and isotopic measurements of small carbon quantities. It is however unlikely that this difference was caused by an uncharacterized contaminant, because this contaminant should also have had affected the alcohol- and acid-treated samples, which were processed at the same time with the same equipment. The isotopic results for solvent treated powders are nearly indistinguishable within error, whereas the concentrations differ significantly (see **Figures 6 and 7**). Hence it is unlikely that contamination is simply a result of solvents changing the surface properties of the sand powder.

Samples treated with DCM show once again the highest contamination (**Figure 6**) with an average $\delta^{13}C$ value of -27.8 ± 0.2 ‰ (n=2, **Figure 7**). This value is consistent with the results presented in the two other studies using DCM (-27.2 ± 0.8 ‰ in section 2 and -28.7 ± 2.8 ‰

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in section 3). These results obtained in three independent laboratories with different solution brands suggest that DCM has a mean carbon isotopic composition of -27.9 ‰ despite the exact values not being measured for each solution. Similarly, the *n*-hexane contamination on quartz has a $\delta^{13}C$ value of -29.5 ± 1.1 ‰, which is close to the value obtained on montmorillonite (-27.6 ± 0.6 ‰ in section 3), even though the solvents come from different laboratories. By contrast, ethanol does not contribute to carbon contamination and it may help to remove some of the contamination introduced by *n*-hexane (**Figure 6**). HCl treatment also appears to not add measureable amounts of organic contamination to the sand and may also help to clean the sample of impurities to some degree (**Figure 6**).

5. CONCLUSIONS

Organic solvents are sometimes used to remove modern organic matter from old rock samples, in order to clean them to obtain more reliable analyses of the bulk organic matter (i.e. kerogen). However, when applied to samples with low carbon content, this 'cleaning' process can be responsible for a non-negligible carbon contamination, inducing changes in TOC and $\delta^{13}C$ values. In order to quantify the effect of this contamination, three independent studies performed in different laboratories yielded similar results. We show that cleaning treatments with methanol, *n*-hexane and dichloromethane contaminate rock samples when used directly on sample powder, regardless of the grain size. This pollution is associated with changes in $\delta^{13}C$ values, which tend to homogenize all samples around the isotopic composition of the solvent deduced from this study as between -27 and -29 ‰. In the future, it would be interesting to have a direct estimate of the isotope composition(s) of blanks with solvents, maybe after several heating steps in order to fully address the source of the contamination(s).

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Wright et al. (1997) has already demonstrated the occurrence of non-negligible dichloromethane and methanol contaminations in low C micrometeorites. Our results extending this finding to rock matrices are consistent with the previous observations that the proportion of contamination depends on the solvent used, with DCM being the most contaminating product. Ethanol is the only solvent that does not seem to contaminate rock samples and even appears to inhibit contamination. However, in cases of pre-existing contamination by hydrocarbons, bitumens, oils or drilling fluids, polar solvents such as ethanol will not be able to quantitatively remove these non-polar contaminants by extraction. The degree of contamination was also found to depend on the mineralogy of the sample. Some minerals like meta-montmorillonite (heated at 500 °C) capture carbon contaminants more efficiently than others, such as "metakaolin". However, we did not observe such a correlation between contamination rate and mineralogy in natural samples. To identify the exact processes implied in this sequestration it would be important to do more experiments on various minerals with particular properties such as chlorite but also on natural samples with varying TOC content, kerogen types and thermal maturities. In light of our preliminary results, we recommend that researchers:

(i) Apply cleaning treatments with organic solvents only to small pieces of rocks (or chips) free of fractures (and not to powders) especially for very low TOC samples,

(ii) Use a final cleaning step (e.g. ethanol cleaning after DCM extraction) as a potential solution to contamination issues based on our important observation that ethanol does not introduce contamination. The use of vacuum and/or heating desorption of solvents and associated contaminants may also represent a good solution but still needs to be tested.

(iii) Restrict interpretations to variations of bulk $\delta^{13}C_{org}$ values significantly greater than a robust estimate of the inaccuracy and imprecision on the data (here ~ 2 ‰, the

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maximum shift induced by solvent treatment on Precambrian sedimentary rocks with low TOC). This recommendation becomes even more important as previous studies have already demonstrated a significant bias on bulk $\delta^{13}C_{org}$ values associated with pre-analysis acid treatment methods (Brodie et al., 2011a and b).

ACKNOWLEDGMENTS

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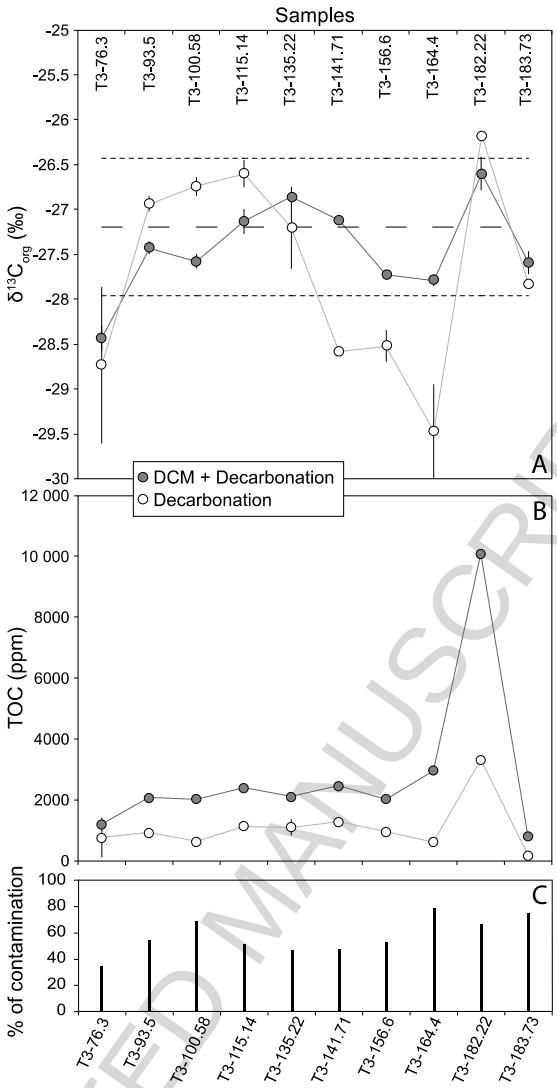

Figure 1. $\delta^{13}C_{org}$ values (A) and TOC contents (B) of decarbonated samples (white) and DCM-treated decarbonated samples (grey) from TCDP3 drill core. The thick black dashed line corresponds to the average $\delta^{13}C$ of the contaminant at -27.2 ‰, calculated by mass- and isotope balance. The thin dashed lines correspond to its standard deviation of ±0.8 ‰ (1σ, see text for details). (C) Proportion of contamination in DCM-treated samples in percent. Note the addition of up to 6770 ppm of organic carbon in DCM-treated samples corresponding to 35 and 79 % of their TOC. This contamination resulted in skewing the $\delta^{13}C_{org}$ values of DCM-treated samples compared to those of directly decarbonated samples, the value of DCM-treated samples approaching that of the contaminant (-27.2 ± 0.8 ‰).

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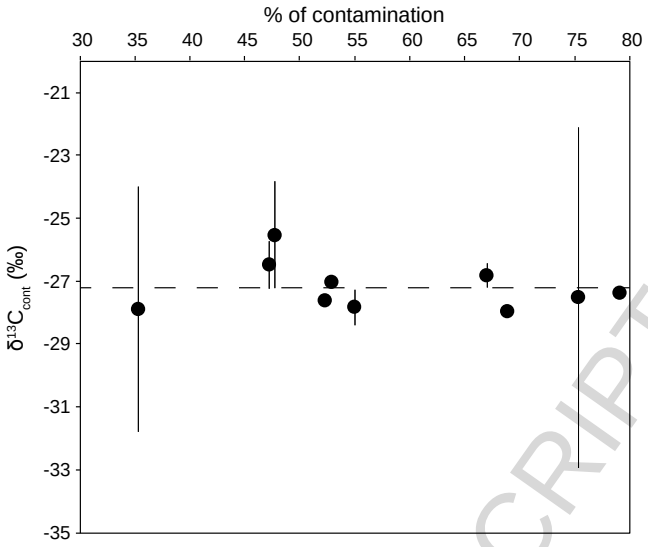

Figure 2. Calculated $\delta^{13}C$ value of the contaminant as a function of contamination proportions in TCDP3 DCM-treated samples. Dashed line indicates average $\delta^{13}C_{cont}$ (i.e. -27.2 ± 0.8 ‰).

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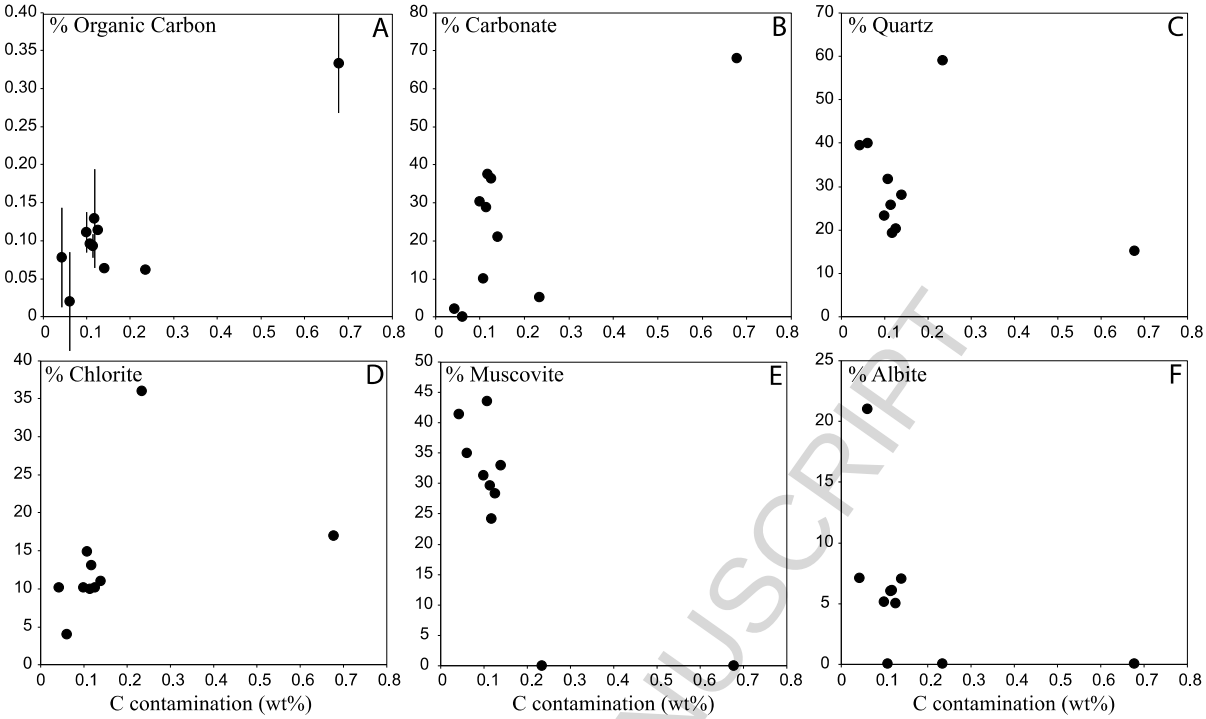

Figure 3. Concentration of C contamination as a function of organic carbon content (A) and mineral proportions (B–F) estimated by XRD analyses in TCDP3 samples. The extent of contamination by dichloromethane–ethanol is not correlated with organic carbon content or the mineralogy of samples.

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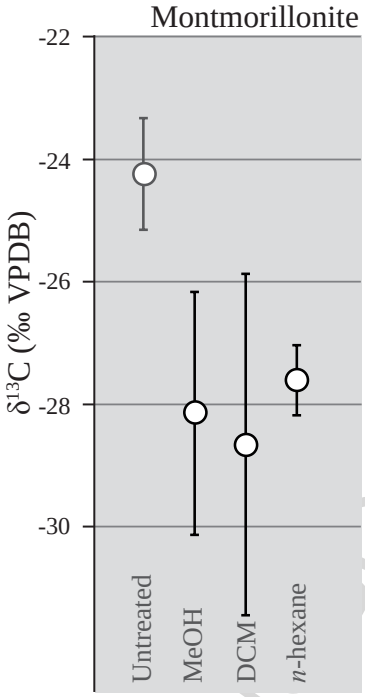

Figure 4. $\delta^{13}C$ values of montmorillonite treated with methanol (MeOH), dichloromethane (DCM) or *n*-hexane compared to the isotopic composition of untreated sample. Note that the $\delta^{13}C$ value of untreated montmorillonite in grey is only approximated (see Table 3 for details).

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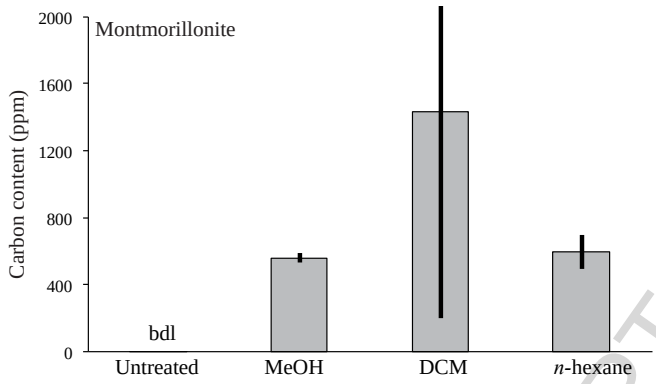

Figure 5. Abundance of organic carbon (ppm) in montmorillonite treated with methanol, DCM or *n*-hexane compared to untreated materials. Note the large difference between untreated material and the different cleanings in the montmorillonite. bdl. below detection limit

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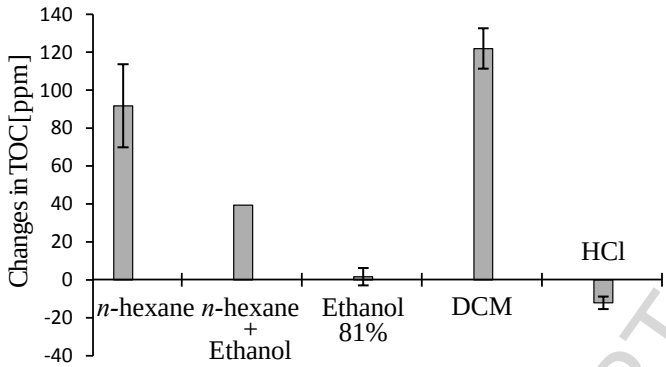

Figure 6. Changes in TOC (ppm) in quartz samples treated with different solvents and HCl acid.

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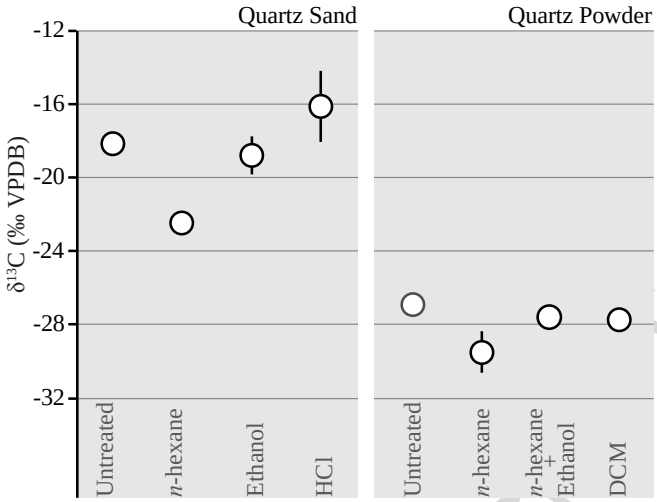

Figure 7. $\delta^{13}C$ values in quartz samples with various grain sizes and after different treatments: (left) sand treated with *n*-hexane, ethanol or HCl and (right) powder treated with *n*-hexane, *n*-hexane with ethanol or dichloromethane (DCM), both compared to the isotopic composition of untreated samples.

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Table 1. Mineralogy of the samples determined by XRD analyses; units in %.

Sample	Lithology	Quartz	Calcite	Ankerite	Chlorite	Muscovite	Albite
T3-76.3	Mudstone	39.4		2.0	10.1	41.4	7.1
T3-93.5	Mudstone + Carbonate	25.7	28.7		9.9	29.7	6.0
T3-100.58	Mudstone + Carbonate	28.0	21.0		11.0	33.0	7.0
T3-115.14	Limestone ± Mudstone	20.2	36.4		10.1	28.3	5.0
T3-135.22	Limestone ± Mudstone	23.2	30.3		10.1	31.3	5.1
T3-141.71	Limestone ± Mudstone	19.2	31.3	6.1	13.1	24.2	6.1
T3-156.6	Mudstone ± Carbonate	31.7		9.9	14.9	43.5	
T3-164.4	Mudstone + pyrite layers	59.0	1.0	4.0	36.0		
T3-182.22	Fe-Oxide carbonates	15.0		68.0	17.0		
T3-183.73	Quartzite	40.0			4.0	35.0	21.0

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Table 2. $\delta^{13}C_{org}$ and TOC measured in TCDP3 samples after DCM treatment and decarbonation or decarbonation alone. The $\delta^{13}C$ value and TOC of the contaminating phase ($\delta^{13}C_{cont}$ and TOC_{cont}) were reconstructed by mass balance calculations (see text). Errors are calculated on duplicate measurements for Acid treatment and triplicate measurements for DCM + Acid treatment.

	DCM + Acid Treatment				Acid Treatment				Contamination				
Samples	$\delta^{13}C$ (‰)	1σ	TOC (ppm)	1σ	$\delta^{13}C$ (‰)	1σ	TOC (ppm)	1σ	Proportion (%)	TOC_{cont} (ppm)	error	$\delta^{13}C_{cont}$ (‰)	error
T3-76.3	-28.4	0.1	1200	0	-28.7	0.9	777	654	35.3	423	1.55	-27.9	3.9
T3-93.5	-27.4	0.1	2067	58	-26.9	0.1	930	156	55.0	1137	0.19	-27.8	0.6
T3-100.58	-27.6	0.1	2033	58	-26.7	0.1	633	25	68.9	1400	0.06	-28.0	0.2
T3-115.14	-27.1	0.1	2400	0	-26.6	0.2	1145	49	52.3	1255	0.04	-27.6	0.1
T3-135.22	-26.86	0.04	2100	0	-27.2	0.5	1109	266	47.2	991	0.27	-26.5	0.8
T3-141.71	-27.12	0.04	2467	58	-28.6	ND	1290	ND	47.7	1177	0.05	-25.5	1.7*
T3-156.6	-27.72	0.03	2033	58	-28.5	0.2	959	8	52.8	1074	0.06	-27.0	0.2
T3-164.4	-27.8	0.1	2967	58	-29.5	0.5	621	18	79.1	2346	0.03	-27.3	0.1
T3-182.22	-26.6	0.2	10100	100	-26.2	ND	3330	ND	67.0	6770	0.01	-26.8	0.4*
T3-183.73	-27.6	0.1	800	0	-27.8	ND	197	ND	75.3	603	0.00	-27.5	5.5*

ND: no duplicate, *calculated with the maximum error obtained on samples.

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Table 3. Average carbon content and $\delta^{13}C$ values measured on kaolinite and montmorillonite samples treated with different solvents; methanol (MeOH), dichloromethane (DCM) and *n*-hexane, compared to untreated materials. If not specified, carbon concentrations and delta values were calculated from triplicate measures. The detailed results are presented in **Supplementary Table 2**. Note that for all the kaolinite samples and untreated montmorillonite, the carbon content is too low (sample intensity equal to blank intensity) to calculate an accurate concentration and to obtain reliable $\delta^{13}C$ values. $\delta^{13}C$ values obtained for those samples (in brackets) are thus uncertain and only given for comparison. The amount of carbon added or removed by the solvent (ΔTOC) calculated from the results are also shown.

		C (ppm)	1σ	$\delta^{13}C$ (‰)	1σ	ΔTOC (ppm)
Kaolinite	Untreated (n=2)	b.d.l.		(-25.38)		
	MeOH	b.d.l.		(-25.45)		< d.l.
	DCM (n=2)	b.d.l.		(-25.32)		< d.l.
	n-hexane (n=2)	b.d.l.		(-25.31)		< d.l.
Montmorillonite	Untreated	b.d.l.		(-24.3)		
	MeOH	562	28	-28.2	2.0	< 562
	DCM	1434	1750	-28.7	2.8	< 1434
	n-hexane	596	102	-27.6	0.6	< 596

b.d.l. (below detection limit)

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Table 4. Average $\delta^{13}C$ values measured in 1) quartz sand untreated and treated with *n*-hexane, ethanol (81 %) or HCl and 2) quartz powder untreated and treated with *n*-hexane, *n*-hexane + ethanol (81 %) or DCM. Changes in TOC (ppm) are calculated as mean values of $TOC_{measured}$ - $TOC_{untreated}$ with $TOC_{untreated}$ of 33.8 ppm in sand and 2.5 ppm in powder.

		$\delta^{13}C$ (‰)	1σ	ΔTOC (ppm)	1σ
Sand	Untreated 33.8 ppm (n=2)	-18.2	0.2	0	2.5
	n-hexane (n=2)	-22.5	0.2	106	22
	Ethanol 81% (n=2)	-18.8	1.0	1.6	9.5
	HCl (n=4)	-16.1	1.9	-12.1	5.2
Powder	Untreated 2.5 ppm (n=1)	-26.9	ND	0	ND
	n-hexane (n=7)	-29.5	1.1	87.6	38.0
	n-hex. + Eth. (n=1)	-27.6	ND	39.4	ND
	DCM (n=2)	-27.8	0.2	122.0	10.6

ND: No duplicate

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HIGHLIGHTS:

– Carbon contamination by organic solvents induces changes in TOC and $\delta^{13}C$ values in low TOC rock samples.

– Contamination rate depends on the solvent used and sample mineralogy.

– Methanol, *n*-hexane and DCM were found to systematically contaminate powdered samples.

– Ethanol is the only solvent that does not seem to contaminate rock samples and even appears to protect against contamination.

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