Subcritical water extraction of organic matter from sedimentary rocks

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HIGHLIGHTS

- Subcritical water extraction of sedimentary rocks can replace solvent extraction.
- 300 °C and 1500 psi represent an effective universal protocol.
- Organic matter types respond differently based on polarities of organic units present.
- Selective extraction of organic compounds is possible using different temperatures.

GRAPHICAL ABSTRACT

Subcritical water extraction of a marine sedimentary rock

ABSTRACT

Subcritical water extraction of organic matter containing sedimentary rocks at 300 °C and 1500 psi produces extracts comparable to conventional solvent extraction. Subcritical water extraction of previously solvent extracted samples confirms that high molecular weight organic matter (kerogen) degradation is not occurring and that only low molecular weight organic matter (free compounds) are being accessed in analogy to solvent extraction procedures. The sedimentary rocks chosen for extraction span the classic geochemical organic matter types. A type I organic matter-containing sedimentary rock produces n-alkanes and isoprenoidal hydrocarbons at 300 °C and 1500 psi that indicate an algal source for the organic matter. Extraction of a rock containing type II organic matter at the same temperature and pressure produces aliphatic hydrocarbons but also aromatic compounds reflecting the increased contributions from terrestrial organic matter in this sample. A type III organic matter-containing sample produces a range of non-polar and polar compounds including polycyclic aromatic hydrocarbons and oxygenated aromatic compounds at 300 °C and 1500 psi reflecting a dominantly terrestrial origin for the organic materials. Although extraction at 300 °C and 1500 psi produces extracts that are comparable to solvent extraction, lower temperature steps display differences related to organic solubility. The type I organic matter produces no products below 300 °C and 1500 psi, reflecting its dominantly aliphatic character, while type II and type III organic matter contribute some polar components to the lower temperature steps, reflecting the chemical heterogeneity of their organic inventory. The separation of polar and non-polar organic compounds by using different temperatures provides the potential for selective extraction that may obviate the need for subsequent preparative chromatography steps. Our results indicate that subcritical water extraction can act as a suitable replacement for conventional...
1. Introduction

The study of organic matter and its storage in the subsurface of Earth has led to a greater understanding of past global biogeochemical processes. The preservation of organic matter in sedimentary deposits represents a direct link to the global cycles of carbon, oxygen and sulphur over geological timescales [1]. Fossil organic matter is primarily the product of selectively preserved biopolymers and newly generated biopolymers collectively termed kerogen, although some information-rich free organic compounds are also present in the organic inventory [2]. To access information contained within fossil organic matter in sedimentary rocks, a method of extracting the organic matter is required. The development of extraction techniques has progressed over decades of dedicated research [3]. The use of organic solvents as extracting agents is the standard method in the area of geochemistry [4,5].

The use of organic solvents, however, has some negative aspects. The production of organic solvents is often difficult, time consuming and expensive. Once produced, organic solvents represent a substantial health hazard to those who work with them. Organic solvents are also potential contaminants of the environment. The deleterious effects of organic solvents have inspired the search for alternative solvents that can be used for extraction of organic compounds from rocks. Supercritical carbon dioxide has showed promising results [6–8] and non-ionic surfactants have been shown to be capable of extracting hydrocarbons from petroleum source rocks [9].

Perhaps the most cost-efficient and least hazardous material to use for extraction is water. Yet at room temperature and pressure water is capable of only extracting polar organic compounds. Fortunately, water can be modified to improve its performance for organic extraction. For example, steam has been used to extract hydrocarbons from petroleum source rocks [10] and subcritical water has been utilised to extract organic materials from Atacama Desert soils [11,12]. Recent work has compared the efficiency of subcritical water extraction alongside organic solvent and surfactant-assisted methods [13] where subcritical water extraction outperformed the aqueous based method involving surfactants, but still lagged behind organic solvent extraction in terms of efficiency.

Subcritical water provides great flexibility during organic extraction. The dielectric constant of liquid water changes with temperature allowing control over its ability to solvate organic compounds of different polarities. The flexibility of subcritical water presents the potential to manipulate conditions to meet the requirements of different organic mixtures. The possibility of tailored extraction is important for sedimentary organic matter because of the varieties present in nature. The ultimate sources of sedimentary organic matter are biological materials such as lipids, lignin, carbohydrates and proteins from plants, algae and bacteria. Variation in the relative contributions from the source organisms leads to different types of organic assemblage [2]. Type I organic matter is dominated by algal remains and typically reflects lacustrine environments. Type III organic matter contains land plant remains, usually in terrestrial or near terrestrial settings. Type II organic matter is intermediate in composition and is found in marine settings. Each type of organic matter is chemically different and, therefore, can be expected to respond in a distinct fashion to extraction protocols.

Once extracted from sedimentary rocks, organic mixtures can be prepared for analysis by analytical instruments. Preparation usually involves column or thin layer chromatography where the polarity of organic compounds is exploited to achieve separation into chemical fractions by elution with organic solvents of varying elution strengths. The resulting fractions can be further separated into individual components by techniques such as gas chromatography. Some extraction techniques are relatively selective so that subsequent preparative chromatography is unnecessary. One example of this approach is provided by supercritical carbon dioxide extraction of carbonaceous meteorites where post extraction preparative steps, and the associated potential loss of already small amounts of valuable extracted material, could be avoided [8].

In this paper we examine the conditions required to extract different types of sedimentary organic matter with subcritical water. Our aim was to develop a replacement for organic solvents for the extraction of organic matter from any mineral matrix and therefore produce a method that can be applied to materials such as soils, recent sediments and sedimentary rocks. Sedimentary organic matter of types I, II and III have been subjected to various temperatures and pressures. Diversity in polarity of organic compounds within some sedimentary organic matter types suggest that fine-tuning the dielectric constants of water provides the opportunity for selective extraction that could eliminate post-extraction fractionation steps prior to further analytical steps.

2. Experimental

2.1. Samples

Sedimentary rocks containing three different types of organic matter were used for subritical water extraction experiments (Table 1). Each sample was washed with solvent (95:5 dichloromethane/methanol (DCM/MeOH) and crushed before initiating the extraction procedure. High performance liquid chromatography (HPLC) grade DCM and MeOH were sourced from Fisher Scientific, UK. The DCM/MeOH wash should have removed any unwanted substances such as plasticisers and surface contaminants from the sedimentary rocks. The samples were then crushed to fine powders and weighed using an analytical balance.

| Sample                                                                 | Organic matter type | Organic matter or carbon content |
|------------------------------------------------------------------------|---------------------|----------------------------------|
| Lower Carboniferous shale, Port Edgar, Midland Valley Scotland, UK     | Type I              | TOC% = 13.43                     |
| Upper Jurassic shale, Kimmeridge Clay, Kimmeridge Bay, UK              | Type II             | TOC% = 3.27                      |
| Upper Carboniferous high volatile bituminous coal, Daw Mill, Warwickshire, UK | Type III            | C% = 81.3                        |
2.2. Organic solvent extraction

Three millilitres of 93:7 DCM/MeOH was added to pulverised source rock samples before sonication using a Sonics & Materials Inc., VCX-130 Vibra-Cell™ ultrasonic processor with a maximum frequency of 20 kHz for 10 min at room temperature. Subsequent centrifugation for 5 min at 2500 rpm effectively settled any suspended sample particles. The solvent supernatants were combined and the total extract was filtered using syringe filters possessing polytetrafluoroethylene (PTFE) membranes with a 0.2 μm pore size. A stream of nitrogen gas was used to reduce filtered supernatants to aliquots of 1 mL and the extracts were transferred to 2 mL vials for analysis. Each sample extraction was performed in triplicate.

2.3. Subcritical water extraction

Fresh pulverised samples were subjected to subcritical water treatment in a purposely built extraction system (Fig. 1). The whole system is an assembly of three main parts housed inside a gas chromatograph oven: a syringe pump, a sample cell and a cooling coil connected to a collection point. Deionised water was first flushed through the entire system and once the system was filled with water the outlet valve and the eluent valve were closed. The oven was then set to a defined temperature. Temperature is by far the dominant control on variability in the dielectric constant of water [14], hence in our experiments we varied temperature but maintained pressure at a standard level to ensure the heated water remained in the liquid state. To stabilise internal pressure at 1500 psi during heating the inlet valve remained open during the temperature ramp and for an additional 5 min after the set temperature was attained. The mode of extraction in the study was static and water remained in the isolated system for set durations. To study the effects of temperature, static extraction duration was fixed at 20 min for 150 °C, 200 °C, 250 °C and 300 °C. To study the effects of duration, extraction at 300 °C was also performed for 30 min, 40 min and 50 min. At the end of the extraction time both the outlet valve and collection point valve were opened simultaneously. The eluent was collected in a large conical flask. The conical flask contained at least 20 mL of DCM prior to eluent collection allowing analytes to readily partition into the organic layer. 10 μL of internal standard (IS) solution of squalane and p-terphenyl (1.156 mg/mL and 0.248 mg/mL, respectively) was added to the DCM organic layer before the eluent was collected. Extraction at 300 °C for 20 min was performed in triplicate to enable calculation of standard deviations. To confirm that the subcritical water extraction procedure was exclusively accessing the soluble organic matter, rather than also releasing compounds by degrading the insoluble high molecular weight kerogen, previously solvent extracted samples were also subjected to subcritical water treatment at 300 °C.

2.4. Post-subcritical water extraction treatment

The eluent and DCM in the conical flask were transferred to a separating funnel where they were shaken and allowed to stand until two distinct phases formed. The more dense bottom layer of DCM was then collected. Another 10 mL portion of DCM was added to the aqueous layer and the liquid–liquid extraction procedure repeated. The DCM layers were combined and treated with anhydrous magnesium sulphate (Fluka, Japan puriss grade ≥98% purity) to remove any traces of water. The volume of DCM solution was reduced on a rotary evaporator and the final extract transferred to pre-weighed vials.

2.5. Extractable organic matter yields

Total yields of extractable organic matter (EOM) of the three different types of sedimentary rocks were calculated using the following approach:

\[
\%\text{EOM} = \frac{EOM_{\text{total}(g)}}{M_{\text{rock}(g)}} \times 100
\]

where \(\%\text{EOM}\) = percentage extractable organic matter, \(EOM_{\text{total}}\) = total extractable organic matter expressed in grams and is the sum of all extracted and identified organic compounds, \(M_{\text{rock}}\) = the mass

![Diagram](https://via.placeholder.com/150)

**Fig. 1.** A schematic representation of the subcritical water extraction system [13]. Briefly, the syringe pump transfers deionised water from the reservoir through a pre-heating coil then to sample cell. The eluent, containing the extracted organic compounds, is passed through a cooling coil before being collected in a flask of organic solvent.
of finely ground types I, II or III organic matter-containing sedimentary rocks in grams.

2.6. GC–MS analyses

Analyte separation was achieved using an Agilent Technologies G3172A gas chromatograph fitted with an Agilent HP-5MS column (29.55 m × 250 μm × 0.25 μm). Helium carrier gas flow rate was 1.1 mL/min. Injection volume was 1 μL and injection mode was splitless. The front inlet temperature was 250 °C and the oven temperature programme was held for 1 min at 50 °C followed by a temperature ramp of 4 °C min⁻¹ to 310 °C, where the temperature was held for 20 min. Total run time was 86 min. Analyte identification was performed using an Agilent Technologies 5973 Mass Selective Detector set in full scan mode and employing a mass range from 50.0 to 550.0 amu. The ionisation source temperature was maintained at 230 °C and mass analyser quadrupole temperature was 150 °C. A nine minute solvent delay was employed. Mass spectra were interpreted by reference to the NIST 2008 mass spectral database. The results are quantitative in that the intensity of an ion is a measure of the response of a compound to the conditions in the mass spectrometer and quantitation relies on comparisons of the relative abundances of compounds or standards present in similar amounts and with identical ionisation efficiencies.

3. Results

3.1. EOM and reproducibility

Subcritical water extraction of solvent extracted rocks produced no organic compounds confirming that the process does not degrade the high molecular weight kerogen present within the samples. The data therefore can be considered as exclusively representing relatively low molecular weight organic compounds, in an analogous fashion to conventional DCM/MeOH extraction. Direct comparison of EOM obtained from organic solvent and subcritical water is possible (Table 2). Relative to organic solvent, the extraction efficiency of subcritical water at 300 °C and 1500 psi is less for type I organic matter but greater for type III organic matter. The chemistry of the organic matter content is exerting a clear control on subcritical water extraction efficiency.

The range of temperatures over which organic matter can be extracted from the different organic matter types displays substantial variability (Table 2). The type I organic matter is only extractable at the highest temperatures with no EOM below 300 °C. Organic matter in type II and type III samples are extractable at all temperatures but with the greatest amount recovered at 300 °C. With 300 °C representing the most efficient extraction conditions for all samples, perhaps the most discriminatory observation is the relative amount of organic matter that can be extracted at low temperatures. Low temperature extraction efficiency decreases in the order type III > type II > type I. The ability of different organic matter types to contribute across all temperature steps is undoubtedly related to the heterogeneity of organic compound types in the various inventories. Type I organic matter is dominantly aliphatic, type III organic matter is a mixture of aliphatic, aromatic and polar compounds, while type II organic matter has an intermediate composition.

3.2. Type I organic matter

Our representative sample of type I organic matter was a Lower Carboniferous lacustrine shale. Direct injection of the DCM/MeOH solvent extract without further fractionation provides an insight into the total EOM present in the rock. The DCM/MeOH extract contained a series of normal alkanes from C₁₅ to C₃₅, with a mode around C₂₅ indicating an algal source for the organic matter (Fig. 2a). Isoprenoidal hydrocarbons were represented by pristane and phytane. Cyclic terpanes were represented by a series of hopenanes and steranes. There were relatively few aromatic or polar compounds in the DCM/MeOH extract indicating an overall aliphatic hydrocarbon-rich sample. Data are consistent with previous work that has examined the organic geochemical constitution of these rocks [15].

Subcritical water extraction of type I organic matter produced different responses with temperature of extraction (Fig. 3). None of the abundant aliphatic compounds observed in the DCM/MeOH extract were evident at temperatures between 150 °C and 250 °C. At 300 °C, however, the majority of aliphatic compounds observed in the DCM/MeOH extract appear in the subcritical water extract. DCM/MeOH extraction does appear to recover more of the components that contribute to the unresolved complex mixture compared to supercritical water at 300 °C.

3.3. Type II organic matter

Our representative sample of type II organic matter was an Upper Jurassic shale. The DCM/MeOH extract contained a series of normal alkanes from C₁₅ to C₃₅, with a mode around C₂₃ indicating an algal source for the organic matter (Fig. 2b). Isoprenoidal hydrocarbons were again represented by pristane and phytane and cyclic terpanes by a series of hopenanes and steranes. A significant unresolved complex mixture indicates the presence of aromatic and polar compounds indicating a partial contribution from terrestrially derived organic materials. Our data are consistent with previous studies that have shed light on the organic constituents of Kimmeridge Clay type II organic matter, and it is known to contain aliphatic, aromatic and sulphur compounds [16,17].

Subcritical water extraction of type II organic matter produced different responses with temperature of extraction. Few of the compounds observed in the DCM/MeOH extract were evident at temperatures between 150 °C and 250 °C (Fig. 4). There were numerous low molecular weight aromatic compounds at temperatures of 200 °C and above (Fig. 4b). Some of the compounds present between 150 °C and 250 °C are polar acids. The low molecular weight aromatic compounds probably reflect significant contributions of land-derived organic matter known to occur in type II organic matter.

Table 2

| Temperature (°C) | Type I EOM (%) | Type II EOM (%) | Type III EOM (%) |
|-----------------|----------------|----------------|-----------------|
| Subcritical water |                |                |                 |
| 150             | 0.000          | 0.001          | 0.0007          |
| 200             | 0.000          | 0.002          | 0.017           |
| 250             | 0.000          | 0.004          | 0.033           |
| 300             | 0.0103 (±0.0055) n = 3 | 0.0087 (±0.0006) n = 3 | 0.0483 (±0.0080) n = 3 |
| Organic solvent |                |                |                 |
| DCM/MeOH        | 0.0533 (±0.0058) n = 3 | 0.0003 (±0.0001) n = 3 | 0.0247 (±0.0103) n = 3 |
Moreover, the low molecular weight aromatic hydrocarbons and acids display relatively high solubilities in water. At 300 °C the subcritical water extract displays concordance with the DCM/MeOH extract from the same sample (Fig. 4d). The majority of aliphatic, aromatic and polar compounds observed in the DCM/MeOH extract appear in the subcritical water extract.

3.4. Type III organic matter

Our representative sample of type III organic matter was an Upper Carboniferous high volatile bituminous coal. The DCM/MeOH extract contained a range of alkylated aromatic, phenolic and oxygen-containing aromatic compounds (Fig. 2c). Isoprenoidal
Fig. 3. Subcritical water extract of a type I organic matter containing sample at (a) 150 °C, (b) 200 °C, (c) 250 °C and (d) 300 °C. The isolation of extractable hydrocarbons was most efficient at 300 °C and produced long chain saturated hydrocarbons as well as the isoprenoidal hydrocarbons pristine and phytane. Vertical scales normalised to the highest peak.
Fig. 4. Subcritical water extract of a type II organic matter containing sample at (a) 150 °C, (b) 200 °C, (c) 250 °C and (d) 300 °C. Increasing temperature led to change in dielectric constant of water and the extraction of different classes of organic compounds. Vertical scales normalised to the highest peak.
hydrocarbons were represented by phytane. Our data are consistent with previous studies that have investigated the organic constituents of high volatile bituminous coals [18].

Subcritical water extraction of type III organic matter produced different responses with temperature of extraction. Significant amounts of organic compounds are extracted at even the lowest temperature. At 150 °C the subcritical water extract contains a number of low molecular weight alkylated aromatic units (Fig. 5a). At 200 °C the responses alkylated and oxygen-containing aromatic units become more obvious and there are more contributions from higher molecular weight units (Fig. 5b). Above 200 °C the responses alkylated and oxygen-containing aromatic units increase further (Fig. 5c). Contributions from higher molecular weight units become even more significant at the highest

Fig. 5. Subcritical water extract of a type III organic matter containing sample at (a) 150 °C, (b) 200 °C, (c) 250 °C and (d) 300 °C. Increasing temperature led to a change in the dielectric constant of water solvent and the extraction of different classes of organic compounds. Vertical scales normalised to the highest peak.
The temperature of 300 °C and the aromatic responses are joined by aliphatic contributions (Fig. 5d).

3.5. Duration of extraction time

To assess the influence of extraction time the duration of static heating was varied from 20 to 50 min for each sample while maintaining the extraction temperature and pressure at 300 °C and 1500 psi. EOM values were used to enable an assessment of extraction time on yield (Table 3). The length of extraction time has minimal impact on the yield of extracted hydrocarbons from sedimentary rocks containing type I organic matter. EOM values for 20, 30, 40 and 50 min treatment with hot water show only very minor differences between them and there is no clear indication of a benefit from extending extraction duration beyond 20 min. The observation of similar extraction yields for various temperatures was also the case for the type II organic matter containing sample. The type III organic matter containing sample also displays constant yields from experiments with 20–40 min extraction duration, but when a duration of 50 min was used the yield declined.

4. Discussion

4.1. Organic matter type and temperature

Subcritical water extraction is an effective technique for the isolation of hydrocarbons and related compounds from sedimentary rocks. Yet the efficiency of extraction is highly dependent on the temperature used and the type of organic matter present in the rocks. If the temperature at which extractable organic matter appears is examined, the influence of organic matter type becomes evident (Figs. 3–5; Table 2). The temperature at which extractable organic compounds appear is lowest for type III organic matter (150 °C), intermediate for type II organic matter (200 °C) and highest for type I organic matter (300 °C).

The influence of temperature on the ability to extract organic matter of different types can be explained by the increase in overall polarity of the organic inventories moving from type I to type III. At room temperature, polar organic compounds are more soluble in water than non-polar compounds. As temperature increases, the dielectric constant of water decreases and the ability of water to solvate non-polar compounds is enhanced. Hence, at low temperatures (150 °C) the polar compounds in type III organic matter are extracted by water, which has a dielectric constant around 45 equivalent to somewhere between acetonitrile and dimethyl sulfoxide (Fig. 6). At moderate temperatures (200–250 °C) low molecular weight aromatic units are extracted from type II organic matter, when the water has a dielectric constant between 40 and 32 equivalent to somewhere between dimethyl sulfoxide and methanol (Fig. 6). At relatively high temperatures (300 °C) the non-polar compounds in type I organic matter are extracted, when the water has a dielectric constant of 20 close to that of acetone (Fig. 6).

The efficiency of extraction and its relationship to temperature can be examined quantitatively by reference to the EOM data. For type I organic matter, significant EOM is only observed at the highest temperature of 300 °C (Table 2). In the extractions of type II organic matter there is a four-fold increase in the EOM from 200 °C to 300 °C (Table 2). For type III organic matter there is a two-fold increase of EOM between 200 °C and 300 °C (Table 2). A trend of increasing EOM with temperature is evident for all organic matter types but is least conspicuous for those organic matter types with chemical heterogeneity (type II and especially type III) where the range in polarities of components provide contributions to each temperature stage.

For general extractions, higher temperatures are more efficient for these hydrocarbon-rich rocks and, although lower temperatures provide significant yields for certain types of organic matter, 300 °C and 1500 psi represent a useful universal extraction protocol for organic matter-rich rocks.

4.2. Extraction duration

Overall the optimal duration for subcritical water extraction of all organic matter types found in sedimentary rocks is 20 minutes. Longer extraction times do not necessarily correlate to higher

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**Table 3**

| Duration (min) | Type I EOM (%) | Type II EOM (%) | Type III EOM (%) |
|---------------|-----------|--------------|-----------------|
| 20            | 0.010     | 0.009        | 0.048           |
| 30            | 0.012     | 0.005        | 0.067           |
| 40            | 0.009     | 0.006        | 0.009           |
| 50            | 0.012     | 0.008        | 0.055           |

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Fig. 6. Change in dielectric constant of water as a function of temperature. At relatively moderate temperatures (200 °C) the polar compounds in types II & III organic matter are extracted by water, which has a dielectric constant of 35, equivalent to somewhere between acetonitrile and methanol; at relatively high temperatures (300 °C) the nonpolar saturated hydrocarbons in types I, II and III organic matter are extracted, when the water has a dielectric constant of 20, close to that of acetone.
yields of EOM (Table 3). For sedimentary rocks containing types I and II organic matter, variation in extraction duration with hot water produces negligible effects. For sedimentary rocks containing type III organic matter, very long extraction durations lead to a decline in yield. The variation in sensitivity to duration of subcritical water extraction for the different organic matter types is most likely related to chemical structure. Type I and type II organic matter assemblages contain substantial amounts of aliphatic structures while type III organic matter is dominated by aromatic units. Oxidation of aromatic constituents during lengthy subcritical water extraction experiments is a previously recognised issue [13] and may account for the drop in yield for type III organic matter-containing sedimentary rocks observed for the longest extraction times (Table 3).

4.3. Potential for selective extraction

Compounds that make up the organic inventory of sedimentary rocks can display differences in polarity. The variable polarities in organic mixtures is exploited in post extraction fractionation steps which isolate compound classes based on their similarity to elution solvent strength. Inevitably the use of post extraction fraction steps make compound isolation more expensive, lengthy and labour intensive. Subcritical water extraction provides the ability to modify temperature and therefore dielectric constant and solvent strength. Our data reveal that selective extraction by subcritical water extraction is a possibility for organic matter-containing sedimentary rocks. Polar organic compounds are usually problematic for gas chromatography-based analysis because their polar and reactive nature can cause them to perform badly during chromatographic separation and can even irreversibly damage instrument components. The extraction of polar compounds at lower temperatures followed by the subsequent selective extraction of analytically amenable non-polar compounds at higher temperatures presents a means to avoid post extraction fractionation steps.

5. Conclusion

The experimental results in this study represent one of the very few case studies of hot water extraction of hydrocarbons from organic-rich rocks. The data provide evidence that subcritical water can act as an efficient substitute for the more hazardous and commonly used organic solvents. A universal extraction protocol for all organic matter types in sedimentary rocks includes a temperature of 300 °C, pressure of 1500 psi and duration of 20 min. The ability to control temperature and therefore dielectric constant of water also provides the opportunity to selectively extract specific compound classes thereby avoiding lengthy and labour intensive post extraction fractionation steps prior to detailed analysis by gas chromatography and mass spectrometry.

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