

## Organic chemical signatures of New Zealand carbonate concretions and calcite fracture fills as potential fluid migration indicators

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### Abstract

Macroscopic calcite crystals are common in sedimentary strata, occurring both as tectonic veins and also filling one or more generations of septarian rupture or later brittle fractures in calcareous concretions. Traces of hydrocarbons are frequently present in calcite crystals, especially near active petroleum systems, and are routinely the object of fluid inclusion studies linking source and migration pathway. Such calcites are shown here also to contain fatty acids in widely varying amounts ranging from 0.2 to more than 5  $\mu\text{g/g}$ . Vein calcites examined are typically near the lower figure, close to analytical blank levels, and this is also true of some concretionary fracture fill calcites, notably those from the Palaeocene Moeraki 'boulders'. Other concretionary fracture fill calcites (Jurassic, Scotland; Eocene, Waikato Coal Measures and associated marine strata) have much higher fatty acid contents, especially those filling later brittle style fractures. Although usually less abundant than the fatty acids in the concretions themselves, they lack the long chain *n*-acids derived from terrestrial vegetation and are commonly dominated by dioic acids. Exceptionally, in the calcitic septarian fill of a sideritic Coal Measures concretion, their abundance far exceeds that of concretion body fatty acids. They appear to be fluid transported, probably in aqueous solution, and have molecular signatures potentially distinctive of maturing organic matter sources from which the fluids derived.

### Keywords

calcite, siderite, fatty acids, concretions, septarian, fractures, geofluids, hydrocarbons

### Introduction

Calcite is a common filling and cementing mineral in sedimentary strata, occurring both in tectonic veins and also filling one or more generations of septarian fractures in calcareous concretions. Traces of hydrocarbons are frequently present in calcite crystals, especially near active petroleum systems,

and are routinely the object of fluid inclusion studies linking source and migration pathway (e.g. Volk et al., 2005; Hall et al., 1997). However, fluid inclusions may be absent or small and consequently difficult to study. Average hydrocarbon abundance in macroscopic calcite is naturally very low because of minute oil and aqueous phase miscibility. On the other hand, Pearson et al. (2005) have shown that calcite fracture fills lacking significant fluid inclusions in Jurassic concretions can contain substantial amounts of fatty acids, presumed to be bound in salt form at either inter- or intra-crystalline sites. Dissolving the calcite in mineral acid releases free fatty acids amenable to chromatographic analysis. Pearson and Nelson (2005) studied a range of calcite fracture fills encompassing tectonic veins, early brown and later yellow/white septarian sparite fills and concretion body micrites and microsparites. Widely varying abundances of fatty acids were found and discussed therein. In this article we present quantitative fatty acid abundances for selected concretion body, early brown calcite and later yellow/white calcite sample sets (including new Scottish Jurassic data) and focus on a Waikato Coal Measure sideritic septarian concretion as an illustration of trapped fatty acids and their possible application as a signature for migrating fluids.

A new model for the origin of septarian structure and its timing is discussed in detail in Hendry et al. (2006). Of particular relevance is their conclusion that early ruptures (septarian cracks proper), now filled or partly filled with brown calcite, probably develop prior to most carbonate cementation of the associated concretion body. Fibrils of bacteria colonising spheroidal volumes of soft sediment impart sufficient rigidity for shrinkage tears to develop as water loss accompanies bacterial degradation in the near sediment surface. Residual bacterial mucilage engulfed as carbonate cement grows in the developing ruptures is responsible for the brown colouration and high polar organic content of the early brown calcite. Yellow/white calcite often fills residual rupture volumes and is the sole filling of other fractures (sometimes present)

that do not taper and crosscut the brown calcite-filled ruptures. They have geometries more typical of brittle fractures and are therefore later features, post-dating carbonate lithification of the concretion.

### Samples and Methods

Fig. 1a illustrates classic septarian structure in which both early brown and later white calcites sequentially fill the ruptures. In this example brittle fractures are absent and ruptures represent an internal shrinkage of around 40%. Fig. 1b is the sideritic concretion AW1 described by Pearson and Nelson (2005) from Waikato Coal Measures near Huntly (Awaroa opencast, Rotowaro) with atypical septarian fracture of low crack volume, having features of both shrinkage and brittle fracturing, and a single calcite fill. Reddening of AW1 is superficial due to surface weathering and internally the body siderite is dark grey and the calcite almost white (very pale yellow). Other samples reported here come from the Jurassic of central southern England (courtesy J.D. Hudson,

University of Leicester, locality details in Pearson et al., 2005) and Staffin, Isle of Skye, Scotland (locality details in Pearson et al., 2005). New Zealand samples comprise a slice of Moeraki 'boulder', Palaeocene, Oamaru (courtesy D. Lee, University of Otago) and concretions from the Eocene Waikato Coal Measures and overlying Rotowaro Siltstone (Rotowaro opencast sites, sampling courtesy of Solid Energy). All samples except the Coal Measures sideritic concretion are calcitic and of marine depositional origin.

Fatty acids were extracted by procedures detailed in Pearson et al. (2005) as modified by Pearson and Nelson (2005). Briefly, chlorinated solvent extracts after decomposition of carbonate with HCl were fractionated into lipids and polars in a two phase solvent system. After methylation, lipids were further separated by thin layer chromatography to yield fatty acid methyl esters (FAMES). Analysis was by GCMS using an  $nC_{17}$  FAME internal standard.

### Fatty Acid Abundance and Molecular Distribution

Selected fatty acid abundances for five concretion body and fracture fill triplets or pairs are plotted in Fig. 2. These vary widely from 0.2 to more than 5  $\mu\text{g/g}$ . Vein calcites examined (data not shown) are typically near the lower figure, close to analytical blank levels, and this is also true of some concretionary fracture fill calcites, notably those from the Palaeocene Moeraki 'boulders'. Other concretionary fracture fill calcites (Jurassic, Scotland; Eocene, Waikato Coal Measures and associated marine strata) have much higher fatty acid contents, especially those filling later brittle style fractures. Although usually less abundant than the fatty acids in the concretions themselves, they lack the long chain  $n$ -acids derived from terrestrial vegetation and are commonly dominated by di-acids. Exceptionally, in the calcitic septarian fill of sideritic Coal Measures concretion AW1, their abundance far exceeds that of concretion body fatty acids.

An approximate indication of the different structural types and molecular range is provided in Fig. 2 by the colour bars representing the selected acids. Although this necessarily involves some simplification of information from the chromatograms, it makes inter-sample comparison easier. Full fatty acid ion chromatograms are shown in Fig. 3 for AW1 concretion body siderite and septarian calcite fill.

Long chain  $n$ -acids, represented in Fig. 2 by  $nC_{28}$ , and minor  $nC_{29}$  alkanes, derive mainly from terrestrial



**Fig 1:** (a) Septarian concretion (locality unknown) showing classic development of ruptures and two phases of calcite fill. (b) Siderite concretion AW1 from Waikato Coal Measures with calcite filled septarian fractures.

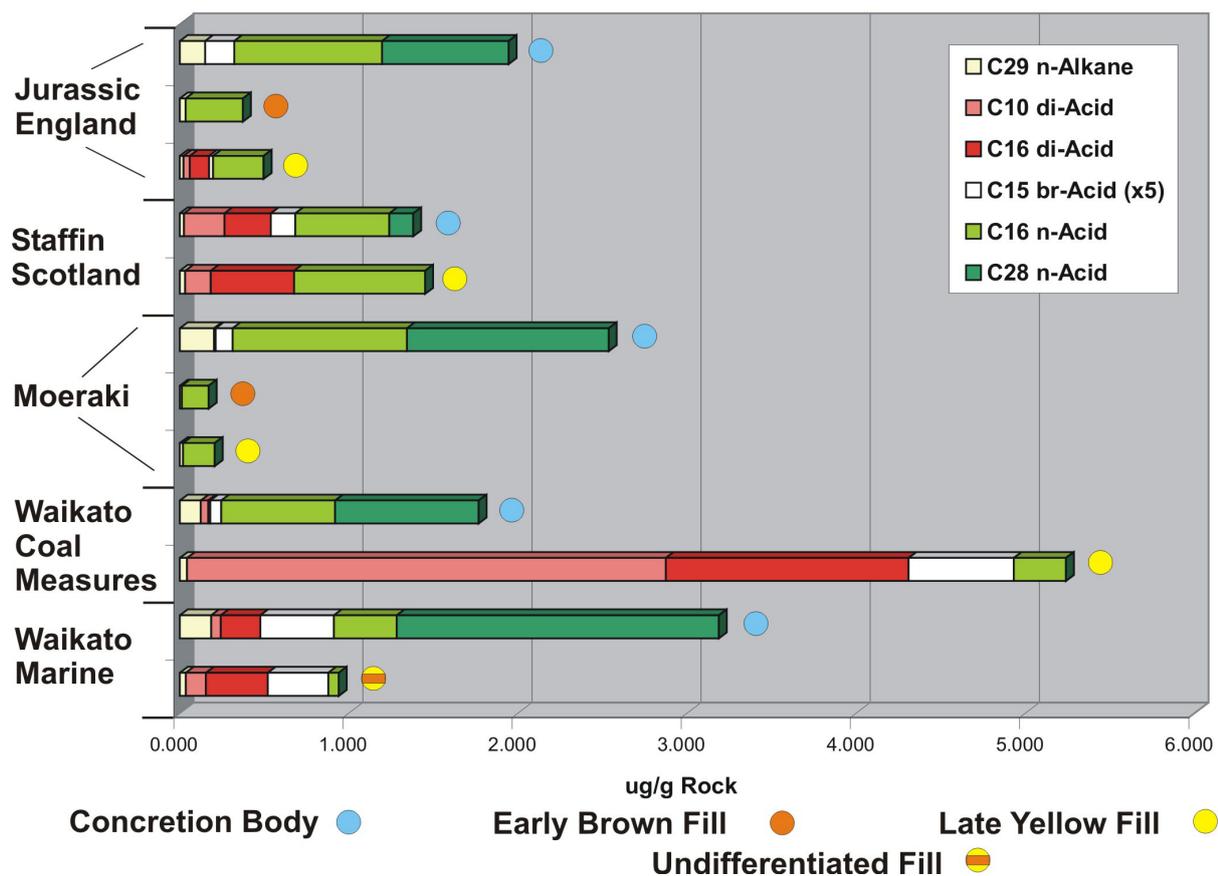


Fig. 2: Selected fatty acid abundances in concretions and corresponding septarian fracture fills from localities described in Pearson and Nelson (2005) and Pearson et al. (2005)

plant waxes and are found only in the concretion body extracts. This is easily understood because concretion body extracts have a mixed origin. They comprise both the solvent soluble part of concreted host mudrock kerogen (original sedimentary organic matter of both water column and terrestrial origin entombed in the concretion) and lipids (including fatty acids) trapped within body calcite microspar crystals. Even though brown calcite fill contains probable bacterial biomass, true detrital kerogen is clay-associated and absent, as also from the later yellow/white calcites. Plant wax derivatives are therefore not found in fracture fill calcites.

Short chain *n*-acids, represented by  $nC_{16}$ , have a multitude of origins, being present even in reagent blanks, and although universally present are non-diagnostic of source.

On the other hand, both medium and short chain di-acids occur, at first sight randomly, in some late yellow calcites and some concretion bodies but are not prominent in any early brown calcites. They may occur in the late yellow calcite and not in the corresponding concretion body (e.g. Jurassic, England) or vice-

versa (e.g. Northland concretion BP2 in Pearson and Nelson, 2005). Our current model for septarian concretion formation (Hendry et al., 2006) allows for pervasive calcite replacement of bacterial biomass in the proto-concretion body and/or calcite infilling of residual porosity continuing during sediment burial over 10s to perhaps 100s of m. It is consistent with this model that concretion body calcification may overlap brittle fracturing and growth of the later yellow calcite fill, though equally it may be complete before then. A logical interpretation of the occurrence of the di-acids therefore is that they are transported, perhaps as fatty acid salts, from an external source by fluids responsible for the late yellow calcite fill. Water solubility of short chain fatty acids is high, decreasing rapidly with chain length and negligible above  $C_{18}$ . Although the solubility of di-acids and their salts is higher than corresponding *n*-acids, they exhibit the same declining trend with molecular size which may account for the absence of long chain acids of any structural type in fracture fill calcites.

### Hydrocarbons and Maturity

Pearson and Nelson (2005) reported a full range of alkane biomarker maturity parameters for concretion  
2006 New Zealand Petroleum Conference Proceedings 3

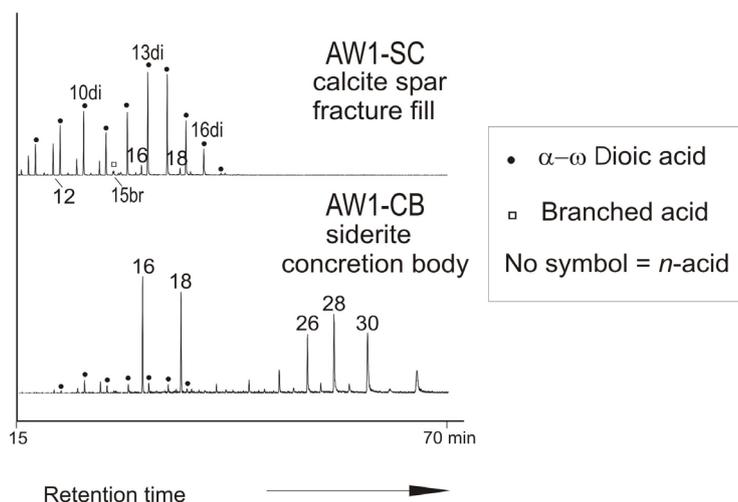


Fig. 3: Fatty acid signatures (GCMS  $m/z$  74+98) of AW1 siderite concretion and corresponding calcite septarian fracture fill.

body and fracture fill lipid extracts. Concretion bodies are all immature to marginally mature (*sensu* petroleum generation: Tissot and Welte, 1984) while those fracture fill calcites examined appear to be at least marginally mature. Fig. 4 illustrates hydrocarbon ion chromatograms for the same AW1 siderite body and fracture fill calcite whose fatty acid chromatograms appear in Fig. 3. This Coal Measures sideritic body (AW1-CB) is significantly more mature than most other concretions analysed. Its hopane S/S+R ratio is fully equilibrated and  $\alpha\beta$  steranes are dominant, but it has residual odd-even predominance in the  $n$ -alkane distribution and traces of immature biomarkers (norhopane,  $\beta\beta$  hopane and oleanene). In the calcite fill (AW1-SC) the immature biomarkers and  $n$ -alkane odd-even predominance are absent. The hydrocarbons recovered from this fracture fill are close to the detection limit and lack distinctive source-diagnostic markers: the hopane and sterane signatures are ubiquitous and identical for all fracture fills (both vein and septarian) examined. Likewise maturities vary little: all appear at least marginally oil-window mature irrespective of concretion body maturities.

### Fluid Signatures and Philosophical Comment

In the absence of fluid inclusions large enough to sample, our hydrocarbon data suggest that the scope for biomarker extraction and detection in vein or fracture fill calcites is limited. Recoveries of hydrocarbons are close to detection limit ( $<0.2\mu\text{g/g}$ ) and some interference by solvent contaminants is inevitable. Either because of this, or

otherwise, only ubiquitous steranes and hopanes are observed that carry little or no source information content.

In contrast, substantial amounts of fatty acids are recovered from many of the same fracture fill calcites, in one case (Waikato Coal Measures) much in excess of  $5\mu\text{g/g}$  (the calculated total of selected quantified acids only). Fatty acid signatures of fracture fill calcites are extremely variable and full data are presented in Pearson and Nelson (2005). They lack the long chain  $n$ -alkanoic acids associated with particulate sedimentary organic matter and the absence of other long chain acids is consistent with transport either of the acids or their salts in aqueous solution. The erratic presence or absence of di-acids in both concretion bodies and late calcite fracture fills suggests their entrapment is serendipitous depending on timing of calcite precipitation relative to the release of di-acids to migrating fluids.

While the origin of di-acids is not well established (see Pearson et al., 2005 for discussion) they have been recovered from calcite associated with early mature kerogen in the Green River Formation of the western USA (Burlingame and Simoneit, 1968). Although our data are currently limited and the link is in no sense proven, it seems reasonable to suggest that the high abundance of these acids in the Waikato Coal

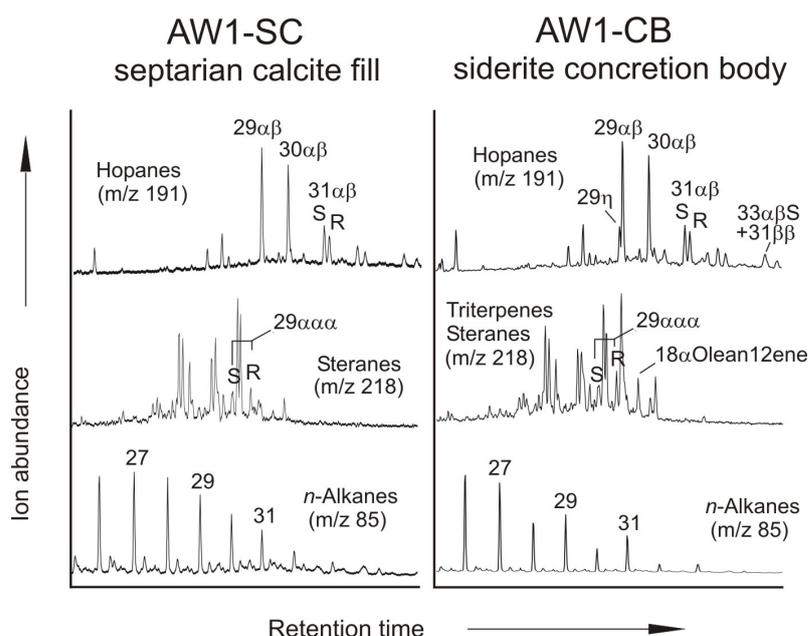


Fig. 4 : GCMS ion chromatograms showing alkane biomarker (hopane, triterpene and sterane) and normal alkane signatures of extracts from Waikato Coal Measures siderite concretion AW1 and corresponding calcite septarian fracture fill.

Measures concretion (AW1) is due to their sourcing by the maturing underlying coals. The molecular distribution of di-acids (Fig. 3) in both the siderite body and late calcite fill of this concretion is almost identical, although their abundance is very different. Likewise the concretion and calcite fill pair from the overlying immature marine formation (AW10, Pearson and Nelson, 2005) have similar di-acid distributions that differ somewhat from AW1. It may be that fracture fills in both these concretions (of non-marine (AW1) and marine (AW10) depositional origin) tapped fluids which were not identical but derived ultimately from the underlying maturing coals. Significantly, corresponding calcite fill from the Moeraki concretion (immature marine formation with no coals or other maturing organic source in the vicinity) is almost devoid of fatty acids and di-acids are completely absent (Fig. 2). The Staffin Jurassic concretion (Isle of Skye, Scotland) occurs in strata intruded nearby by Tertiary igneous rocks and although the concreted shales themselves are unaffected and thermally immature it is not unlikely that late crystallising calcites here also tapped fluids circulating in contact with more mature organic matter closer to the igneous centre.

Since fatty acids are known to be an early maturation product of kerogen (Tissot and Welte, 1984), it may be that oil prone source rocks in their maximum expulsion phase leave no detectable fatty acid fluid signature on the migration pathway. Nevertheless, it is to be anticipated that further study of fatty acids trapped in concretion fracture fills and tectonic veins (though significant vein occurrences have yet to be recorded) has the potential to provide information on fluid circulation history during the early to middle burial stages of petroleum basins.

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