

# **Silica diagenesis promotes early primary hydrocarbon migration**

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## **ABSTRACT**

We present evidence that hydrocarbon source rocks can be preconditioned for primary hydrocarbon migration at an early stage of catagenesis by pore-scale processes linked to silica diagenesis. The evidence comes from a detailed petrographic and geochemical study of the Jordan Oil Shale (JOS), an immature to early mature Upper Cretaceous to Paleogene source rock developed on the platform regions of Jordan. Diagenesis of biogenic silica led to silicification of the source rock interval and the growth of chert nodules. Localization of bitumen veins in reaction rims around these nodules is used to argue that silica diagenesis promotes the early mobilization of hydrocarbons from the geochemically identical, disseminated bitumen within the host mudstones. We propose a model in which early-formed bitumen migrated into neo-forming Mode 1 fractures that formed as a result of the crystallization pressure imposed from the growing chert nodule. Hydraulic fracturing occurred under elevated bitumen fluid pressures that approached lithostatic stress values under burial depths of the order of 1000 m. The recognition that silica diagenesis can promote the early migration of neo-forming bitumen raises the possibility that primary hydrocarbon migration may occur earlier and at shallower depths than predicted by solely kinetic modelling approaches wherever silica diagenetic reactions are coeval with catagenesis.

## INTRODUCTION

Primary hydrocarbon migration is the process by which hydrocarbons are expelled from a mature source rock (Magoon and Dow, 1994). Primary migration may occur either via hydraulic fracturing (Mandl and Harkness, 1987) or diffusion through the organic phase (Stainforth and Reinders, 1990; Thomas and Clouse, 1990). Previous studies advocating a dominance of hydraulic fracturing have been based on source rocks at later stages of catagenesis (Parnell and Carey, 1995; Rodrigues et al., 2009). However, there has been a lack of direct samples (e.g. cores) of source rocks at an early stage of catagenesis to provide diagnostic evidence of the critical first stages of mobilisation of the early-formed bitumen (*sensu* Pepper, 2017).

We present the results of a petrographic and geochemical study of 15 cores of the Jordan Oil Shale (JOS). This Upper Cretaceous to Paleogene source rock is widely developed and exhibits maturity values of up to 0.6 Ro in boreholes, representative of early thermal maturation. Maturity values increase eastwards across Jordan, reflecting the burial and later uplift history. Remarkably, therefore, the west-to-east core transects straddle the very earliest stages of catagenesis, where the kerogen phase is just converting to bitumen (Abu-Mahfouz et al., 2019). Previous studies of these cores (Ali Hussein et al., 2014, 2015, Alqudah et al., 2015; Huggett et al., 2017; Hooker et al., 2017; Abu-Mahfouz et al., 2019) described the sedimentology, diagenesis and structure. Here, we focus specifically on the distribution of early-formed bitumen and, in particular, the development of bitumen veins (BVs). These veins are highly clustered within chemically altered ‘reaction rims’ around chert nodules found within the source rock interval. Our aims are to evaluate the physical and chemical

conditions leading to primary hydrocarbon migration at the earliest stages of catagenesis in the JOS and to explain the development of the bitumen vein networks.

## **GEOLOGICAL SETTING**

The JOS is a highly TOC-enriched Upper Cretaceous–Lower Paleogene source rock that was deposited in local, isolated depocentres in a carbonate platform bordering the Neo-Tethys Ocean (Powell and Moh'd, 2011). The area underwent rift flank uplift in the later Neogene following the establishment of the Dead Sea Rift System (Feinstein et al., 2013). This uplift resulted in an eastward tilt from the outcropping rim of JOS at the Dead Sea escarpment, to reach maximum present-day burial depths of just over 1000 m in the east of Jordan towards the Arabian Platform. Representative burial history plots can be found in Abu-Mahfouz et al. (2019, their Fig. 3).

Our study area is located in central and southern Jordan (Fig. 1a; Fig. DR1 in the GSA Data Repository<sup>1</sup>), and is based on 15 fully cored boreholes. The cored intervals encompass the Upper Cretaceous to Eocene intervals of the Belqa Group but the interval of interest includes the upper Al-Hisa Phosphorite (AHP) and lower Muwaqqar Chalk Marl (MCM) (Fig. 1b), where extensive bitumen occurrences have been observed in the cores (Abu-Mahfouz et al., 2019).

The Cretaceous–Paleogene strata of Jordan (Powell & Moh'd, 2012; Huggett et al., 2017) exhibit a complex diagenetic history. Chert beds, chert nodules and displacive carbonate concretions are observed in all 15 cores. Silica diagenesis has been attributed to thermal conversion of biogenic silica (Powell and Moh'd 2011; Huggett et al., 2017). Two types of chert nodules are recognised: (1) an early suite recognisable as such by being cross-cut by early formed calcite veins (Hooker et al., 2017; Abu-Mahfouz, 2019) and compactional deformation of sedimentary laminae,

and (2) a later suite, characterised by reaction rims around their perimeters (Fig. DR2), absence of compactional deformation of host laminae and no evidence of cross-cutting by early calcite veins. These younger chert nodules (Type 2) are, however, cross cut by BVs. They conform to diagnostic criteria of replacive nodule growth (Selles-Martinez, 1996), and form our main study focus.

## **METHODS**

30 samples were collected from the cored intervals of the JOS in systematic transects from the organic-rich mudstone across the nodule reaction rims and into the chert nodules in order to compare textures and compositions along these transects. Samples were examined in thin section and SEM, and subjected to extensive geochemical analysis to establish bulk mineralogical compositions and total organic carbon (TOC). Methods and equipment used for geochemical and petrographic analysis are described in Table DR1.

## **BITUMEN DISTRIBUTION**

Bitumen veins are found within all the cores, predominantly in the upper section of the AHP and the basal sections of the MCM (Fig. 1b), but with an increased intensity eastwards as burial depth increases (Abu-Mahfouz et al., 2019). This interval of concentrated bitumen veins corresponds to the interval with the most extensive development of type 2 chert nodules in all cores (Fig. 2).

Bitumen is observed in two contrasting habits, (1) disseminated throughout the pore network of the cemented, organic-rich mudstone (Fig. 2), and (2) within opening-mode fractures (veins) in the altered regions immediately surrounding the type 2 chert nodules (Fig. 2, DR2), and cross-cutting nodule margins. The bitumen in the disseminated form occurs within intra-skeletal and inter-granular pores that are

largely occupied by organic matter (kerogen), implying a local derivation of the bitumen from the kerogen (see Abu-Mahfouz et al., 2019, for detailed descriptions). The bitumen veins in contrast, range from microvein sizes (apertures of <100 microns) to macroveins with apertures of up to 1 cm, and up to 30cm tall. They are characterised by irregular fracture walls, lack of evidence for any shear displacement, and 100% bitumen fill (Fig. 2). Previous organic geochemical analysis (Abu-Mahfouz et al., 2019) showed that in all the cores, both the matrix disseminated and the vein-hosted bitumen have identical chemical characteristics, implying that only short-range (bed-scale) migration can have occurred in such low permeability fine-grained rocks, and the bitumen for the veins was sourced in the immediate surrounds.

## **REACTION RIMS AROUND CHERT NODULES**

Petrographically, the reaction rims appear to be a transition from the cemented siliceous carbonate mudstone of the main bulk of the source rock, to the >95% SiO<sub>2</sub> composition of the nodules. Ghosts of fossils are seen within these nodules (Fig. 2), implying replacive alteration of carbonate grains to microcrystalline quartz (Maliva and Siever, 1988; Selles Martinez, 1996). The bitumen within the reaction rims is concentrated in the form of micro- or macro-veins, with a corresponding reduction of the disseminated bitumen relative to that in the unaltered source rock (Fig. 2).

SEM imagery shows that there is a progressive increase of microcrystalline quartz across the reaction rims towards the nodule margins, and this phase increasingly occupies pore space, displaces matrix bitumen and replaces carbonate grains (Fig. 3; Fig. DR3-DR5). Quantification of these changes is uncertain, but compositional data (Figs. 2-3; DR3; DR6; Table DR2) shows that the carbonate fraction reduces from typical values of 40-50% within the unaltered host source rock to 30-40% within the

reaction rims. Most significantly, the average TOC value of 14% in the unaltered host reduces to 6% within the reaction rims (Fig. 4; Table DR2).

## DISCUSSION

What does the dramatic reduction in TOC values within the reaction rims imply, and can it explain the distribution of BVs? It is difficult to calculate the precise reduction in porosity corresponding to the observed reduction in TOC values in the reaction rims. Cementation of the host source rock occurred before the replacive chert nodules grew (Huggett et al. 2017), so we can rule out mechanical compaction to explain the compositional change. This is corroborated by the absence of any differential compaction of laminae around nodule margins. Instead, the observed reduction of TOC and the carbonate phases was balanced by the increased silicification in the reaction rims, implying that silicification led to the reduction in TOC. Within nodule centres, this process culminated in an almost complete displacement of the original organic matter and derivative bitumen and the replacement of carbonate fractions by microcrystalline quartz, with minor (<4%) residual phases. This compositional change is clearly expressed in the progressive textural change from original organic-filled pore space to pore-filling microcrystalline quartz across the reaction rims.

The cross-cutting of reaction rims by BVs means that the progressive silicification seen within the reaction rims must either be synchronous with or post-dated by their formation. Since there are no bitumen veins within the host mudstone outwith the reaction rims, it is argued here that the silicification and vein formation must be directly related. We suggest that this causal link could be physical, for example connected to stress, fluid pressure or temperature, or chemical, such as a chemically induced change in pore fluid composition, pH, wettability, or bitumen composition.

A link between silica diagenesis and accelerated catagenesis has been invoked previously by Lichtfouse and Rullkötter (1994), from analysis of hopane/sterane parameters associated with a silica diagenetic front in the Japan Sea. They suggested that the accelerated catagenesis was due to mineral and textural changes during opaline silica diagenesis, but did not specify a precise mechanism. The biomarker analysis on the JOS conducted by Abu-Mahfouz et al. (2019) showed no such comparable changes in hopane/sterane, or any other chemical differences between the host source rock bitumen and the vein bitumen, so we exclude this possible chemical or kinetic explanation for the localisation of the BVs to the reaction rims.

Can the localisation and clustering of the BVs be explained by any obvious physical processes? Having eliminated mechanical compaction of the host because of the replacive nature of the nodules, we exclude any stress localisation explanation relating to differential compaction as a fracture forming mechanism. Catagenetic volume changes are known to result in bitumen fluid pressures sufficient to form bitumen-driven hydraulic fractures (c.f. Parnell et al., 2000; Cobbold et al., 2013). However, since the JOS is only at an early catagenetic stage it is not clear that the limited kerogen conversion would have led to hydraulic fracturing through volume change (Abu-Mahfouz et al., 2019).

The BVs and microveins are nevertheless clear evidence for fluid-driven, Mode I fracture propagation in which a single phase fluid (bitumen) exerted sufficient pressure to exceed the minimum confining stress plus the tensile strength (Mandl and Harkness, 1987; Price and Cosgrove, 1990). Assuming a tensile strength of 3-4 MPa (Miller et al., 2013) and a typical  $K_0$  ratio for mudrocks of 0.7 (Price and Cosgrove, 1990), then from the typical 1000 m burial depth and overburden density of 2.2 g/cc, we estimate that the bitumen pressure must have exceeded a value of c. 18-20 MPa.

173 Could diagenesis have produced significant bitumen overpressure? Silicification in  
174 the reaction rims clearly involved progressive cementation of existing pore space,  
175 displacement of organic matter and replacement of carbonate grains and cement.  
176 These volumetric changes would almost certainly have required micromechanical  
177 changes at the pore scale, which could have translated into temporary transfer of  
178 vertical stress (overburden load) into fluid pressure increase. Of all these changes, the  
179 most volumetrically significant is crystal growth (quartz) into pore space occupied by  
180 bitumen (Figs. 2 and 3).

181 Based on these observations of compositional changes associated with the reaction  
182 rims, we therefore propose a model in which the bitumen in pore spaces was  
183 displaced under pressure by the growth of microcrystalline quartz (Fig. DR7). The  
184 magnitude of this ‘displacement pressure’ must have been equivalent to the  
185 crystallization pressure, also known as the force of crystallization (Maliva and Siever,  
186 1988). The crystallization pressure of quartz under these conditions ( $> 40$  MPa,  
187 Maliva and Siever, 1988; Moreno and Gibbons, 2007) is considerably higher than the  
188 bitumen pressure needed to form bitumen-driven Mode I fractures, so this mechanism  
189 matches the theoretical requirements for an explanation of bitumen vein formation.

## 190 **CONCLUDING REMARKS**

191 In conclusion, the diagenetically-induced mobilisation of bitumen from the  
192 disseminated pore networks into a neo-forming fracture network that we infer from  
193 the observations of the JOS points to a set of linked pore-scale processes operative at  
194 the earliest stage of catagenesis. This may in turn point to a more general mechanism  
195 for primary oil migration involving diagenetically-induced fracturing. This process  
196 may be important for many other source rocks deposited with a high biogenic silica



fraction (e.g. the Monterey Formation). The mechanism could, however, extend more widely to any source rocks experiencing replacive diagenesis at the critical stage of early maturation, where crystallization pressure has the potential to exert a significant impact on the micromechanics of the organic-rich sediments.

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## FIGURE CAPTIONS

Figure 1. (A) Map of Jordan showing the location of the cored boreholes. The red double arrow outlines the cross-section shown in Fig. DR1. (B) A columnar section showing the lithology of the studied cored intervals along with a representative trend (from core outlined in red in Figure 1a) of vertical distribution of bitumen veins against the three lithological units. Note the clustering of the bitumen veins at the

bottom of the section. AHP, Al-Hisa Phosphorite Formation; MCM, Muwaqqar Chalk Marl Formation; Umm Rijam Chert Limestone Formation.

Figure 2. Core photograph showing the bitumen distribution in the reaction rim (RR; yellow-dotted shape) associated with chert nodule hosted by organic-rich mudstone in the Lower Unit of the study succession. The white-dashed arrow shows the direction of bitumen vein propagation. Note the marked difference in bitumen distribution and form, ranging from disseminated bitumen (B) filling the pore spaces in the organic-rich mudstone, developing into bitumen filaments (BF) in the transitional zone (TZ) within the RR (Inset 1), to developed bitumen veins (BV) in the RR (Inset 2), to bitumen microveins in the chert nodule (Inset 3). Note the presence of fossil ghosts (G; outlined in beige) in the chert nodule.

Figure 3. Backscattered Electron images (BSE) showing the development of bitumen veins (BV) within a reaction rim (RR) and adjacent chert nodule observed in the Lower Unit of core. Qz; Quartz. Note the change in composition and bitumen content from the host mudstone towards the chert nodule. Yellow dotted shapes are fossil ‘ghosts’ in the chert nodule.

Figure 4. Histogram showing the TOC data of the analysed reaction rims and their host organic-rich mudstone. Samples B1-B9 were taken from 9 cores from the Lower Unit (see Figure 1b). Note the reduction in TOC values in the reaction rims.

<sup>1</sup>GSA Data Repository item 2019xxx, petrographic and geochemical data (including Figures DR1-DR6 and Table DR1-DR2), is available online at [www.geosociety.org/pubs/ft2019.htm](http://www.geosociety.org/pubs/ft2019.htm), or on request from [editing@geosociety.org](mailto:editing@geosociety.org) or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

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