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Diagenetic Carbonate Concretions in Devonian organic-rich mudrocks of the Appalachian Basin: How to predict their occurrence while drilling horizontal oil and gas wells

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Summary

Numerous diagenetic alterations to mudstones play roles of varying importance in the exploitation for fossil fuel and critical mineral commodities. Biotic and thermal alteration produce pores which store hydrocarbon within organic material, the dissolution and reprecipitation of silica tests can occlude porosity but provide structural rigidity to certain facies, descending oxygen fronts can mobilize and redeposit metals and critical minerals along specific horizons. Here, we discuss the occurrence of diagenetic carbonate concretions hosted by mudstone dominated sequences in the Appalachian Basin, how they form, and how to identify them. Such concretions encountered while drilling horizontal shale wells negatively affect drilling operations by reducing drilling rates, damaging bits, and requiring excessive steering corrections to penetrate or extricate the bit from the concretion horizon. Carbonate concretions form by the anaerobic oxidation of methane in a narrow zone perhaps just a few meters below the seafloor. Crucial to this mechanism is a slowing or pause in sedimentation rate that would have held the zone of carbonate precipitation at a fixed depth long enough for concretions to grow. Using this model, we attempt to predict the size and location of concretions to avoid encountering them while drilling. Field observations of Upper Devonian shale-hosted concretion dimensions suggest that Marcellus-hosted concretions up to three feet in length are possible. Hiatuses in sedimentation and potential concretion horizons were predicted using uranium to organic carbon ratios. The attachment of uranium to organic carbon macerals occurs across the sediment-water interface. Therefore, an increase in the abundance of uranium per unit organic carbon indicates a cessation in sedimentation and the potential for concretion growth. Indeed, when comparing well log response to core, uranium to organic carbon excursions predicted the location of two concretion horizons.

Background

The Middle and Upper Devonian black and grey shale succession of the Appalachian Basin accumulated as part of the Catskill Delta Complex, an eastward-thickening wedge of clastic marine and terrestrial deposits shed to the west and southwest (present coordinates) from the rising Acadian highlands of eastern New York and New England (Friedman and Johnson, 1966; Woodrow, 1985; Faill, 1985; Ettensohn, 1985). The basin was an elongate northeast-southwest trending foreland basin centered at approximately 30o south latitude (Scotese and McKerrow, 1990) formed by thrust-load-induced subsidence related to the Acadian oblique collision of the Avalonian microplate and Laurentia (Faill, 1985; Ettensohn, 1985, 1987; Ferrill and Thomas, 1988; Scotese and McKerrow, 1990; Rast and Skehan, 1993). The basin was bounded on its east and southeast by the Acadian highlands and on the west and northwest by the Findlay-Algonquin Arch or a precursor arch (Scotese and McKerrow, 1990; Rast and Skehan, 1993; Bose and Bartholomew, 2012; Blakey, 2019; Fig. 1). Inferred Devonian paleogeographic reconstructions (Blakey, 2019) show the Marcellus basin's connection with the global (Rheic) ocean to the southwest as a narrow seaway (Ettensohn, 1985, 1987).

Carbonate concretions are a common diagenetic feature of organic-rich mudstones of the Appalachian Basin (Criss et al., 1988; Coniglio and Cameron, 1990; Lash and Blood 2004; Blood et al., 2013; 2017). Indeed, almost every major organic-rich shale unit in the basin host stratally confined concretions. These concretions are interpreted to have formed in association with the anaerobic oxidation of methane (AOM) and consequent enhanced alkalinity (Lash and Blood, 2004a,b; Lash, 2015a,b, 2018). Each concretionary horizon is interpreted to reflect the diagenetic signature of AOM within the sulfate methane transition zone (SMTZ), a diagenetic horizon of indeterminate thickness along which downward-diffusing seawater sulfate and upward-diffusing methane are consumed by a consortium of methane-oxidizing archea and sulfate-reducing bacteria (Reeburgh, 1976; Hoehler et al., 1994; Niewöhner et al., 1998; Hinrichs et al., 1999; Borowski et al., 1999; Boetius et al., 2000; Paull et al., 2000). Low sedimentation rates focus the diagenetic effects of AOM, maintaining elevated pore water alkalinity within the SMTZ for an extended period of time (Borowski et al., 1999; Rodriguez et al., 2000; D'Hondt et al., 2004; Snyder et al., 2007; Dickens and Snyder, 2009).

Canfield and Raiswell (1991) argue convincingly that the timing of concretion growth is best deduced by assessing the degree of compaction of encapsulating shale at the time of concretion formation. The wrapping of Devonian concretions by laminated shale is consistent with their formation at shallow burial depths early in the compaction history of these deposits (Lash and Blood, 2004b). Further, SEM analysis of host shale samples collected from adjacent to lateral edges of concretions reveals a modestly open clay grain microfabric (Lash and Blood, 2004b). Shale samples collected centimeters away from these areas, however, display a strongly oriented platy grain microfabric (Lash and Blood, 2004b). The former deposits are interpreted to have occupied pressure shadow regions of host sediment that were shielded by adjacent rigid carbonate during early and shallow mechanical compaction (Lash and Blood, 2004b). A shallow depth of concretion formation is further suggested by the pervasive occurrence of randomly oriented clay grains reminiscent of clay floccules within concretions (e.g., O'Brien, 1981; O'Brien and Slatt, 1990; Bennett et al., 1991; Slatt and O'Brien, 2013). The depositional texture of the host clay was likely shielded from compaction-related grain reorientation by the precipitation of calcium carbonate soon after deposition.

The duration of formation of the studied concretions cannot be quantified, yet micro-textural features suggest that they precipitated rapidly at shallow depth, perhaps several meters to a few tens of meters below the sediment-water interface (SWI; Lash and Blood, 2004a,b). The uniformly very-fine grain size (15 – 25 μm) of matrix carbonate and lack of textural evidence of growth banding evince a rapid growth history of a single generation of calcite microspar (Selles-Martinez, 1996; Mozely, 1996; Raiswell and Fisher, 2000, 2004; Gaines and Vorhies, 2016).

Concretions hosted by black shale display depositional laminae inherited from the host sediment that accumulated under oxygen-depleted conditions thereby limiting or precluding the activity of bioturbating organisms (Lash and Blood, 2004a). It is noteworthy that laminae do not thin systematically from concretion centers to edges as would be expected of carbonate masses that precipitated radially coincident with burial-related compaction. Rather, it appears that the concretion masses formed at an essentially steady depth below the sediment-water interface. Indeed, the omnipresence of spherical algal cysts and clay floccules within concretions is suggestive of a generally pervasive growth history that entailed the infilling of void space in the host sediment. However, the fact that the infilling of pore space by calcite cement may be attended by some degree of grain displacement (e.g., Raiswell and Fisher, 2000; Bojanowski and Clarkson, 2012) cautions against inferring a simple relationship between the abundance of carbonate cement and sediment porosity. Indeed, Lash and Blood (2004a) argued that the passive infilling of pore space within host sediment associated with the formation of concretions of the Rhinestreet Formation was accompanied by some displacement of siliciclastic grains.

The prevailing view of calcium carbonate precipitation driven by AOM holds that the $\delta^{13}C$ of pore water and authigenic carbonate should reflect the isotopic composition of the methane substrate (i.e., less than -30 ‰ V-PDB; Borowski et al., 1997; Aloisi et al., 2000). However, recent investigations of pore fluid geochemistry of methane-charged sediments have revealed relatively high δ^{13}CDIC (dissolved inorganic carbon) values (> - 20 ‰ V-PDB) within SMTZs reflecting the commingling of DIC generated by organic matter degradation and methanogenesis at depth with that produced in situ by AOM at the SMTZ (Rodriguez et al., 2000; Borowski et al., 2000; Sivan et al., 2007; Snyder et al., 2007; Kastner et al., 2008; Dickens and Snyder, 2009; Chatterjee et al., 2011; Kim et al., 2011; Malinverno and Pohlman, 2011).

The modestly ^{13}C-enriched stable carbon isotope values documented from concretions throughout the Devonian shale succession of the Appalachian Basin by previous studies (Dix and Mullins, 1987; Siegel et al., 1987; Criss et al., 1988; Coniglio and Cameron, 1990; Lash and Blood, 2004a; Lash, 2015a,b) could reflect abnormally high DIC contributions from organoclastic sulfate reduction (OSR) in the bacterial sulfate reduction zone (BSRZ) (Nyman and Nelson, 2011; Teichert et al., 2014). Indeed, Raiswell and Fisher (2004) posited that large calcium carbonate concretions described from outcrop may originate in the BSRZ. They add, though, that calcium carbonate precipitated in this diagenetic zone is limited to no more than porous, low-density masses of approximately 1.5 wt. % calcite rigid enough to preserve the depositional clay grain microfabric of the host sediment. Raiswell and Fisher (2004) further suggest that the dense bodies of concretionary cement observed in outcrop and core likely record the diagenetic imprint of the faster rates of sulfate reduction and consequent elevated alkalinities generated in association with AOM focused at the SMTZ by diminished sedimentation rates. Thus, the Middle and Upper Devonian concretion horizons are interpreted to reflect growth histories that were initiated within the BSRZ. However, it was not until the nascent concretions were buried to the SMTZ, perhaps a few tens of meters below the SWI (e.g., Borowski et al., 2013), that the dense carbonate masses observed in field exposure formed as a consequence of the passive infilling of porosity. Thus, the discrete calcium carbonate-bearing stratigraphic horizons hosted by the Middle and Upper Devonian shale succession of the Appalachian Basin preserve the record of paleo-SMTZs, each one associated with an episode of reduced sedimentation rate (Lash, 2018).

Theory

When drilling horizontal wells in organic-rich mudstones, a geologic model is often employed to determine the best facies in which to drill the wellbore (Blood, 2010; 2011; Blood and Lash, 2014). As it happens, such “target” zones are often the same intervals of strata conducive to the formation of diagenetic carbonate concretions. Predicting the size and stratigraphic occurrence of concretions is significant owing to the negative impacts they can have on horizontal drilling in organic-rich mudstones. Indeed, wellbores encountering concretion horizons are often characterized by: (1) slower to erratic ROPs owing to the bit transitioning between softer mudstone and harder carbonate (Fig. 1); (2) bit deflections in seemingly random directions, resulting from the oblique encounter of the drill bit with the sloping edges of concretions, and (3) erratic gamma ray signatures resulting from the bit passing from more radioactive mudstone into and out of less radioactive carbonate concretions which may cause errors in geosteering interpretations (Fig. 1). If the location of diagenetic carbonate concretion horizons can be predicted ahead of the drill bit, time and money are saved along with increasing the amount of the wellbore that is in hydrocarbon producing rock.

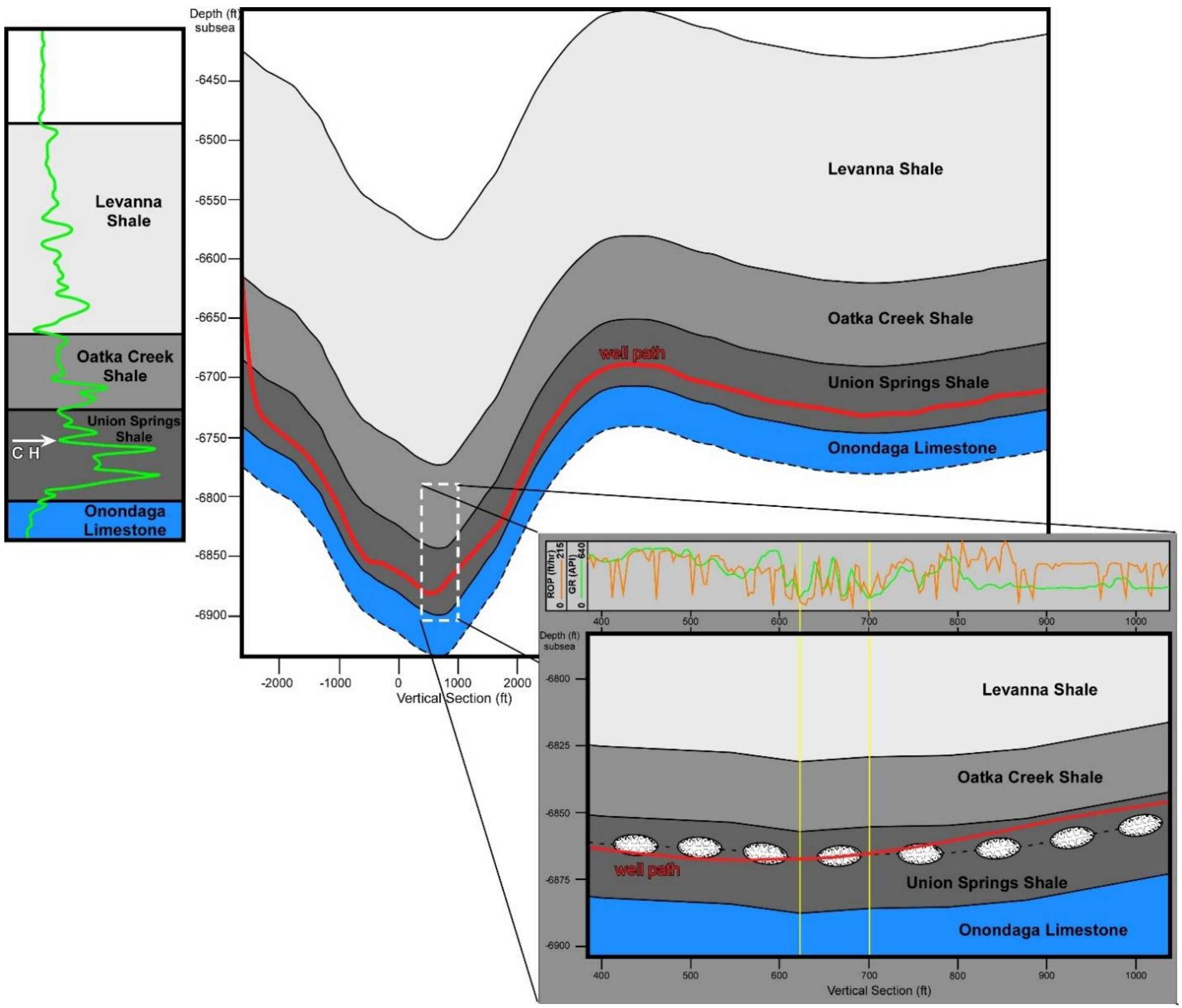

***Figure 1**: Marcellus Shale well geosteer depicting well path through stratigraphic section. Call out box denotes where the wellbore encountered a concretion horizon (CH) within the vertical yellow lines. Note that through this section both ROP and GR vary where concretions are encountered.*

Results and Discussion

Vertical cores through the Marcellus Shale that encounter concretions provide an opportunity to estimate their minimum horizontal and vertical dimensions. Analysis of the bed dip of shale in contact with the edge of the concretion yields insight to how the wellbore encountered the concretion. If the beds and upper contact of the concretion are parallel to regional bed dip, then the wellbore likely drilled through the center of the concretion, while sloping beds would suggest the wellbore penetrated the concretion off center. In the latter scenario the vertical dimension of the concretion should be treated as a minimum, or an ellipse should be fit to match the slope of the carbonate-shale contact to estimate the vertical dimension.

The horizontal dimension was estimated using the relationship to the vertical dimension of concretions hosted by the Rhinestreet Shale (Fig. 2; Lash and Blood 2004). Lash and Blood (2004) demonstrated a largely uniform relationship of horizontal to vertical dimension of concretions less than approximately 24 inches (60 cm) in height. However, concretions greater than 60 cm in height have a tendency towards larger and variable horizontal dimensions. Lash and Blood (2004) suggested these characteristics reflect a more pronounced hiatus in sedimentation and the restriction of carbonate growth to a narrow zone defined by the presence of both methane and sea water sulfate. As a result, the estimation of the horizontal dimension of concretions over 24 in (60 cm) in height is less accurate. The horizontal dimension of concretions less than 24 in (60 cm) then, may be expressed by the following equation where H = horizontal dimension (cm) and V = vertical dimension (cm):

$$H = 0.5209 * V \tag{1}$$

The vertical dimension of 30 concretions encountered in Marcellus Shale cores in Pennsylvania and West Virginia were measured and range from 1.3 to 30.5 in (3.4 to 77.5 cm). Using equation one, horizontal dimensions of concretions range from 2.6 to 58.6 in (6.5 to 148.9 cm; Fig. 2).

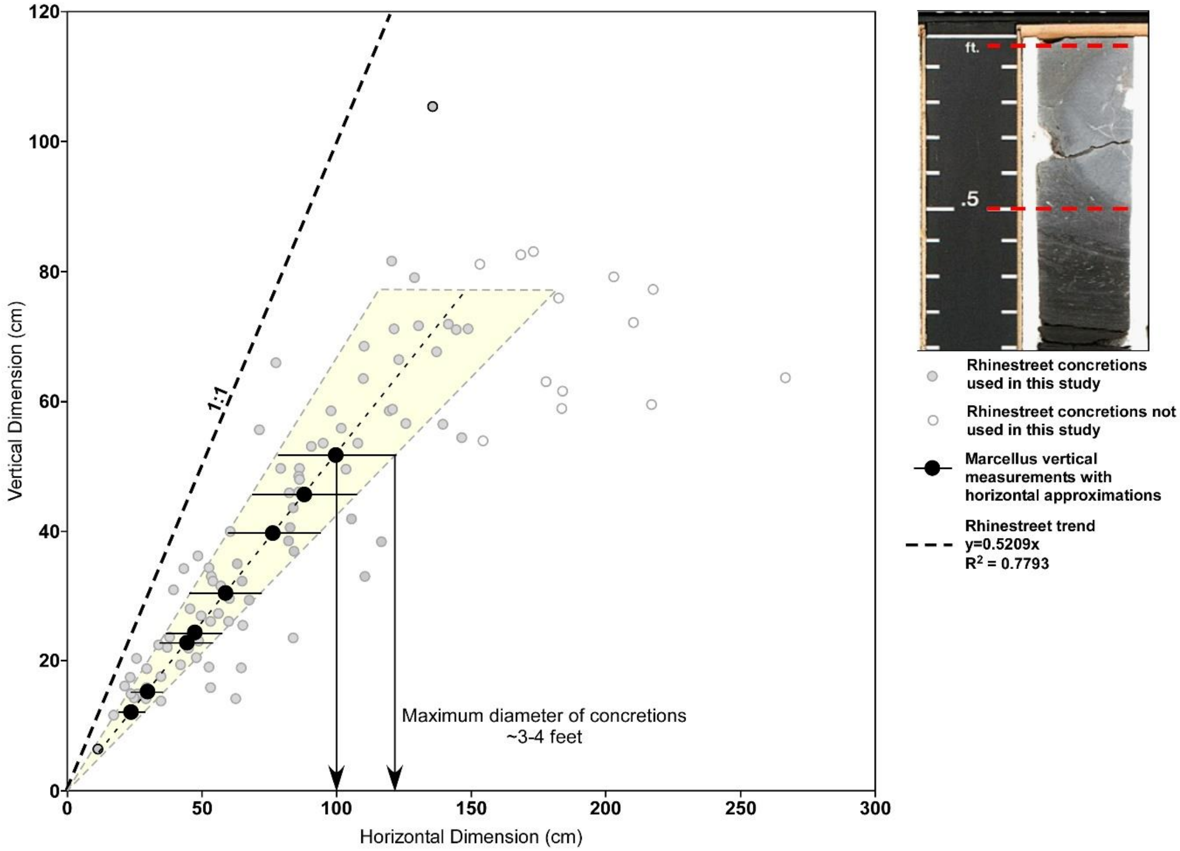

***Figure 2**: Plot of Rhinestreet Shale-hosted concretion dimensions. Yellow area indicates one standard deviation about the mean for the data population. Black circles represent measured vertical dimensions of some Marcellus Shale concretions from core. The horizontal bar accounts for possible range in modeled horizontal dimension.*

Determining the location of concretion horizons on geophysical well logs require two approaches; (1) the direct identification of concretions encountered in wellbores using geophysical well log response, and (2) a model that predicts stratigraphic horizons that potentially host concretion horizons. The latter model is necessary given that concretions are not always encountered within the depth of investigation of logging tools (usually less than a few feet) run in a vertical wellbore, however they may be encountered when drilling horizontally. Concretions often manifest on geophysical well logs as a drop in GR API, an increase in bulk density (RHOB), approaching 2.7 gm/cc, and a photo electric factor (PE) approaching 5.0. It is noteworthy that these responses may be subdued when measured downhole by the influence of the surrounding rock, especially those instances where the concretion is smaller than the depth of investigation of the tools. For example, a concretion hosted by black shale with a GR signature of 300 API, may manifest as a subtle drop or inflection in GR, as opposed to a well-defined carbonate of a few tens of API in value. Further, the high RHOB and PE of pyrite (4.99 gm/cc, 17 b/e respectively) can provide a similar although often greater increase in RHOB and PE.

Due to the discontinuous nature of carbonate concretions, they are not always encountered in a vertical wellbore. Therefore, a model is necessary to predict the stratigraphic intervals in which concretions may occur. Given that concretions are cited along fossil SMTZs during a hiatus in sedimentation, we look at U to TOC relationships in effort to predict these hiatuses. Under reducing conditions, uranium attaches to organic carbon across the sediment water interface. The amount of U present in the rock then becomes a function of (1) the abundance of organic matter acting as a substrate for U attachment, (2) the amount of U present in the sea water, and (3) the amount of time organic matter is exposed at the sediment-water interface allowing for U attachment (Fisher and Wignall, 2001; Lüning and Kolonic, 2003 and references therein). We have no evidence that indicates fluctuations in the in the U content of Middle and Upper Devonian seawater. Therefore, hiatuses in sedimentation and subsequent condensation can manifest as an increase in U/TOC in the organic-rich portions of the shale successions (Fig. 3). We suggest that at or within a few feet of these peaks are stratigraphic horizons that may host carbonate concretions.

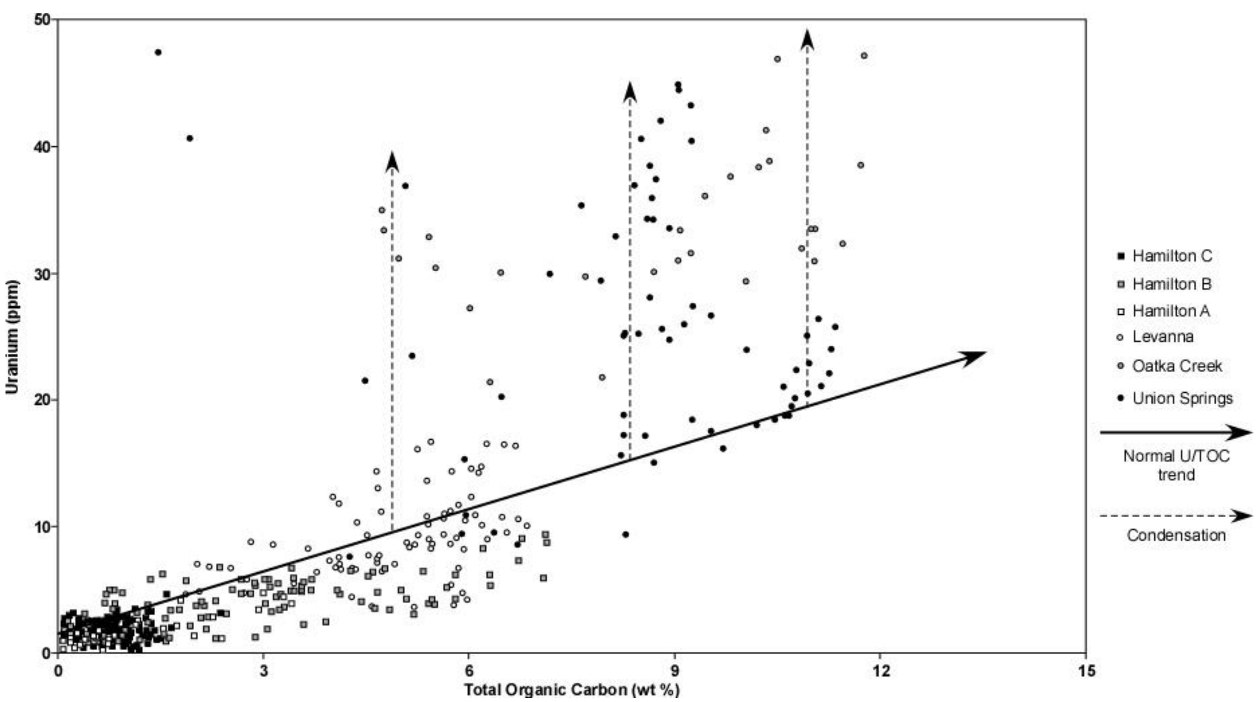

Figure 3*: Scatter plot of TOC vs U for various units of the Hamilton Group. Heavy black arrow indicates the normal trend of increasing U with increasing organic carbon abundance. Vertical dashed arrows indicate possible condensation or hiatuses allowing increased attachment of U to organic carbon.*

Conclusions

In summary, carbonate concretions can pose a challenge or hazard to horizontal drilling operations in shale. However, an accurate geologic model which allows for the prediction of the size and stratigraphic location can help wellbore planners and geosteerers avoid these zones and drill more efficient wells. Finally, it is worth noting the degree to which seemingly "academic" studies, in this case copious amounts of fieldwork and research into the formation of carbonate concretions, may ultimately lead to discoveries of significant economic importance.

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