Element cycling in the Middle to Upper Triassic Shublik Formation: mineralization vs. recycling of biolimiting nutrients in an unconventional resource play

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Abstract

The Triassic Shublik Formation in northern Alaska is one of the major source rocks in North America, having generated much of the petroleum in Prudhoe Bay and associated fields. The middle Shublik Formation, the focus of this study, is a highly phosphatic, organic-rich carbonate mudstone interval. Apatite cements can occur as phosphatic peloids, steinkerns, elongate or angular nodules, and shells or shell fragments. We propose a model whereby phosphatization is favored in early diagenetic environments that have low concentrations of dissolved iron relative to reactive organic matter in the pore water sulfate reduction zone.

Background Statement and Aims

The Middle to Upper Triassic Shublik Formation is a mixed siliciclastic-carbonate-phosphatic unit with significant organic-rich intervals. It is a major source rock in northern Alaska, having generated much of the oil in Prudhoe Bay and associated fields (Peters et al., 2006, and references therein). The Shublik is also being evaluated and tested as a self-sourced resource play (Houseknecht et al., 2012; Duncan and Bird, 2013; Scheirer et al., 2014). The phosphatic component in the Shublik Formation represents the largest Triassic - age phosphorite deposit in the world (Dumoulin et al., 2019; Trappe, 1994; Cathcart and Gluskoter, 1991), yet this aspect of the Shublik Formation is often over-looked in favor of its excellent source quality. While the Shublik Formation is not the only phosphatic-rich source rock (e.g., Miocene Monterey Formation), enrichment of phosphatic minerals is not a widespread attribute of known source rocks. Our aim here is to characterize the variability of phosphate occurrence in the middle interval of the Shublik Formation, focusing on the likely origin of phosphatic cements with respect to other observed pre-compaction cements. This information will allow for a better understanding of phosphatic enrichment in the middle Shublik Formation. It will also provide a clearer picture of early diagenetic processes, particularly cementation, in organic-rich carbonate mudstones, leading to more robust models of porosity evolution and reservoir quality in these important resource plays.
Geologic Background
The Shublik Formation was deposited during the Early to Late Triassic in Arctic Alaska as a southward-thinning (present-day coordinates) wedge along a low-angle, passive margin shelf (Whidden et al., 2018 and references therein). A recent revised stratigraphic interpretation subdivided the Shublik Formation into five second-order sequences from Anisian to late Norian age (247 – 210 million years ago, Ma), with much of the phosphatic strata occurring in the Ladinian to early-middle Norian MCC1, MCC2 and MCC3 intervals (~242 – 217 Ma; Dumoulin et al., 2019; Whidden et al., 2018; Fig. 1). The MCC1, MCC2 and MCC3 units were also identified as containing notably lower amounts of terrigenous siliciclastic material in comparison to the upper and lower Shublik Formation units, with accumulation of biogenic calcareous deposition (Whidden et al., 2018).

Bivalves of the genera *Halobia* and *Monotis* were rapidly evolving species in the Triassic and are widely used as the main index fossils for the Shublik Formation (McRoberts, 2010). These bivalves had very thin shells, and hence are commonly referred to as “flat clams” (McRoberts, 2010). They frequently occur on bedding planes as monospecific or paucispecific accumulations that can be laterally extensive and are found in rocks deposited in a variety of environments from shallow to deep water, and oxic to dysoxic conditions (McRoberts, 2010). Flat clams are considered an example of an opportunistic species that colonized environments with fluctuating oxygen levels (Savrda and Bottjer, 1991). Halobiid flat clams are in the MCC2 and MCC3 units studied here.

Materials and Methods
This study focused on core data from three wells drilled in the National Petroleum Reserve in Alaska (NPR-A; Fig. 2). The collected cores penetrated the Carnian to early Norian aged MCC2 and MCC3 units (Fig. 1). Samples of core were collected at tightly spaced intervals (<4” or 10 cm), as remaining core material allowed. Seventy-nine samples from Ikpikpuk 1, sixteen samples from Inigok 1 and twelve samples from North Inigok 1 were collected, for a total of 107 samples. Previous work on thermal maturity indicated that the Shublik Formation in all three wells is in the late oil to gas window (Threlkeld et al. 2000).

Each sample was cut into two pieces. One piece was prepared for thin sections, and one piece was analyzed for geochemistry. Each thin section was prepared at 20-micron thickness, double-polished, and half-stained to distinguish ferroan from non-ferroan calcite. The samples for geochemical investigation were crushed and analyzed for total organic carbon (TOC). Ikpikpuk 1 and Inigok 1 samples were analyzed by an outside laboratory on a LECO instrument; North Inigok 1 samples were analyzed in-house at the U.S. Geological Survey’s Petroleum Geochemistry Research Laboratory on a LECO 744 carbon analyzer instrument. Samples analyzed for TOC were not extracted to separate kerogen from bitumen. Given the thermal maturity levels of these three cores, it is not clear if these TOC values represent spent kerogen, residual/migrated bitumen or a combination of the two.

Splits of the crushed powders from Ikpikpuk 1 were also analyzed for mineralogy using semi-quantitative X-ray diffraction (XRD). A sub-set of five polished thin sections from Ikpikpuk 1 were selected for analysis using a scanning electron microscope (SEM), based on petrographic microfacies interpretations. Energy-dispersive spectroscopy (EDS) was used to determine mineralogy at specific locations using the SEM. The Ikpikpuk 1 core is ~30’ (9.1 m) in length, while the Inigok 1 core is ~9.5’ (3 m) long, and the North
Inigo k 1 core is ~8' (2.4 m) long. Microfacies observations and interpretations were made for all three cores; however, the stratigraphic interpretations herein are based on the Ikpikpuk 1 core because wireline log interpretations (Rouse et al., 2019, 2017) suggest that the core represents most of MCC2, thus placing it into a defined sequence stratigraphic framework (Whidden et al., 2018).

Results

Optical Petrography and Scanning Electron Microscopy
Petrographic descriptions of 107 thin sections provided observations to define three end-member carbonate microfacies, with a large range of transitional microfacies. The carbonate mudstone descriptive nomenclature used herein is based on Dunham (1962) for recognizable depositional textures and Wright (1992) for fabric-destructive diagenetic textures, as summarized by Flugel (2010, p. 349). Additionally, the term cement is used to describe authigenic minerals that infill any primary or secondary pore space (Milliken and Olson, 2017). Carbonate microfacies 1, the flat-clam microfacies (FCF), can be classified as a halobiid bioclastic wackestone to packstone (Fig. 3a). The detrital component (both autochthonous and allochthonous) primarily consists of shells and shell fragments from halobiid bivalves that are predominantly oriented parallel to bedding, with fragments of echinoderms, brachiopods, benthic foraminifera, and radiolarians, as well as 20% or less (visual estimation) silt-sized, sub-angular quartz and feldspar grains along with remnants of terrigenous organic material. Micro-bioturbation, recognized by circular swirl patterns (Flugel, 2010) defined by shell fragments is common in this microfacies (Fig. 3b). Diagenetic components
include microspar, pyrite, dolomite, clay, plagioclase feldspar, quartz, bitumen and phosphatic particles. Semi-quantitative XRD results identified illite as the dominant clay component, while SEM-EDS analyses on spot sites revealed kaolinite booklets (Fig. 3c). Phosphatic peloids are common, and elongate phosphatic nodules occur parallel to bedding (Fig. 3d). Intermingled microspar, clay, plagioclase, quartz, apatite and pyrite occur as pre-compaction cements.

Several samples near the base of the Ikpikpuk 1 core contain 40% - 60% quartz and feldspar (visual estimation) intermixed between the flat clam shells, and are described as carbonate microfacies 1.1, silty FCF (Fig. 4a). Between the depths of 10,294' and 10,287' quartz and feldspar grains are rare, comprising <5% (visual estimation). Above 10,287', the amount of silt-size quartz grains and shell fragments (rather than whole shells) increase gradually in the upper half of the Ikpikpuk 1 core. Low-angle cross-bedding, subtle scour surfaces and shelly, peloidal lag deposits also become more common in samples from the upper half of this core. This carbonate microfacies 1.2 is described as transported FCF (Fig. 4b). Pre-compaction cement mineralogy in both silty FCF and transported FCF is like that described for end-member FCF. In addition, transported FCF has common phosphatized shells (usually echinoderm plates or bivalve shell fragments), phosphatic steinkerns, and abundant, well-sorted, phosphatic peloids. Centimeter-scale irregular, angular phosphatic nodules are present in many of the transported FCF samples; however, elongate, bedding-parallel nodules are absent from this microfacies.

Carbonate microfacies end-member 2, bioclastic sparry microfacies (BSF), can be classified as a halobiid bioclastic sparry packstone to grainstone. This microfacies consists of halobiid and other shells and shell fragments cemented by equant mosaic spar (Fig. 4c); shell-nucleated bladed calcite occurs on the long edges of some shells and shell fragments. Several samples have thin beds (<1” or 2.5 cm) comprised of mainly echinoderm plates with significant calcite syntaxial rim cement. Bedding-parallel orientation of shells and shell fragments is common (Fig. 4c). Thin intervals (1 cm or less) have evidence of low-angle cross-bedding, as well as frequent occurrences of shell fragments. This microfacies often occurs interbedded with one of the other microfacies on the scale of a thin section. It was observed as vertically distinct beds or as patches of equant mosaic spar within the FCF and transported FCF microfacies. BSF most commonly occurs in the lower part of the Ikpikpuk 1 core. Phosphatic peloids (Fig. 4c) and steinkerns, bedding-parallel phosphatic nodules (similar to Fig. 3d) and phosphatized shell fragments are all common in this microfacies.
Carbonate microfacies end-member 3, the granular spar microfacies (GSF), can be described as a bioclastic cementstone to sparstone (Fig. 4D). This microfacies is made up of granular spar cement enclosed by thin layers of bitumen, and <50% bioclastic grains (visual estimation). The granular spar cement partially to completely obliterates depositional textures. This facies occurs throughout the Ikpikpuk 1 core and can be vertically distinct or small patches within the other microfacies. Phosphatic occurrences include steinkerns, angular nodules and peloids. Lastly, the basal two samples from Ikpikpuk 1 were comprised of silt-sized quartz grains with patches of calcite cement (particularly in the lower two samples) and small, very abraded fossil fragments. These samples are described as calcareous siltstone.

**Geochemistry, Semi-quantitative XRD Results and Authigenic Mineral Phases**

TOC values in the Ikpikpuk 1 well range from 0.06 – 4.26 weight percent (wt. %); Ikpikpuk 1 values shown on Fig. 5a). For the Inigok 1 well, TOC values are 1.29 – 4.03 wt. %, and for the North Inigok 1 well, TOC values are 1.04 – 4.03 wt. %. The wt. % apatite in the Ikpikpuk 1 samples, as measured by semi-quantitative XRD, increases upsection (Fig. 5a). It is notable that the amount of apatite does not track TOC content. The highest amounts of apatite occur in transported FCF samples above 10,287’ (3136 m; Fig. 5a).

Figure 5b illustrates the temporal trend in wt. % for total clay, quartz and total carbonate. Specific mineral phases identified by semi-quantitative XRD analyses include quartz, plagioclase feldspar, calcite, dolomite, apatite, pyrite, and illite in Ikpikpuk 1 samples. Note that these XRD analyses do not distinguish between detrital, biogenic and authigenic mineral phases; for example, the weight percent calcite includes both biogenic and diagenetic forms. Diagenetic quartz crystals intergrown with calcite or kaolinite can be seen in SEM images, in addition to the detrital silt-sized grains described in thin section. Biogenic and authigenic calcite are both common in FCF and BSF samples. Forms of biogenic calcite include flat clam and other bivalve shells, echinoderm plates and spines, brachiopod shells, and benthic foraminifera. Authigenic calcite is present as various forms of spar, including microspar, equant, granular and shell-nucleated bladed spar. Dolomite occurs both as euhedral rhombs and intergrown with calcite.
Figure 5: Total organic carbon (TOC) in weight percent (wt. %) and semi-quantitative XRD data for Ikpikpuk 1. (A) TOC (blue curve) and apatite (red curve) vs. depth; (B) total clay (green curve), quartz (purple curve), and total carbonate (orange curve) vs. depth.
Pyrite is commonly framboidal, although it can also occur as euhedral crystals. Apatite most commonly occurs intergrown with clay as cement between shells or shell layers (Fig. 3c), or as oval peloids. In SEM images, apatite and calcite were frequently observed to be intergrown. Apatite also nucleated on bivalve shell edges, replaced echinoderm plates and spines and infilled articulated bivalve shells to form steinkerns. Phosphatic nodule geometries are either elongate, parallel to bedding forms or irregular, angular, randomly oriented shapes.

Discussion

Ikpikpuk 1 samples from FCF, silty FCF, transported FCF, and BSF are predominantly composed of biogenic and authigenic components. Flat clams, either in-situ and closely associated with the phosphatic cements or transported fragments, are a major component of these facies (Figs. 3, 4). Other body fossils identified include echinoderm plates and spines, small bivalves, benthic foraminifera, brachiopod fragments, radiolarians, sponge spicules, and rare conodonts. Evidence for micro-bioturbation is common (Fig. 3b). The activities and metabolic processes of these organisms likely played a crucial role in the development of MCC2 and MCC3 as organic-rich, phosphatic, carbonate mudstone sequences. The FCF, silty FCF, transported FCF, and BSF are interpreted to represent carbonate microfacies that most closely record depositional and early diagenetic processes in the studied cores of the middle Shublik unit. GSF samples, which were characterized by roughly equidimensional granular calcite spar crystals (Fig. 4d), often have little of the original depositional fabric preserved due to extensive fabric-destructive diagenesis. As such, this carbonate microfacies obscures textures, fabrics and possibly mineralogy related to the depositional and early diagenetic processes that are the main focus of this study. Therefore, this carbonate microfacies will not be discussed further. Further, the calcareous siltstone microfacies occurs in the lowermost part of the Ikpikpuk 1 core, and is interpreted to represent relative lowstand deposits, such that fine-grained terrigenous siliciclastic material was transported to the depositional site. As these samples represent a siliciclastic microfacies rather than a carbonate microfacies, they do not contribute to understanding depositional and early diagenetic processes in carbonate microfacies.

FCF is interpreted to represent the background sedimentation pattern within MCC2 and MCC3. The presence of flat clam shell fragments and occasional abraded echinoderm and other shell fragments implies some degree of energetic disturbance on the sea floor. Transported FCF, silty FCF, and BSF have evidence for more substantial energetic events, including silt-sized detrital quartz grains, abundant shell fragments often in individual, thin (1 to 20 mm thick) beds, low angle cross-bedding, and minor scour surfaces. BSF is interpreted to have been significantly influenced by early diagenetic processes, such that calcite precipitated as equant mosaic spar cement within pore spaces between shells and shell fragments, and as syntaxial rim cement associated with echinoderm plates.

In the Ikpikpuk 1 core, there is an overall increase upsection in the number of samples with evidence of transport, particularly low-angle bedding features and the numbers and sizes of shell fragments. This upward increase in transported FCF samples is interpreted to represent an increase in the frequency of higher energy events within a shallowing-up sequence. Over this same core interval, the amount of apatite (as determined by XRD analysis) also increases upsection (Fig. 5). These observations suggest a connection between transport processes and increased apatite concentrations, perhaps due to winnowing.

Abundant halobiid flat clams, micro-bioturbation, overall low-diversity benthic fossil assemblages and preservation of significant amounts of organic carbon all suggest that the porewaters at the sediment-water interface were predominantly suboxic during deposition of FCF, and likely became anoxic (redox boundary) close to the sediment surface. Episodic energetic events would have re-introduced oxygen into the pore waters causing the oxic-anoxic redox boundary to shift deeper into the sediment, before gradually migrating closer to the seafloor due to oxygen being consumed by metabolic processes (i.e., aerobic respiration) faster than it could be replenished by diffusion.

Episodic energetic events such as storms or currents mixed the uppermost sediment column, ensuring that phosphorus and iron, released during organic matter mineralization, were recycled and bioavailable.
in the overlying water column. Oxygen, calcium, and magnesium from seawater were also resupplied to the pore waters to support biologic processes in the uppermost sediment column. Based on observational data, Morse et al. (2007) suggested that calcite cement precipitation may be inhibited by the presence of organic matter, thereby favoring apatite precipitation. Additionally, large volumes of seawater are needed to provide sufficient calcium and carbonate ions for significant amounts of cement to form, implying that seawater was repeatedly flushed through the near-surface sediment pores (Morse et al., 2007). Mosaic sparry calcite and syntaxial rim cements in BSF samples are interpreted to have precipitated from replenished, oxic, marine pore waters with shell fragments acting as nucleation sites. These episodic energetic events served to disrupt, winnow, and concentrate grains and particles such as shells, shell fragments, and peloids. Larger events had the potential to disturb tens of centimeters of the sediment column, transporting and re-depositing both phosphatic material within the upper sediment column, and biogenic particles close to the sediment-water interface with remaining undegraded organic matter. During quiescent intervals between episodic energetic events, phosphatization may have recommenced, leading to multiple episodes of apatite mineralization. The relationship between apatite concentrations and transport processes may be because the transported beds contain both allochthonous and autochthonous phosphatized grains and particles.

Although high concentrations of phosphorus are associated with organic-rich strata (i.e., Miocene Monterey Formation, Permian Phosphoria Formation), organic-rich strata are not always associated with a significant phosphatic component (i.e., Late Cretaceous Eagle Ford Group, Late Cretaceous Hue Shale). Current models for phosphogenesis closely link phosphate and iron, as follows. Phosphorus is released into the water column or pore waters during organic matter mineralization, whereupon it adsorbs onto available iron oxyhydroxides (Fe-oxides), producing iron-bound phosphorus (Defforey and Paytan, 2018; Marz et al., 2008). With burial, Fe-oxides are easily reductively dissolved, releasing dissolved phosphorus into the pore waters (Taylor and Macquaker, 2011; Marz et al., 2008). Depending on the depth of the redox boundary, some of this pore water phosphorus is recycled back to the water column through diffusion and/or sediment reworking (bioirrigation and/or energetic events), while the rest re-adsorbs onto undissolved Fe-oxides or is incorporated into authigenic apatite (Marz et al., 2008). Although studies have concluded that apatite formation is enhanced by burial of iron-bound phosphorus (i.e., Lenstra et al., 2018; Tsandev et al., 2012), there are many siliciclastic source rocks in the rock record that do not have noticeably high phosphate abundance (as noted above), suggesting that this model cannot account for all phosphate occurrences.

We propose that the key to the formation of phosphate in some source rocks, but not others, is the amount of available iron relative to the amount of organic matter that reaches the sea floor. The major source of iron in the oceans is fluvial runoff (Libes, 2009). Some authors have commented that phosphatic rocks typically form in shelf to slope settings with high primary productivity and low detrital input (e.g., Libes, 2009; Filippelli, 2011). The dominance of biogenic components in MCC2 and MCC3, coupled with a relative paucity of siliciclastic grains throughout most of these units, also suggests that the studied interval in the Ikpikpuk 1 core may have been iron limited (Taylor and Macquaker, 2011). In addition, Lillis et al. (1999) presented data from MCC3 in the Phoenix 1 well north of the Barrow arch (Fig. 1) that indicated moderate sulfur enrichment of the organic matter, further supporting the interpretation that the studied interval was iron-depleted.

Hydrogen sulfide ($H_2S$) is a by-product of organic matter mineralization by sulfate reduction. If organic matter delivery to the sediments is sufficiently high, a fraction of the organic matter will be anaerobically respired by sulfate reduction below the oxic-anoxic redox boundary. Larger amounts of organic matter delivery to the sediments and more oxygen-depletion in the sediments will result in higher concentrations of $H_2S$ (as well as phosphorus) being released into the pore waters, given sufficient sulfate concentrations. Dissolved iron reacts rapidly with $H_2S$ to form pyrite. When sufficient iron is present, most or all of the $H_2S$ is removed from the pore waters and precipitated as pyrite (or its precursors). In iron-limited early diagenetic environments, however, the relative absence of iron allows $H_2S$ to be oxidized at the sulfidic / oxic interface resulting in lower pH in the pore waters (Taylor and Macquaker, 2011). Furthermore, bacterial iron reduction, an acid-consuming reaction, is also minimized in an iron-limited environment, further favoring lower pH conditions (Taylor and Macquaker, 2011). Precipitation of hydroxyapatite (a precursor to apatite) is favored over calcite in lower pH conditions (Fig. 4 of Taylor and
Macquaker, 2011; Berndmeyer et al., 2012; Coleman, 1985). It is notable that XRD data illustrate that where wt. % total carbonate decreases above 10,287', there is a corresponding increase in wt. % apatite (Fig. 5). This model provides a potential mechanism for significant phosphorus sequestration in the sediment column and may explain why large phosphatic accumulations do not occur in all organic-rich strata.

Localized high concentrations of dissolved phosphorus can also occur due to irregular distribution of organic matter (Konhauser, 2007). This may promote apatite precipitation in localized microenvironments such as within articulated shells, forming the steinkerns that are common within MCC2 and MCC3. Notably, pyrite occurs adjacent to apatite within phosphatic peloids but is rare within phosphatized steinkerns. The pyrite within these peloids may represent the available dissolved iron; once this iron was consumed, H₂S concentrations increased below the oxic / sulfidic interface, thus lowering pH and favoring apatite precipitation. The steinkerns, on the other hand, may represent microenvironments isolated from pore waters and a source of dissolved iron, leading to apatite precipitation due simply to high concentrations of dissolved phosphorus from degradation of organic matter confined within the organism.

Conclusions
Petrographic analysis of carbonate mudstone thin sections from the middle Shublik Formation in three cores from NPR-A indicate that this organic-rich interval primarily consists of biogenic and authigenic constituents, with minor terrigenous siliciclastic input throughout most of the studied section. Background sedimentation processes within the middle Shublik are represented by the halobiid bioclastic wackestone to packstone microfacies. Shells and shell fragments are mainly oriented parallel to bedding, with some abraded fragments, suggesting minor energetic disturbance of the sea floor. Associated silty halobiid bioclastic wackestone to packstone and transported halobiid bioclastic wackestone to packstone microfacies are evidence that more significant episodic energetic events disrupted, winnowed and concentrated biogenic and phosphatic grains and particles. These events also modified pore water chemistry through recycling of old pore waters back to the water column and replenishing upper sediment column pore waters with seawater.

The occurrence of significant apatite in the middle Shublik Formation may be related to low concentrations of dissolved iron relative to available organic matter in the sulfate reducing zone. H₂S is produced during anaerobic respiration (i.e., bacterial sulfate reduction), and quickly reacts with dissolved iron to form pyrite. However, if H₂S continues to accumulate in pore waters after the available dissolved iron is taken up by pyrite, then the pH is lowered, favoring apatite precipitation over calcite. This model may account for the occurrence of significant phosphatic accumulations in some source rocks such as the Shublik, while also explaining why many other source rocks are not phosphate-rich. Further work on authigenic phases and associated pore water chemistry will help elucidate changes in pH and alkalinity that play a key role in determining the paragenetic sequence of mineralization in mudrocks.

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References


