# Sequence stratigraphy, titania diagenesis and relationship to petroleum system modelling

Final Report

OERA Research Project number 400-191

Total project duration: 1 October 2018–31 December 2020

Georgia Pe-Piper

Department of Geology, Saint Mary's University, Halifax, NS B3H 3C3

(902) 420 5744

gpiper@smu.ca

Submitted 4 January 2021

OERA Leading Collaborative Energy Research

NOVA SCOTIA

## 2. Executive Summary

Titania ($TiO_2$) minerals are a minor and rather overlooked component of the diagenetic assemblage in sandstone reservoirs, but are important indicators of the availability of organic acids. Although Titanium (Ti) is typically considered immobile during diagenesis, large quantities of diagenetic titania minerals were observed in the Cretaceous sandstones of known oil- and/or gas-producing fields in the Scotian Basin. These minerals can potentially provide information on fluid flow and migration of hydrocarbons in the basin. Recent studies suggest that Ti mobility in pore water is enhanced by organic acids, so that diagenetic titania minerals occur most commonly either at marine lowstands during eodiagenesis, or during late diagenesis associated with petroleum maturation and migration. Representative samples at various depths from wells in the central Scotian Basin were selected to determine the distribution of diagenetic titania polymorphs. The polymorphs were identified by Raman spectroscopy as rutile, anatase, and brookite. Sedimentary facies, burial depth, temperature, and salinity were investigated to evaluate their relationship to the different titania polymorphs.

Diagenetic anatase was seen both during early diagenesis replacing phytodetritus and during late diagenesis precipitating as neoformed crystals with sharp, straight edges. It has been proposed that humic acids at lowstands result in the dissolution of Ti-bearing minerals and the mobilization of Ti early in the burial history of sandstones, favouring the authigenesis of anatase as pH increased. Diagenetic brookite appears late in the diagenetic paragenesis, occurring in pores as euhedral crystal clusters, as isolated crystals in secondary porosity in completely silicified sandstones, in secondary enlarged remnants of primary pores, and along enlarged intergranular boundaries. Brookite is the most abundant titania polymorph and was predominantly observed in petroleum reservoir sandstones above the free water line, i.e. where hydrocarbon concentration is high. In contrast, anatase was mostly observed below the free water line. Brookite is commonly associated with sphalerite, the transport of which requires high-temperature saline fluids. Large amounts of halogens in the deep basinal fluids derived from the Argo Salt Formation, together with the release of organic acids during hydrocarbon formation, resulted in the complete dissolution of Ti-bearing minerals in deeply buried sandstones, transport of Ti in the form of chelate complexes with $Ti^{4+}$, and the precipitation of diagenetic titania in the up-dip parts of the basin. The abundance of brookite, rather than anatase, in sandstone reservoirs is associated with decreasing pH at the oil-water interfaces. In addition, the decrease in $F^-$ ions and increase of $Cl^-$

ions due to the precipitation of fluorapatite and absorbance of $F^-$ in calcite cements, may have preferentially favoured brookite formation.

The widespread occurrence of diagenetic titania minerals in the Scotian Basin is thus related to the salt tectonics and availability of halogens in formation waters. The occurrence of brookite late in diagenesis, after silica and carbonate cementation, confirms results from fluid inclusion studies, which show that hydrocarbon charge was also relatively late. The distribution of brookite vs. anatase in reservoirs can provide detailed information on the filling and drainage of reservoir rocks and may thus be applicable to detailed reservoir engineering in producing fields.

# 3. Table of Contents


2. Executive Summary ........................................ 2
4. Project objectives ........................................ 5
5. Methodology ........................................ 6
6. Key findings and Outcomes ........................................ 8
   Introduction ........................................ 8
   Observations ........................................ 8
   Interpretation ........................................ 17
7. Conclusions and Impact ........................................ 19
8. Recommendations and Future Considerations ........................................ 20
9. Financial ........................................ 21
10. Highly Qualified Personnel (HQP) Summary ........................................ 21
11. Dissemination ........................................ 222
12. References ........................................ 22


**Figures**


Fig. 1. Location of studied wells ........................................ 6
Fig. 2. Stratigraphic and diagenetic context of titania polymorphs ........................................ 7
Fig. 3. Crystal structures and Raman spectra of titania polymorphs ........................................ 8
Fig. 4. BSE images of titania polymorphs ........................................ 19
Fig. 5. Titania polymorphs from oil and gas fields ........................................ 20
Fig. 6. Titania polymorphs from other dry wells ........................................ 21
Fig. 7. Titania polymorphs related to free water level in producing fields ........................................ 21
Fig. 8. Plot of TiO2 vs. halogens for diagenetic titania polymorphs ........................................ 16
Fig. 9. Paragenetic sequence of diagenetic minerals ........................................ 16
Fig. 10. Processes of Ti mobility and precipitation ........................................ 18


**Tables**


Table 1. Chemical composition of different titania polymorphs ........................................ 15
Table 2.. Details of dissemination ........................................ 21

## 4. Project objectives

Diagenetic titania minerals are widespread in the Scotian Basin and can potentially provide information on fluid flow and migration of hydrocarbons in the basin. Recent studies suggest that Ti mobility in pore water is enhanced by organic acids, so that diagenetic titania minerals occur most commonly (a) at lowstands during eodiagenesis, and (b) during later diagenesis associated with petroleum maturation and migration. Previous studies of titania authigenesis in the presence of hydrocarbons have mostly focussed on organic-rich soil and black shales. Anatase is the dominant titania phase mineral to precipitate with bitumen and/or at oil-water contacts in shales and siltstones (Fuchs et al. 2015; Schulz et al. 2016; Liu et al. 2019), whereas brookite has been reported in some bitumen-bearing samples (Parnell et al. 2017). In natural systems, growth and stability of titania polymorphs is mainly controlled by local pH conditions (Zhang and Banfield, 2014).

The objectives of this study were: (1) To characterize and classify diagenetic titania minerals by polymorph (rutile, anatase, brookite), morphology, mineral chemistry, relationship to other minerals and hence diagenetic paragenesis. (2) To confirm the relationship between late diagenetic titania and hydrocarbon migration, to characterize the polymorphs formed, and thus assess the use of titania polymorphs as “pathfinders” for hydrocarbon charge. (3) To relate hydrocarbon charge, inferred from titania minerals, to diagenetic paragenesis and fluid inclusion data, and thus re-evaluate the thermal and charge history of well-known parts of the Scotian Basin and to recommend suitable parameters for petroleum system modelling. The overall motivation of the project was to try to integrate the hydrocarbon charge evidence from diagenetic titania with existing fluid inclusion and sequence stratigraphy data, to better constrain the complex thermal history of the Scotian Basin.

OERA has identified that reservoir quality is a severe exploration risk in the Scotian Basin. OERA has also identified petroleum system modelling as one of its research priorities. This study was designed to investigate an innovative approach to constraining the timing of hydrocarbon migration in the basin, in relation to diagenetic and structural evolution of fairways and reservoirs. It thus contributes to the understanding of reservoir quality as influenced by diagenesis and provides information to validate petroleum system modelling that is at present inadequately constrained in terms of thermal evolution and timing of hydrocarbon charge. We supervised a

Nova Scotian M.Sc. student, Alexis Imperial, to carry out the necessary analytical work to deliver this study.

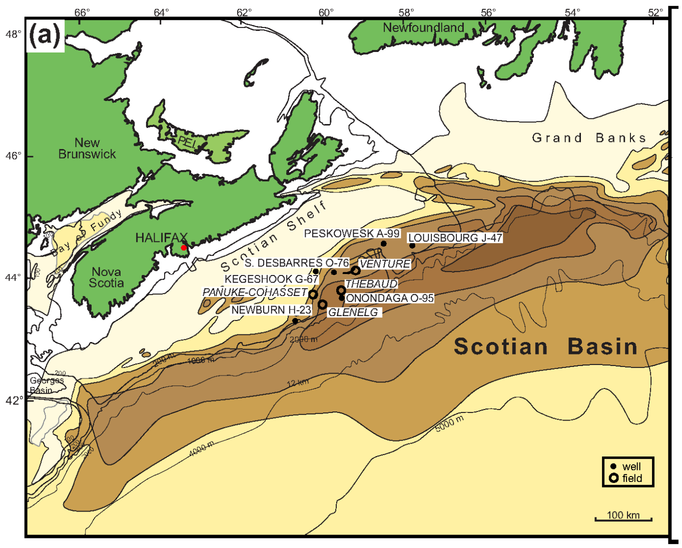


Figure 1. Map of Scotian Basin showing wells that were sampled.

## 5. Methodology

Representative samples at various depths from wells in the central Scotian Basin (Fig. 1) were selected to determine the distribution of diagenetic titania polymorphs (Fig. 2). The polymorphs were identified by Raman spectroscopy as rutile, anatase, and brookite (Fig. 3). The different titania polymorphs were compared with sedimentary facies, burial depth, and temperature and salinity interpreted from fluid inclusions (Fig. 2; Karim et al., 2012; Pe-Piper 2016). To further understand diagenetic titania precipitation and its relationship with hydrocarbons, a more detailed investigation of grain size, bed thickness, permeability and porosity were studied on four known oil and/or gas producing fields: Venture, Thebaud, Glenelg and Cohasset-Panuke. Texture and morphology of the polymorphs were analyzed using scanning electron microscope-backscattered electron images together with transmitted and reflected light microscope images. Selected samples were analysed by electron microprobe for trace element composition including halogens. Distribution of the different polymorphs was compared with the sequence stratigraphic position of the samples, based on Karim et al. (2010) for Thebaud and Glenelg and Gould et al. (2012) for Panuke-Cohasset and Venture.

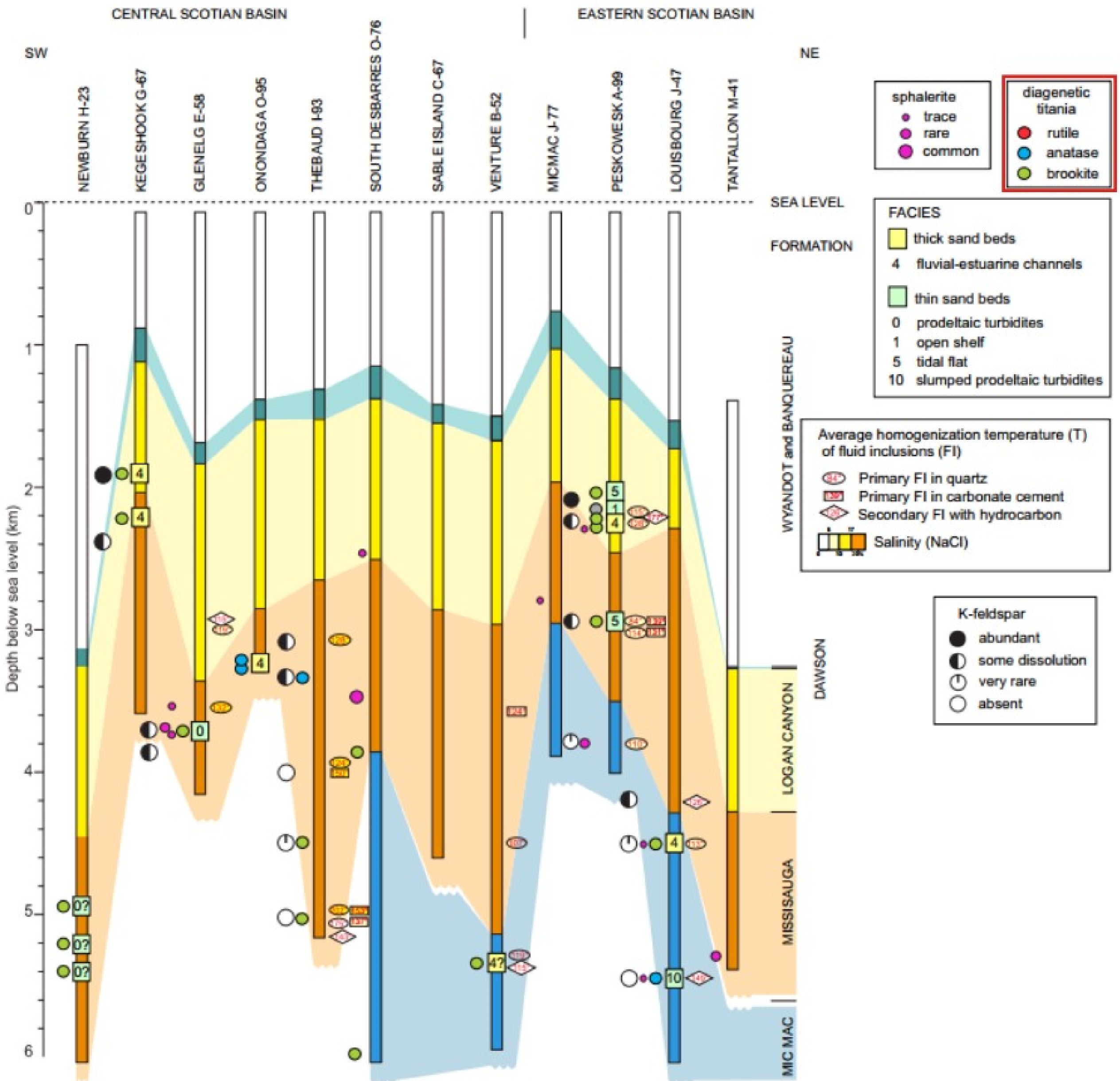


Figure 2. Types of titania polymorphs in their stratigraphic and diagenetic context. Fluid inclusions and K-feldspar from Pe-Piper et al. (2015).

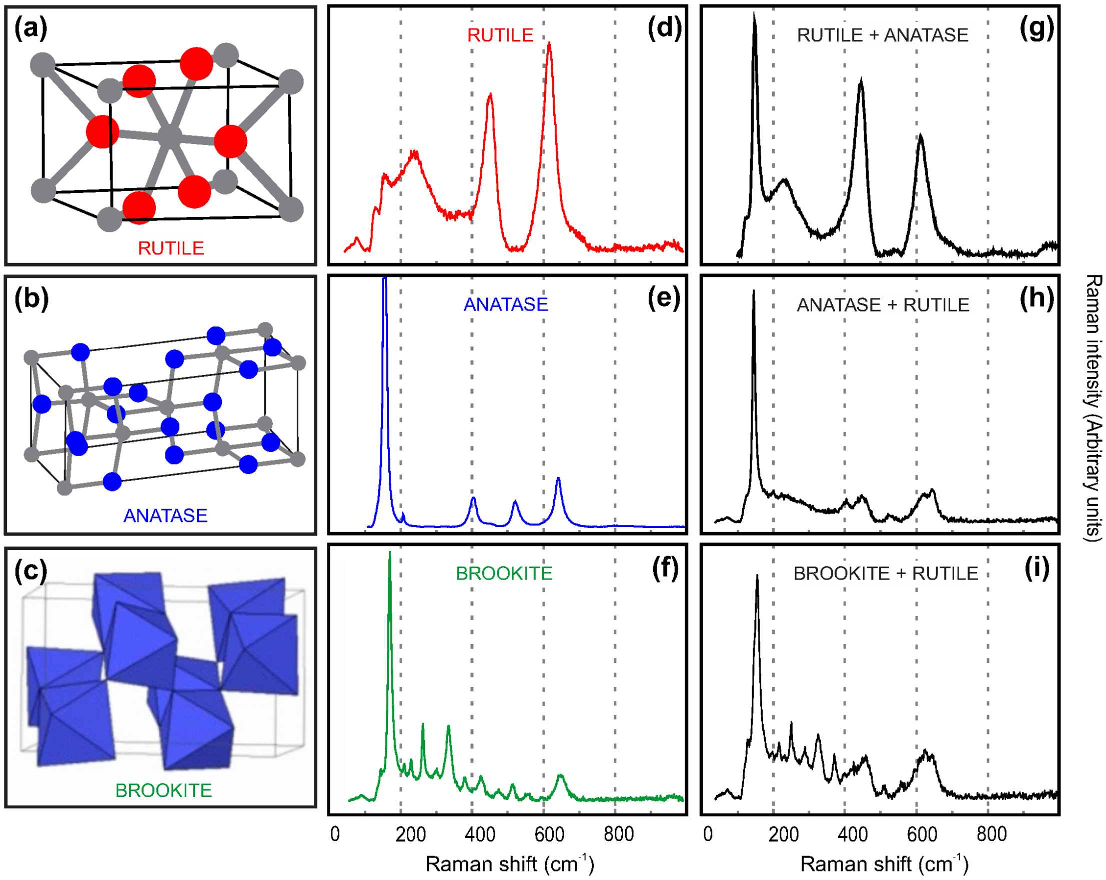


Figure 3. Crystal structure of the three titania polymorphs and examples of their Raman spectra.

## 6. Key findings and Outcomes

### Introduction

The detailed results will be publicly available in an M.Sc. thesis by Alexis Imperial, that will be completed and defended in 2021. The principal findings are also presented in a paper at present in advanced draft form. They were also presented in a poster at the Energy3 Conference.

### Observations

Diagenetic rutile is rare and was seen to rim detrital quartz crystals. Diagenetic anatase primarily occurs as a replacive mineral, usually replacing rutile and phytodetritus, and is demonstrably of eodiagenetic origin. In some cases, neoformed euhedral diagenetic anatase appears to fill pores while anhedral-subhedral crystals of anatase have precipitated adjacent to detrital rutile grains. Diagenetic brookite is predominantly neoformed, occurring in pores as euhedral crystal clusters or as isolated crystals in secondary porosity in completely silicified sandstones, in secondary enlarged remnants of primary pores, or along enlarged intergranular boundaries. Similar to anatase, some diagenetic brookite appear to have precipitated near altered or dissolved detrital rutile crystals. Brookite is the most abundant titania polymorph and predominantly occurs in sandstones that have evidence of transit of deep basinal fluids, based on fluid inclusion data and the presence of the hydrothermal mineral sphalerite. The observed regional titania polymorph distributions (Fig. 2) provide a background against which variability due to the effects of petroleum migration can be assessed.

Textural relationships of the titania polymorphs with other diagenetic minerals suggest at least two stages of titania precipitation. Most rutile appears as framework grains and shows evidence of pedogenic alteration of ilmenite (Fig. 4a). Early mineralization of titania resulted in the precipitation of anatase associated with the partial dissolution of detrital rutile and pseudomorphic replacement of phytodetritus before sediment compaction and quartz overgrowths (Figs. 4c and 5f). Sponge-like neoformed anatase was also observed along framework quartz before calcite cementation, hindering the formation of quartz overgrowths (Fig. 6d). These textures of anatase suggest precipitation early in the paragenetic sequence, in places below sequence boundaries as the result of flux of meteoric waters and biogeochemical processes (Pe-Piper et al. 2011).

Later precipitation of diagenetic titania minerals in the Scotian Basin is associated with extensive dissolution of Ti-bearing minerals including early diagenetic titania minerals. Euhedral crystals of anatase and brookite partially or completely fill pores that display an evident framework grain outline (Figs. 5a, 6b and 6c). In Cohasset A-52 2230.38m, clean euhedral anatase with straight edges fills the remaining pore already partly filled by brookite (Fig. 5a, pos. a). Brookite engulfs quartz overgrowths (Fig. 4e), while late anatase and brookite both engulf or replace the two growth phases of chlorite rims recognised by Gould et al. (2010) (Figs. 4e, position a; 5e, position a).

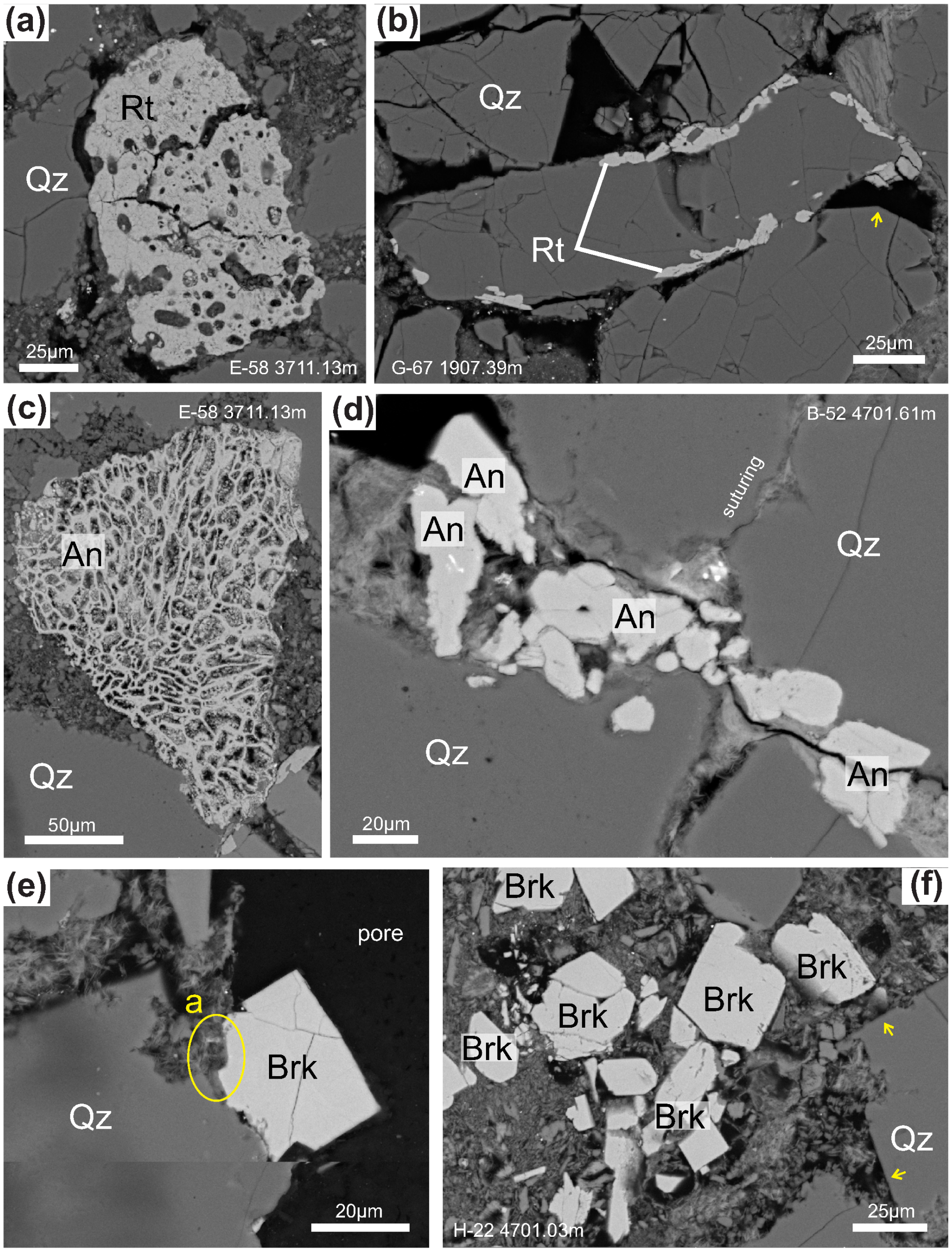


Figure 4. Representative backscattered electron images of main occurrences of diagenetic titania minerals. (**a**) Ilmenite grain pedogenically altered to rutile (Rt). (**b**) Diagenetic rutile rimming quartz overgrowth. (**c**) Anatase (An) replacing uncompacted phytodetritus with quartz (Qz) framework grains lacking overgrowths. (**d**) Cluster of euhedral anatase precipitating along fracture of sutured quartz. (**e**) Isolated crystal of brookite in pore semi-attached to a framework quartz grain (**f**) Cluster of clean brookite (Brk) crystals with straight edges in pore. Yellow arrows indicate quartz overgrowths.

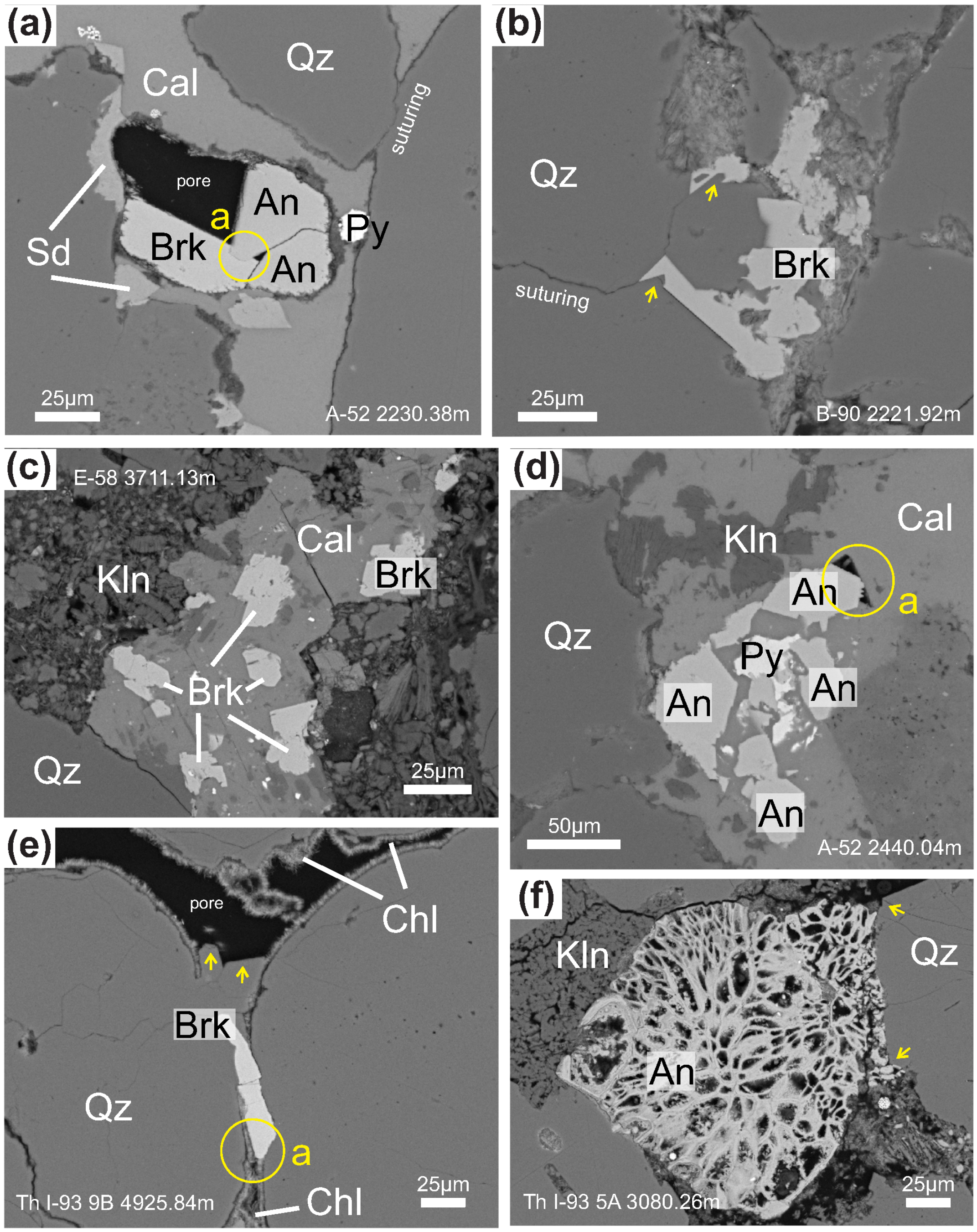


Figure 5. Representative backscattered electron images of occurrences of diagenetic titania from four oil- and/or gas-producing fields (Panuke-Cohasset, Glenelg, Thebaud and Venture fields). **(a)** Brookite and anatase fills a framework pore. **(b)** Brookite occurring along quartz grain boundaries, engulfing overgrowths. **(c)** A cluster of brookite in partly dissolved calcite cement. **(d)** Cluster of clean anatase crystals in calcite cement with pyrite. **(e)** A single brookite in intergranular quartz boundary overprinting chlorite rims. **(f)** Pseudomorphic anatase replacing phytodetritus material.

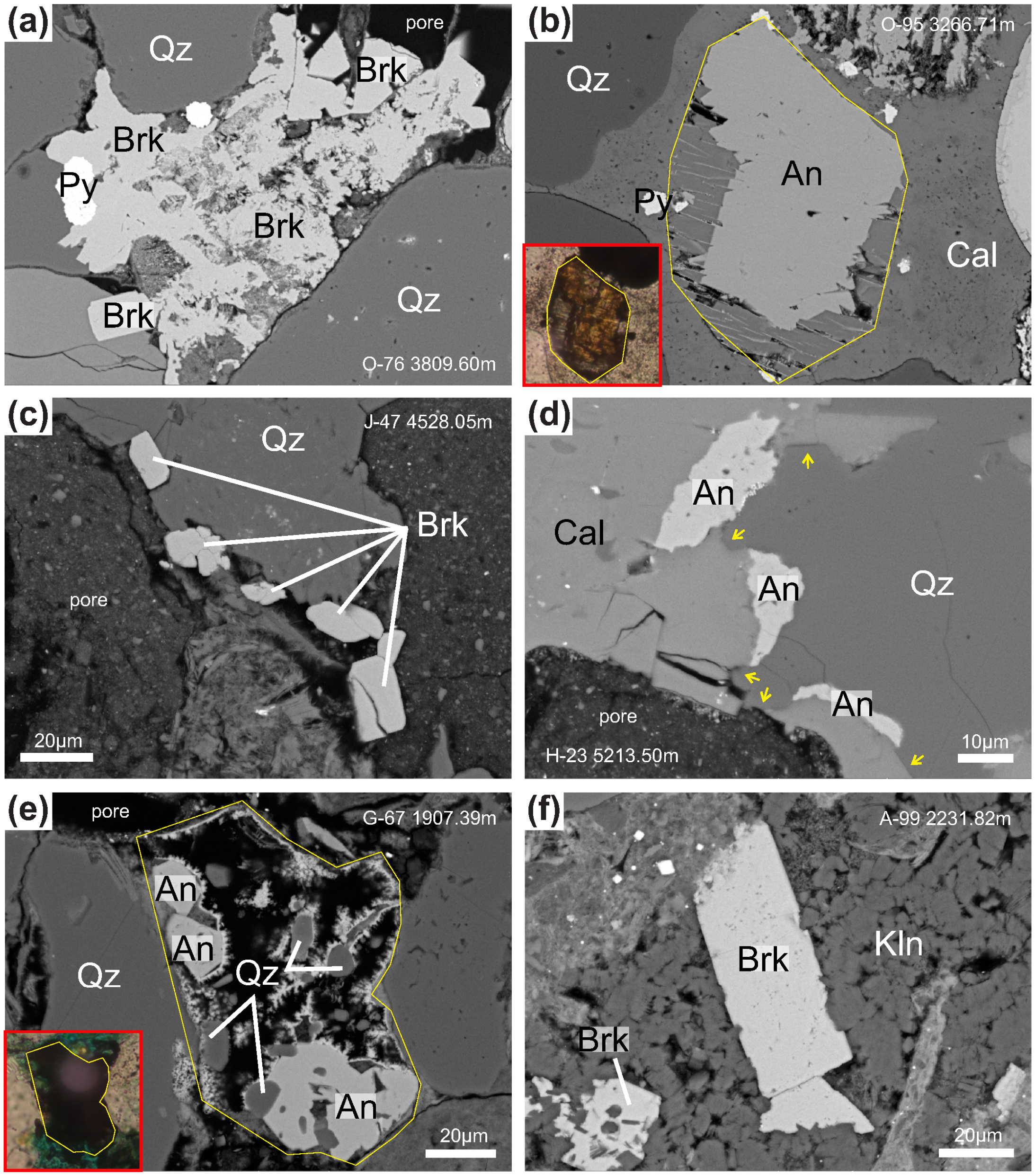


Figure 6. Representative backscattered electron images of diagenetic titania minerals from other wells (South Desbarres O-76, Onondaga O-95, Louisburg J-47, Newburn H-23, Kegeshook G-67, Peskowesk A-99. South Desbarres O-76, Onondaga O-95 and Louisburg J-47. **(a)** Brookite (Brk) precipitating clean crystals with straight edges outwards?. **(b)** Diagenetic anatase (An) and calcite (Cal) replaced a framework grain. **(c)** A string of euhedral brookite crystals occurring along a fracture. **(d)** Sponge-like anatase in between calcite and quartz (Qz) crystal boundary engulfing quartz overgrowths. **(e)** Anatase partially replacing a framework grain with quartz **(f)** Brookite crystals in pore among cross-cutting booklets of kaolinite (Kln). Yellow arrows indicate quartz overgrowths.

Secondary porosity resulting from the fracturing and dissolution of quartz also appears to be another important site of late titania precipitation. Rutile, anatase and brookite have all been observed to precipitate in fractures and in dissolution voids in quartz crystals. The dissolution of detrital rutile and of quartz suggests either a hot and/or very acidic fluid circulation in the basin at the time. Secondary fluid inclusions from fractures cutting quartz and carbonate cement commonly contain hydrocarbons (Karim et al. 2012). Previous work of diagenesis in the Scotian Basin identified that titania minerals occur with late diagenetic sphalerite, which requires high temperatures and saline fluids for transport and precipitation (Pe-Piper et al. 2015).

Unexpectedly, titania minerals from reservoir sandstones of Panuke-Cohasset, Glenelg, Thebaud and Venture fields show a systematic variation with the free water level (Fig. 7). Anatase predominantly occurs below estimated free water levels recorded in well history reports. In contrast, brookite mainly occurs above free water levels of all four oil-/gas-producing fields. Diagenetic rutile appears randomly distributed.

The trace element chemistry of titania polymorphs (Table 1) shows that diagenetic brookite has the lowest $TiO_2$ (mean 94.1 wt%) content compared to diagenetic anatase (~96.8 wt%) and diagenetic rutile (~96.1 wt%). Diagenetic anatase and brookite from the Thebaud and Venture fields on average have lesser $TiO_2$ content (<94 wt%) compared to anatase and brookite from Panuke-Cohasset and Glenelg (>94 wt%). These latter two fields resemble wells lacking significant hydrocarbons, including Peskowesk A-99, Kegeshook G-67 and Newburn H-23.

Metal trace impurities in diagenetic anatase and brookite differ between polymorphs and between oil-/gas-producing fields. In all four fields, brookite has elevated amounts of FeO (>0.6 wt%) and $V_2O_3$ (>0.55 wt%) (Table 1). Brookite from non-producing wells also had higher amounts of FeO, $V_2O_3$ and $Al_2O_3$, when compared to anatase from the same wells. In the Venture field, $V_2O_3$ is higher while $Al_2O_3$ is lower in both brookite and anatase, when compared to other oil-/gas-producing fields. Brookite analyses from non-producing wells have relatively lower $Al_2O_3$ content compared to oil-/gas-producing fields. Brookite from the Thebaud field has high contents of $Nb_2O_5$, whereas brookite from the Glenelg field has elevated amounts of BaO. Unfortunately, data are not available to compare the trace-element content of the titania polymorphs with trace-element contents of associated oils.

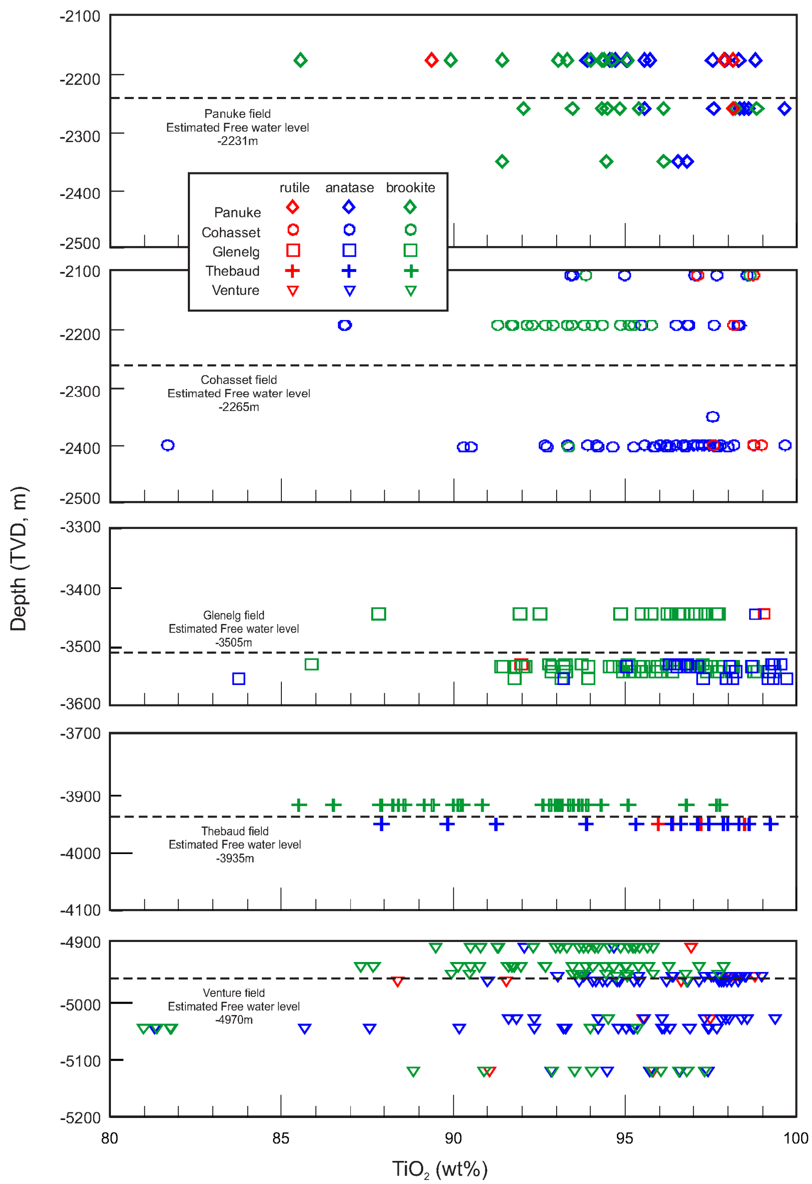


Figure 7. Distribution of all diagenetic titania minerals, both replacive and neoformed, in the Panuke-Cohasset, Glenelg, Thebaud and Venture fields in relation to each field's free water levels (shown by dashed line, from well history reports).

Table 1. Mean compositions (wt %) of diagenetic titania polymorphs from producing oil/gas fields

| | Anatase | | | | Brookite | | | | Rutile |
|---|---|---|---|---|---|---|---|---|---|
| | Panuke-Cohasset | Glenelg | Thebaud | Venture | Panuke-Cohasset | Glenelg | Thebaud | Venture | All |
| $TiO_2$ | 96.25 | 98.04 | 96.20 | 96.63 | 93.85 | 95.76 | 93.14 | 93.84 | 97.48 |
| $V_2O_3$ | 0.4528 | 0.3572 | 0.4538 | 0.4956 | 0.5658 | 0.4832 | 0.5596 | 0.7097 | 0.4416 |
| CaO | 0.3660 | 0.1341 | 0.5190 | 0.4161 | 0.3233 | 0.1314 | 0.1780 | 0.3392 | 0.4130 |
| MgO | 0.0089 | 0.0028 | 0.0130 | 0.0133 | 0.0151 | 0.0039 | 0.0041 | 0.0083 | 0.0000 |
| $SiO_2$ | 0.3949 | 0.5289 | 0.8203 | 0.3441 | 0.5733 | 0.6442 | 0.6310 | 0.6675 | 0.3328 |
| $SnO_2$ | 0.0462 | 0.0332 | 0.0388 | 0.0383 | 0.0423 | 0.0479 | 0.0482 | 0.0436 | 0.0209 |
| FeO | 0.4340 | 0.4932 | 0.3988 | 0.4535 | 1.3274 | 0.9507 | 1.4012 | 1.2922 | 0.4120 |
| $Cr_2O_3$ | 0.0096 | 0.0152 | 0.0126 | 0.0137 | 0.0624 | 0.0891 | 0.1153 | 0.1326 | 0.0707 |
| $Nb_2O_5$ | 0.5516 | 0.2251 | 0.4036 | 0.4559 | 0.2135 | 0.2108 | 1.3180 | 0.6157 | 0.3113 |
| MnO | 0.0066 | 0.0448 | 0.0099 | 0.0103 | 0.0045 | 0.0071 | 0.0051 | 0.0111 | 0.0220 |
| $ZrO_2$ | 0.3025 | 0.1219 | 0.1604 | 0.3126 | 0.3156 | 0.2191 | 0.4265 | 0.5354 | 0.0000 |
| $Al_2O_3$ | 0.1521 | 0.1075 | 0.1509 | 0.1198 | 0.7132 | 0.7578 | 0.6047 | 0.5633 | 0.0408 |
| $Na_2O$ | 0.0745 | 0.0729 | 0.0651 | 0.0690 | 0.0771 | 0.0738 | 0.0696 | 0.0778 | 0.0665 |
| BaO | 0.0103 | 0.0499 | 0.0000 | 0.0091 | 0.0115 | 0.1256 | 0.0202 | 0.0284 | 0.0000 |
| $MoO_3$ | 0.0123 | 0.0177 | 0.0146 | 0.0129 | 0.0135 | 0.0133 | 0.0176 | 0.0095 | 0.0000 |
| $K_2O$ | 0.0380 | 0.0126 | 0.0268 | 0.0222 | 0.0192 | 0.0139 | 0.0171 | 0.0138 | 0.0022 |
| $P_2O_5$ | 0.0132 | 0.0109 | 0.0151 | 0.0197 | 0.0369 | 0.0338 | 0.0354 | 0.0211 | 0.0000 |
| F | 0.0004 | 0.0114 | 0.0170 | 0.0072 | | 0.0148 | | 0.0145 | |
| Cl | 0.0002 | 0.0076 | 0.0094 | 0.0053 | | 0.0104 | | 0.0223 | |
| Total | 99.13 | 100.29 | 99.31 | 99.45 | 98.16 | 99.59 | 98.60 | 98.91 | 99.62 |

Chlorine (Cl) and fluorine (F) content within diagenetic titania minerals shows no variance between anatase and brookite. However, diagenetic anatase and brookite from oil-/gas-producing fields show higher Cl content (0-0.02 wt % Cl) compared to anatase and brookite from the non-producing (wet) wells Peskowesk A-99, Kegeshook G-67 and Newburn H-23 (<0.01 wt % Cl) (Fig. 8a). In addition, diagenetic titania minerals appear to have more F (up to 0.05 wt %) than Cl incorporated in their crystal structures (Figs. 8b).

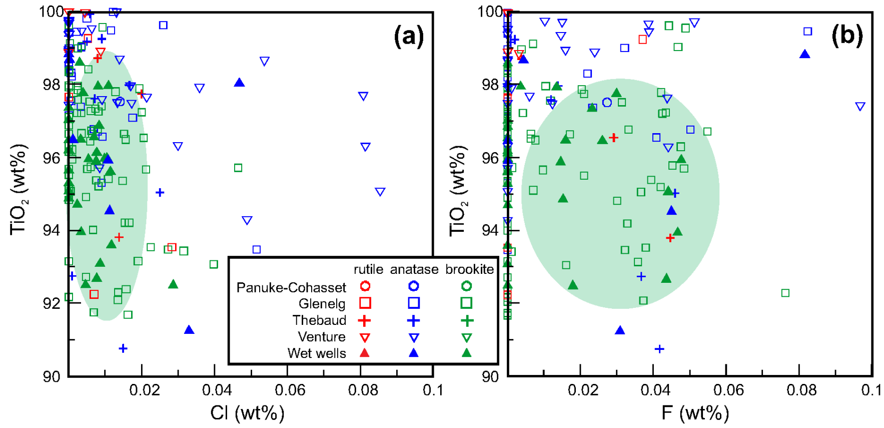


Figure 8. Binary plots of $TiO_2$ vs halogens (Cl and F) for diagenetic titania minerals using electron microprobe data.

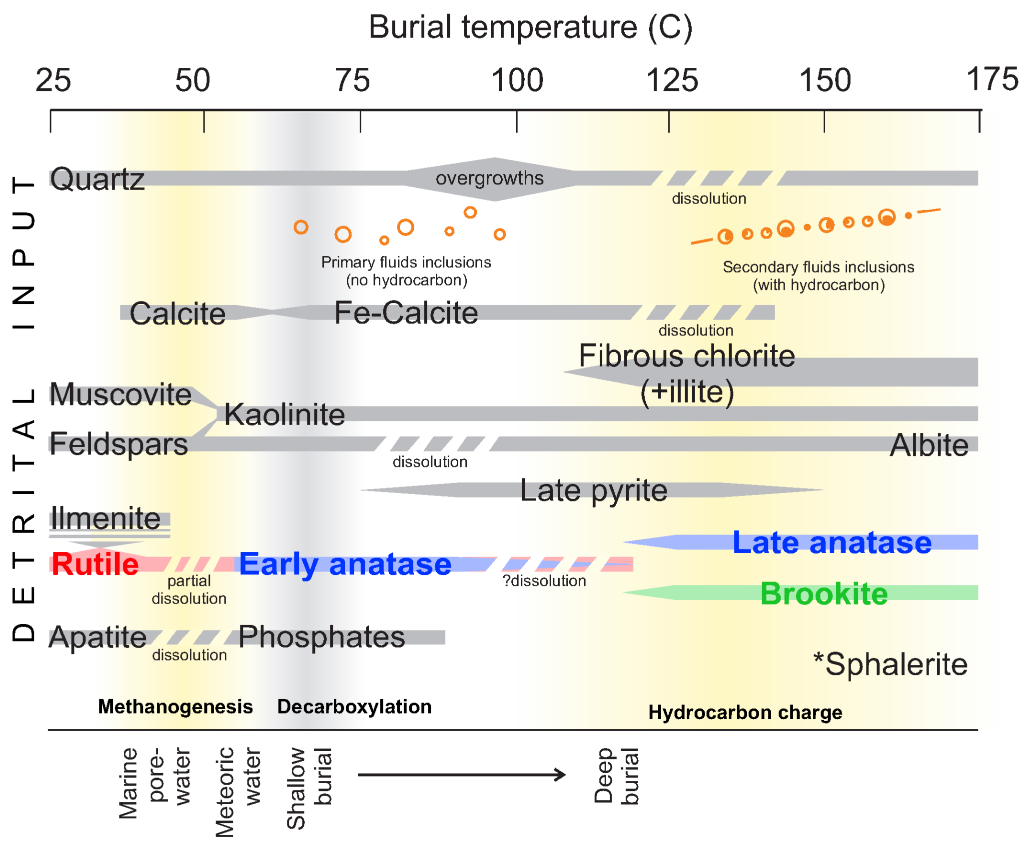


Figure 9. Paragenetic sequence of titania polymorphs (rutile, anatase and brookite) in the Scotian Basin with respect to other minerals and fluid circulation in the basin.

**Interpretation**

Textural relationships of the titania polymorphs with other diagenetic minerals suggest at least two stages of titania precipitation. Diagenetic titania minerals were observed during early diagenesis (eogenesis) predating quartz overgrowth and again during late diagenesis (mesogenesis) post-dating quartz overgrowths and chlorite rims (Fig. 9) and associated with various indicators of hot, saline, corrosive basinal fluids (Pe-Piper et al. 2015).

Almost no analyses of metals in crude oil are available for the Scotian Basin. However, in other basins, trace concentration of Ti in crude oil, typically 2–4 ppm (Hardaway et al. 2004) but as high as 11 ppm (Fuchs et al., 2015), suggests an ability of hydrocarbon fluids to dissolve titanium. Porphyrins are important metal-transporting agents in petroleum (Manning and Gize, 1993), responsible for high concentration of Ni and V in crude oil. The chemical behaviour of $Ti^{4+}$ is similar to $Ni^{2+}$ and $V^{2+}$, suggesting similar solubility in hydrocarbon fluids.

The presence of halogens (Cl and F) in aqueous solutions increases Ti solubility. Titania solubility is higher in F-rich brines compared to Cl-rich brines, particularly at lower temperatures and pressures.

The shales of the Scotian Basin have a high Ti abundance (~1.6 wt% $TiO_2$), double that of global average shales (Pe-Piper et al., 2008), suggesting unusually abundant supply of Ti by rivers. This supply was principally as grains of ilmenite and its alteration products (Pe-Piper et al. 2005). Mineralization of early anatase in the shallow part of the Scotian Basin was facilitated by humic acids released from meteoric waters. Chelate complexes of $Ti^{4+}$ with humic acids caused the mobilization of $Ti^{4+}$ and the partial dissolution of Ti-bearing detrital minerals (Fig. 10). As pH increases, anatase precipitated along cell walls of phytodetritus or adjacent to detrital rutile.

Precipitation of late anatase and brookite was facilitated by organic acids produced during hydrocarbon migration and by halogen-rich brines. Similar to humic acids, organic acids (oxalic and acetic) and $Cl^-$ and $F^-$ formed chelate complexes with $Ti^{4+}$, completely dissolving detrital Ti-bearing minerals and eogenetic titania. As pH increases, Ti will precipitate forming anatase aggregates. Anatase will be the first phase to form as it has the lowest surface energy. As pH continues to increase, microcrystalline anatase will precipitate. At conditions of low pH, aggregates of anatase will convert to brookite and brookite crystals may continue to grow.

Hydrocarbon fluids released during hydrocarbon charge during mesodiagenesis facilitated transport of Ti and precipitation of titania minerals in the Scotian Basin. Distribution of titania minerals in reservoir sandstones suggest brookite precipitation is synchronous with hydrocarbon charge. The occurrence of brookite above the free water line confirms the association of brookite with hydrocarbons.

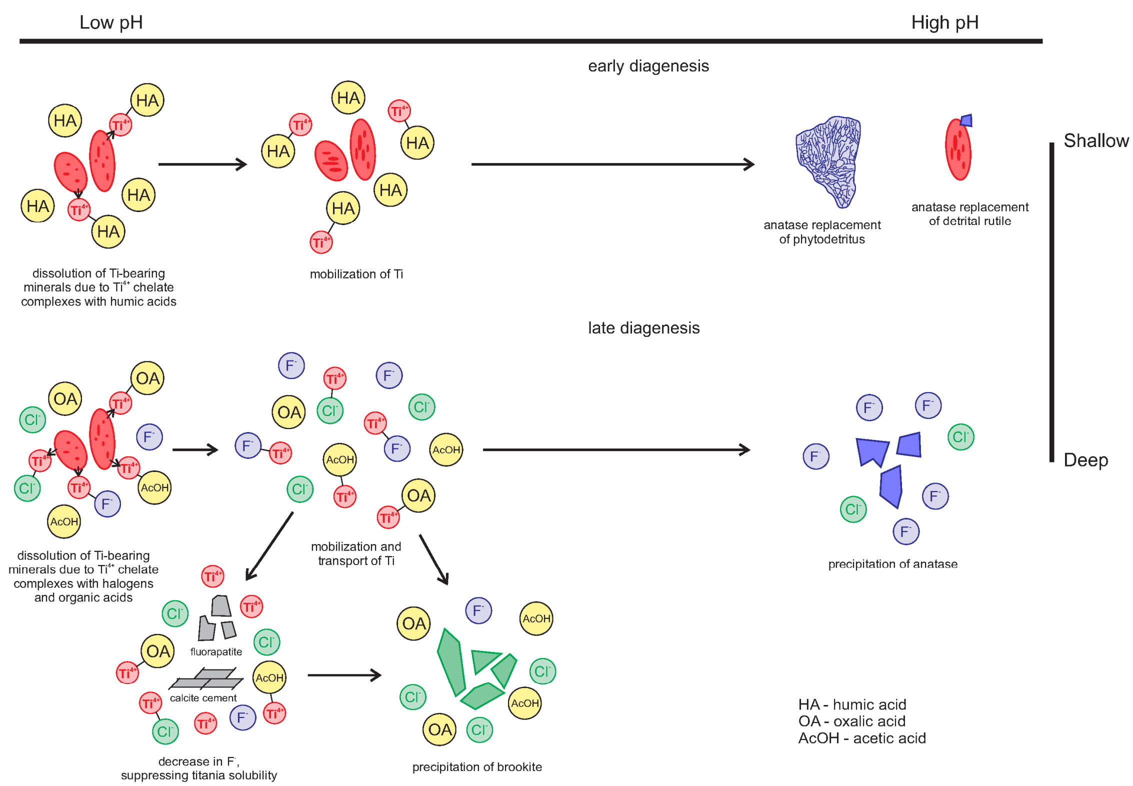


Figure 10. Processes of Ti mobility and titania polymorph diagenesis in the Scotian Basin

# 7. Conclusions and Impact

Modern analytical techniques allow the characterization and classification of diagenetic titania minerals according to polymorph type, morphology, trace-element chemistry, relationship to other minerals and hence diagenetic paragenesis (Objective 1). The methodological protocol we have used can be readily applied to detailed studies of individual fields or to scoping studies of other basins.

The distribution of late diagenetic brookite and anatase in hydrocarbon reservoirs is controlled by the distribution of water and hydrocarbons, with brookite dominant above the free water level. More generally, diagenetic brookite appears to be a "pathfinder" for hydrocarbon migration through secondary porosity formed by corrosion and fracturing of thick sandstone fairways, and is associated with late diagenetic minerals including sphalerite, barite, ferroan chlorite and ankerite. Halogens play an important role in the dissolution and transport of Ti, either from buried early diagenetic anatase or from Ti-bearing ferromagnesian minerals (Objective 2). The study provides new insights into the linkages between titania minerals and hydrocarbons in petroleum basins, with both halogens and organic matter important for the dissolution and transport of Ti. Patterns developed during eodiagenesis, related to sequence stratigraphy, were largely obliterated in reservoir sandstones during mesodiagenesis. The most innovative direct result of this study for petroleum geology is at the reservoir level: the recognition of past free water levels from anatase and brookite distribution.

Temperatures recorded in primary fluid inclusions in quartz overgrowths and ferroan calcite cements are within the normal oil window. Yet hydrocarbons were trapped almost solely in later secondary fluid inclusions, and the evidence of late diagenetic brookite also indicates that most hydrocarbon charge was later. Advection of hot basinal fluids through spaced fairways of channel sandstones favoured rapid growth of diagenetic silica and ferroan calcite, in turn favouring trapping of fluid inclusions. These measured trapping temperatures do not represent regional temperatures in shales. (Objective 3). The study has confirmed that from a petroleum modelling point of view, hydrocarbon charge was "late". As with some other diagenetic minerals in the Scotian Basin, halogen-rich formation waters are important in facilitating transport of elements, in this case Ti to form brookite.

## 8. Recommendations and Future Considerations

Within the time and budgetary constraints of this study, we have met the original objectives of the study and have shown the potential for using titania polymorphs for tracking hydrocarbon migration within the Scotian Basin. The following are desirable future actions:

1. The lack of analyses of the metal content of oils from the Scotian Basin, other than from the Thebaud field, was a serious limitation to understanding the causes of different behaviour of titania polymorphs in different fields.

2. The definition of free water level from brookite and anatase was quite clear in Cohasset, Venture and Thebaud, but less pronounced in the Panuke and Glenelg fields. The reason for this is unknown, but further investigation might yield interesting insights.

3. To test and develop the application of the method to reservoir engineering, a follow up study is needed in collaboration with an industry reservoir engineering team. One possibility would be a detailed study of the Venture field, where the filling sequence of reservoirs was resolved by Richards et al. (2008).

4. To test the wider applicability of the method, it would be useful to evaluate basins with (a) less bulk Ti in shales than the Scotian Basin; and (b) basins lacking significant availability of halogens from salt deposits.

**financial information redacted**

## 11. Dissemination

| Refereed publications: |
|---|
| Imperial, A., Pe-Piper, G., Piper, D.J.W. and Grey, I. (in final draft). Identifying pseudorutile and kleberite using laser Raman microspectroscopy. . |
| Imperial, A., Pe-Piper, G., Piper, D.J.W. and Clyburne, J. (in advanced draft form). Titania polymorphs as indicators of hydrocarbon migration in the Scotian Basin. |
| **Abstracts:** |
| Imperial, A., Pe-Piper, G., Piper, D.J.W.. 2019. The use of titania polymorphs as indicators of mesodiagenesis at hydrocarbon charge. Atlantic Geoscience Society Colloquium, Fredericton February 2019. |
| Imperial, A., Pe-Piper, G., Piper, D.J.W.. 2019. The use of titania polymorphs as indicators of mesodiagenesis at hydrocarbon charge. Energy3 conference, Halifax, October 2019. |
| Imperial, A., Pe-Piper, G. and Piper, D.J.W., 2020. The use of titania polymorphs as indicators of mesodiagenesis at hydrocarbon charge. Atlantic Geoscience Society Colloquium, Truro, February 2020. |
| **Awards:** |
| Alexis Imperial 2019. Best graduate poster at Energy 3 conference, Halifax. |
| **Other:** |
| M.Sc. thesis in preparation |

Note that preparation of the M.Sc. and publications has been delayed by COVID-19.

## 12. References

Fuchs, S., Schumann, D., Williams-Jones, A.E., & Vali, H., 2015. The growth and concentration of uranium and titanium minerals in hydrocarbons of the Carbon Leader Reef, Witwatersrand Supergroup, South Africa. *Chem Geol.* 393-394, 55–66.

Gould, K., Pe-Piper, G. & Piper, D.J.W., 2010. Relationship of diagenetic chlorite rims to depositional facies in Lower Cretaceous reservoir sandstones of the Scotian Basin. *Sedimentology*, 57, 587–610.

Gould, K.M., Piper, D.J.W. & Pe-Piper, G., 2012. Lateral variation in sandstone lithofacies from conventional core, Scotian Basin: implications for reservoir quality and connectivity. *Canadian Journal of Earth Sciences*, 49, 1478–1503.

Hardaway, C., Sneddon, J. & Beck, J.N., 2004. Determination of metals in crude oil by atomic spectroscopy. *Analytical Letters*, 37 (14), 2881–2899.

Karim, A., Pe-Piper, G. & Piper, D.J.W., 2010. Controls on diagenesis of Lower Cretaceous reservoir sandstones in the western Sable Subbasin, offshore Nova Scotia. *Sedimentary Geology*, 224, 65–83.

Karim, A., Pe-Piper, G., Piper, D. J.W., & Hanley, J. J., 2011. Thermal and hydrocarbon-charge history and the relationship between diagenesis and reservoir connectivity: Venture field, offshore Nova Scotia, eastern Canada: *Canadian Journal of Earth Sciences*, 48, 1293–1306.

Karim, A., Hanley, J.J., Pe-Piper, G., & Piper, D.J.W., 2012. Paleohydrogeological and thermal events recorded by fluid inclusions and stable isotopes of diagenetic minerals in Lower Cretaceous sandstones, offshore Nova Scotia, Canada. *AAPG Bulletin*, 96: 1147–1169.

Liu, Z.-R.R., Zhou, M.-F., Williams-Jones, A.E., Wang, W., & Gao, J.F., 2019. Diagenetic mobilization of Ti and formation of brookite/anatase in early Cambrian black shales, South China. *Chemical Geology*, 506, 79–96.

Manning, D.A. & Gize, A.P., 1993. The role of organic matter in ore transport processes. In *Organic Geochemistry*, Engel, M.H. & Macko, S.A.. Plenum Press, New York, pp. 547–563.

Parnell, J., Bowden, S. & Muirhead, D., 2017. Subsurface biodegradation of crude oil in a fractured basement reservoir, Shropshire, UK. *Journal of the Geological Society*, 174. 655–666.

Pe-Piper, G., 2016. Reservoir quality and sediment delivery: Mesozoic Scotian Basin. Report to OERA, 125 p.

Pe-Piper, G., Piper, D.J.W., & Dolansky, L., 2005. Alteration of ilmenite in the Cretaceous sandstones of Nova Scotia, southeastern Canada. *Clays and Clay Minerals*, 53, 490–510.

Pe-Piper, G., Triantafyllidis, S. & Piper, D.J.W., 2008. Geochemical identification of clastic sediment provenance from known sources of similar geology: the Cretaceous Scotian Basin, Canada. *Journal of Sedimentary Research*, 78, 595–607.

Pe-Piper, G., Karim, A., & Piper, D.J.W., 2011. Authigenesis of Titania Minerals and the Mobility of Ti: New Evidence From Pro-Deltaic Sandstones, Cretaceous Scotian Basin, Canada. *Journal of Sedimentary Research*, 81: 762–773

Pe-Piper, G., Piper, D.J.W., Zhang, Y., & Chavez, I., 2015. Diagenetic barite and sphalerite in middle Mesozoic sandstones, Scotian Basin, as tracers for basin hydrology. *AAPG Bulletin*, 99: 1281–1313.

Pe-Piper, G., Sangster, C. & Zhang, Y., 2017. Diagenetic F-rich ferroan calcite and zircon in the offshore Scotian Basin, eastern Canada: Significance for understanding thermal evolution of the basin. *American Mineralogist*, 102, 1542–1555.

Richards, B., Fairchild, L.H., Vrolijk, P.J., & Hippler, S.J. 2008. Reservoir Connectivity Analysis, Hydrocarbon Distribution, Resource Potential and production Performance in the Clastic Plays of the Sable Subbasin, Scotian Shelf. Central Atlantic Conjugate Margins Conference, August 13–15, 2008, Halifax, N.S., Canada. (Extended abstract.) Available for download at http://www.conjugatemargins.com/downloads/publications/Extended%20Abstracts-Revised.pdf

Schulz, H.-M., Wirth, R., & Schreiber, A. 2016. Nano-crystal formation of $TiO_2$ polymorphs brookite and anatase due to organic- inorganic rock-fluid interactions. *Journal of Sedimentary Research*, 86: 59–72.

Zhang, H.Z., & Banfield, J.F., 2014. Structural characteristics and mechanical and thermodynamic properties of nanocrystalline $TiO_2$. *Chem. Rev*. 114 (19), 9613–9644.