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2 DIAGENETIC F-RICH FERROAN CALCITE AND ZIRCON IN THE OFFSHORE SCOTIAN

3 BASIN, EASTERN CANADA: SIGNIFICANCE FOR UNDERSTANDING THERMAL

4 EVOLUTION OF THE BASIN

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11   ABSTRACT

12   In the Scotian Basin, offshore eastern Canada, an unusual combination of high heat flow

13 in the Cretaceous and the abundance of halite has resulted in unusual diagenetic minerals such as

14 sphalerite. The Newburn H-23 well is the most distal well in the basin with good core samples

15 and has two previously unknown diagenetic mineral occurrences: fluorine-rich ferroan calcite

16 and diagenetic zircon. This study uses SEM backscattered electron images and EDS analyses,

17 EMP WDS mineral analyses and Raman spectroscopy to determine mineral chemistry and

18 textures in order to investigate the diagenetic and thermal significance of these minerals.

19   Late diagenetic Fe-calcite contains 1–2.5 wt% fluorine, mostly from adsorption, but

20 rarely as small fluorite crystals. Fluoride is also adsorbed on the surfaces of some framework

21 minerals and chlorite. Fluoride was transported in highly saline formation brines derived from

22 the Argo salt Formation. Zircon grains, 20–40 μm in size, have crystal outlines which are

23 straight adjacent to pores, partially lobate filling porosity, and cross cutting other grains: these

24 may be diagenetic. Some zoned detrital zircon grains show 1–3 μm wide diagenetic outgrowths.

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25   Neoformation of diagenetic zircon requires temperatures of >250°C. Transport of zirconium is

26   favoured by ligands in low pH solution, principally fluoride and phosphate anions, with

27   zirconium mobilized during the alteration of metamict detrital zircon under low-grade

28   metamorphic conditions. The presence of diagenetic sphalerite and the documented mid

29   Cretaceous thermal event in the Scotian Basin indicate conditions that could have been suitable

30   for the formation of diagenetic zircon in this well. Suitable geological conditions for such

31   diagenetic formation of zircon will be found in a subsiding rift basin with early evaporites that is

32   affected by a subsequent phase of volcanism due to new rifting or subduction.

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34   **Keywords**: diagenesis, zircon, ferroan calcite, fluorine, Scotian Basin

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INTRODUCTION

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41   Diagenetic minerals preserve an important record of fluid flow and paleotemperatures in

42   the development of hydrocarbon basins. The Scotian Basin (Fig. 1) is a passive continental

43   margin basin with an unusual diagenetic history. Thick halite accumulated during Late Triassic

44   rifting (Holser et al. 1988), and as a consequence, formation waters in the basin are highly saline.

45   The Jurassic basin was located at the northeast end of the incipient Atlantic Ocean, and the

46   thermal effects of subsequent rifting between the Grand Banks and Iberia in the Cretaceous were

47   felt throughout the basin (Bowman et al. 2012). In the latest Jurassic and early Cretaceous, the

48   basin was a uniquely large depocenter on the eastern North American margin, accumulating

49   several kilometers of sandy deltaic sediment derived from the uplift of the Labrador rift (Zhang

50   et al. 2014). This sediment loading drove an active salt tectonic system (Albertz et al. 2010), with

51   salt detachments and extensional listric faulting providing pathways for diagenetic fluids (Pe-

52   Piper et al. 2015).

53   The unusual combination of high heat flow some 100 Ma after initial rifting of the basin,

54   and the abundance of halite in the basin has resulted in unusual diagenetic minerals in wells in

55   the more proximal parts of the basin on the Scotian Shelf, including sphalerite and Mn-rich

56   siderite (Pe-Piper et al. 2015). In this study, we investigate diagenesis in the only deep-water

57   well in the Scotian Basin with a long record of sandstone diagenesis in sidewall cores, the

58   Newburn H-23 well, drilled in 977 m water depth to a total depth of 6070 m. This well provides

59   the most basinward set of sandy core samples of any well in the Scotian basin. Therefore, as

60   diagenetic fluids originated the deep basin depocenter and migrated up-dip through the basin,

61   this well provides information about the early fluids. The purpose of this study was to investigate

62   diagenetic minerals in the most basinward setting possible. Particular attention is paid to two

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63   diagenetic minerals, zircon and a fluorine-rich ferroan calcite (F-rich Fe-calcite), in order to

64   better understand the evolution of both temperature and diagenetic fluids in the basin.

65   REGIONAL GEOLOGICAL SETTING

66   The early stages of Triassic rifting in the Scotian basin produced syn-rift clastic

67   successions and salt deposits (Fig. 2). As rifting continued into the Jurassic, the deposition

68   became dominated by carbonate rocks. This was followed by fluvial, deltaic, and shelf

69   deposition of the sandstones and shales of the Upper Jurassic and Lower Cretaceous Missisauga

70   and Logan Canyon Formations (Wade and MacLean 1990), with principally shales and some

71   sandy turbidites in deep water. Later deposits in the Upper Cretaceous and Cenozoic are shales

72   and lesser chalks.

73   The Scotian Basin has been strongly influenced by salt tectonics (Albertz et al. 2010).

74   The Upper Triassic-(?) Lower Jurassic Argo Formation salt was remobilized, principally in the

75   Jurassic and Cretaceous, with widespread salt expulsion creating accommodation beneath the

76   Scotian Shelf (Cummings and Arnott 2005), when extensive allochthonous salt bodies were

77   emplaced on the Scotian Slope (Kendell 2012). The Newburn H-23 well is located in zone II of

78   Shimeld (2004), which is dominated by vertical salt structures, with autochthonous salt overlying

79   syn-rift clastic sedimentary rocks and Meguma terrane basement (Fig. 1b; Deptuck et al. 2009).

80   Basin modeling for the Scotian Basin (Williamson 1995; OETR 2011) suggests that most

81   maturation and hydrocarbon charge took place during the Cretaceous. Fluid inclusions show that

82   hydrocarbon transport postdated silica overgrowths and the main carbonate cements, but that

83   some secondary fluid inclusions in fractures contain hydrocarbons (Karim et al. 2012). In the

84   central Scotian Basin, the C-isotope composition of carbonate cements and fluid inclusions in

85   cements indicate a period of flow of hot (<175°C and <23 wt.% $NaCl_{eq}$) basinal brines in the

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86   Aptian-Albian (Wierzbicki et al. 2006; Karim et al. 2012). At this time, regionally high heat flow

87   in the northern Appalachians that resulted in high vitrinite reflectance in the lower Cretaceous

88   Chaswood Formation on land and widespread paleomagnetic resetting of basement rocks

89   (Bowman et al. 2012). Barite and sphalerite are widespread late diagenetic minerals in deeply

90   buried sandstones.

91   In the Newburn H-23 well, thin sandstone and siltstone beds are present in the Albian

92   Cree Member of the Logan Canyon Formation, and the Barremian−Hauterivian Upper and

93   Middle Missisauga Formations (Fig. 3). These beds were interpreted as deep-water turbidites

94   prior to drilling, but biota (OETR 2011) and sedimentary structures indicate an outer shelf

95   depositional environment.

96   **METHODS**

97   Polished thin sections were made from rock slices from 21 sidewall cores, of which 12

98   had fine sandstone or siltstone layers and were studied in detail (Fig. 3). Diagenetic minerals

99   textures were studied from backscattered electron (BSE) images acquired by scanning electron

100 microscope (SEM), supplemented by elemental X-ray maps of selected features acquired by

101 SEM. Minerals were identified by energy dispersive spectroscopy (EDS) analysis using the

102 SEM, and wavelength dispersive spectroscopy (WDS) chemical analyses were obtained by

103 electron microprobe (EMP).

104   The SEM analysis was completed in the Regional Analytical Centre at Saint Mary's

105 University using a LEO 1450 VP SEM acquiring the BSE images and EDS chemical analyses of

106 minerals. This SEM has a maximum resolution of 3.5 nm at 30 kV. It is equipped with an INCA

107 X-max 80 mm^2 silicon-drift detector (SDD) EDS system that has a detection limit >0.1%. A

108 tungsten filament produces a 10 μm beam, calibrated with a cobalt standard. Elemental X-ray

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109   mapping data were processed by the QuantMap package in Oxford Instrument's INCA program.

110   The color bar at the bottom of each elemental mapping image is scaled to EDS analysis (volatile

111   free) and values are presented as oxides to facilitate comparison with standards.

112   Minerals requiring fluorine analysis were analyzed at the Regional Electron Microprobe

113   Centre at Dalhousie University, using a JEOL-8200 electron microprobe with a Noran 133 eV

114   energy dispersive spectrometer and five wavelength spectrometers. Fluorite (~49 wt.% F) was

115   chosen as a standard for fluorine, with fluorapatite analyzed as a control, because SEM-EDS

116   analysis suggested fluorine contents as high as ~25 wt.%. Diffracting crystal LDE1 is more

117   sensitive than other crystals in the microprobe spectrometers and is thus chosen for F analysis.

118   The measured elements and different standards for calibration of each element and the element

119   distribution for each channel (spectrometer) with different diffracting crystal are listed in

120   Supplementary Table 1.

121   Raman laser (LRM) spectroscopy was completed in the Regional Analytical Centre at

122   Saint Mary's University using a Horiba Jobin-Yvon LabRam HR confocal instrument. The LRM

123   uses a 100mW 532 nm Nd-YAG diode laser from Toptica Phonotics and a Synapse charge-

124   coupled device from Horiba Jobin-Yvon. The LRM also uses a 100x Olympus MPlanN objective

125   for images and analysis. The detector is cooled to -50 $^{\circ}$C, and a minimal working distance

126   between the objective and sample is used to reduce interference. A 25 μm confocal hole

127   diameter, and 600 grooves/mm grating was used for all analyses, yielding a spectral resolution of

128   approximately 20 mm. Spectra were collected using an accumulation of three, ten second

129   acquisitions with a laser spot size of approximately 1 μm at 50% laser power. The spectra were

130   collected in two spectral windows 200-4000 cm^{-1} and 200-2600 cm^{-1}. The analyzed polished thin

131   section had all carbon coating removed using methanol to increase the intensity of the peaks.

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132   **DATA PRESENTATION**

133   **Fluorine-rich ferroan calcite**

134   Sandstone and siltstone layers show diagenetic minerals similar to those described

135   elsewhere in shallow water wells in the Scotian Basin (Karim et al. 2010; Gould et al. 2010; Pe-

136   Piper et al. 2015). Unusual diagenetic ferroan calcite (Fe-calcite) grains with elevated fluorine

137   content (2−27 wt.%) were identified using SEM EDS analyses in five samples. The term ferroan

138   calcite is applied to calcite with 1–6 mole % $FeCO_3$; magnesian calcite has 1–7 mole % $MgCO_3$.

139   One sample with F-rich Fe-calcite was from the Cree Member (4353.5 m), the others from the

140   Middle Missisauga Formation (most common at 5403.6 m and 5407 m, also present at 5213.5 m

141   and 5408.5 m) (Supplementary Table 2). EDS analyses of F are imprecise, but in EMP analyses,

142   fluorine totals range between 1 wt.% and 2.5 wt.% in F-rich Fe-calcite. Fluorine was also found

143   in diagenetic chlorite with concentrations as high as 6.9 wt.%,.

144   Textural evidence suggests that the F-rich Fe-calcite is a late diagenetic mineral.

145   Framework grains comprise quartz, lithic clasts, K-feldspar, albite and muscovite, together with

146   small amounts of volcanic glass. Quartz grains have overgrowths that have resulted in complete

147   silica cementation in many areas, but with some pores bounded by euhedral quartz crystal faces.

148   Calcite, Mg-calcite and Fe-calcite engulf originally detrital quartz and feldspar grains (Fig. 4A).

149   Fe-calcite and F-rich Fe-calcite engulf quartz overgrowths (Figs. 4C, 4D, and 4E positions a) and

150   Fe-calcite surrounds and replaces ankerite that may have replaced framework feldspar (Fig. 4C).

151   Earlier Mg-calcite and calcite are replaced by later F-rich Fe-calcite (Fig 4F) and Fe-calcite (Fig.

152   4B). Chlorite fills dissolution voids in F-rich Fe-calcite and calcite (Fig. 4F), cuts F-rich Fe-

153   calcite (Figs. 4D and 4E), and engulfs silt sized quartz (Fig. 4E). Late siderite forms rims (Fig.

154   4A) on or fills secondary dissolution voids (Fig. 4B) in Fe-calcite. It is associated with late

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155   diagenetic sphalerite and barite (Fig. 3). The paragenetic sequence for the minerals which

156   interact with F-rich Fe-calcite is thus: quartz overgrowths → ankerite + calcite + Mg-calcite →

157   Fe-calcite + F-rich Fe-calcite → *dissolution* → fibrous chlorite → siderite ± sphalerite ± barite.

158   EMP data from a variety of diagenetic calcite grains show that the Mg content of Fe-

159   calcite increases steadily from 0.1 to 0.3 wt.% as Fe increases, whereas fluorine ranges from 0 up

160   to 2.5 wt.% in the Fe-calcite (Figs. 5A, 6A) and shows no correlation with Fe content (Fig. 5C).

161   There is no fluorine in the Mg-calcite and there is no correlation between Mg and fluorine in the

162   Fe-calcite (Fig. 5B), despite the relationship suggested by several studies that a higher Mg

163   content increases the adsorption of fluoride (F^-) onto calcite (Rude and Aller 1991).

164   The question of how F^- is incorporated in calcite has been further investigated by Raman

165   spectroscopy. In the literature, both F^- adsorption and surface precipitation of fluorite on calcite

166   have been proposed (Budyanto et al., 2015). Raman spectral analyses were performed on F-rich

167   Fe-calcite crystals from sample 5403.6 m in order to determine if fluorine is present as fluorite

168   on the F-rich Fe-calcite surface (Supplementary Appendix 1). All of the analyses returned calcite

169   as the major mineral phase (Fig. 7), however two analyses, ~2 μm apart, showed minor peaks

170   which correspond to peaks from fluorite. When compared to the EMP analyses (Supplementary

171   Appendix 1, and Supplementary Table 3), no relationship was found between areas which have

172   high fluorine content and those areas which have fluorite spectral lines. This suggests that

173   fluorite surface precipitation probably occurred as patches in the F-rich Fe-calcite and was not

174   the only method by which fluorine was incorporated into the F-rich Fe-calcite analyses. Since no

175   fluorite peaks were found in the other analyzed grains, it seems that F^- adsorption onto Fe-calcite

176   was predominant, and the conditions which favored the surface precipitation of fluorite did not

177   persist throughout the entire period of formation of the F-rich Fe-calcite.

178   The question of how F^- is incorporated in calcite has been further investigated by

179   elemental mapping of a sandstone sample (5408.5 m) with F-rich Fe-calcite cement (Figs. 8 and

180   9). This was to determine if fluorite microcrystals can be seen; if minerals other than calcite were

181   hosts for fluorine; and if textural distribution of fluorine provides evidence for timing of F^-

182   enrichment. The area mapped (Fig. 8A) has framework grains of quartz, albite and muscovite

183   and an apparently deformed lithic clast largely pseudomorphed by calcite and chlorite. This lithic

184   clast includes a few 5–10 μm quartz grains, a 40 μm long muscovite flake, a 10 μm grain of

185   titania, and (from EDS analysis) some phosphate. Most of the chlorite is fibrous or platy, with a

186   porous, diagenetic appearance (Fig. 8B). Secondary porosity has delicate chlorite fibers (Fig.

187   8B), suggesting that the porosity formed by volume reduction from a precursor, rather than by

188   dissolution of chlorite. The calcite appears sparry with abundant secondary porosity particularly

189   along crystal boundaries (Fig. 8C). The silica overgrowths partly engulf albite and show euhedral

190   faces against residual porosity. Some secondary porosity formed by dissolution along crystal

191   boundaries in the silicate mineral framework (position c in Fig. 8A).

192   In the lithic clast, fluorine is strongly positively correlated with the presence of calcite

193   (Figs. 9B and 9C). Lower abundances of fluorine are present in the chlorite. Morphologically

194   similar late chlorite in another sample with a similar lithic clast (Fig. 4E) also contains fluorine

195   (up to 3 wt. %). Fluorine is also present in the outermost few microns of the framework silicate

196   minerals (Fig. 9B, where the white line marks the edge of quartz and albite). In many cases,

197   especially in the albite, the high fluorine is related to the presence of secondary porosity, but this

198   is not the case in some of the silica overgrowths on the right side of the image (unless the

199   porosity is out of the plane of the thin section). The resolution of the elemental mapping is not

200   sufficient to distinguish between surface adsorption of F^- and surface precipitation of fluorite, but

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201   no evidence has been seen for precipitation of fluorite, such as the presence of larger crystals of

202   fluorite in any of the samples. Furthermore, F^- is adsorbed onto chlorite and the margins of

203   framework quartz. In the case of chlorite (Fig. 8B), the F^- may be in the observed µm-scale

204   porosity, but image resolution is insufficient to determine if there is nano-scale porosity in the

205   quartz (Figs. 8A and 9D). We thus conclude that there is predominantly F^- adsorption rather than

206   fluorite precipitation.

207   **Diagenetic zircon**

208   The zircon grains from the Newburn H-23 well range in size from ~20 µm to ~40 µm

209   (Fig. 10) and appear to be euhedral or subhedral and clean, with rare dissolution voids and

210   fractures. Crystal outlines in relationship to porosity may be straight (euhedral) (Figs. 10A, 10B,

211   10C, and 10F), partially lobate (Fig. 10F), appearing to partly fill porosity (Figs. 10A, 10B, and

212   10D), and cross cutting framework and cement minerals including chlorite (Figs. 10D and 10F),

213   calcite (Fig. 10B), kaolinite, K-feldspar, and quartz (Figs. 10D and 10H): such textures are

214   commonly present in late diagenetic minerals. On the other hand, at least some of the small

215   euhedral zircons could be detrital framework grains. High magnification images of some of such

216   zircon grains (Fig. 11) show outgrowths (Figs. 11A, 11B, and 11C), dissolution accompanied by

217   dark patches (Fig. 11D), and internal zoning of the main zircon crystal (Fig. 11A). This suggests

218   that although small euhedral zircon grains could be detrital, some have diagenetic outgrowths.

219   LA-ICPMS U-Pb dating of selected zircons was attempted, but no reliable data were obtained

220   because of the small size of the grains and the low content of radiogenic products, indicating a

221   Late Mesozoic age or younger.

222   **DISCUSSION**

223   **F-rich Fe calcite**

224   The F-rich Fe-calcite is common in the deeper studied samples, late in their paragenesis,

225   and seems to be associated with dissolution, fibrous chlorite lining secondary porosity and late

226   siderite. These observation suggest that the origin of the fluorine enrichment is related to deep

227   burial diagenetic processes.

228   Fluorine tends to concentrate in aragonite when the parent solution is depleted in

229   magnesium, whereas it concentrates in calcite, when the parent solution is enriched in

230   magnesium (Rude and Aller 1991), and as magnesium concentrations rise, so too does the

231   concentration of fluorine in calcite (Kitano and Okumura 1973). Dissolution of aragonite and

232   Mg-calcite during diagenesis releases F^- into pore waters, where it may be consumed during the

233   formation of fluorapatite or adsorbed during the reprecipitation of calcium-iron carbonates, Fe-

234   oxyhydroxides, and Mn-oxides (Rude and Aller 1991). In the case of calcite and Fe-calcite, F^-

235   has been shown to be removed from solution by: a) by adsorption onto the surface of calcite,

236   demonstrated in calcite nano particles, at low F^- concentrations (<5 ppm) (Budyanto et al., 2015)

237   and high pH (Padhi and Tokunaga 2015); and b) from the precipitation of fluorite on the surface

238   of the calcite at concentrations greater than 10 ppm (Budyanto et al., 2015) and low pH (Padhi

239   and Tokunaga 2015).

240   Carbonate cements in the Newburn H-23 well show a complex history of formation,

241   dissolution, and re-precipitation. Ankerite, calcite and Mg-calcite are the earliest diagenetic

242   carbonate minerals, which were later replaced by Fe-calcite and F-rich Fe-calcite, and finally by

243   siderite (Fig. 4). Of these minerals only Fe-calcite contains fluorine >1 wt.%, suggesting that the

244   conditions for fluorine enrichment existed under only particular diagenetic conditions that post-

245   dated the main release of bicarbonate ions associated with maturation of organic matter (Karim

246   et al. 2012), but predating high temperature corrosive brines that precipitated fibrous chlorite,

247   late siderite and sphalerite seen farther up-dip in wells on the Scotian Shelf (Pe-Piper et al.

248   2015).

249   High F^- contents of formation waters are always associated with high Cl^- contents

250   (Worden 1996). At the concentrations of Cl^- estimated from saline fluid inclusions with 20%

251    $NaCl_{eq.}$ (Karim et al., 2012), concentrations of 10-20 ppm of F^- are expected in formation waters.

252   The correlation of F^- with Cl^- indicates that the principal source of both halogens to formation

253   waters is from evaporites (Worden 1996). Samples of halite from the salt canopy at the

254   Weymouth A-45 well contain fluorite inclusions (G. Pe-Piper, unpublished data). The strong

255   influence of the Argo salt on formation waters and diagenesis, with hydrocarbon charge during

256   late diagenesis (Pe-Piper et al., 2015), indicate that conditions of F^- concentration >10 ppm and

257   low pH (from organic acids) are likely to have obtained.

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259   **Diagenetic zircon**

260   The small euhedral zircons with textural relationships suggesting a late diagenetic origin

261   (Fig. 10) may alternatively be volcanogenic, derived from Early Cretaceous volcanoes to the

262   northeast. They are morphologically comparable with the smaller zircons dated by Piper et al.

263   (2012). Zircon would have experienced less dissolution and overgrowth at temperatures ~100 °C

264   than the major framework minerals quartz and feldspar, thus appearing to be of later diagenetic

265   origin. The U-Pb data are consistent with either a diagenetic or detrital origin.

266   Zircon is typically thought of as being a refractory mineral which endures all the stages

267   of diagenesis with minimal effect on its composition and crystal structure. However, several

268   recent studies suggest that zircon may be more susceptible to dissolution and overgrowths than

269   previously thought. Diagenetic zircon described in the literature (Rasmussen 2005; Bojanowski

270   et al. 2012) shows varying morphologies, some of which resemble the morphologies of zircon of

271   this study. Outgrowths similar to those in Figure 11 have been shown to form as minute irregular

272   crystals attached to detrital zircon grains (Rasmussen 2005, their figs. 3 and 4). These irregular

273   crystals are typically less than 3 μm in size and are commonly in "frilly rims" that partly

274   surround detrital zircon, and can also line the surface of fragments of detrital zircon (Rasmussen

275   2005, their figs. 5, 6).

276   Detrital zircon grains from low grade metamorphic rocks have darker patches in BSE

277   images, similar to those in our Figure 11D, that represent zones of low temperature dissolution

278   and reprecipitation of metamict zircon. Such zircon alteration has been reported from rocks with

279   a maximum temperature of 300-350°C (Hay and Dempster 2009). The liberated zirconium is

280   mobilized from areas of low temperature alteration and forms outgrowths on the margins of

281   unmodified zircon crystals.

282   Analogous dissolution and reprecipitation of existing zircon grains is also reported in

283   anchimetamorphic sedimentary rocks, where it is facilitated by high concentrations of F^-,

284   phosphate (PO_4^{3-}), and carbonate in hydrothermal fluids at temperatures as low as 270° C

285   (Bojanowski et al., 2012). Irregular outgrowths, similar to those in our Figure 11, form in

286   prehnite-pumpellyite grade shales at 250° C (Rasmussen 2005).

287   The characteristics of the fluids responsible for the mobilization of zirconium vary. High

288   concentrations of zirconium have been documented in alkaline fluids with pH values of ~10

289   (Vard and Williams-Jones 1993) and ~12 (Kraynov et al., 1969). Solubility experiments by Aja

290   et al. (1995) on zirconium bearing minerals showed that $Zr(OH)_{4(aq)}$ is the dominant form in

291   which zirconium is transported in solution over a wide variety of pH conditions. However, the

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292   mobility of zirconium is promoted by the presence of ligands in solution, principally F^- and PO_4^{3-}

293   anions (Gieré 1990), which form complexes with zirconium and allow for the typically immobile

294   element to be transported in solution. F^- is particularly effective under acid conditions (Aja et al.,

295   1995), as a content of between 0 and 6 wt.% F^- in solution increases the solubility of zirconium

296   by its square (Rubin et al., 1993). Decreases in ligand activity within a solution facilitate the

297   removal of zirconium from solution, particularly during the formation of minerals which contain

298   the complexing elements (Gieré 1986, 1990). Aja et al. (1995) suggested that zirconium is

299   transported by F^- rich, calcium (Ca^{2+}) deficient fluids which precipitate fluorite and zirconium

300   bearing phases when the fluids interact either with Ca^{2+} rich fluids or calcium bearing host rocks

301   which destabilize the zirconium and F^- complexes. Clay minerals such as kaolinite and chlorite

302   can adsorb F^- onto their surfaces by exchanging hydroxyl groups (OH^-) for F^- at surface active

303   hydroxyl sites (Du et al., 2011). At low concentrations the exchange can only occur if the OH^-

304   group is protonated by H^+ from a low pH solution. However, as concentrations of F^- increase to

305   >5 ppm for kaolinite and >100 ppm for chlorite, the exchange no longer requires low pH

306   solutions.

307   In the Newburn H-23 well, several late diagenetic minerals contain F^- and PO_4^{3-} anions,

308   including apatite, fluorapatite, fluorite, and F-rich Fe-calcite. Since these anions are major

309   ligands for zirconium, precipitation of these minerals may have led to the precipitation of

310   diagenetic zircon outgrowths. Calcite is present in the majority of studied samples; it is generally

311   an early formed mineral and is easily dissolved by highly acidic fluids such as the ones required

312   to transport zirconium. Calcite grains in the Newburn H-23 well commonly show dissolution

313   voids, replacement by other minerals, and ragged grain boundaries. The dissolution and

314   replacement of these grains would have produced pore fluids rich in Ca^{2+}, and could have mixed

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315 with the F^- and PO_4^{3-} rich fluids which were complexing zirconium, thereby precipitating apatite,

316 fluorapatite, fluorite, and F-rich Fe-calcite.

317 Chlorite and kaolinite are common pore filling minerals in the Newburn H-23 well. SEM

318 analysis did not detect fluorine in any grains of kaolinite, however several analyses of chlorite

319 grains showed the presence of fluorine (Fig. 9). The acidic solution carrying zirconium and its

320 ligands would have facilitated the exchange of OH^- groups and the adsorption of F^-. Such

321 surficial adsorption onto chlorite and other framework grains may have played a role in the

322 removal of F^- ligands from zirconium bearing fluids. Based on the estimate of 10–20 ppm F^- in

323 the Scotian Basin brines, the critical concentration of 100 ppm for adsorption of F^- on chlorite

324 was probably achieved only under exceptional local conditions.

325 In summary, two processes led to removal of ligands from solution and consequent

326 precipitation of zircon. (1) Formation of fluorine and phosphorus bearing minerals such as

327 apatite, fluorapatite, fluorite, and F-Fe-calcite via the dissolution of calcite, and interaction of the

328 zirconium bearing fluids with liberated Ca^{2+}; and (2) the surficial adsorption of F^- onto chlorite

329 and framework grains.

330 The high temperature diagenetic mineral sphalerite is present in all studied stratigraphic

331 levels in the Newburn H-23 well. A salinity of ∼17% $NaCl_{eq}$ is required for major transport of

332 zinc in chloride complexes (Hanor, 1996), although some brines with >10% salinity may

333 transport zinc (Giordano, 2002). Crystallization of sphalerite generally occurs at temperatures of

334 140°-200°C (Samson and Russell, 1987). This is a little lower than temperatures in the literature

335 for diagenetic zircons (∼270°C) and outgrowths (∼250°C) (Rasmussen, 2004; Bojanowski et al.

336 2012).

337 **Thermal history of the Scotian Basin and its relationship to diagenetic zircon**

338   A widespread thermal event in the Scotian Basin during the Aptian-Albian is recorded by

339 volcanism in the Orpheus graben and enhanced heat flow in terrestrial basins (Bowman et al.

340 2012), high homogenization temperature of primary fluid inclusions in quartz overgrowths and

341 carbonate cements (Fig. 12), and by strongly negative δ^{13}C in carbonate cements of that age

342 (Karim et al. 2012). This event increased the temperature of circulating brines, as shown in

343 calculated trapping temperatures in quartz overgrowths that are as high as 228°C and in

344 carbonate cements as high as 189°C in the Lower Missisauga Formation in the Thebaud well

345 (Karim et al. 2012). This thermal event was likely the result of a regional process in the mantle,

346 probably related to the rifting of Iberia and the Grand Banks (Pe-Piper et al. 2007). This event

347 increased the regional geothermal gradient to 55°C/km (Karim et al. 2012). The presence in the

348 Glenelg field, up-dip from Newburn H-23, of diagenetic sphalerite post-dating carbonate

349 cements, was correlated with Albian-Cenomanian movement on the Balvenie salt Roho system

350 (Pe-Piper et al. 2015).

351   Flow of hot brines was potentially sourced from compaction of sediment in the deep

352 basin and migration along detachment faults, down-to-basin listric faults, and permeable

353 sandstones (Pe-Piper et al. 2015). Seaward of Newburn H-23, the original Triassic rift basin with

354 autochthonous salt lies about 3.5 s below the Albian K095 seismic marker (Fig. 1B: Deptuck et

355 al. 2009), which using an average seismic velocity of 4.0 km/s (Shimeld 2004) gives a burial

356 depth of 7 km. Using a geothermal gradient of 40°C/km based solely on lithospheric cooling and

357 a sea floor temperature of 30°C, as justified by Karim et al. (2012), the temperature of the

358 authochthonous salt would conservatively be 310°C. Using an elevated geothermal gradient of

359 55°C/km as suggested by Wierzbicki et al. (2006) and Karim et al. (2012), the authochthonous

16

360   salt and underlying syn-rift sediments and continental basement rocks would reach temperatures

361   of >400°C, resulting in low-grade metamorphism. At these temperatures, pre-existing zircons

362   would suffer low temperature dissolution as described by Hay and Dempster (2009).

363   Normally at such low-grade metamorphic temperatures, zircon alteration is pervasive in

364   metamict zircon and dissolution-reprecipitation processes occur locally, producing outgrowths

365   on the margins of original zircon crystals (Hay and Dempster 2009). However, in the presence of

366   high F^- ion concentrations from interbedded halite, and under somewhat acid conditions from the

367   maturation of organic matter, zirconium dissolved from zircons will complex with F^- and is

368   capable of long-distance transport in migrating basinal brines (Fig. 12). It produced outgrowths

369   on pre-existing zircons in sandstone at Newburn H-23 (Fig. 11) and may have precipitated

370   neoformed diagenetic zircon crystals (Fig. 10A, E). The formation of outgrowths on zircon

371   grains in metamorphic environments have been suggested to form as the result of a decrease in

372   temperature during retrograde metamorphism (Hay and Dempster 2009). The outgrowths

373   metamorphic rocks are commonly found to be interfingered with muscovite and chlorite,

374   suggesting that they are contemporaneous with or younger than these metamorphic minerals. The

375   formation of similar diagenetic outgrowths of zircon in the Newburn H-23 well may also be an

376   indicator of cooling following a period of elevated geothermal gradient in the Aptian–Albian,

377   during which zirconium was readily released from zircon. The unusual occurrence of diagenetic

378   zircon, at least as outgrowths, in the Newburn H-23 well is the result of two geological

379   conditions: the high heat flow after deep burial of syn-rift clastic sediments and salt, and the

380   presence of halite as a source of F^- ions.

IMPLICATIONS

381

382   This study has shown that hot brines with F^- contents of >10 ppm, derived from deep

383   burial of thick halite successions, can be recognised from high F content of diagenetic ferroan

384   calcite. Such brines are also able to complex with zirconium from dissolved metamict detrital

385   zircon under low grade metamorphic conditions of deep burial to produce diagenetic zircon

386   outgrowths and probably neoformed zircon crystals. Zircon diagenesis is favored by elevated

387   heat flow producing a geothermal gradient >50°C/km, in order to achieve metamorphic

388   temperatures at which zirconium is readily released from zircon. Suitable geological conditions

389   are found where a subsiding rift basin with early evaporites is affected by a subsequent phase of

390   volcanism due to new rifting or subduction.

391

CONCLUSIONS

392

393   The Newburn H-23 well is the closest well with samples for diagenetic studies to the

394   deep-water depocenter of the Scotian Basin. It has late-diagenetic fluorine-rich ferroan calcite

395   cement, with <2.5 wt.% fluorine, mostly at a <1 μm scale presumably by adsorption, but also

396   locally as small fluorite crystals. Fluorine is also apparently adsorbed on the surfaces of some

397   framework minerals and in chlorite. The abundance of fluorine is related to the highly saline

398   formation brines derived from the Argo salt Formation.

399   The unusual occurrence of outgrowths on zircons, and the possible presence of

400   neoformed diagenetic zircon, is the result of zirconium mobility in the presence of >10 ppm

401   concentration of F^- in formation brines. It also required high temperatures (likely ~400°C) in

402   syn-rift clastic sediment interbedded with the Argo salt Formation, resulting from regional high

403   heat flow in the Aptian–Albian, some 60 Ma after initial sea-floor spreading in the basin, that led

404   to low-grade metamorphic dissolution of patches of metamict zircon.

405

406   **ACKNOWLEDGEMENTS**

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534
535

536   FIGURE CAPTIONS

537   **Fig. 1: A:** Isopach map of the Scotian Basin showing location of Newburn H-23 well and

538   inferred paleorivers and volcanic centers in the Early Cretaceous. Base map modified from Wade

539   and MacLean (1990), volcanic centers from Bowman et al. (2012), and paleorivers and major

540   faults from Zhang et al. (2014). **B:** Cross section of part of the Scotian Basin showing geological

541   setting of the Newburn H-23 well. Stratigraphic interpretation from Deptuck et al. (2009) based

542   on 3-D seismic data.

543

544   **Fig. 2:** Stratigraphic column of the Mesozoic rocks of the Scotian basin. Modified from Weston

545   et al. (2012).

546

547   **Fig. 3:** Stratigraphic column for the Newburn H-23 well from the top of the targeted "turbidite"

548   interval showing litho- and biostratigraphy, lithology (from cuttings descriptions and wireline

549   logs), paleo-water-depth estimates from microfossil assemblages, gamma ray log, sidewall core

550   sample locations, and presence of key minerals. (Data from Chevron et al. 2002; Kidston et al.

551   2007; OETR 2011; Weston et al. 2012). brt = barite; F-Fe cal = fluorine-rich ferroan calcite; sp =

552   sphalerite; zrn og = zircon outgrowths.

553

554   **Fig. 4:** Representative BSE images of textures of Fe-calcite and other carbonates from the

555   Newburn H-23 well. Framework quartz grains appear dark. **A:** Fe-calcite engulfs albite, K-

556   feldspar, and quartz, perhaps in an original feldspathic lithic clast, and is partly replaced by

557   siderite [4353.5 m]. **B:** Calcite and Mg-calcite with microporosity are replaced by Fe-calcite.

558   Siderite fills a dissolution void in Fe-calcite [5213.5 m]. **C:** Ankerite engulfs albite, probably

25

559   from an original feldspar framework grain. Fe-calcite surrounds and replaces ankerite and

560   engulfs quartz overgrowths (position a) [5213.5 m]. **D:** Fibrous chlorite cuts F-rich Fe-calcite. F-

561   rich Fe-calcite engulfs quartz overgrowths (position a) [5403.6 m]. **E:** F-rich Fe-calcite engulfs

562   quartz overgrowths (position a). Chlorite cuts F-rich Fe-calcite and engulfs silt-sized quartz

563   [5403.6 m]. **F:** Calcite and F-rich Fe-calcite have dissolution voids filled by chlorite. Calcite has

564   been partly replaced by F-rich Fe-calcite [5407 m]. The contact between calcite and F-rich Fe-

565   calcite is marked by the dashed line.

566

567   **Fig. 5:** Bi-plots of calcite analyses using EMP data showing **A:** chemical definition of Calcite,

568   Fe-calcite and Low Mg-calcite; **B:** variation of F with Mg; **C:** variation of F with Fe.

569

570   **Fig. 6:** Ternary diagram of calcite EMP data from the Newburn H-23 well. **A:** Analyses plotted

571   on a fluorine, iron, and magnesium ternary diagram in element wt.%. **B:** Analyses plotted on a

572    $CaCO_3$, $FeCO_3$, and $MgCO_3$ ternary diagram in mole%.

573

574   **Fig. 7:** Raman spectra analyses (RSA) of F-rich Fe-calcite [5403.6 m]. Compare with reference

575   spectral lines for calcite (dashed grey lines) and fluorite (dashed black lines). **A-C:** Backscattered

576   electron images showing location of spots used for RSA analyses (1) to (7). Dots indicate

577   locations of EMP analyses (green= F-Cal; blue = F-Fe-Cal; magenta= Chl); dark minerals are

578   various calcites, bright minerals are mostly chlorite.

579

580   **Fig. 8:** BSE images from sample 5408.5 m showing a lithic clast which has been affected by late

581   cementation of F-calcite and chlorite. The location of the elemental mapping of Fig. 9 is shown.

26

582   In image (**A**), a = euhedral face of quartz overgrowth; b = Fe-calcite postdates quartz

583   overgrowth; c = secondary dissolution along quartz grain boundaries. (**B**) Detail of lithic clast,

584   showing porosity and platy and fibrous habits of chlorite. (**C**) Detail of Fe-calcite showing sparry

585   habit and porosity.

586

587   **Fig. 9:** BSE image **A:** and quantitative element mapping images **B-I:** from SEM-EDS analysis of

588   sample 5408.5 m showing the distributions of F, CaO, SiO_2, FeO, Al_2O_3, TiO_2, K_2O and Na_2O.

589   See location in Fig. 8. The color bar in the elemental maps is scaled to the quantitative EDS

590   analysis (wt.%). The intergranular boundaries are marked by solid white line.

591

592   **Fig. 10:** Representative BSE images of textural relationship of zircon to other minerals. **A:**

593   Sample 4313.5m. Zircon with sharp crystal outlines against silicate mineral and a dissolution

594   void. Trachytic lithic clast (position a). **B:** Sample 5213.5m. Zircon appears to cut framework

595   grains and F-calcite. **C:** Sample 5403.6m. Zircon with straight crystal outlines towards chlorite

596   (position a). **D:** Sample 5403.6m. Euhedral faces of zircon in contact with quartz and probably

597   engulfs chlorite (position a) and with euhedral crystal outlines towards both. **E:** Sample

598   5408.5m. Zircon fills pore and engulfs quartz. **F:** Sample 5961.7m. Zircon with straight crystal

599   outlines in contact with quartz and pore. **G:** Sample 5961.7m. Zircon cuts chlorite and is

600   euhedral against porosity. **H:** Sample 5961.7m. Zircon fills pore and engulfs quartz. **I:** Sample

601   5962m. Zircon and drilling mud (DM) fill porosity.

602

603   **Fig. 11:** High magnification BSE images of zircon grains. **A:** Sample 4313.5m. Zircon grain

604   showing a dark rim which is probably an outgrowth of diagenetic zircon. **B:** Sample 5403.6m.

605   Zircon grain showing outgrowths (arrows), some of which are in contact with quartz (dashed

606   line). **C:** Sample 5961.7m. Zircon grain showing abundant outgrowths (arrows). **D:** Sample

607   5961.7m. Zircon grain with abundant dissolution voids and dark patches which correspond to

608   areas with dissolution voids.

609

610   **Fig. 12**. Summary transect from Newburn H-23 to the Glenelg and Thebaud fields, showing

611   inferred thermal evolution and flow of formation waters. Measured average homogenization

612   temperatures for fluid inclusions from Karim et al. (2012): calculated entrapment temperatures

613   taking into account confining pressure tend to be tens of degrees higher. Albian geothermal

614   gradient of 40°C/km based on assumption of simple lithospheric cooling after Triassic rifting;

615   55°C/km estimated by Karim et al. (2012) from fluid inclusion studies and data of Bowman et al.

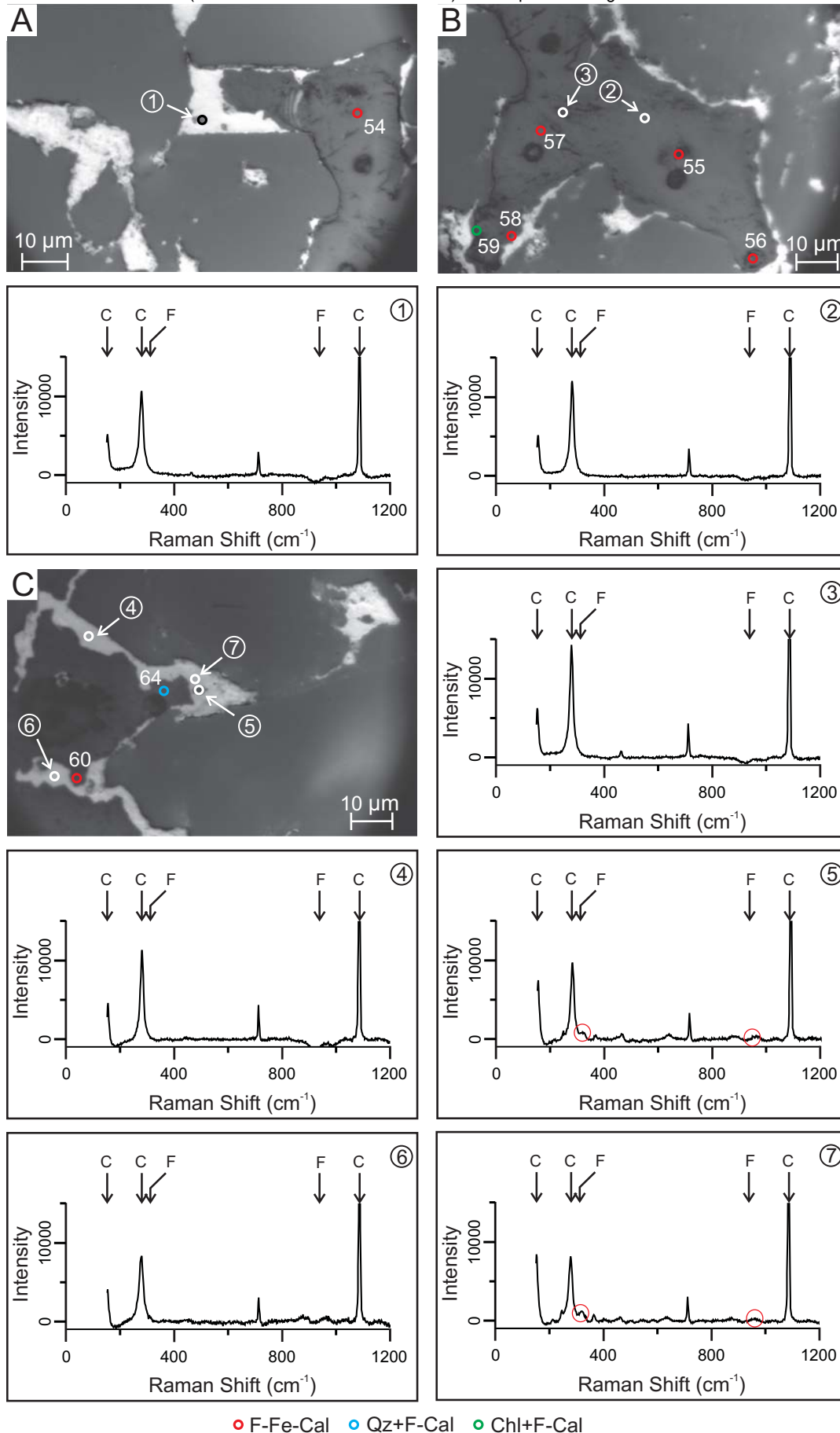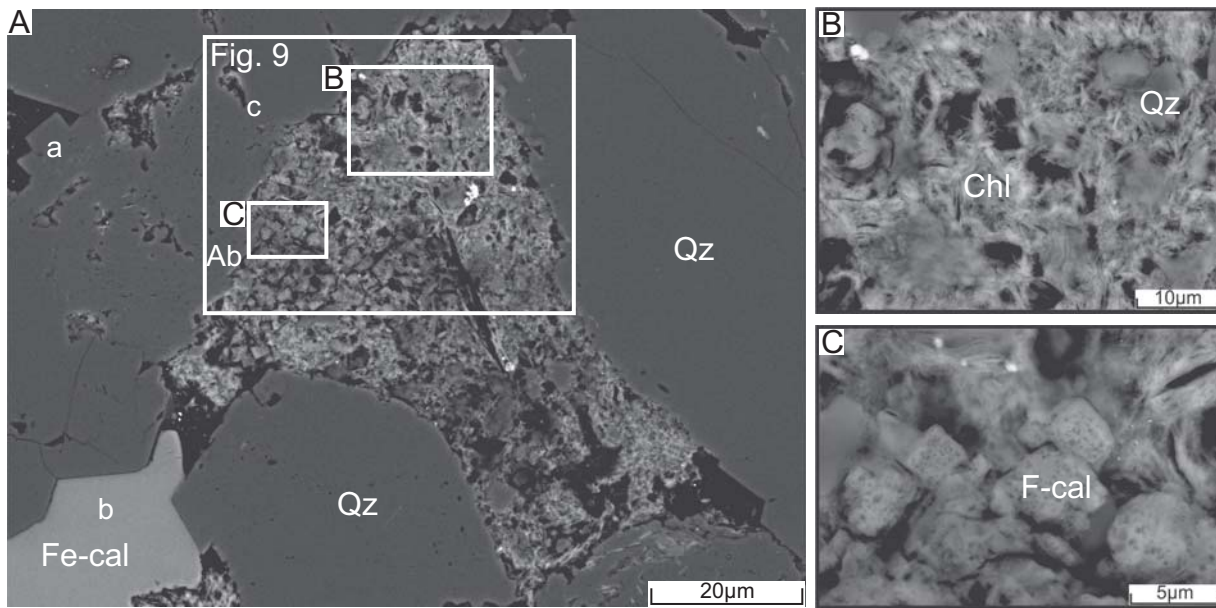616   (2012).

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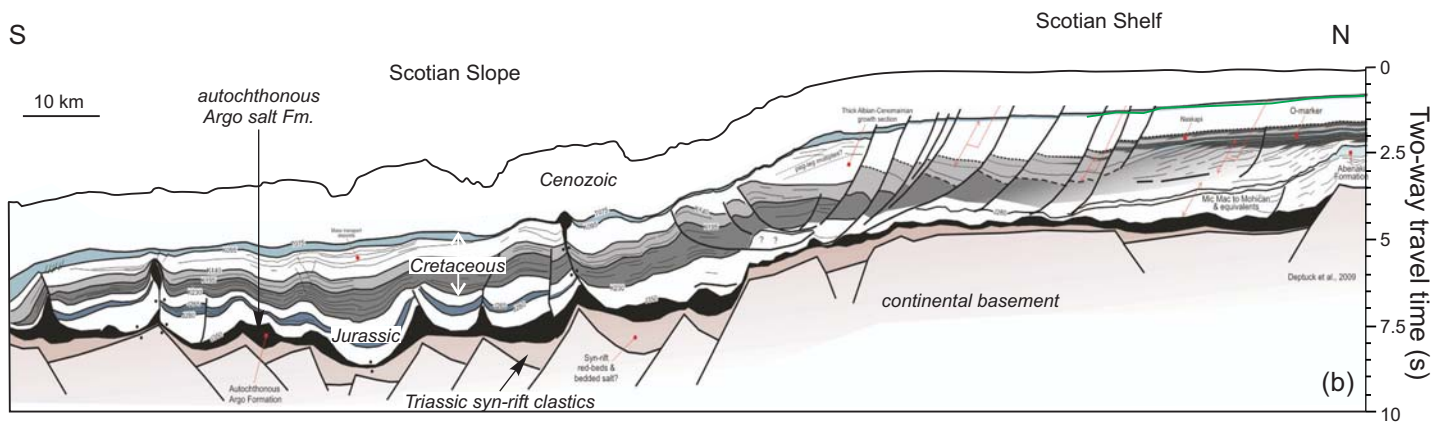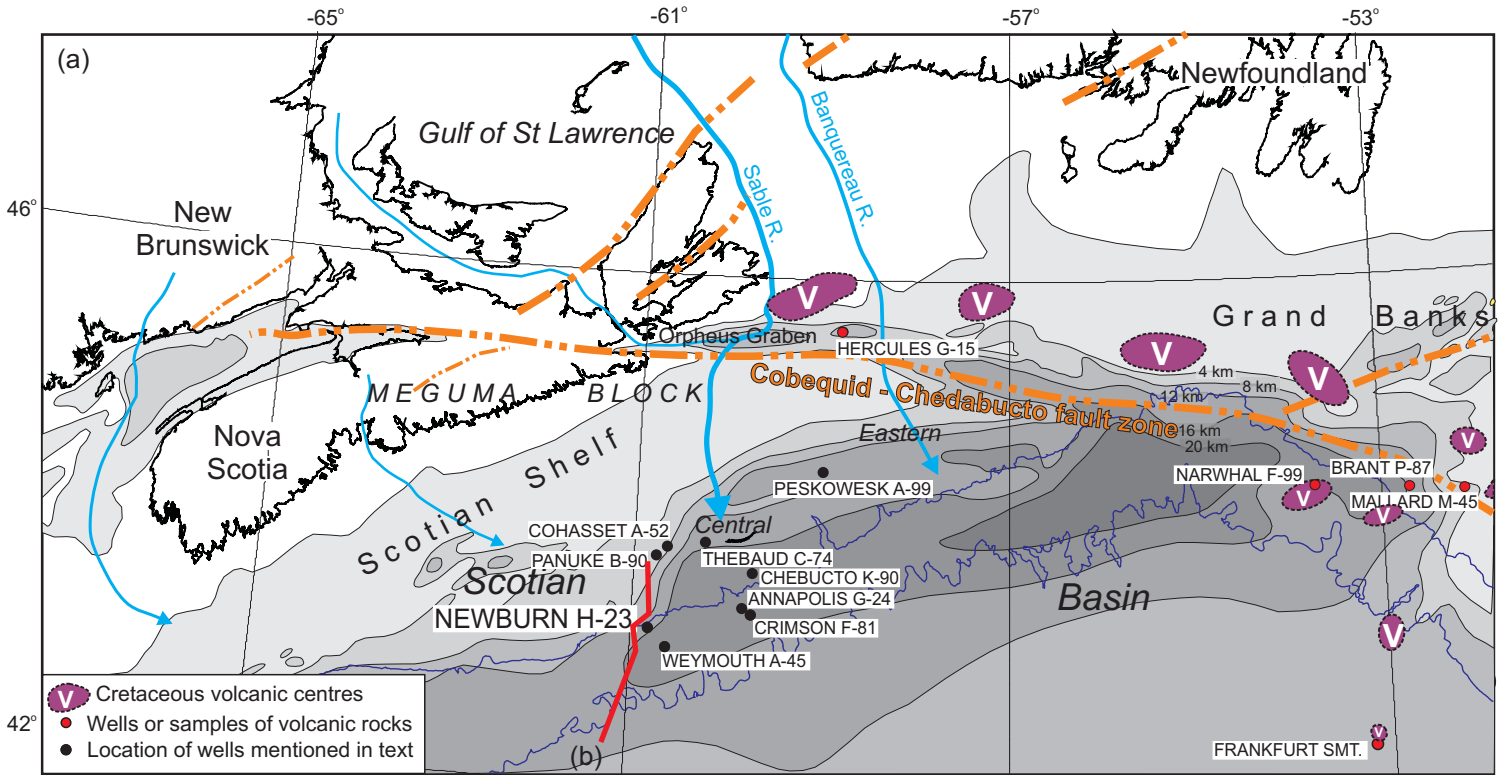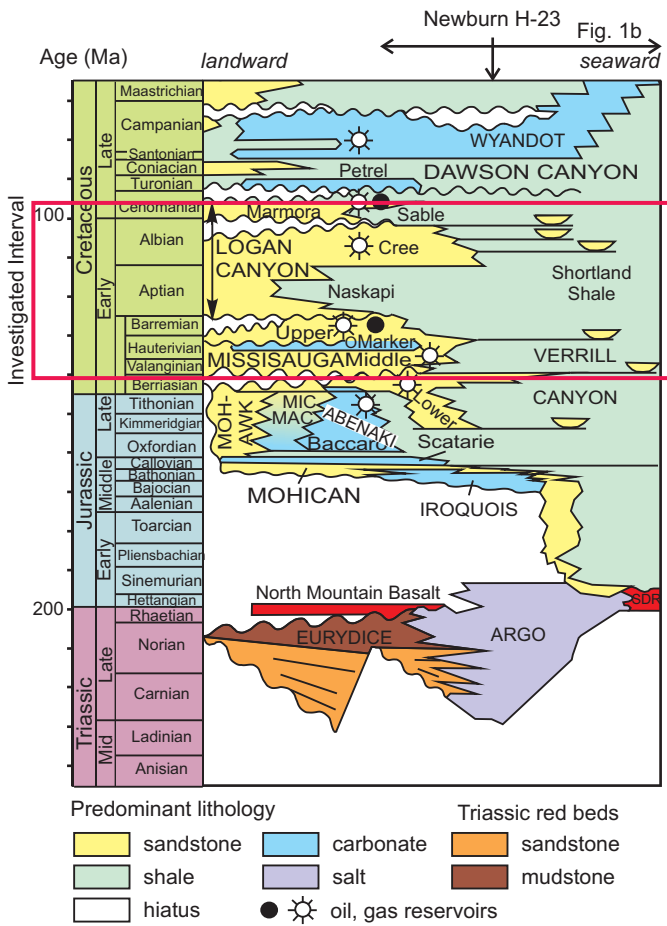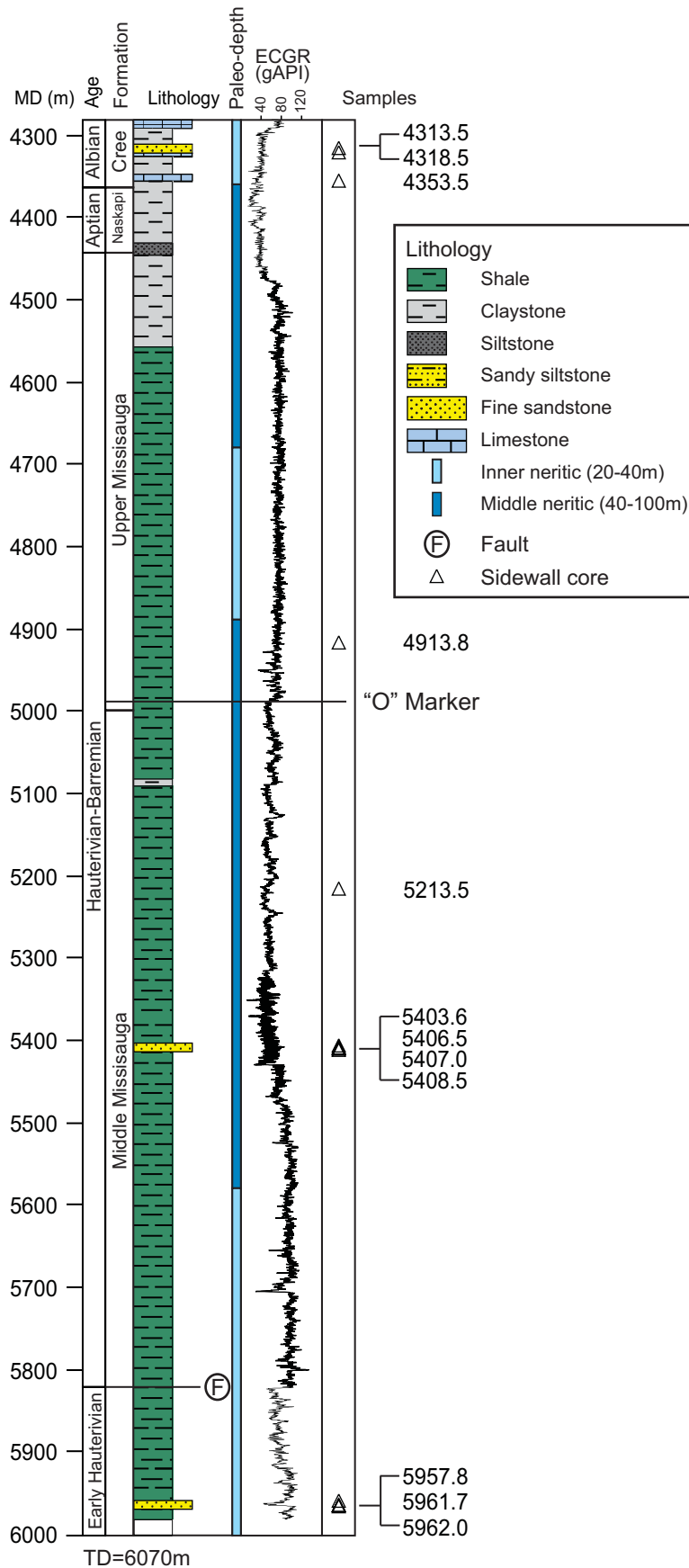
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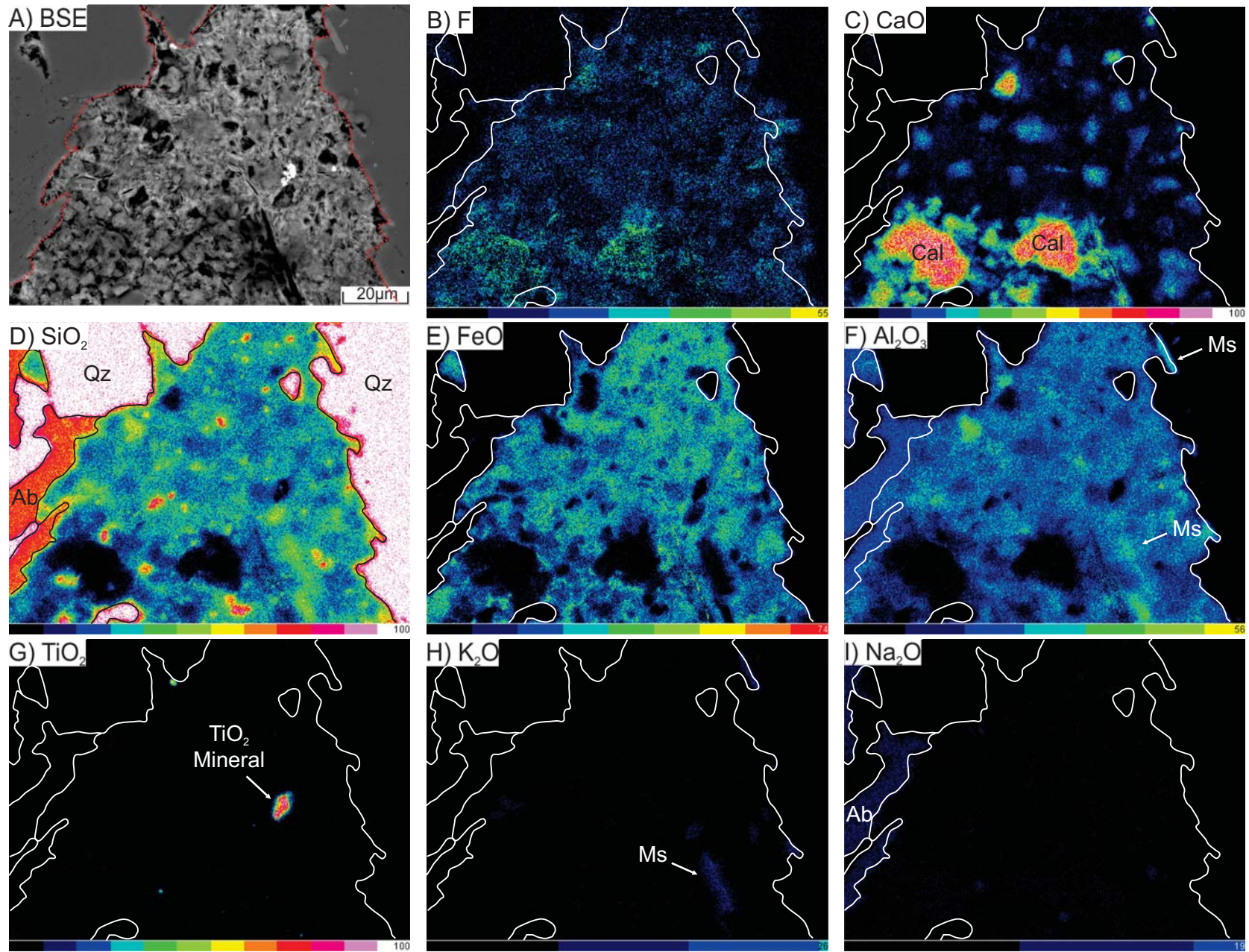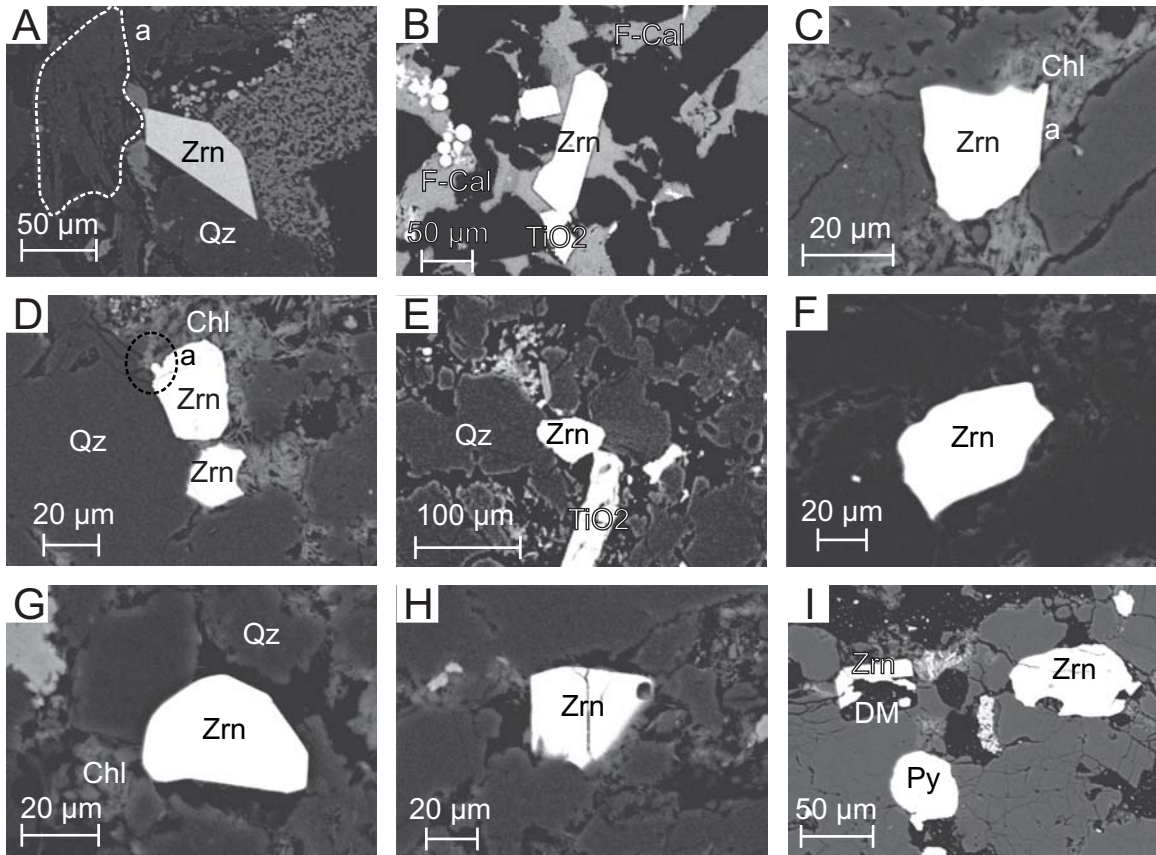
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Figure 12