Running Head: CHARGE CONTRAST IMAGING OF CARBONATES

Title: CHARGE CONTRAST IMAGING (CCI): REVEALING ENHANCED DIAGENETIC FEATURES OF A COQUINA LIMESTONE

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ABSTRACT

Charge Contrast Imaging (CCI) is a low-vacuum scanning electron microscope (LV-SEM) technique that can be induced through partial surface charge suppression of uncoated nonconductive samples, imaged with a suitable detector such as a gaseous secondary electron detector (GSED). The technique commonly produces results similar in style to that of SEM-cathodoluminescence (SEM-CL), providing information on zoning, twinning, annealed fractures, and subtle chemical changes. The current work outlines an example from a Brazilian Lower Cretaceous coquina limestone, in which both optical and SEM-CL imaging produces a limited response from much of the sample. Backscattered electron (BSE) imaging typically suggests only a hint of the cement present, whereas CCI clearly displays a rich and varied cement stratigraphy. The earliest cement displays strong CCI, but appears mainly dark under CL imaging conditions (SEM-CL and optical CL). Later-stage manganese-“enriched” carbonate cement displays luminescence with both optical and SEM-CL, as well as a CCI response. Therefore CCI can provide additional information on cement zonation in an area where CL cannot.
INTRODUCTION

Charge contrast imaging (CCI) has been recorded from a number of minerals, of which one of the first notable examples was that of zonation within gibbsite (Griffin, 1997; Griffin, 2000; Robertson et al., 2004). It has previously been noted that CCI gives results similar to that seen with scanning-electron-microscope-based cathodoluminescence (SEM-CL), with notable geological examples being the zonation of zircons, annealed cracks in quartz, features in cordierite and biotite (Watt et al., 2000), and zonation in calcite crystals (Doehne and Carson, 2001). In addition to this, Cuthbert and Buckman (2005) illustrated examples of garnet that displayed fine-scale internal structure and compositional variation that were not observable by means of optical-CL.

The underlying causes of CCI are thought to be closely allied to those in CL imaging, such as changes in chemical composition and breaks or miss-orientation in crystal structure (see Griffin, 1997). In the case of CCI, instead of these factors causing the release of photons, subtle differences in surface charge cause slight differences in electron emission and hence variation in contrast (Doehne and Carson, 2001). In particular, variation in contrast has been linked to the increase in emission of near-surface secondary electrons (SE1), associated with lower gas pressure (Fig. 1), with SE1 electron generation enhanced by crystal defects and hence displaying brighter signal (Watt et al., 2000).

Polished thin sections of carbonates are commonly examined by SEM, utilizing either backscattered (BSE) imaging or SEM-CL. The latter in particular has been used to good effect to illustrate complex diagenetic zonation in carbonates (Lee, 2000; Lee et al., 2005). Nevertheless, not all carbonates exhibit strong cathodoluminescence. In
this paper, a carbonate coquina from the Cretaceous of Brazil is used to illustrate this, where large areas display poor cathodoluminescence (both optical and SEM-CL) and limited information from BSE imaging. This coquina is known to have a complex paragenetic history (Tavares et al., 2015). CCI was investigated to determine the potential of the technique to elucidate information on the paragenetic history in this unit. It also compares and discusses the CCI response to that of SEM-CL and considers the implications for the mechanisms behind CCI as well as its usefulness in the study of carbonates with respect to CL.

MATERIALS & METHOD

The sample (PET 8) was collected from the São Sebastião Quarry, in the Lower Cretaceous lacustrine coquina limestones from the Morro do Chaves Formation, Sergipe-Alagoas Basin, NE Brazil (see Câmar et al., 2014; Tavares et al., 2015). Material examined herein was collected as part of a program for modeling wireline log responses from carbonate outcrops (Corbett et al., 2013) and was collected from approximately 32 meters of the base of the sequence recorded by Tavares et al. (2015, their Fig. 10), in a facies (Cmi) interpreted as lake delta deposits in a high energy carbonate platform, between storm wave base and fair-weather wave base (Tavares et al., 2015).

The sample was prepared as two standard polished thin sections (25 mm by 48 mm in size), cut perpendicular to bedding. The uncoated samples were examined in a Quanta 650 FEG SEM and an XL30 ESEM with LaB6 filament. Both were pumped to a vacuum of 0.7 - 0.8 Torr (~ 93 - 107 Pa), with other operating conditions: 20 kV, spot size 3.5 to 5.2, and working distance of around 10 mm. All CCI imaging was carried out via a standard large-field gaseous secondary electron detector (LF-GSED),
offset from the axis of the column. Changes in bias were noted to be significant in controlling the CCI phenomena, with a bias of approximately 50% proving optimal for image quality. Contrast of features can be improved by increasing the bias, although this can lead to flaring along the sides of the image. Thin sections were also examined under the same conditions using a BSE detector, and a Gatan mini SEM-CL detector at 20 - 30 kV, spot size 4.5 – 6, and a dwell time of 2.5 to 5 ms. Elemental dispersive x-ray analysis (EDX) was performed with an Oxford Instruments X-max nitrogen 150 mm detector using the “Aztec” mapping module and “INCA” spectral analysis.

RESULTS

BSE imaging clearly differentiates between silicate grains and carbonate phases, as well as illustrating the presence of dissolution features (Fig. 2A). Subtle differences in gray level suggest the presence of differing carbonate cements (Fig. 2A), with optimization requiring long scan times and large spot sizes. SEM-CL observations generally display poor luminescence, with occasional luminescent areas containing some information on cement zoning (Fig. 2B).

At low voltage (5-10 kV), the GSED detector produces images similar to high-vacuum SE images (Fig. 3A, B). Higher voltage (20-30 kV) increases energy input into the sample surface and induces conditions suitable for CCI (Fig. 3C, D). CCI shows a more complex picture, with two distinct phases of cement (Figs. 2C, 4D, 5B, D). Early cement is well defined, displays strongly developed growth lines (Fig. 4D), simple zoned cements (Fig. 4A, B), and occasionally complex multiple cores (Fig. 4F). This is followed by a later phase of coarser cement that is more poorly imaged by the CCI method: flatter in appearance, with less contrast, and less well defined, although still displaying subtle information such as twinning within the later cement.
phase (Fig. 4D). These features are found throughout the thin-sections, and are clearly observed. CCI may also exhibit closely spaced lamellar twinning (Fig. 4D, F) and cleavage structures (Fig. 3D). In addition details on shell structure are occasionally observed, including thickly laminated units running parallel to shell margins (Fig. 4C) and granular, possibly neomorphic cements (Fig. 4E).

The early-stage cements are developed on either side of solution seams, associated with concentrations of clay and quartz as well as on the internal and external surfaces of “corroded” ovoid to circular “bioclastic” material and shells forming a biomoldic cement (Fig. 5A, B). Bioclastic material varies from hundreds of microns to several millimeters in size (Fig. 5A-D). The later-stage cement typically infills the centers of shells and other dissolution voids (Fig. 5B, D). In most cases solution structures are earlier than cements, although in at least one case a linear solution seam was observed passing through an occurrence of late-phase cement (Fig. 5E, F).

Elemental mapping, line scans, and point analysis indicate that early-phase cements that display intricate features with CCI typically lack Mn, Fe, or other minor elements (Fig. 6), with the exception of sporadic areas containing minor Mg (Fig. 6E), or minor cement zones with Mn typically between 0.25 and 0.8 wt% (Figs. 7C, 8F). Late-stage cements show less strongly developed structure with CCI (but are luminescent through SEM-CL) and contain Mn (Figs. 6C, 7C, 8, 9), up to 1.38 wt% (Table 1). To a lesser extent, they can also contain Fe (Figs. 6D, 7D, 8, 9) up to 0.32 wt% (Table 1). In this second phase of cement, the Fe content is typically lower than that of Mn (Figs. 7E, f, 8B, D, F, Table 1).

DISCUSSION
BSE imaging provided limited information on the paragenesis of the samples analyzed (Figs. 2A, 5A, C). Gray level SEM-CL images are more illuminating, but acquisition is too time consuming, commonly requiring greater than 30 minutes per image. Furthermore, SEM-CL exhibits large areas that are poorly luminescent, which form the bulk of the sample (Fig. 2B). Similarly, optical CL of other coquina material, nearby in the quarry, also contains large areas that do not luminesce, although zoning can be apparent in the luminescent portion (Fig. 10). In contrast, CCI reveals a detailed portrait of the cement zonation and paragenesis of these samples (Figs. 2C, 4, 5B, D, F, 6A, 7A), which would otherwise be only partially visible, or not visible at all using other techniques. Features such as the two major phases of cement (Figs. 2C, 3C, D, 4D, 5D) can be imaged within seconds by CCI and provide important details on the carbonate that are otherwise not clearly observed. The CCI technique also displays intricate details on cement zonation (Fig. 4A, B).

Comparison of CCI and CL Images

As previously indicated by a number of authors, for a range of geological and mineralogical samples, CCI is generally comparable to CL (Watt et al., 2000; Doehne and Carson, 2001; Cuthbert and Buckman, 2005). The present study on a carbonate sample broadly confirms these findings (Fig. 11). In general, charge contrast (CC) images from the present study show an inverse relationship to corresponding SEM-CL images, with dark parts of CC images being bright in CL and light parts being dark (Figs. 2B, C, 11C-F). This is also the observed case with other carbonate samples observed by the authors. This simple relationship is complicated by the ability of CC images to invert their gray level (Figs. 9A, 11A, 12) with changes in, amongst others, spot size, dwell time, and pixel density, which does not happen with CL. Similar inversions in gray level are also observed with changes in magnification.
In addition, individual areas of CC images can display discrete variation in gray level that are not picked out by CL (Fig. 13). The latter and the occurrence of inversions in gray level can complicate interpretation when using the CCI technique and comparison with CL. The origins of these differences are discussed in the next section (Underlying Mechanisms of CCI).

The CC images display exceptional resolution, with cement growth phases in the order of 150 nm to 1 μm clearly observed (Fig. 14). Such CC images are superior to SEM-CL images in terms of sharpness and resolution (see Fig. 11G, H) as well as speed of acquisition (seconds for CC as opposed to 30 minutes or more for SEM-CL).

In addition, by study of matched pairs of CC and SEM-CL images, areas that show no detail by SEM-CL can exhibit excellent detailed information with the CCI technique (Figs. 7A, B, 9A, B, 11G, H). Conversely, it can also be observed that in some cases SEM-CL can display additional information that is not always observed by the CCI technique (Figs. 6B, 11D, F).

Underlying Mechanisms of CCI

As with other CCI examples (Griffin, 1997; Griffin, 2000), it is not always clear as to the underlying mechanisms that cause charge contrast differences with this coquina limestone. It is likely that the differences between the two phases of cement by CCI are induced by cation-substituted impurities in the carbonate lattice: the later cement contained impurities of Mn with in some cases Fe as well, which is not seen to such a degree in the earlier phase of cement (Figs. 6, 7, 8, 9, Table 1). Concentration of Mn and Fe can be directly related to CC image brightness (Figs. 6, 7, 8, 9, Table 1), with all measured concentrations of Mn and Fe around or below 1 wt%. The brighter second phase of cement often contains higher amounts of Mn than Fe (Figs. 7E, F,
8B, D, F), with variation in brightness reflecting differences in the amount of both elements (Fig. 9A, Table 1).

In at least one case, fine-scale zonation observed by the CCI technique was associated with areas showing slight enrichment in Mg (Fig. 6E). In other cases, the sub-µm growth zones already noted (Fig. 14), which are common in the early cement, do not always show any systematic variation in impurity concentration across them. This may be due to the detection limits of elemental x-ray analysis in SEM. Therefore the occurrence of impurities in the low parts per million (~ 100 ppm) cannot be excluded. Some micro-zonation seen in the earlier phase of cement (Figs. 7A, 8E) do show a correlation with the occurrence of Mn (Figs. 7E, 8F), indicating a compositional control for the occurrence of micro-zonation in both cases. The occurrence of lamellar twinning (Fig. 4D, F) suggests that contrast differences may in some cases be a reflection of crystal orientation, resulting in different surface charge between lamellae.

As previously indicated, changes in spot size, dwell time, image pixel resolution, as well as magnification can cause the gray level contrast to invert (Fig. 12), a feature that has been noted by previous authors (Robertson et al., 2004; Watt et al., 2000). The reversals displayed by CCI provide information concerning the mechanism behind the technique. At low imaging magnification the later cement is generally darker than the early phase. However, increasing magnification, larger spot sizes, slower scan rates (dwell time), or increased pixel density all cause a reversal in brightness between the cement phases (Fig. 12). This change reflects an increase in charge input into the surface of the sample. Under any given pressure, an increase in surface charge must lead to an increase in image brightness as less charge neutralization will occur. However, to achieve a reversal of contrast (between the two
phases of cement), this suggests either a difference in surface electrical conductivity (with the later cement phase being less conductive), or a physical barrier preventing charge dissipation (from the enclosed pods of late cement). This could take the form of lattice defects or physical breaks between the cement phases. The latter is likely to be the cause of some of the variation in gray level seen along the boundary between the two cement phases (Fig. 13). Therefore it is possible that differences in CCI-gray level may not be directly related to composition, or to near-surface lattice dislocations, but reflect a physical disjunction between domains of cement, which is the overriding factor at higher levels of energy input.

Relative Benefits of CCI vs. CL

The similarities between CC and CL imaging are close enough that even given uncertainties over the exact mechanisms behind CCI, the technique shows great promise. CCI has a number of potential advantages over SEM-CL. In the first place, with SEM-CL, imaging of carbonates typically requires a dwell scan time in the order of 400 - 800 µs (Reed and Milliken, 2003), or much longer as observed herein and noted in Lee et al. (2005), whereas with CC good images are easily achievable at scan rates between 5 and 20 µs. Secondly, a common problem of using SEM-CL with carbonates is the smeared nature of images, caused by the long latency of the red light emitted by such samples (Reed and Milliken, 2003). It is possible to minimize this smearing by using an appropriate color filter (Reed and Milliken, 2003), through longer dwell times or alternatively the CCI technique may be used as a more convenient method.

Carbonate cements often show an increase in cathodoluminescence from initial to final cement phase, with the initial phase often being dark (Boggs and Krinsley,
 Differences in cathodoluminescence occurring due to an initial lack of CL activators (such as Mn), or too much quencher such as Fe (Machel, 1985; Machel et al., 1991; Boggs and Krinsley, 2006; Hiatt and Pufahl, 2014). From the current study, given the general lack of Mn (or other CL activators) from the early phase of cement, one would not expect any CL emission from this phase. Contrast shown with the CCI technique is often best developed in the early cement phase; therefore, CC presents an ideal method for examining carbonate zoning in otherwise low CL emission zones of cement (particularly the early phase of cementation), which is also likely to apply to other carbonate facies (see Future of CCI in Carbonate Studies).

Relative Drawbacks of CCI vs. CL

It should be noted that in several cases a slow SEM-CL scan illustrated zonation in the later phase of cement (at the boundary between the two cement phases) that was not shown by CC (Fig. 6B and also Fig. 11D, F). This clearly illustrates that there is not always a simple relationship between CC and CL imaging.

As previously indicated, from the current carbonate samples, the gray level brightness using CCI cannot always be related directly to chemical or crystal defects, as brightness can flip and become inverted. Therefore a degree of care should be taken when taking and interpreting CC images. Nevertheless, as long as parameters such as spot size, voltage and scan rate remain unchanged, then inversion generally occurs only as magnification is increased. As long as the user is aware of this possibility, inversion of the brightness does not cause a major problem.

It was also noted that a 90° change in scan rotation produced an unexpected change in observed charge contrast (Fig. 15). This may be caused by a change in the relationship between the orientation of the cement zones, in respect to the direction of
scanning, affecting the way that surface charge is built up and dissipated. The latter will clearly have a potential effect on results when viewing and comparing different areas, although it did not appear to represent a major concern in the present study. It is worth noting that the above effect occurs only when applying scan rotation, and is not observed where structures are differentially oriented with respect to the normal scanning direction.

These points do not necessarily detract from CCI as a technique, as it clearly illuminates cement zonation in carbonate facies in a fashion similar to SEM-CL.

**Future of CCI in Carbonate Studies**

Given the points outlined, it is clear that the CCI technique should have more widespread use in the study of carbonate facies. Recent observations on a range of Proterozoic and Devonian carbonate samples indicate that this is the case, illustrating twinning and cement zonation (Fig. 16).

It is likely that a combination of CL and CC could be used to maximize the collection of data on both cement and cement stratigraphy. CCI can be used rapidly over large areas to obtain detailed information on features of carbonate samples, with confirmation from selected areas by optical or SEM-CL. CCI also offers the potential of high-resolution imaging of cement zoning as illustrated herein (Fig. 14).

**CONCLUSIONS**

In comparison to SEM-CL, CCI is quick and, simple, and requires only a low-vacuum SEM equipped with a GSED detector.

The current study indicates that cement zonation seen in these carbonates by CC has an underlying compositional cause, while features such as lamellar twinning are likely
to have been produced due to differences in crystal lattice orientation. Therefore, CC can be used in a similar fashion to that of SEM-CL and optical-CL in the study of carbonate facies.

It is anticipated that use of the technique will provide enhanced cement information for carbonate samples (e.g., cement zonation, twinning, and cleavage), as has been shown for other geological materials (Watt et al., 2000; Cuthbert and Buckman, 2005), especially with initial cement phases, which are commonly nonluminescent (see Boggs and Krinsley, 2006). Compared to SEM-CL, the CCI technique also offers good potential for the study of carbonate cements at the sub-μm scale; as images are less fuzzy and have improved spatial resolution.

Interpretation of CC images should take into consideration factors such as the potential for gray level inversion (brought about by increased energy input) and the effects of electrical isolation through breaks and open fractures (giving gray level variations not necessarily linked to composition, lattice orientation, or defects). These all affect electrical dissipation and have the capability of altering any signal from charge contrast controlled through compositional differences and crystal lattice defects. Nevertheless the technique produces results analogous to SEM-CL, with which it can be favorably compared. A combination of both CC and SEM-CL is likely to be advantageous in the interpretation of cements and cement stratigraphy in carbonate facies.
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REFERENCES


FIGURE CAPTIONS

Figure 1. Illustration of the difference of the source of imaging electrons between normal GSED imaging and CCI, modified after Watt et al. (2000). A) Normal GSED imaging under high gas pressure. Full charge suppression at the surface, leading to imaging from SE2 electrons produced when BSE, escaping from deeper within the sample, collide with gas molecules in the chamber. B) Charge contrast (CC) imaging with GSED, at lower gas pressures. Charge suppression at the surface is incomplete, allowing SE1 emission, which varies depending on factors such as lattice defects, composition, and surface conductivity.

Figure 2. Micrographs of the same area taken as A) BSE, B) SEM-CL and C) CC. In part A note presence of quartz (Q) and solution seam (SS). White arrows indicate subtle changes in gray level, demarcating variation in cement chemistry. Image in part B demonstrates that large areas of the sample appear dark under CL. Note the blurred nature of CL image due to latency of light emission. CCI image (C) shows two phases of cement (1, 2), with detail in the cement phase that is dark under CL. All magnifications x100.

Figure 3. Charge contrast micrographs of the same area at different voltages: A) 5 kV, B) 10 kV, C) 20 kV, D) 30 kV. All other settings: pressure 0.8 Torr, bias 50%, spot 3.5, dwell time 10 μs, 768 x 512 pixels. Little definition is visible in the first two micrographs (A, B) while a nuanced image is visible at higher voltage (C, D) due to increased energy input and incomplete charge suppression; parts C and D both clearly display two phases of cement (1, 2), these are just visible in part B but unseen in part A. Cleavage is also evident (cl). All image magnifications x200.
Figure 4. Examples of structure and cement observed with CCI. A, B) Cement zonation in first cement phase. Arrows indicate direction of growth. Image magnification x1600 and x1250 respectively. C) Laminar shell fabric. Image magnification x100. D) Early cement (1) and later phase cement (2), with arrows indicating the direction of growth, also the occurrence of thin lamellar twins (tw). Image magnification x200. E) Shell fabric with granular texture (possibly neomorphic). Image magnification x175. F) Example of lamellar twining (tw) and zoned cement centered on multiple granular core (arrow). Image magnification x1500.

Figure 5. Paired BSE and CC micrographs respectively. A, B) Centered on complete shell, both upper and lower surfaces show solution seams (ss). Quartz (Q) and clay (C) are concentrated along the shell interfaces and are partially embedded within the shell. Shell replaced by early stage cement (1) initiated on both upper and lower surfaces, growing inwards, as well as a later cement (2) forming in the middle of the shell. C, D) Spherical to ovoid bioclastic particles, bounded by dissolution surfaces (ss). Particles display initial early cement (1) growing inwards from dissolution surfaces (arrows indicate direction of growth), followed by later stage cement (2). E, F) Late-stage cement (2) crosscut by solution seam (ss), other annotations as in parts A-D. A-D Image magnification x100, E, F x800.

Figure 6. CC and CL images of the same area (A, B respectively), with corresponding x-ray dot maps for Mn, Fe and Mg (C-E, respectively). X marks a bright rim of
cement seen in SEM-CL that is not seen in CCI, corresponding to areas with Mn but no Fe (X1 has Mn and Fe). Y marks an area that exhibits fine cement zoning, best seen in CCI and to a lesser extent in SEM-CL. This corresponds to an area with slight enrichment in Mg. A - D Image magnifications x180, E x90.

Figure 7. Micrographs, EDX maps and line scans from same area. A) CC image exhibiting both phases of cement (1, 2), B) SEM-CL image of the area in part A. Note that the SEM-CL image is blurred compared to CC and zonation in cement phase 1 is hardly visible. C, D) X-ray dot maps for Mn and Fe respectively for the area imaged in parts A and B. E, F) linescans for Mn and Fe from lines indicated in part A, showing increase in both elements passing from the early to later cement (E) and a reduction in Mn in transect across an early phase cement crystal in the later cement phase (F). Trends in line scans can be equated with variation in gray level in both CC and SEM-CL images. All image magnifications x330.

Figure 8. CC micrographs (A, C, E) and line scans (B, D, F) showing Mn and Fe variation across marked transects in CC micrographs. All line scans show increase in Mn relative to Fe passing from early-generation cement (1) to late-stage cement (2). Magnification in A, C, and E x2000, x600, and x100 respectively.

Figure 9. Matched pair of A) CC and B) SEM-CL micrographs, as well as C) Mn and D) Fe maps from EDX analysis. Locations 1-9 refer to EDX analyses where Mn and Fe were measured (Table 1). Key: Star = Mn only, circle = Mn greater than Fe, and
square = neither Mn nor Fe. Points 3, 4, and 9 are in the early cement phase and have no Mn or Fe. Points 2 and 8 are at the transition between the two cement phases and contain Mn but no Fe. Points 1, 6, and 7 are in the later cement phase and contain both Mn and Fe, while point 5 is at a later stage in the same cement phase and contains only Mn. Note that these variations in Mn and Fe are reflected in the gray level of both images. In this case both CC and SEM-CL show the same trends (due to image inversion in the CC image), with darker parts of images containing no Mn nor Fe, bright areas with only Mn, and intermediate-gray level areas with both Mn and Fe. Note that SEM-CL image is blurred in comparison to that for CC. C, D) EDX maps for Mn and Fe respectively, from the same area as in parts A and B. All image magnifications x100.

Figure 10. Optical-CL micrographs of a thin section of coquina limestone from São Sebastião quarry, displaying A) luminescent late-stage calcite cement surrounded by typical nonluminescent phases of calcite, and B) detail of cement zoning in luminescent area. Both image magnifications x100. Images courtesy of Ana Carolina Tavares (UFRJ), part A from bed 14a and part B bed 16b; 4 and 10.5 meters above the samples examined by CCI and from within the same facies (Tavares et al., 2015, their Fig. 10).

Figure 11. Comparison between matched sets of micrographs for A, C, E, G) CC and B, D, F, H) SEM-CL. CC images are sharper and display more detail. Asterisk in parts D and F indicate detail in SEM-CL images that are not observed with CCI. Arrows in (C) and (G) indicate where details are clearer in CC as opposed to SEM-
CL. Parts A and B image magnification x800; parts C and D x200; parts E and F x300; parts G and H x250.

Figure 12. Paired CC micrographs of the same area under differing conditions. A, B) Spot size 2.5 and 5.5 respectively; C, D) dwell time 10 µs and 100 µs respectively; E, F) pixel resolution 768 x 512 and 6144 x 4096 respectively. Unless already stated, other settings: pressure 0.8 Torr, bias 50%, spot 3.5, dwell time 10 µs, pixel resolution 768 x 512. Note that all images display two phases of cement (1, 2) and that in all cases the cement phases invert in terms of their gray level due to increased energy input. All image magnifications x200.

Figure 13. CC micrograph showing variation in gray level between crystals (1-8) in the first phase of cement, attributed to differences in electrical connectivity to each other. Arrows indicate breaks in connectivity (with sharp distinctive crystal boundaries), while dotted lines mark areas where contemporaneous cement crystals appear continuous with no boundary between them. Crystals sharing a continuous boundary are a similar gray level, those with breaks differ in gray level. Gray level appears to be size-independant. Image x125.

Figure 14. Fine-scale cement zonation observed by CCI. A) Fine zonation of cement and change in crystal growth vector indicated by termination of face (arrow). B) Zoom-in of area marked by box in part A, cement zones approximately 150 nm to around 1 µm. Image magnifications x4250 and x8500 respectively.
Figure 15. Charge contrast image quality seems to vary based on scan rotation. Normal scan mode (A) was found to have significantly higher definition than scanning at 90° from normal (B). Both image magnifications x500.

Figure 16. CC micrographs of other carbonates. A) Zoned cement from Frasnian reef carbonate, Canning Basin, Australia, displaying well-developed cement zonation comparable to that seen with SEM-CL. B) Lamellar twinning, from Neoproterozoic Nama Group, Namibia. C-F) Zoned cement from Famennian reef carbonate, Canning Basin, Australia. Parts D and F are SEM-CL images of parts C and E, illustrating the relationship between CC and CL. Images courtesy of Madina Taubassova, Secile Iipinge, and Reece Adam (MSc project students, Institute of Petroleum Engineering, Heriot-Watt University, 2015). Image magnification: A, x100, B, x250, C, D, x500, E, F, x250.
High gas pressure

Low gas pressure

SE2 electrons
SE1 electrons
Backscattered electrons
Gas atoms
Positive ions
Sample surface
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<th>Point</th>
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Table 1. Mn and Fe wt% from points 1 – 9 in Figure 9.