

Radiaxial fibrous calcites as low-magnesian calcite cement precipitated in a marine-meteoritic mixing zone

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ABSTRACT

Radiaxial fibrous calcite (RFC) has previously been interpreted as a marine or replacive cement. Study of the Dongjeom Formation (Early Ordovician), Korea, shows that RFC can form in marine-meteoritic mixing zones as a low-magnesian calcite (LMC) cement. RFC in the shallow-marine Dongjeom Formation occurs in arenaceous limestones at the top of a transgressive facies overlying a regressive facies. It shows well-developed growth zonation, and lighter oxygen isotope values and more radiogenic strontium isotope ratios than those of Early Ordovician marine calcite. Such petrographic and chemical evidence indicates that the RFC was precipitated as a primary LMC cement in a marine and meteoritic mixing zone. Owing to the unique environment of formation, the Dongjeom RFC is characterized by growth zonal fabric comprising alternating subzones, which may indicate precipitation from varying fluids. In addition, this study documents the importance of substrate for development of RFC. Early 'nucleation' for RFC occurred mainly on microcrystalline skeletal grains and internal sediments, whereas on homogeneously altered substrates, thin-coated banding structure developed, ultimately forming coarse crystalline spar. This suggests that microcrystalline substrates are preferred sites for nucleation of RFC.

Keywords Growth zone, low-magnesian calcite, mixing zone, radiaxial fibrous calcite, substrate.

INTRODUCTION

Radiaxial fibrous calcite (RFC) is a common pore-filling fabric in ancient limestones and is defined by a distinctive combination of curved twins, convergent optic axes and divergent subcrystals within a single crystal (Bathurst, 1959; Davies, 1977; Lohmann & Meyers, 1977; Mattes & Mountjoy, 1980; Saller, 1986). The petrographic and geochemical origins of this fabric are highly controversial. It was believed initially that RFC is of neomorphic origin from a fibrous aragonite precursor (Kendall & Tucker, 1973). Kendall (1985) reinterpreted RFC as cement precipitated directly from sea water. Recently, Wilson & Dickson (1996) suggested that RFCs are replacive in origin, and the presence of RFC in limestones may provide a distinctive petrographic proxy of earlier magnesian calcite cement precipitated in a

generally warm, CaCO₃-saturated marine environment. The presence of microdolomite inclusions in some RFCs has led researchers to conclude that they were originally high-magnesian calcite (HMC; Davies, 1977; Lohmann & Meyers, 1977; Kendall, 1985; Mazzullo *et al.*, 1990). However, some RFCs do not have microdolomite inclusions, suggesting that they may not have originated from HMC (Woo *et al.*, 1993).

This study describes the petrography and geochemistry of RFC from the Early Ordovician Dongjeom Formation, Korea. Petrographic and geochemical studies indicate that the RFC cement formed in a marine-meteoritic mixing zone. Especially under cathodoluminescence, the RFC shows growth banding that consists of alternating subzones indicative of successively varying pore fluid compositions, as is common in mixing zones.

GEOLOGICAL AND STRATIGRAPHIC SETTING

The Dongjeom Formation constitutes the lowermost strata of Ordovician rocks in the Joseon Supergroup. The Joseon Supergroup comprises lower Palaeozoic strata distributed in eastern central Korea (Fig. 1) and consists mostly of carbonate rocks with interbedded siliciclastic rocks. It ranges from Early Cambrian to Late Ordovician in age (Lee, 1988). The part of the Korean Peninsula to which the study area belongs is regarded as part of the Sino-Korean (north China) Block (SKB; Kobayashi, 1966; Reedman & Um, 1975). Development of extensive carbonate platform deposits in the SKB (Feng *et al.*, 1989;

Meng & Ge, 1996) indicates that, during the Cambro-Ordovician, the SKB was a stable setting, such as passive margin or cratonic interior.

The Dongjeom Formation conformably overlies the Late Cambrian Hwajeol Formation, which consists mostly of ribbon rock and flat-pebble conglomerate deposited in deep-shelf environments (Park, 1985; Park & Han, 1985), and is conformably overlain by the Dumugol Formation, which consists of limestone, dolomitic limestone, argillaceous limestone and shale deposited on shallow to deep ramps (Lee & Kim, 1992; Kim & Lee, 1998). The Dongjeom Formation is about 50–70 m thick and comprises brownish fine- to coarse-grained sandstone, marl to shale with some intercalated flat-pebble

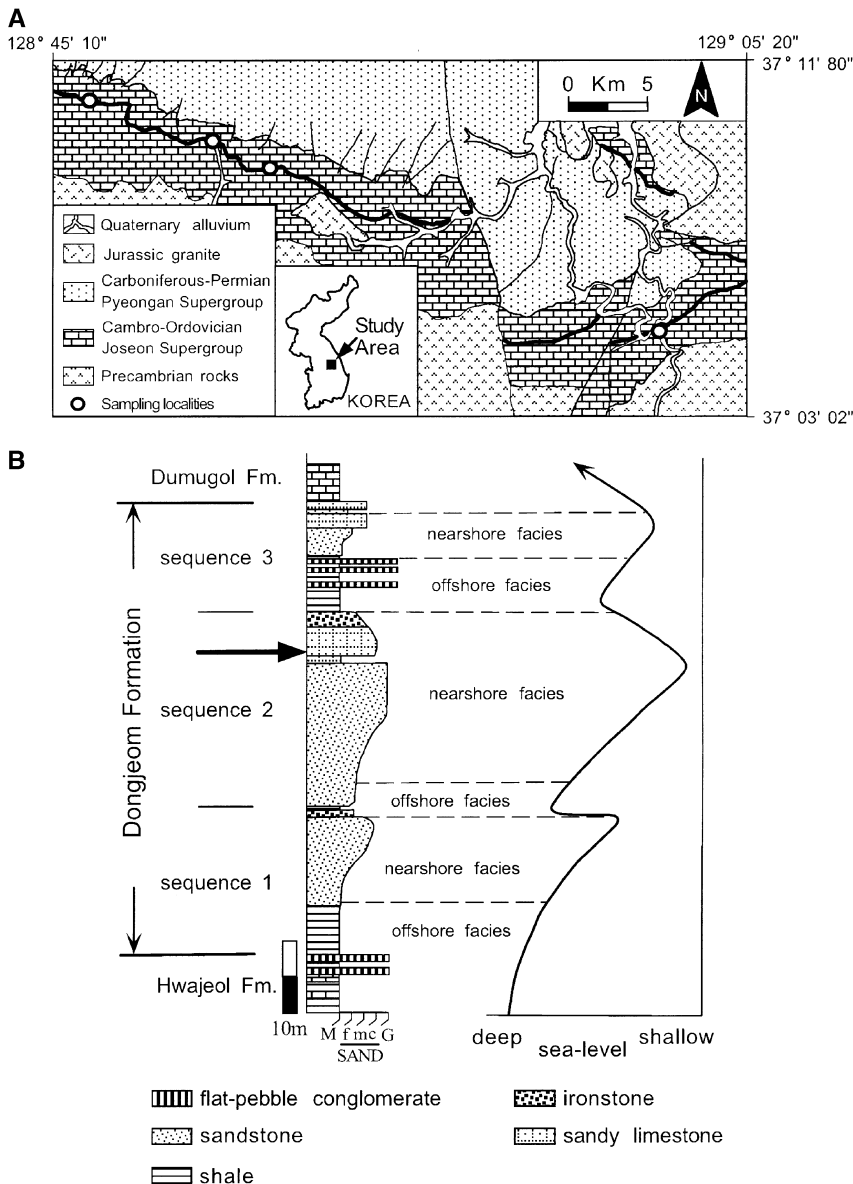


Fig. 1. (A) Simplified geological map of the study area (modified after GICTR, 1962). The dark heavy line in Cambro-Ordovician rocks represents the distribution of the Dongjeom Formation. The studied sections are Dumugol, Teoggol, Sesong and Gumunso from west to east. (B) Simplified columnar section of and a relative sea-level curve for the Dongjeom Formation (after Kim & Lee, 2000). Thick arrow in sequence 2 indicates the stratigraphic position at which RFC occurs. (M, mud; G, gravel; f, fine; m, medium; and c, coarse.)

conglomerates and ironstones. Sedimentary structures such as herringbone cross-bedding and hummocky cross-stratification are occasionally observed. The Dongjeom Formation is composed of three coarsening-upward sequences, each representing changes from offshore to shallow nearshore environments (Kim & Lee, 1999, 2000; Fig. 1B). On the tops of the lower two sequences, ironstone beds occur as condensed sections, separating each sequence (Kim & Lee, 2000). The Dongjeom Formation was dated as Early Ordovician (Tremadoc) by the conodont fauna of the underlying Hwajeol Formation and the overlying Dumugol Formation (Lee & Lee, 1971; Lee, 1988; Jeong & Lee, 2000).

Although the Early Ordovician was a time of relative sea-level highstand, the earliest Tremadoc, when the Dongjeom Formation was deposited, was a time of worldwide regression (Fortey, 1984). Relative sea level generally dropped from the uppermost part of the Hwajeol Formation to the top of sequence 2 of the Dongjeom Formation. Afterwards, sea level rose continuously through sequence 3 to the overlying Dumugol Formation, and carbonate facies became dominant on the Joseon platform. Sequence 3 of the Dongjeom Formation is a transitional zone from siliciclastic facies to carbonate facies of the Dumugol Formation. The carbonate content in sequence 3 sandstones is significantly higher than in sandstones of sequences 1 and 2. RFC in the Dongjeom Formation is concentrated in arenaceous limestones in the top part of the middle sequence, the stratigraphic interval of which comprises higher order regression facies in the lower three-quarters and higher order transgression facies in the upper one-quarter. In the same stratigraphic interval at another locality, Woo (1992) reported the presence of RFC that underwent meteoric diagenesis. He suggested that the sediments were subaerially exposed during a subsequent eustatic sea-level drop (Woo, 1989, 1992).

METHODS

Polished thin sections were examined under a standard petrographic microscope and under cathodoluminescence (CL; model CCL 8200MK3a). Some samples were stained using the method of Dickson (1966). The operating conditions of CL were 700 μ A and 16 kV. By these methods, the growth zones of calcite cements were clearly discriminated. A Jeol JXA-733A electron microprobe was used for Mg, Fe, Sr

and Mn analyses of calcite cements. Operating conditions were 15 kV accelerating voltage, 2–10 nA sample current, 5 μ m beam diameter and 100 s count time. For analyses of oxygen, carbon and strontium isotope compositions, powdered samples of the growth zones were drilled from polished rock chips using a dental drill. Sampling was based on the results of standard light microscopy of thin sections and binocular microscopic examination of polished chips. Samples were roasted under vacuum (450 °C for 1 h) to remove organic contaminants and reacted with phosphoric acid at 50 °C. Stable isotope analyses were performed using a Prism series II model mass spectrometer. Precision of stable isotope analyses is $\pm 0.1\%$ (PDB) for carbon and oxygen. For Sr isotope analyses, powdered samples were washed three times with Milli-Q water and leached in 2.5 N HCl at room temperature in an ultrasonic bath. Insoluble residues were removed by centrifugation. $^{87}\text{Sr}/^{86}\text{Sr}$ ratio measurements were carried out on a Micromass VG Sector 54-30 mass spectrometer in single collector mode (2σ external analytical precision: NBS 987 = $0.710118 \pm 12 \times 10^{-6}$, $n = 12$). Total procedural blank level for Sr was around 100 pg. Stable and strontium isotope compositions were analysed at the Korea Basic Science Institute.

RESULTS

Paragenesis

The arenaceous limestones consist mostly of calcite, quartz (up to 25%) and dolomite (5–8%). The carbonate components are skeletal grains, internal sediments, calcite cements, replace euhedral dolomites and late baroque dolomites in veins (Fig. 2). Four types of calcite cement are distinguished on the basis of petrographic texture: RFC, equant spar, bladed spar and echinoderm overgrowths. All phases are non-ferroan according to chemical staining. CL reveals three growth zones in the calcite cements. The paragenesis of diagenetic stages is interpreted as follows: micritization of some skeletal grains, dull to bright CL zone 1 (Z1) calcite cementation, stabilization and dissolution of echinoderms and Z1 cements, finely subzoned non- to dull CL zone 2 (Z2) calcite cementation, dull to bright CL zone 3 (Z3) calcite cementation and alteration of Z3 cements.

The Z1 calcite cements precipitated as overgrowths on some echinoderms. They show

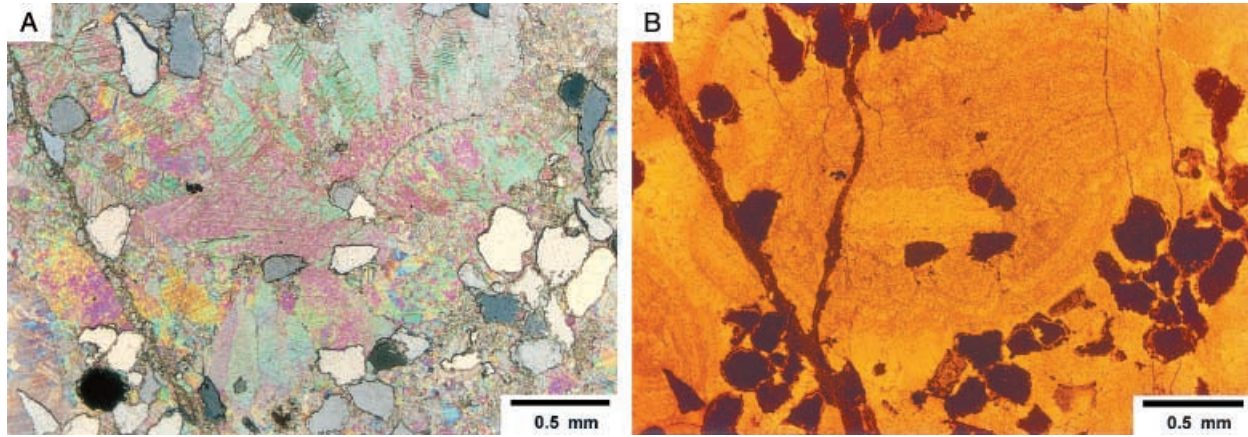


Fig. 2. (A) Cross-polarized light photomicrograph showing arenaceous limestone. It consists mostly of calcite, quartz and dolomite. (B) CL photomicrograph of the same field of view as (A). Note that finely alternating growth zoning develops on various substrates. Echinoderm grain in the centre forms coarse crystalline spar, whereas RFCs develop other microcrystalline grains.

homogeneous CL without any growth zoning. Both echinoderm grains and Z1 calcite cements contain rhombic microdolomites showing red CL (Fig. 3). The Z2 calcite cements occur as both RFC and coarse crystalline spar (Fig. 4). They not only developed as first-generation cement on the internal sediments and skeletal grains, but also grew on Z1 cements (Figs 4 and 5). Z2 calcite cements have a finely alternating CL texture of non- and dull luminescent subzones, sometimes truncating each other (Figs 4–6). Some Z2 calcite cements show ‘contouring texture’ formed by dissolution by meteoric water (cf. Walkden & Berry, 1984; Fig. 7). The Z3 calcite cements occur as bladed and equant spar in intergranular pores, and as overgrowths upon Z2 cements as RFC

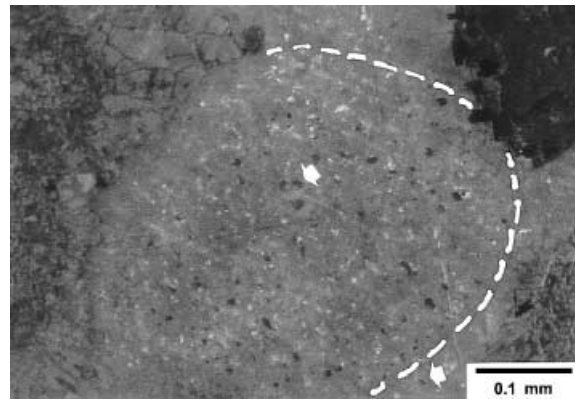


Fig. 3. CL photomicrograph showing echinoderm and its overgrowth (Z1). Echinoderm fragment is delineated by dashed line. Microdolomites (arrows) are present in both.

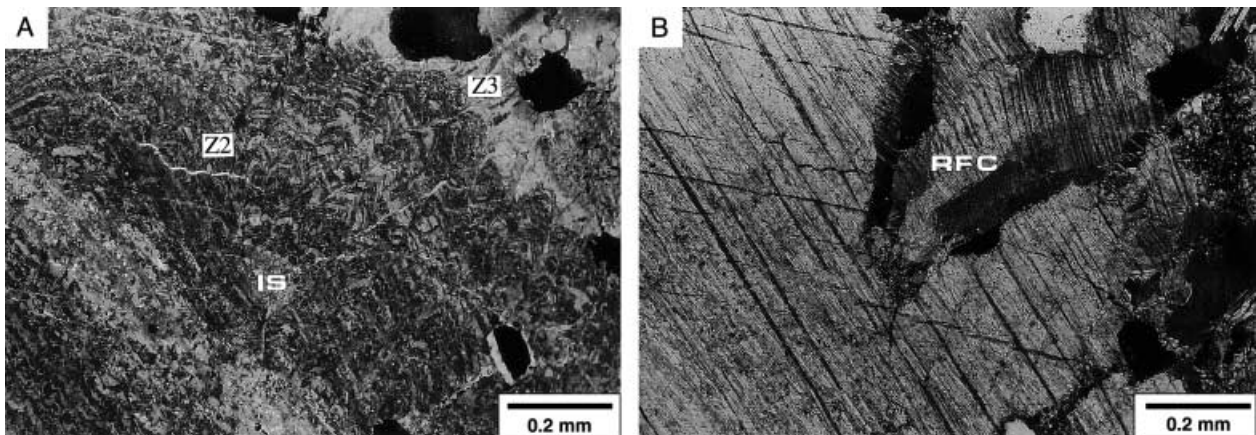


Fig. 4. (A) CL photomicrograph showing that development of RFC is substrate dependent. Z2 calcite cements have a finely alternating texture between non- and dull luminescent subzones. Z2 cements forming RFC nucleated on internal sediments (IS). In contrast, Z2 cements formed overgrowth of coarse crystalline spar on homogeneously altered substrates. (B) Cross-polarized light photomicrograph of the same field of view as in (A). Note that amalgamated Z2 cement is spar, whereas Z2 cement nucleated on internal sediments occurs as RFC.

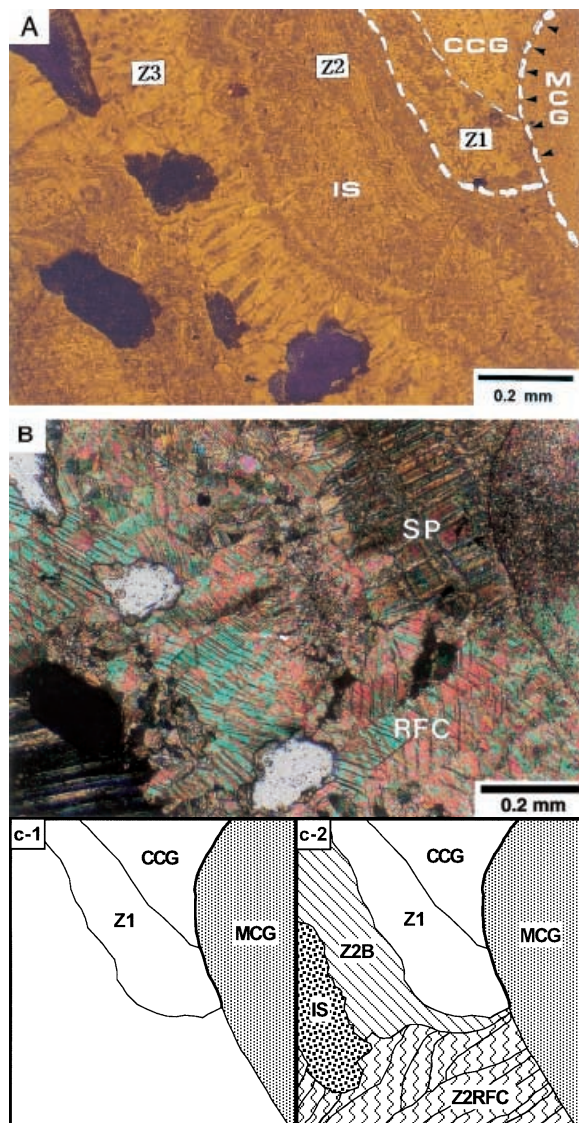


Fig. 5. (A) CL photomicrograph showing three calcite cement zones (Z1, Z2 and Z3). Note that Z2 cements nucleated selectively on a skeletal microcrystalline grain (MCG) and on internal sediments (IS). The dashed lines indicate boundaries between allochems and cement, and between Z1 and Z2 cements. The boundary between skeletal grains (arrowheads) suggests that dissolution and compaction has occurred. (B) Cross-polarized light photomicrograph of the same field of view as in (A). As in Fig. 4B, amalgamated Z2 cement is spar (SP), whereas Z2 cement nucleated on internal sediments and on the microcrystalline substrate occurs as RFC. (C) Line drawings of upper right part of (A) showing dissolution–compaction and Z2 precipitation during early diagenesis. After precipitation of Z1 cement on a coarsely crystalline grain (CCG), dissolution and compaction occurred at the boundary between a CCG and a microcrystalline grain (MCG), indicating that the coarsely crystalline grain and Z1 cement, composed originally of HMC, were selectively dissolved along the boundary in contact with the microcrystalline grain (C-1). After the dissolution–compaction event, both substrates experienced coeval Z2 cementation (C-2). However, RFC (Z2RFC) was developed only on a microcrystalline grain and internal sediments (IS), whereas on altered and dissolved substrates, a thin-coated banding structure (Z2B) was developed, ultimately forming coarsely crystalline spar.

(Figs 2, 5 and 8). Z3 calcite cements show a relatively homogeneous CL and have some microdolomite inclusions (Figs 2, 5 and 8). Z1 and Z2 calcite cements are devoid of arenaceous minerals such as quartz, which are concentrated in Z3 cements (Fig. 2).

Radial fibrous calcites

RFCs occur as 0.5 to 1.5 mm thick isopachous (Figs 2 and 5) or fan-shaped (Fig. 4) cements on internal sediments and skeletal grains. They exhibit irregular composite crystal boundaries and acute crystal terminations. RFCs contain few inclusions, as indicated by their clear appearance. They are composed of Z2 cement only, or Z2 and successive Z3 cements. The development of RFC is largely related to nucleation of Z2 cements on micritic substrates. In RFCs, Z2 cements nucleated directly on substrates such as internal sediments and skeletal grains that have microcrystalline textures (Figs 4 and 5). In contrast, on altered, but not micritic and dissolved substrates, such as echinoderm fragments, Z2 cements did not form RFC, but precipitated as overgrowths of coarse crystalline spar (Figs 4 and 5).

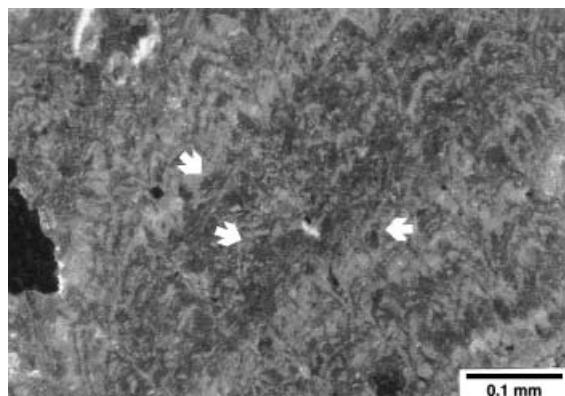


Fig. 6. Close-up CL photomicrograph of Z2 cement. Alternating subzones of Z2 calcite cements have internal truncation structures between some subzones (arrows).

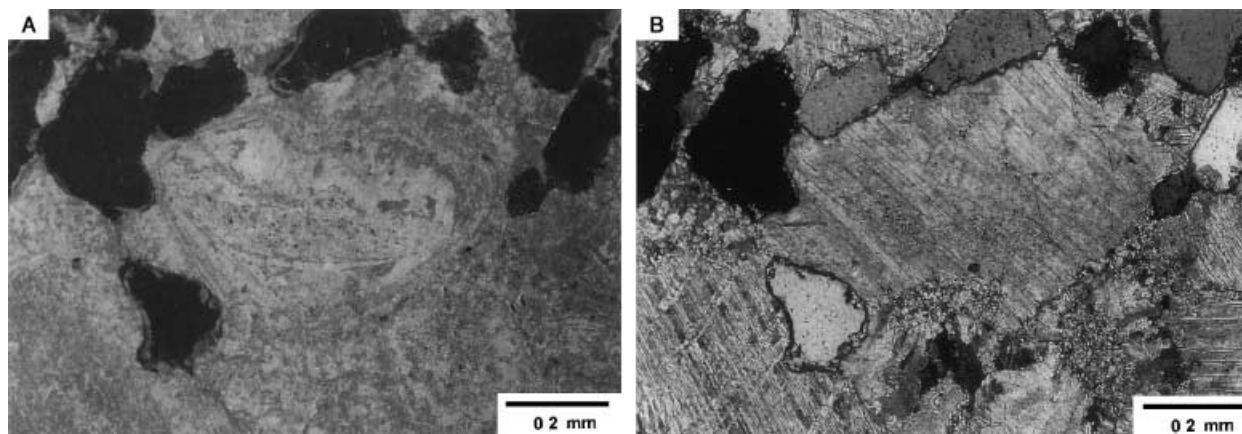


Fig. 7. (A) CL photomicrograph showing contouring texture (centre) of Z1 calcite cement caused by dissolution by meteoric water (Walkden & Berry, 1984). Dark grains are quartz. (B) Cross-polarized light photomicrograph of the same field of view as in (A).

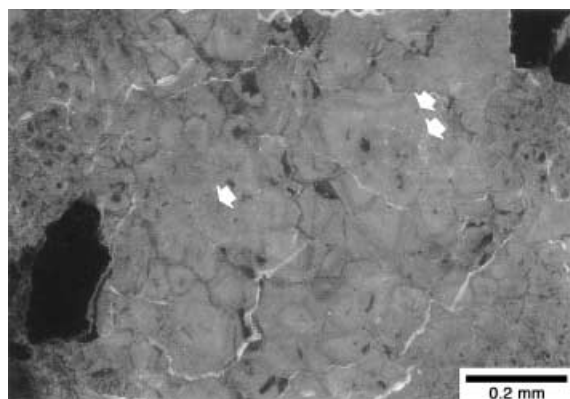


Fig. 8. CL photomicrograph showing equant spars of Z3 cements. Some microdolomites (arrows) are shown in Z3 cements.

Elemental and isotopic composition

The elemental and isotopic composition of calcite cements is shown in Tables 1 and 2. Mn (average 850 p.p.m.), Fe (average 2530 p.p.m.) and Sr (average 350 p.p.m.) contents of Z2 calcite cements plot between fields of marine and meteoric calcites (Fig. 9), whereas Z1 and Z3 cements have a relatively wide range of elemental compositions. Elemental compositions of Z3 cements are similar to those of calcite cements reported by Woo (1992). Stable isotopic compositions of RFCs are relatively uniform (Fig. 10). $\delta^{18}\text{O}$ values ($n = 7$) of Z2 cements range from -14.7 to -16.7‰ (PDB), and $\delta^{13}\text{C}$ values ($n = 7$) range from -0.3 to -0.6‰ (PDB; Fig. 10). $\delta^{18}\text{O}$ values ($n = 7$) of Z3 cements are from -14.1 to -15.3‰ (PDB), and $\delta^{13}\text{C}$ values ($n = 7$) are from -0.3 to -1.0‰ (PDB; Fig. 10). The $\delta^{18}\text{O}$ values of Z2 and Z3 cements are much lower than those of Early

Ordovician marine calcites (Veizer *et al.*, 1999). However, $\delta^{13}\text{C}$ values are similar to those of Early Ordovician marine calcites (Veizer *et al.*, 1999). $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of four Z2 and three Z3 cements are from 0.71137 to 0.71148, and from 0.71274 to 0.71280 respectively. $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are more radiogenic than those of Early Ordovician marine calcites (about 0.7090; Veizer *et al.*, 1999).

INTERPRETATION AND DISCUSSION

Diagenetic environment of calcite cementation

Sediments containing calcite cements were deposited in nearshore environments during the transitional stage from regression to transgression (Choi, 1990; Kim & Lee, 1999). Most calcite cements in the present study have general features of marine calcites, such as fibrous textures, isopachous fringes, association with internal sediments and non-ferroan compositions. However, there are some questions about the diagenetic environment of Z2 cements, especially regarding the change of composition in calcite cements. First, the presence of microdolomites within Z1 and Z3 cements suggests that they formed originally as high-magnesian calcite (HMC; Lohmann & Meyers, 1977; Leutloff & Meyers, 1984). The absence of microdolomite and alteration textures in Z2 calcite cements suggests that they precipitated as low-magnesian calcite (LMC). Although it has been reported that LMC precipitated directly from marine environments during the Early Ordovician (Wilson *et al.*, 1992; Kim & Lee, 1996), it is unlikely that calcites

Table 1. Trace element composition (in p.p.m.) of calcite cements.

| Zone 1 | Mn | Fe | Sr | Mg | Zone 2 | Mn | Fe | Sr | Mg | Zone 3 | Mn | Fe | Sr | Mg |
|--------|------|------|------|------|--------|------|------|-----|------|--------|------|------|------|------|
| | 800 | 1190 | 200 | 1840 | | 1250 | 2230 | 330 | 2120 | | 990 | 4540 | 620 | 2620 |
| | 400 | 1130 | 840 | 2570 | | 1360 | 2470 | 280 | 2410 | | 1770 | 3130 | 160 | 1370 |
| | 330 | 440 | 690 | 3900 | | 1620 | 3420 | 130 | 2400 | | 880 | 3130 | 590 | 1780 |
| | 370 | 980 | 640 | 3080 | | 290 | 2540 | 330 | 1850 | | 1110 | 2720 | 80 | 1320 |
| | 1030 | 1390 | 380 | 1600 | | 780 | 3250 | 420 | 2720 | | 1320 | 1770 | 320 | 1550 |
| | 40 | 120 | 1160 | 710 | | 1180 | 2200 | 360 | 1840 | | 1570 | 1330 | 280 | 1360 |
| | 150 | 60 | 880 | 1350 | | 1180 | 3500 | 120 | 2260 | | 1380 | 2860 | 330 | 1670 |
| | 780 | 3240 | 700 | 2060 | | 1060 | 1950 | 160 | 1450 | | 1070 | 2800 | 300 | 1440 |
| | 640 | 2780 | 440 | 1420 | | 1070 | 2740 | 320 | 2410 | | 1110 | 4050 | 520 | 2010 |
| | 570 | 1070 | 550 | 1570 | | 590 | 1280 | 20 | 1830 | | 560 | 2730 | 470 | 1270 |
| | 1180 | 2060 | 140 | 1670 | | 740 | 2900 | 550 | 1820 | | 290 | 2240 | 820 | 2020 |
| | 350 | 260 | 1150 | 790 | | 850 | 3380 | 640 | 2420 | | 2520 | 3350 | 20 | 1540 |
| | 1030 | 2590 | 300 | 1990 | | 480 | 2320 | 420 | 4420 | | 290 | 2730 | 500 | 1860 |
| | 640 | 1150 | 50 | 2880 | | 920 | 2210 | 460 | 1540 | | 1030 | 3340 | 220 | 1490 |
| | 330 | 60 | 780 | 1370 | | 370 | 2320 | 850 | 2260 | | 780 | 3240 | 700 | 2060 |
| | 720 | 2630 | 170 | 1900 | | 40 | 3060 | 430 | 2560 | | 640 | 2780 | 440 | 1420 |
| | 570 | 2400 | 300 | 1890 | | 660 | 3070 | 540 | 1950 | | 570 | 1070 | 550 | 1570 |
| | 570 | 630 | 50 | 3630 | | 770 | 2980 | 450 | 2400 | | 1180 | 2060 | 140 | 1670 |
| | 1630 | 3110 | 460 | 2360 | | 1290 | 1970 | 80 | 1890 | | 680 | 2400 | 330 | 1650 |
| | 820 | 3740 | 440 | 2180 | | 960 | 2150 | 200 | 1550 | | 1290 | 3330 | 700 | 1810 |
| | 780 | 2560 | 230 | 2100 | | 1170 | 4000 | 90 | 3010 | | 1540 | 2060 | 470 | 1390 |
| | 780 | 2070 | 440 | 2120 | | 850 | 1780 | 160 | 1370 | | 1430 | 3280 | 190 | 1800 |
| | 790 | 2930 | 300 | 2030 | | 530 | 2360 | 750 | 1610 | | 2100 | 2950 | 390 | 1570 |
| | 780 | 1240 | 380 | 1730 | | 500 | 2880 | 590 | 1920 | | 570 | 1620 | 640 | 3320 |
| | 290 | 2240 | 820 | 2020 | | 750 | 3120 | 280 | 1900 | | 140 | 350 | 770 | 930 |
| | 640 | 2780 | 523 | 1420 | | 930 | 1470 | 350 | 1530 | | 180 | 440 | 230 | 4910 |
| | 570 | 1070 | 550 | 1570 | | 1110 | 1740 | 190 | 2120 | | 1700 | 1210 | 50 | 1420 |
| | 660 | 3060 | 450 | 1950 | | 530 | 2950 | 540 | 2800 | | 1240 | 1670 | 320 | 1470 |
| | 720 | 2872 | 170 | 1600 | | 220 | 3120 | 590 | 2180 | | 750 | 690 | 250 | 2680 |
| | 620 | 2790 | 390 | 1560 | | 320 | 3500 | 270 | 2510 | | 390 | 1840 | 600 | 2030 |
| | 1110 | 2963 | 350 | 2040 | | 920 | 2690 | 300 | 2290 | | 820 | 1480 | 320 | 2610 |
| | 150 | 60 | 880 | 1350 | | 750 | 2580 | 220 | 2030 | | 220 | 580 | 580 | 1560 |
| | 780 | 3240 | 700 | 2060 | | 1030 | 3170 | 650 | 1800 | | 820 | 170 | 280 | 2980 |
| | 640 | 2780 | 440 | 1460 | | 640 | 1560 | 440 | 1730 | | 1110 | 90 | 150 | 2690 |
| | 570 | 1070 | 550 | 1570 | | 570 | 2330 | 540 | 2050 | | 720 | 290 | 400 | 2230 |
| | 1180 | 2060 | 140 | 1670 | | 1100 | 2420 | 70 | 2550 | | 1320 | 490 | 260 | 3500 |
| | 350 | 260 | 1150 | 790 | | 640 | 2740 | 350 | 1880 | | 570 | 720 | 150 | 1280 |
| | 1030 | 2590 | 300 | 1990 | | 1280 | 1560 | 360 | 1610 | | 350 | 260 | 1150 | 790 |
| | 640 | 1150 | 50 | 2880 | | 1030 | 1240 | 270 | 3870 | | 1030 | 2590 | 300 | 1990 |
| | 330 | 60 | 780 | 1370 | | 750 | 1670 | 100 | 1680 | | 640 | 1150 | 50 | 2880 |
| | 720 | 2630 | 170 | 1900 | | 1320 | 2420 | 430 | 1940 | | 1280 | 1390 | 550 | 2570 |
| | 570 | 2400 | 300 | 1890 | | 1140 | 3030 | 280 | 2730 | | 140 | 1300 | 320 | 1700 |
| | 570 | 630 | 50 | 3630 | | | | | | | 1030 | 380 | 90 | 2480 |
| | 780 | 3240 | 700 | 2060 | | | | | | | 860 | 1480 | 470 | 2090 |
| | 640 | 2780 | 440 | 1420 | | | | | | | 540 | 230 | 430 | 2040 |
| | 570 | 1070 | 550 | 1570 | | | | | | | 180 | 520 | 1150 | 890 |
| | | | | | | | | | | | 330 | 90 | 780 | 1370 |
| | | | | | | | | | | | 720 | 2630 | 170 | 1900 |
| | | | | | | | | | | | 570 | 2400 | 300 | 1890 |
| | | | | | | | | | | | 890 | 2310 | 410 | 2470 |
| | | | | | | | | | | | 1250 | 1480 | 220 | 1820 |
| | | | | | | | | | | | 500 | 470 | 80 | 3000 |
| | | | | | | | | | | | 820 | 260 | 670 | 2180 |
| | | | | | | | | | | | 330 | 140 | 1040 | 1310 |
| Mean | 657 | 1818 | 481 | 1924 | Mean | 846 | 2530 | 355 | 2172 | Mean | 891 | 1752 | 413 | 1949 |

Table 2. Isotopic composition of calcite cements.

| Zone 2 | $\delta^{18}\text{O}$ (‰) | $\delta^{13}\text{C}$ (‰) | $^{87}\text{Sr}/^{86}\text{Sr}$ | Zone 3 | $\delta^{18}\text{O}$ (‰) | $\delta^{13}\text{C}$ (‰) | $^{87}\text{Sr}/^{86}\text{Sr}$ |
|--------|---------------------------|---------------------------|---------------------------------|--------|---------------------------|---------------------------|---------------------------------|
| | -15.9 | -0.3 | 0.71141 | | -15.1 | -0.3 | 0.71274 |
| | -15.9 | -0.4 | 0.71137 | | -15.3 | -0.3 | 0.71275 |
| | -16.7 | -0.4 | 0.71137 | | -14.9 | -0.3 | 0.71278 |
| | -16.3 | -0.3 | 0.71145 | | -14.7 | -0.5 | 0.71275 |
| | -14.7 | -0.3 | 0.71148 | | -14.4 | -1.0 | 0.7128 |
| | -14.7 | -0.3 | 0.71139 | | -14.1 | -0.6 | 0.71274 |
| | -15.2 | -0.6 | 0.71148 | | -14.1 | -0.6 | 0.71277 |
| Mean | -15.6 | -0.4 | 0.71142 | Mean | -14.7 | -0.5 | 0.71276 |

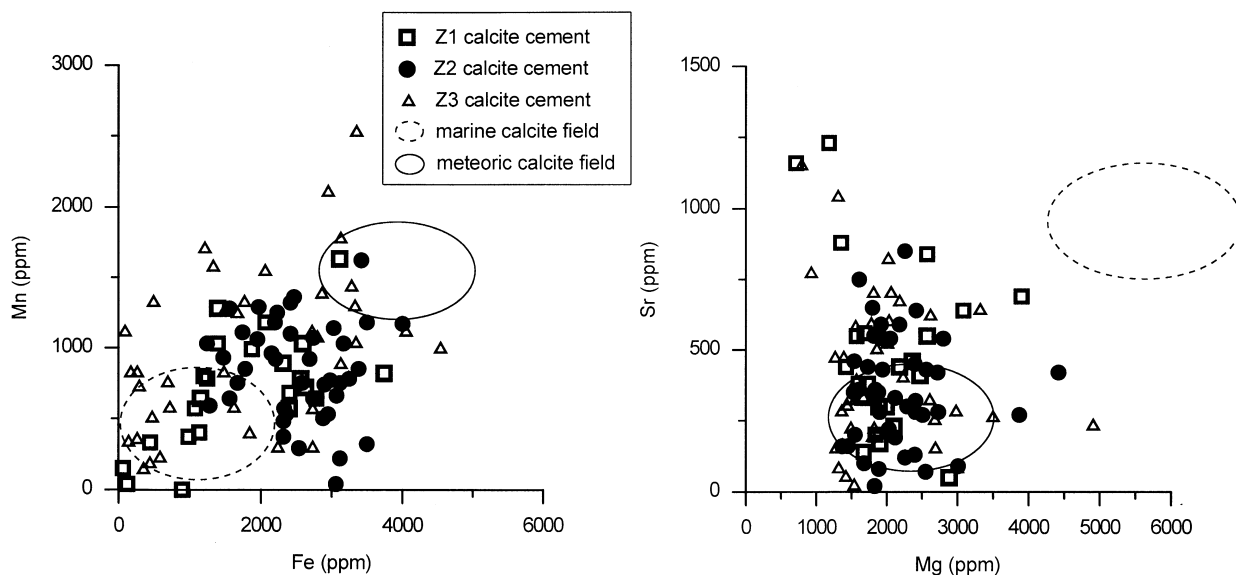


Fig. 9. Scatter diagrams of element compositions (Mn vs. Fe, and Sr vs. Mg) for early calcite cements. Fields for marine and meteoric calcites (Dickson, 1990) are shown for reference. Elemental compositions for Z1 and Z3 calcite cements vary widely from marine to meteoric calcite fields, whereas Z2 calcite cements plot between marine and meteoric calcite fields. Based on textural observation, Z1 and Z3 cements were originally high-Mg calcites precipitated from sea water and were altered to low-Mg calcites under the influence of meteoric waters during very early diagenesis. In contrast, Z2 cements originated as low-Mg calcites.

precipitated from normal sea water would have changed from HMC (Z1) to LMC (Z2) and then to HMC (Z3). Secondly, Z2 cements have many finely alternating growth subzones indicative of changes in fluid chemistry during precipitation. Calcite cements from marine environments are commonly non-luminescent and have few growth zones, whereas non-marine cements are compositionally zoned as a result of variations in Mn and Fe contents (Hemming *et al.*, 1989; Reeder, 1991). Truncation between subzones also indicates compositional variations in fluids during Z2 cementation. Also, the alteration of echinoderms and Z1 cements (HMC) to LMC before Z2 cementation suggests that fluids that precipitated Z2 cements were different from normal sea water. Finally, although it is presumed that there must

have been relatively high porosity during early diagenesis, dissolution–compaction appears to have occurred before the early stage of Z2 cementation (Fig. 5). After the dissolution–compaction event, both substrates experienced coeval Z2 cementation. Only echinoderm grains and Z1 cement, composed originally of HMC, were dissolved at grain contacts. This early dissolution–compaction indicates that meteoric water entered the unit before Z2 cementation (cf. Hird & Tucker, 1988).

The above lines of evidence suggest that Z2 cements precipitated from fluids different from those for Z1 and Z3 cements. If the Z1 and Z3 cements were of marine origin, the Z2 cements may not have precipitated from normal sea water, but from diluted water, probably marine-meteoric

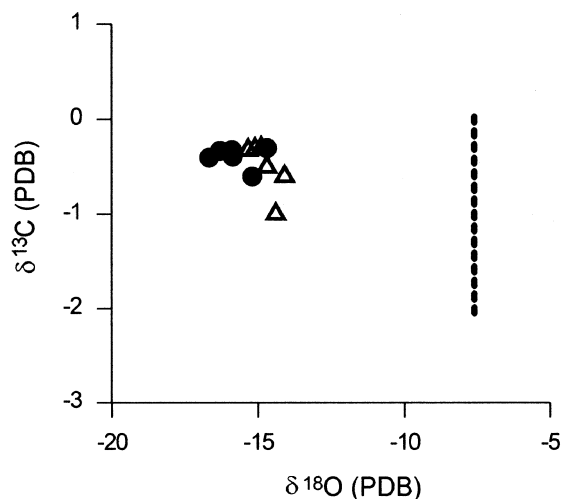


Fig. 10. Carbon and oxygen isotopic compositions of Z2 (dots; $n = 7$) and Z3 (triangles; $n = 7$) calcite cements. The $\delta^{18}\text{O}$ values of RFC are more depleted than literature data (dotted line; Veizer *et al.*, 1999) for Ordovician marine calcites. However, $\delta^{13}\text{C}$ values are similar to the literature data.

mixed waters of variable chemistry. The influx of meteoric water into the examined stratigraphic interval is supported by the occurrence of ironstone characterized by chamosite facies in a superjacent stratigraphic interval (Kim & Lee, 2000). The chamosite facies is known to form near river mouths, which have a high influx of weathering products (Odin, 1985). In addition, Woo (1992) reported the occurrence of RFCs altered by meteoric water in the same stratigraphic interval

at another locality. Therefore, it is interpreted that, through time, calcite cementation occurred in a marine zone (Z1), in a mixing zone (Z2) and again in a marine zone (Z3; Fig. 11).

Development of the mixing zone could be related to the regressional phase of the Dongjeom sequence (cf. Muchez & Viaene, 1994). After Z1 cementation, incursion of meteoric water occurred into sediments, resulting in the formation of a mixing zone. In this zone, before Z2 cement precipitation, HMCs such as echinoderms and Z1 cements were altered to LMC or partially dissolved and compacted and, subsequently, LMC (Z2) precipitated. In the mixing zone, a CL contouring texture (Fig. 7) was formed by dissolution of Z1 cement (cf. Walkden & Berry, 1984), a process known as 'mixing corrosion' (James & Choquette, 1984; Wicks *et al.*, 1995).

The influx of meteoric water was variable, probably controlled by factors such as climate or rainfall. Thus, the chemical composition of mixed water would have been changed continuously, resulting in the development of alternating subzones in the Z2 cements. In this process, RFCs formed selectively upon microcrystalline skeletal grains and internal sediment. As sea level rose again, meteoric water was replaced by sea water in pore spaces, from which HMC (Z3) cements precipitated. Homogeneous CL and the occurrence of microdolomite within Z3 cements suggest that they were altered to LMC during diagenesis.

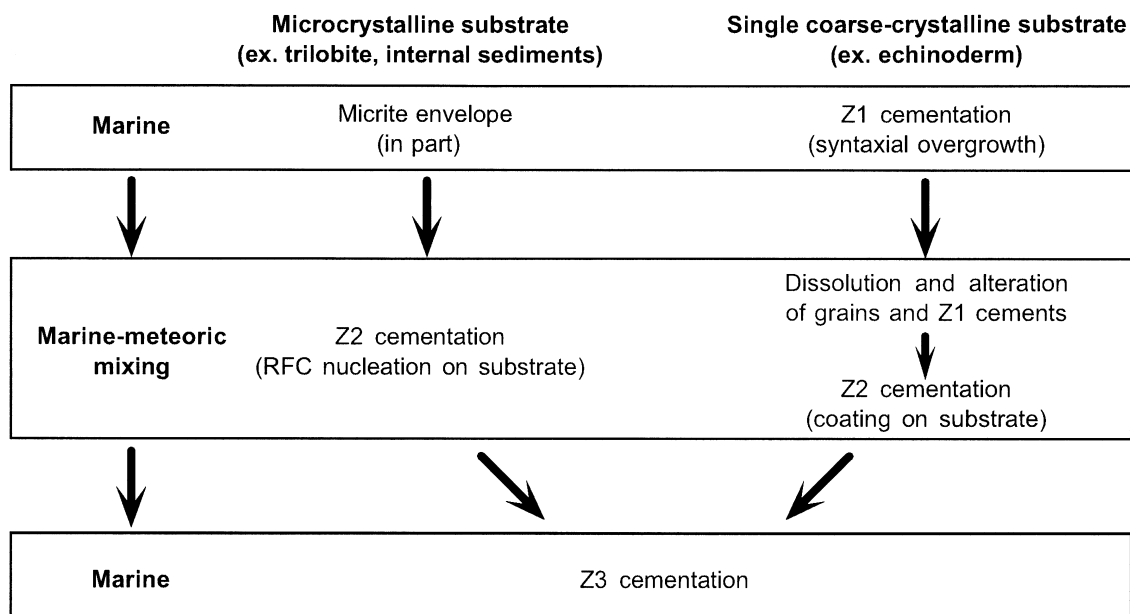


Fig. 11. Flow chart showing the early diagenesis of the examined arenaceous limestone. Conclusively, RFC developed selectively on microcrystalline substrates.

Elemental and isotopic results support the above interpretation. The preservation of finely luminescent growth subzones in Z2 cements suggests that they have not been altered since formation. Thus, their elemental and isotopic values are probably related to primary conditions of precipitation. Minor element (Mn, Fe and Sr) contents of Z2 calcite cements mostly plot between fields of marine and meteoric calcites (cf. Dickson, 1990; Fig. 9). In contrast, minor element contents of Z1 and Z3 cements show a wide range, which suggests that both cements were altered after precipitation. The overlap of carbon and oxygen isotopic compositions between Z2 and altered Z3 cements suggests that they had a similar isotopic composition before burial (Fig. 10). Lighter $\delta^{18}\text{O}$ values of Z2 and Z3 cements than those of marine calcites coeval with Ordovician sea water suggest that both cements were influenced by meteoric waters. The similarity of isotopic compositions of Z2 cements to those of Z3 cements that were altered by meteoric water supports a mixing zone origin for Z2 cement (including RFC). Continental waters have higher $^{87}\text{Sr}/^{86}\text{Sr}$ values than that of coeval sea water. Thus, more radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of Z2 and Z3 cements than those of Ordovician marine calcites also support the above interpretation. Tobin *et al.* (1997) also reported that Ordovician marine-meteoric mixing zone calcite cements with high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (0.7117–0.7119) were formed by an influx of meteoric water. Alternatively, lighter oxygen isotopic compositions and higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of Z2 and Z3 cements may indicate that they have undergone recrystallization and water–rock interaction, respectively, during burial diagenesis. However, if they originated during burial diagenesis, it is unlikely that the Z2 cements would show such petrographic and geochemical characteristics as loose displacive texture, rare inclusions, well-preserved growth zones and non-ferroan compositions. Arenaceous grains such as quartz are mainly present floating in Z3 calcite cements (Fig. 2). This may suggest that Z1 and Z2 calcite cements displaced arenaceous minerals during their growth, indicating that sediments were still loose when they grew. RFC is occasionally interpreted to have been of replacive origin during burial (Kendall & Tucker, 1973; Wilson & Dickson, 1996). Replacive calcite commonly contains inclusions or ghosts of its precursor (Lohmann & Meyers, 1977; Sellwood *et al.*, 1989; Wilson & Dickson, 1996). However, the studied RFC is clear with few inclusions. Also, Dongjeom RFC has a

non-ferroan composition. Calcites formed under reducing conditions, especially during burial, are commonly enriched in Fe because they originated from subsurface brines that interacted with siliciclastic rocks (Choquette & James, 1987; Tucker & Wright, 1990). Collectively, all the lines of evidence presented above favour the formation of Z2 cement, including the RFC, in a marine-meteoric mixing zone.

Wider implications for the origin of RFC

The examined RFC has many growth zones (under CL), which indicates that they are primary in origin. Thus, this study supports the interpretation of Kendall (1985) that RFC is a primary cement precipitated directly on substrates.

It has generally been believed that RFC is a typical fabric of early marine cementation (Dickson, 1990; Tucker, 1991). The results of this study indicate that RFC can also form in mixing zones.

This study also documents the importance of substrate characteristics for the development of RFC. Early nucleation of RFC is mostly developed on skeletal microcrystalline grains and internal sediments, which is attributed to preferential nucleation on them for growth (Figs 4, 5 and 11). However, on altered to dissolved substrates, a thin-coated banding structure is developed, ultimately forming coarse crystalline spar (Figs 4, 5 and 11). These observations suggest that microcrystalline substrates are preferred in nucleating RFC cements. Thus, substrate fabric is an important control on RFC formation.

CONCLUSIONS

RFC in the shallow-marine Dongjeom Formation occurs in arenaceous limestones in the top of the middle sequence, which is interpreted to represent transgressive facies following a regression. The Dongjeom RFC is characterized by growth zonal fabric comprising alternating subzones indicative of varying fluid composition. Petrographic and chemical studies indicate that Dongjeom RFC was precipitated directly on substrates as LMC in a marine and meteoric mixing zone. This study supports previous work that concluded that RFC is a primary cement precipitated directly on substrates. However, the results of the present study extend the environmental conditions of RFC precipitation to the mixing-zone environment. Moreover, this study documents

the importance of substrate for the development of RFC. Early nucleation for RFC occurred mainly on microcrystalline skeletal grains and internal sediments. However, on homogeneously altered substrates, thin-coated banding structure developed, ultimately forming coarse crystalline spar. This suggests that microcrystalline substrates preferentially nucleate RFC cements.

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