Diagenesis and Evolution of Microporosity of Middle–Upper Devonian Kee Scarp Reefs, Norman Wells, Northwest Territories, Canada: Petrographic and Chemical Evidence¹

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ABSTRACT

The Middle-Upper Devonian Kee Scarp reef complexes of Norman Wells, Northwest Territories, Canada, are oil-producing, stromatoporoiddominated carbonates. Episodic increases in the rate of sea level rise produced multiple cycles of reef growth that exhibit backstepping characteristics. These carbonates, composed of invariably altered limestones, have original interskeletal, intraskeletal, and intergranular porosity, mostly occluded by nonferroan, dull luminescent cements. Secondary porosity, represented by micropores of various types, developed during diagenesis by aggrading neomorphism and dissolution. The micropores represent the main reservoir porosity in the Kee Scarp limestone. Micropores in the Kee Scarp limestone can be classified into four categories based on their shapes: (1) stepwise rhombic, about 1 μ m to 2 μ m in diameter, developed mainly in stromatoporoids; (2) intercrystalline rhombic, about 1 µm in diameter, developed mainly in algal aggregates; (3) microvugs, $4 \,\mu m$ to $10 \,\mu m$ in diameter, developed mainly in algal aggregates; and (4) microchannels, about 12 μ m in length and 0.5 μ m in width, developed in algal aggregates and stromatoporoids. The stepwise rhombic and microvugs are developed mainly at the Kee Scarp reef margin and constitute the best type of reservoir porosity.

Petrographic, chemical, and isotopic studies of Kee Scarp reef components reveal a complex diagenetic history involving marine fluids modified by increasing water/rock interaction and burial. Early diagenetic processes include marine cementation and micritization followed by neomorphic replacement of high-Mg calcite and aragonite reef components, resulting in the creation of the first generation of microporosity via dissolution on a micron scale. Later diagenesis, represented by microfracturing and cementation, with two generations of equant calcite and stylolitization, was responsible for the second generation of microporosity. Very minor silicification, dolomitization, and vertical fracturing occurred at variable depths. Portions of well-preserved marine cements, stromatoporoids, and rare crinoids of postulated high-Mg calcite precursor mineralogy have escaped diagenetic alteration and preserve the original marine δ^{18} O and δ^{13} C signatures (-4.7 ± 0.3‰ PDB for oxygen; 1.0 ± 0.4‰ PDB for carbon). Minor and trace element data show less preservation of the postulated original marine composition. Neomorphic stabilization of skeletal components caused further depletion in δ^{18} O but very little change in δ^{13} C, an argument for modification of the original marine fluids with increasing burial. Variations in magnitude of water/rock interaction with depth, facies changes, and porosity modifications probably exerted some control on fractionation and distribution of stable isotopes and trace elements in reef components.

INTRODUCTION

Microporosity is common and very important in ancient limestone reservoirs in the Paleozoic, Mesozoic, and Tertiary deposits of North America (Loucks and Sullivan, 1987; Kopaska-Merkel, 1988; Dravis, 1989; Kaldi, 1989; Perkins, 1989), North

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¹Manuscript received October 24, 1994; revised manuscript received June 5, 1995; final acceptance September 11, 1995.

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This research was supported by a grant from NSERC (to ISA). We wish to extend our thanks to Imperial Oil Company for providing samples, data, and support. Special thanks are due lain Muir (formerly Imperial Oil, now Wascana Energy), Mark McMurry (Imperial Oil), and Warren Chriasty (Imperial Oil) for their valuable information and help during and after the sampling period. Thanks are also due to Ingrid Churchill and John Robinson (University of Windsor) for their help in chemical analysis and SEM. An earlier version of this paper benefited from critical reviews by A. D. Desrochers, G. Burrowes, H. Qing, and P. W. Choquette.





Africa (Bebout and Pendexter, 1975; Holail and Lohmann, 1994) and Asia (Friedman, 1983; Moshier, 1989b). These limestones are shallowwater deposits exhibiting various kinds of chalky texture. Such chalky textures resulted from microporosity developed within the matrix component of these rocks, but is different from that of true chalks, which are deep ocean accumulations of calcareous nanofossil tests with abundant inter- and intraparticle microporosity. Terms other than "chalky porosity" have been used in the literature, such as "matrix microporosity," "intramicrite porosity," and "pin-point porosity." Moshier (1989a) suggested that microporosity is produced by neomorphism, which converts metastable calcium carbonate [aragonite (A) and high-Mg calcite (HMC)] into a stable phase, low-Mg calcite (LMC). This may be attributed to the volume change accompanying the partial elimination of Mg²⁺. In their study of Upper Cretaceous chalks from Egypt, Holail and Lohmann (1994) argued that the chalky porosity resulted during early lithification, extensive recrystallization, and chemical equilibrium of micrite. Development of microporosity has been found to be facies controlled (Dravis, 1989; Kaldi, 1989).

Norman Wells oil field, which lies in Northwest Territories, Canada, along the Mackenzie River, produces from the Upper-Middle Devonian Kee Scarp Formation. The reservoir is composed mainly of stromatoporoid-rich carbonates that have original interskeletal, intraskeletal, and intergranular porosity, mostly occluded by cement (Muir et al., 1985; Kaldi, 1989). The main reservoir porosity is represented by micropores of various types. The micropores (4–8 µm) occur as intercrystalline microvoids within the present LMC stromatoporoid, algal, and matrix components that make them different from other examples in which microporosity is dominant in mud-supported carbonate sequences. Kaldi (1989), in his petrologic study of Kee Scarp reef complexes, attributed the formation of microporosity to a mixed marine-meteoric environment early in the diagenetic history.

In this paper, we demonstrate, using both petrologic and geochemical evidence, that microporosity formed in two diagenetic stages, early and late, in shallow to intermediate burial from modified marine fluids. Our goals are to (1) evaluate facies control on the occurrence, distribution, and shape of micropores; (2) quantify the nature of the diagenetic pore waters and the conditions of the diagenetic environments that dominated during the stabilization of the Kee Scarp carbonates using petrographic, chemical, and isotopic evidence; and (3) quantify chemical changes during diagenetic stabilization of metastable carbonate phases and show their relationship to the evolution of microporosity.

GEOLOGIC SETTING

The Upper-Middle Devonian Kee Scarp Formation at Norman Wells lies beneath the Mackenzie River in the Northwest Territories of Canada (Figure 1), about 1500 km north of Edmonton, between latitude $65^{\circ}14'56''$ N to $65^{\circ}17'54''$ N and longitude $126^{\circ}47'28''$ W to $126^{\circ}59'41''$ W. The reef occupies an area 15-25 km long and 6-8 km wide and has a general northeastsouthwest trend. The regional structural dip of the



Figure 2—Schematic cross section across Norman Wells reef complex showing different reef cycles (modified from West and Doyle-Read, 1988).

reef complex beds is 4.5° to the southeast. Oil has accumulated in the updip part (northwest) of the reef bioherm, under the Mackenzie River, but no gas cap was formed (Kempthrone and Irish, 1981). The original oil in place is estimated to be 10^8 m^3 . Norman Wells oil production peaked at 5516 m³/day in July 1992 (Chriasty et al., 1994). At the present time, more than 300 wells have been drilled through the reservoir as a part of a line-drive waterflood, enhanced oil recovery project.

Growth of the reefs was affected by the paleogeography of the area. The reef complex developed trending approximately 25° north relative to the paleoequator, where the Devonian trade winds and paleocurrents provided sufficient nutrients (Habicht, 1979). This paleogeography explains the preferential growth of reefs, with steep flanks and highly developed porosity and permeability on the north side (Fischbuch, 1984; Kaldi, 1989).

RESERVOIR STRATIGRAPHY AND DEPOSITIONAL HISTORY

The Kee Scarp reef complex is underlain by the Hare Indian shale formation and overlain by the Canol shale formation (Figure 2). At least one, or as many as several kilometers of post-Middle Devonian sediments were present but were removed by erosion during the pre-Albian uplift (Feinestein et al., 1991). This process was confirmed by observations that fracture widths increase with decreasing reservoir depth. This width increase has been attributed to the unloading of rocks by erosion that made the fractures open wider under lower confining stress (Kempthrone and Irish, 1981; West and Doyle-Read, 1988). Bassett and Stout (1967) and Braun (1977) suggested that a pre-Canol unconformity existed between the Canol shale formation and the Kee Scarp Formation. However, Muir and Dixon (1984) recognized a conformable relationship between the Canol shale and the pre-Canol deposits in the Rampart Formation, in the Mackenzie Mountains, that is equivalent to the subsurface Kee Scarp Formation.

The Kee Scarp Formation at Norman Wells consists of 10 carbonate megacycles of reef growth (Figure 2), formed by major episodic increases in the rate of sea level rise, and each major cycle has minor increments (Muir et al., 1985). This reef buildup exhibits shallowing-upward cycles that end with backstepping that resulted from an abrupt change to deeper water conditions (Braun, 1977; Muir and Dixon, 1984; Muir et al., 1985; West and Doyle-Read, 1988; Kaldi, 1989).

According to Muir and Dixon (1984) and Muir et al. (1985), the depositional history of the Kee Scarp Formation can be summarized as follows. (1) A rapid rise of sea level near the beginning of Givetian time drowned the Hume platform to a depth of 150 m or more. (2) Deposition of the Hare Indian Formation and progradation continued with a slow rise in sea level so that the formation approached wave base and became a site of in-situ sedimentation on a relatively shallow water ramp. (3) The rising sea level drowned the ramp and was accompanied by growth of branched corals and cylindrical stromatoporoids on topographic highs (shallow-water sites) toward sea level that resulted in development of a basinward-submerged platform lithofacies (K1). The stromatoporoid-coral



Figure 3—Core photographs of some Kee Scarp lithofacies. (A) Sample from tidal flat facies. Note a vertical calcite vein on the left and a vertical stylolite on the right. (B) Part of the large stromatoporoid with the possibility of the presence of horizontal and vertical microfractures. (C) A bulbous stromatoporoid illustrating the internal fracture pattern. (D) Nodular and stromatoporoid-rich limestone illustrating solution seams and a vertical calcite vein.

fauna continued to grow with the sea level rise; these fauna created shoals on the carbonate platform with surrounding deeper water (K1B-K2A). (4) Progradation of reef cycle 1 (K2B) was followed by subsequent aggradation of reef cycles 2 and 3 (K2C-K3B). Reefs grew upward and laterally, and colonized the margins of the highs on the platform to shelter an interior lagoon where *Amphipora* wackestones and tidal flat facies were deposited. (5) A rapid rise in sea level affected the area, causing an upward backstepping of the reef margin (K3C-K4) and onlapping of Canol shale. This rapid rise in sea level may have caused a deficiency of nutrients for more reefal growth or expansion and also changed the depositional environment from a restricted lagoonal environment to a more open marine environment.

Lithofacies	Rock Type	Diagenetic Features
PLATFORM LIMESTONES Shoal Limestones	Rudstone and floatstone platform carbonates (K1A-K1B) having corals and stromatoporoids embedded in skeletal pelloids and algal aggregate matrix.	Organic borings and geopetal fills. Syntaxially cemented crinoids. Early bladed calcite and later equant calcite spar. Rare poikilotopic and botroyoidal cement. Selective dolomitization affecting matrix and associated with stylolites.
BASIN AND FORESLOPE-TOE LIMESTONES		
Nodular Lime Mudstones	Laminated, brown pelloidal micrite with nodule texture (Figure 3B) and scattered skeletal debris of corals (<i>Thamnopora</i>).	Syntaxially cemented crinoids (7%). Horizontal irregular stylolites and solution seams. Vertical, high-amplitude stylolites (Figure 5F) along which bitumen accumulates.
Basinal Laminites	Argillaceous micrite and mudstones with scattered debris of corals <i>(Thamnopora)</i> , cylindrical stromatoporoids, and gastropods.	Horizontal irregular stylolites and solution seams.
FORESLOPE LIMESTONES In-Situ Foreslope Limestones Cylindrical Stromatoporoid Foreslope Limestones	Rudstones of cylindrical stromatoporoids with minor corals (<i>Ampbipora</i>) downslope of the reef margin in the high circulation environment.	
Middle Foreslope Stromatoporoid Limestones	Boundstones and rudstones of microcracked bulbous and cylindrical stromatoporoids (40–50%) (Figure 3C) with minor branched corals (<i>Thamnopora</i> , 10%).	Syntaxially cemented crinoids. Geopetal fills. Horizontal irregular to smooth stylolites. Early fibrous cement followed by equant calcite spar (Figure 5C). Selective minor dolomitization (2%) in cements. Selective silicification of some stromatoporoids. Late vertical coarse calcite infilling veins.
Stromatoporoid Rubble Subfacies	Rudstones of mixed fragments of stromatoporoids in skeletal or pelloidal grainstone matrix.	Rare syntaxially cemented crinoids. Early fibrous followed by late drusy equant calcite cements.
Carbonate Sands	Grainstones and packstones of skeletal fragments, interbedded with micrite.	Syntaxially cemented crinoids.
REEF MARGIN LIMESTONES	Boundstones and rudstones of in-situ massive to tabular stromatoporoids.	Organic boring and geopetal fills. Equant calcite cement in galleries. Minor dolomitization in cements.
REEF FLAT LIMESTONES	Rudstones, but rare boundstones, of abraded fragments of stromatoporoids in coarse skeletal grainstone matrix.	Syntaxially cemented crinoids. Clear, equant calcite cement. Horizontal irregular stylolites. Selective dolomitization in cements.
REEF INTERIOR LIMESTONES		
Tidal Flat Limestones (Interior Lagoons) Subtidal Lagoonal Limestones	Mudstones and packstones of algae, algal aggregates, scattered corals <i>(Amphipora),</i> and cylindrical stromatoporoids (5%) in pelloidal to micritic matrix.	Horizontal, irregular to smooth and high- amplitude (0.8 cm) stylolites. Three generations of calcite cements, one early acicular and two late equant calcite. Rare poikilotopic cement.
Open Marine Lagoon Limestones	Rudstones and floatstones of bulbous and cylindrical stromatoporoids with minor <i>Amphipora</i> in pelloidal packstone to grainstone algal matrix.	Horizontal irregular stylolites along which hydrocarbons accumulate. Selective dolomitization in cements.
Restricted Lagoon Limestones	Floatstone and rudstones of mainly <i>Amphipora</i> with cylindrical and tabular stromatoporoids in pelloidal to micritic, skeletal packstone matrix.	Horizontal columnar stylolites with high amplitude (0.5 cm). Early turbid fibrous calcite cement followed by late equant calcite cements.

Table 1. Summary of Lithofacies, Rock Types, and Main Diagenetic Features of Kee Scarp Formation

(1) Shoal limestones were deposited in open marine conditions and constitute the majority of the carbonate platform deposits (K1-K2). These deposits consist mainly of rudstones and floatstones containing cylindrical stromatoporoids and branching corals set in a micritic matrix.

(2) Basin and foreslope-toe limestones and shales were deposited in lower energy, relatively deep water settings, and consist of nodular lime mudstones and basinal laminites.

(3) Foreslope limestones consist of either (a) insitu cylindrical stromatoporoids, *Amphipora* and coral bearing rudstones, or middle foreslope wafercylindrical stromatoporoids, crinoids and brachiopod-bearing rudstones and floatstones, or (b) allochthonous, coarse, stromatoporoid debris with a carbonate sand matrix or pelloidal grainstones and packstones.

(4) Reef margin limestones, which were formed in the highest energy environment, consist of insitu, thick, tabular stromatoporoids or broken, reworked fragments of these organisms.

(5) Reef flat limestones consist of the rubble of massive stromatoporoids and encrusting and cylindrical stromatoporoids as well as *Amphipora* rudstones in the leeward part of the rubble zone.

(6) Reef interior limestones consist of (a) cyclic, shoaling-upward deposits, mainly pelloidal packstones, stromatoporoid floatstones, and rudstones, and *Amphipora* grainstones, or (b) tidal flat deposits, mainly pelloidal mudstones to packstones and cyanobacterial, laminated mudstones with fenestral texture and mud-filled cavities (Figure 3A).

METHODOLOGY

The data and interpretations presented in this study were based on detailed examination of 150 samples totaling more than 495 m from five cores in Norman Wells. Four of these cores have margin positions within the reef structure (G-24x, G-36x, O-45x, and P-9x), and one was central (MR-1) (Figure 1). An additional seven cores were sampled and visually examined as well (J-21x, MR-4, P-8x, K-40x, R-34x, and P-21y). Polished slabs and uncovered thin sections were stained for Fe-calcite using a mixture of potassium ferricyanide and alizarine red-S according to the method outlined by Lindholm and Finkelman (1972). All thin sections were examined by cathodoluminescence microscopy using a Technosyn 8200 MKII Model cold cathodoluminescence stage at a voltage of 15 kv and current intensity of about 425 µA. In addition, some thin sections were dyed with a blue fluorescent dye for the recognition of microporosity (Yangus and Dravis, 1985). Thirty-six samples, representing all the facies exhibited by the studied cores, were examined by scanning electron microscope (SEM) to study the diagenetic textures and microporosity. Clean, polished, small slabs were etched with 50% acetic acid for two minutes, plated with gold or aluminum, and examined using a NANOLAB-7 SEM. Porosity data were obtained by mercury injection capillary pressure analysis at Imperial Oil Laboratory, Calgary, Alberta, Canada.

Various generations of calcite cements, fossil components, and matrix were sampled for carbonand oxygen-isotopic analysis and minor and trace element analysis employing a microscope-mounted drill assembly to extract 0.5–4 mg (for isotope analysis) and 100–250 mg (for element analysis) of powdered carbonates from polished slabs. The samples for isotope analysis (n = 149) were reacted with 100% phosphoric acid at 25°C. All gas extractions were done at the Stable Isotope Laboratory, University of Windsor. The evolved CO₂ was analyzed for C and O isotopes using a SIRA-12 mass spectrometer at the University of Ottawa. The δ^{18} O and δ^{13} C values are reported relative to PDB. Precision was better than 0.1‰.

Sixty-nine samples were separated for chemical analysis. The powdered samples were digested in 20 ml of 6% (v/v) HCl for four hr (e.g., Brand and Veizer, 1980). Ca, Mg, Na, Sr, Fe, and Mn were determined using a Varian Spectra AA300 spectrometer. The average accuracies, as compared to 1C standard, are Ca (0.3), Mg (10.0), Na (9.0), Sr (7.5), Fe (9.0), and Mn (2.3) relative percent. All discussion in the text is based on elemental concentrations recalculated on a 100% carbonate (insoluble residue-free) basis.

PETROGRAPHY AND PARAGENETIC SEQUENCE OF KEE SCARP LITHOFACIES

The classification of Kee Scarp lithofacies as outlined by Muir et. al. (1985) is adapted in this study for describing the main petrographic and diagenetic characteristics. Table 1 summarizes the main depositional and diagenetic features of these lithofacies. For more details, see Azmy (1992).

The main skeletal framework in the studied limestones is composed of stromatoporoids, corals, and algae, and algal aggregates, crinoids, and mollusks. These fossils show variable degrees of preservation in response to their original mineralogy and shell structure. Fairly well-preserved, non-luminescent, calcitic microstructures are present in some stromatoporoids and crinoids as well as early cements of a presumably marine precursor, which attests to their original high-Mg calcite



Figure 4—Paragenetic sequence of the Kee Scarp Formation showing relative timing of diagenetic features and diagenetic stages or environments. The sequence of events is based on petrographic relationships as well as chemical data.

mineralogy. Such textural preservation of these skeletal components is corroborated by the preservation of their original chemistry (see following paragraphs).

The paragenetic sequence shown in Figure 4 is based on petrographic observations, spatial distribution, cross-cutting relationships among depositional and diagenetic fabrics, cements, stylolitization and fracturing, and geochemical evidence. Diagenetic processes can be grouped into three stages (Figure 4): marine or syngenetic stage, shallow burial or epigenetic stage, and intermediate burial stage.

With accretion of the reef buildup, marine boring commenced contemporaneously with marine cementation, represented by non-luminescent, fibrous cement followed by the inclusion-rich equant calcite (Figure 5c), syntaxial cementation, and internal sedimentation (Figure 5b). Burial of the Kee Scarp reef complex at shallow depths was accompanied by early silicification and the formation of some compactional features such as in-situ broken shells, closed packed grains, and microstylolites (fitted fabrics) (Figure 5a). This was followed by the deposition of the early generations of dull, prismatic, and drusy equant calcite cements. As a result of increasing compaction, solution seams and smooth stylolites developed, and diagenetic stabilization started to affect the rock components, especially the stromatoporoids, which resulted in the development of the first generation of microporosity in stromatoporoids in addition to leaching of some grains.

With further burial, a later phase of silicification occurred, and microcracks developed in stromatoporoids (e.g., Figure 3B, C), cutting all cements and acting as conduits for further active solutions that caused the development of the second generation of microporosity. At this stage horizontal irregular stylolites, high-amplitude columnar stylolites, and vertical stylolites developed (Figure 5f). The development of the late vertical fractures that were filled with the late generations of burial, red to dull, drusy equant calcite cement (calcite veins), occurred at a deeper burial stage (Figure 3B, D). Kempthrone and Irish (1981) and West and Doyle-Read (1988) described these fractures and their significance for the oil recovery program at Esso. Kaldi (1989) suggested that the spatial/temporal relationship between fractures and microporosity



Figure 5—Photomicrographs of various diagenetic features. (a) Fitted fabrics between skeletal grains in shoal limestone facies. (b) Late equant cement (A). Notice the pores, developed by organic borings, filled later by sediments and cement to form a geopetal structure (B). (c) Two generations of marine cements; fibrous calcite (A) followed by inclusion-rich equant calcite (B). (d) Coarse drusy equant calcite cement in secondary pore space. (e) Same calcite cement as in d but under cathodoluminescence. Notice multiple generations of prismatic and equant calcite. (f) Large-scale columnar stylolite with bitumen in its apex. is weak. Late calcite cement also occupies some pores (Figure 5d, e). Minor dolomitization occurred by replacement and is associated mainly with stylolitization. Oil accumulation in the reservoir might have occurred after the late burial cementation because such cement includes some bitumen traces.

Major exposure of Kee Scarp reefs to meteoric diagenesis was discounted for these reasons: no apparent subaerial exposure features, such as disconformities between reefal facies, paleokarsts, or caliche deposits (cf. James and Choquette, 1984) were observed; meniscus cements and moldic porosity (e.g., Dravis, 1989) are not present in Kee Scarp lithofacies; furthermore, chemical and isotopic evidence do not support meteoric diagenesis (see following paragraphs). Geologic evidence from formations deposited after the Kee Scarp reef complex does not support any major exposure to meteoric waters until the Cretaceous (e.g., Muir et al., 1985; Feinestein et al., 1991; Al-Aasm et al., 1993).

MICROPOROSITY DESCRIPTION AND CLASSIFICATION

Despite the high porosity values recorded (Azmy, 1992) in some facies (e.g., reef margin and foreslope facies), the rocks of these facies show no significant macroporosity because most primary pores are occluded by cementation; therefore, a different type of porosity (i.e., microporosity) developed in these rocks.

Microporosity is developed extensively in the Kee Scarp facies in the skeletal components (i.e., stromatoporoids, algae, and corals) and matrix. Development of microporosity increased the total porosity values measured in some facies to 18.7% and the permeability to 36 md (e.g., reef margin facies; M. McMurry, 1992, personal communication). SEM studies reveal that four types of microporosity, mostly in the range of $1-10 \,\mu$ m, developed in Kee Scarp carbonates, and these types are related to the types of rock components and facies. The four types are (1) stepwise (rhombic) micropores, (2) intercrystalline microrhombic pores, (3) microvugs, and (4) microchannels.

Stepwise-shaped micropores (Figure 6A) have a diameter of $1-2 \mu m$. They occur as intercrystalline microvoids between microrhombic calcite crystals ranging in size from 2 to $6 \mu m$. This type of micropore commonly was observed in reef margins and grain shoals at the reef margin where it occurs in stromatoporoids (mainly tabular species), algae, and crinoids. The studied samples have a porosity of about 14% and a permeability of about 4.5 md. Intercrystalline microrhombic pores are intercrystalline micropores (Figure 6B) having a diameter of

 $1-1.5 \,\mu\text{m}$ and may be interconnected by pore throats of about 0.3 µm in diameter. They occur as microvoids between euhedral to subhedral microrhombic calcite crystals ranging in size from 2 to 4 μ m. This type commonly was observed in algal aggregates and corals of the foreslope facies. The studied rocks that have this type of microporosity exhibit porosity values up to about 13% and have a permeability of about 3 md. In some samples, dark and light zones were observed in the rock components (allochems and matrix), and the light zones were found to have better developed microporosity than the dark zones. Microvugs are relatively large intercrystalline microvoids (Figure 6C) of irregular shape and have diameters ranging from 4 to 10 µm. They were observed mainly in algal aggregates of the grain shoal facies. Such micropores are usually isolated but are sometimes interconnected through pore throats that are 1-3 µm in diameter or through the other types of micropores. A microvug is bigger than average microrhombic calcite crystals. Microvugs are rare in reef margin facies. Microchannels are channellike intercrystalline micropores (Figure 6D) that are about 0.5 µm wide and up to 16 µm long or sometimes longer. Microchannels are usually branched and common in cemented matrix (algal aggregates and micrite of platform shoal facies). Rocks with abundant microchannels have low porosities (about 2%) but high permeability (about 4.2 md) (Azmy, 1992) because of the connectivity and branching of these microchannels.

GEOCHEMISTRY OF KEE SCARP REEF COMPONENTS

Major and Minor Elements

Results of the chemical analysis of the Kee Scarp reef components can be obtained from the authors upon request. Chemical analyses of different fossil components, represented by stromatoporoids, algae and algal fragments, crinoids, and corals, show relatively low to moderate Mg (1372-35,920 ppm), Sr (208-1373 ppm), and Na (33-443 ppm), but low Fe (3-150 ppm) and Mn (3-441 ppm), compositions. Few analyses were performed on late equant calcite cement. This cement is low-Mg calcite (Mg average = 4481 ppm), with Sr (424-711ppm), Mn (20-109 ppm), Na (28-227 ppm), and Fe (10-77 ppm). The low concentrations of Mn and Fe in the studied components can be attributed to the presence of somewhat oxidizing conditions and/or low concentrations of these elements in diagenetic fluids (cf. Budd, 1989).

Sr, Mg, and Na in skeletal components display a recognizable increase in concentration with depth



Figure 6—SEM micrographs of different shapes of micropores in Kee Scarp rock components. (A) Stepwise micropores in stromatoporoids in grain shoal facies. (B) Intercrystalline (rhombic) micropores in algal aggregates of foreslope facies. (C) Microvugs in algal aggregates of grain shoal facies. (D) Microchannels in cemented micritic matrix in platform facies. (E) Enhanced microporosity along a microcrack (K) in a stromatoporoid. (F) Late big microvug in cement, reef margin facies.



Figure 7—Trace element-depth cross plots of Kee Scarp skeletal components. Depths are below surface. (A) Mg vs. depth (Core MR-1). (B) Na vs. depth (Core MR-1). (C) Sr vs. depth (Core P9X). (D) Mn vs. depth (Core P9X). The concentrations of these elements increase with depth.

(Figure 7). These relationships can be explained in terms of variations of porosity and permeability and hence flow paths of diagenetic fluids. They also may reflect a somewhat closed system for diagenetic stabilization of Kee Scarp reef components (cf. Machel, 1988; Moshier, 1989a).

Stable Isotopes

Skeletal Components

The stable carbon and oxygen isotope compositions of various skeletal components from all cores are plotted in Figure 8. Texturally preserved microstructures of some stromatoporoids and corals have similar δ^{18} O and δ^{13} C values relative to the postulated carbonates precipitated in equilibrium with Middle-Upper Devonian seawater (Popp et al., 1986; Veizer et al., 1986; Carpenter et al., 1991). However, many of the diagenetically more altered skeletal components, represented by algae, stromatoporoids, and crinoids, show a negative shift in their δ^{18} O values (range from -6 to -11), which may reflect partial re-equilibration and stabilization (HMC to LMC) by diagenetic fluids (Brand and Veizer, 1980; Al-Aasm and Veizer, 1986). However, their δ^{13} C values fall within the range of Devonian carbonates (Figure 8).

A negative relationship between δ^{18} O values of skeletal components and porosity (Figure 9) demonstrates the impact of increasing diagenetic alteration of these components on porosity.

Nonskeletal Components

Figure 10 shows the isotopic compositions of different calcitic cement generations. Early fibrous, syntaxial, and inclusion-rich equant cements of

presumably marine origin have isotopic values similar to Devonian marine calcite that argue for the preservation of their original isotopic signatures. Later cements, represented by equant calcite and fracture-fill calcite, have more negative δ^{18} O values but similar δ^{13} C values. The very late fracture-fill calcite has the most depleted δ^{18} O values (Figure 10).

Isotopic compositions of other nonskeletal components, represented by micrite and peloids, are similar to isotopic compositions of late equant cement (δ^{18} O for micrite ranges from -6.3 to -10.6‰, average -8.6‰; δ^{13} C = 0.3 to 2.6‰, average 1.5‰; and δ^{18} O for peloids = -8.6 to -11.1‰, average = -9.8‰; and δ^{13} C = 1.0 to 2.5‰, average = 1.9‰).

DISCUSSION

Field relationships, petrographic characteristics, chemistry, and stable isotopes of the Kee Scarp carbonate components delineate a complex diagenetic history. Most of the diagenetic features, including mineralogical stabilization, cementation, silicification, and microporosity creation, are a result of the influx of marine and modified marine diagenetic fluids under shallow to intermediate burial conditions.

Constraints on the Evolution of Microporosity

Shapes and distributions of micropores in Kee Scarp limestones are controlled by two main factors: facies type and the depositional and diagenetic history of the rock.

Facies Type

The influence of facies type on the shape and distribution of micropores includes two subfactors: lithologic control and biogenic control. Table 2 summarizes the magnitude of the presence of microporosity in different facies and fossil components.

Lithologic Control—SEM studies show that stepwise micropores are developed mainly in reef margin facies; however, they also occur in open lagoon, grain shoal facies and upper foreslope facies. Trace amounts of this type of porosity occur in other types of facies. We suggest that the highly developed microporosity in reef margins is related to the wave action and organic boring that developed a good void system in reef margin facies (cf. Kaldi, 1989). Such voids later acted as conduits for the diagenetic solutions that caused the development of microporosity by neomorphism or dissolution. The intercrystalline microrhombic pores are



Figure 8—Oxygen vs. carbon stable isotope values of skeletal components of Kee Scarp Formation. The box represents the postulated ranges for Devonian carbonates (see text for details).

abundant in all facies except for the reef margin, where they are rare. This type of microporosity could possibly be produced by further dissolution of the stepwise micropores as suggested also by Kaldi (1989). Microvugs commonly are observed in grain shoals at the reef margin but rarely coexist with other types of micropores. Generally, microvugs are expected to develop in any facies where they are believed to be developed by intense dissolution. Their abundance probably depends upon the amount and degree of saturation of the diagenetic fluids and the response of the rock components to these fluids. The grain shoal components are fine-grained, so they respond strongly to dissolution that results in such microvugs.

Microchannels are developed in some shoal facies but may coexist with other types of porosity. These microchannels look as if they were developed in the cemented components of the rock (cemented matrix), and they usually do not connect any intercrystalline micropores. They are interpreted to be developed by dissolution along preexisting microfractures. Development of microchannels increased the permeability of the rocks but not the porosity.

Microporosity is dominant in the north side of the Kee Scarp reef complex (Figure 11), with the lowest porosity values occurring in the center, east, and south sides of the reef complex. This porosity distribution illustrates that the porosity is facies controlled, being high in reef margin and low in



Figure 9—Oxygen isotope values vs. porosity of various skeletal components. Porosity values represent total measured porosity of bulk samples.

reef interior facies. This spatial distribution pattern of porosity could also be related to paleoenvironmental conditions (e.g., supply of nutrients, trade winds, and paleocurrents) (cf. Habicht, 1979; Fischbuch, 1984; West and Doyle-Read, 1988). These environmental conditions allowed greater growth of major reef skeletal framework where most of the secondary microporosity formed.

Biogenic Control—The distribution of shapes of micropores is influenced also by the type of skeletal components. Stepwise micropores generally are observed to be more common in stromatoporoids (especially in the tabular type) than in algae, algal aggregates, or micrite, but they are poorly developed in crinoids and are not observed in corals. This is probably because of the nature of the skeletal structure of these fossils and their precursor mineralogy, which respond differentially to neomorphism (see following discussion).

Intercrystalline microrhombic pores commonly are observed in most types of facies where they possibly are independent of the skeletal structures of the fossils. Microvugs may also be formed in all types of biofacies by intensive dissolution, so biofacies type is not restricted to any skeletal structure but possibly is determined by particle size.

Depositional and Diagenetic History of the Rock

Development of microporosity is controlled by several depositional and diagenetic factors: (1) original mineralogy, (2) stabilization of precursor components, (3) crystal habit, (4) degree of cementation, and (5) degree of dissolution.



Figure 10—Oxygen vs. carbon isotope values of various generations of calcite cements and micrite in Kee Scarp reefs.

Original Mineralogy—The original mineralogy (aragonite vs. calcite) controls the texture of microporosity, especially in the matrix (lime-mud) where micrites (0.5-2 μ m) derived from calcitic muds exhibit fine, equant, microrhombic, and calcite crystals. The texture of these micrites may be due to the abundance of calcite nuclei in the stabilizing mud, whereas those derived from aragonitic mud exhibit coarser microspar (about 5 µm) textures because calcite would have nucleated on widely spaced seeds in mud and aragonite (Lasemi and Sandberg, 1984). SEM studies of algal aggregates, which mainly represent the matrix of the Kee Scarp limestones, suggest a precursor of HMC as evidenced by the presence of microdolomite inclusions in the matrix (e.g., Lohmann and Meyers, 1977). The same phenomenon of occurrence of microdolomite was observed in the stromatoporoids at Kee Scarp reefs, which may indicate that the original mineralogy of the stromatoporoids in Kee Scarp facies was HMC and not A (cf. Rush and Chafetz, 1991). This theory is confirmed by the absence of aragonite relics in these components of the rock and by the fairly well preserved nature of stromatoporoid microstructures in comparison to aragonitic mollusks of the same rock. The HMC precursor mineralogy of most of the Kee Scarp limestones may be the reason for the development of micropores between microrhombic calcite crystals (average size $2-4 \mu m$) where the stabilization of HMC is accompanied by a slight change in volume. No clear stepwise or intercrystalline rhombic micropores were observed in corals that had an aragonitic precursor.

Stabilization of Precursor Components— Preservation of the original skeletal structures of

		Sti	romator	oroi	ds	Α	lgae, M	latrix			Crin	oids			Cora	ıls	
Facies	Porosity (%)	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
Lagoon	6.8 (4.0-11.8)	++	+++	+	+	+	+++	+	+	_	-	_	_	-	_	_	_
Reef margin	13.4 (9.6-18.7)	+++	+	+	+	+++	+	+	+	-	_	-	-	-	-	-	_
Foreslope	2.5 (1.9-2.8)	++	+++	+	+	++	+++	+	+	++	_	-	-	-	+++	-	_
Shoal	4.7 (0.2-14.0)	+++	+++	+	+	+	++	+++	++	-	_	-	-	-	-	-	_
Sand flat	6.8 (6.3-7.2)	-	+++	+	+	-	+++	+	+	-	-	-	-	-	-	-	-

Table 2. Summary of the Lithofacies Control on Types of Microporosity in Kee Scarp Limestones*

*The numbers denote the type of microporosity observed: (1) stepwise micropores, (2) intercrystalline (rhombic) micropores, (3) microvugs, and (4) microchannels. The symbols (+++), (++), (+), and (-) represent main, minor, trace, and absent. The observations and porosity data are based on SEM study and porosity measurements of wells from all facies.

microporous components indicates that the stabilization of the metastable phase occurred slowly, through discrete, self-contained, reaction zones on solid-liquid interfaces on each component (thinsolution film principle) (Pingitore, 1976; Brand and Veizer, 1980; Veizer, 1983; Al-Aasm and Veizer, 1986). Destruction of original structures of some highly replaced components may be due to stabilization of metastable phases by an intensive fast solution-precipitation process.

Crystal Habit—We observed that stepwise micropores are developed between euhedral microrhombic calcite crystals (Figure 6A), whereas the intercrystalline microrhombic pores are developed between subhedral to anhedral microrhombic crystals (Figure 6B). This difference in development could be a function of progressive dissolution of crystals (cf. Kaldi, 1989). Development of microvugs or microchannels is believed to be independent of a definite crystal habit.

Degree of Cementation-Retention of microcrystalline porosity and preservation of microrhombic calcite textures in the Kee Scarp Formation require that cementation be inhibited or stopped shortly after stabilization of the original particles of the rock components, or possibly that the relatively low permeability of these components contributed to that preservation. This preservation of microporosity may occur by isolation of the deposit from a significant additional source of carbonate cement and by restricting the source of cements to the local dissolution process (stabilization process). Such conditions can be accommodated in a somewhat closed system and in low water:rock ratio diagenesis (Moshier, 1989a). However, some destruction of microporosity can be observed in Kee Scarp carbonates in zones (halos) along the peaks of columnar stylolites, whereas the central area inside the peak exhibits preserved, unaltered micropores. This phenomenon is suggested to be caused by calcite cements deposited from solutions moving through the stylolites. Mechanical compaction may contribute to the reduction of microporosity

(Moshier, 1989a), which is observed in the distribution of microporosity in the Kee Scarp limestones where an inverse relationship between development of microporosity and depth can be recognized in some cores studied. However, the relative retention of microporosity shows that burial compaction was moderate.

Degree of Dissolution—Passage of undersaturated fluids through the rock components resulted in the development of secondary microporosity, which is observed in the halos (zones) of enhanced micropores along the microcracks (average diameter of 2-10 μ m) that are developed in highly replaced and/or neomorphosed stromatoporoids with relative poor microporosity. The microcracks acted as conduits for undersaturated fluids where dissolution, caused by the fluid, can be traced along the microcrack. The situation in microcracks is different from that in relatively bigger columnar stylolites (amplitude about 0.8 cm) because stylolites are much wider conduits than microcracks, so they allow larger volumes of solution to flow through them, which may destroy the microporosity in the adjacent parallel zones by cementation. However, the early smooth horizontal stylolites and solution seams could possibly contribute to the development of microporosity in the rock components. Morse and Mackenzie (1993), in their geochemical modeling study on carbonate transport in subsurface sedimentary environments, suggested that in the stylolite and fracture developmental stages, fluid flow is restricted to these features, with minor exchange with the matrix calcite and the source of carbonate in the diagenetic fluids internally.

A phenomenon of development of dark and light zones is observed in some rock components (e.g., algae, algal aggregates, pelloids, and stromatoporoids) of the Kee Scarp limestones. Moshier (1989b) studied a similar phenomenon and explained the distribution of the dark and light porous matrix as a primary depositional fabric related to bioturbation. In this study, however, the



Figure 11—Total porosity thickness map of Kee Scarp reef (K1A–K4) (modified after West and Doyle-Read, 1988). Also shown in this map are the Kee Scarp reef outline and the oil-water (O/W) contact for the field.

distribution of these zones is suggested to be related to the differential leaching of these zones because SEM studies revealed better microporosity in the light zones. The isotopic results show lighter δ^{18} O for the light zones, which are suggested to be more diagenetically altered than the dark ones.

Microvugs and microchannels are developed by dissolution where, in restricted cases, some large microvugs (about 17 μ m in diameter) were seen to have developed in the cement in the reef margin facies (Figure 6F).

Diagenetic Environment of Microporosity Formation

We suggest that microporosity in the Kee Scarp carbonates has been generated at shallow to intermediate burial realms from modified marine fluids. Stabilization of the Kee Scarp reefs by meteoric water has been discounted for the reasons discussed in a previous section.

In addition to the absence of meteoric diagenetic features, there are four burial environment features that confirm the burial origin of the microporosity. (1) The development of microcracks in stromatoporoids and the occurrence of well-developed microporosity around these microcracks (Figure 6E) indicate that a phase of microporosity developed in the burial environment after compaction that led to the formation of the microcracks. (2) The preservation of microporosity indicates that it developed after burial cementation. (3) The leaching of echinoid ossicles that shows some microporosity developed within them indicates a burial origin because a wholesale dissolution of echinoids is extremely rare in freshwater systems (cf. Dravis, 1989). (4) The burial-derived cements occluding inter- and intraparticle pores have very negative stable isotopic oxygen signatures ($\delta^{18}O =$ >-10‰), which is consistent with the precipitation in the burial environment (relatively high temperature) (Choquette and James, 1987).

Chemical and Isotopic Constraints

Partial factor analysis of trace elements and stable isotopes of Kee Scarp reef components (Table 3), shows that three factors control relationships between trace elements and stable isotopes. Factors 1, 2, and 3 can be interpreted as a response to diagenetic alteration and cementation of reef components. These processes are accompanied by an increase in temperature due to burial and modification of pore water chemistry (e.g., Veizer, 1983). The lack of a co-variant relationship between $\delta^{18}O$ and δ^{13} C reflects increasing temperature, and the δ^{13} C values are buffered by the carbonate phase in the system. Some skeletal components and early cements show fairly good preservation of their inferred textural and isotopic attributes; however, their trace element concentrations were changed upon interaction with diagenetic pore waters. Such a phenomenon has been observed by other investigators in carbonate diagenesis (Al-Aasm and Veizer, 1982, 1986). Such preservation of original textural and isotopic signatures could argue for a semiclosed diagenetic condition during stabilization of the metastable carbonate phases (cf. Al-Aasm and Veizer, 1986).

	Factor 1	Factor 2	Factor 3
Log I.R.	0.03459	0.13959	0.15756
Log CaO	-0.07571	-0.72290	0.1599
Log Mg	0.22078	0.58876	0.18190
Log Sr	<u>0.85733</u>	0.23031	-0.11290
Log Na	-0.22557	0.75330	0.03364
Log Fe	0.21322	0.22175	<u>-0.79902</u>
Log Mn	-0.12074	0.05522	0.24706
δ180	<u>-0.89775</u>	0.15267	-0.07536
$\delta_{13}C$	0.16678	0.21017	<u>0.85918</u>
Variation (%)	23.5	17.5	16.5
Eigen value	2.11484	1.57813	1.48087
Interpretation	Diagenetic stabilization	Diagenetic stabilization	Diagenetic stabilization (late cemen- tation)
*N = 45			tation)

Table 3. Partial Varimax Rotated Factor Analysis of Trace Elements and Stable Isotopes of All Studied Kee Scarp Reef Components*

Petrographic, SEM studies, and porosity measurements reveal a clear relationship between the evolution of microporosity and the degree of diagenetic alteration of skeletal reef components. The negative relationship between oxygen isotopes and porosity (Figure 9) indicates that increasing diagenetic alteration of fossils was accompanied by depletion in δ^{18} O values. This depletion is more pronounced in stromatoporoids than in algae or other skeletal components because their original microstructure may have allowed diagenetic fluids to move through more freely.

The downward increase of Mg, Sr, and Na and the decrease of Fe and Mn in skeletal components reflects the difference in magnitude of their distribution coefficients and hence the diagenetic fluids (cf. Veizer, 1983). These differences reflect variations of the concentrations of these elements along fluid flow paths. The direction of diagenetic fluid paths could have been vertical and downward so that the depletion of Mg, Sr, and Na from the solid phase was inhibited with increasing depth (Machel, 1988). The generally low concentrations of Mn and Fe in reef components may reflect that the diagenetic fluids were poor in Fe and Mn.

Diagenetic Pore Water Evolution

Geologic, petrographic, and stable isotope data can be combined to deduce changes in the oxygen isotope composition of pore water in Kee Scarp reefs during diagenesis. The relationships among mineral δ^{18} O values, pore water δ^{18} O values, and temperature for diagenetic phases from Kee Scarp



Figure 12—Oxygen isotope composition of pore water ($\delta^{18}O_{00}$ SMOW) vs. crystallization temperature (°C) for Kee Scarp reef components. Isotopic composition of calcite is shown as contours ($\delta^{18}O_{00}$ PDB). The equation relating temperature, $\delta^{18}O_{water}$, and $\delta^{18}O_{mineral}$ is (10³ln $\alpha_{cal-water} = 2.78 \times 10^6 T^{-2} - 2.89$) (Friedman and O'Neil, 1977). Zone I represents carbonate precipitated in equilibrium with Devonian seawater (Veizer et al., 1986; Carpenter et al., 1991); zone II represents the inferred onset of diagenetic stages at shallow burial; and zone III represents the inferred onset of diagenetic stages at intermediate burial. The arrows show the pore water evolution.

reefs are shown in Figure 12. A pore water evolution path has been suggested to fit these curves to insert the range of possible temperatures and water δ^{18} O values in an order consistent with the observed paragenetic sequence (Figure 4), and in a way that is compatible as much as possible with the geologic history of the area.

Some independent constraints on temperature during diagenesis of the Kee Scarp reef components were used to constrain the evolution of δ^{18} O of diagenetic water. These constraints were the minimum temperatures at which certain diagenetic processes occurred (e.g., earlier stylolitization) and sequence of diagenetic events. Other geologic and vitrinite reflectance studies (Link and Bustin, 1989) in nearby areas were also used for this purpose. Fluid inclusion measurements from Kee Scarp reef components were not determined. Accordingly, at this stage, such an approach of constraining pore water evolution should be treated with caution.

Studies of the thermal maturation of organic matter in the Mackenzie River area (Link and Bustin, 1989; Feinestein et al., 1991) show that an uplift, probably caused by the Ellesmerian orogeny, resulted in the discontinuity between the Devonian and Cretaceous (Pugh, 1983). This uplift led to the erosion of about 1–2 km of the sediments (Link and Bustin, 1989; Feinestein et al., 1991). The time of the erosion can be constrained with certainty only between the Late Devonian and Cenomanian (Feinestein et al., 1991). The paleotemperature required for the maturation of organic matter in the Norman Wells area is suggested to range between 65 and 100°C, and the geothermal gradient is estimated to be about 45-50°C (Feinestein et al., 1991). Assuming a surface temperature of about 20°C, a burial depth of about 1.7 km could be calculated for the Middle-Upper Devonian of the study area (Feinestein et al., 1991).

Three main diagenetic events with concurrent changes in δ^{18} O pore water are envisaged (Figure 12). During stage 1 (zone I), marine cements and formation of reef components were initiated at a temperature of about 20°C and $\delta^{18}O_{water}$ of about -5‰ SMOW, similar to Devonian seawater. During stage 2 (zone II), shallow burial with an increase in burial temperature and stabilization of metastable reef components, accompanied by formation of the first generation of microporosity, commenced with slight enrichment in δ^{18} O of diagenetic fluids at a temperature of about 40-50°C. During stage 3 (zone III), increasing burial with continued stabilization of reef components, compaction (e.g., late vertical stylolitization and fracturing), and cementation was associated with depletion of δ^{18} O of precipitated cements, enrichment in δ^{18} O of diagenetic fluids, and an increase of temperature to about 120°C. Such enrichment may have been caused also by increasing water-rock interaction during burial diagenesis, which led to the enrichment of the waters with heavy oxygen (18O) relative to the light isotopes (16O) (Land and Prezbindowski, 1981; Al-Aasm et al., 1993).

According to the highest temperature obtained from that hypothetical curve, and assuming that the sediment-water interface temperature was about 20°C and the geothermal gradient about 45-50°C/km (Link and Bustin, 1989; Feinestein et al., 1991), the maximum depth of burial may have been at least 2 km.

CONCLUSIONS

The Middle-Upper Devonian Kee Scarp reef complexes at Norman Wells, Northwest Territories, are oil-producing, stromatoporoid-rich carbonates associated with reefal buildup.

(1) Diagenetic dissolution and neomorphism of reef components resulted in the development of microporosity, which is the dominating porosity type in the reservoir. The diagenetic features observed in the rocks suggest a shallow to intermediate burial environment of diagenesis caused by pore water of a marine-derived origin. SEM studies reveal that stromatoporoids, algae, and matrix components have responded to diagenesis at different rates depending on the precursor mineralogy and their architectural buildup. Microporosity was found to be facies controlled where it is better developed in the reef margin, foreslope, and grain shoals facies. The response of rock components to diagenesis was affected by the amount of porosity of the skeletal framework of the fossils where stromatoporoids show faster response to diagenesis than the other components. This response is attributed to the open skeletal structures of the fossils.

(2) Microcracks in stromatoporoids acted as conduits for fluids that enhanced microporosity by dissolution, whereas big stylolites had the opposite effect.

(3) The retention of microporosity indicates that it developed under moderate mechanical compaction and in a somewhat closed system at low water:rock ratios in which the system was isolated from external sources of cements where the source of the later cements was restricted to the local dissolution through stabilization (neomorphism) and was so limited in time that it did not destroy the microporosity.

(4) Stabilization of metastable skeletal reef components and cementation occurred in marine-dominated diagenetic waters, and was later modified by increasing burial temperature and rock-water interaction.

(5) Some skeletal components have preserved their textural and isotopic composition relative to their ambient Devonian seawater; however, minor and trace elements show less preservation of the postulated original marine composition.

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