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GEOCHEMISTRY OF CARBONATE ROCKS OF LATE CAMBRIAN AGE, NORTHWESTERN WYOMING, AND INFERENCES FOR STRONTIUM ISOTOPIC COMPOSITION OF LATE CAMBRIAN SEAWATER

by

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Approved by:

Major Professor

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CONTENTS

C. 2	37 37	Page
Acknowledgements	• • • •	Vi
Introduction	• • • •	1
Scope of the investigation	• • • •	1
Location of the area of study	• • • •	4
Regional geology		8
Geology of the Upper Cambrian rocks	• • • •	12
Dunoir Member	••••	12
Open Door Member	• • • •	15
Laboratory procedures	• • • •	16
Preparation of samples	• • • •	16
Crushing	• • • •	16
Reagents	• • • •	16
Laboratory wares	• • • •	17
Atomic absorption spectrophotometry	• • • •	17
Preparation of samples	• • • •	17
Instrumental analyses	• • • •	17
Mass spectrometry	• • • •	18
Preparation of samples	• • • •	18
Instrumental analyses	• • • •	19
Petrography	• • • •	20
Results		21
Elemental abundances	• • • •	21
Dunoir Member	• • • •	21
Open Door Member		29

Strontium isotopic abundances 37
Pilgrim Limestone 37
Dunoir Member 45
Open Door Member 52
Stable isotopic abundances
Discussion
Elemental abundances
Carbon isotopic abundances 70
Oxygen isotopic abundances
Strontium isotopic abundances
87 sr/ 86 sr ratio of the Late Cambrian sea
Conclusions 96
Peferences sited

ILLUSTRATIONS

Fig	rure Page
1.	Sampling locality, 40 km northwest of Cody,
	Wyoming, northwestern Bighorn Basin 5
2.	Location of the cored well, Bighorn Basin, Wyoming 6
3.	Sampling locality, 20 km west of Dubois, Wyoming,
	northwestern Wind River Basin 7
4.	Major structural features of Wyoming 9
5.	Generalized stratigraphic diagram of Precambrian
	and early Paleozoic time-stratigraphic and rock
	units, northwestern Wind River Basin, Wyoming 14
6.	Vertical profiles of chemical data from the Dunoir
	Member, Wind River Basin outcrop
7.	Comparison of Sr/Ca ratios of rocks from the Dunoir
	and Open Door members, with Sr/Ca ratios in
	limestones from littoral and lagoonal environments 28
8.	Vertical profiles of chemical data from rocks of the
	Open Door Member, Wind River Basin outcrop 33
9.	Sketch of a sample of the Pilgrim Limestone, showing
	sampling sites41
10.	Profile of strontium isotopic ratios across a
	sample from the Pilgrim Limestone 42
11.	Strontium-content profile across the sample from
	the Pilarim Limestone

12.	Rubidium-content profile across the sample from
	the Pilgrim Limestone 44
13.	Scatter-plot of 87 Sr/86 Sr versus Ca/Mg, Dunoir
	Member, limestone outcrops48
14.	Scatter-plot of 87 Sr/86 Sr versus Sr/Ca, Dunoir
	Member, limestone outcrops49
15.	Scatter-plot of 87 Sr/86 Sr versus Sr-content, Dunoir
	Member, limestone outcrops50
16.	Scatter-plot of 87sr/86sr versus Mn-content, Dunoir
	Member, limestone outcrops 51
17.	Scatter-plot of 87Sr/86Sr versus Ca/Mg, Open Door
	Member, outcrop samples
18.	Scatter-plot of 87 Sr/86 Sr versus Sr/Ca, Open Door
	Member, outcrop samples57
19.	Scatter-plot of 87Sr/86Sr versus Sr-content, Open
	Door Member, outcrop samples
20.	Scatter-plot of 87 Sr/86 Sr versus Mn-content, Open
	Door Member, outcrop samples59
21.	Scatter-plot of Ca/Mg versus δ^{18} 0, Dunoir Member 62
22.	Scatter-plot of Sr/Ca versus 6 180, Dunoir Member 63
23.	Scatter-plot of 87 Sr/ 86 Sr versus 6^{18} O, Dunoir and
	Open Door members
24.	Diagenetic trends for aragonite, high-Mg calcite and
	low-Mg calcite, upon stabilization with meteoric
	water

TABLES

Tabl	Le	Page
1.	Chemical data for the Dunoir Member	24
2.	Chemical data for the Open Door Member	31
3.	Elemental abundances in the three carbonate phases	
3	from sample OD24 from the Open Door Member	. 36
4.	Isotopic data of a hand specimen of the Pilgrim	
	Limestone from southwestern Montana	40
5.	Strontium isotopic abundances in samples of the	
	Dunoir Member	47
6.	Strontium isotopic abundances of samples of the	ės.
	Open Door Member	54
7.	Strontium, carbon and oxygen isotopic abundances	
	of three carbonate phases from sample OD24 from	*
18	the Open Door Member	55
8.	Stable isotopic abundances in samples from the	
	Dunoir Member and the Open Door Member	61

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INTRODUCTION

Scope of the Investigation

Strontium in the oceans is derived primarily from the weathering of (1) old continental silicate rocks, (2) young submarine volcanic rocks, and (3) carbonate rocks. These sources, depending on their Rb/Sr ratios and their ages, have contributed strontium of different isotopic compositions to seawater at different times in the past. Because crustal rocks are enriched in Rb and because the $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ ratio in them would increase with time due to the radioactive decay of ⁸⁷Rb to ⁸⁷Sr, Wickman (1948) suggested that this average increase in the 87 Sr/86 Sr ratio of the crust may be recorded in the seawaters that are receiving influxes of strontium from the continent. Early works by Gast (1955), Gerling and Shukolyukov (1957) and Ewald et al. (1956) failed to confirm the predictions of Wickman. investigators noted that the range of variation in 87sr/86sr ratios in carbonate rocks of Precambrian-to-Recent age is much less than that predicted by Wickman. With improved analytical capabilities, later studies have shown conclusively that the strontium isotopic composition of seawater has varied randomly with time (Peterman et al., 1970; Biscaye and Dasch, 1971; Veizer and Compston, 1974;

Tremba et al., 1975; Veizer and Compston, 1976; Faure et al., 1978).

A review of the strontium isotopic studies on fossils and sedimentary carbonate rocks reveals that we now have a broad knowledge of the variation of strontium isotopic composition of seawater with time. The specific nature of the variation is better known for post-Devonian time because of the large number of strontium isotopic data on rocks and well-preserved fossils from that time. However, due to a lack of availability of well-preserved fossils, the strontium isotopic composition of the early Paleozoic is not well documented. Much of our existing knowledge of the isotopic variation during the early Phanerozoic and the Precambrian comes from the studies by Veizer and Compston (1974, 1976). In their work of 1974, these authors stressed that, in the absence of well-preserved fossils, carbonate rocks can be used to determine the isotopic composition of strontium of the seawater from which the carbonate precipitated. Carbonate rocks are, however, affected to varied degrees by post-depositional events. The effects of the post-depositional events on the 87sr/86sr ratios of carbonate rocks have to be carefully evaluated prior to assigning any isotopic value to contemporary seawater.

Recognizing that additional data are needed for the early Paleozoic, the present study is an attempt to contribute strontium isotopic data for the Late Cambrian Epoch. To achieve this objective, carbonate rocks from the Dunoir and Open Door members of the Upper Cambrian Gallatin Formation, from northwestern Wyoming, were studied. Major and trace-element compositions, petrography and stable isotopic data were obtained and utilized to assess the effect of post-depositional alterations and their possible effects on the ⁸⁷Sr/⁸⁶Sr ratios of the carbonate rocks. It is hoped that the data presented in this study will contribute to a growing body of information regarding the strontium isotopic composition of seawater during the Phanerozoic.

An extended part of this investigation was to analyze the strontium isotopic composition of Upper Cambrian carbonate rocks from a cored well in the Bighorn Basin of northwestern Wyoming. The purpose was to determine the feasibility of the use of strontium isotopic data as a stratigraphic tool in geologic settings where the strata are repeatedly faulted and where stratigraphic relationships in the subsurface are difficult to establish.

Location of the Area of Study

Carbonate rocks from the Dunoir Member and Open Door Member of the Upper Cambrian Gallatin Formation, northwestern Wyoming, were the focus of this study. Samples of the Dunoir Member were collected from an outcrop in the northwest part of the Bighorn Basin, at a location in the SW1/4 SE1/4, Sec. 31, T56N, R104W, approximately 40 km northwest of Cody (Fig. 1). Samples of both the Dunoir and the Open Door members were obtained from a cored well, located in the SW1/4 SE1/4, Sec. 20, T48N, R103W, in the Bighorn Basin (Fig. 2). Samples of both members were also obtained from the northwest part of the Wind River Basin, from an outcrop in Warm Spring Canyon, in the NE1/4 SW1/4, Sec. 30, T42N, R108W, approximately 20 km west of Dubois (Fig 3).

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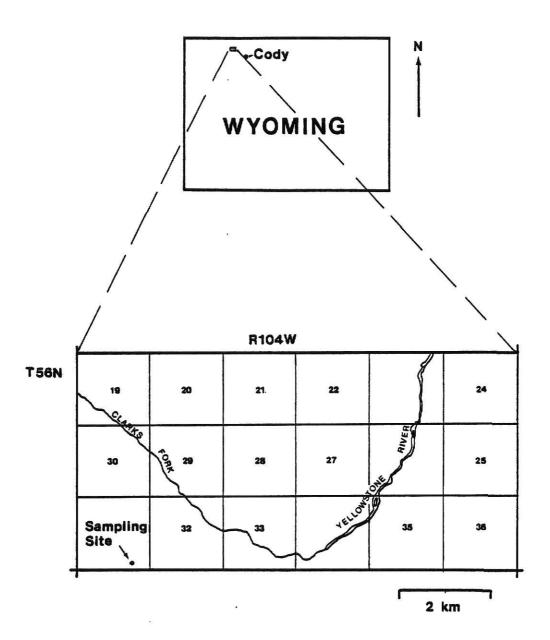


Figure 1. Sampling locality, 40 km northwest of Cody, Wyoming, northwestern Bighorn Basin.

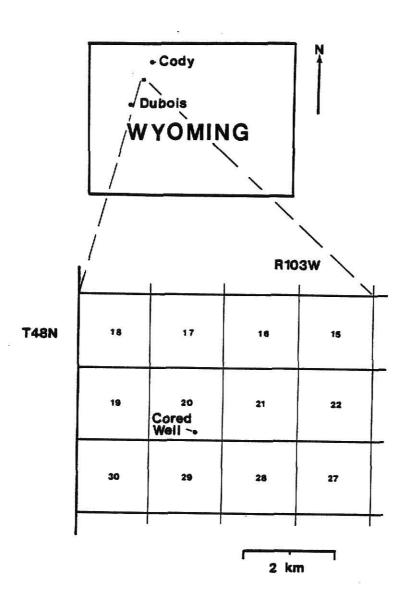


Figure 2. Location of the cored well, Bighorn Basin, Wyoming.

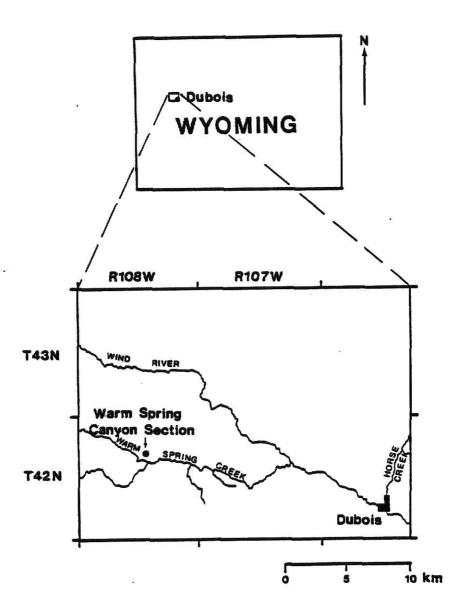


Figure 3. Sampling locality, 20 km west of Dubois, Wyoming, northwestern Wind River Basin (after Moore, 1977).

REGIONAL GEOLOGY

The regional geology of northwestern Wyoming and adjacent areas has been discussed by Foster (1947), Sloss (1950), Keefer (1957, 1970), Thomas (1965) and Keefer and Van Lieu (1966), among others. The geologic framework of northwestern Wyoming consists of several mountains and intermontane basins (Fig. 4). The major mountains in this area include the northwest-southeast trending Bighorn Mountains, Wind River Mountains, Gros Ventre Mountains, and Beartooth Mountains, and the east-west trending Owl Creek Mountains. The intermontane basins lie within a region in which Paleozoic and Mesozoic shelf sediments were deposited non-conformably over a continental cratonic crust of gneiss, schist and granite. This region, between deep and mobile geosynclines to the west and the stable craton to the east, is referred to as the Rocky Mountain Foreland. The rocks of most of the mountains surrounding the basins are Precambrian crystalline rocks and Paleozoic sedimentary rocks that have been uplifted in broad, tilted or flat-topped block anticlines. The less resistant Mesozoic sediments are eroded, though some remnants crop out as hogback ridges.

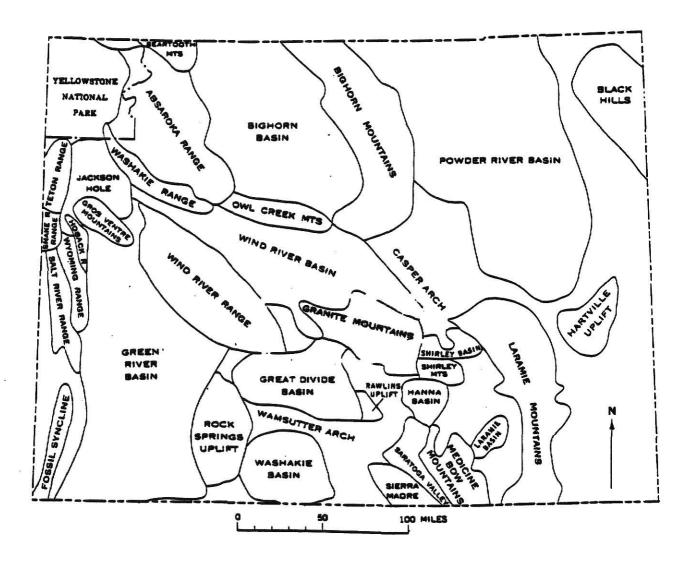


Figure 4. Major structural features of Wyoming (from Moore, 1977).

The Bighorn Basin and the Wind River Basin, from which samples for the present study were collected, are the prominent structural basins in the area (Fig. 4). Bighorn Basin is a northwest-southeast trending, elliptical intermontane basin with many peripheral anticlinal folds. The basin is situated on the eastern shelf of the Cordilleran geosyncline. The Bighorn Basin is bounded on the east by the Bighorn Mountains, on the south by the Owl Creek Mountains, on the west by the Yellowstone-Absaroka volcanic plateau, and on the north by a low structural saddle separating it from the Crazy Mountain syncline of central Montana. The Bighorn Basin is markedly asymmetric, with its steep side on the west. The Wind River Basin, which covers approximately 22,000 km², is also a northwestsoutheast trending, elliptical intermontane basin. bounded on the west by the Wind River Mountains, on the northwest by the Washakie Range, on the north by the Owl Creek Mountains, on the east by the Casper Arch, and on the south by the Granite Mountains. The deepest parts of this structurally asymmetrical basin are along the north and east margins.

The present geologic framework of mountains and structural basins evolved in at least four episodes of deformation during the Laramide Orogeny, which extended from

the Late Cretaceous to the Eocene. Post-Laramide regional uplift, local vertical adjustments, major erosional events and glaciation of the surrounding mountains played a major role in developing the modern topography.

Geology of the Upper Cambrian rocks

In northwestern Wyoming, the Late Cambrian Epoch is represented by the Gallatin Formation, which is underlain by the Middle Cambrian Gros Ventre Formation and overlain by the Upper Ordovician Bighorn Dolomite (Fig. 5). The Gallatin Formation, which is 66 to 99 m thick, is divided into two members. The Dunoir Member is the lower member and consists of an upper 8 to 11 m thick unit of grainstone that contains a 0.5 to 0.6 m thick unit of quartz arenite in the middle. The lower unit of the Dunoir Member consists of microsparite, pseudosparite and biosparite. The Open Door Member is the upper member of the Gallatin Formation and consists of 38 to 80 m of thin-bedded, gray limestones that are underlain by 10 to 16 m of green mudrock.

Dunoir Member. -- Miller (1936) stated that carbonate rocks were deposited during a marine transgression from the west during the Middle Cambrian Epoch. Sedimentation occurred on a gently sloping broad shelf on which there were zones of high and low energy. Near the end of the Middle Cambrian, local uplift in northwestern Wyoming caused the sea to retreat slightly but to remain over a major part of the region to the east.

The Dunoir Member can be differentiated into lower and upper sequences. The lower units are composed of massive, laminated, ripple cross-laminated, and cross-bedded carbonate rocks deposited in channels and in subtidal, intertidal and tidal-flat environments. The upper units are composed of a thick, laterally continuous sequence of fossiliferous, dolomitic oomicrosparite that formed in a shoaling subtidal environment (Moore, 1977).

Local uplift in northwestern Wyoming exposed the rocks of the Middle Cambrian Gros Ventre Formation and created a tidal flat that became dissected by channels. An ooid shoal was formed off-shore from the tidal flat creating a lagoon. Subsidence drowned the area, and a thin sequence of lagoonal sediments was deposited. Further subsidence caused the ooid shoal to migrate over the lagoonal sediments, thus completing the Dunoir carbonate sequence. Later, normal marine conditions were re-established and the green shale and limestone of the Open Door Member of the Gallatin Formation were deposited (Moore, 1977).

	SER.	FM.	MEMBER	. LITH	OLO	GY
ORDOVICIAN	UPPER	BIG- HORN	LEIGH		9 m 48 m	DOLOSTONE
	UPPER	GALLATIN	OPEN DOOR		60 m	MICRITE
	ח	GA	DUNOIR		14 m	MICRITE (OÖLITIC)
CAMBRIAN	Ш	GROS VENTRE	PARK SHALE		123 m	MICRITE CONGLOMER- ATIC MICRITE SHALE AND SUBLITHARENITE
3	CAI	BORE	DEATH CANYON		42m	MICRITE
)	WOLSEY SHALE		50 m	MICACEOUS SHALE AND SUBLITHARENITE
			FLATHEAD		71m	QUARTZ ARENITE, SUBARKOSE, ARKOSE
PRE- CAMBRIAN	PRECAMBRIAN		CAMBRIAN	关注公公	au	ARTZ MONZONITE

Figure 5. Generalized stratigraphic diagram of Precambrian and early Paleozoic time-stratigraphic and rock units, northwestern Wind River Basin, Wyoming (from Martin et al., 1980).

Open Door Member. -- The Open Door Member of the Gallatin Formation overlies the Dunoir Member and is overlain by the Ordovician Bighorn Dolomite. The Open Door Member can be differentiated into an upper limestone unit and a lower green-shale unit. The upper unit consists of gray to brown, thin-bedded calcarenite, thin- to thick-bedded calcilutite and thin-bedded dolostone. Many of the carbonate rocks are burrowed and some show small-scale ripple marks. Carbonate rocks of the Open Door Member show extensive neomorphism which is observed in both the matrix and allochemical constituents in the limestone. The Open Door Member was deposited in a broad, shallow, transgressing epeiric sea with a low-angle bottom slope under conditions of low energy. The environment was shallow sublittoral, and there was no tidal fluctuation (Fischer, 1965).

LABORATORY PROCEDURES

Preparation of Samples

Erushing.—All field samples were trimmed to remove weathered portions. Parts of the samples were retained for thin-section preparation, and the remaining samples were thoroughly cleaned with distilled and demineralized water and broken to about pebble—size. The chips were examined under a binocular microscope, and any obvious secondary vein-rock or non-carbonate phases were rejected. The samples were washed again with distilled and demineralized water and reduced to powder using a pre-cleaned "diamonite" mortar and pestle. The powders were sieved to a 80-100 mesh size and ground in a pre-cleaned agate mortar and pestle for about 10 minutes. The agate—ground samples were then stored in plastic sample bottles which had been pre-cleaned in a 6 N hydrochloric—acid bath and rinsed several times.

Reagents. -- Hydrochloric and nitric acids used in the laboratory procedures were distilled in a Vycor-glass acid-distilling apparatus and stored in precleaned Nalgene-bottles. Water that was used for washing and dilutions was distilled in a commercial distiller and demineralized by passing through demineralizing columns.

<u>Laboratory wares</u>.—To avoid any contamination from within the laboratory, all the glassware used was constructed of Vycor-glass. Teflon beakers were used for all dissolutions and column-chromatographic separations.

All laboratory wares were soaked in a 6 N hydrochloric-acid bath for at least two hours and then rinsed thoroughly with distilled and demineralized water prior to use.

Atomic Absorption Spectrophotometry

Preparation of samples.—A weighed amount of the agateground sample was wetted with water and dissolved in 0.1 N Vycor-distilled hydrochloric acid. This normality (0.1 N) has been shown to leach negligible amounts of cations from the clay minerals in the carbonate rocks (Chaudhuri and Brookins, 1979). The insoluble residues were filtered out and used to determine the insoluble-residue content. A part of the filtrate was retained for isotopic analyses, and the remaining filtrate was diluted initially to specific volumes (usually 50 or 100 ml). After appropriate dilutions, the solutions were used to determine the concentrations of Ca, Mg, Mn and Sr.

<u>Instrumental analyses</u>.—The diluted solutions were analyzed using a Perkin-Elmer 305B Atomic Absorption Spectrophotometer. Artificial standard solutions were

prepared by diluting commercial standards (Fisher-brand) to the linear ranges of the instrument. The instrument settings that were used were those recommended by the manufacturer. The analyses have a maximum error of about 5 percent.

It is assumed that, due to the low normality of the acid used to dissolve the carbonate rocks, negligible amounts of cations were leached from the non-carbonate phases. Bearing this in mind, the weights of the insoluble residues were subtracted from the weights of the whole-rock samples to yield the weight of the carbonate fractions.

Assuming that the carbonate fractions contributed all the cations, the elemental abundances were recalculated to those of rocks composed only of carbonate phases.

Mass Spectrometry

Preparation of samples.—An amount of the rock solution, containing approximately 30 ug of Sr, was pipetted into a clean teflon beaker and evaporated to dryness. The salts were redissolved in 3 ml of 2 N Vycor-distilled hydrochloric acid. The solution was carefully transfered into pre-calibrated ion-exchange columns containing a cross-linked Dowex 50W—X8 cation-exchange resin. After elution with a pre-determined volume of 2 N HCl, strontium chloride

was collected in teflon beakers and evaporated to dryness. The residue was redissolved in 3 N nitric acid and evaporated. The nitrates were used for mass-spectrometric analyses.

The separation of Rb from the carbonate rocks required the removal of Ca, which caused an interference in the analyses. Ca was separated by passing the sample through a cation-exchange resin. The solution was then reacted with 3 to 4 ml of double-distilled perchloric acid to convert the salts to perchlorates. The solution was evaporated to near-dryness and redissolved in methanol. This solution was refrigerated for 24 hours, causing the precipitation of Rb-perchlorate. The supernatent liquid was discarded. The residue was converted to nitrates by the addition of 3N nitric acid, and mounted in the mass spectrometer.

Instrumental analyses. -- Mass spectrometric analyses were performed on a 6-inch radius, 60-degree sector, Neirtype instrument (Nuclide Corporation, Model 6-60S).

Nitrated samples were evaporated onto pre-cleaned tantalum filaments and mounted in the source of the mass spectrometer. Ions were collected by a Faraday-cup configuration and the signal multiplied by a Cary Vibrating Reed Electrometer. Ion-beam intensities were recorded on a

strip-chart recorder from which peak heights were read. All calculations were standardized to the ⁸⁶Sr/⁸⁸Sr value of 0.1194.

Petrography

Thin-sections of 23 rocks were prepared using standard techniques and mounted on clean glass slides using epoxy cement. Thin-sections were examined for identification of minerals and for the relative chronology of the minerals. Special attention was given to the identification of clastic fragments, if any, and to the recognition of any post-depositional features. Since detailed petrography was beyond the scope of this study, quantitative estimations of mineralogy by point-counts were not attempted. Detailed petrography of the rocks of the Dunoir and the Open Door members has been done by Fischer (1975) and Moore (1977).

RESULTS

Elemental Abundances

Dunoir Member. -- Insoluble-residue contents and Ca, Mg, Rb, Sr and Mn abundances were determined for eight carbonate rocks from the Dunoir Member. Of these, five samples were collected from an outcrop in the Wind River Basin, and three from an cutcrop in the Bighorn Basin. Two other samples that have been interpreted to be from the Dunoir Member were collected from a cored well in the Bighorn Basin. Ca, Mg, Rb, Sr and Mn contents were also determined for a carbonate cement in a sandstone that is interbedded with the limestone of the Dunoir Member. The results of these analyses are given in Table 1. The Ca contents in these rocks range from 37.68 to 40.83 percent, Mg from 0.17 to 0.66 percent, Sr from 164 to 442 ppm, and Mn from 140 to 360 ppm. contents in all of these rocks are less than 0.5 ppm. variations of these elements, the Ca/Mg ratios and the Sr/Ca ratios, within a stratigraphic section in the Wind River Basin are shown in Figure 6. The Mg and Sr contents are mostly uniform, except in the lower part of the section where the Mg contents increase and the Sr contents decrease.

On the basis of Ca/Mg ratios, Chilingar (1957) classified carbonate rocks into seven categories. These are

magnesian dolomite (Ca/Mg = 1 to 1.5), dolomite (Ca/Mg = 1.5 to 1.7), calcareous dolomite (Ca/Mg = 1.7 to 3.5), highly dolomitic limestone (Ca/Mg = 3.5 to 16), dolomitic limestone (Ca/Mg = 16 to 60), slightly dolomitic limestone (Ca/Mg = 60 to 105) and calcitic limestone (Ca/Mg greater than 105).

Based on this classification, the carbonate rocks of the Dunoir Member, with Ca/Mg ratios between 60.9 and 223.3, are either slightly dolomitic limestone (DU84, RS1 and RS2) or calcitic limestone (DU90, DU92, DU96, DU106 and RS4).

The Sr contents of the rocks which range from 164 to 442 ppm are lower than the average Sr concentration of 500 ppm reported by Degens (1965) for Paleozoic carbonate rocks. Veizer and Demovic (1974) studied the distribution of Sr in carbonate rocks of Mesozoic age from Central Western Carpathians and showed that there is distinct facies control of the distribution of Sr. According to these authors, 1000 Sr/Ca ratios between 1 and 5 in carbonate rocks represent a lagoonal environment of deposition, whereas 1000 Sr/Ca ratios between 0.25 and 0.9 represent a littoral environment of deposition. The 1000 Sr/Ca ratios (0.4 to 1.17) obtained for the samples of the Dunoir Member were compared with the range of values reported by Veizer and Demovic (1974). With the exception of two samples (RS2 and RS4), the Sr/Ca ratios of the samples are within the range for a littoral

environment (Fig. 7). Martin et al. (1980) reported that the Dunoir Member was deposited in lagoons near the shore and in mud-ooid and quartz-sand shoals. The interpretation of a littoral environment, based on the Sr/Ca ratios, agrees with the interpretations of Martin et al.

Table 1. Chemical data for the Dunoir Member.

Sample	Ca	Mg	Rb	sr	Mn	Insoluble
						Residue
	(pct)	(pct)	(ppm)	(ppm)	(ppm)	(pct)
	Wind	River Ba	sin - Ou	tcrop s	amples	
DU106	38.03	0.23	<0.5	324	335	4.21
DU102	40.74	1.24	<0.5	164	255	78.82
DU96	40.47	0.31	<0.5	305	168	3.59
DU92	37.76	0.18	<0.5	297	342	4.95
DU90	37.97	0.17	<0.5	347	360	10.21
DU84	40.21	0.66	<0.5	276	313	8.93
			_			
	Bigi	norn Basi	n - Outc	rop sam	ples	
RS4	40.83	0.38	<0.5	396	140	12.05
RS2	37.68	0.49	<0.5	442	300	6.17
RS1	40.13	0.41	<0.5	230	306	5.30
Bighorn Basin - Core samples						
CW5472	40.83	0.35	<0.5	283	189	2.35
CW5477	40.52	0.55	<0.5	261	165	70.61

Table 1. (Continued)

Sample	Ca/Mg	1000 Sr/Ca	$1/sr \times 10^3$					
	Wind River Basin	- Outcrop Sam	ples					
DU106	165.3	0.853	3.08					
DU102	33.9	0.402	6.10					
DU96	130.5	0.754	3.28					
DU92	209.8	0.787	3.36					
DU90	223.3	0.915	2.88					
DU84	60.9	0.687	3.62					
Bighorn Basin - Outcrop Samples								
RS4	107.4	0.970	2.52					
RS2	78.9	1.172	2.26					
RSl	97.9	0.572	4.35					
Bighorn Basin - Core samples								
CW5472	116.6	0.693	3.53					
CW5477	73.7	0.644	3.83					

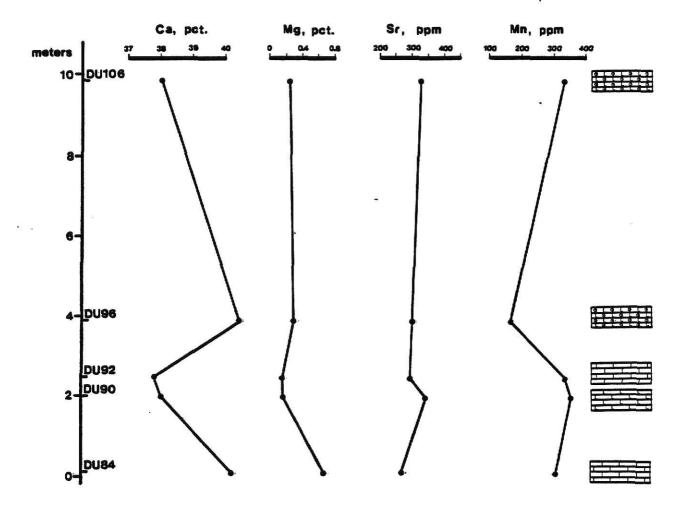


Figure 6. Vertical profiles of chemical data from the Dunoir Member, Wind River Basin outcrop.

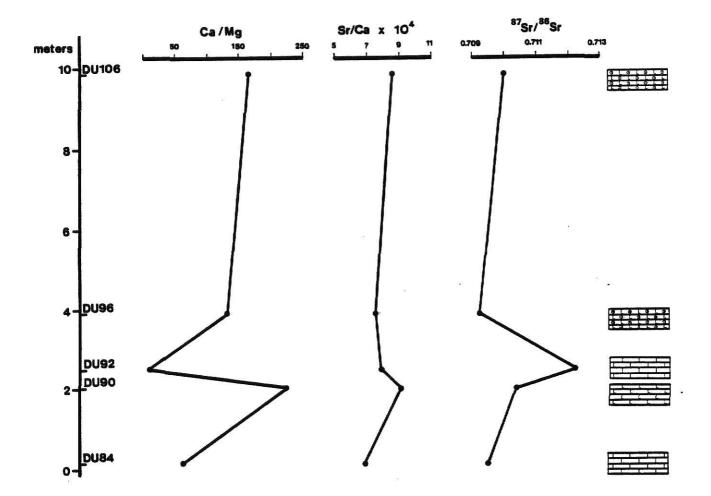


Figure 6. (Continued)

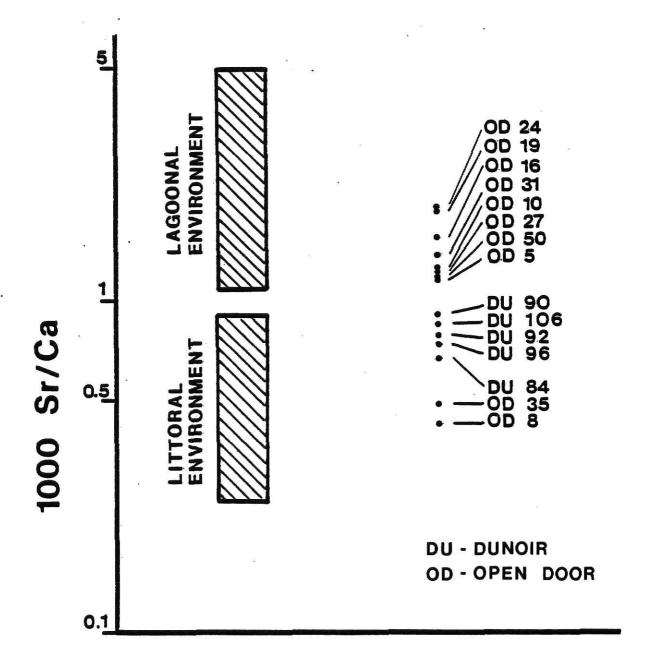


Figure 7. Comparison of Sr/Ca ratios of rocks from the Dunoir and Open Door members, with Sr/Ca ratios in limestones limestones from littoral and lagoonal environments (after Veizer and Demovic, 1974).

Open Door Member .-- Insoluble-residue contents and Ca, Mg, Rb, Sr and Mn contents were determined for ten samples of the Open Door Member from an outcrop in the Wind River Three samples that have been interpreted to be from Basin. the Open Door Member were collected from a cored well in the Bighorn Basin. The results of these analyses are given in Table 2. The Ca contents in these rocks range from 15.33 to 41.54 percent, Mg from 0.12 to 9.17 percent, Sr from 76 to 739 ppm and Mn from 69 to 498 ppm. The Rb contents in all these rocks are less than 0.5 ppm. The variation of these elements, the Ca/Mg ratios and the Sr/Ca ratios, within a stratigraphic section in the Wind River Basin is shown in Figure 8. The Ca content is low (15.33 percent) at the top of the Open Door Member, and it ranges between 37.13 and 40.61 percent in the rest of the section. The Mg content is 9.17 percent for the uppermost sample, but decreases to 1.47 and 1.65 percent for those directly below. Lower in the section, the Mg contents decrease even further to 0.12 to 0.68 percent. The samples with low Sr and high Mn contents are from the top of the section, but otherwise the Sr (173 to 739 ppm) and Mn values (69 to 199 ppm) appear to vary randomly within the section.

On the basis of their Ca/Mg ratios, the rocks of the Open Door Member are classified as dolomite (OD35),

dolomitic limestone (OD19, OD27, OD31 and CW5287), slightly dolomitic limestone (OD8 and OD16) and calcitic limestone (OD5, OD10, OD24, OD50, CW5277 and CW5416).

The 1000 Sr/Ca ratios of the rocks from the Open Door Member were compared with the 1000 Sr/Ca values reported by Veizer and Demovic (1974). With the exception of two samples (OD8 and OD35), the rocks of the Open Door Member plot within the range for lagoonal environment of deposition (Fig. 7), which is in accordance with the shallow, lowenergy environment interpreted for the Open Door Member by Martin et al. (1980).

Table 2. Chemical data for the Open Door Member.

Sample	Ca	Mg	Rb	Sr	Mn	Insoluble
	1					Residue
	(pct),	(pct)	(ppm)	(ppm)	(ppm)	(pct)
	Wind 1	River Bas	sin - Ou	tcrop S	amples	
OD35	15.33	9.17	<0.5	76	252	2.29
OD31	39.65	1.47	<0.5	555	102	7.94
OD27	38.52	1.65	<0.5	476	69	3.72
OD24	37.13	0.25	<0.5	716	104	3.54
OD19	40.61	0.68	<0.5	739	145	5.31
OD16	40.16	0.42	<0.5	642	110	4.80
OD10	40.55	0.19	<0.5	509	131	7.47
OD8	40.08	0.43	<0.5	173	199	11.00
OD5	37.18	0.35	<0.5	415	179	8.29
OD50	39.80	0.12	<0.5	476	193	3.78
Bighorn Basin - Core Samples						
CW5277	40.14	0.39	<0.5	185	498	18.39
CW5287	41.54	1.54	<0.5	177	455	50.39
CW5416	39.92	0.33	<0.5	208	368	7.43

Table 2. (Continued)

Sample	Ca/Mg	1000 Sr/Ca	$1/sr \times 10^3$
	Wind River Basin	- Outcrop Sam	ples
OD35	1.7	0.496	13.16
OD31	27.0	1.400	1.80
OD27	23.3	1.237	2.10
OD24	148.5	1.929	1.40
OD19	59.0	1.819	1.35
OD16	95.6	1.555	1.60
OD10	213.4	1.255	1.96
OD8	93.2	0.433	5.76
OD5	106.2	1.116	2.41
OD50	331.7	1.196	2.10
6	Bighorn Basin	- Core Samples	6
CW5277	102.9	0.462	5.39
CW5287	26.9	0.427	5.64
CW5416	120.9	0.521	4.81

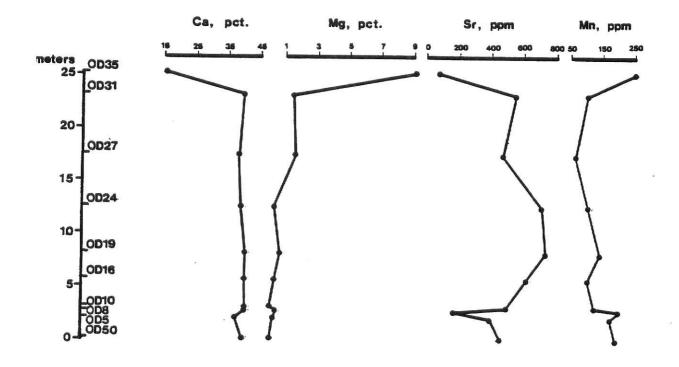


Figure 8. Vertical profiles of chemical data from rocks of the Open Door Member, Wind River Basin outcrop.

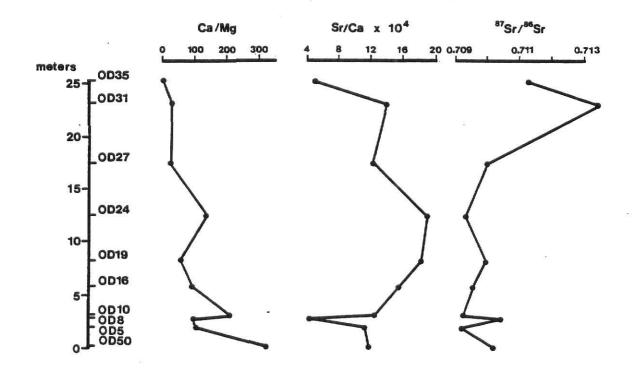


Figure 8. (Continued)

Fragments of trilobite, micrite and a sparite-enriched carbonate sample were collected from a hand-specimen (OD24) of the Open Door Member, and their Mg, Rb, Sr and Mn contents were determined. The results of the analyses are given in Table 3. The Sr and Mn contents of the fossil and the sparite are similar, whereas the micrite has lower concentrations of these two elements. The Mg contents of the micrite (0.25 percent) and sparite (0.26 percent) are similar, whereas the Mg content of the fossil is somewhat lower (0.20 percent).

Table 3. Elemental abundances in the three carbonate phases from sample OD24 from the Open Door Member.

Sample	Mg	Rb	Sr	Mn
,	(pct)	(ppm)	(ppm)	(ppm)
Fossil	0.20	<0.5	515	99
Micrite	0.25	<0.5	460	94
Sparite	0.26	<0.5	525	104

Strontium Isotopic Abundances

Pilgrim Limestone. -- The Pilgrim Limestone of southwestern Montana is correlated with the Dunoir Member of northwestern Wyoming (Lochman-Balk, 1972). A sample of the Pilgrim Limestone (Fig. 9) was obtained from the Indiana University Field Station collection from a location at South Boulder Creek in Madison County, Montana. The sample of the Pilgrim Limestone is traversed by a 5 mm-thick calcite vein. To study records of any chemical variations that may have resulted from fluids which deposited the vein-calcite, eight samples, including one from the vein, were collected from along a traverse across the rock (Fig. 9). The samples were analyzed for their 87 Sr/86 Sr ratios and Sr contents. Rubidium concentrations were determined in four of the eight samples. The results of the analyses are given in Table 4. Unless indicated otherwise, the isotopic data have a maximum error of 0.0003.

As the rocks are Late Cambrian in age, the radiogenic growth of 87 Sr due to the decay of 87 Rb, must be subracted from the measured 87 Sr/ 86 Sr ratios to find the initial 87 Sr/ 86 Sr ratios of the samples. As the Rb/Sr ratio of the vein-carbonate is low (0.001), negligible growth of 87 Sr can be expected. Even if it is assumed that the maximum age of

the vein is similar to that of the host-rock, the initial 87 Sr/86 Sr of the vein would be 0.71939. A considerably younger age for the vein would make the initial 87 Sr/86 Srratio the same as the measured 87 Sr/86 Sr ratio. The Rb/Sr ratios, measured for three samples of the host-rock, are slightly higher than that of the vein and hence corrections for the radiogenic growth of 87sr must be made for these samples. Assuming an age of about 500 million years, the calculated initial ratios of the host-rock samples range between 0.70982 and 0.71000. Although the Rb content of 8L was not measured, its value can be reasonably estimated from the extrapolation of concentrations measured for the 3L and 17L samples, which have Rb contents of 6.20 and 6.82 ppm, respectively. Based on this estimated value of Rb, and making an appropriate correction for the radiogenic growth, the initial 87sr/86sr ratio of 8L would be 0.71028. The profile of the initial (corrected) 87Sr/86Sr ratios of the five samples, together with the measured (uncorrected) $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ ratios of other samples across the vein, is shown in Figure 10. A similar plot for the Sr concentrations shows a high Sr content (557 ppm) in the vein and considerably lower values (107 to 334 ppm) in the host-rock (Fig. 11). A plot of the Rb contents versus the locations of the four samples that were analyzed, shows that the vein

is depleted in Rb compared to the host-rock (Fig. 12).

Table 4. Isotopic data of a hand specimen of the Pilgrim
Limestone from southwestern Montana.

Sample	Rb	Sr	$87_{\rm Rb}/86_{\rm Sr}$	87 _{Sr/} 86 _{Sr}	87 _{Sr/} 86 _{Sr}
	(ppm)	(ppm)		(measured)	(initial)
17L	6.82	283	0.700	0.71033	0.70982
8L	فلت فالروين	221	100 cm	0.71088	400 May 400
3L	6.20	107	0.168	0.71122	0.70999
CV	0.88	557	0.004	0.71941	0.71939
3R		251	-	0.71095	
5R		313	-	0.71016	
8R		334	500 to to	0.71055	:
32R	22.6	195	0.336	0.71247	0.71000

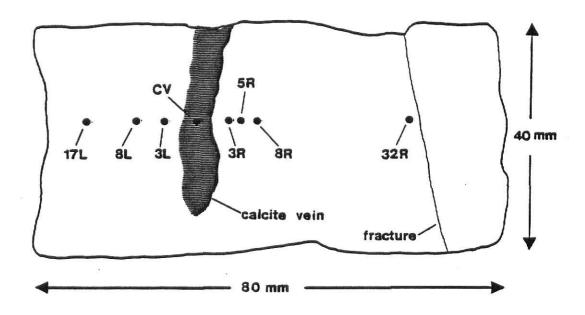


Figure 9. Sketch of a sample of the Pilgrim Limestone, showing sampling sites.

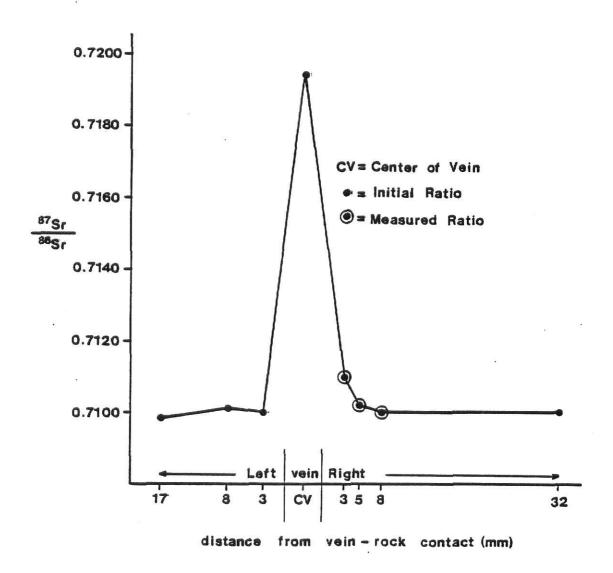


Figure 10. Profile of strontium isotopic ratios across a sample from the Pilgrim Limestone.

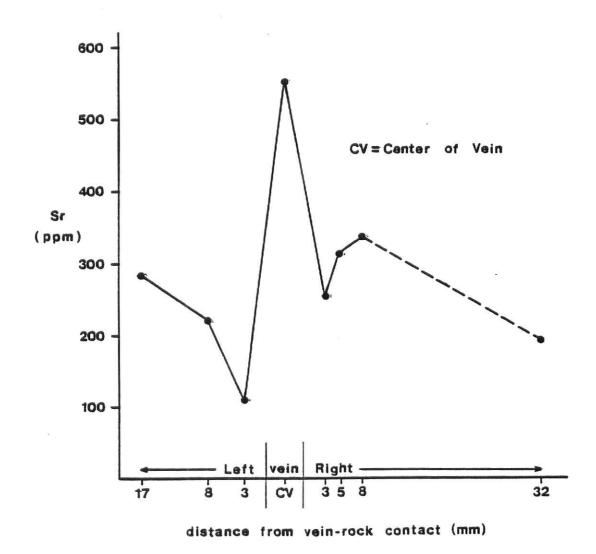


Figure 11. Strontium-content profile across the sample from the Pilgrim Limestone.

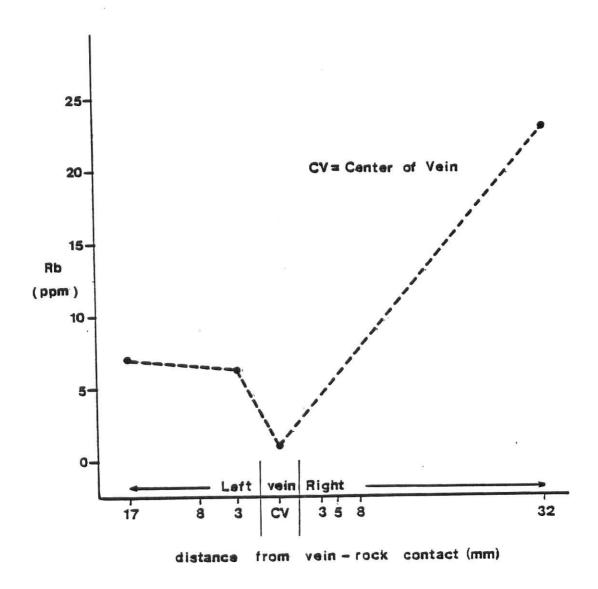


Figure 12. Rubidium-content profile across the sample from the Pilgrim Limestone.

Dunoir Member. ——Strontium isotopic abundances were measured for eight samples of limestone from the Dunoir Member and for carbonate cement of a sample (DU102) of a sandstone in the Dunoir Member. Six of these samples were collected from an outcrop in the Wind River Basin and three from an outcrop in the Bighorn Basin. In addition, two samples that have been interpreted to be from the Dunoir Member, were obtained from a cored well in the Bighorn Basin. The results of these analyses are given Table 5.

As the Rb/Sr ratios are low, the ⁸⁷Sr/⁸⁶Sr ratios are considered to be the initial ⁸⁷Sr/⁸⁶Sr ratios. The ⁸⁷Sr/⁸⁶Sr ratios of the samples from the Wind River Basin range from 0.70924 to 0.71234, whereas the ⁸⁷Sr/⁸⁶Sr ratios in the samples from the Bighorn Basin are 0.70962, 0.70979 and 0.71082. The two samples from the cored well in the Bighorn Basin yielded ⁸⁷Sr/⁸⁶Sr ratios of 0.70967 and 0.71479. The higher ratio of 0.71479 was obtained in a sample that had an insoluble-residue content of 70.6 percent.

Vertical distribution of $87 \, \mathrm{sr}/86 \, \mathrm{sr}$ ratios of samples within the stratigraphic section of the Dunoir Member in the Wind River Basin is shown in Figure 6. With the exception of one sample (DU92), whose $87 \, \mathrm{sr}/86 \, \mathrm{sr}$ ratio is 0.71234, the

remaining samples from the Wind River Basin have 87 sr/86 sr ratios between 0.70924 and 0.71040. No apparent trends are observed between the 87 sr/86 sr ratios and other factors, including the Ca/Mg ratios, the Sr/Ca ratios, the Sr contents, and the Mn contents (Figs. 13, 14, 15, 16). The coefficients of correlation for these plots are less than 0.3.

Table 5. Strontium isotopic abundances in samples of the Dunoir Member.

Sample 87_{Sr/86_{Sr}}

Wind River Basin

DU106 0.71000

DU102 (cement) 0.71367

DU96 0.70924

DU92 0.71234

DU90 0.71040

DU84 0.70950 ± 0.00003

Bighorn Basin - Outcrop Samples

RS4 0.70962 ± 0.00002

RS2 0.71082

RS1 0.70979 ± 0.00002

Bighorn Basin - Core Samples

CW5472 0.70969 ± 0.00004

CW5477 0.71479 ± 0.00002

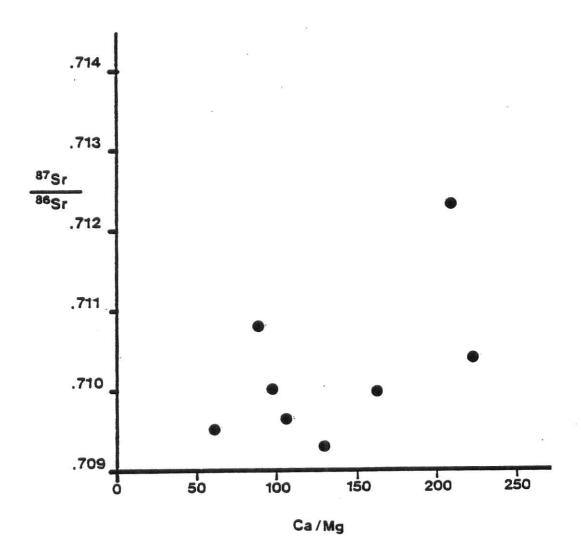


Figure 13. Scatter-plot of ⁸⁷Sr/⁸⁶Sr versus Ca/Mg, Dunoir Member, limestone outcrops.

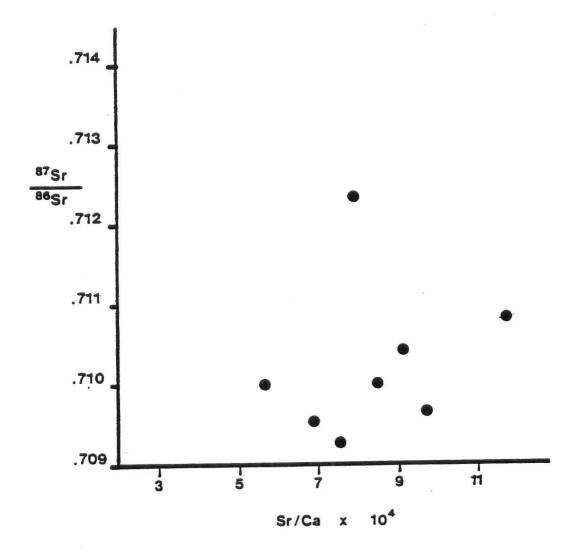


Figure 14. Scatter-plot of ⁸⁷Sr/⁸⁶Sr versus Sr/Ca, Dunoir Member, limestone outcrops.

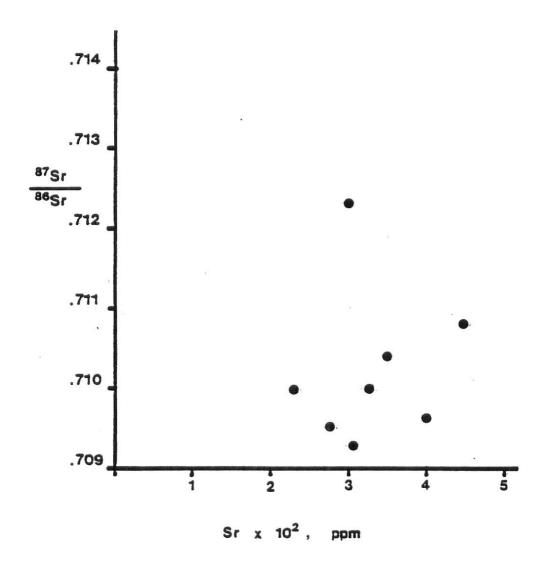


Figure 15. Scatter-plot of ⁸⁷Sr/⁸⁶Sr versus Sr-content,

Dunoir Member, limestone outcrops.

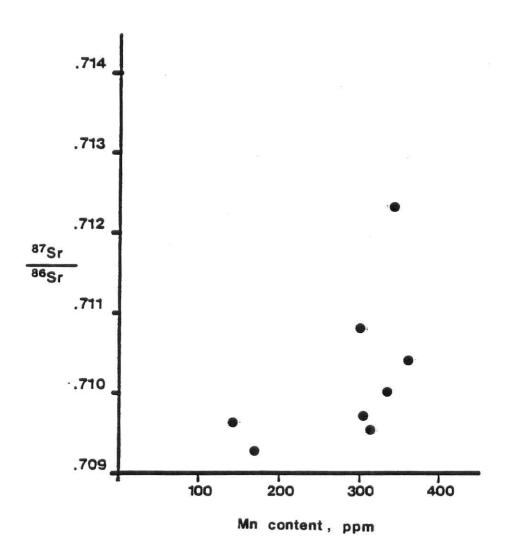


Figure 16. Scatter-plot of ⁸⁷Sr/⁸⁶Sr versus Mn-content,
Dunoir Member, limestone outcrops.

Open Door Member. -- Strontium isotopic data were obtained for ten samples of the Open Door Member from the Wind River Basin. In addition, three samples that have been intrepreted to be from the Open Door member, were collected from a cored well in the Bighorn Basin and analyzed for their 87 Sr/ 86 Sr ratios. As the Rb/Sr ratios in these samples were low, the measured 87sr/86sr ratios are considered to be the initial ratios. The results of these analyses are given in Table 6. Vertical distribution of 87 Sr/86 Sr ratios of the Open Door Member is shown in Figure 8. The 87 Sr/86 Sr values range from 0.70916 to 0.71351. upper part of the Open Door Member has high 87Sr/86Sr ratios of 0.71132 and 0.71351. In the lower part of the Open Door Member, the 87 Sr/86 Sr ratios fluctuate randomly within the range of 0.70916 to 0.71055. The 87 Sr/86 Sr ratios of the samples of the Open Door Member do not show any predictable trends with either the Ca/Mg ratios (Fig. 17) or the Sr/Ca ratios (Fig. 18). No apparent trend can be found between the ⁸⁷Sr/⁸⁶Sr ratios and either the Sr or the Mn contents (Figs. 19, 20). Excepting data from the rocks that have been dolomitized, the coefficients of correlation for these latter plots are less than 0.3.

Sr isotopic abundances were determined for three carbonate phases (a fragment of trilobite, a micrite and a

sparite-enriched sample) from a hand-specimen (OD24) of the Open Door Member. The results of the analyses are given in Table 7. The 87 Sr/ 86 Sr ratio (0.70916) of the sparite is lower than that of the associated micrite (0.70938). The fossil fragment yielded an intermediate 87 Sr/ 86 Sr ratio of 0.70928.

Table 6. Strontium isotopic abundances of samples of the Open Door Member.

Sample	87 _{Sr/} 86 _{Sr}				
Wir	nd River Basin				
OD35	0.71132				
OD31	0.71351				
OD27	0.70997				
OD24	0.70924				
OD19	0.70997				
OD16	0.70959 ± 0.00002				
OD10	0.70931 ± 0.00001				
OD8	0.71055				
OD5	0.70922 ± 0.00002				
OD50	0.71031				
Bighorn Basin - Core Samples					
CW5277	0.70979 ± 0.00001				
CW5287	0.71266 ± 0.00002				
CW5416	0.71034 ± 0.00002				

Table 7. Strontium, carbon and oxygen isotopic abundances of three carbonate phases from sample OD24 from the Open Door Member.

Sample	$87_{Sr}/86_{Sr}$	$\delta^{13}C$	δ18 _O	$\delta^{18}O$
		(per mil)	(per mil)	(per mil)
		(PDB)	(PDB)	(SMOW)
Fossil	0.70928		Title time can	-
Micrite	0.70938	+0.95	-7.32	+22.83
Sparite	0.70916	+0.88	-7.79	+22.34

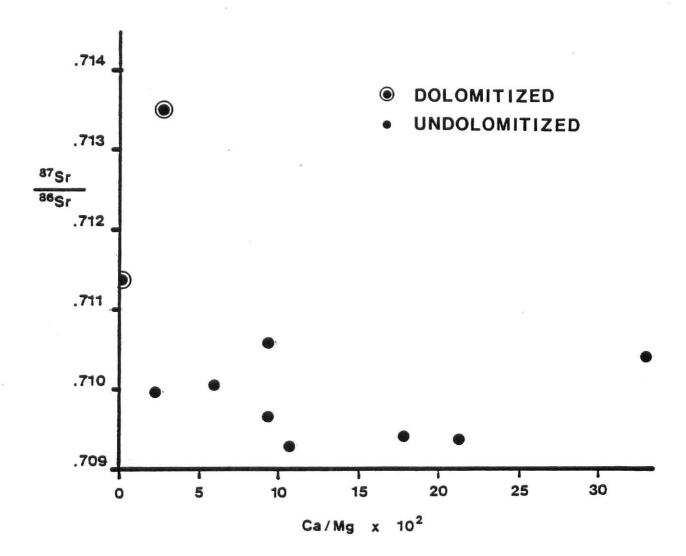


Figure 17. Scatter-plot of ⁸⁷Sr/⁸⁶Sr versus Ca/Mg, Open Door Member, outcrop samples.

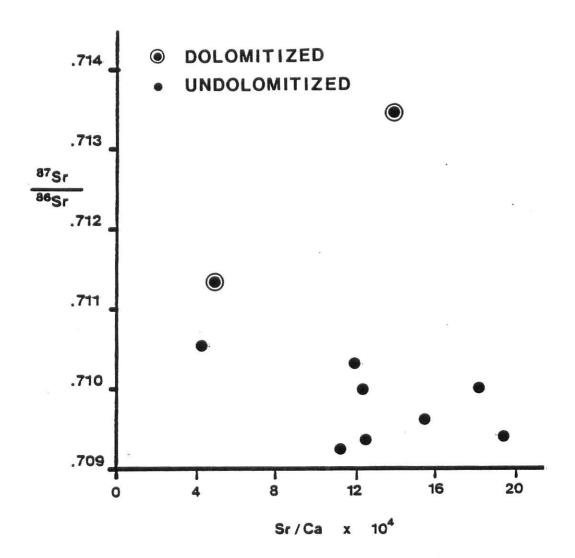


Figure 18. Scatter-plot of ⁸⁷Sr/⁸⁶Sr versus Sr/Ca, Open Door Member, outcrop samples.

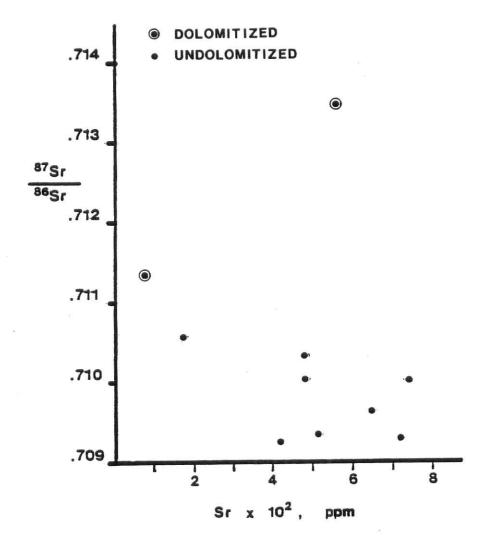


Figure 19. Scatter-plot of ⁸⁷Sr/⁸⁶Sr versus Sr-content, Open Door Member, outcrop samples.

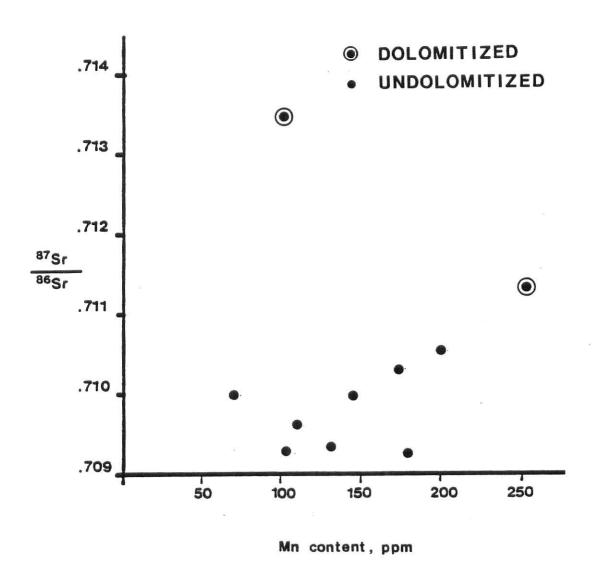


Figure 20. Scatter-plot of ⁸⁷Sr/⁸⁶Sr versus Mn-content, Open Door Member, outcrop samples.

Stable isotopic abundances. -- Oxygen and carbon isotopic abundances were obtained for six samples of the Dunoir Member. Four samples of the Open Door Member, including the micrite and sparite phases from a sample (OD24) were also analyzed for their stable isotopic abundances. The results of these analyses are given in Table 8.

The δ^{13} C values in the samples from the Dunoir Member are negative, ranging from -1.54 to -0.33 per mil, whereas those of the Open Door Limestone are positive and range from +0.44 to +1.05 per mil. The δ^{18} O (SMOW) values for the Open Door Member have a narrow range of +22.06 to +22.83 per mil. The lowest δ^{13} C value was obtained from a carbonate cement in a sandstone (DU102) from the Dunoir Member. No apparent trends are observed between the δ^{18} O values and the Ca/Mg ratios, the Sr/Ca ratios, or the 87 Sr/ 86 Sr ratios (Figs. 21, 22, 23).

Table 8. Stable isotopic abundances in samples from the Dunoir Member and the Open Door Member.

Sample	Unit	$\delta^{13}c$	δ 18 ₀	6 18 O	
		(per mil)	(per mil)	(per mil)	
		(PDB)	(PDB)	(SMOW)	
DU106	Dunoir	-1.08	-9.22	+20.87	
DU102	Dunoir	-1.54	-9.57	+20.50	
DU96	Dunoir	-0.42	-7.48	+22.66	
DU92	Dunoir	-0.38	-8.86	+21.24	
DU 90	Dunoir	-0.43	-6.96	+23.20	
DU84	Dunoir	-0.33	-7.01	+23.14	
OD24S	Open Door	+0.88	-7.79	+22.34	
OD24M	Open Door	+0.95	-7.32	+22.83	
OD19	Open Door	+1.05	-7.5 3	+22.06	
OD50	Open Door	+0.44	-7.66	+22.47	

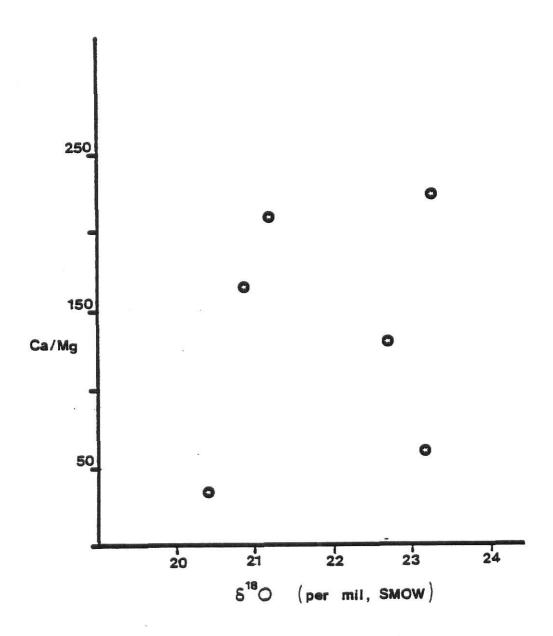


Figure 21. Scatter-plot of Ca/Mg versus δ^{18} O, Dunoir Member.

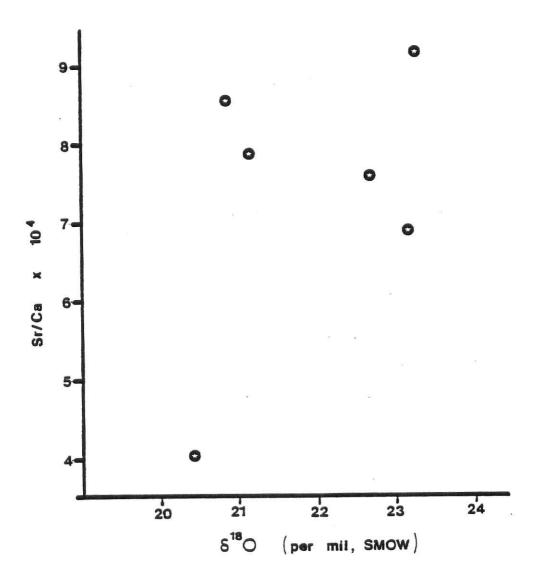


Figure 22. Scatter-plot of Sr/Ca versus δ^{18} 0, Dunoir Member.

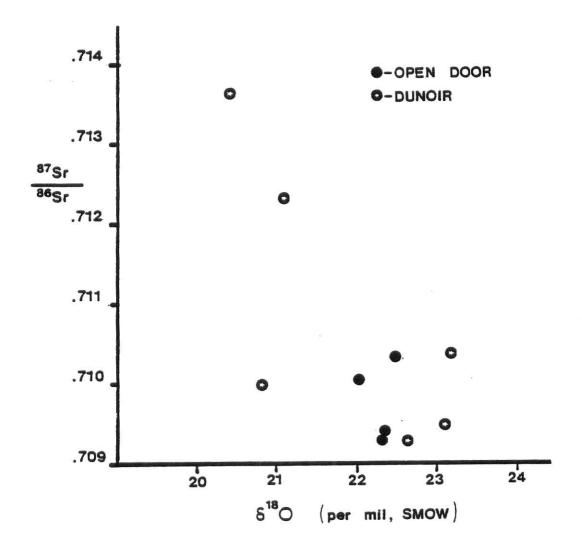


Figure 23. Scatter-plot of $^{87}\text{Sr}/^{86}\text{Sr}$ versus $\delta^{18}\text{O}$, Dunoir and Open Door members.

DISCUSSION

Any isotopic variation within the carbonate rocks can be ascribed either to (1) the effects of diagenesis, during which isotopically different Sr was introduced into the carbonate rocks, or (2) random fluctuations in the isotopic composition of Sr in seawater. Therefore, it is imperative that, prior to ascribing any particular ⁸⁷Sr/⁸⁶Sr value to the seawater from which the carbonate rocks were precipitated, the measured isotopic abundances should be evaluated in the light of possible diagenetic processes which could have altered, to varied degrees, the $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ ratio of the carbonate rocks. Information from petrographic examinations, stratigraphic considerations, trace-element abundances and stable-isotope data should be combined to provide a sound basis from which the role of diagenesis in altering the strontium isotopic composition of the rocks can be critically assessed.

Elemental Abundances

Extensive neomorphism, which is to be expected in carbonate rocks as old as Cambrian, is observed in both the Dunoir and Open Door members. Examination of thin-sections of samples from the two members reveals the recrystallization of micrite to microspar or pseudospar.

Usdowski (1963; cited by Chilingar et al., 1979) compared the average Mg contents of recrystallized limestone and unaltered limestone, and found them to be 0.7 percent and 4.7 percent, respectively. Chilingar et al. (1979) suggested that during recrystallization, Mg is expelled to the interstitial fluids, matrix or the cement, where they are available for other diagenetic processes either in the immediate vicinity or at remote localities. The random and sparse occurrence of dolomite rhombs in the rocks of the Dunoir Member could have resulted from Mg expelled by inversion and recrystallization.

The behavior of Sr in carbonate rocks has been studied by several workers (Harris and Mathews, 1968; Kinsman, 1969; Shearman and Shirohammadi, 1969; Bathurst, 1975; Al-Hashimi, 1976; Baker et al., 1982), and there is a consensus that Sr is expelled during diagenesis. Brand and Veizer (1980) related increasing textural maturity, and increases and

decreases in elemental abundances, to the degree of diagenesis. These authors stated that during diagenetic equilibration of the original carbonate phases with meteoric water, there would be an increase in Mn, Fe and Zn content, and a decrease in Sr and Na content. Mg content would either increase or decrease depending on whether the original carbonate phase was high-Mg calcite, low-Mg calcite or aragonite. Furthermore, on the basis of Sr/Ca ratios and Mn contents, Brand and Veizer (1980) attempted to deduce the original mineralogy of ancient carbonate rocks that experienced diagenetic equilibration with varied amounts of water.

A plot of the Sr/Ca ratios versus Mn contents (Fig. 24) defines fields that depict the depletion of Sr from the original minerals (aragonite, high-Mg calcite or low-Mg calcite), with increasing digenetic equilibration with meteoric waters (represented by increasing Mn contents). Within the range of 40 to 300 ppm of Mn in stabilized carbonate rocks, the differences in the Sr content of the original mineralogical phases are still preserved, although the absolute concentrations of each phase are lowered. The Sr/Ca ratios and the Mn values for all samples of the Dunoir Member, and most of the samples of the Open Door Member, plot within fields that suggest aragonite or low-Mg calcite,

or both, were the original minerals in the carbonate rocks. Two samples of the Open Door Member (OD8 and OD35) plot within fields that suggest that high-Mg calcite or aragonite, or both, were the original minerals in the carbonate rocks. The original mineralogy of one sample (OD27) could not be deduced from the data.

According to Brand and Veizer (1980), carbonate rocks containing more than 300 ppm of Mn represent an "open" diagenetic system that has equilibrated with large quantities of meteoric water. The chemical differences in the carbonate phases diminish as the system becomes progressively open. In samples that have Mn contents of about 500 ppm or more, the recognition of the original mineralogy becomes impossible. Most of the samples of the Dunoir Member plot within the "open-system" part of the diagram (Fig. 24), suggesting that the rocks of the Dunoir Member had undergone diagenetic stabilization with large quantities of meteoric water. On the other hand, the samples of the Open Door Member, having Mn contents less than 300 ppm and 1000 Sr/Ca ratios less than 2, appear to have undergone equilibration with lesser amounts of meteoric water than the rocks of the Dunoir Member.

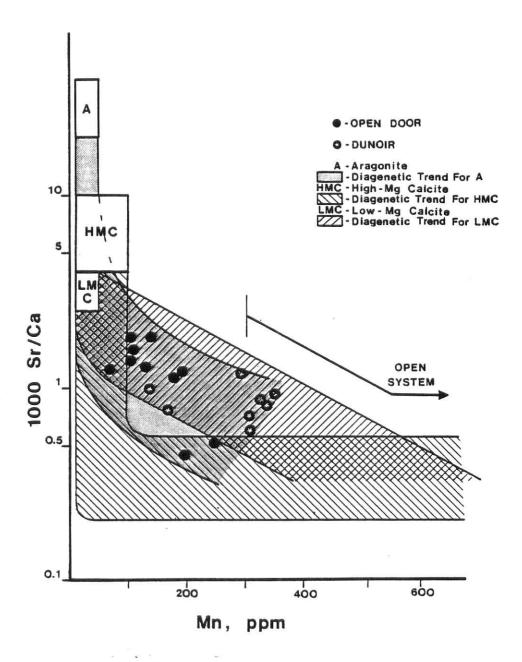


Figure 24. Diagenetic trends for aragonite, high-Mg calcite and low-Mg calcite, upon stabilization with meteoric water (after Brand and Veizer, 1980).

Carbon Isotopic Abundances

The $\delta^{13}\text{C}$ values for the Dunoir and Open Door members (Table 8) are similar to those reported for many Paleozoic limestone rocks by Keith and Weber (1964). Hudson (1977) reported that marine limestone has initial $\delta^{13}\text{C}$ values of 0 ± 2 per mil, which may be altered during diagenesis by the introduction of light or heavy carbon. During early diagenesis, decay of organic material will most likely introduce 12C-enriched bicarbonate into the pore waters, which then would be available for exchange with the carbonate host-rock or for precipitation as carbonate cements. Based on this argument, Hoefs (1973) stated that, with increasing diagenesis, marine limestone can become progressively lighter in carbon isotopic composition. 12C-enrichment will be especially marked during early diagenesis; however, during late diagenesis, the isotopic values of the carbonate rocks could become similar to those for average marine limestone by equilibration with waters that had equilibrated with marine limestone (Hudson, 1977).

The different $\delta^{13}C$ values of the Dunoir Member (-0.33 to -1.08 per mil) and the Open Door Member (+0.44 to +1.05 per mil) can be explained by the difference in the composition of the biochemical accumulates in these two

units. Isotope fractionation by marine organisms ("vital effects") are known to cause variation in the carbon isotopic composition of skeletal fragments (Hoefs, 1973). Alternatively, the difference in the carbon isotopic composition can be explained as a result of different degrees of response to isotopic equilibration of the carbonate materials with fresh water. This postulate of the fresh water being a causative factor in the isotopic differences between the two units, receives support both from the carbon isotopic data of a rock whose stratigraphic position would favor receiving light carbon during diagenesis and from the fresh-water origin for the carbonate cement of a sandstone that is interbedded with the limestone. The most negative δ^{13} C value (-1.54 per mil) obtained in the Dunoir Member was from a sample located at the top of the unit, near the basal shale unit of the Open Door Member. An introduction of light carbon from the overlying shale or an introduction of fresh water along the bedding-plane between the shale and the limestone beds could account for the negative δ^{13} C values in the limestone. A cogent argument, based on the high 87sr/86sr ratio, can be advanced for the cement to have derived from continental Thus it appears that the enrichment of light carbon in the Dunoir Member, as compared to the Open Door Member,

reflects a greater involvement of fresh water in the Dunoir Member. Additional support for this conclusion comes from the Mn and Sr/Ca ratios, which indicate that the rocks of the Dunoir Member are characteristic of open-system diagenesis in contact with meteoric water (Fig. 24).

The limited range of isotopic compositions of samples from an individual member indicates that (1) either the original carbonate had nearly uniform isotopic composition, or (2) that any dispersion in the isotopic values that may have existed in the original allochemical constituents were destroyed by continued adjustment to achieve isotopic equilibrium with ambient water. The actual process that led to the near uniformity in the carbon isotopic values is not clearly understood from the present data. However, the distinction between the carbon isotopic compositions of the two members (Dunoir: -1.54 to -0.33 per mil; Open Door: +0.44 to +1.05 per mil) is clearly evident, and it indicates that any tendency for isotopic equilibration was limited, perhaps restricted to a few meters within a rock unit.

Oxygen Isotopic Abundances

A major question concerning the oxygen isotopic data of carbonate rocks is to what extent diagenesis has altered their primary isotopic compositions. If the nature and magnitude of the secondary processes and their attendant isotopic changes can be identified, then it may be possible to estimate the isotopic composition of the oceans at the time of the deposition of the carbonate phases.

Although the oxygen isotopic compositions are broadly similar, the samples from the Dunoir Member (+20.87 to +23.20 per mil) have a wider range of δ^{18} O than those of the Open Door Member (+22.06 to +22.83 per mil). Keith and Weber (1964) reported an average δ^{18} O of +19.5 per mil for marine limestone of Cambrian age. Compared to this average value, the samples from the Dunoir and Open Door members are enriched in 18 O. The range of the isotopic values of the two limestone units could have resulted from an isotopic exchange with fresh water; however, this is not apparent from the available δ^{18} O values and the elemental data.

The two most $^{18}\text{O-depleted}$ samples are from the Dunoir Member. The lower $\delta^{18}\text{O}$ values can be explained by oxygen isotopic exchange between the carbonate and percolating fresh water. This postulate receives support from the

strontium isotopic data for at least one of the samples (DU92) which has the highest 87 Sr/86 Sr ratio.

A comparison of the oxygen isotopic values of the Dunoir Member and the Open Door Member reveals that some of the samples from the Dunoir Member have δ^{18} 0 values higher than those of the Open Door Member. From the oxygen isotopic data, it may be suggested that these samples from the Open Door Member experienced a greater degree of opensystem recrystallizatiion in contact with fresh water. This is contrary to what the Mn contents and Sr/Ca ratios suggest (Fig. 24). The apparent contradiction is best resolved by considering that an inherent difference between the primary values of the two carbonate units is still preserved, although a difference not necessarily of the same magnitude. The difference in primary isotopic values can be attributed to oxygen isotopic compositions of carbonate precipitates influenced by isotope fractionation by organisms ("vital effects") (Hoeffs, 1973). At least for some of the rocks, the isotopic exchange with fresh water was of limited extent.

Lack of any apparent correlation either between the $\delta^{18}{\rm O}$ values or between the Ca/Mg ratios and the $\delta^{18}{\rm O}$ values excludes consideration of dolomitization as a causative

factor in producing the varied δ^{18} O values in the carbonate rocks. Although the Mg contents of these rocks are low, small amounts (less than 5 percent) of randomly distributed dolomite rhombs have been found in the thin-sections of these rocks. Theoretically, dolomites that are in oxygen isotopic equilibrium with calcite will be 3.1 per mil higher than the associated calcite (Friedman and O'Neil, 1977). Small amounts of dolomite, whose oxygen isotopic compositions were most likely derived from the ambient water, are unlikely to produce any measureable changes in the inherent oxygen isotopic composition of these carbonate rocks.

The oxygen isotopic composition of a sparry calciteenriched carbonate (+22.34 per mil) from the Open Door
Member was found to be nearly identical to that of the
associated micrite (+22.83 per mil). The dissolutionprecipitation phenomenon, which is an attribute of the
micrite-sparite transformation, should conserve the isotopic
similarity, unless there is an introduction of isotopically
different carbon dioxide that would alter the isotopic
composition of the resultant precipitate. The preservation
of the isotopic identity could also be achieved if the
dissolution was essentially the result of a pressuresolution effect. The phenomenon of pressure-solution could

also account for the oxygen isotopic similarity between the sparite and the micrite. However, based on the difference in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the sparite-enriched sample and the associated micrite, it is suggested that there may have been an introduction of carbonate that had an oxygen isotopic composition similar to that of the micrite.

Strontium Isotopic Abundances

A carbonate rock is a multi-component system, consisting essentially of allochemical and orthochemical components and silicate minerals such as clays and glauconites that may be detrital or diagenetic. As the strontium isotopic composition of seawater is essentially uniform at a particular time (Peterman et al., 1970; Biscaye and Dasch, 1971; Faure, 1977; Burke et al., 1982), the knowledge of the strontium isotopic composition of the past oceans can be obtained from the investigation of primary allochemical constituents. However, it is an established fact that the chemical compositions of primary allochemical constituents are diagenetically modified to different degrees, and that secondary carbonate that is generated at different times during diagenesis can have varied chemical composition. Under certain conditions, these chemical modifications can erase, to a great extent, the original isotopic memory of the carbonate rock and imprint secondary isotopic values, which could be significantly different from those of the primary carbonate. In addition to the effects of the secondary alterations, the contribution of radiogenic ⁸⁷Sr from silicate fractions can also adversely affect the primary isotopic composition of the carbonate rocks. This possibility of isotopic disturbance arising from the

silicate fraction dictates that only those carbonate rocks low in insoluble residues can be considered suitable for strontium isotopic investigation. By minimizing or eliminating the effect of silicate minerals, through the proper selection of samples, the effects of diagenesis on the primary isotopic values of the carbonate rocks can be carefully evaluated. This, then would permit the determination of the most probable strontium isotopic values of the contemporary seawater.

With the exception of a few samples that are enriched in \$7\$sr and which will be discussed later, the \$7\$sr/86\$sr ratios of most of the samples of the Dunoir and the Open Door members range from 0.70916 to 0.71055. This range of values can be explained in two ways. One possibility is that the values represent varied \$7\$sr/86\$sr ratios of the contemporary seawater. Alternatively, the \$7\$sr/86\$sr ratios could have been initially uniform but were altered to varied degrees by diagenesis at some later stage. Clearly then, the understanding of the nature of the influence of diagenesis in the primary isotopic composition of the carbonate rock is essential to arrive at a logical conclusion concerning the cause of the strontium isotopic variations observed among the samples of both the Dunoir and the Open Door members.

In previous discussions on the trace-element abundances, it has been shown that the Open Door Member experienced a lesser degree of open-system recrystallization with meteoric waters than the Dunoir Member. If these waters had strontium isotopic compositions which were different from that of the limestones, then one could expect to find some relationship between the trace-element data and the $87 \, \mathrm{sr/86} \, \mathrm{sr}$ ratios. Normally, increasing diagenetic equilibration with meteoric waters is accompanied by decreasing Sr content and Sr/Ca ratio, and an increasing Mn content (Brand and Veizer, 1980). However, no apparent relationships are observed between the $87 \, \mathrm{sr/86} \, \mathrm{sr}$ ratios and other factors, including the Sr contents, the Mn contents, the Ca/Mg ratios and the Sr/Ca ratios (Figs. 13-20).

The lack of any apparent relationships between the isotopic and the elemental data suggests that the strontium isotopic variations in the carbonate rocks were not the results of varied degrees of chemical and isotopic exchange with fresh water. Lack of uniformity of the isotopic values either within a member or between the two members leads to a conclusion that, for the most part, pervasive open-system recrystallization was nonexistent. The extent to which the pore fluids were effective in homogenizing the isotopic composition of the carbonate rocks, and thereby giving a

qualitative estimate of the amounts of fluid-circulation, can be established by examining the isotopic composition of different components of the carbonate rocks on a small scale.

To what extent the allochemical and orthochemical components differ in their strontium isotopic compositions was investigated by analyzing micrite, sparry calciteenriched carbonate and a fragment of a trilobite from a small hand specimen of the Open Door Member. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio (0.70916) of the sparite, which is indoubtedly of secondary origin, is slightly lower than that of the associated micrite (0.70938). The fossil-fragment in the same hand specimen yielded an intermediate 87 Sr/86 Sr ratio of 0.70928. The isotopic difference on such a small scale is contrary to what can normally be expected from diagenetic changes. With increasing diagenesis, in the presence of large volumes of water, various carbonate components would strive to attain isotopic homogeneity. The fact that the strontium isotopic differences do exist among various components, on a small scale, suggests that diagenesis did not entirely obliterate their isotopic memory.

Continental meteoric waters commonly have high $$^{87}{\rm Sr}/^{86}{\rm Sr}$$ ratios because of their contact with Rb-bearing

silicate minerals. Considering that contact with such waters would tend to increase the 87sr/86sr ratio of marine carbonate rocks, the somewhat lower 87 Sr/86 Sr ratio of the sparite, as compared to the micrite, probably suggests that the waters involved in the formation of sparite had a history of association primarily with low 87Sr-bearing carbonate minerals rather than high 87sr-bearing silicate minerals. Nearly identical carbon and oxygen isotopic values between the sparite and the micrite suggest that the chemical components of the sparite were primarily remobilized from carbonate materials of local origin. Any major influx of continental waters would have produced a substantially lower $\delta^{18}O$ value. The suggestion of an involvement of a limited amount of fresh water raises the possibility that much of the strontium in the sparite was locally derived from carbonates of marine origin.

Lithification history of sedimentary carbonate rocks encompasses a change from an unconsolidated carbonate mass, with porosity of 40 to 70 percent, to a limestone composed usually of low-Mg calcite with porosity of 3 percent or lower (Pray and Choquette, 1966). Although there is an increase in volume by as much as 8 percent from inversion of high-Mg calcite and aragonite to low-Mg calcite, the bulk of the primary porosity reduction to a value as low as 3

percent is attributable to the introduction of cement. Compaction is generally considered to be a minor factor in the reduction of porosity. Bathurst (1975) remarked that cementation of carbonate muds and sands begins early, before compaction, and much of it occurs under an overburden pressure exerted by a few tens of meters of sediment. further stressed that the vast reduction of porosity through cementation demands: (1) a large supply of calcium carbonate from a source immediately outside the pore systems, and (2) a very efficient means of transporting the dissolved calcium carbonate and depositing it in the pores. In addressing the question of source of the cement, Bathurst commented that the products and processes of cementation can be related to three basic diagenetic environments: the subaerial, freshwater eogenetic; the submarine eogenitic; and the deepcrustal mesogenetic environments. The most important requirements are that the carbonate sediments should contain more than one solid-carbonate phase and that fluid-flow should permit dissolution-precipitation to proceed in the pore system on a large scale.

Near-surface cementation is a process common to many
Recent carbonate sediments. Thus submarine eogenetic and
subaerial fresh-water eogenetic environments play a dominant
role in the history of cements for many carbonate rocks.

The concept of donor and receptor limestones, wherein calcium carbonate is dissolved from a lime-mud or limestone (donor) and then deposited in a mass of lime-mud and sands (receptor), may account for the strontium isotopic variation observed for the carbonate rocks of the Dunoir and Open Door members. The transport of large quantities of calcium carbonate between formations that consist of two or more carbonate phases that have different solubilities and strontium isotopic compositions can result in the precipitation of the carbonate as a cement. This precipitation can generate not only isotopic differences among beds but also within a bed, depending upon the disposition of the pore systems and hence the paths of the fluid flow. Considering that the fluid moving through carbonate rocks will soon achieve a state of saturation with respect to calcium carbonate, the transport of the carbonates probably will be no farther than a few meters. As the cementation appears to occur early and under overburden pressure of a few meters, the donor of calcium carbonate, hence of strontium, can be nearly the same age as the receptor. Under this circumstance, the redistribution of strontium from the donor to the receptor will reveal the range of isotopic composition of strontium from these two sources.

If the cementation was subaerial, in a fresh-water eogenetic environment, small amounts of strontium would have been present in that water before it came into contact with the donor calcium carbonate. By coming into contact with the donor, the transporting fluid will have the strontium isotopic composition essentially the same as that of the donor. This becomes all the more apparent when one considers that the unstable calcium carbonate minerals (aragonite, high-Mg calcite) removed from the donor contain several hundred parts per million or more of strontium. Under this condition, the isotopic composition of the donor and the amount introduced will control the extent of strontium isotopic variation of the receptor. In the event of cementation in a submarine eogenetic environment, any variation in the isotopic composition in the receptor will depend upon: (1) the amount of strontium received from the donor, and (2) the extent of isotopic exchange that occurred between the seawater and the donor of carbonate cement. Because much of the lithification is early, the isotopic variation in the receptor will be in response to the varied isotopic composition of the contemporary seawater, from which the carbonate of both the donor and the receptor precipitated. The earlier discussion on the oxygen and carbon isotopic data on the limestone of the Open Door and

the Dunoir members favored primarily a marine source for these isotopes. The trace-element data, especially the Sr/Ca ratios and the Mn contents, suggest stabilization of the rocks in the presence of a large supply of fresh water. For the limestone units of the Dunoir and the Open Door members, lithification accompanied by cementation in either the subaerial, fresh-water eogenetic or the submarine eogenetic environments, or both, are compatible with the trace-element and isotopic data. The diagenesis in either environment will most likely preserve the range of strontium isotopic composition of contemporary seawater represented by the values of the primary carbonate mud and sand, and the newly-formed cement.

Cementation of the carbonate mud and sand leads to stabilization of the carbonate rocks. After much cementation has occurred in the early stage of lithification, little or no isotopic exchange or migration occurs between the residual pore fluids and either the overlying unconsolidated mass or the interstitial fluids associated with them. This proposition receives support from the observation made by Hofmann et al. (1972), who reported that the pore fluids associated with partially cemented carbonate materials from deep-sea cores of Cretaceous age have strontium isotopic compositions similar

to those of Cretaceous seawater. Similarly, the limestone of the Open Door and the Dunoir members can be kept isolated from contact with fluids of geologically later time. The isolation of the newly-lithified rock is greatly favored when the diagenesis has produced a stable, nearly monomineralic carbonate phase. The isotopic diffusion at this point is extremely slow. The study of the calcite-vein within a hand specimen from the Pilgrim Limestone shows that no effect of the ⁸⁷Sr-enriched introduced strontium can be found in the host-rock only a few millimeters away from the vein (Fig. 9). The same reasoning can be applied to explain why there is no isotopic homogeneity of a limestone at the time of its cementation.

Although most of the samples have their 87 Sr/ 86 Sr ratios between 0.70916 and 0.71055, there is one sample from the Dunoir Member and two from the Open Door Member that are significantly enriched in 87 Sr. The 87 Sr/ 86 Sr ratios of these samples range from 0.71132 to as high as 0.71350. The two samples of the Open Door Member (OD31 and OD35) are also high in Mg contents, and one of them is a dolostone (OD35). Their stratigraphic positions are also noteworthy. These two samples of the Open Door Member are located in the upper part of the unit, near the unconformity between the Open Door Member and the overlying Bighorn Dolomite. The

dolomitization appears to be restricted to the upper 1.5 meters of the Open Door Member, suggesting that the proximity of the samples to the unconformity made them highly susceptible to contact with continental waters. Therefore, the high 87 Sr/86 Sr ratio of the two samples from the Open Door Member can be explained by their contacts with ⁸⁷Sr-enriched meteoric water as a result of their proxmity to the unconformity. The high 87 Sr/86 Sr ratio in the sample (DU92) from the Dunoir Member, however cannot be explained in terms of its stratigraphic position. Elemental abundances do not provide any evidence that neomorphism of the rock took place in contact with percolating fresh water. The only available explanation at this time for the high 87Sr/86Sr ratio is that the sample contains about three percent feldspar, which may have provided radiogenic strontium at the time of acid-dissolution of the carbonate rock in the laboratory.

Two samples (CW5472 and CW5477) from a cored well in the Bighorn Basin have been interpreted to be from the Dunoir Member and three samples (CW5277, CW5287 and CW5416) from the same well, to be from the Open Door Member. Two samples (CW5287 and CW5477) that have high insoluble-residue contents, have high 87 Sr/86 Sr ratios that are attributed to the contribution from the silicate fraction. These values

are rejected. The remaining three samples (CW5277, CW5472 and CW5416) have 87 Sr/86 Sr values that range from 0.70969 to 0.71034. This range of 87 Sr/86 Sr values of the samples that have the lower insoluble-residue contents, is well within the ranges for the outcrop samples of the Dunoir (0.70924 to 0.71040) and Open Door (0.70916 to 0.71055) members. As these strontium isotopic ratios differ completely from reported values (0.7077 to 0.7088) for the overlying Bighorn Dolomite (Peterman et al., 1970), the Cambrian age for the core samples is confirmed. Although no values have been reported for the underlying Gros Ventre Formation, values reported for other Middle Cambrian rocks only partially overlap those of the Dunoir and Open Door members, so in theory these might be distinguished. Thus the strontium isotopic data can be useful for stratigraphic correlation in the subsurface, although in this case it could not be used to distinguish between two members of the same formation.

87 Sr/86 Sr Ratio of the Late Cambrian Sea

The strontium isotopic abundances of samples from the Dunoir and the Open Door members fall into two groups: one with values between 0.70916 and 0.71055 that define the isotopic composition of a great majority of the samples, and the other with values between 0.71132 and 0.71352 that represent the composition only of a few samples. samples with the high 87 Sr/86 Sr ratios are those that showed extensive dolomitization and had trace-element data that suggested open-system recrystallization. Considering a high probability that these rocks recrystallized in contact with fresh water having Sr isotopic compositions perceptibily different from those of the marine carbonate rocks, the high 87 Sr/86 Sr ratios between 0.71132 and 0.71352 cannot be representative of the strontium isotopic composition of the seawater in which these rocks were precipitated. question then is whether the range of the 87sr/86 Sr from 0.70916 to 0.71055, manifested by most of the samples, is representative of the Late Cambrian seawater in which they were deposited.

The rocks that have strontium isotopic values between 0.70916 and 0.71055 show evidences of neomorphism. The stable isotopic data do not give any clear-cut evidence of

any pervasive influx of fresh water during the diagenetic recrystallization of the carbonate deposits, although the trace-element data of the Dunoir Member tend to suggest open-system recrystallization. In earlier discussions on trace-element and isotopic data, arguments have been made that fluids involved in neomorphism were essentially of seawater composition, or that the fluids remobilized chemical components from within the sequence of the Upper Cambrian carbonate rocks, without significantly altering the overall chemical or isotopic composition of these rocks. This neomorphic process probably involved very little introduction of Sr that was externally derived and isotopically different from that in the carbonate rocks, except for those rocks that are adjacent to the unconformity between the Cambrian and Ordovician rocks. Strontium isotopic differences that exist among the different components within a hand specimen are suggestive of the lack of pervasive migration of fluids through these rocks that would otherwise have resulted in their isotopic homogeneity.

A pertinent question at this point is whether the range of 87 Sr/86 Sr ratios from 0.70916 to 0.71055, manifested by most of the samples, is the result of radiogenic strontium that was derived from local continental water. The chemical data from the rocks of the Dunoir and Open Door members

suggest that the range of 87 Sr/86 Sr ratios is not the effect of local drainage. Firstly, the Open Door Member, which was deposited in a lagoonal environment, shows the same strontium isotopic distribution as the rocks of the Dunoir Member, which were deposited closer to the shore. If periodic influxes of continental water contributed radiogenic strontium to the seawater, it would be possible to observe higher 87 Sr/86 Sr ratios in the rocks of the Dunoir Member than those of the Open Door Member. However, higher ratios are not identified.

Continental waters are commonly associated with high Mn contents (Veizer and Demovic, 1974) and high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. It therefore follows that, if continental waters contributed a large amount of radiogenic ^{87}Sr , then a corresponding increase in Mn content would also be observed. Poor correlations between the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and the Mn contents of the rocks of the Dunoir and Open Door members raise doubts about the local drainage being the controlling factor in the observed isotopic range.

Another strong argument against the effects of local drainage on the $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ ratios, comes from the fact that there is remarkable agreement between the data presented in this study (0.70916 to 0.71055) and the $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ ratios

(0.70914 to 0.71053) reported by Veizer and Compston (1974), for Australian carbonate rocks of Late Cambrian age. The agreement of the isotopic values is suggestive of uniformity in the strontium isotopic composition on a global scale, in which case the 87 Sr/ 86 Sr ratios are those of the Late Cambrian seawater.

At any particular geologic time, seawater is considered to be uniform in its strontium isotopic composition. reproducibility of 87 Sr/86 Sr ratios in rocks of similar age from different geographical localities, where the different geologic settings are likely to produce different secondary effects, is still considered to be the best test for ascertaining the strontium isotopic composition of seawater. The ⁸⁷Sr/⁸⁶Sr ratios measured in the Upper Cambrian rocks from the Bighorn Basin (0.70962 to 0.71082) are similar to the values for rocks from the Wind River Basin (0.70924 to 0.71040). A sample of the Pilgrim Limestone from southwestern Montana yielded 87Sr/86Sr ratios ranging from 0.70982 to 0.71000. The close agreement between the data presented in this report (0.70916 to 0.71055) and the values (0.70914 to 0.71053) reported by Veizer and Compston (1974) for Upper Cambrian carbonate rocks from Australia has been mentioned above. The agreement between the two sets of data from Australia and North America is remarkable.

reproducibility of the isotopic values among Upper Cambrian carbonate rocks suggests that the strontium isotopic composition of the Late Cambrian seawater varied between 0.70916 and 0.71055.

Acceptance of the range of the strontium isotopic values raises two pertinent questions. Is this range of the isotopic values possible for a time interval as long as the Late Cambrian? Did the isotopic composition of the seawater change as observed in the carbonate rocks?

The ⁸⁷Sr/⁸⁶Sr values for the Dunoir Member and the Open Door Member fluctuate randomly within a vertical sequence. This fluctuation is not a representation of the variation of the strontium isotopic composition of the contemporary seawater. Clearly, the three different ⁸⁷Sr/⁸⁶Sr ratios (0.70916, 0.70928 and 0.70938) measured in three carbonate phases from within a hand specimen of the Open Door Member cannot represent three separate isotopic values for nearly the same seawater. In earlier discussions of the trace-element, stable isotopic and strontium isotopic data, the differences within a hand specimen have been attributed primarily to the internal redistribution of strontium within the marine carbonate sequence.

The observed ⁸⁷Sr/⁸⁶Sr values in the Dunoir Member and the Open Door Member could have resulted from the mixing, within the stratigraphic units, of Sr of different isotopic composition. It is apparent, however, that there were at least two sources, the isotopic compositions of which can be described by the highest and the lowest ⁸⁷Sr/⁸⁶Sr ratios of 0.71055 and 0.70916, respectively.

The strontium isotopic data presented in this study are for the rocks of the Upper Cambrian, which spans a time interval of approximately 15 million years (Faure, 1977). difference of 0.0014 exists between the highest and the lowest 87Sr/86Sr ratios. Considering the dispersion that exists in strontium isotopic values for other geologic periods, the spread in the 87sr/86sr for the Late Cambrian is not unusual. For example, the difference between the highest and the lowest 87sr/86sr values is 0.0010 for both the Neogene, which spanned 24 million years, and the Late Permian, which spanned 15 million years (Faure, 1977). It is, therefore, evident that a single 87 Sr/86 Sr value cannot be ascribed to a particular geologic period or epoch that may cover a time interval of several million years. However, until the time-dependent variation of the isotopic composition of seawater is refined to small and discrete intervals of time, such as a million years, the assigning of

ranges of 87 Sr/86 Sr ratios would be more appropriate than assigning a single 87 Sr/86 Sr value. Geochemists are in the process of studying rocks that represent small intervals of time, and data are being added to a growing body of information regarding the strontium isotopic composition of seawater during geologic time.

CONCLUSIONS

The results of this study support the following conclusions:

- Based on Sr/Ca ratios and Mn contents, the rocks of the Dunoir Member appear to have undergone diagenesis in a relatively more open system than the rocks of the Open Door Member.
- Carbon and oxygen isotopic composition of the carbonate rocks are similar to values reported for Paleozoic marine carbonate rocks.
- 3. Excepting the rocks that have been dolomitized, the \$87\$sr/86\$sr ratios of the limestone from the Dunoir and Open Door members range between 0.70916 and 0.71055.

 The dolomitized rocks have \$87\$sr/86\$sr ratios greater than 0.71132.
- 4. The ⁸⁷Sr/⁸⁶Sr ratios of core samples are within the range of ⁸⁷Sr/⁸⁶Sr ratios obtained for outcrop samples. However, based on ⁸⁷Sr/⁸⁶Sr ratios, stratigraphic correlation could not be made between the core samples and outcrop samples at the level of formation members.

- 5. The range of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the carbonate rocks is similar to the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios reported for Australian carbonate rocks of equivalent age.
- 6. The strontium isotopic composition of the Late Cambrian seawater appears to have varied between 0.70916 and 0.71055.

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GEOCHEMISTRY OF CARBONATE ROCKS OF LATE CAMBRIAN AGE, NORTHWESTERN WYOMING, AND INFERENCES FOR STRONTIUM ISOTOPIC COMPOSITION OF LATE CAMBRIAN SEAWATER

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This study was an attempt to provide information regarding the strontium isotopic composition of the Late Cambrian seawater. To achieve this objective, carbonate rocks from outcrops of the Dunoir and Open Door members of the Gallatin Formation of Late Cambrian age in northwestern Wyoming were analyzed. In addition, samples of the two members from a cored well were analyzed to determine the feasibility of the use of strontium isotopic data as a stratigraphic tool in geologic settings where the strata are repeatedly faulted and where stratigraphic relationships are difficult to establish. The Ca contents in the limestones range from 37 to 40 percent, Sr from 164 to 739 ppm and Mn from 104 to 498 ppm. The dolomitic rocks have Mg contents that range from 1 to 9 percent, Ca from 15 to 39 percent, Sr from 76 to 555 ppm and Mn from 69 to 252 ppm. contents in all the carbonate rocks were less than 0.5 ppm. Based on the Sr/Ca ratios and Mn contents, the rocks of the Dunoir Member are interpreted to have undergone diagenesis in a relatively more open system than the rocks of the Open Door Member. The carbon isotopic abundances in the carbonate rocks range from -0.33 to +1.05 per mil (PDB), and oxygen isotopic abundances range from +20.87 to +23.14 per mil (SMOW). The carbon and oxygen isotopic compositions of the carbonate rocks are similar to those reported for

Paleozoic marine carbonate rocks. Excepting the rocks that have been dolomitized, the 87sr/86sr ratios of the limestones of the Dunoir and Open Door members range between 0.70916 and 0.71055. The dolomitized rocks have 87 Sr/86 Srratios that are greater than 0.71132. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the core samples are similar to the 87 Sr/86 Sr ratios of the outcrop samples; however, no distinction could be made between the rocks of the Dunoir and the Open Door members on the basis of 87 Sr/86 Sr ratios. The range of 87 Sr/86 Srratios (0.70916 to 0.71055) of the limestones of the Dunoir and Open Door members is similar to the 87 Sr/86 Sr ratios (0.70914 to 0.71053) reported for Australian carbonate rocks of Late Cambrian age. This agreement between the two sets of data from North America and Australia is suggestive of uniformity in strontium isotopic composition of seawater on a global scale, in which case, the range of the 87sr/86sr ratios is that of the Late Cambrian seawater.