# GEOCHEMISTRY OF CARBONATE CEMENTS IN SURFICIAL ALLUVIAL CONGLOMERATES AND THEIR PALEOCLIMATIC IMPLICATIONS, SULTANATE OF OMAN

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ABSTRACT: Early diagenetic carbonate cements are a common feature of Quaternary alluvial conglomerates in Oman. Cements are formed in the vadose and, more commonly, phreatic zones from near-surface groundwaters. In drainage areas underlain by the Semail Ophiolite, groundwaters have $Mg^{2+}/Ca^{2+}$ ratios greater than two, and cements are often dolomite or high-magnesium calcite in addition to low-magnesium calcite. In drainage areas underlain by limestone, groundwaters have $Mg^{2+}/Ca^{2+}$ ratios of around one or less and cement mineralogy is nearly always low-magnesium calcite. The oxygen and carbon stable isotopic ratios of the cements vary widely, from $-10.6‰$ to $+3.0‰$ PDB and from $-10.0‰$ to $+0.7‰$ PDB, respectively. Cement $\delta^{18}O$ values principally reflect variation in rainfall $\delta^{18}O$ over a time scale of several thousand years. Rainfall and cement $\delta^{18}O$ values probably are inversely correlated with the amount of rainfall, which is related to the frequency and intensity of the Indian Ocean monsoon. Thus, cement $\delta^{18}O$ is potentially a proxy indicator of relative rainfall and monsoon activity. For each of three sampling areas, $\delta^{13}C$ is positively correlated to $\delta^{18}O$. Cement $\delta^{13}C$ values are also related to rainfall amount because rainfall controls the plant population. Greater plant respiration of isotopically depleted $CO_2$ to shallow groundwaters and burial of organic material in conglomerate deposits results in lower cement $\delta^{13}C$ values compared to periods of lesser plant activity.

## INTRODUCTION

Alluvial conglomerates, either as valley-fill deposits or alluvial fans, are major components of terrestrial depositional systems, particularly in areas of high relief. To date, the study of alluvial fans has concentrated almost wholly on their morphology and sedimentology, although application of this information to paleoenvironmental studies is also common. One major component of any alluvial fan system, and one that has received scant attention, is early diagenetic cements. In a recent compilation of 19 papers on alluvial fans, only one mention of cements is made in the entire volume (Rachocki and Church 1990). The relatively few papers that do concentrate on cements in alluvial conglomerates are either outcrop-scale descriptions (Lattman 1973; Reeves 1983) or concentrate only on pedogenic carbonates (e.g., Schlesinger 1985). Only Barnes and O'Neil (1971) previously investigated the elemental and isotopic chemistry of cements in alluvial conglomerates. Yet early cementation, not necessarily associated with pedogenesis, may be common in such conglomerates (e.g., Spötl and Wright 1992). Cementation surely both affects and reflects the hydrology of depositional systems and is a major factor in the preservation of alluvial deposits (Maizels and McBean 1990).

A further interest in carbonate cements in alluvial systems is their potential as paleoclimate indicators. While the depositional history (e.g., Abrams and Chadwick 1994) and morphology (e.g., Maizels and McBean 1990) of alluvial gravels have been used to interpret various aspects of climate at the time of deposition, cements themselves seem never to have been utilized. Yet, because early carbonate cements are precipitated near-surface from shallow groundwaters, their oxygen and carbon stable isotopic ratios certainly hold information about near-surface environmental conditions. Stable isotopes of pedogenic carbonates have long been used as paleoclimate indicators (Cerling et al. 1977), and recent work (Hays and Grossman 1991) suggests that the isotopic composition of meteoric cements should also be useful as a paleoclimate tool.

Here, we discuss the origin and geochemistry of carbonate cements in

alluvial conglomerate deposits in Oman, where recent uplift of the Oman Mountains has resulted in deposition of extensive coarse, alluvial deposits in and around the mountains. The goals of this study are to (1) document the types of early carbonate cement in alluvial gravels in Oman, (2) determine what controls their mineralogy in various locations underlain by different rock types, and (3) determine what controls the isotopic composition of carbonate cement, with particular emphasis on the role of climate.

## BACKGROUND

The geology of Oman has received much study (see, e.g., Robertson et al. 1990; Peters et al. 1991) and is renowned for the world's largest and best exposed obducted ophiolite complex. The basic stratigraphy of the Oman Mountains region is summarized here because the rocks weathering at the surface are the clastic sources of recent surficial deposits. The composition of clasts in the conglomerates affects the chemistry of shallow groundwaters and early diagenetic cements.

The stratigraphic column of Oman can be divided into four major rock units: (1) the Precambrian to Cretaceous allochthonous succession of sedimentary rocks, mainly carbonates, underlying the ophiolite, (2) the Hawasina Complex of overthrusted marine sediments, which range from shallow-water limestones to radiolarites, (3) the Semail Ophiolite, a mafic to ultramafic section of oceanic crust and mantle, and (4) late Maastrichtian to Tertiary neo-autochthonous shallow-water carbonates (Glennie et al. 1974). Thus, of the four main rock units, three are mainly carbonate and dominantly limestone. The ophiolite varies somewhat in composition, with the crustal rocks composed mainly of gabbros and basalts, and the mantle sequence dominantly serpentinized harzburgite (olivine and orthopyroxene) (Glennie et al. 1974; Lippard et al. 1986).

The modern climate of Oman is hot and arid. For example, Sohar, on the north coast of Oman, has a mean annual air temperature over the last 30 years of 26.2°C, with monthly averages from 19.7° to 33.1°C, annual average rainfall of 104 mm, and annual potential evapotranspiration of 2630 mm (Food and Agriculture Organization, United Nations, 1987). Rainfall can locally be quite intense, however, with several years' average falling in one event.

The Oman Mountains are a rugged terrain of high topographic relief (> 1500 m) with a typical mountainous-desert geomorphology and a highly dissected drainage pattern. Coarse alluvial sediments partly fill intramontane wadis and empty onto gravel plains on either side of the mountains. Gravel thicknesses within the mountains can be as much as 100 m. On the margins of the Oman Mountains, alluvial gravel fans extend tens to hundreds of kilometers to the north and south, and the total thickness is probably several hundred meters (Maizels 1987 and references therein), though individual depositional units are usually much thinner (Maizels 1987; Abrams and Chadwick 1994).

The ages of the alluvial gravels are not precisely known. No attempts at directly dating the deposits have been made. Extensive alluvial gravel formation, however, is unlikely prior to development of significant relief in the Oman Mountains, which has mainly taken place since the Miocene (Glennie et al. 1974; Mann et al. 1990 and references therein). For the Batinah coast area, Abrams and Chadwick (1994) tentatively correlated the gravel sequence in Oman to that of Saudi Arabia, suggesting ages from Late Pliocene to recent. South of the Oman Mountains, the oldest alluvial conglomerates are probably Late Pliocene in age (Maizels 1987).

## SAMPLES AND METHODS

Sampling sites were chosen to reflect the variety of rock types found at the surface. A total of 63 samples were taken mainly from three areas (Fig 1): (1) Wadi Hashimi, within the Oman Mountains, (2) south of the Oman Mountains, near the town of Barzaman, in the Wadi Andam drainage, and (3) near Sur, in the northeast corner of Oman. The Wadi Hashimi area is in the northern Oman Mountains about 60 km southwest of the town of Sohar. The drainage area of the wadi is composed entirely of the ophiolite complex. The wadi fill is composed of at least two generations of well-cemented gravels, approximately 80 m of which have been exposed by later downcutting. The younger generation was deposited as a terrace within the older eroded gravels. Most samples were taken from two measured sections within the wadi. A number of additional samples were taken from two other wadis in the same area, Wadi Ahin and Wadi Sudari.

The second sampling area was within the Wadi Andam drainage, near the town of Barzaman, about 50 km south of the Oman Mountains (Fig. 1). The catchment of the wadi now extends into the Semail Ophiolite, but most of its drainage is from areas floored by the Hawasina Complex of limestones and cherts. The exposed gravels are exhumed remnants of wadi paleo-channel courses, and at least 12 paleochannel generations have been identified (Maizels and McBean 1990). Clast composition changes systematically through the sequence, with the older generations having up to 80% chert and few ophiolite clasts and the younger generations containing less than 10% chert and over 90% ophiolite clasts (Maizels and McBean 1990). We sampled from paleochannel generations that we thought we could confidently identify: 1, 2, 3, 6, 7, 8, and 9.

Samples were also taken from several locations near the town of Sur in northeast Oman. The area is surrounded mainly by the Maastrichtian to Tertiary carbonate platform, though some outcrops of the Hawasina Complex are also found in the drainage area. Clasts of the gravels are accordingly mainly biogenic limestones together with lesser amounts of cherts. Samples were mainly collected from an ∼ 60 m thick sequence of gravels exposed in a wadi 2.5 km south of the town. Additional samples were collected from gravels along the coastal outcrops about 10 km east of town and 15 km west of the town, and from the Wadi Falaij, 25 km south of town.

Eight water samples were collected from perennial springs or pumped from wells. Standing surface waters were not sampled. Temperature and pH were measured during collection, and alkalinity was measured in the field by titration within 24 hr. A split of each sample was poisoned with HgCl. These samples were later analyzed for $SO_4^{2-}$, $NO_3^{2-}$, $PO_4^{3}$, $Ca^{2+}$, $Mg^{2+}$, and $Sr^{2+}$ by ion chromatography. Unpoisoned samples were analyzed for $Cl^-$ and $Na^+$, also by ion chromatography. Hydrogen and oxygen isotopic ratios were also measured on the unpoisoned portion of each sample.

Thin sections were prepared from all samples and were studied using a variety of techniques, including a standard light microscope and UV fluorescence. In addition, a few samples from each area were studied under cathodoluminescence (CL). For CL work, polished, aluminum-coated thin sections were bombarded with a 30 keV electron beam at a current density of 0.3 $\mu A/mm^2$.

The mineralogy of the cements was determined by X-ray diffraction (XRD). A small amount of cement was either drilled from the pore spaces, if enough cement was present, or scraped by hand from clast surfaces. The position of the 10.4 reflection relative to a quartz internal standard was used to estimate the magnesium concentration (Goldsmith et al. 1961). Estimated error is ± 1 mole %.

Approximately 5 mg of the same powder used for XRD analysis was used for determination of carbon and oxygen stable isotope ratios. For samples containing one mineral, or where there was only a trace concentration of a second carbonate, the samples were analyzed using an on-line automated carbonate preparation system linked to a VG Prism ratio mass spectrometer. The four samples containing both calcite and dolomite were

leached in an off-line system, at 50°C, to obtain analyses from each mineral. The $CO_2$ produced was collected and purified in three steps: (1) the $CO_2$ evolved after 15 minutes was collected, (2) gas evolved from 15 to 30 minutes was pumped away, and (3) $CO_2$ was again collected after approximately 12 hr. Tests with mixtures of calcite and dolomite of known composition show that the first portion of gas collected is almost wholly from calcite, with only minor contamination from dolomite, and the second aliquot of gas is only from dolomite. Analytical reproducibility for standard materials in both on-line and off-line systems is 0.08‰ for $\delta^{18}O$ and 0.04‰ for $\delta^{13}C$. All analyses are reported relative to the PDB standard, and all samples were corrected using the phosphoric acid fractionation factor for calcite at the appropriate temperature. No correction for the difference in phosphoric acid fractionation factors between dolomite and calcite was applied to the dolomite samples.

## RESULTS

### Mineralogy

Carbonate cements in the alluvial gravels are dolomite, low-magnesium calcite (LMC), and high-magnesium calcite (HMC). Dolomites are generally calcium-rich, ranging from 41 to 50 mole % magnesium. HMC compositions are from 7 to 13 mole % magnesium, and LMC from 1 to 4 mole % magnesium (Table 1). Cement composition is strongly dependent on location (Table 2). Within the Oman Mountains, the majority of samples contain HMC or dolomite, though calcite is also common. In the Barzaman and Sur areas, the great majority of the cements were calcite. Only one sample contained HMC and 5 samples contained dolomite (Table 2). Calcites from the Sur area all have comparatively low magnesium contents (Table 1). In general, the cements within any one sample are of only one composition. Only 10 of 63 samples have two minerals, usually HMC or dolomite in addition to calcite, and one sample contained HMC and dolomite (Table 1).
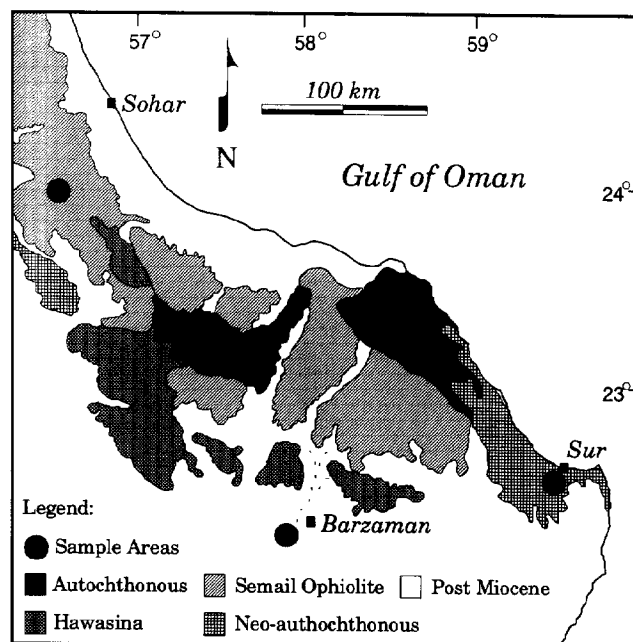


Fig. 1.—Generalized geologic map of Oman Mountains in northeast Oman showing the three major sampling areas and the four major rock units. See text for details of rock units.

TABLE 1.—*Cement mineralogy and isotopic composition*

| Sample | Location | Mineralogy | $\delta^{13}C$ | $\delta^{18}O$ | mol% Mg |
|---|---|---|---|---|---|
| OM92- | Oman Mountains | | | | |
| 1 | Wadi Al Hashimi | HMC + DOL | -8.1 | -1.1 | 10 |
| | | | -8.5 | -2.7 | 47 |
| 2 | - | HMC | -6.2 | 0.1 | 13 |
| 3 | - | CAL | -7.6 | -1.9 | 1 |
| 4 | - | HMC | -1.9 | 1.5 | 7 |
| 5 | - | HMC | -5.5 | 0.6 | 11 |
| 6 | - | HMC | -6.6 | 0.4 | 10 |
| 7 | - | CAL | -3.9 | -0.6 | 4 |
| 8 | - | CAL | -7.7 | -2.3 | 1 |
| 9 | - | CAL ≫ DOL | -0.3 | 2.0 | 4 (44) |
| 10 | - | CAL | -7.0 | -1.1 | 2 |
| 11 | - | CAL | -0.2 | 3.0 | 4 |
| 75 | - | CAL | -5.3 | -0.2 | 1 |
| 76 | - | DOL | -8.0 | -1.3 | 45 |
| 12 | - | CAL ≫ DOL | -1.8 | 2.7 | 2 (47) |
| 13 | Wadi Sudari | CAL + DOL | -9.7 | -2.3 | 2 |
| | - | | -8.6 | -2.2 | 46 |
| 15 | Wadi Al Hashimi 2 | HMC ≫ DOL | -3.8 | -1.7 | 10 (48) |
| 16 | - | DOL | -6.3 | 0.1 | 47 |
| 17 | - | DOL | -6.1 | -1.3 | 46 |
| 18 | - | DOL | -5.9 | -1.0 | 47 |
| 19 | - | CAL + DOL | -6.7 | 0.6 | 4 |
| | - | | -5.2 | 2.2 | 41 |
| 20 | - | DOL | -5.2 | 2.6 | 42 |
| 21 | - | DOL | -5.5 | 1.6 | 44 |
| 22 | - | DOL | -5.5 | 0.0 | 50 |
| 23 | - | DOL | -4.4 | -0.0 | 45 |
| 24 | Wadi Ahin | CAL | -6.8 | -2.2 | 4 |
| 25 | - | CAL | -7.0 | -3.2 | 2 |
| 26 | - | CAL | -6.2 | -1.5 | 2 |
| 27 | - | CAL + DOL | -6.6 | -1.0 | 1 |
| | - | | -7.6 | 0.1 | 44 |
| 77 | - | DOL | -8.0 | -0.7 | 46 |
| 78 | - | DOL | -7.8 | -0.3 | 44 |
| 79 | - | CAL | -6.9 | -0.5 | 2 |
| | Sur Area | | | | |
| 30 | 2.5 km S of Sur | CAL | -9.1 | -9.1 | 1 |
| 31 | - | CAL | -9.3 | -9.4 | 1 |
| 32 | - | CAL | -8.8 | -9.0 | 1 |
| 33 | - | CAL | -10.0 | -10.6 | 1 |
| 34 | - | CAL | -9.3 | -9.7 | 1 |
| 35 | - | CAL | -8.4 | -8.8 | 1 |
| 36 | - | CAL | -9.0 | -9.3 | 1 |
| 37 | - | CAL | -9.0 | -8.8 | 1 |
| 38 | Coast E of Sur | CAL | -5.7 | -6.9 | 1 |
| 39 | - | CAL | -5.9 | -6.5 | 1 |
| 40 | Wadi Falaij | CAL | -1.8 | -3.3 | 1 |
| 41 | - | CAL ≫ DOL | -4.2 | -4.5 | 2 (43) |
| 42 | - | CAL | -4.3 | -4.8 | 1 |
| 73 | Coast W of Sur | CAL | -4.7 | -4.6 | 1 |
| 74 | - | CAL | -4.3 | -5.2 | 1 |
| | South of Oman Mountains | | | | |
| 60 | Huqf Area | CAL | 0.7 | -0.5 | 2 |
| 61 | - | CAL ≫ DOL | 0.3 | -0.9 | 4 (47) |
| 62 | Barzaman (6)* | CAL | -6.6 | -3.2 | 2 |
| 63 | - (6) | CAL | -5.6 | -2.7 | 1 |
| 64 | - (6) | CAL | -7.6 | -3.1 | 2 |
| 65 | - (7) | CAL | -3.5 | -1.6 | 2 |
| 66 | - (7) | CAL | -3.5 | -0.9 | 2 |
| 67 | - (8) | HMC + CAL | -6.5 | -2.5 | 10 (2) |
| 68 | - (2) | CAL | -7.6 | -7.3 | 2 |
| 69 | - (1) | DOL | -8.2 | -6.7 | 44 |
| 70 | - (3) | CAL | -6.3 | -5.7 | 2 |
| 71a | - (9) | CAL | -5.1 | -1.7 | 2 |
| 71b | - (9) | CAL | -4.9 | -1.0 | 2 |
| 72 | - (7) | DOL | -5.6 | -1.6 | 42 |

\* Numbers refer to gravel sequence as identified by Maizels and McBean (1990).

TABLE 2.—*Mineralogy by location*

| Location | No. w/LMC* | No. w/HMC | No. w/DOL |
|---|---|---|---|
| Wadi Al Hashimi | 8 | 5 | 4 |
| Wadi Sudari | 1 | 0 | 1 |
| Wadi Al Hashimi 2 | 1 | 1 | 9 |
| Wadi Ahin | 5 | 0 | 3 |
| S of Sur | 8 | 0 | 0 |
| Wadi Falaij | 3 | 0 | 0 |
| Coast | 4 | 0 | 0 |
| Barzaman | 10 | 1 | 2 |

\* Number of samples containing LMC, etc.

## Petrography of Cements

Extent of cementation, crystal size, and cement morphology vary widely. The least cemented samples have micritic or finely crystalline cements developed only at grain-to-grain contacts (Fig. 2B). These cements often show a meniscus morphology. In some cases, poorly cemented samples also contain finely crystalline pendant cement on the undersides of clasts. Micritic cements are often found together with fine internal sediment, which is preferentially found on the upper surface of clasts (Fig. 2A). HMC cements are present almost exclusively as micrite.

The most common cement morphology is fine to medium crystalline isopachous cement, and in most samples it was precipitated directly onto clasts as the first layer of cement. Isopachous cements range from a discontinuous fringe of poorly formed rhombs of dolomite (Fig. 2C), to continuous rims of very fine spar (Fig. 2D), to medium-grained isopachous crystals (Fig. 2E). The most completely cemented samples are also the most coarsely crystalline. These are mainly hypidiotopic (Gregg and Sibley 1984) blocky dolospar, and drusy pore-filling calcite (Fig. 2G).

In the great majority of samples only one generation of cement is seen. There can, however, be as many as three to four different cement layers (Fig. 2F). In about 10% of the samples, isopachous cement is precipitated on top of a micritic meniscus cement. In several samples there are multiple generations of isopachous cement (Fig. 2F). Internal sediment cemented by micrite is also found on top of isopachous cements in a few samples.

Porosity in the conglomerates is dominantly original intergranular porosity. A secondary porosity type of lesser importance is an unusual type of moldic porosity. After cementation there often appears to be further weathering of the ultramafic clasts, which results in dissolution of the outer surfaces of clasts and possibly the inner surfaces of cements. The result is an envelope of porosity between the cement and the ultramafic clast. In one or two instances a later generation of cement was precipitated within this pore space, i.e., on the inside surface of the original cement.

**Cathodoluminescence and UV Fluorescence.**—All samples were also studied under blue UV light. The UV fluorescence characteristics of cements were highly dependent on grain size. Micritic cements, particularly the vadose micrite cements, usually showed medium to bright fluorescence. The coarser-grained sparry cements were almost uniformly nonfluorescent and homogeneous (Fig. 2 G, H). Multiply zoned spar cements were found in only two samples.

Ten samples were also analyzed using CL. Only one showed alternating bright and dull luminescing zones. In all others, the cements were nonluminescent and nonzoned (see also Stalder 1975). Small discrete areas in some samples were slightly luminescent.

## Water Chemistry

Results on chemical and isotopic analyses of the waters (Table 3) in general agree with a much more extensive study of ground waters and surface waters by Neal and Stanger (1985 and references therein) and show that the ground waters and surface waters are of three types: hyperalkaline (pH > 11), $Ca^{2+}-OH^-$ springs, (Sample OW-1); a $Na^+-Cl^-/Mg^{2+}-HCO_3^-$ type water with $Mg^{2+}/Ca^{2+}$ ratio greater than about 3(OW 2-5); and a similar water with $Mg^{2+}/Ca^{2+}$ around 1(OW 6-8). Oxygen and hydrogen isotopic ratios for all waters fall into a relatively narrow range, from ±1‰ $\delta^{18}O$ (vs. SMOW) and ±10‰ $\delta D$.

The hyperalkaline water discharges along either the basal thrust of the ophiolite or where the crust-mantle boundary within the ophiolite crops out. Because of their very high pH and high $Ca^{2+}$ concentrations, these waters have partial pressures of $CO_2$ far below atmospheric $p_{CO_2}$. Upon reaching the surface, they immediately absorb $CO_2$ from the atmosphere and precipitate calcite or aragonite, which results in locally large accumulations of travertine and locally cements gravels. On a large scale, such
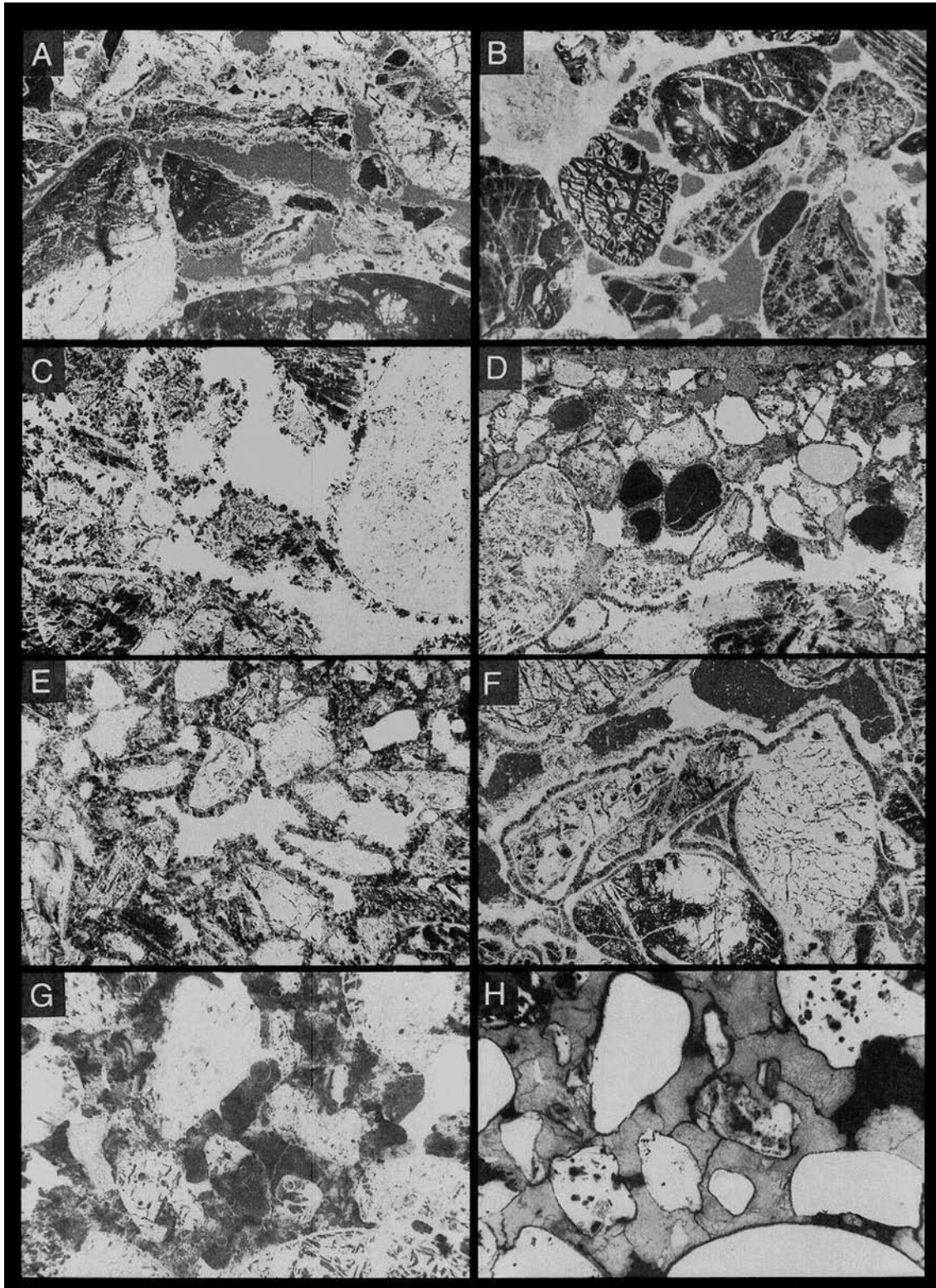
FIG. 2.—Thin-section photomicrographs: A) OM92-25, calcite-cemented vadose silt and pendant calcite spar, both vadose-zone cements, plane light (PL); B) OM92-66, vadose micrite cement (PL); C) OM92-18, isopachous fringe of poorly formed dolomite rhombs, crossed-polarized light (CPL); D) OM92-61, thin fringe of isopachous calcite spar (CPL); E) OM92-5, medium-grained, isopachous dolomite spar (CPL); F) OM92-22, multiple generations of dolomite cements, both microspar and dolomicrite (PL); G) OM92-71b, blocky pore-filling calcite (CPL); H) same as G but viewed under blue fluorescence showing typical uniform fluorescence. Photomicrographs A D, E, G, and H are 2.5 mm, B and F are 1.0 mm, and C is 0.5 mm across the bottom, respectively.

TABLE 3.— Water samples: isotopic and major-element chemistry by location

| Location: | Sur | Barzaman | | Oman Mountains | | | | |
|---|---|---|---|---|---|---|---|---|
| Component | OW-8 | OW-7 | OW-6 | OW-5 | OW-4 | OW-3 | OW-2 | OW-1 |
| δD (‰ SMOW) | 4.8 | 3.9 | 2.4 | 5.9 | -4.5 | -4.1 | -4 | -9.3 |
| δ¹⁸O (‰ SMOW) | 0.3 | 0.5 | 0.1 | 0.0 | -0.6 | -0.6 | -0.9 | -2.4 |
| pH | 7.56 | 7.44 | 7.68 | 7.95 | 8.99 | 8.47 | 10.3 | 11.57 |
| Tot Alk (meq) | 4.82 | 5.91 | 5.36 | 4.86 | 3.66 | 4.75 | 3.32 | 6.94 |
| Cl mmol | 13.1 | 21.0 | 5.2 | 4.7 | 1.9 | 2.8 | 5.6 | 6.1 |
| SO₄² - | 11.1 | 8.0 | 1.5 | 0.5 | 0.4 | 0.4 | 0.4 | 0.0 |
| Na⁺ - | 17.79 | 22.97 | 6.35 | 3.86 | 2.02 | 2.15 | 6.78 | 9.44 |
| Mg²⁺ - | 4.36 | 5.88 | 2.13 | 2.04 | 1.51 | 2.24 | 0.90 | 0.02 |
| Ca²⁺ - | 5.79 | 3.79 | 1.60 | 0.71 | 0.30 | 0.50 | 0.07 | 1.27 |



FIG. 3.—Cross plot of $\delta^{18}O$ vs. $\delta^{13}C$ for carbonate cements from each of the three sampling areas. Linear-regression data for each area: for Oman Mountains $r^2 = 0.51$, slope = 1.00; for Barzaman $r^2 = 0.67$, slope = 0.54; for Sur Area $r^2 = 0.97$, slope = 1.10.

waters are also found as deeper groundwaters throughout the mantle sequence rocks in the Oman Mountains (Neal and Stanger 1985).

The major difference between the other two waters is their $Mg^{2+}/Ca^{2+}$ ratio. Waters with $Mg^{2+}/Ca^{2+}$ ratios generally greater than 2 are found in drainage basins composed mainly of mafic and ultramafic rocks where near-surface weathering of Mg bearing minerals results in Mg-rich waters, though specific reactions are difficult to define (Neal and Stanger 1985; Stanger and Neal 1994). In drainage basins that are partly or wholly within carbonate terranes the groundwaters are similar in overall composition but usually have $Mg^{2+}/Ca^{2+}$ ratios of 1 or lower due to carbonate dissolution (Neal and Stanger 1985; Stanger and Neal 1994). Both of these waters have $Na^+$ and $Cl^-$ contents well in excess of local precipitation, which contains on average 6 ppm $Cl^-$ (Neal and Stanger 1985).

### Stable Isotope Results

Isotopic results are shown in Table 1 and Figure 3. Overall, $\delta^{18}O$ varies from -10.6‰ and +3.0‰ and $\delta^{13}C$ from -10.0‰ to 0.7‰. For individual areas there is somewhat less variation. Samples from the Sur area tend to have the lowest and the Oman Mountains the highest $\delta^{13}C$ and $\delta^{18}O$ values (Fig. 3). There is a positive correlation between oxygen and carbon isotopic values for individual areas (Fig. 3). This relationship is expressed best in the Sur area and most poorly in the Oman Mountains. The stable isotope values are not correlated to cement composition.

### DISCUSSION

#### Cement Formation

The alluvial conglomerate cements in Oman precipitate from shallow groundwaters in both the vadose and, more commonly, the phreatic zones. The observed meniscus and pendant cement morphologies are typical of vadose-zone cement. Micrite-cemented, fine-grained internal sediment, often termed "vadose silt", also suggests vadose-zone cementation. The great majority of the carbonate cements, however, do not show these features, but consist of fine to coarse isopachous or pore-filling cement and are interpreted to be phreatic in origin. All cements must have precipitated relatively near surface, because none of the conglomerates have ever been buried to more than perhaps 100 m or so. All the cements appear to be primary precipitates because there is no replacement of framework grains, and no "floating grain" textures are observed.

Lack of cathodoluminescence is also consistent with near-surface precipitation. It indicates cement precipitation under mainly oxidizing water conditions with low Mn concentrations. Lack of zoning in either CL or UV light suggests that the cements formed in a relatively short time, during which pore-fluid chemistry was relatively constant. Different cement generations were the exception when viewed under plain light. CL and UV study generally confirms that what appear in plain light to be individual cement layers, even coarsely crystalline examples, are not actually composed of multigeneration cements precipitated over long time periods.

In contrast to many desert areas, carbonate cementation of alluvial
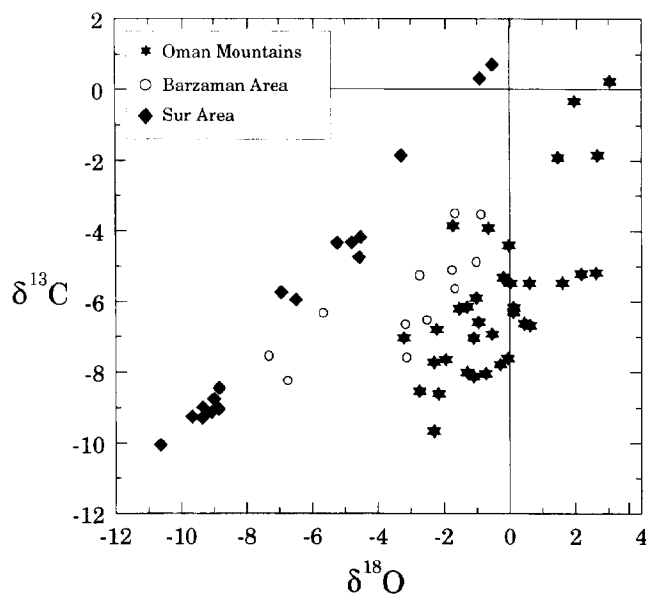
gravels in Oman is apparently not chiefly associated with pedogenesis. There is an almost complete lack of either well-developed massive or laminated calcretes and even of any typical pedogenic calcrete structures such as nodular textures, brecciation, rhizocretions, or pisoids (Wright 1992). In addition, most Quaternary pedogenic calcretes or dolocretes are relatively thin 1-3 m layers (Wright and Tucker 1991), whereas the cemented gravel zones in Oman may be up to 50 m thick. Lack of pedogenic carbonate formation may be due to scant vegetative cover and lack of significant soil formation in most areas. By some definitions (Wright 1992), the phreatic cements found in Oman could be termed groundwater calcretes, though they are often fairly coarse-grained and do not generally form in discrete layers.

The specific mechanisms of precipitation are not precisely known. Wright and Tucker (1991) suggested that the most likely causes for precipitation of groundwater calcretes are $CO_2$ degassing, evapotranspiration, or the common-ion effect during mixing of groundwaters. Without long-term monitoring of groundwater chemistry it is difficult to evaluate the relative importance of these mechanisms in Oman. The latter, however, seems least likely because there is generally only one shallow groundwater type in a given drainage. In Oman, it is also possible that rapid weathering of unstable ultramafic clasts results in release of $Ca^{2+}$ and $Mg^{2+}$ and $OH^-$ to the groundwaters, which would promote carbonate precipitation.

The main control on cement mineralogy and composition is bedrock type, which controls the $Mg^{2+}/Ca^{2+}$ ratio of the surface waters. As explained above, weathering of ultramafic rocks in drainage areas of the Oman Mountains results in surface waters with $Mg^{2+}/Ca^{2+}$ ratios usually greater than 2, and precipitation of HMC and dolomite cements is common (Table 2). The precise relationship between the magnesium content of the samples and the $Mg^{2+}/Ca^{2+}$ ratios of the groundwaters is less clear. Of the samples collected for this study, none had magnesium contents between 13 and 40 mole %, though Stalder (1975) reported one example of HMC with 30 mole % in the Oman Mountains. Barnes and O'Neil (1971), in a study of quite similar cements, found a much wider range of magnesium contents, with up to 50 mole % magnesium found in calcite-like structures. The samples analyzed by Barnes and O'Neil, however,

were only as old as 7000 yr B.P. The scarcity of very magnesium-rich calcites in Oman, despite modern groundwaters with a wide range of $Mg^{2+}/Ca^{2+}$ ratios, may simply be due to the highly metastable nature of such compositions and the greater age of the Oman gravels.

In contrast to the Oman Mountains, the bedrock types in the Sur and Barzaman areas include carbonate rocks. Surface waters in both areas have $Mg^{2+}/Ca^{2+}$ ratios around 1 or lower, and LMC is the main cement mineral (Table 2). The bedrock control on groundwater composition shows that changes in cement composition from LMC to HMC to dolomite are not related to changes in depositional environment, and thus the compositions are not themselves environmental indicators.

## Stable Isotopes

Oxygen Isotopes.—The oxygen isotopic composition of carbonate cement is directly controlled by temperature and the isotopic composition of the precipitating fluid. For the cements studied here, however, temperature is not likely to have directly played an important role, because all the samples are products of near-surface precipitation, where temperature is likely to have been relatively constant. Changes in average near-surface water temperatures as large as 10°C would result in an approximately 2.5‰ change in isotopic values. Thus, the large range in cement oxygen isotope values is most likely due to changes in the isotopic composition of meteoric water as opposed to a direct effect of temperature.

Given that the variation in $\delta^{18}O$ of the cements reflects variation in $\delta^{18}O$ of meteoric water, a second factor to consider is whether the changes in $\delta^{18}O$ of the meteoric water are directly related to changes in $\delta^{18}O$ of rainfall, or whether varying degrees of evaporative enrichment are superimposed on a relatively constant rainfall value. Several studies have suggested that the isotopic composition of near-surface carbonates is in general well correlated to that of rainfall without significant enrichment from evaporation (e.g. Cerling 1984; Hays and Grossman 1991). Such may not be the case, however, for extremely arid areas. For example, Schlesinger (1985) found that soil waters in the Mojave desert were as much as 8‰ enriched in $^{18}O$ compared to regional rainfall.

In Oman, however, the surface and groundwater isotopic values are only about 1–2‰ enriched in $\delta^{18}O$ and 10‰ enriched in $\delta D$ relative to rainwater (rainwater data from Neal and Stanger 1985), which indicates a small evaporative water loss. The isotope data contradict Neal and Stanger's (1985) explanation of the high $Na^+$ and $Cl^-$ contents of groundwater, which they attributed to an approximately 90% evaporative enrichment of rainwater. Such a high evaporative water loss in an arid climate (average relative humidity = 60%) would result in more than 20‰ enrichment in $\delta^{18}O$ (Gonfiantini 1986), not the observed 1–2‰. Overall, the isotopic composition of groundwater in Oman is close to that of rainwater.

With respect to the elevated salinity of the surface waters and groundwaters, it is likely that there is significant dry deposition of salts on the ground surface during the lengthy periods between rainfall events. Many of these salts could then be dissolved during subsequent rainfall. Rapid infiltration of the rain and dissolved surface salts into the coarse, porous surface sediments would raise the salinity of the groundwaters yet prevent significant evaporation.

On the whole, the varying oxygen isotopic compositions of the cements studied here are thought to reflect variations in rainfall values, with only minor effects due to evaporative enrichment. What, then, is causing the observed variation in $\delta^{18}O$ of cements and probably also of rainfall? First, two possible causes of variation do not appear to play a major role. One is an orographic effect. In many areas of significant relief, $\delta^{18}O$ of rainfall is inversely correlated to altitude (e.g., Siegenthaler and Oeschger 1980). The oxygen and hydrogen stable isotopic ratios of the water samples, however, do not vary more than 1‰ and 10‰, respectively, for samples taken from a variety of locations within the Oman Mountains (Neal and Stanger 1985). The values are also similar to those of water samples from

outside of the Oman Mountains. Furthermore, the cement samples from within the Oman Mountains have the highest $\delta^{18}O$ values, not the lowest. The lowest cement $\delta^{18}O$ values are from the Sur area, less than 50 masl (Table 1). The observed differences in isotopic compositions of cements from different areas probably are the result of them being of different ages (see discussion below) rather than being a reflection of geographic variation in the isotopic composition of rainfall.

Second, it might be expected that in the areas with high concentrations of marine carbonate clasts, dissolution of the clasts would buffer the isotopic values, particularly $\delta^{13}C$, toward the marine values of the rocks. This process is also thought to be of minor importance, because the samples from the area with the highest carbonate clast content, the Sur area, have the lowest $\delta^{13}C$ values.

Another possibility is that $\delta^{18}O$ of rainfall varies with temperature, in which case the $\delta^{18}O$ values of the cements would be a paleotemperature tool. For mid- to high-latitude areas, the $\delta^{18}O$ of rainfall is fairly well correlated to temperature (Dansgaard 1964), an observation that forms the basis of much isotope-based paleoclimatology. Stable isotope ratios of carbonates in continental sediments have been used for quite some time as paleoclimate indicators. The carbonates used, however, have been almost exclusively pedogenic, and rarely have isotopic values from meteoric calcite cements been used to interpret aspects of paleoclimate. Hays and Grossman (1991), however, recently discussed possible uses of $\delta^{18}O$ of meteoric calcites as paleotemperature indicators. Their data indicate that for coastal areas, and for areas with mean annual temperatures above 15°C, the $\delta^{18}O$ values of meteoric calcites (and presumably other carbonate minerals) "will vary minimally with temperature" (Hays and Grossman 1991). The conclusion of Hays and Grossman is in accord with data on $\delta^{18}O$ of rainfall at lower latitudes, where no correlation to temperature is observed (Dansgaard 1964; Rozanski et al. 1993). Thus, it seems unlikely that temperature variation controls the isotopic composition of either rainfall or meteoric cements in Oman.

More likely is that rainfall $\delta^{18}O$ is related to the amount of rainfall in Oman. At low latitudes, there is often an inverse correlation between rainfall amount and its $\delta^{18}O$ value; this is particularly true of oceanic islands (Rozanski et al. 1993). The "amount effect" is in some cases related to changes in the source of rainfall throughout the year, particularly in areas affected by a monsoonal climate (Rozanski et al. 1993). Isotopic analyses of rainfall from New Delhi, India illustrate this effect and provide a short-time-scale analogy to what may be occurring over much longer time scales in Oman. In New Delhi, average monthly rainfall increases greatly during the Indian Ocean summer monsoon, June through September, and the isotopic composition of rainfall in those months is much lower than during the rest of the year (Rozanski et al. 1993). The result is an overall inverse correlation between $\delta^{18}O$ of rainfall and amount.

At present, there is no increased seasonal rainfall in northern Oman associated with the Indian Ocean summer monsoon. Only the coastal highlands area of southwest Oman receives monsoonal rainfall. For the late Pleistocene and early Holocene, however, lacustrine deposits in the Ar Rub' Al Khali desert (McClure 1976), in north-central Oman, and increased spring discharge in the Oman Mountains (Clark and Fontes 1990) attest to periods of increased rainfall in central and northern Oman. The timing of the most recent "pluvial" period, around 9000 yr B.P., corresponds to a period of intensified monsoonal circulation off the coast of the Arabian Peninsula (Clemens and Prell 1990 and references therein). Thus, the 9000 yr B.P. pluvial event has been interpreted as indicating northward extension of the summer monsoon rainfall to cover most or all of Oman (McClure 1976; Clark and Fontes 1990).

If the effect of the monsoon on the isotopic composition of rainfall in New Delhi can be used as an analogy for Oman, then the likely effect of northward extension of the monsoon would be to increase rainfall and simultaneously decrease the isotopic composition of rainfall. We suspect that such a relationship is the principal cause of the variations in $\delta^{18}O$ of
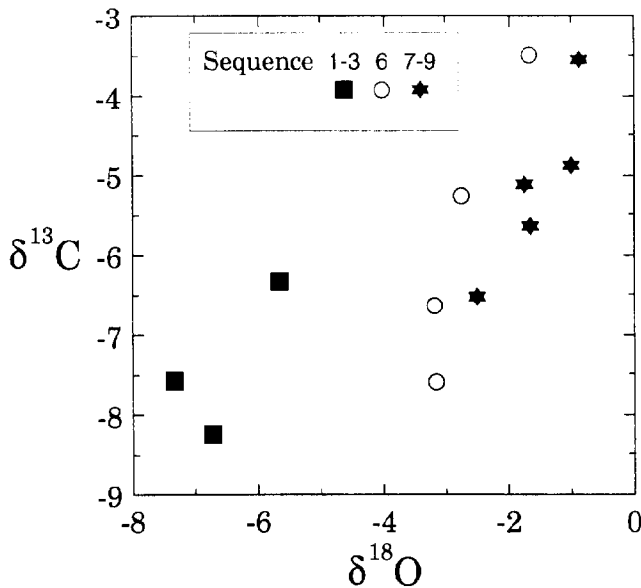
Fig. 4.—Stable isotope data of different generations of gravels (Maizels and McBean 1991) from the Barzaman area.

the carbonate cements. Over a time scale of probably several thousand years, greater frequency and amount of monsoonal rainfall results in lower cement $\delta^{18}O$ values.

There is also an independent qualitative assessment of past rainfall that can be directly related to our stable isotope measurements. Maizels and McBean (1990) used the geomorphology of successive generations of alluvial channel gravels from the Barzaman area of Oman to interpret paleoclimate. They concluded that, in general, the earlier paleochannel generations "resulted from more prolonged annual river flows than those of the later generations, and those of the present day" (Maizels and McBean 1990). Isotopic measurements of cement from a number of the same paleochannel generations (Fig. 4) show that the earlier channel generations have more negative $\delta^{18}O$ values ($-5.66‰$ to $-7.34‰$) than later generations ($-3.17‰$ to $-0.87‰$). Thus, the geomorphological evidence supports the interpretation that rainfall amount and cement $\delta^{18}O$ are inversely correlated.

Our results from Oman suggest that the isotopic compositions of meteoric cements or pedogenic carbonates from low latitudes may have potential as a paleo-rainfall indicator. Another possible example is provided by the work of Rossinsky and Swart (1993), who studied Holocene calcrete formation in the Caribbean region. They found that the oxygen isotopic ratios of calcrete increase fairly regularly along a transect from south Florida through the Bahamas, from a mean of $-3.82‰$ in south Florida to $-1.76‰$ in Caicos. They attributed this trend to variation in evaporation rates. Along the same transect, however, average annual rainfall decreases regularly, from an annual mean of 1513 mm in Miami to 605 mm in Caicos (Rossinsky and Swart, 1993). Thus, the calcrete $\delta^{18}O$ is inversely correlated to rainfall amount. The reasons for the correlation are not entirely clear, however, because rainfall isotopic data are insufficient to fully evaluate whether $\delta^{18}O$ of rainfall and amount are inversely correlated in this region.

Carbon Isotopes.—The carbon isotopic ratios of the carbonates can be used to help identify the sources of $CO_2$ to the groundwaters. Carbon isotopes are fractionated such that for equilibrium conditions at 25°C there is about a 10‰ enrichment in $\delta^{13}C$ values of carbonate relative to dissolved $CO_2$ (Bottinga 1969; Emrich et al. 1970). Thus the range of $\delta^{13}C$ values of carbonate cements in Oman indicates $\delta^{13}C$ values for $CO_2$ from

about $-8‰$ to $-20‰$. These values suggest substantial variation in the relative amounts of the two possible sources of $CO_2$: (1) atmospheric $CO_2$ ($-7‰$), and (2) the local flora (average = $-25‰$) via root respiration or oxidation of organic matter incorporated in the gravels. The higher $\delta^{13}C$ values are compatible with an almost pure atmospheric source of $CO_2$. The lower values indicate mainly plant-sourced $CO_2$, although still with an atmospheric component. Mixing of respired and atmospheric $CO_2$ sources is typical of soils with low soil respiration rates (i.e., low plant cover) and would be expected for an arid area with sparse vegetation.

For each of the three different areas sampled there is, to varying degrees, a positive correlation between oxygen and carbon isotopes (Fig. 4). Such correlations often have been reported for isotopic values of pedogenic carbonates (e.g., Salomons et al. 1978; Cerling 1984; Schlesinger 1985). Cerling (1984) attributed this correlation to related variations in $\delta^{18}O$ of rainfall and in the fraction of $C_3$ vs. $C_4$ flora with temperature. Schlesinger (1985) suggested that in the Mojave Desert the correlation was caused by seasonal variations in plant growth and evaporation of soil waters, with lower ratios during times of higher seasonal rainfall, when more plant respiration should be expected, and higher ratios during times of lower rainfall, when more evaporative enrichment of $\delta^{18}O$ and less plant activity occurred.

In Oman, this correlation is best explained by a mechanism similar to that proposed by Schlesinger (1985), but where evaporation is not a factor affecting $\delta^{18}O$. Rather, as suggested above, variations in rainfall amount are inversely correlated to the $\delta^{18}O$ of rainfall over longer time periods. During periods of higher rainfall, when both rainfall and cements have more negative $\delta^{18}O$ values, there is more extensive plant cover on the land surface. More extensive plant cover results in more extensive respiration of $^{13}C$-depleted $CO_2$ into soil waters from plant roots and/or more plant organic material available for bacterial conversion to isotopically depleted $CO_2$. Conversely, during periods of lower rainfall, indicated by less negative $\delta^{18}O$ values, there is less extensive plant cover and less to no input of plant-derived $CO_2$ into soil waters.

SUMMARY

Early carbonate cements are an almost ubiquitous component of alluvial conglomerates in Oman. The cements are precipitated in both the vadose and, more commonly, phreatic groundwater zones. Cementation ranges in degree from minor amounts of meniscus cements only at grain-to-grain contacts to sparry cements completely occluding intergranular pore space. The carbonate cements found include low-magnesium calcite, high-magnesium calcite, and dolomite. Cement composition is ultimately controlled by the near-surface rock types available for weathering. In areas underlain by ultramafic rocks, shallow groundwaters with $Mg^{2+}/Ca^{2+}$ ratios generally greater than two are found, and HMC and dolomite are common as cements. In areas underlain by carbonate rocks, the near-surface groundwaters have $Mg^{2+}/Ca^{2+}$ ratios less than one, and LMC is the predominant cement mineral.

The oxygen and carbon stable isotope ratios of the cements range widely, from $+3.0‰$ to $-10.6‰$ and from $+0.7‰$ to $-10.0‰$, respectively, even though all the cements are near-surface precipitates. The $\delta^{18}O$ values of the cements are thought to be inversely related to the amount of rainfall on a time scale of several thousand years. The amount of rainfall is a function of the frequency and intensity of the Indian Ocean monsoon. Thus, for Oman, cement $\delta^{18}O$ is potentially an indicator of paleo-rainfall amounts and monsoon activity. The oxygen isotopic composition of meteoric cements from other low-latitude settings may also be related to rainfall amount. For each of the three sampling areas, $\delta^{18}O$ values are positively correlated to $\delta^{13}C$. The cement $\delta^{13}C$ values are also inversely related to the amount of rainfall, because rainfall controls the plant population. During periods of relatively high rainfall, increased plant populations should result in higher input of isotopically depleted, plant-respired

$CO_2$ to soil waters and shallow groundwaters, and in greater incorporation of organic material into alluvial deposits. The net result should be carbonate cements with lower $\delta^{13}C$ values as compared to times of low rainfall.

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