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Petrology and isotope geochemistry  
of calcite in a south Texas roll-type uranium deposit

By

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Abstract

Calcite occurs in nearly equal amounts throughout the altered tongue, ore zone, and reduced barren ground in the Benavides roll-type uranium deposit, south Texas. Petrographic and oxygen isotopic studies indicate that, prior to mineralization, calcite formed in reduced rock, as a result of oxidation of fault-derived methane to  $\text{CO}_2$ . The  $\delta^{13}\text{C}$  of this calcite was isotopically light (less than -30 permil). During mineralization, calcite was dissolved in the altered tongue and reprecipitated ahead of the migrating roll-front. This calcite had  $\delta^{18}\text{O}$  values that reflect precipitation from meteoric ground waters. After mineralization, carbonate was removed from caliche at the surface and reprecipitated in the host rock throughout the altered tongue, ore zone, and downdip into reduced barren ground. This calcite had a  $\delta^{13}\text{C}$  value of about -6 to -8 permil. Authigenic calcite in the altered tongue of the Benavides deposit contrasts greatly with the absence of calcite in the altered tongues of roll-type deposits in the Wyoming Tertiary basins.

## Introduction

Calcite is common in host rocks of roll-type uranium deposits and occurs typically in a marked spatial asymmetry to the redox boundary. In several Wyoming deposits, calcite is absent or strongly depleted in oxidized rock updip from the roll-front, but is abundant in reduced rock in and slightly downdip from ore (Harshman 1972, 1974; Dahl and Hagmeier, 1974; Rackley, 1972). Calcite occurs both as a cementing material in ore and as concretionary masses localized around large accumulations of carbonized plant debris. Petrographic observations of samples from Wyoming deposits have established that this calcite may either predate or postdate the major uranium-bearing phases (Melin, 1964; Harshman, 1972). These geometric and petrographic relationships may be explained by a mechanism in which diagenetic and epigenetic calcite is destroyed at the redox boundary by acid solutions developed via pyrite oxidation (Melin, 1964, Granger and Warren, 1969; Harshman, 1972; Rackley, 1972). Pre-ore calcite may be formed diagenetically from carbonate species released during organic decay processes. Additional calcite can be formed in reduced rock as an epigenetic phase by redeposition from initially acid solutions produced at the redox boundary; as the solutions move downdip, they are progressively neutralized by reactions with the host rock. The range of paragenetic relationships between uranium bearing phases and calcite suggests the presence of both diagenetic and epigenetic carbonate in the Wyoming roll-type deposits.

Stable isotopic studies of carbon and oxygen in calcite have proved a valuable adjunct to petrographic work in understanding the genesis of calcium carbonate (Hudson 1977). Carbon in calcite may have a distinctive ratio of  $^{13}\text{C}/^{12}\text{C}$  depending upon the source of carbon. Marine carbonates have  $\delta^{13}\text{C}$  values close to 0 permil. Keith and Weber (1964) obtained an average value of  $+0.6 \pm 1.6$  permil for 321 selected samples of marine carbonates and an average value of  $-4.9 \pm 2.8$  permil for 183 freshwater carbonates. In contrast, organic matter is systematically enriched in the light isotope  $^{12}\text{C}$ . Values of  $^{13}\text{C}$  for most terrestrial plants fall in the range -24 to -28 permil although some aquatic, desert, and salt marsh plants are heavier (-6 to -19 permil; Smith and Epstein, 1971). When these organic materials are oxidized and the  $\text{CO}_2$  is precipitated, the resulting carbonate will likewise be enriched in  $^{12}\text{C}$  relative to carbonate in marine and freshwater limestone. Because methane is isotopically lighter than organic matter, oxidation of methane to  $\text{CO}_2$  can provide carbonate carbon with  $\delta^{13}\text{C}$  less than -30 permil (Hudson, 1977).

The major study on  $\delta^{13}\text{C}$  in roll-type uranium deposits is that of Cheney and Jensen (1966). Who reported  $\delta^{13}\text{C}$  values of calcite associated with uranium in the Gas Hills district, Wyoming. Values of  $\delta^{13}\text{C}$  for carbonate cement in sandstone, much of which was associated with organic debris, range between +1 and -33.2 permil with a majority of the samples in the range of -10 to -27 permil. These data indicate that oxidation of organic matter was an important carbon source for the calcite.

$$\delta^{13}\text{C} = \frac{(^{13}\text{C}/^{12}\text{C})_{\text{sample}} - (^{13}\text{C}/^{12}\text{C})_{\text{standard}}}{(^{13}\text{C}/^{12}\text{C})_{\text{standard}}} \times 1000$$

See techniques section for discussion of the standard

The oxygen isotopic content of a carbonate precipitated from water depends principally upon the isotopic composition and temperature of the water. At equilibrium, there is a temperature dependent isotope separation between the isotopic ratio of water and that of the carbonate (fig. 1). It is therefore possible to determine the isotopic composition of the depositional waters if an estimate of the temperature of formation can be made. Meteoric waters are highly variable in their oxygen isotope ratio due in part to a pronounced latitude effect as reflected in mean annual air temperature (fig. 2). Cheney and Jensen (1966) measured  $\delta^{18}\text{O}$  on the same carbonate suite as was studied for  $\delta^{13}\text{C}$ . They reported a large range of oxygen isotopic composition of +18 to -10 permil with a mean of +7 permil. The mean value reflects deposition from water highly enriched in  $^{16}\text{O}$ .

Detailed studies of calcium carbonate associated with roll-type uranium deposits are limited to a few examples from the Wyoming Tertiary basins. In this paper we report on abundance, distribution, petrography, and isotopic composition of calcium carbonate from a roll-type uranium deposit in the south Texas coastal plain.

#### Description of Deposit

The Benavides uranium deposit is located near the town of Bruni in Webb County, Texas and occurs in the Oligocene and Miocene Catahoula Tuff. The sample suite and geologic setting have been described previously by Goldhaber and Reynolds (1977), Reynolds and Goldhaber (1978), Goldhaber and others (1978). Samples were obtained primarily from core holes (1-9) drilled perpendicular to the trend of a roll-front (fig. 3). The core fence is subparallel to the regional dip (northwest to southeast). Core 1 is at the updip end of the core fence and core 9 at the downdip end. It is believed,

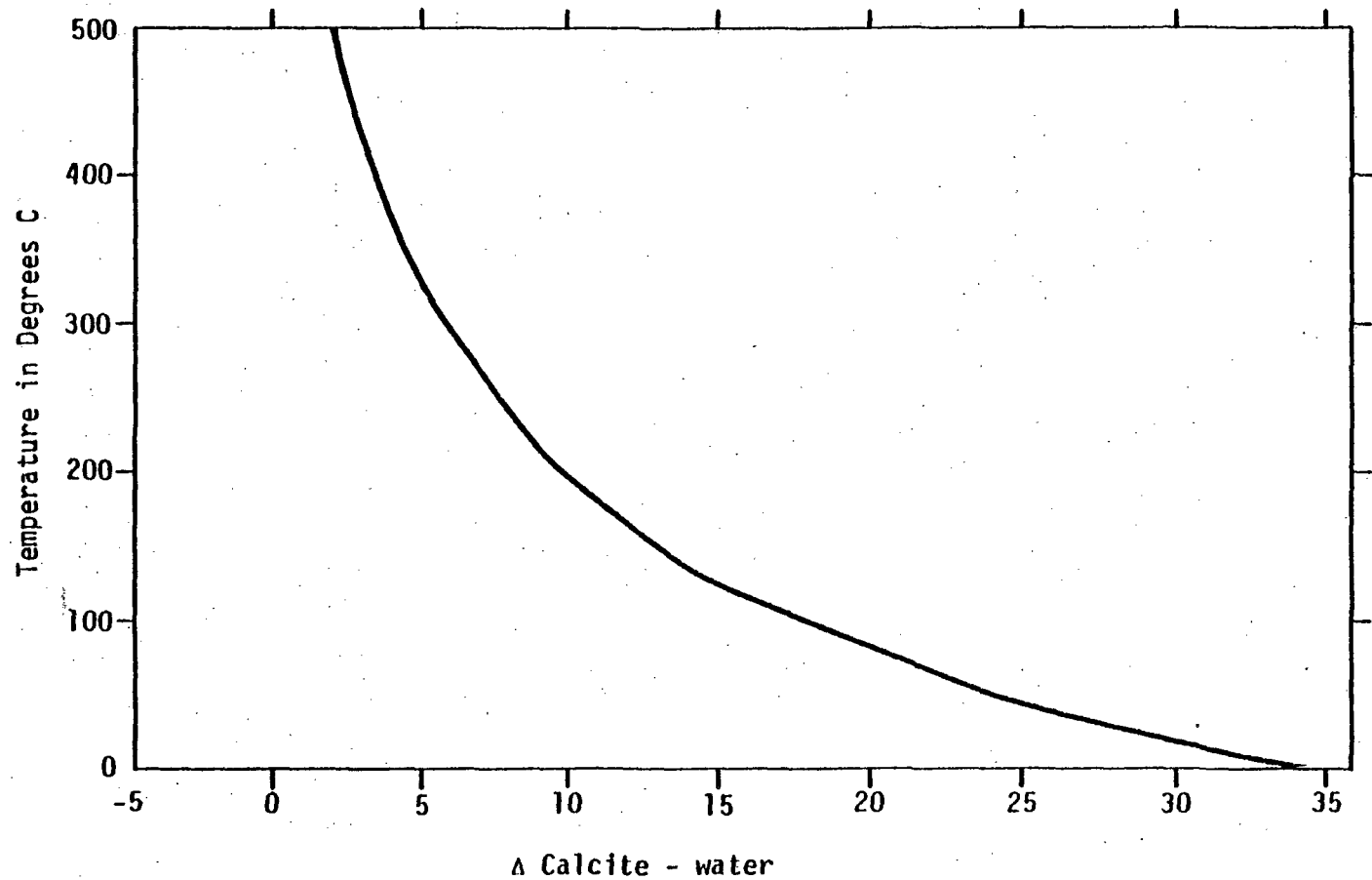


Figure 1.--Isotopic separation of oxygen isotopes in calcite and water,  $\Delta$  ( $\Delta = \delta^{18}\text{O calcite} - \delta^{18}\text{O water}$ ) as a function of temperature. Modified from Friedman and O'Neil, 1977.



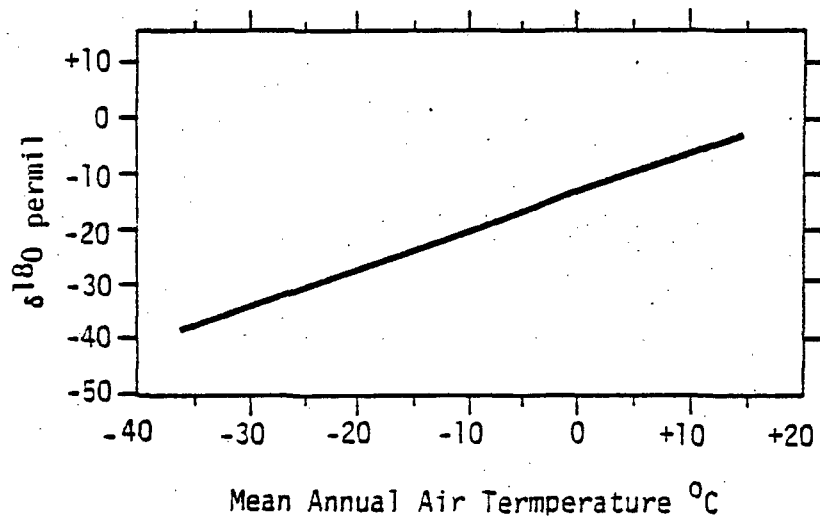


Figure 2.--Oxygen isotopic composition of meteoric water as a function of mean annual temperature. Modified from Faure, 1977.

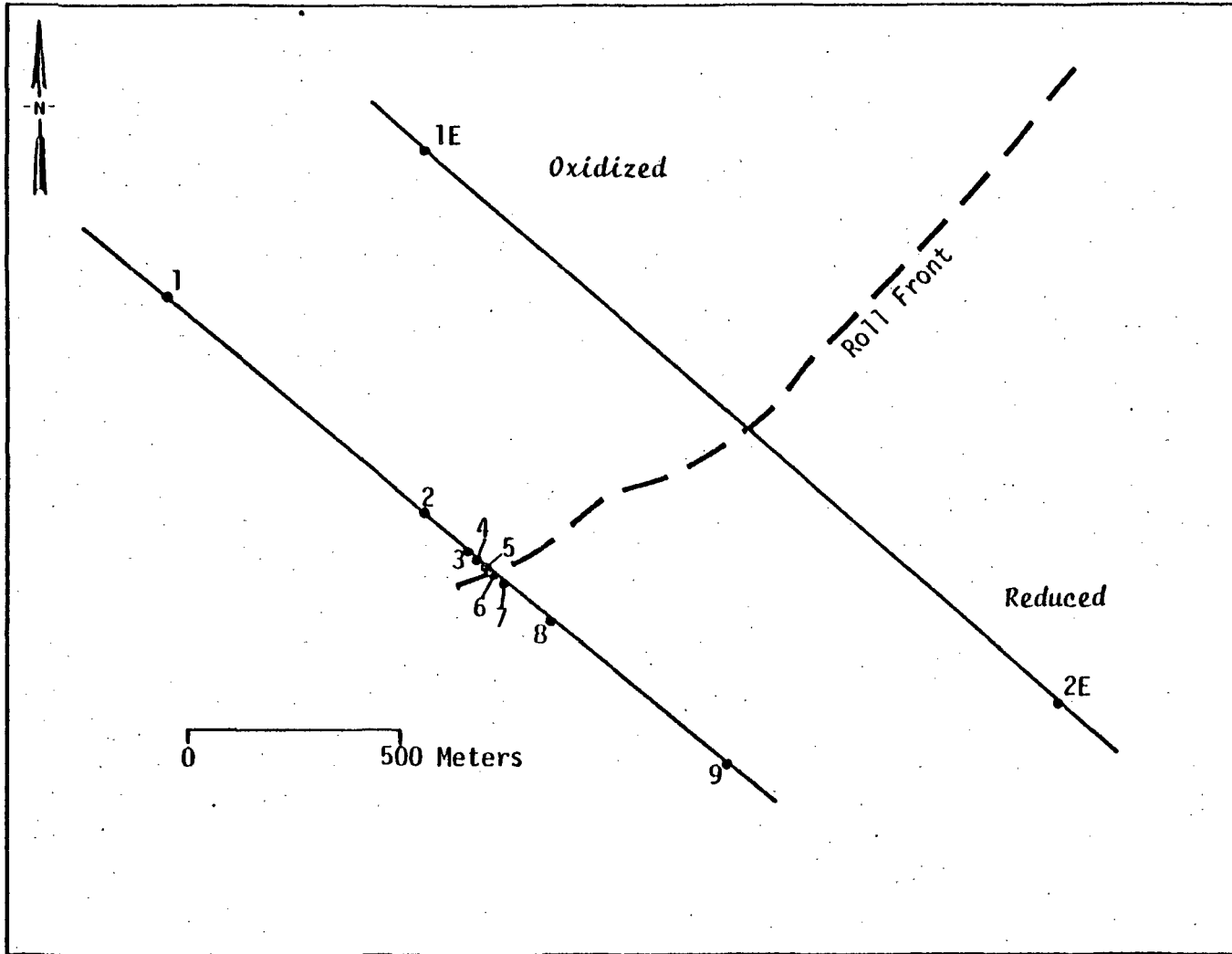


Figure 3.--Plan view of the south Texas roll front (dashed line) showing location of core holes (circles) along two fences (solid lines).

based upon previous work (Reynolds and Goldhaber, 1978; Goldhaber and others, 1978), that the deposit formed in two stages. The first (pre-ore) stage involved sulfidization of the host rock by  $H_2S$  emanating from a fault located downdip from the present position of the roll. Subsequent invasion of the sulfidized host rock by oxygenated, uranium-bearing ground water established a redox boundary and resulted in mineralization.

### Techniques

The complete data set on the abundance of carbonate, as determined by Wyoming Mineral Corp., was presented in a previous report (Goldhaber and Reynolds, 1977). Petrographic data are based on study of 19 thin sections and 29 polished thin sections. In addition, 5 of the polished thin sections were examined by the cathodoluminescence technique using a Nuclide model ELM 2B luminescope operated at 11 kv and 0.2 ma beam current.

Carbon and oxygen isotope ratios were measured on carbon dioxide liberated by reaction with 100 percent phosphoric acid from selected samples and the evolved  $CO_2$  analyzed by comparison with PDB carbonate standard on a Nier-type mass spectrometer. Results of isotopic analysis are reported in standard notation;  $^{18}O$  is expressed similarly in terms of  $^{18}O/^{16}O$  ratios relative to the SMOW (Standard Mean Ocean Water) standard.

### Results

Carbonate abundance is summarized in figure 4, which is a plot of the average (mean) values of carbonate from individual cores as a function of core position. Where the cored interval contained both reduced (upper and lower limb) and oxidized (altered tongue) material (cores 2 to 5), only the oxidized samples were averaged. The carbonate contents averaged in this way are

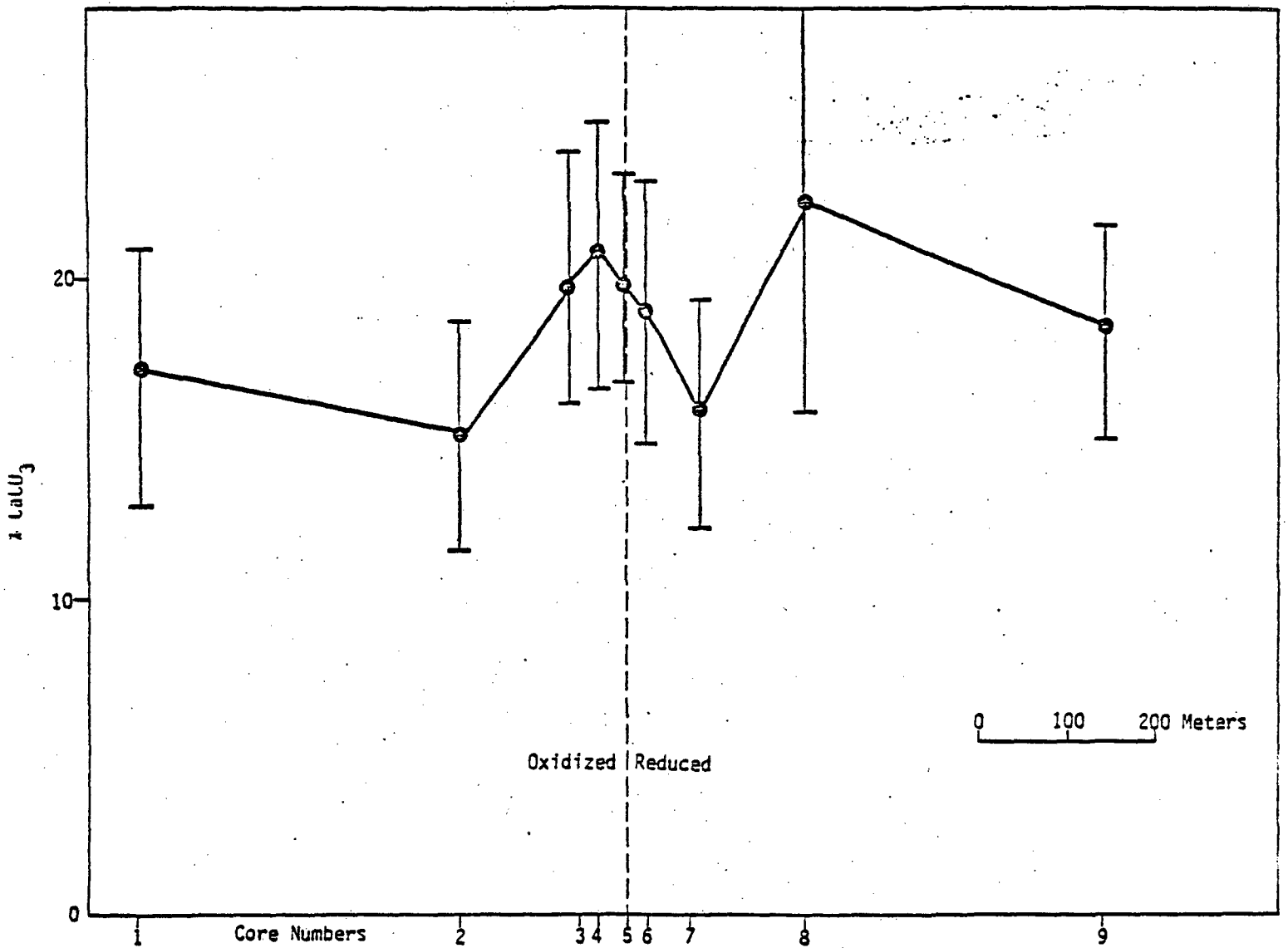


Figure 4.--Plot of average calcite abundance (percent by weight of the bulk rock) as a function of core position along core fence. Vertical bar represents  $\pm$  one standard deviation from the mean. Dashed line indicates oxidized-reduced interface.

consistently high along the entire core fence and show no strong systematic trends. There is no indication of anomalously low values in the oxidized tongue, as have been reported from Wyoming. Enrichment in reduced rock ahead of the roll is not marked, although the highest carbonate contents are found in core 8.

Petrographic studies of thin sections and polished thin sections reveal that calcite is the only carbonate phase. Three types of calcite were identified; authigenic micritic calcite, authigenic sparry calcite, and detrital calcite. No consistent paragenetic relationships were noted between authigenic micritic and sparry calcite. These two types were present in nearly equal amounts. Detrital calcite, identified conclusively only on the basis of very rare reworked microfossils is, nevertheless, abundant in some Catahoula sands. McBride and others (1968) reported that detrital calcite comprises as much as 20 percent (and averages 5.5 percent) of the framework grains in the Catahoula samples that they studied. These carbonate rock fragments were chiefly micritic and were derived from Cretaceous marine sedimentary rocks exposed to the west of the Catahoula outcrop belt (McBride and others, 1968).

Our observations of the polished thin sections reveal clear relationships between calcite and detrital and authigenic opaque phases. Authigenic calcite was observed commonly as rims around pyrite and marcasite in reduced rock. In the oxidized tongue, calcite was also seen to be later than ferric oxide phases (limonite) which are themselves pseudomorphic after iron disulfides. Because marcasite formed during development of the uranium roll (Goldhaber and others, 1978), as did the ferric oxides in the altered tongue (Reynolds and Goldhaber, 1978), it may be concluded that at least a portion of the calcite was precipitated after the mineralization.

Under the luminoscope three types of carbonate were identified: (1) micrite which luminesces various shades of orange; (2) sparry calcite which likewise luminesces orange; and (3) nonluminescent sparry calcite. The nonluminescent sparry calcite occurs both alone and in association with luminescent calcite. In the latter occurrence, the nonluminescent sparry calcite invariably formed a core which was rimmed by either luminescent micrite or, more typically by luminescent sparry calcite. Nonluminescent calcite was present throughout the deposit and constituted 5 to 20 percent of the calcite grains examined. If as noted by McBride and others (1968) detrital carbonate is micritic, the nonluminescent material is probably authigenic. We cannot, however, as yet relate this nonluminescent calcite to other observations presented in the study.

Carbon and oxygen isotopic results are contained in table 1. Trends in carbon and oxygen isotopes contrast greatly. Whereas carbon ranges broadly in its isotopic composition between -5.2 and -25.4 permil, oxygen isotopes are essentially constant with a range of only 0.7 permil (-24.4 permil to -25.1 permil). Carbon isotope values vary as a function of calcite abundance (fig 5). Samples with high calcite concentrations are systematically enriched in the light isotope  $^{12}\text{C}$ . Systematic trends in the  $\delta^{18}\text{C}$ -weight percent  $\text{CaCO}_3$  relationships are shown in figure 6. In samples from the updip part of the core fence (illustrated by data from core 2), variation in calcite abundance corresponds to only slight changes in  $\delta^{13}\text{C}$ . However, in samples located well ahead of the roll front (illustrated by data from core 8) variation in calcite abundance corresponds to major changes in  $\delta^{13}\text{C}$ . Calcite abundance and  $\delta^{13}\text{C}$  for samples from cores 4 and 6 between cores 2 and 8 show intermediate behavior. These data demonstrate that the isotopically lightest portion of the calcite carbon is localized preferentially downdip ahead of the redox boundary.

Table 1.--Carbon and oxygen isotope values from the Benavides deposit, south Texas

Core No.	Depth in meters	$\delta^{18}\text{O}$	$\delta^{13}\text{C}$	
1	29.6 - 30.8	24.89	-6.73	
	31.7 - 32.9	24.95	-6.67	
2	33.8 - 35.1	24.54	-5.97	
	42.5 - 43.0	24.92	-5.20	
	43.3 - 43.7	24.46	-5.80	
	44.2 - 45.0	24.64	-5.79	
4	34.4 - 35.1	24.70	-9.33	
	35.1 - 35.7	24.64	-8.69	
	36.0 - 36.3	24.79	-8.95	
	36.6 - 36.9	24.64	-7.59	
	36.9 - 37.2	24.63	-8.69	
	37.2 - 37.5	24.86	-6.22	
	37.8 - 38.4	24.79	-8.49	
	38.7 - 39.6	24.71	-7.94	
	42.1 - 42.4	24.74	-6.72	
	44.2 - 44.8	24.92	-8.31	
	6	33.5 - 33.8	24.82	-7.80
		36.3 - 36.9	24.90	-7.76
		39.0 - 39.3	24.75	-8.55
41.8 - 42.4		24.71	-6.67	
7	34.7 - 35.7	24.82	-8.83	
	35.7 - 36.3	24.87	-7.31	
	36.3 - 37.2	24.58	-12.81	
	43.3 - 44.2	25.06	-5.57	
8	32.0 - 32.9	24.88	-11.89	
	33.8 - 35.1	24.55	-19.09	
	35.1 - 35.7	24.56	-25.40	
	35.7 - 36.0	24.50	-22.06	
	36.9 - 37.8	24.24	-18.87	
	40.2 - 41.5	24.63	-9.15	
	44.7 - 45.6	24.83	-8.15	
	9	36.6 - 37.8	24.52	-6.49
		40.8 - 41.8	24.40	-9.39
		42.7 - 43.6	24.39	8.13
45.7 - 46.9		24.64	7.99	

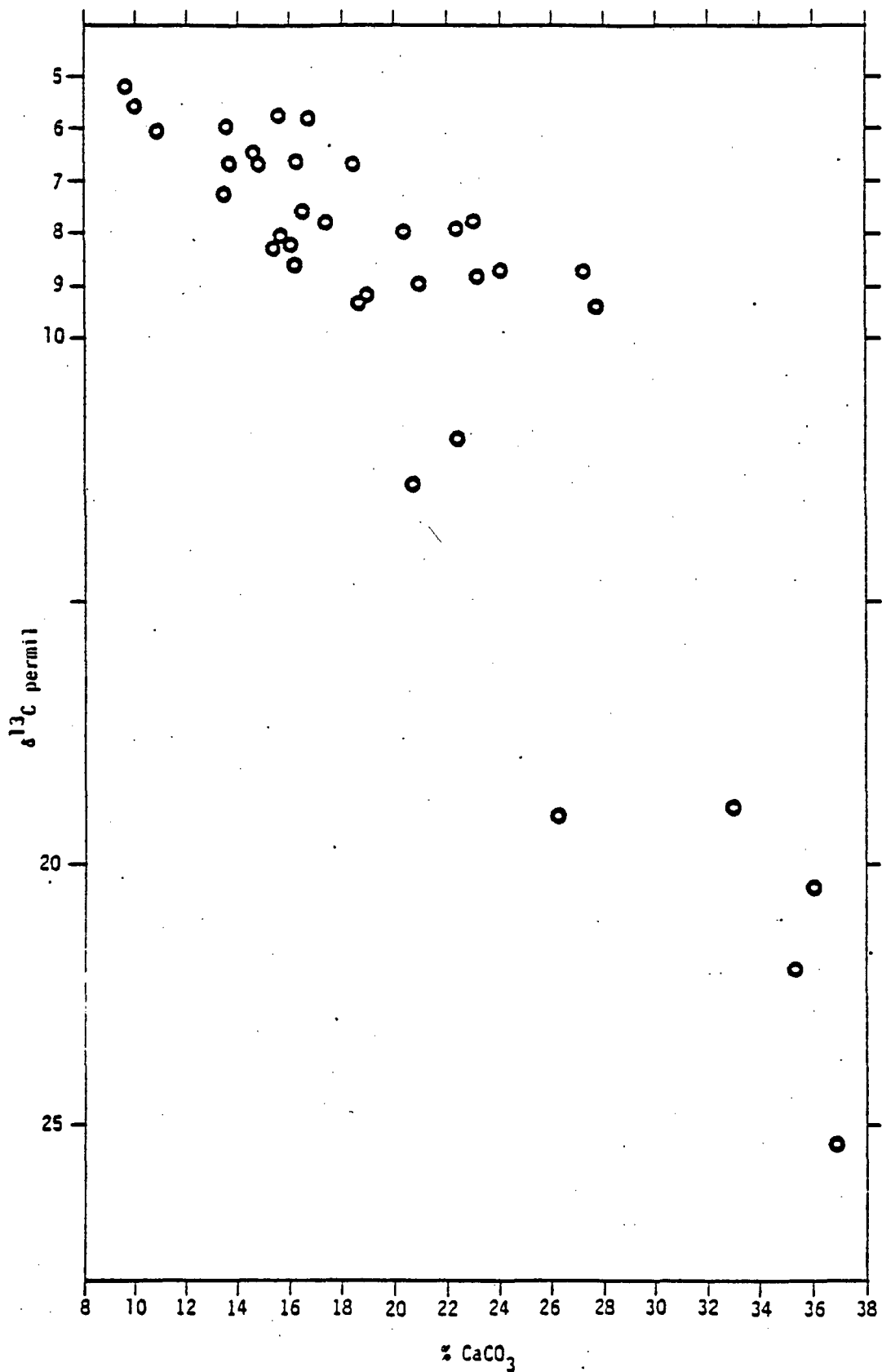


Figure 5.--Plot of carbon isotopic composition ( $\delta^{13}\text{C}$ ) against carbonate abundance for all samples in the study.



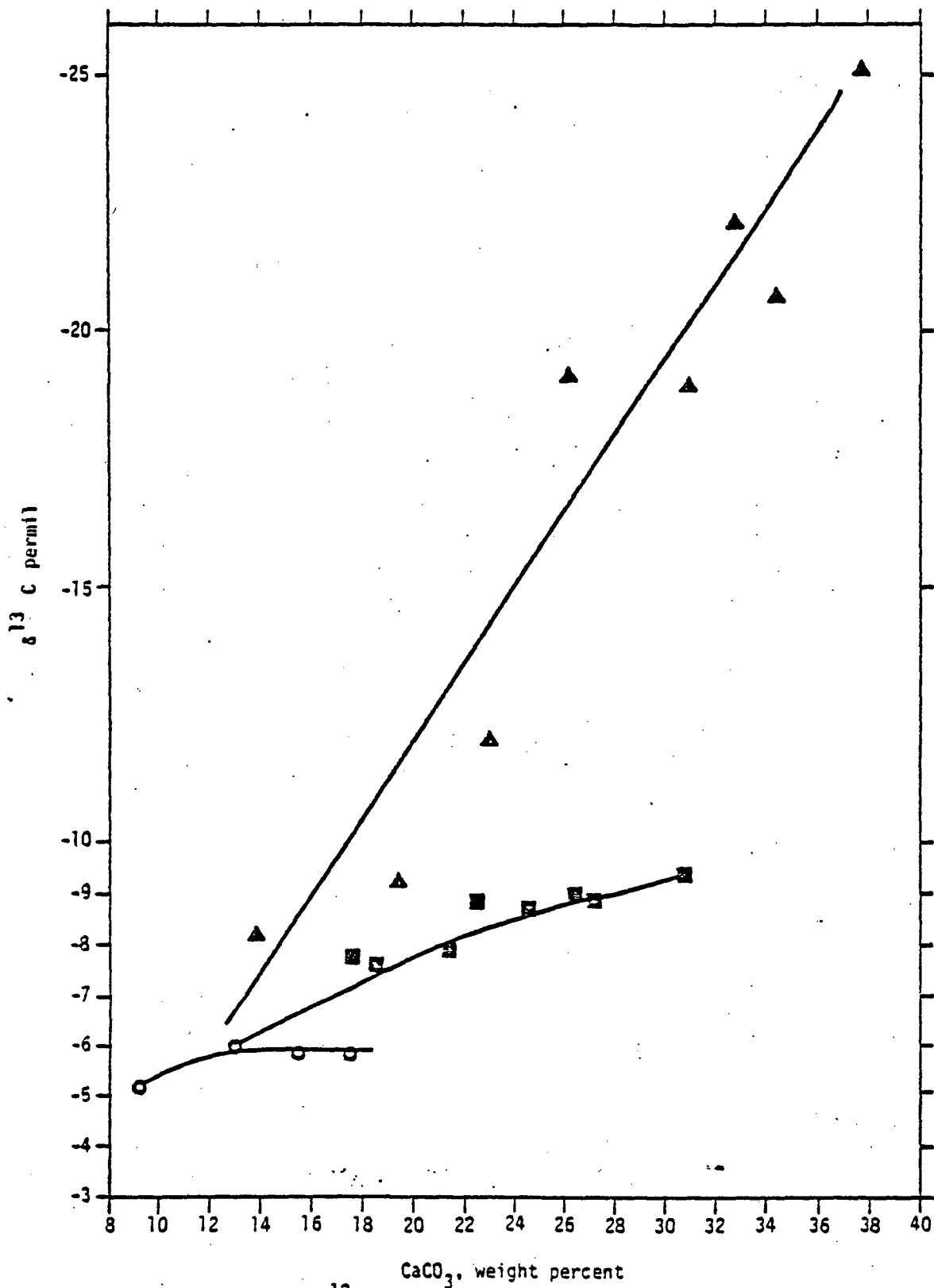


Figure 6.--Plot of  $\delta^{13}\text{C}$  against carbonate abundance for individual cores:  
 ○ data from core 2; ■ data from cores 4 and 6; ▲ data from core 8.  
 The curves through the data points are "best-fit" lines drawn by hand.

## Discussion

The petrographic and geochemical data from the Benavides deposit are useful for determining the origin of the calcite. The most important petrographic observation in this context is that much of the calcite was introduced after mineralization. This conclusion is based upon the observation that calcite forms rims around limonite and marcasite both of which formed during ore deposition. Clearly, however, some detrital carbonate was present prior to ore deposition.

Because oxygen isotopes of calcite are inherited from depositional waters, the constancy of the oxygen isotopic data (table 1) demonstrate that the calcite was deposited from a water of fixed isotopic composition and temperature. Alternatively, the entire carbonate oxygen reservoir may have been reequilibrated after deposition with water of a fixed isotopic value. This second possibility is not likely because although calcite may exchange oxygen isotopes at  $T > 150^{\circ}\text{C}$  (for example, Clayton and others, 1968), exchange at earth surface temperatures is very slow.

Calcite from marine Cretaceous rocks in south Texas has an oxygen isotopic composition ( $\delta^{18}\text{O}$ ) in the range from +24.2 to +27.2 with a mean of approximately +26.3 (Prezbindowski, 1977). These values are, for the most part, heavier than those of the calcite in the Benavides deposit (table 1). Any quantitatively significant amount of detrital marine carbonate bearing its original oxygen isotopic compositions would thus cause a deviation of the  $\delta^{18}\text{O}$  values from what is observed. Therefore, detrital carbonate is present in low abundance or its oxygen isotopic value has been altered by dissolution and reprecipitation.

The relationships between oxygen in water and in calcite can give some indication of the  $\delta^{18}\text{O}$  of the water from which this carbonate was

precipitated. Estimation of the appropriate temperature for use in this calculation is uncertain but it is likely that the depositional waters at shallow depth approximate the mean annual temperature. For the Benavides area, the mean annual temperature is 22°C (Ruffner, 1979). At this temperature, calcite would have a  $\delta^{18}\text{O}$  value which is 28 permil heavier than the depositional waters (fig. 1). The water in equilibrium with Benavides carbonate, therefore, would have a  $\delta^{18}\text{O}$  value of about -3 permil, which is very close to that expected for Gulf Coast meteoric water (Clayton and others, 1966; Friedman and others, 1964). It has also been shown that Gulf Coast formational brines are considerably heavier than -3 permil ranging between +2 and +9 permil (Clayton and others, 1966). To produce the observed calcite  $\delta^{18}\text{O}$  from such brines would have required a temperature of 50 to 150°C (fig. 1) which is highly unlikely.

The carbon isotopic composition of calcite is useful for determining the source of carbonate carbon. The  $\delta^{13}\text{C}$  value of much of the carbonate in the Benavides deposit suggest a nonmarine, soil-related source for the carbon. Many of the measured values (-2.1 to -6.7 permil) fall within the range expected for fresh-water limestones. When this range is broadened to reflect soil carbonates which typically have  $\delta^{13}\text{C}$  values of -9 to -12 permil (Salomons, 1975), most of the carbon isotope data is included. Apparently, detrital calcite from nearby Cretaceous limestones, which have  $\delta^{13}\text{C}$  values in the range -1 to +6 permil and a mean of +2.5 permil (Prezbindowski, 1977), has made little or no contribution to the observed  $\delta^{13}\text{C}$  values. This conclusion is consistent with petrographic observation that detrital calcite is a minor constituent in the host rock of the Benavides deposit, and consistent with  $\delta^{18}\text{O}$  data.

Clearly, however, there is an additional, much lighter, carbon component in some parts of the deposit, as for example in core 8 (fig. 6). Assuming that calcite in the sample in core 8 from the depth 35.1 to 35.7 m (with a carbon isotope ratio of -25.4 permil and 38.5 percent calcite) is a mixture of a component of "light calcite" (28.5 percent) and one with a  $\delta^{13}\text{C}$  of -5.5 permil (10 percent), then the isotopic ratio of the "light component" ( $\delta x$ ) is solved by the formula

$$\frac{10}{38.5} (-5.5) + \frac{28.5}{38.5} (\delta x) = -25.4$$

The  $\delta^{13}\text{C}$  of the light component ( $\delta x$ ) is -32.3 permil. The assumption of 10 permil  $\text{CaCO}_3$  with an isotopic composition of -5.5 permil is justified upon inspection of the plot of data from several cores (fig. 6) which show this as a likely end member common to each. Carbonate carbon of -30 permil and lighter is very likely formed by oxidation of methane to  $\text{CO}_2$  (Hudson, 1977; Donovan, 1974). Methane oxidation requires atmospheric oxygen, and therefore probably occurs in a near-surface environment dominated by ground water rather than in formation waters which are anoxic.

Based on the petrographic and isotopic data presented above, the following processes led to calcite precipitation in the Benavides deposit:

(1) Pre-ore processes. Methane was introduced into the host sand from a deep-seated source in association with hydrogen sulfide. Whereas the hydrogen sulfide reacted with iron in the host sand, methane was essentially unreactive in the environment and migrated updip. The methane was oxidized to  $\text{CO}_2$  and subsequently precipitated as calcite in a zone of mixing a fault-derived fluid and oxygen-charged ground water. The  $\delta^{13}\text{C}$  of this calcite was  $<-30$  permil, and the  $\delta^{13}\text{C}$  values were either dominated by local ground water or by a mixture of ground water and brine. Detrital calcite was present in the host rock but was a minor constituent.

(2) Ore-stage processes. Calcite, (primarily methane derived but some detrital), located updip from the present roll front, was dissolved by ground water acidified by oxidation of iron disulfide minerals during mineralization, and was reprecipitated downdip ahead of the roll. At this stage, carbonate was absent from the altered tongue but isotopically light calcite (with  $\delta^{18}\text{O}$  reflecting precipitation from local ground water) was present in reduced rock.

(3) Post ore-stage processes. Following the ore-forming process, calcite developed in soils at the surface overlying the deposit. This soil carbonate was subsequently dissolved during a climatically wet interval and reprecipitated in the host rock in the subsurface. This carbonate had a  $\delta^{13}\text{C}$  value of about -6 permil. The  $\delta^{18}\text{O}$  of this carbonate was dominated by local meteoric water as was the calcite that formed during mineralization.

The above described mechanism accounts for the presence of post-ore calcite in reduced rock and, unlike the Wyoming deposits, in the oxidized tongue. It also accounts for the wide range of observed  $\delta^{13}\text{C}$ , for constancy of  $\delta^{18}\text{O}$ , and for the systematic variations of  $\delta^{13}\text{C}$  as a function carbonate abundance (fig. 6).

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