Redox conditions of calcite cementation interpreted from Mn and Fe contents of authigenic calcites

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ABSTRACT

Mn and Fe contents of cathodoluminescent (CL) calcite cements that formed in shallow fresh-water aquifers can be used to infer the redox potential of the pore fluids from which they formed. A semi-quantitative geochemical model relating these factors is based upon the assumption that the Mn$^{2+}$ and Fe$^{2+}$ concentrations of the ground waters were controlled by the Eh-dependent solubility of manganese and iron minerals and that the Mn and Fe concentrations of calcite cements precipitating from these solutions can be related to their concentrations in solution by distribution coefficients. Although the qualitative model of Oglesby (1976), Carpenter and Oglesby (1976), and Frank and others (1982) correctly relates calcite CL to the redox conditions of precipitation, numerous inconsistencies arise when it is compared to hydrogeochemical data for modern ground waters and to petrographic observations of CL-calcite sequences. First, the model defines redox conditions for calcite precipitation incompatible with those reported from modern ground waters. Second, the wide range of diagenetic conditions proposed by the model for precipitation of brightly luminescent calcite is incompatible with the observation that this is volumetrically the least important cement type. This model also fails to account for the Fe contents reported for many nonluminescent calcite cements. Finally, the Eh predicted from the Mn content of the calcite cements is considerably more oxidizing than that predicted from the Fe content. In part, these inconsistencies reflect the difficulty of estimating ancient redox conditions from calcite Mn and Fe contents because of the variable composition, crystallinity, and thermodynamic stability of Mn- and Fe-oxyhydroxide minerals.

A geologically reasonable, internally consistent model of the redox conditions of calcite cementation can be derived by assuming that the ground-water 2$\Delta$Mn$^{2+}$ and 2$\Delta$Fe$^{2+}$ were controlled by equilibrium with a poorly crystalline ferric hydroxide [$\Delta G_{f}^{0}\text{Fe(OH)}_{3} = -696.5$ kJ mol$^{-1}$] and a fictive MnO$_2$* with an apparent $\Delta G_{f}^{0} = -549.3$ kJ mol$^{-1}$.* These modifications to the existing model make it internally consistent so that similar Eh conditions of calcite precipitation are defined on the basis of Mn and Fe. Furthermore, the revised geochemical model defines Mn$^{2+}$ and Fe$^{2+}$ concentrations and redox conditions that are compatible with those reported from ground waters. Modern carbonate aquifers can thus provide a useful analog to interpret the distribution of CL-zoned calcite cements in ancient carbonate rocks, allowing a more refined understanding of paleo-aquifer systems and the prediction of diagenetic facies and cement distribution in ancient carbonate sequences.

INTRODUCTION

Cathodoluminescence (CL) in calcite cement (Fig. 1) results from trace-element substitution for Ca$^{2+}$. Although various trace elements are capable of influencing calcite CL (Machel, 1985), it is well known that the elements exerting the major control over CL in diagenetic calcite cements are Mn$^{2+}$ and Fe$^{2+}$ (Sommers, 1972; Meyers, 1974; Oglesby, 1976; Glover, 1977; Meyers, 1978; Meyers and Lohmann, 1978, 1985; Pierson, 1981; Frank and others, 1982; Grover and Read, 1983; Fairchild, 1983; ten Have and Heijnen, 1985). Mn$^{2+}$ activates CL, whereas Fe$^{2+}$ serves as a quencher. The exact concentrations of Mn and Fe needed to activate or quench CL, respectively, are poorly constrained. More than a few tens to 100 ppm Mn seem to be required to activate luminescence, however (Pierson, 1981; ten Have and Heijnen, 1985). The intensity and color of luminescence are also dependent on the relative proportions of Mn and Fe (Table 1). In general, calcite with Mn$>$Fe will luminesce brightly, whereas calcite with Mn$<$Fe exhibits dull luminescence. CL becomes progressively more dull with increasing Fe content but is not extinguished at Fe concentrations less than 10,000 ppm (Pierson, 1981; Fairchild, 1983).

Mn and Fe contents of calcite cements reflect pore-water chemistry prevailing during carbonate precipitation. Various studies (Oglesby, 1976; Carpenter and Oglesby, 1976; Meyers, 1978; Meyers and Lohmann, 1978; Frank and others, 1982; Grover and Read, 1983; Machel, 1985; Dorobek, 1987; Kaufman and others, 1988; Niemann and Read, 1988) have sug-

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<tr>
<th>Mn and Fe composition of calcite cement*</th>
<th>Mn and Fe composition of pore waters in equilibrium with calcite†</th>
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<tr>
<td>Mn &lt; 100 ppm</td>
<td>Mg$^{2+}$ $\approx$ 10$^{-4}$ m (1.2 ppb)</td>
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<tr>
<td>Fe &lt; 200 ppm</td>
<td>Fe$^{2+}$ $\approx$ 10$^{-8}$ m (8.8 ppb)</td>
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<tr>
<td>Brightly luminescent calcite Mn 400-9,000 ppm Fe &lt; 2,000 ppm</td>
<td>Mg$^{2+}$ $\approx$ 10$^{-7}$ (4.7-105 ppb)</td>
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<tr>
<td>Dully luminescent calcite Mn 100-3,000 ppm Fe 200-10,000 ppm</td>
<td>Fe$^{2+}$ $\approx$ 10$^{-5}$ (88 ppb)</td>
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*Based on reported values from calcite cements that formed in shallow, fresh-water aquifers by Meyers, 1978; Grover and Read, 1983; Niemann and Read, 1988; Meyers and Lohmann, 1955; Donitzek, 1983; and Graum, 1983.
†$D_{\text{Mn, calcite}} = 15$ (Pegrum, 1978); $D_{\text{Mn, calcite}} = 4$ (Ishihara, 1983).

Figure 1. Microphotographs of cathodoluminescent-zoned calcite cements. Scale bar equals 0.5 mm for both photos. Note the paucity of brightly luminescent calcite (BR) relative to nonluminescent (NL) and dully luminescent (DL) calcite cements in each example. A. Middle Ordovician calcite cements described in Grover and Read (1983). Crinoid grain (CR) overgrown by nonluminescent calcite cement which was succeeded by brightly luminescent calcite and a final void-filling, finely subzoned, dully luminescent calcite. B. Mississippian calcite cements described in Niemann and Read (1988). Fenestral cavity is lined by nonluminescent calcite cement which is overgrown by a thin rim of brightly luminescent calcite. These were followed by a second generation of nonluminescent calcite and a later void-filling dully luminescent calcite.

suggested that the increasing Fe and Mn contents in the commonly observed sequence of CL zonation from nonluminescent to brightly luminescent to dully luminescent reflects a progressive decrease in Eh. Implicit in this geochemical model is the assumption that the Mn$^{2+}$ and Fe$^{2+}$ concentrations in the diagenetic water were governed by equilibrium reactions with Mn- and Fe-bearing mineral phases whose solubilities were controlled by the pH and Eh conditions of the ground water and that these minerals were present in the system during the precipitation of authigenic carbonate. Because pore-water pH in carbonate aquifers is generally restricted to a relatively narrow range (between 6.5 and 8.5) due to carbonate buffering, variations in dissolved Mn$^{2+}$ and Fe$^{2+}$ are attributed primarily to changes in redox conditions. The Mn and Fe contents of calcite precipitated in equilibrium with these pore waters are determined by the Mn/Ca and Fe/Ca ratios of the pore waters and the corresponding distribution coefficients. Carbonate buffering limits the Ca$^{2+}$ content in the pore water (generally between 30 and 200 ppm). The Mn and Fe compositions of diagenetic calcites therefore should largely reflect the Eh conditions prevailing during the various stages of calcite cementation.

In this paper, we evaluate the geochemical model proposed by Oglesby (1976), Carpenter and Oglesby (1976), and Frank and others (1982) which uses calcite Mn and Fe contents to define diagenetic environments of CL calcite precipitation. It will be shown that numerous inconsistencies in the model limit its ability to define redox conditions of calcite cementation consistent with those observed in modern carbonate aquifers or those inferred from ancient calcite cements. These inconsistencies arise from the use of Mn- and Fe-oxyhydroxide phases with different thermodynamic stabilities than those actually governing Mn$^{2+}$ and Fe$^{2+}$ in modern ground waters. We propose modifications to the model which make it internally consistent and define diagenetic environments of precipitation for CL calcite cements compatible with those observed in shallow, fresh-water aquifers. The proposed modifications to the existing geochemical model are a substantive improvement and show that hydrogeochemical data from modern aquifers can provide a modern analog to paleoaquifer systems, allowing a more refined understanding of regional calcite cementation in ancient carbonate sequences.

PREVIOUS WORK

Based on the hypothesis that Mn and Fe contents (and consequently, the CL) of authigenic calcite cements reflect pore water $\delta_{\text{Mn}^{2+}}$ and $\delta_{\text{Fe}^{2+}}$ which were governed by redox reactions, Oglesby (1976), Carpenter and Oglesby (1976), and Frank and others (1982) with proposed diagenetic environments of precipitation for nonluminescent, brightly luminescent, and dully luminescent calcite cements. Model constructed assuming equilibrium with MnO$_2$ (pyrolusite), FeOOH (goethite), and calcite; total sulfur concentrations are negligible. Boundary between nonluminescent/brightly luminescent and brightly luminescent/dully luminescent fields calculated at $\delta_{\text{Mn}^{2+}} = 10^{-7}$ and $\delta_{\text{Fe}^{2+}} = 10^{-7}$, respectively. Shaded area represents range of Eh-pH measurements reported for shallow ground waters by Baas Becking and others (1960), Edmunds (1973), and Edmunds and others (1987).
Oglesby (1976), and Frank and others (1982) proposed a geochemical model that broadly defined diagenetic environments of precipitation for calcite cements, relating cathodoluminescence to the solution Eh (Fig. 2). This model correctly relates calcite CL to the redox conditions of calcite precipitation. Our work, however, indicates that numerous inconsistencies in the model become evident when it is compared to hydrogeochemical data for modern carbonate aquifers and to geological observations of natural calcite cements.

The first problem is that although Oglesby (1976), Carpenter and Oglesby (1976), and Frank and others (1982) did confine their model to a narrow pH range (6.5 to 8.5) compatible with known ground waters in carbonate aquifers, they made no attempt to confine the model to Eh values observed from modern aquifers. Consequently, the diagenetic environments proposed for formation of nonluminescent calcite and the uppermost portion of the brightly luminescent field are incompatible with measured Eh values reported for shallow fresh ground waters (for example, Baas Becking and others, 1960; Edmunds, 1973; Edmunds and others, 1982; and Dorobek (1987). These nonluminescent calcite cements containing iron cannot have formed in the nonluminescent diagenetic environment defined by the model.

In order to improve the internal consistency of this otherwise useful model, we propose the following reassessment of the geochemical controls over Fe and Mn incorporation into CL calcite cements.

**ESTIMATING THE GEOCHEMICAL CONDITIONS OF CALCITE CEMENTATION**

**Carbonate Equilibria**

Shallow meteoric ground waters in carbonate aquifers are generally low in ionic strength (ionic strength < 0.05) and the estimated activity coefficients for Ca$^{2+}$, Mn$^{2+}$, and Fe$^{2+}$ using the Debye-Hückel equation are greater than 0.5. Furthermore, in these dilute, simple solutions, the
with respect to calcite at a given $P_{CO_2}$ and temperature (Back and Hanshaw, 1970; Plummer and others, 1976). As a first approximation, however, the ground water may be assumed to be in equilibrium with calcite. In many carbonate aquifers, carbonate equilibria calculations assuming open-system conditions (constant $P_{CO_2}$) more closely approximate observed ground-water chemistry than when a closed-system approach is used (Freeze and Cherry, 1979, p. 257). This observation is utilized in subsequent calculations. The parameters relating to carbonate equilibria used in the subsequent calculations to estimate nominal geochemical conditions are given in Table 2. The selection of these parameters fixes the $a_{Ca^{2+}}$ of the diagenetic waters near $10^{-2.8}$ ($\approx 70$ ppm), compatible with reported values from carbonate ground waters (Back and Hanshaw, 1970; Langmuir, 1971; Plummer and others, 1976; Edmunds and others, 1987).

It is emphasized that these and subsequent calculations specifically apply to Ca sequences that formed during calcite cementation in shallow meteoric aquifers (Meyers, 1978; Grover and Read, 1983; Niemann and Read, 1988; Meyers and Lohmann, 1985; Dorobek, 1987; Grams, 1987; Goldstein, 1988). Late-stage calcite cements may form under deeper burial conditions by warm saline fluids as indicated by petrographic, isotopic, and fluid-inclusion studies (for example, Nelson, 1985; Dorobek, 1987), and the conclusions developed here cannot be directly applied to these cases.

In order to construct Eh-pH diagrams for the Fe-CO$_2$-S-H$_2$O and Mn-CO$_2$-S-H$_2$O systems, an estimate for total sulfur activity is needed. For the calculation of stability fields, total sulfur, $S_T = 10^{-3}$ m ($\approx 10$ ppm), characteristic of fresh ground waters, is used. Note that this value is too low for coastal aquifers undergoing salt-water intrusion and mixing of sea water with fresh water; however, it is reasonable for most fresh waters. The formation of FeSO$_4$(aq) and MnSO$_4$(aq) is relatively insignificant in waters having $SO_4^{2-}$ concentrations less than $10^{-3}$ m (Hem, 1970, 1985). Therefore, they are not considered in subsequent calculations.

### Mn$^{2+}$ and Fe$^{2+}$ Contents

Under equilibrium conditions, the relation between the concentration of a trace element in calcite and the trace-element composition of the pore waters may be expressed by the distribution coefficient (D) of the trace element (Me$^{2+}$), where

$$D = \frac{(Me^{2+}/Ca^{2+})_{CAL}}{(Me^{2+}/Ca^{2+})_{SOLN}}.$$  

Because only ions with the same valence state readily substitute for Ca$^{2+}$ in calcite cement, only the concentrations of the reduced species, Fe$^{2+}$ and Mn$^{2+}$, are important in determining the amount of Mn and Fe incorporated into a diagenetic calcite, because Fe$^{3+}$ and Mn$^{6+}$ cannot substitute for Ca$^{2+}$.

Therefore, the $\delta_{Mn^{2+}}$ and $\delta_{Fe^{2+}}$ in the pore water at the time of calcite precipitation may be approximated from their concentrations in the calcite using distribution coefficients for Mn ($D_{Mn}$) and Fe ($D_{Fe}$). Distribution coefficients for Mn and Fe in calcite are influenced by precipitation rate (Lorens, 1981; Dromgoole and Walter, 1987; Mucci, 1988) and temperature (Bodine and others, 1965). Lorens (1981) indicated that $D_{Mn}$ varies from 5 at rapid precipitation rates to almost 70 at very slow rates of precipitation, and one may infer that $D_{Fe}$ exhibits similar behavior. In subsequent calculations, we use $D_{Mn} = 15$ (Pingetore, 1978) and $D_{Fe} = 4$ (Ichikuni, 1983). If the effective distribution coefficients for Mn and Fe during calcite cementation varied even _an order of magnitude_ from these values due to rate effects, the estimated solution Eh would be in error by only 0.06 volts, which will not significantly affect the conclusions developed in this paper. Temperature-induced variations in $D_{Mn}$ and $D_{Fe}$ are

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Figure 4. Calculated pore water Mn$^{2+}$ and Fe$^{2+}$ activity ranges for the various calcite CL zones superimposed on equilibrium activity contours of Eh-pH diagrams, assuming pore-water equilibrium with MnO$_2$ (pyrolusite) and amorphous Fe(OH)$_3$. Lower limit of $a_{Fe^{2+}}$, $a_{Mn^{2+}}$ are terminated at $10^{-9}$, calcites precipitating from such solutions would contain no detectable Fe and Mn. Note that the Eh range defined by the reported range of Mn concentrations for authigenic calcites is considerably more oxidizing for any given CL zone than that defined from Fe composition. This relation is maintained throughout pH range of interest. Shaded area represents range of Eh-pH measurements reported for shallow ground waters by Baas Becking and others (1960), Edmunds (1970), and Edmunds and others (1987). Note that Eh predicted on basis of Fe content is consistent with these observations, whereas Eh expected on basis of Mn content is more oxidizing.

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**Notes:**

- Effects of ion pairing are negligible (Hem, 1985). The error in assuming that the activity of ionic species is approximately equal to the concentration can be neglected as even an order of magnitude of error in estimating the solution chemistry will change the estimated Eh by a small amount (<0.06 volts). Consequently, in this paper, the activities of ionic species are assumed to be equal to their concentration in solution, and the terms are used interchangeably. It is emphasized that this approach applies specifically to shallow meteoric ground waters.

- An estimate of $a_{Ca^{2+}}$ is needed in order to use distribution coefficients to evaluate the $a_{Fe^{2+}}$ and $a_{Mn^{2+}}$ in the pore water. Ground waters in carbonate aquifers may be undersaturated, supersaturated, or saturated.
also of no concern, because the model applies specifically to shallow meteoric ground waters (~25 °C). $D_M$ is not significantly affected at temperatures lower than 100 °C (Bodine and others, 1965), and $D_F$ should exhibit similar behavior. The reported variations in calcite Mn and Fe contents therefore cannot be attributed solely to changes in the distribution coefficients due to precipitation rate and/or temperature, and it is reasonable to assume that calcite Mn and Fe contents are influenced chiefly by the composition of the pore water.

Table 1 lists Mn$^{2+}$ and Fe$^{2+}$ concentration ranges of the various calcite CL zones that were used in this study to estimate Mn$^{2+}$ and Fe$^{2+}$ composition of the diagenetic waters that precipitated the calcite cements. These concentrations are based on reported values from various studies of calcite cements that formed in shallow, fresh-water aquifers (Meyers, 1978; Meyers and Lohmann, 1985; Grover and Read, 1983; Niemann and Read, 1988; Dorobek, 1987; Grams, 1987). The calculated pore-water Mn$^{2+}$ and Fe$^{2+}$ activities are robust estimates; the equilibrium Eh of the pore water from which the calcite precipitated will change only 0.06 volts for an order of magnitude of error in estimating $a_{Fe^{2+}}$ and $a_{Mn^{2+}}$ resulting from variation in the distribution coefficients. Consequently, the error would have to be considerable before the proposed modified geochemical model or the conclusions developed in this paper are significantly affected.

**Eh-pH Diagrams**

There are numerous difficulties in relating activities of redox-related dissolved species in natural waters to measured Eh values. Many of these result from mixed potentials arising from disequilibrium between numerous redox couples in the solution, so that it is generally not possible to attribute measured Eh values to a single master redox couple (Lindberg and Runnells, 1984). In particular, Pt electrode measured Eh does not adequately reflect the effects of the O$_2$aq/H$_2$O redox couple which can result in considerable discrepancy between measured Eh and Eh computed from the dissolved-oxygen content. The Fe$^{2+}$/Fe(OH)$_3$ redox couple, however, more closely approaches equilibrium with respect to Pt electrode Eh than that computed for the O$_2$aq/H$_2$O couple (Lindberg and Runnells, 1984). Various studies have demonstrated that Pt electrode Eh values are compatible with Eh estimated from the Fe$^{2+}$ content and pH of natural ground waters, assuming equilibrium with iron oxyhydroxide minerals with stabilities between Fe(OH)$_3$ and crystalline FeOOH (Barnes and Back, 1964; Back and Barnes, 1965; Hem, 1970, 1985; Fayard, 1971; Whittemore and Langmuir, 1975; Stoufer, 1975). Furthermore, the redox potential of Mn redox couples is also unrelated to the potential calculated from the O$_2$aq/H$_2$O redox couple (Bohn, 1970) but can be related to the Pt electrode Eh assuming equilibrium with a Mn-oxide phase more stable than pyrolusite (discussed below). These lines of evidence suggest that Pt-electrode–measured Eh more closely reflects redox conditions as defined by the iron and manganese equilibria than that provided by other indicators (for example, the O$_2$aq/H$_2$O redox couple). In this model, we are concerned only with the Eh of the solutions as reflected by the iron and manganese redox equilibria so that disequilibrium among other redox couples is of no concern.

Another problem in relating activities of redox elements in solution to
Eh conditions is that internal disequilibrium for any given redox couple is common (Lindberg and Runnells, 1984); however, given the time scale of calcite cementation in shallow aquifer systems (>10^6 yr, see Dorobek, 1987; Niemann and Read, 1988), redox reactions between cations in solution are comparatively instantaneous (see for example Table 6.3, p. 475, in Basolo and Pearson, 1967); furthermore, the dissolution and precipitation rates of iron and manganese oxyhydroxides are also quite fast (Cornell and others, 1976; Sarana and Warren, 1969; Malati, 1983). Stumm and Morgan (1981, p. 468–469) indicated that redox reactions involving Mn and Fe oxyhydroxides are rapid (minutes to hours) in solutions containing organic compounds. Furthermore, Mn-oxide reduction and subsequent increase in Mn^{2+} in solution occurs soon after the onset of reducing conditions in flooded soils (Patrick and Turner, 1968). Thus it is reasonable to assume that Mn and Fe contents of authigenic calcite will reflect long-term, average equilibrium between Fe^{2+} and Mn^{2+} in solution and iron and manganese oxyhydroxides.

Based on the above discussion, if the pore waters were in equilibrium with Mn and Fe oxyhydroxide phases of known thermodynamic stability, Mn^{2+} and Fe^{2+} contents of the diagenetic environment can be interpreted in terms of redox conditions. Eh-pH diagrams for the FeCO_2-S-H_2O and Mn-CO_2-S-H_2O systems define the activity contours for Fe^{2+} and Mn^{2+} in solutions at equilibrium with iron and manganese oxyhydroxides, respectively, for which free-energy data are available in the literature (Fig. 3). These diagrams show that a small change in Eh or pH will cause a significant change in Fe^{2+} and/or Mn^{2+} concentration and that Mn^{2+} concentrations should be much higher in pore waters at any given Eh and pH value than Fe^{2+}.

When the Mn^{2+} and Fe^{2+} solution concentration ranges estimated for each CL zone (Table 1) are superimposed on their respective activity contours (Fig. 4), the redox conditions defined from the Mn content of the calcites do not coincide with those defined on the basis of Fe. This relation is maintained throughout the pH range of interest. Because the Mn and Fe are coprecipitated with the calcite cement, they should define similar redox conditions. Thus, one or more of the assumptions used to relate the Fe^{2+} and Mn^{2+} content of the calcite cement (and hence their cathodoluminescence) to the Eh conditions of their formation must be altered to account for this behavior.

Because Eh-pH diagrams are constructed using logarithmic functions, the discrepancy between the Eh values determined using Fe and Mn cannot simply be due to the choice of distribution coefficients, as the estimated pore water $\alpha_{Fe}$ and/or $\alpha_{Mn}$ would have to be in error by over ten orders of magnitude in order for them to define similar Eh conditions. Other assumptions ($P_{CO_2}$, calcite equilibria, total sulfur) also cannot account for the discrepancy. No matter what reasonable values of $P_{CO_2}$, $\alpha_{O_2}$, and $\phi_S$ are used, the difference remains.

The only reasonable explanation for this discrepancy is that the pore waters are not in equilibrium with the Fe and Mn oxyhydroxide phases considered in construction of the stability diagrams. This could reflect (a) Fe- and Mn-oxyhydroxide phases were not present; (b) disequilibrium between pore-water Fe^{2+} and Mn^{2+} with Fe- and Mn-oxyhydroxide

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Figure 7. Mass-balance model of equilibrium Mn and Fe uptake into calcite cement. A. Pore space in CaCO_3 sediment is incrementally cemented by calcite under successively lower Eh conditions (from "A" to "B"). Initial Mn content: 100 ppm as MnO_2; initial Fe content: 500 ppm as Fe(OH)_3; these initial Mn and Fe concentrations are compatible with those reported for modern marine CaCO_3 sediments with little or no terrigenous component (Friedman, 1969; Rao, 1981, 1986). Mn and Fe in the calcite cement are assumed to be derived from the admixed Mn- and Fe-oxyhydroxides within the CaCO_3 sediments; Ca^{2+} is transported to the site of calcite cementation by ground water and was derived from carbonate dissolution updip. B. Resulting profile of the Mn and Fe concentrations of the calcite cement. Under the oxidizing conditions defined by the nonluminescent field, MnO_2 and Fe(OH)_3 are relatively stable; this is reflected by the low Mn and Fe contents of calcites forming under these conditions. Under the moderately reducing conditions defined by the brightly luminescent field, MnO_2 is progressively dissolved to yield increasing Mn^{2+} to the fluid; however, Fe(OH)_3 remains relatively stable. This results in precipitation of calcite with Fe << Mn. The sudden depletion in Mn from the brightly to dully luminescent fields reflects loss of MnO_2, which was progressively dissolved under the more reducing conditions. The location of this boundary and the maximum concentrations of Mn that are attained depend on the initial Mn content of the CaCO_3 sediment. Under the reducing conditions defined by the dully luminescent field, Fe(OH)_3 is progressively dissolved to yield Fe^{2+} to the pore water, which is reflected by the elevated Fe contents of these late calcites.
Iron and Manganese Solubility Controls

Numerous ground-water studies have demonstrated that Fe$^{2+}$ in most ground waters is in equilibrium at the observed pH and Pt electrode determined Eh with iron oxyhydroxide minerals with apparent solubilities between that of amorphous Fe(OH)$_3$ and crystalline FeOOH (Barnes and Back, 1964; Back and Barnes, 1965; Hem, 1970, 1985; Fayard, 1971; Whittemore and Langmuir, 1975; Stoufer, 1975) and is compatible with the Eh-pH diagrams shown here (Figs. 3, 4). The variable stability of the iron oxyhydroxide phases, however, make the exact determination of Eh from solution Fe$^{2+}$ concentrations impossible. Unfortunately, these studies have been confined to ground waters in siliciclastic aquifers, which are different in mineralogy from carbonate aquifers and are not necessarily buffered by carbonate equilibria, and they therefore may not be directly applicable.

Only a few hydrogeochemical studies of fresh ground waters in carbonate aquifers have been reported which provide Eh, pH, and Fe$^{2+}$ analyses. The thermodynamic stability of the Fe hydroxides governing Fe$^{2+}$ solubility in these waters can be evaluated by estimating the apparent standard free energy of formation of a hypothetical ferric hydroxide phase in equilibrium with the ground water using the Nernst equation, assuming that Pt-electrode-measured Eh potentials approximate the actual Eh. The reported Fe$^{2+}$, pH, and Eh values for two carbonate aquifers (Edmunds, 1973; Edmunds and others, 1987) each yield average estimated
The manganese chemistry in natural systems is extremely complex and not well understood. Reasons for these complexities are numerous: Mn exists in several possible oxidation states and commonly forms complex, nonstoichiometric oxyhydroxides incorporating mixed valence states of Mn; Mn oxides exist in several crystalline states and form coprecipitates with Fe-oxyhydroxides; and the composition and crystalline state of the complex Mn oxyhydroxides vary with the environment in which they formed (Ponnamperuma and others, 1969). More than 150 Mn oxides with compositions ranging from MnO₂ to MnO₂₀ have been described (Dubois, 1936). Detailed studies of Mn oxide mineralogy from various sedimentary environments indicate that Mn oxides other than pyrolusite (MnO₂) are dominant; various workers have identified lithiophorite (Tiller, 1963); lithiophorite, birnessite, todorokite, and hollandite-group minerals (Potter and Rossman, 1979); examples of stoichiometric pyrolusite (MnO₂) are relatively uncommon.

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Consequently, manganese-solubility controls evaluated using Eh-pH diagrams constructed assuming equilibrium with pyrolusite (MnO₂) are not generally applicable to natural systems (Ponnamperuma and others, 1969). Observed Mn²⁺ concentrations are consistently lower than those calculated assuming equilibrium with pyrolusite (Bohn, 1970; Gotoh and Patrick, 1972), indicating that, if the waters are in equilibrium with a Mn oxide phase, it is considerably more stable than pyrolusite. Furthermore, the observation that ground waters nearly always contain higher levels of Fe²⁺ than Mn²⁺ (Seaber, 1965; Hem, 1970), in conflict with the stability diagrams (Figs. 3, 4) which predict that at any given Eh and pH, ApFe²⁺ << Amn²⁺, indicates that most fresh ground waters are not in equilibrium with the pure Mn oxide phases but may be in equilibrium with a thermodynamically more stable compound.

Because the manganese oxide mineralogy of most carbonate rocks is unknown, and thermodynamic data for the complex Mn oxide phases are lacking, apparent standard free energies of formation must be utilized in order to assess manganese solubility controls in shallow aquifer systems. The apparent standard free energies of formation reported for nonstoichiometric Mn-oxides by Brenet and others (1963) and Ponnamperuma and others (1969), indicate that the complex Mn oxides are considerably more stable under reducing conditions than is pyrolusite. We propose that, because no stability data for these phases exist, a fictive MnO₂⁺ phase with a nominal ΔGf° = −549.3 kJ mol⁻¹ be used as a proxy (Ponnamperuma and others, 1969). Stability diagrams constructed using these estimated standard free energies of formation (Fig. 5) demonstrate that the Mn²⁺ activity contours are depressed toward more reducing conditions and define Eh conditions consistent with those predicted from the iron equilibria discussed above.

The proposition that Mn oxide phases more stable than pyrolusite govern ΔMn²⁺ in carbonate aquifers can be evaluated from hydrogeochemical data for modern carbonate aquifers (Edmunds, 1973; Edmunds and others, 1987). Using the Nernst equation (assuming Pt electrode measured Eh approximates Eh as reflected by the Mn equilibria), the average estimated apparent ΔGf° for MnO₂⁺ = −549 kJ mol⁻¹ and −545 kJ mol⁻¹, which compare favorably with those reported by Ponnamperuma and others (1969). Therefore, the choice of a thermodynamically more stable, complex Mn oxide defines Mn²⁺ concentrations compatible with those reported from shallow ground waters in carbonate aquifers.

**THE MODEL**

We propose an internally consistent, geochemical model (Fig. 6) that defines redox conditions of calcite precipitation on the basis of calcite Fe and Mn contents, assuming pore-water Fe²⁺ and Mn²⁺ compositions (Table 1) were governed by thermodynamic equilibrium with Fe and Mn oxyhydroxides similar in stability to those considered here [ΔGf°(Fe(OH)₃) = −696.5 kJ mol⁻¹, ΔGf°MnO₂⁺ = −549.3 kJ mol⁻¹] at 25 °C. The boundary locations are approximate; however, for each order of magnitude error in the estimated pore-water Amn²⁺ and AppFe²⁺, the field boundaries would be shifted by a small amount (∼0.06 volts). Consequently, the error would have to be considerable before the model developed here is greatly affected. Temperature effects on the stability diagram were evaluated using ΔGf° data reported for temperatures other than 25 °C (Naumov and others, 1974; Barner and Scheuermann, 1978; Robie and others, 1978). An increase in temperature of 25 °C will shift the field boundaries downward −0.08 volts, but will preserve the relative geometry of the diagram.

Using this model, we can define calcite Mn and Fe contents (Fig. 7) compatible with those reported by various workers for natural calcite cements (Fig. 8). Furthermore, the mass balance model (Fig. 7) demonstrates that the Mn and Fe contents initially present in “clean” marine
conditions for precipitation of ancient calcite cements which can then be

rather on using it to provide an objective means of estimating the redox

defined from the geochemical model (Fig. 6)

cemented in updip reaches of paleo-aquifer near unconformity and penetrated downdip under confined-aquifer conditions. Dully luminescent calcite formed in distal portion of confined aquifer (from Niemann and Read, 1988). B. Siluro-Devonian Helderberg Group, Virginia and West Virginia: nonluminescent calcite cements formed in shallow aquifers sourced from updip sandstones and passed basinward into dully luminescent calcite (from Dorobek, 1987).

Figure 11. Schematic distribution of CL-calcite cements; cross sections are oblique to strike, and downdip reaches are 40 km maximum from paleorecharge regions; paleo-ground-water flow is from left to right. A. Mississippian Newman Limestone, Kentucky: nonluminescent calcite precipitated in updip reaches of paleo-aquifer near unconformity and penetrated downdip under confined-aquifer conditions. Dully luminescent calcite formed in distal portion of confined aquifer (from Niemann and Read, 1988). B. Siluro-Devonian Helderberg Group, Virginia and West Virginia: nonluminescent calcite cements formed in shallow aquifers sourced from updip sandstones and passed basinward into dully luminescent calcite (from Dorobek, 1987).

CONCLUSIONS

The geochemical model of Oglesby (1976), Carpenter and Oglesby (1976), and Frank and others (1982) proposed that Mn and Fe contents (and the CL) of authigenic calcite should reflect the redox conditions of calcite precipitation. Their model was based on the following assumptions: (a) calcite Mn and Fe contents record pore-waters Mn$^{2+}$ and Fe$^{2+}$; (b) Mn$^{2+}$ and Fe$^{2+}$ in the pore water are governed by equilibrium with Mn- and Fe-bearing minerals; (c) the solubility of these minerals is dependent on the Eh and pH of the pore water; (d) because pore water pH is buffered by carbonate equilibria, Mn$^{2+}$ and Fe$^{2+}$ are primarily affected by Eh conditions. Although these assumptions are largely justifiable, considerable discrepancies exist between the diagenetic conditions defined by their model and those observed in modern carbonate aquifers and inferred from CL-calcite cements. In part, these inconsistencies reflect the difficulty of using Mn$^{2+}$ and Fe$^{2+}$ to define redox conditions because of the variable composition, crystallinity, and thermodynamic stability of Mn- and Fe-oxyhydroxide minerals.

We propose that the existing geochemical model be modified by using Mn- and Fe-oxyhydroxide phases of similar thermodynamic stability to those controlling Mn$^{2+}$ and Fe$^{2+}$ solubility in shallow meteoric ground waters. Using the revised geochemical model developed in this paper, similar redox conditions are expected on the basis of calcite Mn and Fe contents, and the Eh conditions thus defined coincide with those observed in shallow, fresh ground waters. This allows modern aquifers to be used as an analog with which to interpret the distribution of CL-calcite cements in ancient carbonate rocks and permits a more sophisticated approach toward understanding paleoaquifer systems and predicting diagenetic facies and cement distribution in ancient carbonate sequences.
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