Diagenetic responses to sea-level change: Integration of field, stable isotope, paleosol, paleokarst, fluid inclusion, and cement stratigraphy research to determine history and magnitude of sea-level fluctuation

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Abstract Quantifying the history of changes in sea level is an important constraint for modeling sedimentary systems. Integration of diagenetic evidence for subaerial exposure with stratigraphic evidence of paleotopography is important for determining the history of relative changes in sea level. Surfaces of subaerial exposure cut into orogen front orogenic strata from aggradation of sediment into the subaerial realm, from eustatic sea-level falls, or from uplift. Surfaces of subaerial exposure that result from aggradation alone can be distinguished from those that result from eustatic fall or uplift. Exposure surfaces directly overlie strata of subaerial origin or drapes significant paleotopography, and aggradation alone must be ruled out. The minimum relative fall in sea level can be quantified by tracing surfaces of subaerial exposure over reconstructed paleotopography or by determining the depth to which vadose-zone diagenesis occurred. Paleosols, paleokarst, trends in stable isotopes, calcite cement stratigraphy, calcite cement fabrics, and fluid inclusions provide diagenetic records that are useful in identifying ancient surfaces of subaerial exposure and determining the position of ancient vadose zones. Paleosols can be identified using the preserved records of desiccation and weathering, subaerial processes, and phytolith activity. Studies from the Pennsylvanian Helder Formation of New Mexico illustrate that paleosols can be extremely variable in nature and can be used to demonstrate a relative fall in sea level of at least 30 m (100 ft). Paleosol features can develop well below the subaerial surface, and caution must be used in applying this technique. Paleokarst is another useful record of subaerial exposure. Some karstification results in surface landforms, terraces, paleosols, or vertical voids in which there is a clear relationship to an ancient surface of subaerial exposure. The depth of penetration of these karst features that developed in the vadose zone can be used as a minimum estimate of relative-sea-level fall. For karst cavities that cannot be directly associated with a specific surface of subaerial exposure, the age of sediment fills or regional distribution of cavities can provide the most direct link to a particular surface of subaerial exposure. Whole-rock titrants of relatively negative δ13C, relatively positive δ18O, and a baseline shift in δ18O can also reflect ancient surfaces of subaerial exposure. Variability of data from the Helder Formation shows that the trends predicted are not the result of stabilization in a homogeneous, relatively negative δ13C zone but the result of patchy cementation and replacement in a solution of heterogeneous carbon isotopic composition. Preservation of the most negative carbon signatures depends on sampling the highest volumes of soil-precipitated fluids and those in closest proximity to organic structure in soils. Calcareous cements with meniscus or pendant fabrics preserve a record of vadose diagenesis. Vertical pinchouts of calcite-cement compositional zones may reflect surfaces of subaerial exposure. The lateral variability of such cements in the Pennsylvanian Helder Formation and the Laramie-Kansas City Groups of Kansas shows that such cements develop best in paleogeographically high settings. Fluid inclusions can provide a record of diagenesis in the vadose zone. Fluid inclusions trapped in the vadose zone are marked by variable ratios of eutectic liquid to solid phases and show variable fluid inclusions. The distribution of such inclusions in Miocene rocks of Spain demonstrate a relative fall in sea level of at least 50–55 m (160–180 ft).

Accurate modeling of sedimentary systems relies on establishing appropriate constraints on the variables that affect sedimentation. One of the most important variables is the history and magnitude of sea-level change. A part of this history can be determined by analysis of the early meteoric diagenesis of shallow-water sedimentary rocks. In this article we describe techniques by which sea-level history can be determined through the integration of meteoric diagenesis and subaerial exposure with sedimentary facies and paleotopography. We illustrate the importance, strengths, and weaknesses of paleosols, paleokarst, stable isotopic signatures, vadose-zone cement fabrics, cement stratigraphy, and fluid inclusions as records of subaerial exposure and discuss their use for quantifying the history of relative change in sea level. The discussions and case studies are biased toward carbonate and our studies of the Carboniferous and the Miocene, but we also include some findings on sandstones.

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During a relative fall in sea level, shallow-water marine carbonate sediments commonly are exposed subaerially and are subjected to diagenesis by meteoric fluids. The unstable mineralogy of these sediments and the chemically aggressive nature of meteoric water renders carbonates diagenetically impressionable so that they typically preserve a record of the meteoric fluids. Identification of surfaces of subaerial exposure and the paleotopography along these surfaces help to reveal the history and magnitude of relative sea-level falls.

Determining causes of subaerial exposure

Surfaces of subaerial exposure on marine strata can result from (1) uplift, (2) eustatic fall in sea level, and (3) vertical aggradation of sediment into the subaerial realm without uplift or eustatic fall. To quantify the history of sea-level change, we believe that it is important to distinguish subaerial exposure events that resulted from vertical aggradation from those events that resulted from eustasy or uplift.

It is well known that shallow-water carbonate sediments can accrete vertically into the subaerial realm without a fall in sea level. Modern, shallow subtidal carbonate environments can be areas of localized active sediment aggradation into the intertidal and finally into the supratidal or subaerial realm (Enos and Perkins, 1979); such accretion can be followed by progradation of tidal flat and subtidal carbonate sediments over and into the subtidal environment (e.g., Kinsman (1964) and Ginsburg (1971)). Overall, shoaling-upward sequences are common features of the ancient stratigraphic record (Wilson, 1975; James, 1984). Simple aggradation produces a vertical sequence of shallow subtidal to intertidal to supratidal strata capped by a surface of subaerial exposure. However, a similar sequence also can develop from eustatic fall in sea level or tectonic uplift. Therefore, in ancient rocks, distinguishing exposure surfaces caused by aggradation into the subaerial realm from those surfaces caused by eustatic or tectonically induced falls in relative sea level is critical. Three types of observations aid in determining the origin of such surfaces: (1) the vertical sequence of facies relative to the subaerial surface, (2) the paleotopography over which an ancient surface of subaerial exposure can be traced, and (3) the depth to which vadose-zone diagenesis penetrates beneath the exposure surface.

An upward transition directly from marine subtidal strata to a subaerial exposure surface suggests an eustatic fall in sea level or an uplift (Hardie et al., 1986; Goldhammer et al., 1987; Goldstein, 1988b). Such a transition cannot be generated by simple aggradation into the subaerial realm. Even subaerial erosion following aggradation (without sea-level fall) cannot explain such a transition because subaerial erosion would not cut down into the subtidal facies (which would remain below sea level) without a relative fall in sea level.

A surface of subaerial exposure that caps marine limestones can be used to determine the amount of fall in relative sea level by tracing the exposure surface down the paleoslope. Paleotopography can be estimated by determining the thickness of strata that onlap the exposure surface or by estimating the paleoslope through the discrepancy between the preserved topography or bedding and the geopetal fabrics (Playford, 1980) or paleomagnetic indicators (Devaney et al., 1986). Exposure surfaces that can be traced over significant paleotopography must result from eustatic sea-level fall or uplift rather than from simple aggradation into the subaerial realm.

In most coastal settings, during subaerial exposure, the lowest elevation of the water table is that of sea level. Therefore the depth to which the vadose zone penetrated beneath a particular surface of subaerial exposure can be used to estimate the minimum relative fall in sea level. Exceptions to this are arid closed-drainage basins and tectonically depressed regions. With subaerial exposure that results from simple aggradation, significant vadose diagenesis should not extend more deeply than the underlying intertidal strata. With subaerial exposure that results from eustatic fall or uplift, vadose diagenesis may extend more deeply into the underlying strata. The criteria for recognition of vadose diagenesis are covered later.

Determining sea-level history from subaerial exposure

Paleosols, paleokarst, stable isotopic shifts, records of vadose-zone cementation, cement stratigraphic discontinuities, and fluid inclusions are important for identifying events of subaerial exposure and for locating specific ancient surfaces of subaerial exposure. The location of such surfaces over paleotopographic relief and on marine sedimentary facies provides a useful constraint on quantifying the history of relative sea-level change. Determining the depth of vadose-zone diagenesis provides a further constraint on that history. In what follows we summarize various methods for identifying ancient surfaces and events of subaerial exposure and provide examples of their application for tracing sea-level history. Although it is not a comprehensive summary, its purpose is to deal with the most important methods and to concentrate on applications to carbonate rocks.

Paleosols

The easiest means for the identification of ancient surfaces of subaerial exposure are the recognition of paleosols, which are the partial remains of ancient soils. Paleosol formation is characterized by plant activity, desiccation and wetting, and infiltration and evaporation of meteoric water. Horizons containing evidence of such activity provide strong support for subaerial exposure.

Excellent evidence for subaerial exposure are cracks that form during exposure. Root penetration (Klappa, 1980a) and shrinkage and expansion during early desiccation and wetting result in cracks that commonly are filled with internal
sediment or carbonate cement. During subaerial exposure, rapidly percolating vadose water and production of sediment through soil processes encourage sediment to move through pore networks and to be deposited in early pores. However, internal sediment in cracks as by no means diagnostic of subaerial exposure.

The crack patterns resulting from soil processes can be diagnostic of subaerial exposure (fig. 1) (Brewer, 1964; Freyot and Plaziat, 1982). Many such cracks curve around grains rather than cut across them because of the lack of extensive cementation in the sediment. Such short, curved cracks are called curved planes (Freyot and Plaziat, 1982) or circumgranular cracks (Swineford et al., 1958) (fig. 2). Desiccation and wetting also can produce discontinuous, parallel planar cracks (fig. 3), which are commonly classified at fenestrate among geologists (Shinn, 1968, 1983) as joint planes among soil micromorphologists (Brewer, 1964). More extensive cracking may produce a brecciated fabric in which particles can be fitted back together in puzzle-piece fashion (autoclastic breccia, skew planes) (fig. 4). Such a fabric indicates formation in place. Crazed-plane fabrics (Brewer, 1964) can be produced by extensive brecciation and water infiltration, resulting in a fabric in which clasts can no longer be fitted back together (fig. 5) (Mazzullo and Birdwell, 1989; Wright, 1990). In argillaceous palaeosols especially, the clasts (peds) produced by crack formation form diagnostic patterns, including platy, prismatic, columnar (fig. 6), and blocky structures (Rellifalk, 1988).

Preserved upright plants provide strong evidence for palaeosol formation, but preservation of plants in life position is unusual. More commonly, root structures (rhizoliths) are preserved as evidence of palaeosols (Klappa, 1980b). In general, rhizoliths are identified as sinuous, cylindrical pores filled with internal sediment, later spar, or microcrystalline cement (fig. 7). Many rhizoliths are encrusted with multiple concretionary layers of microcrystalline calcite or calcite spar (rhizocrenites) (fig. 8). Rhizoliths can be distinguished from most animal burrows by their tiny sinuous shapes, their downward or outward taper, their tendency to decrease in diameter at branches (fig. 9), and their ability to form integrated systems of root structures with thick, vertical taproots and shallow lateral roots (Klappa, 1980b).

Laminated crusts composed of laminae of micrite and sparry calcite are common features of calcareous palaeosols (fig. 10) (Read, 1976; Wright, 1989). These calcite crusts may be concretionary around rhizoliths and may coat or
Figure 2. Photomicrograph of calcite spar filling complex system of "cruce planes" or "circumgranular cracks" (plane-polarized light; Pennsylvanian Holdville Formation, New Mexico). Other crack types are also present. The cracks result from desiccation and wetting. Scale bar is 250 μm.

Figure 3. Photomicrograph of calcite spar filling discontinuous planar cracks that are subparallel to one another (plane-polarized light; Pennsylvanian Holdville Formation, New Mexico). Such cracks, called joint planes, result from desiccation and wetting. Scale bar is 500 μm.

Figure 4. Photomicrograph of calcite spar filling discontinuous planar cracks that lack any preferred orientation (plane-polarized light; Pennsylvanian Holdville Formation, New Mexico). Such skew planes produce an autochthonously brecciated fabric. Scale bar is 250 μm.

Figure 5. Weathered face of potash spar nodule, Permian Llanoforma Formation, New Mexico. Arrows indicate where extreme in-place crack formation has produced a "cruce plane" fabric in which cracks are well separated by dark potash material. The rest of the nodule face displays dark fillings of joint planes and skew planes. Scale bar is 2 cm.
Figure 6. Outcrop of base of the Osukella Shale Member, Dee Creek Limestone (Pennsylvaniaan), Kansas. Notice columnar structure produced by forma- tion of palaeosol. Scale bar is 5 cm.

Figure 7. Polished slab of palaeosol in Sequane limestone member (Pennsylvaniaan), Kansas. Dark, millimeter- and submillimeter-scale thin sheets are abundant. Note that some form changet features; some are branched, and others are reflected as aligned dark bluffs resulting from infraction of sinuous cylindrical molds with the polished surface. Top central area or area of laminated crust. Horizontal joint planes are present in the lower left corner. Scale bar is 1 cm.

Figure 8. Photomicrograph of concentric overgrowth around a root feature called a 'white vein' (plane-polarized light; Pennsylva- nian Hold Forman, New Mexico). Scale bar is 250 µm.

Figure 9. Outcrop of a Permian shale unit in Kansas. This unit has been penetrated by numerous roots. Arrow points to branched phosphorite in which the decrease in diameter at branches is apparent. Scale bar is 2 cm.
replace particles along bedding, crack, or other surfaces of the host sediment. Many have a porous structure that contains common root molds.

In carbonate palaeosols grains may have multiple irregular coatings of microcrystalline quartz, nannofossil ooze, or microfossil calcite (fig. 11). Other coatings (e.g., that are common in palaeosols are composed of clay minerals or oxidizes (Brewer, 1964).

Sediment can be replaced extensively by micrite in soil environments (Kahle, 1977; James, 1972). Micritization in soils leads to destroy the original fabric of the host rock (fig. 12).

In many calcareous palaeosols calcite has precipitated as chalky, isolated, equidimensional or elongated nodules. Such "calcite nodules" can be recognized in ancient and modern calcareous soils (Esker and Klapp, 1983).

Distinctive colors also have been used to identify palaeosols. Reddish or orangish color, from precipitation of iron oxyhydroxides, is commonly used as an indication of soil formation. However, colors may develop well after subaerial exposure from later oxidizing events. And color may be lost during later bleaching and reduction. Brown and black colors develop from preservation of sulfides and organic matter in palaeosols. However, such dark colors should not be considered diagnostic of palaeosol formation because they can form in other environments (Ward, 1978; Strasser, 1984; Shinn and Lido, 1988).

Microscopic features associated with soil organic activity provide additional support for palaeosol formation. Alveolar textures (e.g., by Labberton (1974). Alveolar-vascular structures of Wright (1986) are microscopic structures that divide pores, forming irregular and cellular septae (figs. 13 and 14). Most of these structures result from calcification and encrustation of rootlet or fungal structures.

Tangential needle fibers of calcite (James, 1972) are subparallel microscopic fibers of calcite in which the long axes of the fibers are parallel to the surface they have encrusted or parallel to the long dimension of an alveolar structure (fig. 15). They most likely are a calcification of a fungal structure associated with soil organic processes (Ward, 1978; Wright, 1984; Callo et al., 1985).

Microbial filaments (Glick, 1912) are more unusual soil-associated structure that is a millimeter- to submillimeter-sized aggregate of calcite prisms (fig. 16). It forms from either
calcification of muscoherzal associations (Klappa, 1978) or other soil-related processes (Freyt and Plutiai, 1982).

Randomly distributed needle fibers of calcite are rare structures that are difficult to preserve, but they have been described in several ancient paleoseys (Solomon and Walkden, 1983; Goldstein, 1988b).

Finding paleosol features provides the evidence necessary to infer an event of subaerial exposure. However, to use the features to constrain sea-level history, the timing of their development and the surface along which subaerial exposure occurred must be determined. It is well known that recent soil features can be superimposed on outcrops of ancient rocks. To disprove such recent superimpositions on ancient rocks, paleosol features should be shown to be early in the diageneric sequence and they should predate diageneric features, such as stylolites and through-going fracture fills. Moreover, a stratigraphic horizon with paleosol features may result from subaerial exposure of that horizon or subaerial exposure of units higher in the stratigraphic sequence. For instance, paleosol-like features can develop at the water table or along permeability discontinuities well below the surface of subaerial exposure (Seminski and Meagher, 1981; Seminski...
and Seidle, 1985) and thus can mimic surfaces of subaerial exposure. For example, if rhizoliths originating from an overlying horizon extend downward to a lower altered horizon, the lower horizon may not represent a discrete surface of subaerial exposure; it could simply represent some of the palaeosol alteration associated with a surface of subaerial exposure higher in the stratigraphic sequence. To distinguish lower altered horizons from the actual surfaces of subaerial exposure, field relationships must demonstrate the presence or absence of a link between the altered horizon and the overlying palaeosol horizon and must determine whether the altered horizon parallels or cuts across stratigraphic surfaces.

Pennsylvanian Holder Formation: An example of the utility of palaeosols in constraining the history of change in sea level is from the Pennsylvanian (Virgilian) Holder Formation of southern New Mexico (Goldstein, 1988b), which consists of approximately 20 carbonate-siliciclastic cycles deposited on the edge of the Pedernal uplift (Wilson, 1967) (fig. 17). The limestone units in the cycles show evidence of shallowing upward but for the most part appear to have been deposited entirely in the subtidal realm. For many Holder cycles, palaeosols are developed within the uppermost meter of the carbonate units (figs. 18 and 19). Rhizoliths, tangential needle fibers of calcite, alveolar texture, irregular coatings on grains, micritized grains, cracks from desiccation, and laminated crusts provide good evidence for palaeosols and thus indicate repeated subaerial exposure during deposition of the Holder Formation. Because most of the palaeosols are developed on subtidal carbonate rocks, simple aggradation into the subaerial realm could not have caused subaerial exposure; a fall in sea level or tectonic uplift is required. Some palaeosols
are laterally continuous and can be traced from the shelf to more basin positions (fig. 26). Their characteristics change laterally in response to different timing of exposure and different paleohydrogeologic setting (Goldstein, 1988b). For one surface onlapping relations hips of overlying beds and original topography on bioturbated 30–50 m (100–160 ft) of paleotopography on marine rocks capped by a single paleosol, indicating a relative fall in sea level of at least 30–50 m (100–160 ft) (Goldstein, 1988b).

Paleokarst Dissolution of limestone can occur during ancient subaerial exposure of carbonate strata. Identification of such paleokarst formation yields valuable evidence for subaerial exposure and provides a further means to determine minimum relative falls in sea level. Dissolution of carbonate sediment is to be expected in strata subjected to chemically corrosive ground water charged with atmospheric or soil CO₂ or mixtures of two different ground waters (Thailkill, 1968; Back et al., 1984; Ford et al., 1988). The key for developing the paleokarst method of tracing sea-level change is, first, the recognition of karst and, second, the establishment of the timing of its formation relative to a particular stratigraphic surface of subaerial exposure. Paleokarst must be related to the surface of subaerial exposure to determine magnitude of sea-level fall through tracing the depth of vadose diagenesis or pedoturbation on the exposure surface.

Kast cavities can have any shape (Palmer, 1991) but are still easy to recognize. They generally cut across the rock fabric to some degree. The walls tend to be smooth from the solution process. Void walls do not fit together in a puzzle-piece fashion, as simple dilational voids would. Karst limestones commonly produce a rubble outcrop, resulting from smaller cavities that dissect the host limestone. Some karst landforms develop at the surface of subaerial exposure or just below a cover of soil. The dissolution at and near the subaerial surface scalps the surface of the carbonate rock to produce tunnel, pinnacle, trough, pit, and other forms. Given adequate outcrops, such forms can be useful in identifying ancient surfaces of subaerial exposure (Esteban and Klappa, 1983; Ford et al., 1988).

In other settings near-surface karst processes develop gradational contacts between an underlying bed of limestone and an overlying bed of reddish siliclastic material. The limestone may contain small interconnected pockets and vugs filled with the siliclastic material, much of which is presumed to be the residue of limestone dissolution. The dissolution of host limestone would have occurred near the subaerial surface as part of a soil profile and thus represents.
Figure 20. Cross section constructed from four stratigraphic sections in the Holker Formation. Surfaces A through F are used for correlation. Correlations with solid lines indicate high confidence; correlations with dashed lines indicate fair confidence; correlations with dotted lines are inferred. H/B is the Holker Formation–Beorn Formation contact. Lower parts of section 1 are basin; lower parts of section 2 are on the shelf edge; lower parts of section 3 are on the shelf crest; lower parts of section 4 are lacustrine. Between sections 1 and 2, notice the onlap/convexity of surfaces A, B, and C. Siliciclastic strata in the basin onlap the slope to reflect significant paleotopography.
subaerial exposure and dissolution (terra rossa paleosol) before deposition of the overlying stratigraphic unit (Goldhammer and Elmore, 1984).

In some settings karst is related to near-surface infiltration and downward percolation of meteoric water through the vadose zone. Such vadose karstification can cause near-vertical solutional voids that extend downward from or just below the subaerial surface. The vertical, pipe, or star-step shape of these cavities generally allows them to be distinguished from caves formed in the phreatic zone (fig. 22) (Wright, 1982; Eisehn and Klapa, 1983; Ford et al., 1988). These large voids may remain open or be filled with speleothems, the sediment residue of dissolution, paleosol material, or sediment of the overlying bed. For quantifying minimum relative fall in sea level, ancient examples of such karst would be easy to relate to a particular surface of subaerial exposure, because the vertical voids would extend upward to or just below the stratigraphic surface at which subaerial exposure occurred. Moreover, because the vertical voids formed mostly in the vadose zone, the depth to which they penetrate can be used as further quantification of minimum relative fall in sea level.

Other karstification produces cavities in which age and origin are unclear, because they do not show an easily understood relationship to a surface of subaerial exposure. For instance, one might find karst cavities within ancient limestones that formed hundreds of meters beneath the surface of subaerial exposure. Because of the complex variables that control karst formation, the shape and position of the solution cavities may yield no clues to their timing or environment of formation. Moreover, some karst cavities develop along preexisting or lithologic discontinuities so that their relationship to a stratigraphic surface mimics one of the aforementioned subaerial-surface-related examples (Wright, 1982; Palmer, 1991). Furthermore, karstification at the water table or a laterally continuous mixing zone could confine karst to a stratigraphic horizon to mimic subaerial-surface-related karst.

There are some other simple criteria that allow paleokarst developed at or just below the subaerial surface (surface paleokarst) to be distinguished from karst cavities that developed well below the subaerial surface (as summarized by Wright (1982)). Surface paleokarst might be overlain by paleosol or terrestrial sediment; it might be associated with features indicative of the vadose zone; it might be truncated by overlying beds; and if it contains solutional
voids that connect to a higher surface of subaerial exposure, and overlying beds should not display evidence of collapse into the cavities.

In settings in which the cavities show no clear isoporic relationship to a surface of subaerial exposure or in which the cavities cannot be demonstrated to have formed in the vadose zone, it may be difficult to interpret minimum relative falls in sea level. To interpret relative falls in such settings, we must determine the age of the cavities relative to a stratigraphic surface. Commonly, karst voids contain stratified fillings of insoluble residue, palaeosol, lag sediment that has filled in from above, fragments of host limestone, and speleothems (fig. 23). The age of infilling can be determined biostratigraphically through examination of the nonworked fossils contained in the cavity fillings. Careful biostratigraphic and paleoecologic study might be necessary to distinguish worked from nonworked fossils. Further dating can be accomplished by comparing karsen-filling lithologies to lithologies higher in the stratigraphic sequence; if a lithologic match is produced, the cavity provides deposition of a particular stratigraphic unit and thus may help in determining the timing and position of the surface of subaerial exposure. The surface of subaerial exposure can be further constrained through mapping of paleokarst networks and by relating the networks to a stratigraphic surface up-section (Craig, 1988).

Stable isotope trends Stable isotopic analyses of whole-rock and multi-component samples commonly are used to identify ancient surfaces of subaerial exposure. The whole-rock method, developed by Allan and Matthews (1982), predicted that stabilization of non-lithified sediment during subaerial exposure could produce a relatively negative carbon signature from plant-derived soil gas CO2, a relatively positive oxygen signature from evaporation, and an overall shift in oxygen isotopic composition because of different diagenetic histories across a buried surface of subaerial exposure (fig. 24). Failing two or more such signatures at an ancient surface was considered sufficient by Allan and Matthews (1983) to identify an event of subaerial exposure. This technique has value in identifying subtle surfaces of subaerial exposure that otherwise would have been missed (Mavor and Matthes, 1983), in verifying other evidence for exposure (Allan and Matthews, 1983), and in identifying surfaces for exploratory purposes.

There are many variables that introduce ambiguity into interpreting whole-rock isotope trends, and therefore corroborating evidence of subaerial exposure is desirable. If significant mineral stabilization or recrystallization does not take place during subaerial exposure, then the predicted isotope trends may not develop. The amount of recrystallization or mineral stabilization during subaerial exposure versus the amount of preserved marine carbonate or later diagenetic phase ultimately will affect the isotopic composition of the whole rock. Moreover, the carbon isotopic composition developed in an ancient limestone that has been subaerially exposed might be related to the isotopic composition and amount of decomposing organic matter, fractionation to
more positive values during carbon dioxide degassing, the contribution of sediment carbon, and the contribution of atmospheric carbon (Furnas-Rinaldi et al., 1968; Hendy, 1971; Cerling et al., 1989). Oxygen isotopic trends might be related to the isotopic compositions of meteoric water, temperature, relative humidity, evaporation, kinetic factors, and the degree of preservation of the original sediment signal (Furnas and Ebihara, 1970; Schonweiss et al., 1978; Lehmann, 1982; Meyers and Swart, 1989). Finally, subsequent diagenetic events can overprint an isotopic signal related to the exposure event.

Isotopic signals in the Holdale Formation A study from the Pennsylvania Holdale Formation of southern New Mexico (Goldstein, 1991b) illustrates the utility and potential ambiguity of the isotopic technique for identification of surfaces of subaerial exposure. Whole-rock samples across paleosol-capped cycles and microcomponent data from paleosol-precipitated phases demonstrate the nature of the isotopic signals. The stratigraphy of the Holdale Formation in the study area (Tooney et al., 1977) consists of several shallowing-upward carbonate cycles. The tops of two of the cycles contain diagnostic paleosol fabrics, such as laminated crest, rhizoliths, alveolar texture, vadose-zone cements, autoclastic breccia, and many other paleosol fabrics (fig. 25).

Soil-forming microcomponents analyzed for their isotopic composition include the layers of vadose-zone cements (ribbon spar), laminated crusts, and rhizoliths. The most obvious feature of the microcomponent isotopic compositions is their variability (figs. 25 and 26). For instance, microcomponent data along a narrow stratigraphic interval (top of unit F) show wide variability in both carbon (about 3%) and oxygen (about 3%) isotopic composition. Moreover, the carbon signal can be spatially related to the distribution of organic matter in the soil. Sample traverses taken adjacent to rhizoliths show that the isotopically lightest signatures develop close to rhizolith cores and get progressively more positive outward (fig. 27). Therefore the isotopic signatures developed during subaerial exposure appear to be spatially or temporally heterogeneous.

The overall variability in isotopic composition of soil-formed microcomponents suggests that compositions diverge away from a "meteoric calcite line" (fig. 26) of variable δ13C and consistent δ18O (Lehmann, 1988). Such divergence is most easily explained by a combination of evaporation and carbon dioxide degassing, but variations in organic flux, root carbon input, atmospheric carbon input, and climatic variations are all possibilities. The more negative carbon isotopic values provide strong support for subaerial exposure, but more positive values appear to be preserved along with them. Comparison of whole-rock isotopic compositions to microcomponent data may or may not show significant deviations. For instance, the top of unit F (fig. 25) shows a negative carbon shift in both whole-rock and microcomponent

Figure 25. Stable isotopic composition of soil-formed microcomponent and whole-rock samples relative to stratigraphic position of two surfaces of subaerial exposure in the Holdale Formation. Letters A through J designate stratigraphic units (detailed discussion by Goldstein [1991b]).
Figure 26. Isotopic composition of soil-formed microcomponents from stratigraphic units F and H (fig. 25). Shaded field approximates the position of a meteoric calcite line at about -5.9‰ 813C. Divergence in the right can be explained by a combination of temporal variation, such as seasonal changes, evaporation, CO2 degassing, or variations in the ratios of components utilized in the system.

Data. On the other hand, the microcomponents on the top of unit F (fig. 25) yield a significantly negative carbon shift, but no negative carbon shift is observed in whole-rock data at the same horizon. At this horizon the whole-rock samples contain only small amounts of pure soil-formed microcomponents. This indicates that whole-rock isotopic signatures are not retained through stabilization of the host sediment during exposure. Apparently, the whole-rock signature is controlled by the amount of soil-precipitated phase that is present. High concentrations of soil phase yield the whole-rock shift, and low concentrations do not. This has important implications for use of the whole-rock isotope technique. In palaeosols a heterogeneity distribution of thin siltflats and laminated crusts formed at or well below a subaerial surface (even at the water table) is well known. Such a distribution could yield vertically and laterally variable whole-rock isotopic signals of questionable relationship to the subaerial exposure surface. The isotopic signals would trace the distribution of soil-precipitated phases rather than the distribution of the subaerial surface.

Whole-rock trends toward more positive 813C values are largely absent in the Holder Formation samples (fig. 25). Although microcomponent data suggest that minor evaporation took place, no heavy oxygen signal is recorded in whole-rock samples near surfaces of subaerial exposure. Apparently, this is caused by the lack of a significant volume of soil microcomponents formed during evaporation. Whole-rock oxygen shifts are also absent across the surfaces, suggesting that these closely spaced cycles have experienced similar diagenetic histories.

Although the whole-rock method of isotopic analysis probably would not have been sufficiently unambiguous to infer subaerial exposure at these surfaces in the Holder Formation, the observed whole-rock compositions at exposure surfaces 1 would have raised suspicion that further investigation was necessary. Furthermore, the relatively negative carbon signatures preserved in the soil-formed microcomponents are useful for providing further evidence of subaerial exposure.

Cement stratigraphy When carbonate strata are subjected to subaerial exposure, infiltration of meteoric water may result in low-magnesium calcite cementation (Bartholomew, 1975; Longman, 1980). Low-magnesium calcite cement can provide a record of the history of subaerial exposure, which in turn allows interpretation of history of sea-level fall. Obviously, the observation of subaerial exposure is calcite cement that preserves evidence of cementation in the vadose zone. The vadose zone may extend well below a surface of subaerial exposure, so care must be taken when relating the vadose zone to the exposure surface. Moreover, because it is unlikely that the vadose zone extends below sea level, the depth below an exposure surface to which vadose-zone
cements extend can be used as a constraint on estimating the minimum amount of fall in sea level. Calcite cements with naylond fabrics (fig. 28) (Panzer, 1969; Grover and Read, 1978), prefilled growth near grain contacts (Meyers, 1974), or meniscus fabrics (fig. 20) (Drum, 1971) provide good evidence of cementation in the vadose zone.

Cement stratigraphy of compositional growth banding in calcite (Meyers, 1974), as revealed by staining, cathodoluminescence, ultraviolet fluorescence, back-scattered electron imaging, and X-ray mapping, can provide a more stable record of subaerial exposure. Vertical changes in the pattern of cement zonation may be caused by cementation associated with buried surfaces of subaerial exposure. Cement zones that precipitated from meteoric water recharged during the exposure event should not be traceable above the exposure surface, but later events should be traceable across it (Meyers, 1974; Wallen, 1987; Goldstein, 1988a; Horbury and Adams, 1989). The position of the ancient exposure surface could be identified by locating the stratigraphic position at which cement zones resulting from an exposure event pinch out upward (fig. 30).

Cross-cutting relationships with features formed during subaerial exposure (see Forewing discussion on paleosols and paleokarst) are essential to show that cement zones are related to subaerial exposure events (Goldstein, 1991a). Merely tracing cathodoluminescent zones relative to stratigraphic surfaces can be misleading because of the complexities of paleoaequifacies and flow. For instance, lateral and vertical changes in cathodoluminescent pattern may be related to such variables as localized sources of iron and manganese or change in redox potential related to one of many aqueous parameters (e.g., rate of fluid flow relative to organic reactions) (Grover and Read, 1983; Domack, 1987; Shear, 1988). The cross-cutting relationships provide an adequate means of distinguishing those changes in cement zonation related to exposure events from those related to compartmentalized flow in the subsurface or those related to stratigraphically localized geochemical features of the subsurface. Further determination of the origin of changes in cement zonation can be aided by geochemical tracer such as stable isotopes and fluid inclusions.

In some rocks complex pore fluid history has produced variable cement zonation that has made lateral and vertical tracing of cement zones difficult (Shear, 1988). In other systems zonation patterns are too observable or are not unique so that identification of surfaces of subaerial exposure is difficult. In some settings subaerial exposure may not result in significant calcite cementation. For these situations cement stratigraphy is not an appropriate method for locating ancient surfaces of subaerial exposure.

Holderness Formation cement zonation In the Holderness Formation limestones cross-cutting relationships with paleosols, features, fissure fillings, early fractures, and clast boundaries in intraformational conglomerates relate calcite cements to events of subaerial exposure (Goldstein, 1988a). Some calcite zones both predate and postdate the paleosol or paleokarst features of a particular horizon, and thus the cement zones are shown to have precipitated during subaerial exposure. Those cement zones that precipitated during the intraformational events of subaerial exposure are early in the paragenetic sequence and predate compaction features and teconic fractures. Vertical tracing of different sequences of those intraformational cement zones reflect at least 15 events of
Figure 30. Hypothetical correlation of cement zones taken from samples vertically in a stratigraphic section. Zonation is somewhat idealized. Between samples E and F, the earliest zones pinch out upward, recording an event of cementation associated with subaerial exposure. Downward pinches of cement zones are related to hydrogeologic and geochemical factors of the freshwater aquifer.

subaerial exposure during which the limestones' underlying surfaces of subaerial exposure were cemented with calcite (fig. 31). In general, these cement zones cannot be traced downward through thick shales and oriented limestones. Apparently, they acted as aquitards during exposure and prevented cementation in underlying strata. The early cements are best developed in a shelf-crescent setting and tend to become less abundant in a basinal or lagoonal direction (figs. 20 and 31) (Goldstein, 1988a). Thus, locating surfaces of subaerial exposure from cement stratigraphy should be most applicable in shelf settings. Lateral tracing of one of the surfaces exhibiting changes in cement zonation reveals that sea level must have dropped 30-50 m (100-160 ft) (fig. 29).

Many of the silicilastic sandstone units in the Holker Formation contain only small amounts of the early meteoric calcite. Subaerial exposure surfaces that exist in the silicilastic units generally have not resulted in calcite cementation of these silicilastics. However, sandstone units that directly underlie the limestones that are capped by surfaces of subaerial exposure may contain early meteoric calcite cement that correlates with the cement zones of the directly overlying limestone. For such a sandstone point-count data from six samples show that the meteoric calcite is developed best in those sandstones that contain a high content of calcareous lithic fragments and bioclasts (fig. 32). This research work suggests that development of early meteoric calcite cement in sandstone was compositionally controlled and that subaerial exposure of limestone appears to be required for development of meteoric calcite cement in underlying strata (Bowman, 1987). Therefore, cement stratigraphy of meteoric calcite cement should be applicable to sandstones only in relatively special situations.

Calcite cements of the Lansing-Kansas City Groups The Pennsylvanian (Missourian) limestones of the Lansing-Kansas City Groups of northwestern Kansas and southwestern Nebraska (fig. 33) show that the cement stratigraphic technique is not universally applicable for locating surfaces of subaerial exposure. These units consist of carbonate-silicilastic cyclic strata that show evidence of repetitive subaerial exposure (Watney, 1980). They were deposited within a relatively paleoepigraphically low area between the Central Kansas uplift and the Las Animas arch. Despite cyclic subaerial exposure, cement stratigraphic patterns have not proven useful in reflecting the events of subaerial exposure. Most of the calcite dolomiscent cement zones postdate compaction. This observation suggests that calcite cements early in the paragenetic sequence postdate at least some burial and may be unrelated to cycle-capping subaerial exposure. The sequence of calcite dolomiscent cement zones is traceable across multiple cycles (fig. 34). Fluid inclusion data indicate calcite cementation from low-temperature brines rather than from freshwater (fig. 35) (Anderson, 1989). Such evidence suggests that calcite cementation took place from brines that refluxed through the Pennsylvanian section during deposition of Permian evaporites.
Figure 32. Percentage of early cement (expressed in percentage of authigenic calcite in occluded porosity) versus percentage of evaporificial carbonate (percentage of the depositional grains that are carbonate as opposed to siliciclastic in composition). Data are from point counts of sandstones and limestones, closely qualifying a surface of subaerial exposure on a limestone (Holder Formation). These coincidences suggest that the amount of early cement increase with increasing carbonate grains in sandstones (Bowman, 1987).

Because the setting of the Lansing–Kansas City Groups was in a relatively paleotopographically low area, its setting probably was not conducive to development of abundant meteoric calcite cement during autunian subaerial exposure (as observed in the Holder Formation). Thus cement stratigraphy in this paleotopographically low setting is not closely related to sea-level history.

Fluid Inclusions During precipitation of calcite from a fluid, some of the fluid can be trapped within the growing crystal. These fluid inclusions can provide useful information on the location of the vadose zone and thus can help to constrain the amount of fall in sea level. The vadose zone is a two-phase system in which both vadose atmosphere and water are present in the pores. Cements that grow in the vadose zone reflect this system because they include all liquid, all gas, and two-phase inclusions with highly variable ratios of gas to liquid (fig. 36) (Goldstein, 1986). The fluid present within these inclusions is 1 atm. Alternatively, fluid inclusions trapped in the low-temperature pheic zone are all liquid; fluid inclusions trapped in high-temperature fluids have two phases with small bubbles and with consistent vapor to liquid ratios, and fluid inclusions that have been naturally overheated may develop small bubbles in some inclusions because of volume increase (Goldstein, 1980, 1990).

Therefore fluid inclusions trapped in the vadose zone remain distinctive by virtue of their combination of one-phase inclusions and two-phase inclusions with highly variable ratios of vapor to liquid. Borehole heating and laboratory heating of such populations can cause reequilibration of some of the inclusions. Most reequilibration affects originally one-phase all-liquid inclusions by increasing their volume and causing nucleation of small vapor bubbles at room temperature. Thus the discrete variability in the vapor-liquid ratio of the vadose inclusion population is preserved in rocks that have been naturally heated. Populations of fluid inclusions with these characteristics can be used to trace the location of ancient vadose zones (Goldstein, 1990).

Miocene of Spain The Miocene marine carbonate strata of southeastern Spain consist of depositional sequences that are separated by stratigraphic breaks (fig. 37), some of which are of ambiguous origin (Fransems, 1989). The stratigraphic breaks can be traced laterally. In one area, Mesa Roja (fig. 38), an ambiguous break can be shown to have at least 50–55 m (160–180 ft) of original depositional relief preserved (Eisebein and Giner, 1980; Fransems, 1989). If this ambiguous break could be demonstrated to be a surface of subaerial exposure, then a minimum drop in sea level of 50–55 m (160–180 ft) could be demonstrated.

Recently, Goldstein et al. (1990) used the distribution of fluid inclusions in calcite cement to demonstrate a vadose-zone signal associated with this stratigraphic break. Limestones within one depositional sequence (DS2, fig. 37) contain common sparry calcite cement. Yet the base of the overlying sequence (DS3, fig. 37) is a porous dolomite that lacks calcite cement. Such a distribution suggests that the calcite cement of DS3 predates deposition of DS3.

 Petrographic examination of the calcite in DS2 reveals fluid inclusions that consist of all liquid, all gas, or gas and liquid with highly variable phase ratios. Such distributions are highly indicative of cementation in a two-phase diagenetic system such as the vadose zone. Furthermore, by crushing the calcite crystal between two glass plates to open the inclusions while immersed in a liquid at 1-atm pressure, the pressure within the inclusions is shown to be approximately 1 atm. This offers further support for a vadose-zone interpretation.

Ice melting temperatures (T_m) were determined for the inclusions (39). Most inclusions yielded T_m of 0.5°C, indicating a freshwater composition. Others yielded T_m as low as −0°C, indicating brackish fluids as saline as 12 wt % NaCl equivalent (Potter et al., 1977). The inclusion data strongly support cementation from the vadose zone. The distribution of cements suggests cementation before deposition of DS3. Therefore the ambiguous break between DS2 and DS3 represents an event of subaerial exposure. Because the surface covers deposition aureole of at least 50–55 m (160–180 ft), a relative sea-level fall of at least that amount can be interpreted for the boundary between the two sequences. Brackish water in some of the inclusion may even suggest proximity to the ancient shoreline during the event of subaerial exposure.
Conclusions

The identification of subaerial diagenesis can provide a useful record of the history and magnitude of sea-level change. Ancient surfaces of subaerial exposure are best integrated with other determinations of paleotopography and depth of vadose diagenesis to provide a quantitative record of minimum relative falls in sea-level. The following diagenetic methods are useful for determining this history.

1. Ancient surfaces of subaerial exposure can develop from aggradation without eustatic fall in sea level or uplift. These surfaces overlie strata that record aggradation through intertidal and supratidal environments, are commonly localized, and do not drape significant paleotopography.

2. If a surface of subaerial exposure caps or vadose diagenesis extends down to strata deposited in a normal marine subtidal environment, eustatic fall in sea level or uplift has occurred.

3. Ancient surfaces of subaerial exposure that drape significant paleotopography result from eustatic fall in sea level or from uplift. The amount of sea-level fall can be quantified by determining the paleotopographic relief through methods such as onlapping relationships and geotop fabric.

4. Palaeossols are useful for identifying ancient surfaces of subaerial exposure but should be used with caution. They may be laterally variable in nature, and palaeossol features can develop well below surfaces of subaerial exposure.

5. Paleokarst provides a useful record of subaerial exposure. Karst cavities that show surface topography, gradational development up to a surface, or vertical voids extending up to a surface are easily related to surfaces of subaerial exposure. Depth of vadose karst provides a minimum estimate of relative sea-level fall. For other karst case histories, similar studies must be conducted to relate timing of karst to specific surfaces of subaerial exposure.

6. Whole-rock trends in stable isotopes are useful exploratory techniques for investigating surfaces of subaerial exposure. The development of such signatures is both laterally and vertically heterogeneous so that identification of surfaces of subaerial exposure is not without ambiguity. The technique is best used with corroborating evidence.

7. Calcite cement that developed in the vadose zone

Figure 33. Location of cores from the Lassen-Kansas City Groups (after Anderson (1989)).
Figure 34. Vertical distribution of cement zones in the Lansing–Kansas City Groups. LS designates limestone reservoir units that are present in stratigraphic sequence. Bar patterns allow pack-
ing of cement zones that occur in the numbered order. The length of each bar corresponds to the percentage of the pore space (that existed before cementation) that is now occluded by the cement. Percentages are averages for each stratigraphic interval and are based on visual estimates from 120 thin sections. No relationship to stratigraphic position is observed at this level of detail after Anderson (1989).

(pendant and network fabrics) provide strong evidence of subaerial exposure. The depth below surfaces of subaerial exposure to which the vadose zone features penetrate can provide higher quantification of the magnitude of relative sea-level fall.

8. Discontinuities in distribution of compositional zones in calcite cement can reflect surfaces of subaerial exposure. Such cement stratigraphic discontinuities can also be related to aquifers or localized geochemistry of aquifers. Geo-

chemical tracer and cross-cutting relationships indicate which cement discontinuities are related to events of subaerial exposure. This technique is most useful in paleo-
topographically high settings. Siliciclastic strata containing significant carbonate detritus and located below exposed limestones may also contain zones of metelic calcite cement.

9. Fluid inclusions trapped in the vadose zone (plane-polarized light) exhibit highly variable ratios of vapor to liquid. Arrows point to fluid inclusions that have different ratios of vapor to liquid. Specimens from Carlsbad Caverns, New Mexico. Scale bar is 25 µm.

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Figure 37. Depositional sequences (DS), terminal carbonate complex (TCC), and megabreccias (MB) (modified from Fransen in 1989) in relation to carbonate strata of Mesa Roldan (modified from Eisele and Gimer in 1980; after Goldstein et al. in 1990).

Figure 38. Location diagram for Mesa Roldan area of southeastern Spain (after Goldstein et al. in 1990).

Figure 39. Frequency histogram of freezing point depression for fluid inclusions in Miocone strata, Mesa Roldan. Most inclusions contain freshwater, whereas some inclusions are brackish and have salinities as high as 1.2 wt % NaCl equivalent (Potter et al., 1978).
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