

# Elemental composition of calcites in late Quaternary pedogenic calcretes from Gujarat, western India

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## Abstract

Pedogenic calcretes commonly exhibit clotted micrite, circum-granular calcite (grain coats) and microspar/spar veins. The three calcite-types with different dimensions were analyzed for their magnesium content to determine the relationship between crystal elongation and magnesium incorporation. The results show a very low MgO content for grain coats and microspars and high values for clotted micrite indicating that the ideal kinetic model does not hold true and several variables govern the end composition of calcites. The magnesium concentrations of meteoric calcites are genetically linked to the evolutionary history of the soil and climate. Grain coats, which are elongated calcites, contain the least amount of Mg and is related to the initial stages of pedogenesis wherein the limiting factor is the Mg/Ca ratio of the parent fluid. Lower magnesium contents arise due to smaller quantities of Mg being released during incipient weathering. Micrite morphology and composition is controlled by the greater availability of Mg ions through weathering, higher  $p\text{CO}_2$  in soil due to increased time-dependent soil respiration, which causes a rise in calcite precipitation rates and clay authigenesis. This in turn exerts a physical control on morphology by occluding pore space and providing numerous nuclei for calcite precipitation. The wide variability in spar cements is inherently controlled by inhomogenities in parent fluid compositions with lower-than-micrite values on account of slower precipitation rates. © 2004 Elsevier Ltd. All rights reserved.

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## 1. Introduction

Calcrete is a common feature of arid, semi-arid and sub-humid landscapes wherein it forms either within the soil profile or through evaporative precipitation from groundwater in the phreatic and capillary-fringe zone (Goudie, 1983; Wright and Tucker, 1991; Tandon and Gibling, 1997; Khadkikar et al., 1998, 2000). It is also referred to as caliche, nari, kunkar, etc. (Goudie, 1983). Calcretes display characteristic fabrics and crystal morphologies in thin-section that aid in their discrimination (Wright and Tucker, 1991). Of these various microfabrics, the most commonly occurring are clotted micrite, circum-granular calcite (grain coats) and microsparitic/sparitic veins. These fabrics contain calcites having different dimensions. The calcite usually is low-Mg, although dolocretes are also known to

occur wherein the carbonate phase is dominantly, if not completely, represented by dolomite.

Little is known about the elemental chemical composition of the carbonate phase of the calcretes. Electron microprobe analysis was carried out by Driese and Mora (1993) on Devonian calcretes from the central Appalachians. They analyzed spar cements and clotted micrite for Mg, Mn and Fe along three traverses, one containing a *Microcodium* spherule, another a micritic rhizolith and the third in a micritic nodule. These analyses yielded Mg concentrations varying from 2149 to 4244 ppm while spar cements had values from 562 to 4389 ppm. Hay and Wiggins (1980) reported microprobe analyses on pellets and ooids in calcrete profiles from California. The range in  $\text{MgCO}_3$  contents in spars was 2.5–5 mol% whereas the pellets and ooids had values between 1.5 and 0.1 mol%. Pliocene to Holocene calcretes from northern Tanzania contained up to 1 mol%  $\text{MgCO}_3$  (Hay and Redder, 1978).

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Herein results of electron microprobe studies on the carbonate phase in calcretes are presented and compared with bulk geochemical analyses on calcrete nodules. Moreover an attempt is made to understand the controls on the composition of meteoric calcites in these calcretes.

## 2. Quaternary geology

The Quaternary sediments in Mainland Gujarat (Fig. 1) provide an excellent repository of information on changing palaeoenvironments over the past 130 kyrs. These sediments have formed under three discrete depositional environments representing an incremental weakening of the Southwest Indian Monsoon (Khadkikar et al., 1999). The stratigraphically lowest deposits (Figs. 1 and 2) represent ancient seasonal rivers that formed under a sub-humid climate and are represented by a higher proportion of conglomerates and calcic Vertisols (Khadkikar et al., 1998, 1999). Stable isotope analyses on calcretes from the Vertisols have shown a dominance of a C3 dominated biomass (Khadkikar et al., 1999). These deposits have been dated using Electron Spin Resonance and luminescence based techniques which given an age bracket between 130 and 80 ka BP (Khadkikar et al., 1999). Upwards through the succession, the deposits become sand dominated and contain sediments deposited by ephemeral rivers (Khadkikar et al., 1999). A prominent ferric-calcisol (*sensu* Mack

et al., 1993) is seen throughout the area (Fig. 2), which documents climatic amelioration between 50 and 20 ka BP (Khadkikar et al., 1999). This phase of sedimentation continued till about 20 ka BP after which it is succeeded by ubiquitous sandy loess deposits; relicts of intense dust storm activity in tandem with the Last Glacial Stage (Khadkikar et al., 1999). The calcretes sampled for the present study come from the older two phases of sedimentation, i.e. deposits of seasonal and ephemeral rivers. Their detailed morphology has been described by Khadkikar et al. (1998), who gave a broad framework of calcrete production and recycling in semi-arid alluvial systems. Samples for microprobe studies were taken from the basal calcic Vertisol at Mahudi and Rayka and from the ferric-calcisol at Dabka. These calcrete samples were preferentially chosen due to their enrichment of calcite and minimal siliciclastic content.

## 3. Methodology

Based on the enrichment of calcium carbonate seen petrographically, three specimens, two of pedogenic calcrete nodules from calcic Vertisols and one of a pedogenic calcrete nodule from a ferric-calcisol, were chosen for electron microprobe analyses. Analyses were carried out on a JEOL 733 electron microprobe equipped with four wavelength dispersive spectrometers and an Oxford Link eXL energy dispersive system at the Department of Earth Sciences,

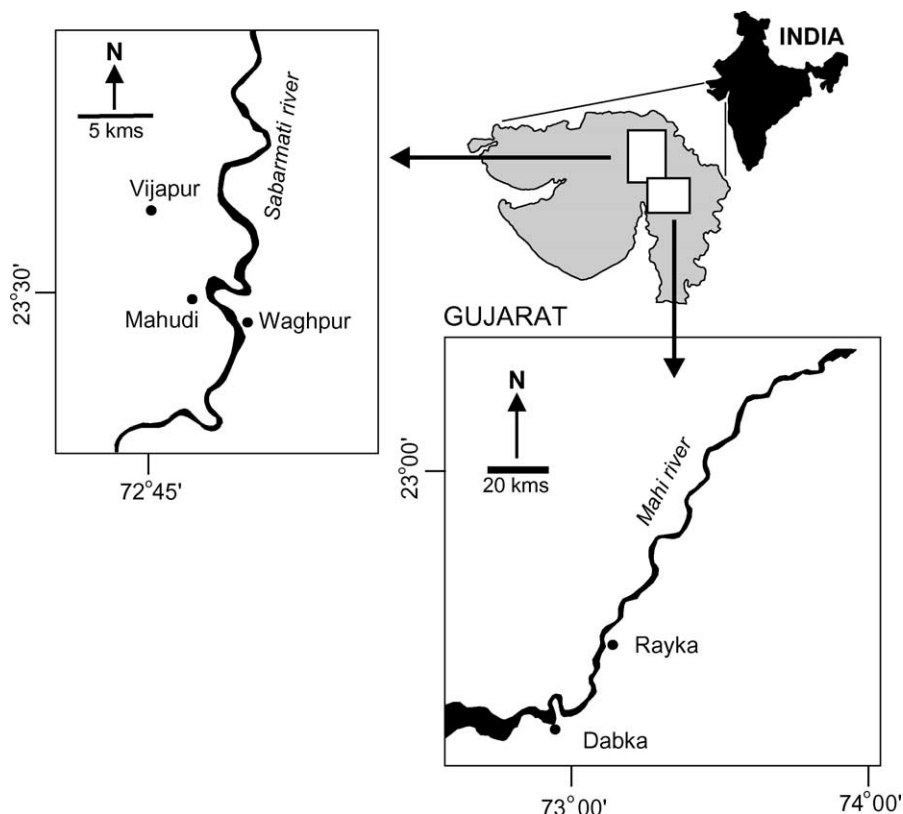


Fig. 1. Location map of the sites from which the calcrete samples were taken.

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