



Isotopic evidence for dolomite formation in soils



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ABSTRACT

Dolomite formation in soils constitute a particular challenge because of: 1) scant magnesium content in continental environments as opposed to the marine medium, 2) the kinetic problem related to the incorporation of magnesium into the carbonate, and 3) the unknown role of soil dolomites in the global carbon cycle.

Pedogenic dolomite formed at deeper soil levels (subsoil) before the development of petrocalcic horizon barriers was investigated in a semiarid region of SE Spain (Guadix–Baza basin). Mineralogical characterization, textural relationships and isotopic data concerning soil dolomite, together with the results of a precipitation experiment, provided fuller knowledge of the processes and conditions governing neof ormation of dolomite in these soils.

In the study case, dolomite enrichment occurs beyond the limit of major biological activity, which coincides with the rooting depth of native perennial plants in the semiarid soils studied. Textural studies reveal the corrosion of inherited dolomite crystals in the upper soil horizons and the formation of dolomite in depth in relation to a clayey material, composed mainly of smectites. Stable isotope distribution in dolomites throughout the profiles indicates a fractionation with depth. This is explained by the formation of dolomites after the dissolution of the pedogenic calcite. The calcite detected in the subsoil is interpreted here as a precursor of the neof ormed dolomites that transport the isotopic signal associated with biological activity of soils to deeper layers. Dolomite formation appears to be favoured by the presence of clay minerals in the precipitation media. Clays retain water during evapotranspiration stages, which drastically change the transport properties of the media and promote the incorporation of Mg into the structure of the neof ormed Ca,Mg-carbonate. As confirmed by laboratory experiments, diffusion-controlled crystal-growth processes lead to the formation a precursory “protodolomite” with disordered Ca,Mg distribution from a fluid locally supersaturated in dolomite.

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1. Introduction

The genesis of calcic and petrocalcic horizons in soils occurs as part of carbonate dissolution–precipitation cycles (Gile et al., 1966; Salomons and Mook, 1976). Detrital limestone and other calcareous materials undergoing decarbonation constitute a source for secondary carbonate accumulation in soils. Biogenic and atogenic CO₂ are alternative sources for the carbon fixation in the soil under physico-chemical conditions stabilizing the carbonate ion. The pedogenic environment is strongly influenced by biological activity: root mats, in addition to associated lichens and microorganisms, contribute directly to mineral

dissolution–precipitation in soils. In fact, pedogenesis begins with intense biological activity in the weathering zone (Wright and Tucker, 1991; Wright, 1992; Cerling and Quade, 1993). Carbonic acid produced in association with biological activity (mainly roots) is the main acid involved in the dissolution of calcium carbonate. The leaching depth of the dissolved carbonate augments with increasing mean annual precipitation and temperature (Arkley, 1963; Stevenson et al., 2005). Carbonate precipitation at the deeper layers results largely from the declining P_{CO₂} in the soil and from the higher concentrations of solutes in the soil solution due to evapotranspiration. In this sense, the carbonation process is favoured in arid–semiarid regimes. Large amounts of soil inorganic carbon, stored in the form of calcium carbonate, have been reported in cultivated mollisols under moderately cold temperatures (5–5.5 °C), and with a mean annual precipitation between 581 and 397 mm (Mikhailova and Post, 2006; Mikhailova et al., 2009), suggesting an increase in the carbonation process with agricultural practices.

Isotopic relationships found in pedogenic carbonates in arid–semiarid ecosystems indicate that carbonate dissolution–precipitation cycles in a

Abbreviations: a.s.l., above sea level; AEM, analytical electron microscopy; apfu, atoms per formula unit; BSE, back scattered electrons; DIC, dissolved inorganic carbon; EDX, energy-dispersion X-ray; FESEM, field-emission scanning electron microscope; MCL, Meteoric Calcite Line; MDL, Meteoric Dolomite Line; OA, oriented aggregated; TEM, transmission electron microscopy; XRD, X-ray diffraction.

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pedogenic environment provoke changes in the isotopic composition of the precipitated carbonate, by inducing significant inputs of biogenic carbon (Cerling, 1984). Biogenic carbon carries a unique isotopic signature, and the biological fractionation processes deplete ^{13}C to negative values (Salomons et al., 1977; Magaritz and Amiel, 1980; Magaritz et al., 1981). Therefore, the pedogenic carbonate will usually have more negative ^{13}C than detrital carbonates.

Modern dolomites are formed only in certain environments such as meteoric, marine, hypersaline, subsurface brines, and hydrothermal (Hardie, 1987). The precipitation of dolomite and dolomitization of previous Ca-rich carbonates are among the least-understood problems encountered in the geochemistry of carbonates: e.g. surface seawater is strongly oversaturated in dolomite, but little evidence is available on the widespread dolomite precipitation in modern, open-marine sediments. To explain the “dolomite problem”, models have emerged ascribing microbial activity to the mediation of dolomite precipitation. Various authors have focused their attention on the role played by the bio-mediation that leads to CO_2 enrichment and raises alkalinity, and presumably drives dolomite formation in Mg-rich environments (e.g. Wright, 1999). In any case, the occurrence of dolomite in the geochemical systems of the earth's surface is often strongly controlled by reaction kinetics (Arvidson and Mackenzie, 1999; Deelman, 2005) and/or mass-transport processes.

The formation of dolomite in soils is rarely reported, its origin being related to parent-material inheritance, to atmospheric Mg^{2+} wet deposition, and to the addition of dolomite contained in atmospheric dust (Ghebre-Egziabhier and St. Arnaud, 1983; Ming, 2002; Goddard et al., 2007; Díaz-Hernández et al., 2011). The occurrence of neoformed dolomite in soils is usually restricted to saline environments (Shermann et al., 1962; Kohut et al., 1995). However, the presence of high-Mg water solutions in soils derived from weathering of serpentinites and basaltic rocks may lead to the formation of authigenic dolomite in non-saline environments (Podwojewski, 1995; Capo et al., 2000). Although the formation of dolomite in soils has been discussed (Drees and Wilding, 1987; Sobecki and Karathanasis, 1987; Bui et al., 1990; Whipkey and Hayob, 2008), no mechanism explaining the precipitation of dolomite in soils has been reported. The incorporation of magnesium into the calcite structure to form high magnesian-calcites and protodolomites under surface conditions is broadly described in the literature (Hardie, 1987 and references therein; Deleuze and Brantley, 1997). Sedimentary and diagenetic dolomites probably precipitated as protodolomites and their isotopic composition was controlled by the protodolomite–water fractionation (Fritz and Smith, 1970). In any case, the incorporation of magnesium to the rhombohedral carbonate structure is not easy and appears to be controlled by kinetic factors (Mucci and Morse, 1983; Putnis et al., 1995; Fernández-Díaz et al., 1996).

2. Scope of the investigation

In this paper, we study the occurrence of pedogenic dolomite in soils of an arid/semiarid region. Calcite is by far the most abundant and best-studied pedogenic carbonate. On the other hand, dolomite is not usually evaluated in soils and its role in the pedogenic processes is scarcely known. Here, we describe the formation of dolomite at soil depths below indurated layers delimited by petrocalcic horizons or caliches. Deeper layers (subsoil) in these types of soils are scarcely studied because caliches are hard to excavate and their features at these depths are irrelevant for soil taxonomy or for judging the soil as a support for plants.

Several reasons underlie this approach: 1) Knowledge of the distribution of carbon in the deep-soil-layer system in semiarid areas is essential to assess soil carbonates (calcite and dolomite) as a sink for atmospheric carbon. However, the carbon distribution in deeper layers (subsoil) has rarely been determined (Jobágyy and Jackson, 2000; Díaz-Hernández et al., 2003). 2) Well-ordered dolomite, together

with protodolomites, has recently been documented in soils (Whipkey and Hayob, 2008). 3) The soils of the study area are particularly rich in inherited dolomites and, therefore, could be suitable for the development of pedogenic dolomites in addition to calcites. 4) Periodic moisture movement to depths below *solum* horizons serves as a regulating factor in maintaining soluble Mg at levels favourable to the precipitation of low-magnesium calcites (St. Arnaud and Herbillon, 1973), and occasionally also leads to the formation of dolomites. 5) The few studies available concerning pedogenic dolomites (St. Arnaud, 1979; Botha and Hughes, 1992; Capo et al., 2000) point to the occurrence of pedogenic dolomites in depth.

The main objective of this research is to demonstrate the formation of dolomite in soils. For this, we firstly studied compositional, mineralogical, and textural variations throughout the soil profiles, finding that dolomite was dissolved in superficial horizons and precipitated at greater depths than was the pedogenic calcite. Also, we analysed the isotopes in calcite and dolomite of the soil samples. This second stage revealed that the biogenic isotopic signature of the pedogenic calcite was transferred to a neoformed dolomite through the dissolution–precipitation cycles that affected the soil carbonates. Finally, we discuss the physico-chemical constraints on the dolomite formation in subsoil. According to the model proposed for the precipitation of dolomite: 1) inherited dolomite constitutes the main source for the Mg^{2+} ; 2) hydrodynamics in the soil studied controls moisture and solute transport properties in the subsoil; and 3) the incorporation of magnesium to the carbonate structure in Mg-rich confined porous media to form dolomite is explained from the standpoint of kinetics.

3. Material and methods

3.1. Geological setting and climate

The Guadix–Baza basin is located in the Betic cordillera (SE Spain, Fig. 1A). The area studied was developed as an endorheic depression from the Late Neogene to the Late Pleistocene (Vera, 1970; Peña, 1985; García-Aguilar and Martín, 2000; Gibert et al., 2007, among others), and occupies about 3500 km². During this period, the basin was filled with alluvial and lacustrine materials for which the composition varies depending on the nature of source materials. Those from the Subbetic ranges (North border) are rich in limestone, while those from the Betic ranges (South border) are rich in quartzite, micaschist, and dolomite (IGME, 1973–1999). The Guadix sub-basin is comprised of fluvial sediments (silts, sands and conglomerates) and the Baza sub-basin is formed mainly by lacustrine deposits (limestones, marly limestones, and gypsum). The rocky relief surrounding the Guadix–Baza depression coincides partially with the Atlantic–Mediterranean divide. The depression is characterized by having elevations ranging from 1500 m a.s.l. (above sea level) on the edges to 650 m a.s.l. at the Guadiana Menor River, the main drain of the area.

The capture of the internal drainage network of the depression by the Guadiana Menor River (a tributary of the Guadalquivir River) modelled the landscape into two main geomorphological groups (Díaz-Hernández and Juliá, 2006):

- 1) Old surfaces (350,000–205,000 yr): S1, S2, S3, consisting of dissected piedmont plains gently sloping towards the centre of the basin (Fig. 1B), capped by caliche soils with thick petrocalcic horizons (Petric Calcisols and Chromic Luvisols, FAO-UNESCO, 1988) (Calciorthids, Paleorthids, Paleargids, Haploxeralfs, Rodoxeralfs and Xerochrepts, following the Soil Taxonomy, Soil Survey Staff, 1999). Dolomite enrichment observed under the petrocalcic horizon (see below) suggests that the formation of dolomite began within this broad time range.
- 2) The youngest surfaces (115,000–48,000 yr): S4 (badlands, with Gypsic, Calcaric and Eutric Regosols, FAO-UNESCO, 1988) (Xerortents,

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