Sedimentary Geology 211 (2008) 1–11

Contents lists available at ScienceDirect

Sedimentary Geology

journal homepage: www.elsevier.com/locate/sedgeo

Silcrete and alunite genesis in alluvial palaeosols (late Cretaceous to early Palaeocene, Duero basin, Spain)

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ARTICLE INFO

Article history:
Received 21 December 2007
Received in revised form 22 July 2008
Accepted 28 July 2008

Keywords:
Silcrete
Alunite
Siderolithic
Fluvial diagenesis
Palaeosols
Duero basin

ABSTRACT

An extensive formation of silcretes occurs in the upper half of a late Cretaceous-to-Palaeocene Siderolithic Unit consisting of conglomerates, sandstones and sandy mudstones along the western margin of the Tertiary Duero basin (Spain). The unit is arranged in fining-upward sequences that were deposited in a fluvial braided system with floodplains subject to periodic events of exposure and drying out. The original mineralogy of the Siderolithic Unit is seen in the less altered levels, where it consists of quartz, illite–white mica, kaolinite and, at the top of the unit, K-feldspar, all coming from the palaeoalteration mantles developed on the metasediments of the Variscan Basement. The unit is characterized by a marked development of alluvial palaeosols at the uppermost part of each sequence. At field scale, the pedogenic structures and features are evident from the mottled pattern, burrowing, cracking planes and root traces; at micromorphological scale, an intense development of birefringent fabrics is seen in clays. Micas and feldspars show evidence of alteration due to hydrolysis, while the more resistant quartz grains show common corrosion gulfs and have become the only surviving elements in the most silicified beds. The neoformed minerals are related to the pedodiagenetic processes developed on the floodplains. The main neoformed phase is opal (probably amorphous silica in origin that aged to opal-CT), which ranges from local cementations in pores to an almost complete replacement of the rock, specially the finest components (matrix). Kaolinite is the most abundant neoformed clay. Locally, veinlets of alunite accompany the opalized levels.

All the processes described occurred in a seasonal tropical climate. During dry episodes, strong evaporation resulted in an increase in pH, favouring the hydrolysis of the original silicates. The paucity of Mg^{2+} and Ca^{2+} in the groundwater would have favoured the increase in pH. In ensuing wetter periods, pHs fell rapidly, resulting in the precipitation of kaolinite and also favouring the precipitation of opal and alunite. The alunite could have formed either by oxidation of the iron sulphides developed in reducing areas of the flood plains or by evaporitic concentration of sulphate in Ca^{2+}- and Mg^{2+}-free groundwaters.

1. Introduction

Silcrete formation on carbonate sediments is a widespread phenomenon in non-marine successions where the silica facies is associated with lacustrine carbonates and/or Mg-clays in closed basins, calcretes/dolocretes and gypcretes (Meyer, 1987; Southgate et al., 1989; Milnes and Thiry, 1992; Armenteros et al., 1995; Nash and Shaw, 1998; Thiry, 1999; Thiry and Ribet, 1999; Nash et al., 2004). In contrast, silcrete genesis on non-carbonate deposits is mainly controlled by a severe scarcity of Mg and Ca and/or prevailing conditions of leaching (Meyer, 1987; Thiry and Millot, 1987; Molina et al., 1997; Thiry and Maréchal, 2001). In addition, some silcrete levels, as is the case of the present study, are associated with alunite [$(KAl_3 (SO_4)_2(OH)_6$], as in examples from Portugal (Meyer and Pena Dos Reis, 1985) and Spain (Saavedra and Sánchez Camazano, 1981; Gómez-Gras et al., 2000). It is known that alunite formation requires acidic conditions to move Al^{3+}; this may result from sulphide weathering and/or ferrolysis (Mcarthur et al., 1991).

The silicification of non-carbonate sediments raises some questions about the provenance and the manner of silica accumulation. Silica may derive from the weathering of silicates in source areas or from the silica coming from the *in situ* alteration of the host silica materials. With regard to timing and the geomorphological framework, it is important to differentiate between silcretes linked to pedogenic–sedimentary sequences (Blanco and Cantano, 1983) and those related to open basin conditions, which generally occur after the uplifting and downcutting of palaeosurfaces (Molina et al., 1997; Thiry and Ribet, 1999).

These issues are explored in the present study. Many works have addressed the silicification of the lowest sedimentary unit (Siderolithic Unit; siderolithic is applied to “a residue, reworked or not, of the intense weathering of the tropical humid type”, Millot, 1964) that lies unconformably over the Variscan Iberian Basement (Iberian Massif) along the western margin of the Duero basin (Bustillo and Martín-Serrano, 1980; Martín Patiño and Saavedra Alonso, 1981;

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0037-0738/$ – see front matter
doi:10.1016/j.sedgeo.2008.07.005

Saavedra and Sánchez Camazano, 1981; Blanco et al., 1982; Blanco and Cantano, 1983). Other studies have focused on the palaeoweathering and associated silicification of this Variscan Basement (Molina and Blanco, 1980; Molina et al., 1987; Molina et al., 1990; Molina et al., 1997; Molina Ballesteros et al., 2007) (Fig. 1). A dismantling of kaolinitic and lateritic mantles, developed during the Mesozoic over the emergent Variscan Basement, was the main source of the resistant minerals and kaolinites of the Siderolithic Unit (Molina et al., 1997).

Two contrasting views about the model of silica emplacement exist. One proposes a planation surface of early Palaeocene age that can be attributed to a single silicification process due to silica coming from both the weathered Iberian Basement and the superficial weathering of the siderolithic cover. In this case, silicification would have been linked to a general water table, although with nourishment from the upper part of bleached horizons (Molina et al., 1997). The other view attributes the silicification at the top of the Siderolithic Unit to episodes that occurred within some fluvial sequences of the Siderolithic Unit. Silica is illuvial–pedogenic in origin, and the migration of silica-rich solutions was essentially vertical (Bustillo and Martín-Serrano, 1980; Blanco and Cantano, 1983).

This work aims to clarify the mechanism of silica precipitation and to establish its relationship with other pedodiagenetic processes, such as those that gave rise to mottled textures, silicate hydrolysis, and mineral neoformations, among which alunite genesis deserves to be highlighted. A parallel study of the sedimentological, textural and mineralogical features of both the silica accumulations and of the host fluvial deposits was carried out to gain a better understanding of the timing and framework of silicification and associated processes.

2. Geological setting

The silicified levels studied here form the upper part of the Siliceous Sandstones also known as the Siderolithic Unit (Siderolithic Unit), (Alonso-Gavilán, 1981; Armenteros et al., 2002). In the Salamanca area the maximum visible thickness of the unit is around 100 m. This unit is situated along the western border of the Tertiary Duero basin in the northern part of Spain, where it outcrops as a discontinuous north–south fringe between the Variscan Basement and the Tertiary Duero basin (Fig. 1). Its age is controversial: some isotopic results on K–Ar from alunite, which is authigenic in this formation, indicate an age from 66 to 57 Ma (Maastrichtian to Tanetian) (Blanco et al., 1982), whereas its correlation with similar successions in the neighbourhood and in Portugal, whose approximate ages are known, indicates a slightly older age (Campanian–Maastrichtian: Armenteros et al., 2002). It constitutes both the preliminary sedimentary phase in the configuration of the Tertiary Duero basin and the first Post-Palaeozoic sedimentation in the area. Its deposits are mainly derived from the weathering mantle developed over the rocks that form the Variscan Basement, extending throughout the western Iberian Peninsula (Fig. 1). This Basement consists of Precambrian and Palaeozoic rocks (mainly from the Cambrian, Ordovician and Silurian) dominated by siliciclastic units subjected to low metamorphism, and by igneous rocks belonging to both the pre-Variscan and Variscan cycles.

3. Sedimentology

The Siderolithic Unit consists of conglomerates, sandstones, and sandy mudstones that are arranged in 0.5–5-m thick fining-upward sequences (Fig. 2). These begin with coarse-grained facies (conglomerates and conglomeratic sandstones) that cover a planar erosive surface and contain white quartz and more abundant brown quartzite clasts 3–6 cm in diameter; larger intraformational clasts (sandy mudstones) are common in some levels. They gradually pass upwards to muddy coarse-to-fine sandstones and sandy mudstones at the top.

The coarse facies are commonly massive to vaguely stratified; some bodies show trough-cross stratification and, to a lesser extent, a crude horizontal stratification and a tabular cross stratification (Fig. 3). Fine muddy sandstones and sandy mudstones are characteristically poorly or very poorly sorted and massive. Coarse facies are made up of: a) sandy conglomerates with an infiltration matrix consisting of sand, silt, and clay-sized, poorly sorted particles; b) medium-to-very coarse-grained sandstones, poorly to moderately sorted, not well rounded, and generally with an abundant (15 to 35%) silty clay matrix;

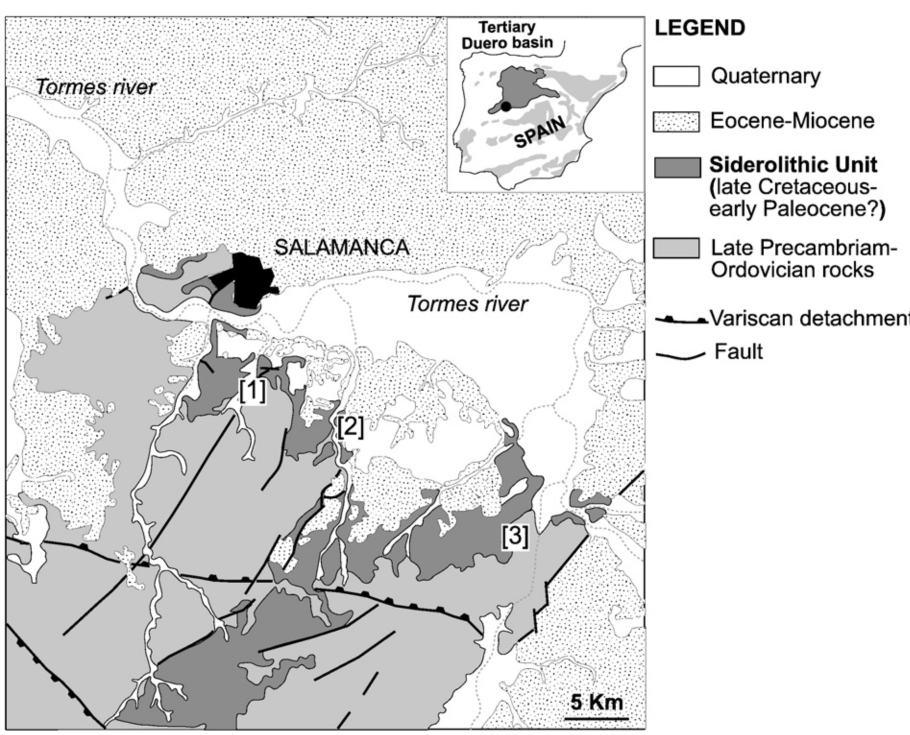

Fig. 1. Geological setting and location of the profiles studied. Stratigraphic sections: 1 Arapiles; 2 Calvarrasa; 3 Bernardo Carpio.