Geoderma 213 (2014) 173–177

Contents lists available at ScienceDirect

Geoderma

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

Rapid communication

A new form of needle-fiber calcite produced by physical weathering of shells

Ximena S. Villagran [a,b,*,1], Rosa M. Poch [c,2]

[a] University of Sao Paulo, Institute of Geosciences, Rua do Lago 562, Cidade Universitária, São Paulo, 05508-080, Brazil
[b] Eberhard Karls Universität Tübingen, Institute for Archaeological Sciences, Rümelinstrasse 23, Tübingen, 72070, Germany
[c] University of Lleida, Departament de Medi Ambient i Ciències del Sòl., Av. Rovira Roure 191, 25198 Lleida, Catalonia, Spain

ARTICLE INFO

Article history:
Received 17 April 2013
Received in revised form 5 August 2013
Accepted 11 August 2013
Available online 10 September 2013

Keywords:
Mytilus edulis
Shell middens
Beagle Channel
Shell weathering

ABSTRACT

Needle-fiber calcite is a common crystal form in soils and sediments from diverse environmental settings, and it has been used as evidence of a specific soil development either past or present. However, it can have either a physicochemical or a biological origin and its ubiquity prevents straightforward use as an environmental proxy. In this paper, we present a new form of needle-fiber calcite, derived neither from biologically mediated mineralization in the soil nor from physicochemical precipitation. This needle-fiber calcite is monocrystalline and prismatic, and is associated with the physical weathering of *Mytilus edulis* (Linnaeus) bivalve shells found in soils from anthropic shell middens located on the northern coast of the Beagle Channel (Argentina). The effects of freeze–thaw cycles can be observed in the local soils and would be responsible for the release of the calcite crystals that make up the outer layer of the shell. In this respect, the new form of needle-fiber calcite would be specific for this process in anthropogenic soils in cold climates, and could provide information on past climatic conditions.

1. Introduction

Needle-fiber calcite, also described as acicular calcite, is a common feature in carbonate soils, calcretes and caves. Many forms, shapes and arrangements of needle-fiber calcite have been identified and two processes are responsible for their formation: physicochemical precipitation; and biomineralization (Phillips and Self, 1987; Verrecchia and Verrecchia, 1994; Wright, 1984).

In sedimentary rocks needle fiber calcite commonly precipitates in interparticle pores, desiccation cracks and dissolution voids. In calcretes and soils, it is observed in root channels and other pores. The arrangements of needle-fiber calcite include meshes of randomly oriented acicular crystals, bundles of subparallel rods forming coatings around pores or grains, and convoluted fabrics that form loose discontinuous infillings (Verrecchia and Verrecchia, 1994).

Verrecchia and Verrecchia (1994) classified needle-fiber calcite into two main morphological groups: monocrystalline rods (M, MA and MB type) and polycrystalline chains (P chains) (see further information in Verrecchia and Verrecchia, 1994). Their varying morphologies are related to the processes behind crystal formation. Only the P chains are produced by dissolution–precipitation under intense evaporation and desiccation (Jones and Kahle, 1993; Verrecchia and Verrecchia, 1994), all the monocrystalline forms are of biochemical origin. M microrods are related to calcified bacteria (Loisy et al., 1999; Phillips and Self, 1987; Verrecchia and Verrecchia, 1994), while MA rods are biomineralizations by fungi in the mycelium bundles (Callot et al., 1985a,b; Verrecchia and Verrecchia, 1994). The MB rods are secondary syntactic crystals growing on MA rods by physicochemical precipitation (Jones and Kahle, 1993; Phillips and Self, 1987; Verrecchia and Verrecchia, 1994).

Although needle-fiber calcite is common in arid and semi-arid environments, it is also frequent in humid and even periglacial environments. This makes them weak environmental proxies (Strong et al., 1992; Verrecchia and Verrecchia, 1994; Wright, 1984), although their isotopic signature could provide some information on microscale paleoenvironmental conditions (Cailleau et al., 2009). Only the MA rods, when well preserved in paleosoils, can be used as evidence of early pedogenesis (Becze-Deàk et al., 1997).

In this paper, we present a new morphological type of needle-fiber calcite and discuss its origins, with special emphasis in its climatic and environmental significance.

2. Regional setting, material and methods

Analyses were done in the archaeological site Tunel VII, a shell midden located on the north coast of the Beagle Channel (Tierra del Fuego, Argentina), which dates from the 18th/19th century AD (Figure 1A).

* Corresponding author at: Eberhard Karls Universität Tübingen, Rümelinstrasse 23, 72070, Tübingen, Germany. Tel.: + 49 70712976470.
E-mail addresses: villagran@usp.br, ximena.villagran@uni-tuebingen.de (X.S. Villagran), rosa.poch@macs.udl.cat (R.M. Poch).
[1] Tel.: +49 70712976470.
[2] Tel.: +34 973 702621.

0016-7061/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.geoderma.2013.08.015

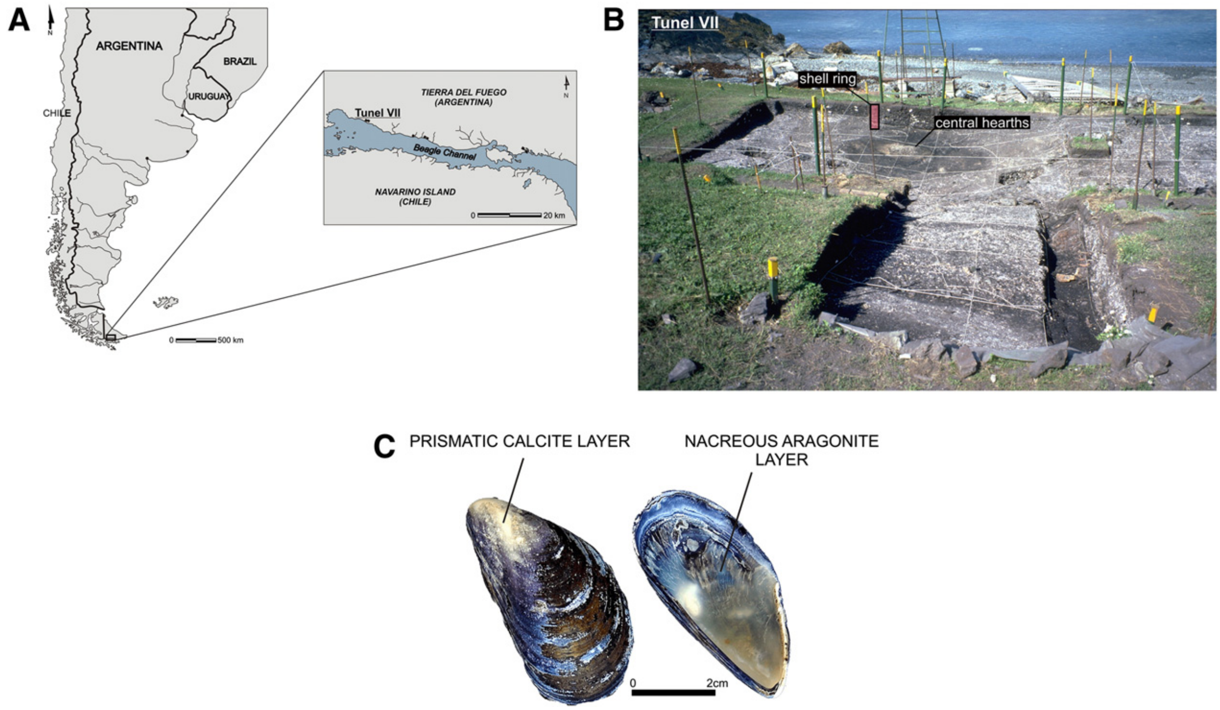

Fig. 1. Map with location of the archaeological shell midden Tunel VII (A). Photograph of the excavation at Tunel VII with location of the sampling column in the shell ring and the central hearths in the habitation hut (B). View of the valve of *Mytilus edulis* with identification of the outer calcite layer and the inner nacreous aragonite layer (C).

The site consists of a small shell ring 3.5–4.0 m in diameter and 30–60 cm high that surrounds a central habitation area. The shell ring resulted from the sequential accumulation of shell and other organic debris (bones, charcoal, plants) around the central hut occupied by the *Yamana* people, the indigenous population of coastal Tierra del Fuego (Vila et al., 2011) (Figure 1B).

The Beagle Channel climate is cold sub-Antarctic with an average temperature of 5 °C, mean annual rainfall of 570 mm and intense wind. Modern vegetation is sub-Antarctic deciduous and evergreen beech forests, with Magellanic moorland occurring along the coast and as patches in the forest (Heusser, 1989, 2003). These climatic and vegetation conditions would have existed in the region since the Middle Holocene (Candel et al., 2009).

A set of sixteen thin sections from Tunel VII was analyzed. Seven thin sections were made out of a 60 cm tall sampling column collected from the shell ring (Figure 1B). Nine thin sections were collected from five uperposed combustion features identified in the central habitation area (Figure 1B), which correspond to ancient hearths used for heating and cooking. Analyses were made under PPL and XPL using an Olympus BX51 optical microscope. SEM observations, with a Hitachi S-70 and Leo 1450 VP electron microscopes, were made on gold or platinum coated archaeological shell of the species *Mytilus edulis* (Linnaeus). This mollusk makes up almost 95% of the faunal assemblage in the shell midden (Estevez et al., 1996; Orquera and Piana, 2001) and is the main clastic component of soils in the archaeological site. Electron dispersive spectroscopy (EDS) was done to provide measurements of major elements.

3. Results

Transparent (PPL), acicular calcium carbonate crystals were observed extensively in the shell ring and in the hearths located closer to the current surface of the site (Villagran et al., 2011a). These crystals have high birefringence, parallel extinction, are negative uniaxial and their size varies from 0.5 to 2 μm thick and 20 to 50 μm long. They appear from the base to the top of the shell ring as randomly oriented monocrystals inside the soil aggregates, or as bundles of parallel crystals, frequently associated with shell fragments (Figure 2A–D).

In the shell ring, the average frequency of free calcite crystals determined by visual estimation is 10–30% in the microfacies that correspond to massive shell tossing events (Figure 2E). The highest concentration of crystals (50%) appears in the angular blocky soil that develops by freeze–thaw during the seasonal abandonment of the site (Figure 2F). This soil is made of partially accommodated prisms of 5 × 5 mm composed of clay and organic matter with inclusions of very fine sand to silt sized fragments of shell and bone, and tissue residues. In the central hearths, the frequency of acicular carbonates varies from 5 to 50%. Of the five hearths analyzed, acicular carbonate is only observed in the upper three hearths, which were lit at moderate temperatures (below 500 °C) (Villagran et al., 2011a).

The acicular crystals from the shell midden seemed to be similar in size, shape, arrangement and composition to the MA rods described by Verrecchia and Verrecchia (1994). However, their frequent association with shell fragments suggested the possibility that crystals could be byproducts of the alteration of mollusk shell.

SEM investigations on archaeological specimens proved that crystals are being massively detached from the outer layer of *Mytilus edulis* shells in the soil (Figure 3A). The smooth and polygonal shaped crystals have a sheet-like arrangement within the shell outer layer, and break into irregular prisms of 10–50 μm long and less than 2 μm thick (Figure 3B). Microprobe analyses with EDS proved that acicular crystals are composed of Ca (~30%) and C (~18%). SEM observations also showed clear differences in shape and arrangement with Verrecchia and Verrecchia's MA rods: crystals are prismatic (with polygonal section); and are single crystals, not paired rods (Figure 3C).

Complementary analyses made with UV fluorescence on the thin sections did not show any difference in color between the needles and the shell fragments. Optical cathodoluminescence (CL) was also done in the shell fragments, but since both the needles and the shells have the same mineralogy, no difference in color would be visible unless the needles were enriched in other components during a supposedly secondary formation. CL analyses on SEM were not done because the uneven topography of the shells would produce a mixture of signals difficult to interpret.