# Opaline chert nodules in maar lake sediments from Camp dels Ninots (La Selva Basin, NE Spain)

## *Nodulos de chert en sedimentos lacustres del maar de Camp dels Ninots (Cuenca de La Selva, NE España)*

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**Abstract:** Chert nodule samples from three different well cores (CC, CP1 & CA) from the lacustrine infill of the Camp dels Ninot maar-diatreme (La Selva Basin) have been studied by means of X-ray diffraction, and optical and electron microscope technique. The chert nodules replace diatomites and carbonates layers, and varies in mineralogy between opal-A to opal-A/CT. The microtexture of the opal-A rich nodules is characterized by smooth microspheres of ~2µm in diameter that forms aggregates of amalgamated microspheres. Commonly, the nodules contain diatoms and their moulds when replacing diatomites, and dolomite or ankerite crystals and their moulds when replacing carbonates. The opal-A/CT rich nodules exhibit a microtexture consisting of microspheres of ~8µm in diameter that form aggregates with botryoidal and finger-like morphologies. Results indicate that the early diagenetic transformation of opal-A to opal-CT is not complete in the studied sediments.

**Key words:** lacustrine, maar, chert nodules, opal-A, opal-A/CT

***Resumen:*** *En el presente trabajo se estudian muestras de 3 testigos de sondeo (CC, CP1 y CA) mediante DRX, microscopio óptico y electrónico a fin de caracterizar los nódulos de chert en el relleno sedimentario lacustre del maar de Camp dels Ninots (La Selva Basin,). Los nódulos de chert reemplazan capas de diatomitas y carbonato, y varían mineralógicamente entre ópalo-A y ópalo-A/CT. La microtextura de los nódulos ricos en ópalo-A se caracteriza por microesferas lisas de ~2µm de diámetro que forman agregados de microesferas amalgamadas. Frecuentemente, los nódulos contienen diatomeas y sus moldes cuando reemplazan diatomitas, y cristales de dolomita y ankerita y sus moldes cuando reemplazan carbonatos. Los nódulos rico en ópalo-A/CT presentan una microtextura con microesferas de ~8µm de diámetro que forman agregados con morfología botroidal. Los resultados indican que la transformación diagenética de ópalo-A a ópalo-CT no es completa en los sedimentos estudiados.*

***Palabras clave:*** *sedimentos lacustres, maar, nódulos de chert, ópalo-A, ópalo-A/CT*

## INTRODUCTION

Chert nodules are very common in the lacustrine sediments of the Camp dels Ninots maar of Caldes de Malavella (La Selva Basin, NE Spain) as menilitic opal. The mineralogy and origin of such chert nodules have been succinctly described from outcrop specimens by Piqué (2008), who identifies the occurrence of opal-A (i.e, amorphous opal) and opal-CT.

Research well cores recovered at Camp dels Ninots maar (Caldes de Malavella), during paleontological and climatic studies, revealed that chert nodules are common in the lacustrine infill of the basin. These cores also allow to study the early diagenetic silica minerals in lacustrine maar environments. Specific objectives of this work are: (i) to characterize the mineralogy of the nodules and (ii) to constrain the origin and diagenetic evolution of the silica.

## GEOLOGICAL SETTING

The Camp dels Ninots maar-diatreme (CNMD) (41° 50′ 06″N, 2° 47′ 51″E; 95 m above sea level) is a Pliocene maar located in Caldes de Malavella (La Selva Basin, NE Spain), with a diameter between 650 and 400 m. La Selva Basin is a Neogene basin bounded by NW-SE faults (Pous et al., 1990) included in

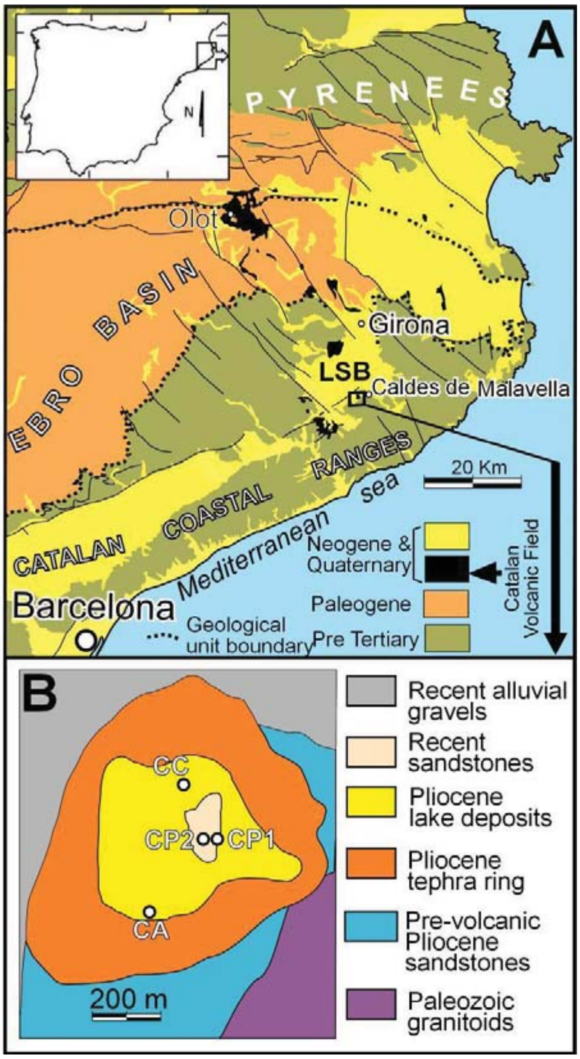



FIGURE 1: A) Location of the Camp dels Ninots maar diatreme within the Iberian Peninsula (upper left) and within the Catalan Volcanic Field. B) Simply geological map of Camp dels Ninots maar with the location of the wells (see the methods). Oms et al., 2015 (modified)

Catalan Volcanic Zone. This zone constitute belongs to the Neogene European Rift System provinces (Fig.1). The origin of the CNMD (Gómez de Soler et al., 2012; Oms et al., 2015) is most probably associated to the faults bounding the La Selva Basin and it is classified as phreatomagmatic (Martí et al., 2011).

The earliest geological study in Camp dels Ninots considered sediments as lacustrine without any mention to volcanism (Vidal, 1882), being Vehí et al. (1999) who identified these sediments as the infill of a maar. During recent years, the maar sediments have been extensively studied due to its well-preserved Pliocene fossil record (Campeny and Gómez de Soler, 2010; Gómez de Soler et al., 2012 Jiménez-Moreno et al., 2013). More recently, the maar structure and infill sediments were thoroughly studied by integrating eight cores and nine electric resistivity tomography cross sections (Oms et al., 2015). The basement of the CNMD is composed by Late Carboniferous to Permian granites, schists, and Pliocene arkoses, clays, sands, and gravels from the La Selva Basin alluvial system (Pous et al., 1990). The lacustrine sediments fill a maar diatreme lake rimmed by a tephra ring-shape. Three main facies (Jiménez-Moreno et al., 2013) are found in the lake sediments: (i) laminated green-to-greyish mudstones composed mainly by clay minerals; (ii) laminated dark mudstone rich in organic matter; and (iii) laminated/massive whitish carbonates. These lacustrine sediments contain frequent early diagenetic silica concretions dominated by chert nodules (menilites) that are the goal of this study. Piqué (2008) noted that these chert nodules replaced or grew within calcite and dolomite layers, as opal-CT lepispheres with botryoidal textures.

## METHODS

Fifty-four core samples have been selected from three wells of the Camp dels Ninots maar (Can Cateura – 31 m (CC), Can Pla 1 – 112 m (CP1), Can Argilera – 75.5 m (CA), Fig.1b) as well as from trench outcrops within the area. Sampling includes: a) the main lithological facies and b) the chert nodules and associated host rocks. Thirty-eight thin sections and ten polished slabs were prepared from the selected core samples. The samples have been studied by optical microscopy, X-Ray powder Diffraction (XRD) and Scanning Electron Microscope (SEM).

The mineralogy of all samples was determined by XRD using a Bruker D8-A25 powder diffractometer equipped with a Cu x-ray source (Cu Kα radiation) and a LynxEye position sensitive detector. The scans were recorded between 3º and 65º (in 2θ) with a 0.05° step size and equivalent integration times of 576 s per step. Phase identification was performed using the Diffrac. EVA software in combination with the Powder Diffraction File (PDF-2) and the Crystallography Open Database (COD).

Thirty-eight thin sections were prepared with standard procedures and examined with a Zeiss Axiophot petrographic microscope. Detailed textural analyses were performed on rock chips with a Scanning Electron Microscope (SEM) JSM-7100F equipped with a dispersive X-ray spectrometer (EDS).

## RESULTS

Core log examination indicates that the highest concentration of diagenetic chert nodules occur within the white carbonate facies, whereas the dark mudstones exhibit the lowest concentrations, showing the greyish facies intermediate concentrations. Regardless of facies, chert nodules appear both at shallow and deep depths, replacing both carbonates and diatomite layers. Chert nodules are usually black (Fig. 2A) or brown in colour, occasionally zoned, and with typical irregular shapes, often planar and semi-spherical with smoothed edges.

XRD analyses indicate that nodules are composed by opal-A (typical broad peak from diffuse scattering centred at lattice spacings of ~4Å) to opal-A/CT (broad peak centred at 4.Å with two minor individual peaks at ~4.09Å and ~4.32Å). The host rock mineralogy is dominated by carbonates (dolomite, ankerite and/or calcite), with subordinate of quartz, feldspars, clays (smectite phases, kaolinite, illite), gypsum and pyrite. Together with carbonates, diatom rich layers are also found in the host rock.

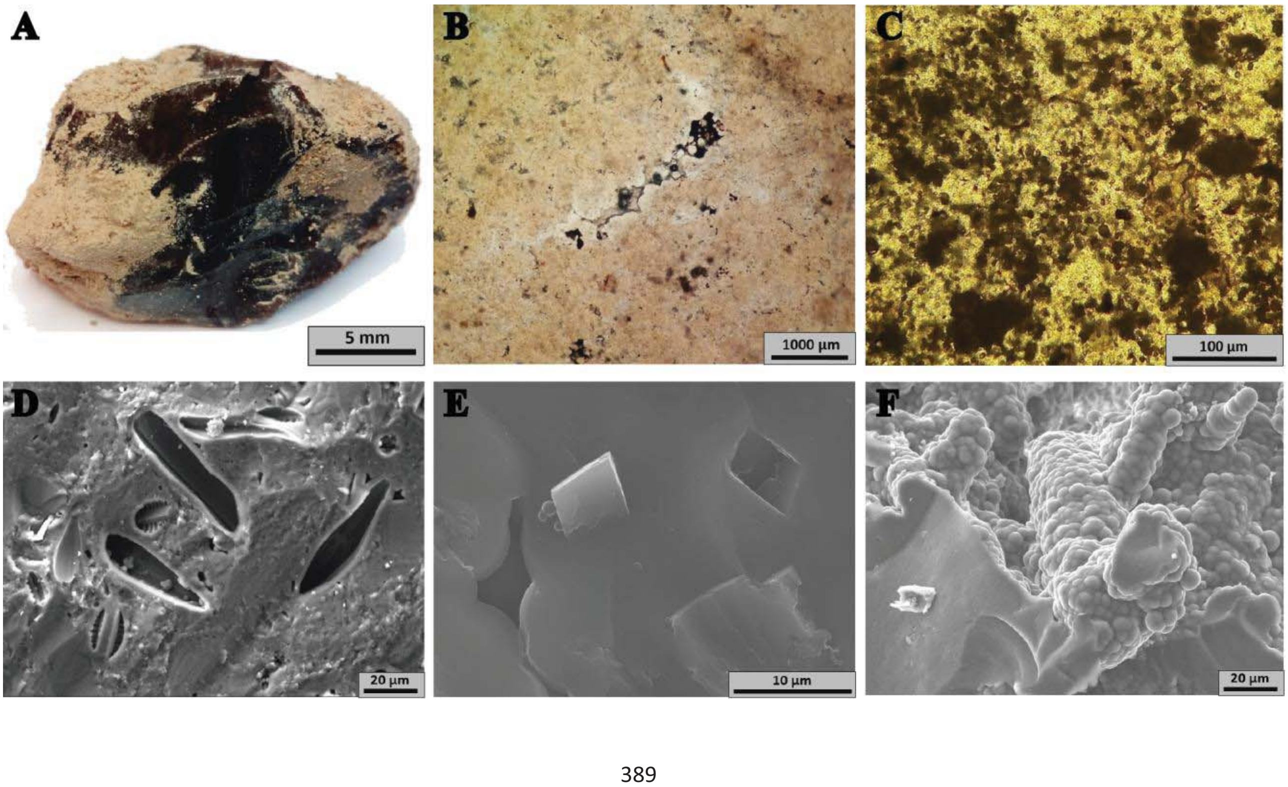
Optical petrographic observations of chert nodules show the typical yellowish to light brown colours of the opal under polarized light (Fig. 2B). The opal-A rich nodules are made of smooth microspheres of ~2µm in diameter forming aggregates of amalgamated microspheres. The opal-A replacing diatomite frequently engulfs diatoms and their moulds that decrease in abundance towards the centre of the nodule (Fig. 2D). Moreover, opal-A nodules replacing carbonate layers typically engulf crystals and their moulds of the carbonate minerals (dolomite and ankerite) (Fig. 2E). The opal-A/CT rich nodules show a microstructure similar to that of opal-A rich nodules characterized by aggregates of microspheres of ~8 µm in diameter (Fig. 2C). Occasionally these microspheres form finger-like aggregates (Fig. 2F). In addition to opal-A and opal-A/CT, petrographic observations indicate the presence of small crystalline areas, likely microquartz crystals, appear within the opaline texture.

**DISCUSSION:**

The occurrence of diatom moulds in opal-A nodules suggests that the dissolution of silica diatom skeletons, which are abundant in the Camp dels Ninots lacustrine sediments, contributed in part to the formation of the nodules. Textural observations indicate that opal-A is formed by microspheres, most probably generated through a dissolution and re-precipitation process (Mackay, 2007). Despite opal-A/CT have been recognized by XRD in Camp dels Ninots, the typical opal-CT bladed lepispheres reported in the literature (e.g., Lynee et al., 2005) are not recognized, indicating that the complete opal-A to opal-CT transformation is not complete in the studied samples.

The transformation from opal-A to opal-CT has been extensively reported in the literature (e.g., Lynee et al., 2005). According to these authors the complete diagenetic transformation of opal-A includes the pass of opal-CT to microquartz frequently with an intermediate phase called moganite. XRD analyses of the Camp dels Ninots nodules do not support further transformation of opal-CT to moganite or microquartz in the studied sediments. However, the presence of small microquartz crystals that appear within the opaline suggests that the transformation may have been

Figure 2: A) Hand specimen of a black and homogeneous chert nodule. B) Photomicrograph of opal-A rich nodule showing the typical yellowish color of the amorphous mass (parallel light). C) Photomicrograph of opal-A/CT rich nodule showing the texture made of clusters of microspheres (parallel light). D) SEM image showing diatom moulds within the opal-A amorphous mass. E) SEM image of an opal-A rich nodule showing the amorphous mass engulfing ankerite crystals. F) SEM image of the opal-A/CT nodule showing a cluster of smooth microspheres of around 8 µm in diameter and finger-likely morphology.



initiated. The low amount of microquartz in the studied sediments probably prevents its record in the XRD scans, which are dominated by opal phases.

## CONCLUSIONS

The study of well cores from Camp dels Ninots reveals the presence of diagenetic chert nodules in almost all the lacustrine sedimentary infill.

Chert nodules are composed by opal-A or opal-A/CT, both showing similar petrographic characteristics. The opal-A nodules are made of microspheres of ~2µm in diameter forming aggregates. Opal-A/CT nodules are usually made of microspheres aggregates showing botryoidal and finger-like morphologies. Typically, the opal-A/CT microspheres are ~8µm in diameter. Our present data suggests that opal-A was partially transformed to opal-A/CT during diagenesis.

The transition from opal-A to opal-A/CT during the diagenesis and its potential evolution to opal-CT and microquartz needs to be further characterized by complementary analytical techniques such as Raman scattering or Si isotopes.

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