Mineralogical and Crystalochemical Characterization of the Sepiolite Deposit from Andrichi (Pranjani Basin, Serbia)

/ MERCEDES SUÁREZ BARRIOS (1), VLADIMIR SIMIC (2), NEVENA ANDRIC (2), EMILIA GARCÍA-ROMERO (3,4),

(1) Departamento de Geología, Universidad de Salamanca. Plaza de la Merced s/n. 37008 Salamanca. Spain.
(2) University of Belgrade, Faculty of Mining and Geology, Djusina 7, 11000 Belgrade, Serbia
(3) Departamento de Cristalografía y Mineralogía. Facultad de Geología. Universidad Complutense de Madrid. Avd. José Antonio Novais s/n. E-28040. Madrid. Spain.
(4) Instituto de Geociencias (IGEO). (Universidad Complutense de Madrid – Consejo Superior de Investigaciones Científicas). Avd. José Antonio Novais s/n, E-28040. Madrid. Spain.

INTRODUCTION

The sepiolite deposit of Andrichi is located in the Pranjani Basin, in the central region of Serbia. It is a sedimentary deposit, Lower Miocene in age, which appears in the transition between alluvial and marginal-lacustrine facies alternating whit dolomite, claystone and siltstone beds (Fig.1). The sepiolite is mostly neoformed in an alkaline-moderately saline environment (Simić et al., 2013).

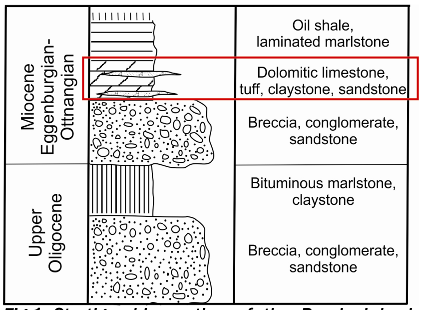

Fig.1 Stratigraphic section of the Pranjani basin (Djurdjević, 1992). Red rectangle comprises the materials studied.

MATERIALS AND METHODS

Six representative samples of the different sedimentary bed of the Andrichi deposit were studied. Samples were labeled from the bottom to the top as AND1 to AND6. Mineralogical composition was obtained by X-Ray Diffraction with the usual methodology for clay studies. A Siemens D-500 diffractometer with CuKα radiation and a graphite monochromator was used.

Particle morphology and textural relationships were established using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Chemical analyses of raw samples were obtained by ICP-AES and ICP-MS. The SEM observations were performed operating at 20kV. Prior to the SEM observation, samples were air dried and Au coated under vacuum in an Ar atmosphere. TEM observations were performed by depositing a drop of diluted suspension on a microscopic grid with collodion and coated with Au. The chemical composition was obtained using analytical electron microscopy (AEM) with TEM, using a JEOL 2000FX microscope equipped with a double-tilt sample holder at 200 kV. The microscope incorporates an OXFORD ISIS EDX spectrometer (136eV resolution at 5.39 keV) and has its own software for quantitative analysis. A PHILIPS CM-20 operating at 200kV was also used.

RESULTS AND DISCUSSION

The sample located at the bottom of the profile, AND1, is a bentonite composed of a trioctahedral smectite, analcime and a mineral of the serpentine group. Samples AND2 to AND6 are very rich in sepiolite. The fibrous mineral can appear with very high purity, as in AND5 sample, where sepiolite only contains very small amounts of smectite, detectable in the glycolated sample (Fig.2). Other samples present impurities of dolomite (AND2 and AND4), or trioctahedral smectite (AND3 and AND6).

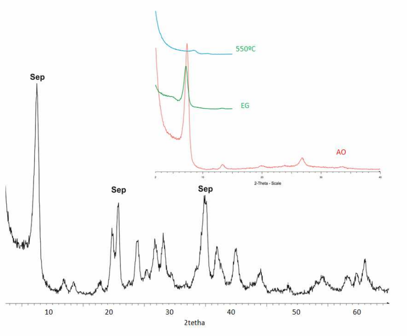

fig 2. RXD patterns of AND5 sample. Raw sample shows the high purity of sepiolite. A small amount of smectite and the variation of the 110 d-spacing can be identified in the glycolated sample (EG-pattern).

Sepiolite shows good crystallinity by XR-diffraction, with narrow and well defined peaks, but it is noticeable the "swelling" that can be detected after glycolation (fig.2). 110 reflection varies from 12.12 Å in the oriented aggregated to 12.34 Å in the glycolated sample. Swelling of

	SiO2	Al2O3	TiO2	FeO	MgO	CaO	Na2O	K2O	P2O5	S	LOI
AND-1	39.69	5.16	0.10	6.73	16.27	0.97	1.50	0.06	0.05	tr.	29.47
AND-2	19.91	0.04	0	0.37	15.95	27.06	0.03	0	0.03	tr.	36.61
AND-3	46.76	0.96	0.02	1.15	24.02	0.43	0.01	0.05	0	tr.	26.60
AND-4	35.77	0.36	0.02	0.43	24.09	18.41	0.03	0.02	0.03	tr.	20.84
AND-5	45.91	0.79	0.03	1.91	23.21	0.14	0.01	0.05	0	tr.	27.95
AND-6	46.30	2.08	0.03	5.61	20.93	1.59	0.01	0.18	0.01	0.80	22.46

Table 1. Chemical composition of the studied samples as % of the major element oxides.

palabras clave: sepiolita, depósito de Andrichi, Cuenca de Pranjani | ***key words:*** sepiolite, Andrichi deposit, Pranjani Basin

* corresponding author: **msuarez@usal.es**

sepiolite has been referred in some occasions, very recently by Pozo et al. (2014). The high d-spacings of 110 reflections together the swelling point to this sepiolite is not a term of the polysomatic series sepiolite-palygorskite recently described by Suárez & García-Romero (2013).

Minority minerals, not detected by XRD, have been observed by SEM. Micrometric and idiomorphic pyrite, benthic lacustrine diatom algae, and scarce apatite grains appear in AND1 sample. This sample shows detritic grains of serpentine (Fig.2-a) while smectite and analcime show textures of neoformation (Fig.2-b). AND3 contains small laminar particles that correspond to Mg-rich smectite. In AND2 and AND4 samples, dolomite appears in micrometric crystals rounded by sepiolite fibres (Fig 2-c). Dolomite crystal are homogeneous in size, between 2 - 5 µm. AND5 sample, the richest in sepiolite sample, shows the typical fibrous morphology of sepiolite (Fig.2-d), sometimes the fibres form plains. In AND6 sample small laminar particles of smectites appear together with the sepiolite fibres and scarce detritic grains of serpentine have been identified in this sample.

The study by TEM shows the typical morphology of sepiolite with nanometric in width fibres, that appear aggregated forming rods of individual laths (Fig. 3). These rods form the characteristic bundles of this mineral.

According to the length, this sepiolite can be classified as Type 2 or intermediate in length and curved fibres after García-Romero & Suárez (2013).

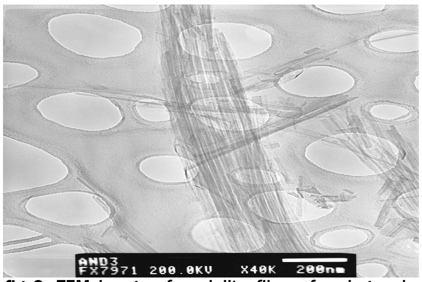

fig 3. TEM image of sepiolite fibres forming rods and bundles.

Preliminary crystallochemical data obtained by AEM analysis in SEM and TEM allow us to obtain the structural formulae for the different phyllosilicates present in the samples. The mean structural formulae are in Table 2.

Serpentine shows full tetrahedral occupation but with very high Si substitution and variable substitution of Mg in the octahedral sheet. Fe^{3+} can reach 0.35 atoms per half unit cell. Smectite formula is very difficult to fit because Mg is the interlayer cation and therefore it is not possible to know the layer charge. To fit this mean structural formula we complete the octahedral sheet at 6 cations and the rest of Mg is assumed as interlayer cation. This result in a saponite.

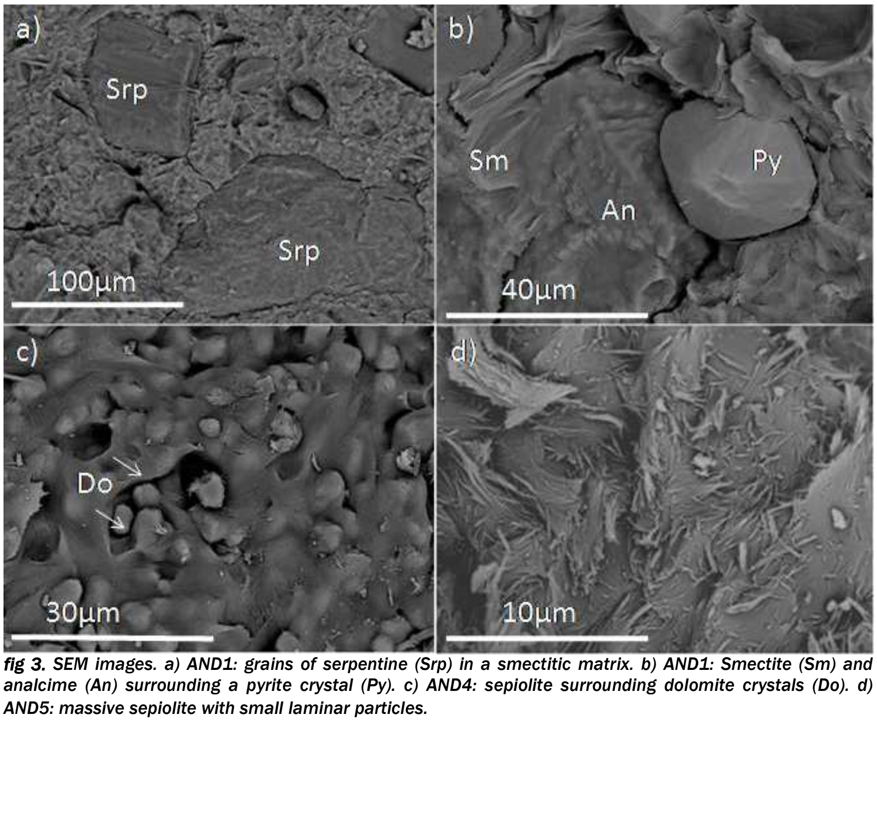

fig 3. SEM images. a) AND1: grains of serpentine (Srp) in a smectitic matrix. b) AND1: Smectite (Sm) and analcime (An) surrounding a pyrite crystal (Py). c) AND4: sepiolite surrounding dolomite crystals (Do). d) AND5: massive sepiolite with small laminar particles.

The mean structural formula of sepiolite corresponds to Type I, or ordinary sepiolite, according to the classification proposed by García-Romero & Suárez (2010). There is a great variability in the point analyzed, with a high standard deviation regarding to the mean formula. Standard deviation for Mg is 0.35 and can be related to the existence of Mg as adsorbed cation because there are several analyses with more than 8 octahedral cations. New analysis of the sample has to be performed to be sure that the Mg appears only as octahedral cation.

Srp	$Si_{2.06}O_5Al_{0.08}Fe^{3+}{}_{0.21}Mg_{2.45}(OH)_4$
Sm	$Si_{7.05}Al_{0.85}Fe^{3+}{}_{0.09}$ $O_{20}Fe^{3+}{}_{0.42}Mg_{5.58}(OH)_4$ $Mg_{0.22}$
Sep	$Si_{11.91}Al_{0.09}O_{30}$ $Al_{0.16}Fe^{3+}{}_{0.11}Mg_{7.64}$ $(OH)_4$ $Ca_{0.08}(OH_2)_4nH_2O$

Table 2: Mean structural formulae for phyllosilicates (Srp: serpentine, Sm: smectite in AND1 sample studied by SEM, and Sep : sepiolite in AND5 sample analyzed by point analysis in TEM).

FINAL REMARKS

The mineralogy of the sedimentary deposit of the Andrichi is mainly composed by trioctahedral phyllosilicates: serpentine, saponite and sepiolite. Sepiolite is the major mineral that can be pure or almost pure. Serpentine is an inherited mineral while saponite and sepiolite probably are neoformed minerals.

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