Applied Clay Science 103 (2015) 1–9

Contents lists available at ScienceDirect

Applied Clay Science

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

Research paper

Clays from Neogene Achlada lignite deposits in Florina basin (Western Macedonia, N. Greece): A prospective resource for the ceramics industry

Ioannis K. Oikonomopoulos [a,*], Maria Perraki [b], Nikolaos Tougiannidis [c], Theodora Perraki [b], Haino Uwe Kasper [c], Marcus Gurk [d]

[a] Core Laboratories LP., Petroleum Services Division, 6316 Windfern Rd., Houston, TX 77040, USA
[b] National Technical University of Athens, School of Mining and Metallurgical Engineering, Division of Geological Sciences, Heroon Polytechniou 9, 15773, Zografou, Athens, Greece
[c] University of Cologne, Faculty of Mathematics and Natural Sciences, Institute of Geology and Mineralogy, Zuelpicher 49a, 50674 Cologne, Germany
[d] University of Cologne, Faculty of Mathematics and Natural Sciences, Institute of Geophysics and Meteorology, Pohligstrasse 3, D-50969 Cologne, Germany

ARTICLE INFO

Article history:
Received 22 August 2013
Received in revised form 30 October 2014
Accepted 3 November 2014
Available online 19 November 2014

Keywords:
Clays
Lignites
Ceramics
XRD
FT-IR
Greece

ABSTRACT

The mineralogical composition and the resulting behavior upon firing of samples from the intercalated clay seams of the Achlada lignite-bearing sequence (west Macedonia, N. Greece) were examined. The resulting data sets were interpreted in order to evaluate the possible use of the studied clays in the production of structural ceramics. The mineralogical composition of the studied clays was accomplished by means of X-ray diffraction (XRD), thermo-gravimetric (TG), differential thermo-gravimetric (DTG) and differential thermal analysis (DTA) and Fourier Transform-Infrared (FT-IR) spectrometry. The clay minerals prevail in all samples, with illite being the dominant phase and kaolinite and chlorite comprising the rest of the clay components. No smectite was found that would negatively affect the produced ceramics. Other mineral phases identified were mainly quartz and feldspars and subordinated siderite. The classification of the clays using appropriate ternary diagrams suggests their possible use in the production of red-stoneware products in ceramic industry. Casting molds were fired at various high temperatures (up to 1300 °C). The mineralogical composition was examined by comparative XRD and FT-IR studies. The results suggested that the formation of both vitrified mass and new crystalline phases, such as Al–Si-spinels and hematite (alpha/a-Fe_2O_3), starts at ~1000 °C. The presence of vitrified mass becomes stronger with increasing firing temperature (~1100 °C), enclosing as the neo-formed phases as the residues of quartz and feldspars. At ~1200 °C mullite [$3Al_2O_3*2SiO_2$] began to form which contributes to the resistance of the ceramic product.

1. Introduction

After the end of the Alpine orogenesis and during the Early Miocene, a period of intense tectonic faulting begins in NW Macedonia. The activity of major and profound faults of NW–SE direction resulted in the formation of the Florina–Ptolemais–Servia (FPS) graben (Fig. 1). This graben extends North of the Greek borders with F.Y.R.O.M. (Monastiri area) and is more than 150 km long (Metaxas et al., 2007). Subsequent tectonic episodes of NE–SW extension resulted in the fragmentation of the FPS graben and the creation of many independent sedimentological basins (Florina, Amynteo, Ptolemaida, Kozani and Serbia) (Pavlides and Mountrakis, 1987).

The basement and the borders of the depression belong to the Pelagonian geotectonic zone, whereas the presented basins are flanked by mountain ranges that are primarily composed of Palaeozoic schists, Upper Carboniferous granites, and Mesozoic limestones (Brunn, 1956).

The Neogene sediments that fill the Florina basin unconformably overlay the basement rocks and include three lithostratigraphic units: (i) the lowest consists of conglomerates, in which thickness fluctuates from 1 m up to 20 m at the west part of the basin. The maximum observed thickness is about 200 m (Pavlides and Mountrakis, 1987). Upwards, a transitional passing into marls, sandy marls, sands, clays and thin lignite horizons is present. The age of this unit has been defined by fossils as late Miocene–early Pliocene (Velitzelos and Petrescu, 1981). (ii) The middle unit, which is observed at the Vevi–Achlada lignite mines, is a clayey formation and contains some thick lignite beds, which alternate mainly with clays and secondly with marls, sandy marls, and sands. Conglomerates and marly limestone lenses

* Corresponding author at: Core Laboratories, Petroleum Services Division, 6316 Windfern Road, Houston, TX 77040, USA. Tel.: +1 713 328 2553; fax: +1 713 328 2170.
E-mail addresses: Ioannis.Oikonomopoulos@corelab.com (I.K. Oikonomopoulos), maria@metal.ntua.gr (M. Perraki), ntougian@uni-koeln.de, geo.Nikolas@gmx.de (N. Tougiannidis), peraki@metal.ntua.gr (T. Perraki), hu.kasper@uni-koeln.de (H.U. Kasper), geogurk@geo.uni-koeln.de, geogurk@web.de (M. Gurk).

http://dx.doi.org/10.1016/j.clay.2014.11.002
0169-1317/© 2014 Elsevier B.V. All rights reserved.

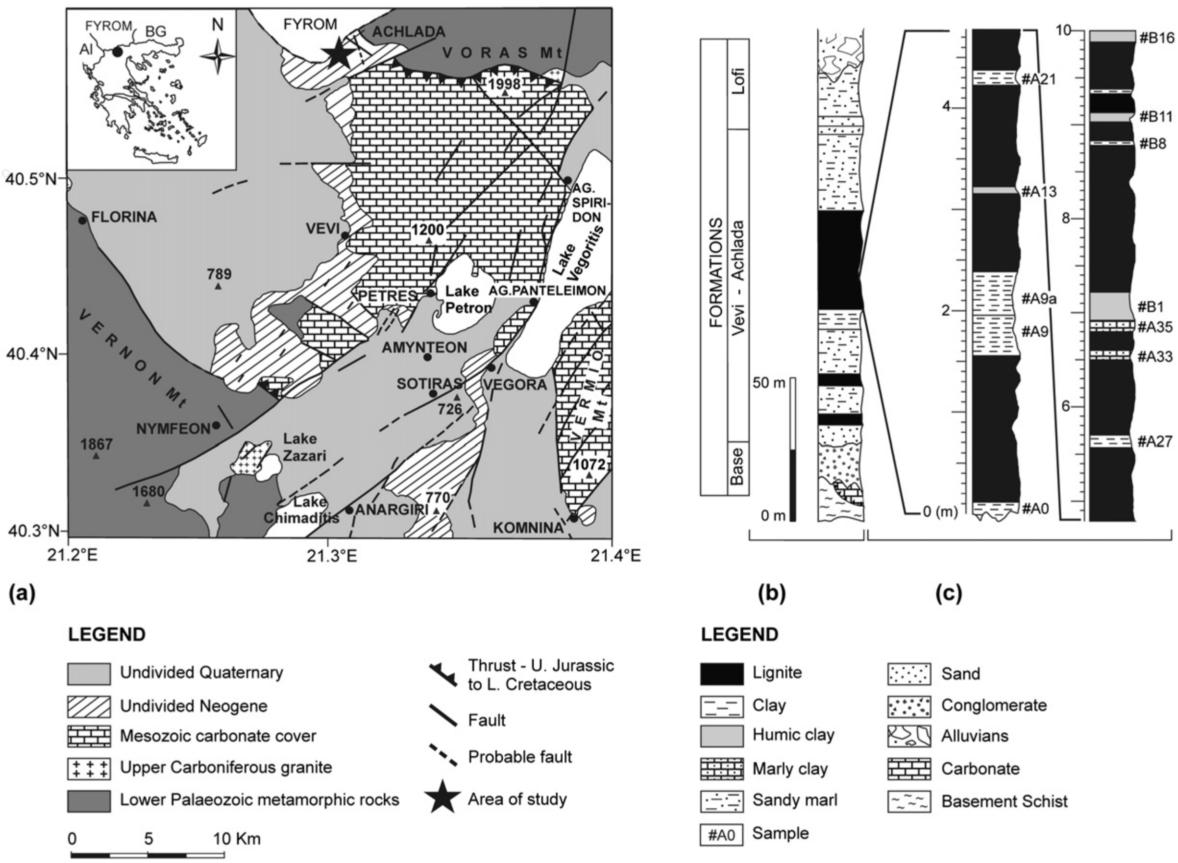

Fig. 1. (a) Geological map of the Florina basin showing the location of Achlada lignite deposits (after Pavlides and Mountrakis, 1987), (b) the generalized lithological column of the Florina basin (after Pavlides and Mountrakis, 1987) and (c) the studied lignite-bearing sequence of the Achlada lignite deposits (NW Greece).

are also occasionally present. Pollen analysis and a microfaunal study (Ioakim, 1984; van de Weerd, 1979) have concluded in an early Ruscinian age (lower boundary: 5.3 Ma) for the lower members of the unit and a late Ruscinian one for the upper members (Koufos, 1982). Current studies (Koukouzas et al., 2009, 2010) have shown that the Achlada deposits belong to the Komnina lignite sequence, which is correlated to chron C3An.1n (6.01–6.28 Ma) (Weber et al., 2012). (iii) The upper unit (Lofi formation) presents alternations of clays, marls, marly breccias, and sandy conglomerates. On the top of this unit, a marly limestone bed is formed on the entire area of the basin, whose thickness is about 10 m. The fossils included in the beds of this unit (*Planorbis*, *Neritina*, *Unio*, *Limnaeus* and other mollusca) are typical of the Pliocene age (Metaxas et al., 2007).

Quaternary sedimentation is represented by limnic and terrestrial sediments such as sandy clays, clay marls, sandy marls, lignites, lateral fans and alluvial deposits (Pavlides and Mountrakis, 1987). Thin sediments of an Upper Quaternary age are also very common in the Florina basin.

The tectonic activity of NE–SW and NW–SE directed faults resulted in the subsidence of the Neogene sediments into the SW (Pavlides and Mountrakis, 1987).

Nowadays, the total area of Florina basin is under exploitation due to the abundance of lignite deposits, which contribute to the national economy. Clays, which are part of the local lignite-bearing sequence, are also exploited along with lignites, but they are not yet evaluated for their economic potential. The research focuses on the mineralogical and chemical compositions of the clays from the Achlada lignite deposits. The transformations of mineralogical phases, during firing of casting molds, at certain temperatures, including formation of new crystalline phases and vitrified mass are also evaluated. During firing, the clays were thoroughly transformed given that minerals in the clay bodies undergo chemical and structural modifications. Both the neoformed phases and the vitrified mass characterize the final ceramic products and also affect strongly their properties, such as the maintenance of their form (Carretero et al., 2002; Jordán et al., 1999; Manning, 1995; Perraki and Orfanoudaki, 2001; Vieira et al., 1999). The knowledge of the origin, diagenesis, and physicochemical composition of the studied clays is essential when sketching out suitable compositions required for ceramic production (Meseguer et al., 2009; Sanfeliu and Jordan, 2009).

The inorganic seams that are included in lignite-bearing sequences have always been regarded as non-usable materials (waste materials) and therefore, as a negative factor during lignite exploitation. These materials also create an additional problem in the environmental rehabilitation of the open lignite mine that they occur. The aim of the present study is to evaluate the possible industrial use of clays from the Achlada lignite deposits (Florina basin, NW Greece) as raw material in the ceramic industry. This is an original research of particular economic interest, since it is the first thorough mineralogical study in Greece concerning the industrial use of the inorganic seams (waste materials), which occur in a lignite-bearing sequence.

2. Materials and methods

The examined clay samples were collected along the studied succession from bottom to top (Fig. 1c).

Mineralogical and chemical analyses as well as firing procedure were conducted on the studied samples in order to identify: (i) the mineralogical composition of the bulk samples, (ii) the transformation of the mineralogical phases during firing of the samples and (iii) the neo-formed mineral phases resulting from firing. Both the bulk samples and the casting molds, which were fired successively at various