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Research paper

Chromium-bearing clays in altered ophiolitic rocks from Crommyonia (Soussaki) volcanic area, Attica, Greece

I. Mitsis[a,*], A. Godelitsas[a], J. Göttlicher[b], R. Steininger[b], P.N. Gamaletsos[c], M. Perraki[d], M.M. Abad-Ortega[e], M. Stamatakis[a]

[a] Faculty of Geology & Geoenvironment, National and Kapodistrian University of Athens, Zografou Campus, 15784 Athens, Greece
[b] Karlsruhe Institute of Technology, ANKA Synchrotron Radiation Facility, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany
[c] Center for Electron Nanoscopy, Technical University of Denmark, 2800 Kongens Lyngby, Denmark
[d] School of Mining and Metallurgical Engineering, National Technical University of Athens, 9 Heroon Polytechniou St., 15773 Athens, Greece
[e] Centro de Instrumentación Científica, Campus Universitario de Fuentenueva, Paseo Prof. Juan Ossorio, s/n, 18003 Granada, Spain

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ABSTRACT

Chromium-bearing clays occurring at Crommyonia (Soussaki), Greece, are studied in detail. In this area Mesozoic ultramafic ophiolitic rocks were affected by a Pliocene volcanic activity continuing, nowadays, with intense post-volcanic phenomena. Particularly, the Cr-bearing clays were formed at the margins of the ophiolite into highly altered serpentinized peridotite. These clays were studied by means of x-ray diffraction (powder-XRD), microscopic (SEM-EDS), nanoscopic (TEM-EDS/STEM-HAADF), and spectroscopic (FTIR, XANES) techniques. The XRD and SEM-EDS studies confirmed smectites and halloysites, with average Cr_2O_3 content ca 6.2 wt% and 4.3 wt%, respectively. The mineralogy and mineral-chemistry of the above unique Cr-clays was also confirmed by TEM-EDS/STEM-HAADF measurements. Subsequent FT-IR investigation indicated the relation of chromium ions with structural hydroxyls whereas a XANES study showed the presence of only Cr(III) in both phases and the absence of Cr(VI). According to the above data, Cr(III) ions should occupy octahedral sites in the structure of the studied clays. Geochemical data indicated high enrichment in Cr, and also in As, Se, Ni, *V*, Sc, Tl, when compared to Upper Continental Crust (UCC), and in Cr when compared to average global peridotite and primitive mantle. The formation of Cr-bearing clays is attributed to additional alteration of serpentinized peridotite minerals (such as Cr-spinels), due to hydrothermal fluids leaching different elements from the volcanic, sedimentary, and ophiolitic rocks of the area.

1. Introduction

It is well known that ultramafic rocks, and particularly peridotites, are unstable at surface or submarine conditions (Hostetler et al., 1966; Mumpton and Thompson, 1966; O'Neil and Barnes, 1971; Coleman, 1977; Wilson et al., 2009). Meteoric water, ground water, or hydrothermal fluids can interact with the primary minerals to form new stable phases. The alteration of ultramafic rocks may result in the local enrichment of elements such as Fe, Ni, Cr, Co in newly formed minerals. Enrichment in chromium has been reported in clays formed by such processes. In the region of Takovo, former Yugoslavia, some illites and smectites contain as much as about 14 wt% Cr_2O_3, whereas in some halloysites the content of Cr_2O_3 reaches up to 11.5 wt% (Maksimovic and White, 1973; Maksimovic et al., 1981). In this area, hydrothermal veins, containing silicified serpentinite, pyrite and cinnabar, cut the serpentinite body and are surrounded by argillic zones, which contain the former Cr-clays. Chromian beidellites, which contain 5.6 to 6.4 wt% Cr_2O_3, localized in serpentinites from the Candelaria mine, Nevada, are regarded as the result of the hydrothermal alteration of the ultramafics (Foord et al., 1987). In the ophiolites of the Baie Verte peninsula, Newfoundland Canada, lenses of listvenites (carbonated peridotites) occur that contain chromium-rich micas (fuchsite) with 4.4 to 7.9 wt% Cr_2O_3 (Chao et al., 1986). The formation of listvenites is regarded as the result of hydrothermal alteration, too (Escayola et al., 2009). In the Almaden mercury mining district, Spain, Cr-rich phyllosilicates (fuchsite, Cr-chlorite and/or Cr-illite) are present in ultramafic enclaves and are the result of hydrothermal alteration of chromian spinels (Morata et al., 2001). Cr-smectites are present also in the vein type magnesite deposit at Malentrata (Tuscany, Italy) and are considered to be the result of interaction of fluids derived from the active Larderello-Travale geothermal field and the Ligurian serpentinites (Boschi et al., 2009). The serpentinite host rock was hydrothermally completely altered by

* Corresponding author.
E-mail address: mitsis@geol.uoa.gr (I. Mitsis).

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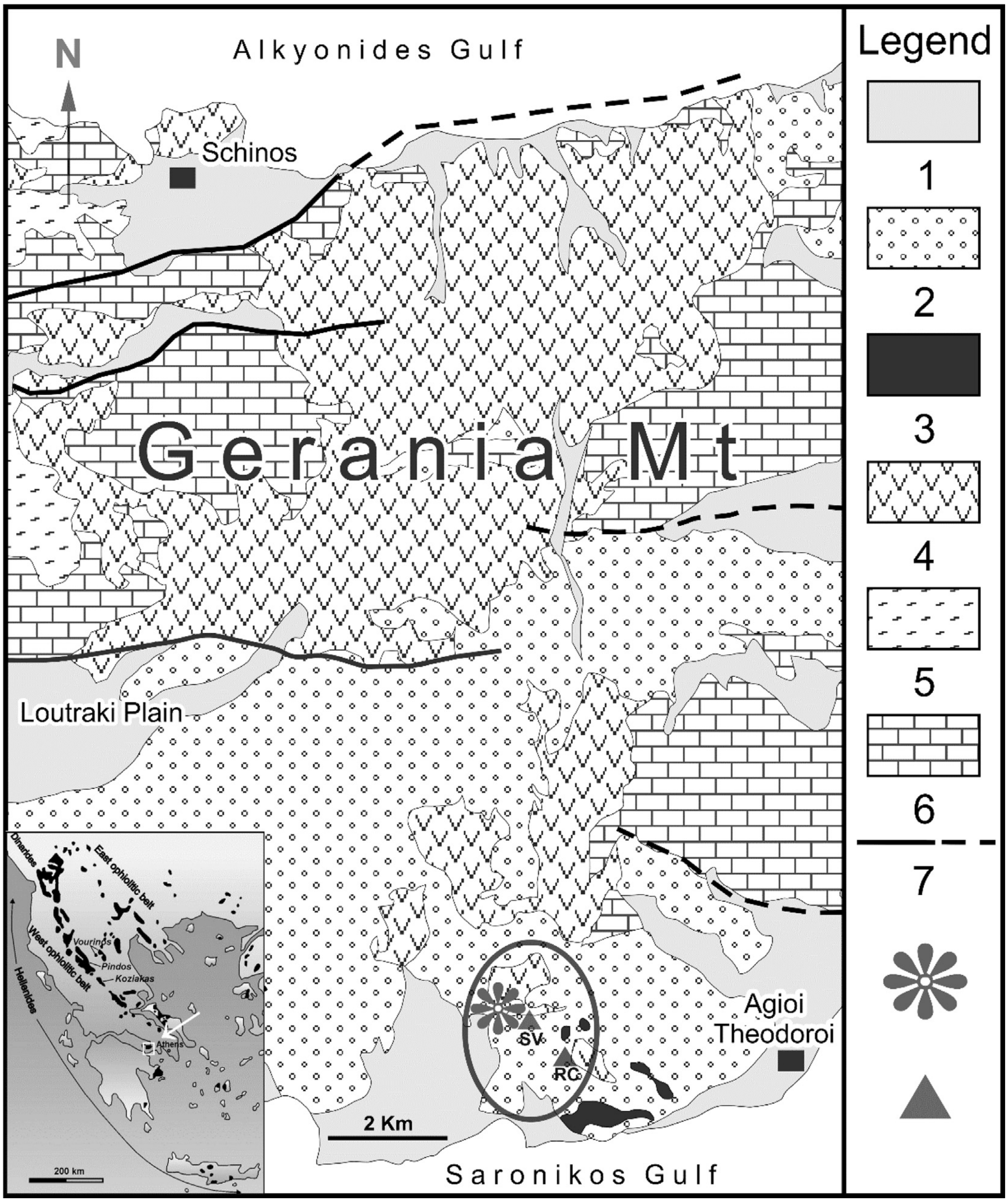

Fig. 1. Crommyonia (Soussaki) volcanic area (Papastamatiou, 1937; Pe-Piper and Hatzipanagiotou, 1997) and sampling locations. 1: Alluvial and scree; 2: Pliocene - Pleistocene deposits; 3: Plio-Pleistocene Volcanics; 4: Serpentinites; 5: Clastic Sediments (Upper Jurassic–Low Cretaceous); 6: Neritic Limestones (Middle Jurassic–Low Cretaceous); 7: Neotectonic Faults; ✻ Volcanic Manifestations; ▲ Locations Sampling in ellipse (SV: Soussaki Volcano; RC: Red Cave). Scale: 1:79.000.

Si- and CO_2 –rich fluids to a friable rock consisting mainly of opal, chalcedony, Al-Mg-Cr phyllosilicates and accompanied by the formation of a network of magnesite and dolomite veinlets and large magnesite/dolomite veins along major tectonic structures. However, besides Cr-clays reported as formed by the decomposition of ultramafic rocks, these Cr-clays are also widely distributed in the Hutrurin Formation, Jordan and Israel (Khoury et al., 1984; Sokol et al., 2011; Khoury, 2012, 2014; Khoury and Al-Zoubi, 2014). These Cr-bearing clays, comprising volkonskoite and Cr-smectite, presented various dioctahedral and trioctahedral compositions, are regarded as the result of infiltration of the varicolored marble (combusted bituminous phosphatic marl) by highly alkaline reducing waters. The source of chromium is attributed to the original bituminous phosphatic marl. The mineral volkonskoite has been reported from several localities (Khoury et al., 1984; Foord et al., 1987 and references therein), but the type locality is the Okhansk region of the Perm Basin Ural Mountains, Russia. The mineral volkonskoite is defined as a dioctahedral member of the smectite group if Cr is the dominant octahedral cation percent (Brindley, 1980).

Preliminary data about occurrences of Cr-bearing clays from the Crommyonia area (Soussaki) in Greece, have been mentioned by Mitsis et al. (2009). In the Soussaki area ultramafic rocks were altered by post-volcanic activity and the associated hydrothermal fluids. In the present paper the Cr-bearing clays are investigated in detail, using a combination of X-ray diffraction, electron microscopic and spectroscopic techniques applied in bulk, microscale and nanoscale, comprising methods as SEM/EDS, HRTEM-AEM/STEM-HAADF and Synchrotron-based techniques. It should be stressed that such a thoroughly study concerning Cr-bearing halloysite and Cr-bearing smectite localized in ophiolitic ultramafic rocks, altered by Pliocene - Pleistocene acid volcanic activity, is presented maybe for the first time.