FORMATION OF SULFATES AT THE THIAPHES AREA OF MILOS ISLAND:
POSSIBLE PRECURSORS OF KAOLINITE MINERALIZATION

AKIS E. KELEPERTSIS
Department of Geology, National University of Athens, Panepistimiopolis, A. Ilia, GR-15784 Athens, Greece

ABSTRACT

The physicochemical conditions at the Thiaphes area of Milos Island are favorable for the recent formation of alunogen, alunite, natroalunite, melanterite, gypsum, sulfur, sylvite, quartz, cristobalite and kaolinite. The local environment is characterized by gas emissions rich in H2S and CO2, thermal waters enriched in SO4 and Na by mixing with seawater, porous and permeable alluvial aluminosilicate-rich soils, and the presence of atmospheric O2. Alterations started in the Quaternary in an acid environment and continue up to the present day in areas of H2S-rich fluids. The hydrated sulfates represent precursors of the very common kaolinite mineralization on the island. Kaolinite was also formed by the hydrolysis of feldspars.

Keywords: hydrothermal alteration, sulfates, kaolinite, acid environment, Milos, Greece.

INTRODUCTION

The island of Milos is located in the central part of the South Aegean active volcanic arc (Fig. 1). Only a small exposure of metamorphic rocks occurs at the southern part of the island; these rocks belong to a flysch formation (phyllites) associated with ophiolites and allochthonous blocks of limestones (Fytikas 1977). Most of the island consists of volcanic rocks (Fig. 2), which are part of the southern Aegean island arc, and which formed during the Pliocene as a consequence of the northward subduction of the African plate beneath the Aegean plate (Fytikas et al. 1984). The volcanic rocks belong to a calc-alkaline series of andesites and rhyolites accompanied by tuffs, ignimbrites and pyroclastic rocks.

On Milos, there is a high-enthalpy geothermal field (Fytikas & Marinelli 1963). The heat flow was responsible for intense hydrothermal activity, which caused widespread bentonization and alunization, kaolinization and the formation of various hydrothermal mineral deposits (kaolinite, bentonite, sulfur, barite, galena, alunite and manganese oxides). Kaolinite deposits are especially large; most of them are being exploited. Kaolinite is used as raw material in the paper and cement industries.

Fumaroles (up to 102°C), submarine gas leakage (> 50°C), thermal springs (up to 75°C) and hot grounds (up to 100°C) are some surface thermal manifestations. At the sites of altered volcanic rocks, active mud volcanos, lignitic deposits, and volcanic emanations (Velinov et al. 1970, Baltatzis et al. 1986), hydrous sulfate (e.g., roseneite, melanterite, römerite, halotrichite, epsomite and alunite) are formed.

This paper reports on the mineralogy and the conditions of formation of sulfate minerals and other secondary products, especially kaolinite, in the Thiaphes area near the village Adamanda (Fig. 2).

GEOLOGY OF THE THIAPHES AREA

The area in which humid–hot soils and gas exhalations occur is approximately 1 km northeast of Adamanda; it is known as Thiaphes, meaning "sulfur concentrations". The soils are unconsolidated alluvial deposits consisting of pebbles, sands, silt and clay derived by weathering of the surrounding geological formations, such as tuffs, rhyolitic and
ryodacitic lavas, and lahars, which are younger than Upper Pliocene (Fytikas 1977).

Where gas emanations take place, the soils are altered and covered with thin layers of secondary minerals that make the soils yellowish, greenish, white and brownish black. The soils are damp, probably as a result of the effect of the underlying geothermal field, whose presence has been confirmed by drilling of the surrounding alluvial deposits.

**ANALYTICAL METHODS**

Powder X-ray diffractometry was used to identify the hydrated sulfate aggregates and the associated material. A Philips PW1010 diffractometer was operated with Ni-filtered CuKα radiation at 36 kV and 24 mA, at the Department of Geology, National University of Athens. The samples (10) were also analyzed by atomic absorption spectrometry for K, Na, Al, Fe, Ca, Co, Ni, Pb, Zn, Cu and Sr. X-ray-diffraction data and chemical results are shown in Tables 1 and 2, respectively.

**RESULTS**

**Mineralogy**

The minerals identified by X-ray diffractometry include alunogen, melaniterite, gypsum, natro-alunite, alunite (all sulfates), quartz, cristobalite, sulfur, halite, and sylvite. Of the two forms of silica, cristobalite is the newly formed mineral present, whereas part of the quartz may be of detrital origin. The aluminosilicates are represented by kaolinite; halite and sylvite also are present.

**Chemistry**

The chemical composition of the sulfate-coated aggregates analyzed is quite simple and is as expected from the mineral determinations; concentrations of the major elements (Al, Ca, K, Na, Fe) correlate well with the mineral assemblages. For example, the sample with high gypsum content (M5) is characterized by a high Ca content; the presence of alu-
KAOLINITE MINERALIZATION, MILOS, GREECE

Fig. 2. Geological sketch map of Milos Island (from Fytikas et al. 1986), with location of the studied area. Symbols: 1 metamorphic basement, 2 Neogene sediments, 3 basal pyroclastic series (Middle-Upper Pliocene), 4 complex of domes and lava flows (Upper Pliocene), 5 pyroclastic rocks, 6 lava domes, 7 Halepa and Plakes domes, 8 rhyolitic complexes (Upper Pleistocene), 9 products of phreatic activity, 10 Quaternary sediments, 11 study area.

nogen $\text{Al}_2(\text{SO}_4)_2\cdot 17\text{H}_2\text{O}$, alunite $\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$, natroalunite $\text{NaAl}(\text{SO}_4)_2(\text{OH})_6$ and kaolinite $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ is reflected by the high Al contents in the samples. Sodium and potassium are present in alunite, natroalunite, halite and sylvite. The high Fe-contents in the samples reflect the presence of melanterite ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), the only iron sulfate detected. Ni, Pb, Zn concentrations are never anomalous, suggesting that other sulfate minerals are absent. Cu, Co and Sr were not detected in the samples, except for a Sr value of 230 ppm in a gypsum-rich specimen. All these results suggest that the altered parent soils, which were affected by the hydrothermal solutions and $\text{H}_2\text{S}$ gases, were low in trace elements (Cu, Pb, Zn, Ni), and this is reflected by their mineralogical composition. The alluvial soils consist of particles derived from the alteration of the surrounding geological formations, which are mainly white tuffs and hydrothermally altered (mainly kaolinized) volcanic rocks. In general, the soils are composed of Si-, Al-, Fe-, K- and Na-bearing silicates. Part of the Na is attributed to contamination of the hydrothermal solutions by seawater.

DISCUSSION:
FORMATION OF ALTERATION MINERALS

Hydrous sulfate minerals typically form in the oxidation zone of sulfide ores (Velinov et al. 1970, Good 1971, Zodrow et al. 1979), but also have been found in areas of volcanic activity (Stamatakis et al. 1987). From field observations and published data (Fytikas 1977), the chemical environment at the Thiaphes area is favorable for the formation of hydrated sulfate minerals. This environment is characterized by $\text{H}_2\text{O}$, $\text{H}_2\text{S}$ and $\text{CO}_2$ emanations and by high humidity from the geothermal field. The $\text{SO}_4$ contents of thermal waters that apparently penetrate the permeable alluvial soils are high and hence pH is low (4.0).

The hydrous sulfates at the Thiaphes area of Milos must be the alteration products formed by the reaction of $\text{H}_2\text{S}$ with alluvial soils in a humid microenvironment of low pH. The abundances of Al-sulfate minerals (alunogen, natroalunite, alunite) reflect the existence of Al-rich minerals in the soils. The occurrence of sulfur in thin layers in the surface around
The formation of gypsum occurs by the transformation of the anorthite component of plagioclase according to the reaction:

$$\text{CaAl}_2\text{Si}_2\text{O}_8 + \text{H}_2\text{SO}_4 + 3\text{H}_2\text{O} \rightarrow \text{anorthite component}$$

$$\text{CaSO}_4\cdot2\text{H}_2\text{O} + \text{Al}_2\text{Si}_3\text{O}_8\cdot(\text{OH})_4$$

gypsum kaolinite

As mentioned before, on Milos there are widespread gaseous emanations, thermal springs, barite and sulfur deposits, etc., as well as many kaolinite deposits. Most of these deposits are aligned along fractures that formed during recent tectonic activity and that favored the surfacing of gases and hydrothermal solutions. These solutions consist of resurgent heated meteoric water mixed in some way with seawater.

Kaolization, alunitization and silicification phenomena had their maximum development in proximity of the high-thermal-gradient sites, as is shown on maps of thermal anomalies (Fytikas 1977). These anomalies, together with the widespread recent volcanic activity on the island, suggest the existence at depth of magmatic bodies, which represent the source of energy for the processes of alteration and mineralization.

The alteration processes are still active today near Thiaphes, giving rise to silica minerals, sulfates, sulfur, chlorides and aluminosilicate minerals (kaolinite). The mineralogy of the kaolinite mineralization includes amorphous phases of silica, cristobalite, quartz, alunite and natroalunite. Gypsum, pyrite and sulfur also are present in a few deposits. A comparison in the mineral associations between the present-day aggregates and the kaolinite deposits shows that sulfate minerals like alunogen and melanterite are absent in the deposits. This absence is reflected in their color: the kaolinized masses have a whitish color, but the recently altered masses of the Thiaphes area are impure, owing to silica minerals, sulfates and iron oxides. In addition, the relative proportions of sulfate minerals to kaolinite are higher in the present-day aggregates than in the kaolinite deposits. In the Kastriani kaolinite mine (Kelepertsis et al. 1988), the proportions of minerals are: 41% kaolinite, 44% cristobalite and amorphous phases, 6% quartz, 2% undetermined minerals and 7% alunite.

Based on the field observations and the above data, two processes of alteration seem to be responsible for the formation of kaolinite: (a) hydrolysis of feldspars and muscovite under conditions of low pH and humidity, and (b) development of early hydrated sulfate facies into sulfates having a higher structural order and a lower water content. These eventually were transformed into kaolinite and other minerals.
according to the following reaction:

\[
\text{Al}_2(\text{SO}_4)\cdot 17\text{H}_2\text{O} + 2\text{H}_4\text{SiO}_4 \rightarrow \text{Alunogen}
\]

\[
\text{Al}_2\text{SiO}_5(\text{OH})_4 + 3\text{H}_2\text{SO}_4 + 16\text{H}_2\text{O}
\]

**CONCLUSIONS**

Fluids at the surface at the Thiaphes area of Milos Island are represented by gases (CO\text{2} and H\text{2}S) and hydrothermal solutions enriched in SO\text{4}\text{-} and Na\text{+}, possibly mixed with seawater. Deep magmatic bodies represent the source of energy for the upward migration of the fluids.

The formation of the sulfate minerals is favored by H\text{2}S-bearing gases emanating at the surface, the low pH of the thermal waters and the high porosity and permeability of the alluvial soils composed of aluminosilicate minerals.

The present-day aggregates consist of alunogen, melanterite, gypsum, alunite, natroalunite, halite, sylvite, sulfur, quartz, cristobalite and kaolinite. According to these studies, the early hydrated sulfate phases may represent the precursors of the minerals in the paragenesis of the late Milos kaolinite deposits. The precursors eventually developed into sulfates with a higher structural order and kaolinite. Kaolinite was also formed by the alteration of feldspars.

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