THE AUTHIGENIC MINERALS FORMED FROM VOLCANIC EMANATIONS AT SOUSSAKI, WEST ATTICA PENINSULA, GREECE

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ABSTRACT

The Soussaki area, situated in the west Attica Peninsula, Greece, represents the northwestern end of the South Aegean Plio-Pleistocene volcanic arc. Postvolcanic phenomena continue to the present day, and include emission of gases such as H_2S, CO_2, and water vapor. Reaction between these fluids and pre-existing rocks, consisting mainly of serpentinite, chert, marlstone, limestone, and subordinate rhyodacitic lava, has resulted in the formation of gypsum, sulfur, silica polymorphs, and Fe and Mg sulfates; kaolinite, anhydrite, carbonates, and Ni and K–Al sulfates also are present in some cases. The authigenic minerals form a crust up to 10 m in thickness on top of partly altered basement rocks. The sulfates, carbonates and silica polymorphs are enriched in Ni, Co and Cr. The chemical formulas of the authigenic minerals and their field relationships suggest that the Fe, Mg, Ni sulfates, as well as magnesite, dolomite and some of opal-CT, are related to hydrothermal alteration of serpentinites, whereas alunite, kaolinite, opal-CT, cristobalite and quartz are associated with the alteration of small bodies of rhyodacite. The major part of the gypsum and anhydrite, and some of the neoformed calcite, aragonite and dolomite, may be caused by the decomposition of the marlstones and limestones of the bedrock.

Keywords: Aegean volcanic arc, sulfate minerals, volcanic emanation, hydrothermal alteration, Greece.

SOMMAIRE

La région de Soussaki, située dans la partie occidentale de la péninsule de l'Attique (Grèce), représente l'extrémité nord-ouest de l'arc volcanique plio-pleistocène. Les phénomènes post-volcaniques continuent jusqu'à ce jour, comme en témoignent les émissions de gaz (H_2S, CO_2, et vapeur). La réaction de ces fluides avec les roches encaissantes (constituées principalement de serpentinites, chert, marnes, calcaires, et laves rhyodacitiques) a abouti à la formation de gypse, soufre, polymorphes de silice, et sulfates de Fe et de Mg; kaolinite, anhydrite, carbonates, et sulfates de Ni et de K–Al sont aussi présents dans certains cas. Les minéraux authigènes forment une croûte épaisse de 10 m sur les roches du socle partiellement altérées. Les sulfates, carbonates et les polymorphes de silice sont enrichis en Ni, Co et Cr. Les formules chimiques des minéraux authigènes et leurs relations sur le terrain font penser que les sulfates de Fe, Mg et Ni, ainsi que la magnésite, la dolomite et, dans certains cas, l'opale-CT, sont liés à l'altération hydrothermale des serpentinites, tandis qu'alunite, opale-CT, cristobalite, et quartz sont associés à l'altération des petits massifs rhyodacitiques. La plupart du gypse et de l'anhydrite et une partie de la calcite, l'aragonite et la dolomite néoformées seraient dues à la décomposition des marnes et des calcaires des roches hôtes.

Mots-clés: arc volcanique égéen, sulfates, exhalations volcaniques, altération hydrothermale, Grèce.

INTRODUCTION

In the Aegean region (Fig. 1), extensive volcanic activity has taken place from Tertiary through to Quaternary times (Innocenti *et al.* 1979, Fytikas *et al.* 1984). The Soussaki area is located about 65 km west of Athens, near the Canal of Corinth (Fig. 2) and represents the northwesterly end of the South Aegean volcanic arc. Here, volcanic activity commenced during the Pliocene and continued through the Pleistocene. Postvolcanic activity is still observed today, manifested as emanations of warm fluids in a localized area of roughly 200 m × 700 m called Psorochoma (Figs. 2, 3) (Papastamatiou 1937, Pe 1972, Innocenti *et al.* 1984, Fytikas *et al.* 1988). This activity is characterized by the emission of hydrogen sulfide, carbon dioxide and water vapor (Papastamatiou 1937).

Basement rock-types of the Soussaki area include pre-Neogene serpentinite and chert, whereas marine and fresh-water marlstone and limestone of Pliocene age partly cover the older rocks (Papastamatiou 1937). Locally, small bodies of dacite–rhyodacite lavas have erupted through the former rocks. The volcanic glass of these rocks is still partly unaffected by the postvolcanic phenomena. The serpentinite basement occurs as elongate bodies near the area of the major center of volcanic emanations.

FIG. 1. The location of the Soussaki area in the south
Aegean arc.

In the area, the reaction of warm, acidic fluids
with the pre-existing rock-types created a series of
authigenic minerals, in particular sulfates, carbonates
and silica polymorphs. Thick, unconsolidated masses
of these secondary minerals up to 10 m in thickness
commonly occur near the sites of fluid emission as
a result of decomposition of silicate minerals in the
pre-existing rocks.

This study discusses the assemblages of the secon-
dary minerals, the distribution of Ni, Co, Cu, Zn
and Cr, and relationships with the type of parent
material. Samples were collected from the sites of
major postvolcanic activity at Psorochoma (Fig. 3).

ANALYTICAL METHODS

Mineralogical determinations were carried out
using X-ray-diffraction analysis. Concentrations of
Ni, Co, Cu and Zn were determined by atomic
absorption analysis, whereas concentrations of Cr
and Pb were determined by colorimetry. All the ana-
lyses were done at the University of Athens. The ana-
lytical results are given in Tables 1 and 2.

MINERALOGY AND GEOCHEMISTRY

The identified authigenic minerals (Table 1) can
be subdivided into chemically related groups as fol-
lows: hydrous ferric and ferrous sulfates: rozenite
$FeSO_4 \cdot 4H_2O$, melanterite $FeSO_4 \cdot 7H_2O$, roemerite
$Fe^{2+}Fe^{3+}{}_2(SO_4)_4 \cdot 14H_2O$; hydrous Mg-bearing sul-
fates: hexahydrite, epsomite; Ca-bearing sulfates:
gypsum, anhydrite; hydrous Ni sulfate: nickel hex-

ahydrite $NiSO_4 \cdot 6H_2O$; native element: sulfur; car-
bonates: magnesite, dolomite, calcite, aragonite; K–
Al hydroxysulfate: alunite; silica polymorphs: opal-
CT, low cristobalite, quartz; clay minerals: kaolinite,
smectite; sulfide: marcasite; oxides–hydroxides:
scarce Fe-oxides, hydroxides.

The sulfate aggregates rich in roemerite and nickel
hexahydrite usually have a green color, whereas those
containing rozenite, epsomite, hexahydrite, melan-
terite, anhydrite, or alunite are white. Melanterite-
and rozenite-rich samples are easily identified
because they exhibit curved, elongate crystals and
silky, cotton-like aggregates, respectively. Opal-CT,
low cristobalite and quartz form hard, massive bod-
ies, black-grey to olive green in color. The presence
of native sulfur gives a yellowish color to aggregates.
Transparent gypsum crystals are widespread in all
the sulfate aggregates, but may form individual
masses up to 5 m thick, especially close to marlstone
and limestone (Fig. 3). In contrast, near serpentinite
masses, magnesite and opal-CT occur in abundance,
in addition to the Ni, Mg and Fe sulfates (Fig. 3).

Most of the ferrous, ferric, nickel and magnesium
sulfates occur as efflorescences on the inner walls of
caves excavated before and during the Second World
War for the extraction of native sulfur. It is notice-
able that the three Fe-sulfates have not been found
together (Table 1). In some caves, different
parageneses have been observed (Table 1), consist-
ing of either alunite with opal-CT, or kaolinite with
quartz, or low cristobalite with opal-CT. In the last
two cases, unaltered volcanic glass is present.

Ni, Co, Cu, Zn and Cr contents of the aggregates
are reported in Table 2. Lead concentrations were
found to be below the detection limit (5 ppm). Nickel
concentrations show an enormous range, from 15
ppm in samples enriched in native sulfur and car-
bonate, to 9800 ppm in samples containing nickel
hexahydrite (Tables 1, 2). Cobalt concentrations
generally follow those of nickel, with values between
5 and 355 ppm. Although Zn and Cu values are rela-
tively low in comparison with the Ni and Co con-
centrations, the former elements do occur in
increased concentrations wherever the Ni and Co
values are high (Table 2, Fig. 4).

A statistical treatment of trace-element concentra-
tions shows that there is a good correlation between
Ni and Co (correlation coefficient $R = 0.89$), moder-
ate correlation between Ni and Zn ($R = 0.64$), Co and
Zn, and poor correlation between Ni and Cu
($R = 0.28$), Cr and Zn (Fig. 4).

DISCUSSION

In the field of volcanic emanations at Soussaki,
the predominance of Fe and Mg hydrous sulfates,
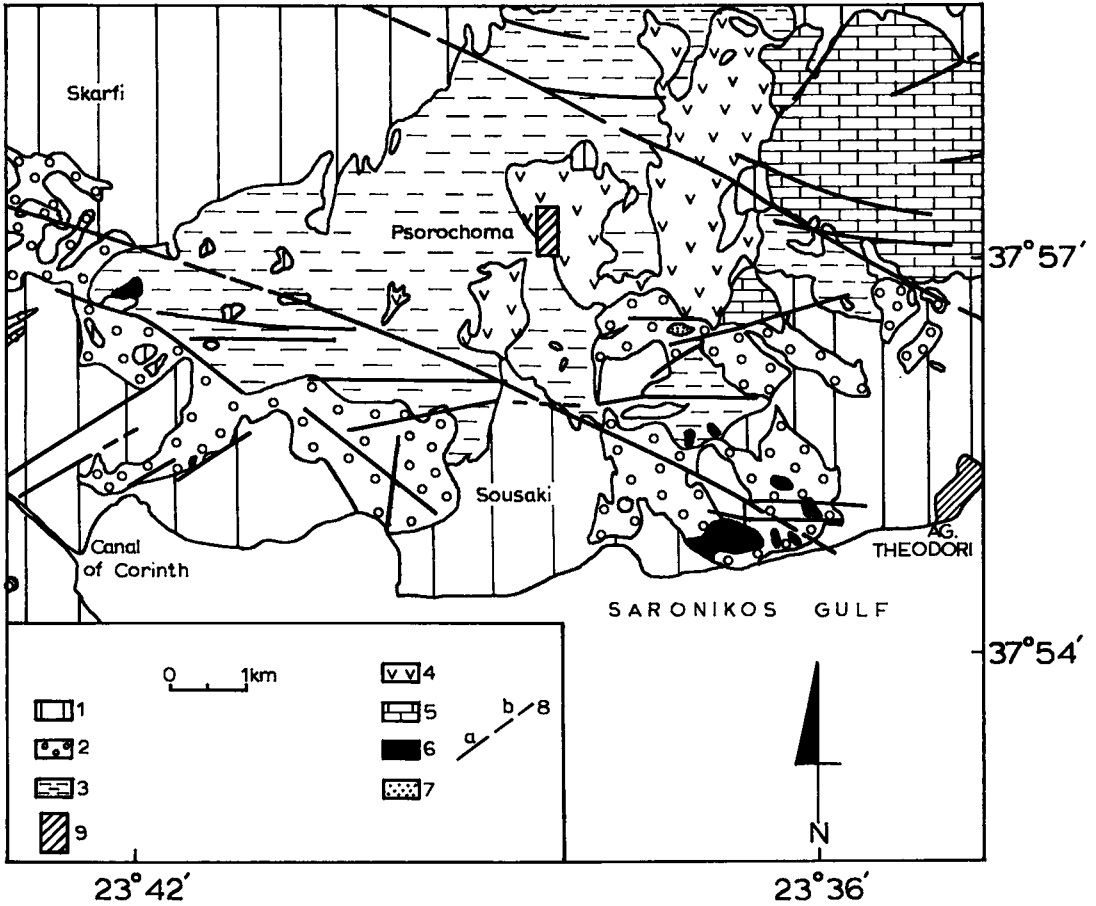the presence of Ni sulfate and a correspondingly high

FIG. 2. Geological map of the Soussaki area (from Fytikas *et al.* 1988, slightly modified). Legend: 1 alluvial deposits, 2 marly limestones, marls, conglomerates of Plio-Pleistocene age, 3 conglomerates, sandstones and marly limestones with lignitic intercalations (Pliocene), 4 ophiolite complex, 5 carbonaceous sequence (Middle Jurassic – Upper Triassic), 6 dacitic lava flows and domes, 7 tuffs, 8 fault (a observed, b inferred), 9 area studied.
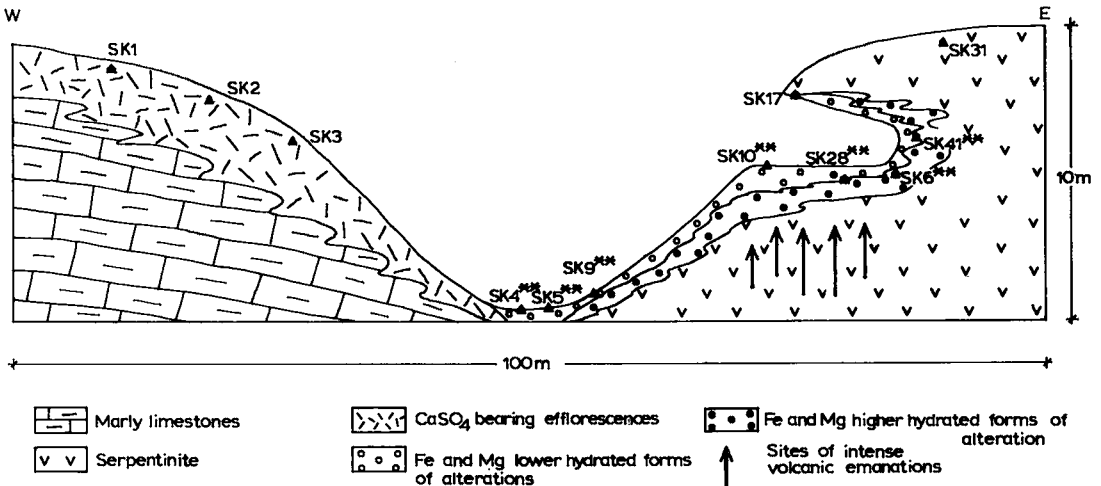
FIG. 3. Schematic cross-section at the southern end of the study area at Psorochoma (see Fig. 2).

TABLE 1. MINERALOGICAL ASSEMBLAGES*
IN THE ALTERATION ZONES

Sample	mineralogical constituents
SK-1	– gypsum (M), calcite (I)
SK-2	– gypsum (M), opal-CT (I)
SK-3	– opal-CT (M), marcasite (T)
SK-4 **	– roemerite (M), gypsum (I), rosenite (T), calcite (T)
SK-5 **	– roemerite (M), gypsum (I), anhydrite (I), rosenite (T), calcite (T)
SK-6 **	– roemerite (M), gypsum (I), melanterite (I), nickelhexahydrite (T), aragonite (T)
SK-8	– opal-CT (M), quartz (I)
SK-9 **	– aragonite (M), roemerite (M), anhydrite (I), epsomite (I), rosenite (T)
SK-10**	– sulfur (M)
SK-15	– quartz (M), opal-CT (I), gypsum (I)
SK-17	– quartz (M), magnesite (M), opal-CT (I), dolomite (I), epsomite (T)
SK-18	– quartz (M), opal-CT (I), low-cristobalite (I)
SK-19	– low-cristobalite (M), dolomite (I), gypsum (I), roemerite (T), epsomite (T)
SK-21	– rosenite (M), gypsum (M), opal-CT, alunite (T)
SK-22	– glass (M), low-cristobalite (I), opal-CT (I), gypsum (T)
SK-23	– rosenite (M), dolomite (M), opal-CT (I), alunite (I)
SK-25	– aragonite (M), glass (M), kaolinite (I)
SK-26	– dolomite (M), quartz (M), glass (I), kaolinite (T), smectite (T)
SK-27	– gypsum (M), low-cristobalite (I), quartz (I)
SK-28**	– rosenite (M), gypsum (I), melanterite (I)
SK-29	– opal-CT (M), dolomite (M), quartz (I), gypsum (I)
SK-31	– serpentine (M), smectite (T)
SK-32	– opal-CT (M), smectite (T)
SK-36	– dolomite (M), quartz (I)
SK-38**	– rosenite (M), roemerite (M), gypsum (I)
SK-39	– opal-CT (M), dolomite (T)
SK-40	– gypsum (M), quartz (I), opal-CT (I)
SK-41**	– rosenite (M), gypsum (I), melanterite (I), hexahydrite (T)
SK-42	– gypsum (M), opal-CT (I)

*. determined by X-ray diffraction (powder method).

Explanatory notes: **. = efflorescences
M = major constituent
I = intermediate constituent
T = trace constituent

TABLE 2. CHEMICAL DATA* ON ASSEMBLAGES
OF SECONDARY MINERALS

Sample	Ni	Co	Cu	Zn	Cr
SK-1	282	25	4	6	
SK-2	67	10	3	4	
SK-3	115	10	27	5	480
SK-4 **	2400	125	7	9	
SK-5 **	2420	210	29	37	
SK-6 **	9800	355	29	55	1150
SK-7	136	15	4	8	
SK-8	892	45	7	6	329
SK-9 **	3400	210	27	39	580
SK-10 **	15	5	4	4	
SK-11	3650	280	29	51	821
SK-12	479	35	9	16	
SK-13	18	10	10	4	
SK-14	584	75	5	7	
SK-15	1100	50	51	–	
SK-16	2600	65	7	48	
SK-17	1820	105	7	29	657
SK-18	1821	100	6	27	1100
SK-19	6120	305	27	63	411
SK-20	3550	150	11	27	
SK-21	1770	85	9	16	493
SK-22	1850	110	39	58	
SK-23	2750	145	28	31	
SK-24	3330	105	18	44	
SK-25	1480	90	17	20	
SK-26	1050	50	20	25	
SK-27	359	35	7	8	
SK-28 **	2040	100	16	31	
SK-29	324	20	31	45	
SK-30	520	40	11	13	
SK-31	3500	230	11	38	
SK-32	1900	130	26	50	780
SK-33	1600	90	35	21	
SK-34	346	20	12	9	
SK-35	1650	85	39	40	
SK-36	663	50	27	9	
SK-37	2420	100	10	51	
SK-38 **	4800	170	7	6	
SK-39	167	10	4	4	
SK-40	419	35	–	12	
SK-41 **	1500	80	9	26	
SK-42	2800	100	24	42	
SK-43	2200	100	6	14	
SK-44	1760	80	6	20	
SK-45	1820	95	11	23	
SK-46	542	150	22	21	

Pb values are less than 5 ppm in all samples analyzed.
*. in ppm
**. efflorescences

concentration of Ni, even in samples in which minerals of the serpentine group were not detected, all show that the main parent material was the serpentinite of the basement. This conclusion is further reinforced by the strong positive correlation between Ni and Co, and the paragenetic association of silica polymorphs with Mg and Fe sulfates and Mg-bearing carbonates.

The appearance of a ferrous and ferric sulfate, roemerite, along with either rozenite or melanterite (ferrous sulfates) may be attributed to variations in the H_2S, H_2O and O_2 concentrations in the microenvironment in which these minerals formed. The presence at the Psorochoma of Mg and Ni sulfates with various amounts of structural water, i.e., i) epsomite $MgSO_4 \cdot 7H_2O$ and hexahydrite $MgSO_4 \cdot 6H_2O$, and ii) morenosite $NiSO_4 \cdot 7H_2O$ (Mitsaki 1981) and nickel hexahydrite $NiSO_4 \cdot 6H_4O$, can be attributed to variations in the temperature and humidity in the microenvironment of alteration. The higher hydrated forms of all of the hydrated sulfates mentioned above have been shown to occur in environments of high humidity (Ehlers & Stiles 1965, Baltatzis et al. 1986). On the other hand, morenosite is easily transformed to nickel hexahydrite at temperatures higher than 31°C (JCPDS 1973).

In the Soussaki area, the paragenesis of alunite, silica polymorphs, kaolinite and relict volcanic glass is indicative of a parent material containing glass, in this case a rhyodacitic–dacitic rock.

One of the most common minerals to be formed from an acid volcanic rock precursor material in areas of intense volcanic emanations, where high H^+ and SO_4^{2-} concentrations occur, is alunite (Hemley et al. 1969). This mineral is formed by the reaction of the above ions with feldspars. According to Holler (1967), the reaction for the potassian end-member is:

$$KAlSi_3O_8 + 6H^+ + 3SO_4^{2-} \rightarrow KAl_3(SO_4)_2(OH)_6 + 9SiO_2 + K_2SO_4$$
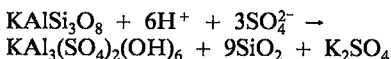
The SiO_2 released from this reaction of the K-feldspar to alunite forms silica polymorphs (Mar-
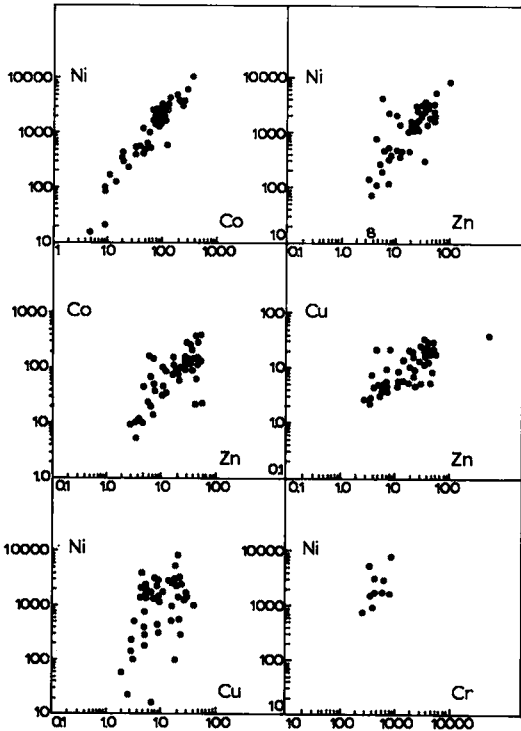
FIG. 4. Trace-element variation diagrams for samples shown in Table 2.

FIG. 5. Schematic representation of the ions mobilized owing to the action of H_2SO_4 and H_2CO_3.

copoulos & Katerinopoulos 1986). Besides alunite, kaolinite also is favored in this acid environment (Hemley *et al.* 1969, Marcopoulos *et al.* 1986).

The combined action of hot hydrogen sulfide (plus sulfurous oxides) with carbon dioxide, high humid- ity and reduced concentration of atmospheric oxygen, has affected the pre-existing rocks through which these emanations have been channeled. A possible association between the parent material and the released ions is shown in Figure 5.

Finally, the combined action of SO_4^{2-}-bearing and HCO_3^-bearing solution on marlstones and limestones favors the formation of Ca- and Mg-rich authigenic minerals such as gypsum, anhydrite, hexahydrite, epsomite, and also aragonite, magnesite, dolomite and calcite.

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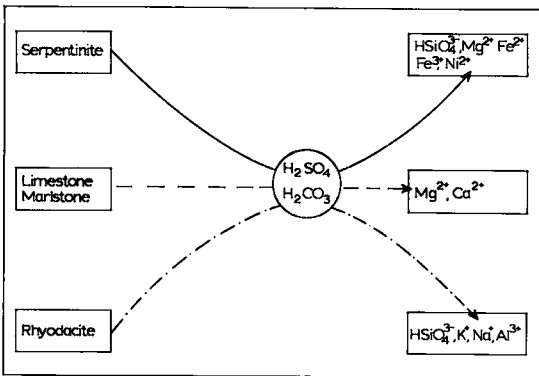
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