

## Sulfate minerals from a mud volcano in the Katakolo area, western Peloponnesus, Greece

MICHAEL G. STAMATAKIS, EMMANUEL G. BALTATZIS, STYLIANOS B. SKOUNAKIS

Department of Geology, National University of Athens, Panepistimiopolis, Ano Ilissia, Athens 15784, Greece

### ABSTRACT

The efflorescences from a mud volcano in the western Peloponnesus, Greece, contain halotrichite, alunogen, voltaite, melanterite, gypsum, and native S. The sulfate minerals were formed by the reaction of carbonates, clay minerals, feldspars, and iron oxides and hydroxides of the basement rocks with  $H_2S$  in the mud-volcano gases. Native S was formed by the oxidation of  $H_2S$  in the atmosphere. Chemical analyses of some major and trace elements are given, and their geochemical behavior is discussed.

### INTRODUCTION

A mud volcano emitting hydrogen sulfide and gaseous hydrocarbons (Karageorgiou, unpub. data) is located in the Katakolo area, western Peloponnesus, Greece (Fig. 1). The orifice of the mud volcano has a diameter of 30 cm, and its inner wall is coated with a thin efflorescence of S, accompanied in places by fibrous, silky-white and cottonlike aggregates of white and pale green minerals. The rocks of Katakolo peninsula are mainly marlstone, claystone, siltstone, conglomerate, sandstone, and limestone. A terra-rosa layer covers them, and thin lignitic layers are interbedded within the aforementioned sedimentary rocks of Pliocene age (Christodoulou, 1970). Diapiric Triassic gypsum-anhydrite rocks, along with dolomite, compose the basement of the Katakolo area (de Loczy, 1955; Konofagos and Komitopoulos, 1986). A fault with a NE-SW direction occurs in the place of gas emanations and extends into Katakolo Bay, where bubbles of gas have also been observed (Karageorgiou, unpub. data). There is no evidence of recent volcanic activity in the western Peloponnesus and the nearby Ionian islands. This paper describes the occurrence of some hydrated sulfates associated with the mud volcano and their probable mode of formation.

### ANALYTICAL METHODS AND RESULTS

Powder X-ray diffractometry and scanning electron microscopy were used for the identification of the minerals that compose the hydrated sulfate aggregates and the loose material around them. Chemical analysis of the sulfate mineral aggregates was done by atomic absorption for Fe, Al, Ca, Mg, Mn, Sr, Ni, Co, and Cu; flame photometry for Na and K; titration for  $SO_4^{2-}$ ,  $Cl^-$ ; and colorimetry for Pb, B, and  $NO_3^-$ . Water was determined by the Penfield method.

The minerals, which were identified by X-ray diffraction, are, in order of their abundance, halotrichite ( $FeAl_2(SO_4)_4 \cdot 22H_2O$ ), alunogen ( $Al_2(SO_4)_3 \cdot 17H_2O$ ), voltaite ( $K_2Fe_3^+Fe_3^+(SO_4)_{12} \cdot 18H_2O$ ), melanterite ( $FeSO_4 \cdot 7H_2O$ ), and gypsum ( $CaSO_4 \cdot 2H_2O$ ). The white to pale green aggregates are especially enriched in halotrichite and voltaite, and the fibrous, silky-white aggregates

consist mainly of halotrichite and alunogen. The brown-to-yellow loose material that lines the mouth of the mud volcano consists of quartz, gypsum, sulfur, calcite, smectite, illite, and iron hydroxides. Sanidine, albite, quartz, calcite, illite, and chlorite occur in the Pliocene claystone of the basement. Iron hydroxides, minor goethite, and also chlorite, quartz, albite, and sanidine have been observed in the terra-rosa. A chemical analysis of the sulfate aggregates is given in Table 1.

### DISCUSSION

Aggregates of halotrichite, alunogen, voltaite, and melanterite have been observed in the oxidized zone of sulfide deposits (Sclar, 1961; Wiggins and Howe, 1967; Velinov et al., 1970; Kravtsov, 1971; Good, 1971; Zodrow and McCandlish, 1978; Zodrow et al., 1979) and also in areas of volcanic emanations (Marcopoulos et al., 1986). However, the development of hydrous sulfates in mud volcanoes has received little attention.

Our in situ observations show that the environment of the present locality is sufficiently wet to allow the formation of highly hydrated sulfate minerals. Indeed, Karageorgiou (unpub. data) has pointed out that in addition to gas emanations, water has been observed gushing intermittently from the volcano's mouth. An analogous correlation between the humidity of the microenvironment and the identity of the sulfate minerals formed has been observed by Sclar (1961) and Gruner and Hood (1971). The absence of rozenite ( $FeSO_4 \cdot 4H_2O$ ) and the exclusive occurrence of ferrous sulfate as melanterite ( $FeSO_4 \cdot 7H_2O$ ) in the area studied, both due to the high humidity of the microenvironment, are well documented from observations on similar mineral assemblages (Ehlers and Stiles, 1965; Gruner and Hood, 1971; Baltatzis et al., 1986).

Concerning the chemical analyses, the analytical values for Fe, Al, Ca, Mg,  $SO_4^{2-}$ , Na, K, and  $H_2O$  (Table 1) are the expected from the X-ray diffraction analysis. The relatively high values of Ni, Zn, and Co correspond to the association between parent material (terra-rosa lateritic layers) and the decomposition products (Fe, Al, sulfates

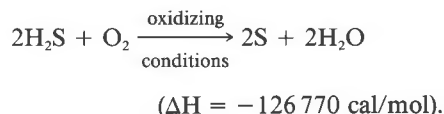


Fig. 1. Locality of the mud-volcano occurrence in the Katakolo area, western Peloponnese, Greece.

rich in Ni, Co, Zn, or probably discrete Ni, Co, Zn sulfates occurring in trace amounts). It is well known that laterites are enriched in Ni and Co (Zeissink, 1969). Chloride anions are available from the adjacent sea water, from dissolution of chloride evaporites that may accompany the anhydrite-gypsum dome, and even from oil-field brines. The last-named source is quite plausible in view of the presence of gas and liquid hydrocarbons in the Katakolo area (Konofagos and Komitopoulos, 1986) and the high values of B observed (Table 1) in the aggregates studied. It is known that, in some regions of mud volcanoes, B-bearing emanations may be found and that the B is derived from oil-field waters (Oborin and Zalkind, 1964). There is a general association between oil-field waters and the presence of high concentrations of B in similar cases (White, 1957; Oborin and Zalkind, 1964;

Aliyev et al., 1966; Rittenhouse et al., 1969; Harder, 1974). The B in oil-field waters is derived from the resinous components of the oil (Gulyayeva et al., 1966). Because the pure sulfates are B free (Harder, 1959, 1974), B will occur as borate minerals admixed with the sulfate aggregates. B in the Katakolo area might also be derived by leaching of the buried evaporitic layers, especially if they contain K salts (Diarov, 1966, 1967; Braitsch, 1971). Karageorgiou (unpub. data) has pointed out the presence of  $\text{NO}_3^-$  in significant quantities in spring waters near the mud volcano. The absence of nitrate minerals from the mud-volcano suite may be due to its reduction to  $\text{NO}$  or  $\text{N}_2$  during the oxidation-reduction reactions of bacterial decomposition (Berner, 1971).

The hydrous sulfates at the Katakolo mud volcano must represent decomposition products formed by  $\text{H}_2\text{S}$  action on pre-existing materials in a humid microenvironment, as indicated by their occurrence at the site of  $\text{H}_2\text{S}$  emanations, the composition of sulfate minerals, and the distribution of the trace elements Ni, Co, and Zn. Gypsum may have formed by the decomposition of calcium carbonates, and the minerals halotrichite, alunogen, voltaite, and melanterite may be due to the decomposition of clay minerals. The Fe and Mn needed for halotrichite, voltaite, and melanterite formation could be derived from terra-rosa decomposition. The abundant native S in the surface around the  $\text{H}_2\text{S}$  emanations is due to the partial oxidation of  $\text{S}^{2-}$  to  $\text{S}^0$  in the atmosphere. The low partial pressure of  $\text{O}_2$  in the atmosphere favors the formation of S instead of  $\text{SO}_2$  (Jensen and Bateman, 1979), according to the reaction



The  $\text{H}_2\text{S}$  in the gas emanations can be attributed to the anaerobic bacterial decomposition of anhydrite and gypsum and/or to the biochemical decomposition of organic material (lignite). Both source materials exist at different subsurface levels in the Katakolo area. The presence of gaseous hydrocarbons is very important for the growth of some species of anaerobic, sulfate-reducing bacteria (Jensen and Bateman, 1979), resulting in the conversion of sulfate to hydrogen sulfide (Barker et al., 1979; Ruckmick et al., 1979), i.e.,

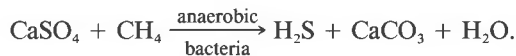


TABLE 1. Chemical analyses of hydrous sulfate aggregates from Katakolo area, western Peloponnese, Greece

Sam- ple	$\text{SO}_4^{2-}$	$\text{H}_2\text{O}$	Fe	Al	Ca	Mg	K	Na	Cl	Mn	Sr	B*	Cu*	Ni*	Co*	Zn*
Ka <sub>ewg</sub>	42.40	40.93	4.10	4.92	3.90	1.10	0.42	1.32	0.44	0.18	0.12	1759	37	810	300	600
Ka <sub>sw</sub>	45.80	37.96	2.90	3.57	5.62	1.29	0.31	1.10	0.36	0.12	0.18	1353	22	650	280	380

Note:  $\text{NO}_3^-$  and Pb were analyzed for but not found.

\* Values in ppm; other values in wt%.

In summary, the major factors that control the occurrence of native S and hydrous sulfates at the Katakolo mud volcano are the presence of H<sub>2</sub>S in the gas emanations from the volcano, the presence of carbonates, clays, and iron oxides and hydroxides in the parent rocks, and the high humidity of the mud-volcano microenvironment.

#### ACKNOWLEDGMENTS

We wish to thank R. C. Rouse and an anonymous referee for their helpful comments on the manuscript of this paper.

#### REFERENCES

- Aliyev, A.G., Aliyeva, G.A., and Osika, D.G. (1966) Distribution of I<sub>2</sub>, Br<sub>2</sub>, NH<sub>4</sub> and B in rock solutions and stratal water of oil deposits in north Dagestan. *Geochemistry International*, 3, 1194–1197.
- Baltatzis, E.G., Stamatakis, M.G., and Kyriakopoulos, K.G. (1986) Rozenite and melanterite in lignitic layers from the Voras mountain, western Macedonia, Greece. *Mineralogical Magazine*, 50, 737–738.
- Barker, J.M., Cochran, D.E., and Semrad, R. (1979) Economic geology of the Mishraq native sulfur deposit, northern Iraq. *Economic Geology*, 74, 484–495.
- Berner, R.A. (1971) *Principles of chemical sedimentology*. McGraw-Hill, New York.
- Braitsch, O. (1971) Salt deposits. Their origin and composition. Springer-Verlag, New York.
- Christodoulou, G. (1970) About the age of Kastro limestones, NW Peloponnesus, Greece. *Greek Geological Society Publication*, 7, 121–136 (in Greek).
- de Loczy, L. (1955) The petroleum-bearing sedimentary basins of Greece. *Proceedings of the Fourth World Petroleum Congress, Rome*, 1, A/2, 148–149.
- Diarov, M. (1966) Boron distribution in potash salts. *Geochemistry International*, 3, 454–459.
- (1967) Behavior of boron during formation of salt deposits. *Geochemistry International*, 4, 159–164.
- Ehlers, E.G., and Stiles, D.V. (1965) Melanterite-rozenite equilibria. *American Mineralogist*, 50, 1454–1461.
- Good, R. (1971) Melanterite-rozenite-pyrrhotite occurrence in Carroll County, Virginia. *Virginia Minerals*, 17, 10.
- Gruner, D., and Hood, W.C. (1971) Three iron sulfate minerals from coal mines refuse dumps in Perry County, Illinois. *Illinois State Academy of Science Transactions*, 64, 156–168.
- Gulyayeva, L.A., Kaplun, V.B., and Shishenina, E.P. (1969) The distribution of boron among the components of petroleum. *Geochemistry International*, 3, 636–641.
- Harder, H. (1959) Contribution to the geochemistry of boron: II. Boron in sediments. In C.T. Walker, Ed., *Geochemistry of boron*, 83–104. Halsted Press, Pennsylvania.
- (1974) Boron. In *Handbook of geochemistry*, no. 5, B1–O3. Springer-Verlag, Berlin.
- Jensen, M.L., and Bateman, A.M. (1979) *Economic mineral deposits*, third edition. Wiley, New York.
- Konofagos, E., and Komitopoulos, N. (1986) New offshore development techniques for marginal oil fields and the Katakolo discovery in the Greek Ionian sea. *Mineral Wealth*, no. 42, 49–62.
- Kravtsov, E.D. (1971) Minerals from the permafrost oxidation zone of the D'yakhtardakh deposit (Abs.). *Zapiski Vsesoyuznogo Mineralogicheskogo Obshchestva*, 100, 282–290.
- Marcopoulos, Th.N., Stamatakis, M.G., and Marandos, J.A. (1986) Minerals neof ormation in Nisyros volcanic emanation field (Abs.). Third Congress of the Geological Society of Greece, Athens.
- Oborin, A.A., and Zalkind, I.E. (1964) Geochemistry of boron in supergene process. *Geochemistry International*, 1, 63–72.
- Rittenhouse, G., Fulton, R.G., Grabowski, R.J., and Bernard, J.L. (1969) Minor elements in oil-field waters. *Chemical Geology*, 4, 189–209.
- Ruckmick, J.C., Wimberly, B.H., and Edwards, A.F. (1979) Classification and genesis of biogenic sulfur deposits. *Economic Geology*, 74, 469–474.
- Sclar, C.B. (1961) Decomposition of pyritized carbonaceous shales to halotrichite and melanterite. *American Mineralogist*, 46, 754–756.
- Velinov, I., Aslanyan, S., Punev, L., and Velinova, M. (1970) Ferrosulfates, halotrichite and alunogen from the oxidized zone of the hydrothermally altered volcanic rocks, near the village of Krusha, district of Sofia. *Bulletin of the Geological Institute, Bulgarian Academy of Sciences, Series Geochemistry, Mineralogy and Petrography*, 19, 243–264.
- White, D.E. (1957) Magmatic, connate and metamorphic waters. *Geological Society of America Bulletin*, 68, 1959–1982.
- Wiggins, L.H., and Howe, K.C. (1967) Mineralogy of the old pyrite mine near Proffit, Albemarle County, Virginia. *Virginia Journal of Science*, 18, 189.
- Zeissink, H.E. (1969) The mineralogy and geochemistry of a nickeliferous laterite profile (Greenvale, Queensland, Australia). *Mineralium Deposita*, 4, 132–152.
- Zodrow, E.L., and McCandlish, K. (1978) Hydrated sulfates in the Sydney coalfield, Cape Breton, Nova Scotia. *Canadian Mineralogist*, 16, 17–22.
- Zodrow, E.L., Wiltshire, J., and McCandlish, K. (1979) Hydrated sulfates in the Sydney coal field of Cape Breton, Nova Scotia. II. Pyrite and its alteration products. *Canadian Mineralogist*, 17, 63–70.

MANUSCRIPT RECEIVED OCTOBER 3, 1986

MANUSCRIPT ACCEPTED MARCH 23, 1987