

LOW-TEMPERATURE ALTERATION OF THE EXTRUSIVE SEQUENCE, TROODOS OPHIOLITE, CYPRUS

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ABSTRACT

The lavas of the Troodos ophiolite have been altered primarily by low-temperature interaction with seawater and by localized hydrothermal upwelling. An uppermost zone of highly oxidized lavas that contain abundant calcite and smectite is believed to be due to seafloor weathering. In a few sections, where thick layers of umber overlie the volcanic pile, the oxidized zone is absent, suggesting that the crust was sealed off from circulating seawater. Below the oxidized zone, the rocks are less pervasively altered and locally contain fresh glass. Assemblages of analcime, natrolite, phillipsite, chabazite and gmelinite are common in the pillow lavas of this sequence whereas assemblages of clinoptilolite, mordenite and celadonite are primarily associated with the massive flows. A basal sequence of more siliceous lava has abundant secondary silica. Alteration in these zones is believed to reflect seawater-rock interaction during or shortly after crustal accretion. Outside the very localized zones of hydrothermal alteration, the Troodos lavas have not been pervasively metamorphosed, and below the upper oxidized zone there are no systematic variations in the intensity or character of alteration with depth. The observed assemblages of secondary minerals can be explained by local variations in permeability, type of cooling unit, temperature, water/rock ratio and initial lava composition.

Keywords: alteration, low-temperature, Troodos ophiolite, Cyprus, ocean crust, permeability, clays, zeolites, oxidation.

SOMMAIRE

Les laves du massif ophiolitique de Troodos ont principalement été altérées par un échange avec de l'eau de mer à basse température et, localement, par jaillissement de fluides hydrothermaux. Une zone supérieure de coulées fortement oxydées, enrichies en calcite et smectite, représenterait une zone de lessivage marin. Où d'épaisses couches d'umbre recouvrent l'empilement volcanique dans quelques sections, la zone oxydée est absente, ce qui indiquerait que la croûte était isolée de l'eau de mer en circulation. En dessous de la zone oxydée, les roches sont moins complètement altérées et contiennent même, ici et là, du verre frais. Des assemblages à analcime, natrolite, phillipsite, chabazite et gmelinite sont courants dans les laves à coussins de cette séquence, et les assemblages à clinoptilolite, mordenite et céladonite sont surtout associés aux coulées massives. Une séquence inférieure de lave plus siliceuse contient beaucoup de silice secondaire. L'altération de ces zones refléterait l'interaction des roches avec de l'eau de mer pendant ou

tôt après la formation de la croûte océanique. En dehors des zones très localisées d'altération hydrothermale, les laves du Troodos n'ont pas été sujettes à un métamorphisme répandu; d'ailleurs, en dessous de la zone supérieure oxydée, on ne trouve aucune variation systématique dans l'intensité ou le caractère de l'altération avec la profondeur. Les assemblages de minéraux secondaires dépendraient des variations locales en perméabilité, type d'unité de refroidissement, température, rapport volumique eau/solide et composition initiale de la lave.

(Traduit par la Rédaction)

Mots-clés: altération, basse température, massif ophiolitique de Troodos, Chypre, croûte océanique, perméabilité, argiles, zéolites, oxydation.

INTRODUCTION

Previous studies, summarized in Honnorez (1981), have shown that alteration in the upper oceanic crust is largely the result of seawater-basalt interaction. The distribution and paragenesis of secondary minerals have been shown to depend upon such factors as lithology, fluid composition, temperature and age (Alt *et al.* 1985, Staudigel *et al.* 1981, Natland & Mahoney 1978). The shallow depth of most Deep Sea Drilling Project holes and the restricted lateral control over each site have limited our understanding of the process of seawater penetration into the crust and the extent of hydrothermal circulation and metamorphism at depth.

Ophiolites provide an alternative for studying *in situ* oceanic crust. Unfortunately, the transportation and emplacement history of many ophiolites have made it difficult to study their original pattern of alteration. Previous students of the Troodos ophiolite concluded that the extrusive sequence had been metamorphosed, resulting in the development of two distinct facies interpreted in terms of axis and off-axis volcanism (Gass & Smewing 1973, Smewing *et al.* 1975). In this paper, we show that the extrusive rocks of the Troodos ophiolite have undergone the same type of low-temperature alteration as that observed in the modern oceanic crust; also, we discuss the physical conditions that control the distribution and paragenesis of the secondary minerals. A more detailed study of the physicochemical conditions active during the different stages of alteration is still underway.

Recent studies of the Troodos Massif of Cyprus have confirmed that it is a fragment of oceanic lithosphere, as suggested by Moores & Vine (1971), although it is now believed to have originated in a subduction-zone environment rather than at a mid-ocean ridge (Moores *et al.* 1984, Robinson *et al.* 1983, Schmincke *et al.*-1983, McCulloch & Cameron 1983). The excellent exposure and relatively undeformed nature of this complex provide a unique opportunity to study the processes of alteration through a complete section of oceanic lithosphere.

Early workers divided the extrusive sequence into the Upper Pillow Lavas (UPL) and Lower Pillow Lavas (LPL) on the basis of color, abundance of olivine phenocrysts, assemblages of secondary minerals and the location of the sulfide orebodies (Bear 1960, Gass 1960). Gass & Smewing (1973) divided the sequence into an axis sequence, consisting of the Lower Pillow Lavas and the Sheeted Dykes, and a younger, off-axis sequence, represented by the Upper Pillow Lavas, based on a supposed metamorphic boundary within the complex.

Robinson *et al.* (1983) have outlined two geochemical suites for the northern flank of the Troodos ophiolite on the basis of glass compositions: 1) a lower andesite - dacite - rhyodacite assemblage of arc tholeiite affinity and 2) an upper picritic basalt - andesitic basalt assemblage with a depleted arc tholeiite affinity. The stratigraphic level of this new geochemical boundary is variable within the extrusive sequence in relation to the old UPL/LPL boundary (Fig. 1). A third suite of highly depleted basalts having "boninitic" affinities has been recognized on the southern flank of Troodos (J.M. Mehegan, pers. comm. 1984).

Detailed studies of stratigraphically controlled sections between the villages of Malounda and Margi (Fig. 2) have shown that the extrusive sequence has not been pervasively metamorphosed. Fresh volcanic glass is preserved sporadically throughout the extrusive sequence, extending downward to the top of the Basal Group (90% sheeted dykes). Furthermore, the distribution of the secondary minerals within the extrusive sequence indicates that there is neither a sys-

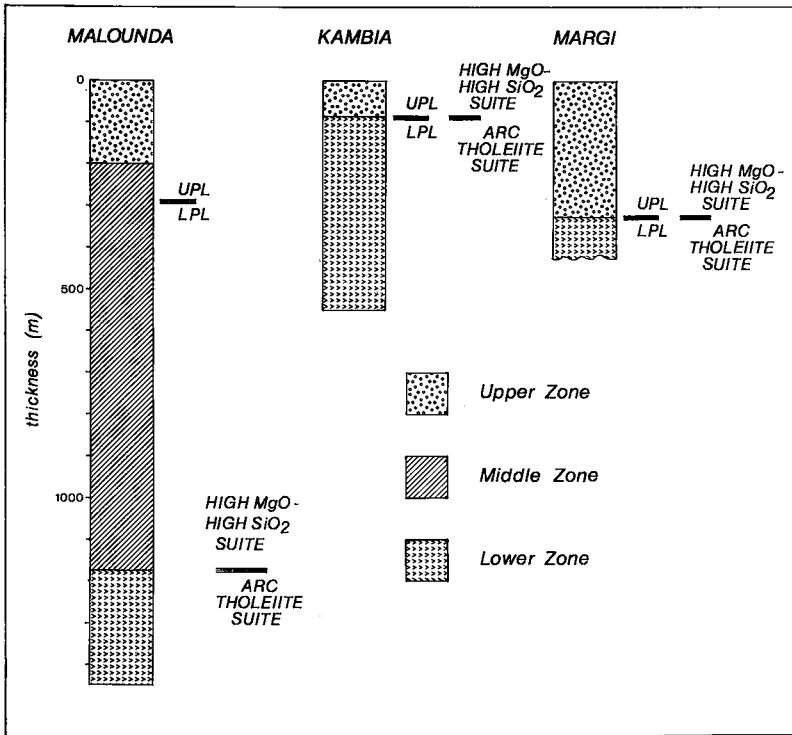


FIG. 1. Schematic representation of the geology of the study areas, outlining the stratigraphic position of the old Upper Pillow Lava/Lower Pillow Lava boundary and the new geochemical suites. Upper zone: aphyric to olivine-phyric basalts and picrites; middle zone: aphyric to slightly olivine-clinopyroxene-phyric basalt to andesitic basalt; lower zone: aphyric to slightly clinopyroxene-plagioclase-phyric andesites - dacites - rhyodacites.

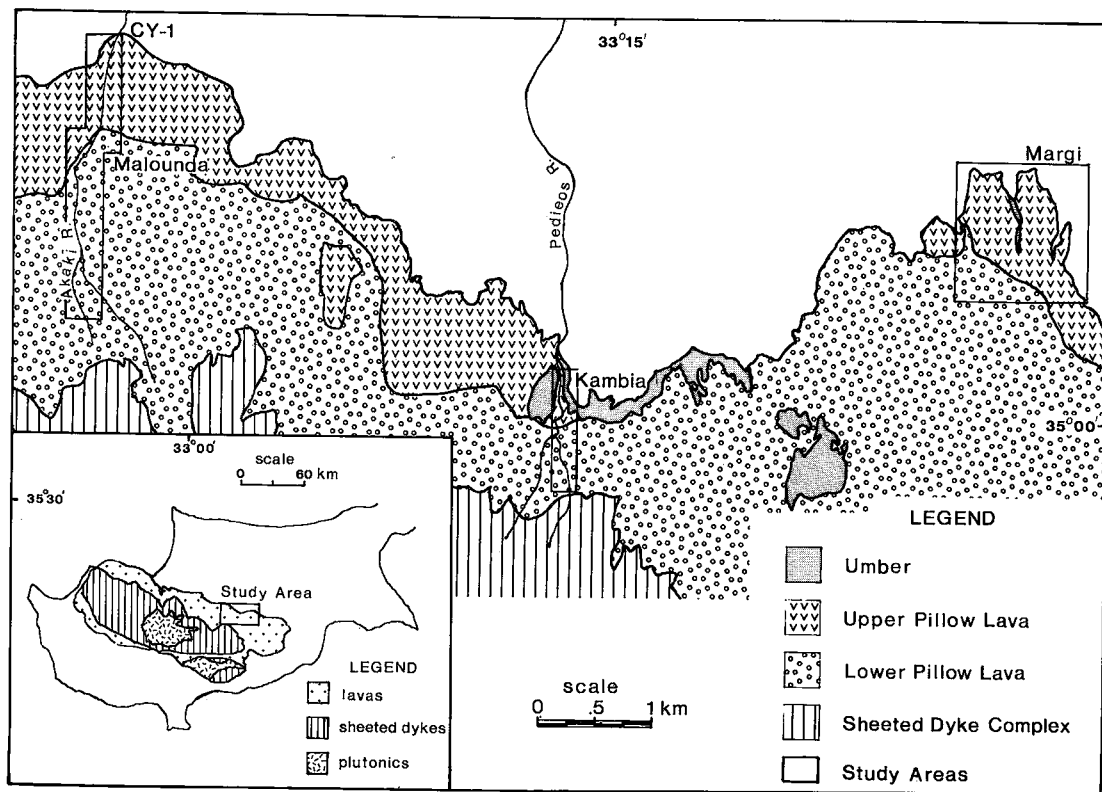


FIG. 2. Geological map of the northeastern portion of the extrusive sequence. The Malounda, Kambia and Margi study areas are outlined. Note that the old Upper Pillow Lava/Lower Pillow Lava boundary is shown. For a comparison of this old boundary with the new geochemical boundary for each study area, see Figure 1.

tematic increase in the intensity of alteration with depth nor a metamorphic boundary within the lavas. Localized zones of high-temperature hydrothermal alteration underlie the massive-sulfide orebodies [International Crustal Research Drilling Group (ICRDG) 1984], but these are spatially restricted and have little overall effect on the lavas. The presence of an oxidized zone in the upper 20 – 200 m of the extrusive sequence and the relationships among the assemblages of secondary minerals, type of cooling unit and host lithology both suggest that alteration was largely due to circulation of low-temperature seawater during and after crustal accretion. Regional reconnaissance has shown that the study area is representative of the alteration in the northern flank of the complex.

REGIONAL GEOLOGY

Recent studies of the lavas on the northern flank of Troodos have shown that the extrusive sequence is composed of numerous lithologic units, ranging from 50 to 200 m in thickness, that are defined on

the basis of color, type of cooling unit and mineralogy (Mehegan & Robinson 1984, Schmincke *et al.* 1983). These units have been grouped into three major stratigraphic sequences referred to as the upper, middle and lower zones. Although the same general sequence is found throughout the area, these zones vary greatly in thickness, lithology and lateral extent.

The basal 500 – 600 m of the extrusive sequence contains aphyric to sparsely clinopyroxene- and plagioclase-phyric massive and sheet flows, pillow lavas and hyaloclastites of andesitic to dacitic composition that comprise the arc tholeiite suite of Robinson *et al.* (1983). Dykes are present throughout this zone and increase in abundance toward its base. This lower zone is overlain by approximately 500 m of green to greyish green pillow lavas and massive flows locally separated by thin layers of hyaloclastite. These aphyric to slightly olivine- and clinopyroxene-phyric units have a basalt to basaltic andesite composition and belong to the high MgO – high SiO₂ suite of Robinson *et al.* (1983). Dykes, sills and coarse-grained basaltic to doleritic bodies

TABLE 1. SELECTED ELECTRON-PROBE DATA ON COMPOSITIONS OF CLAY MINERALS

	celada	celadb	smec ^a	smecd	smec ^e	smec ^f	smec ^g	smec ^h
SiO ₂	45.89	54.22	43.06	47.88	45.42	37.49	38.74	45.61
Al ₂ O ₃	2.76	5.07	11.05	8.52	7.15	9.99	11.52	12.45
FeO*	22.31	15.91	13.85	9.39	7.97	28.78	12.05	1.11
MnO	0.04	-	-	0.24	-	0.06	-	-
MgO	5.15	7.10	16.68	18.26	21.20	7.94	20.26	23.87
CaO	0.63	0.36	0.72	0.97	0.90	2.38	1.95	2.16
Na ₂ O	-	-	-	-	-	0.66	-	-
K ₂ O	5.57	9.08	3.08	2.06	-	-	-	-
Cr ₂ O ₃	0.06	-	-	-	-	-	-	-
Total	82.39	91.74	88.51	87.10	82.64	87.30	84.58	85.20
Cation Proportions on the basis of 20 O								
Si	7.21	7.35	5.94	6.46	6.37	5.69	5.53	6.00
Al	0.51	0.81	1.80	1.35	1.18	1.79	1.94	1.93
Fe	2.93	1.80	1.60	1.06	0.93	3.65	1.44	0.12
Mn	-	-	-	-	-	0.01	-	-
Mg	1.21	1.44	3.43	3.67	4.43	1.80	4.31	4.68
Ca	0.11	0.05	0.11	0.14	0.14	0.39	0.30	0.30
Na	-	-	-	-	-	0.19	-	-
K	1.12	1.57	0.54	0.35	-	-	-	-

* Total iron expressed as FeO; - not detected.

a, b groundmass celadonite (KG:82:303, KG:82:389); c yellowish green groundmass smectite (KG:82:108); d yellowish green groundmass smectite, middle of c (KG:82:108); e orange-brown groundmass smectite, centre of c (KG:82:108); f orange-brown smectite, vesicle lining (KG:82:522); g, h orange-brown smectite in olivine phenocryst (KG:82:008).

are present at this level, but are less abundant than in the underlying sequence. The upper zone at the top of the section is approximately 20 to 300 m thick and consists of aphyric to olivine-phyric pillow basalts and picrites that are also part of the high MgO - high

SiO₂ suite. Intrusive bodies are absent at this stratigraphic level.

METHODS

Samples representing the different assemblages of

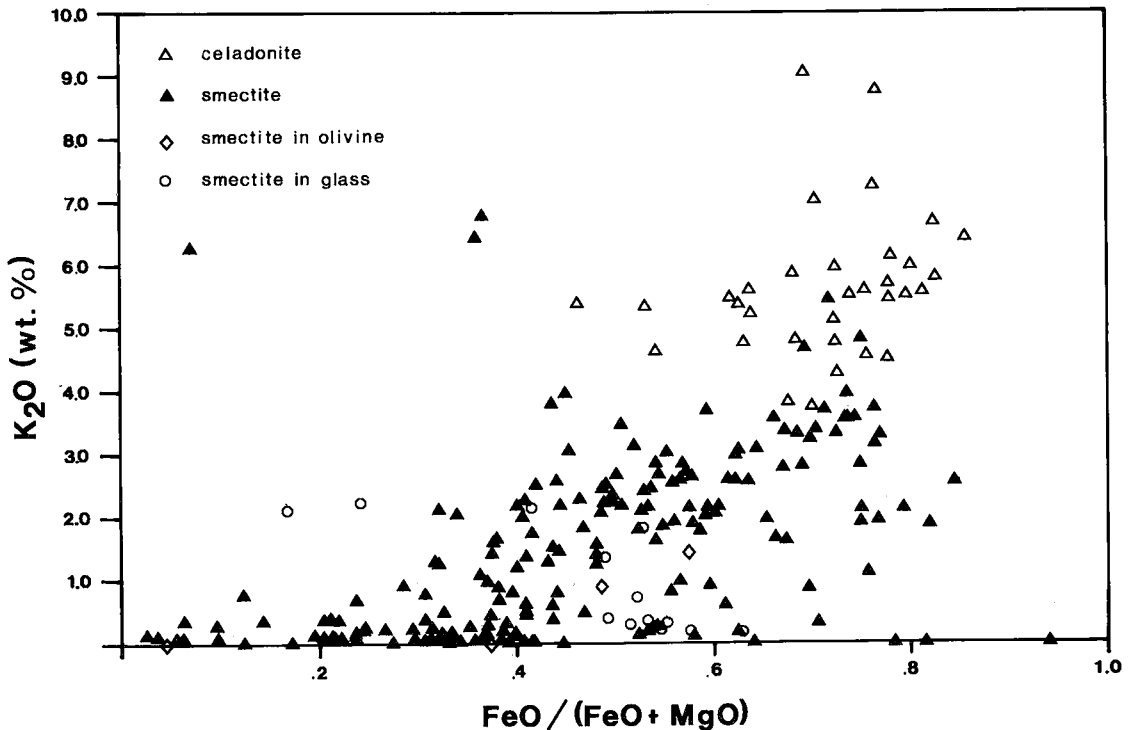


FIG. 3. Composition of clay minerals: wt. % K₂O versus FeO/(FeO+MgO).

secondary minerals and intensities of alteration were collected from stratigraphically controlled sections, chiefly within the Akaki River canyon near Malounda, the Pediaeos River canyon near Kambia and the Margi area. The stratigraphic relations in these areas were defined by Schmincke *et al.* (1983), J.M. Mehegan (pers. comm. 1984) and Bailey (1984), respectively.

Hand-picked secondary minerals were identified on a Philips X-ray diffractometer (CuK α radiation). Oriented smear-slides of clays were scanned from 2° to 40° 2 θ at 1° per minute. Representative samples of the different groups of clays were treated with ethylene glycol and rerun from 2° to 15°. The remaining secondary minerals were scanned from 4° to 60° 2 θ at 1° per minute.

The chemical analyses were obtained using electron-microprobe microanalyzers at Memorial University, St. John's, Newfoundland, the Smithsonian Institute, Washington, D.C. and Dalhousie University, Halifax, Nova Scotia. Mineral paragenesis was determined from the polished thin sections used for microprobe analysis.

SECONDARY MINERALS

The assemblages of secondary minerals consist of

TABLE 2. SELECTED ELECTRON-PROBE DATA ON COMPOSITION OF CARBONATES

	1	2	3
SiO ₂	0.06	0.07	0.01
Al ₂ O ₃	-	0.05	0.02
FeO*	1.16	-	-
MnO	3.14	0.07	0.06
MgO	0.82	0.57	0.56
CaO	56.36	57.39	61.93
Na ₂ O	0.02	0.03	0.03
K ₂ O	0.01	0.02	-
Total	63.11	58.32	62.63

* Total iron expressed as FeO, - not detected.

1 fracture filling calcite, XG82-153

2 groundmass calcite, CY-1:72.75 m

3 calcite in vesicle, CY-1:72.75 m

clay minerals, zeolites, silica, carbonates and iron oxides.

Clay minerals

Clay minerals, by far the most abundant of the secondary phases in the volcanic pile, replace the primary minerals and groundmass material and line or fill vesicles, vugs and veins.

Smectite, the most widespread clay mineral, was identified by its broad basal peak at 16 Å and the subsequent shift to 18 Å upon treatment with ethy-

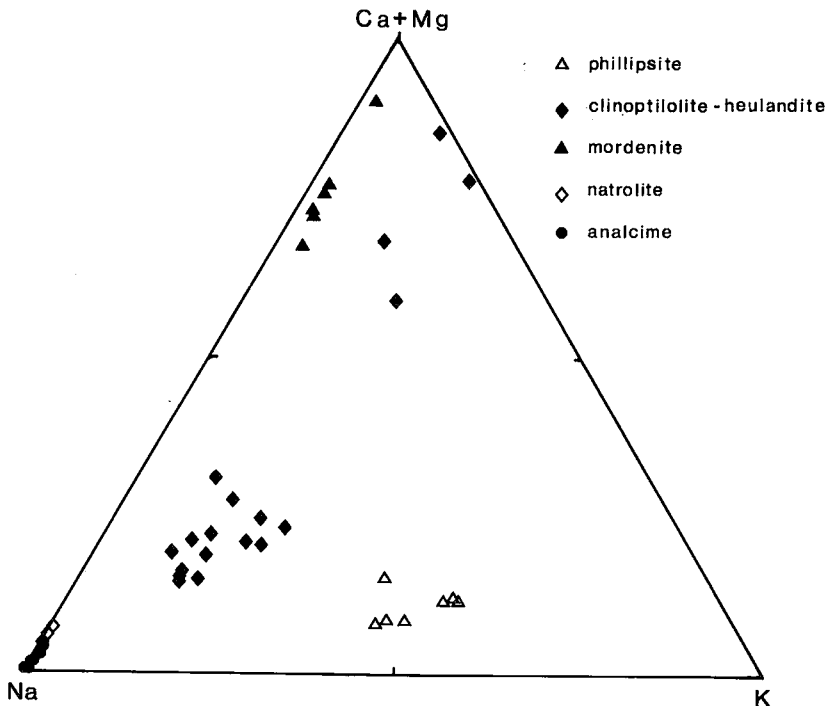


FIG. 4. Triangular plot of the proportion of alkalis [Na - (Ca + Mg) - K] in the zeolites. Data are from samples from the Akaki River section.

lene glycol. Several varieties of smectite have been distinguished on the basis of habit, color and composition. The composition ranges from Mg-rich to Fe-rich with varying K content (Table 1, Fig. 3). Orange-brown to brown smectite is generally Mg-rich, whereas yellowish green smectite is Fe-rich, although some brown varieties in the groundmass are Fe-rich and form oxidized halos around vesicles. Orange-brown, Mg-rich smectite, Fe hydroxides and calcite replace olivine in the upper part of the section. In the middle and lower zones a similar smectite partly replaces plagioclase. Smectite that replaces primary minerals is very finely crystalline, whereas that filling voids is usually fibrous to platy and radiates out from the wall of the cavity. Smectite that replaces groundmass material may be fibrous, radiating, massive or globular.

Celadonite, identified by its basal peak at 10 Å and its distinctive bluish green color, replaces interstitial groundmass-material and partially fills voids, where it occurs as a fibrous, late-stage alteration product. Chemically, celadonite is distinguished from smectite on the basis of FeO/(FeO + MgO) and K₂O content (Fig. 3, Table 1). The general paragenetic sequence of these clay minerals is: Mg-rich, K-poor smectite → Fe-rich smectite with variable K content → celadonite.

Palygorskite was recognized on the basis of the 10.4, 6.4, and 4.5 Å peaks, which remain unchanged upon glycolation and heating (*cf.* Natland & Mahoney 1978). This papyraceous to fibrous mineral is restricted to late-stage, vertical veins in the upper 500 m of the sequence, where it is commonly associated with calcite.

TABLE 3. SELECTED ELECTRON-PROBE DATA ON COMPOSITION OF ZEOLITES

	morda	clinb	olinc	ana1d
SiO ₂	70.76	68.35	67.02	60.95
TiO ₂	0.03	-	-	-
Al ₂ O ₃	10.89	12.58	11.77	23.29
FeO	0.19	-	0.12	-
MnO	0.05	-	-	-
MgO	0.06	-	0.13	-
CaO	3.40	3.46	1.73	-
Na ₂ O	0.96	1.17	5.12	11.68
K ₂ O	0.09	1.04	1.00	0.02
Total	86.48	86.60	86.93	95.97
Cation Proportions				
Si	20.49	29.93	29.63	2.45
Al	3.72	6.49	6.14	1.10
Fe	0.05	-	0.04	-
Mn	0.01	-	-	-
Mg	0.03	-	0.09	-
Ca	1.06	1.62	0.82	-
Na	0.54	0.99	4.40	0.91
K	0.03	0.58	0.56	-
O	48.00	72.00	72.00	7.00

* Total iron expressed as FeO; - not detected.

a mordenite in vesicle of massive flow (KG:82:497); b, c clinoptilolite-heulandite (KG:82:466); d analcime (KG:82:076).

Carbonates

Carbonates are pervasive throughout the upper zone of the extrusive sequence and are locally abundant in the middle and lower zones. Calcite forms irregular patches and stringers in the groundmass of most lithologic units. It is relatively pure, but may contain minor amounts (< 1%) of Si, Mg, Fe, Na and K. A few crystals in narrow, cross-cutting veins have up to 3% Mn (Table 2). Assemblages of calcite, smectite and Fe hydroxides replace olivine phenocrysts in the basalts of the upper zone. Iron-stained, drusy and botryoidal calcite commonly fills cavities in these rocks. Many veins have undergone several stages of calcite growth, as indicated by successive layers of euhedral crystals that are commonly mantled by smectite or celadonite (or both).

Aragonite was identified in one occurrence near the base of the sequence.

Zeolites

Zeolites form distinctive assemblages with other secondary minerals throughout the extrusive sequence. They have been identified petrographically, on the basis of their XRD pattern and on the basis of their Ca, Na and K contents (Fig. 4, Table 3).

Clear, well-formed crystals of analcime, accompanied by sparse, radiating aggregates of pink phillipsite, commonly line fractures and pillow margins, line veins and locally replace groundmass material of both massive flows and pillows. Phillipsite, an alteration product of fresh glass, is the earliest of these two phases. Radiating prisms of natrolite, commonly associated with analcime, occur chiefly in vesicles and vugs. Hexagonal clusters of pinkish orange gmelinite, commonly associated with chabazite, are locally abundant in the upper pillowed units.

Yellowish green rosettes of clinoptilolite line the edges of veins and fracture surfaces in massive and sheet flows and commonly occur as alteration products of fresh glass in hyaloclastite-rich zones. Fibrous mordenite is typically associated with clinoptilolite in vesicles and along pillow margins. Clinoptilolite is distinguished from heulandite by its Al/Si ratio (Mumpton 1960) and by the constancy of the 020 peak upon heating (Boles 1972). Trace amounts of a more calcic phase of this mineral, which may be heulandite, are present in a few carbonate veins (Fig. 4, Table 3).

White to pink, prismatic laumontite fills vesicles of some pillows cut by dykes at the base of the lower zone.

Silica

Secondary jasper, chalcedony, opal-C, opal-CT and clear colorless quartz form chiefly in the voids

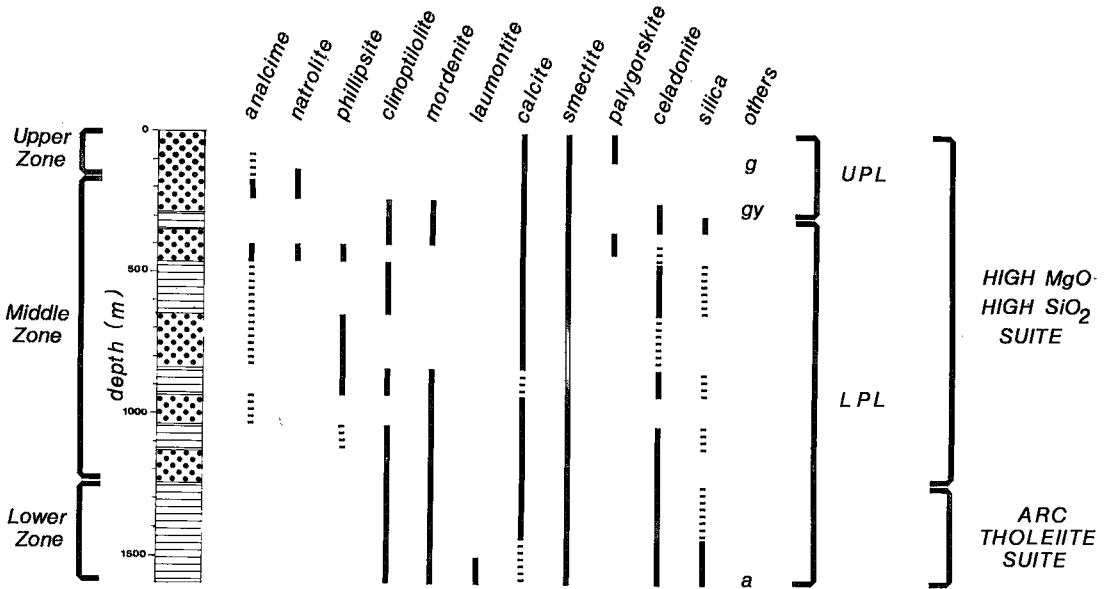


FIG. 5. Distribution of secondary minerals in the Akaki River section. Depth refers to the stratigraphic thickness of the sequence. The small circles represent dominantly pillowed units, and the horizontal lines represent dominantly massive flow-units. The shaded area shows the limit of the oxidized zone in this region. Solid lines indicate that the secondary phase is found throughout the unit, and dashed lines indicate that the secondary phase is locally present. Upper, middle and lower zones refer to the lithologic groupings outlined in the text. UPL/LPL indicates the old boundary outlined by Gass (1960) and others, and the high MgO - high SiO₂ suite/arc tholeiite suite indicates the position of the new geochemical boundary outlined by Robinson *et al.* (1983). Others: g gmelinite, gy gypsum, a aragonite.

of massive flows and dykes. Chalcedony is commonly associated with celadonite in zones of relatively intense alteration within the massive flows. Clear, colorless chalcedony and quartz fill vesicles, vugs and narrow veins, particularly in the lower andesite - dacite - rhyodacite suite. Minor amounts of chalcedony, however, are also present in the massive flows of the high MgO - high SiO₂ suite. Late-stage, fine-grained chalcedony typically occurs in calcite veins throughout the entire extrusive sequence. White to bluish opal-C and opal-CT (classification after Jones & Segnit 1971) form very thin layers on fracture and cooling-joint surfaces in massive and sheet flows.

ALTERATION PATTERNS AND THE DISTRIBUTION OF SECONDARY MINERALS

The distribution of secondary minerals in the extrusive sequence along the Akaki River near Malounda is summarized in Figure 5. Note that different mineral assemblages are common to different types of cooling units and to different stratigraphic zones. The pattern of low-temperature alteration in the Akaki River section and adjacent areas is discussed

below in terms of the three major stratigraphic sequences.

Upper zone

Two styles of alteration characterize the upper 20 - 200 m of the extrusive sequence. Along most of the northern flank of Troodos, the uppermost pillows are green to reddish green in color, highly oxidized and leached. The thick pillow-margins are altered to smectite with minor zeolite and calcite, and some calcareous sediment occurs in interpillow voids. Olivine phenocrysts have been completely replaced by orange-brown smectite, Fe oxides and calcite, and the groundmass material is altered to calcite and yellowish green to orange-brown smectite. Vesicles, veins and fractures are filled with assemblages of smectite, carbonate, zeolites and traces of K-feldspar. Many vesicles have oxidized halos containing radiating to globular masses of orange-brown smectite with minor calcite and yellowish green smectite. The entire oxidized unit is cross-cut by late, vertical veins of palygorskite and calcite.

In the Kambia-Margi area, where the extrusive sequence is overlain by relatively thick layers of amber (Fe-Mn sediment), the upper oxidized zone is ab-

sent. Pillows in the upper 2–5 m of the section have grey, highly altered interiors, but fresh glassy rinds are typically preserved. Interpillow spaces contain umberiferous sediment, with minor calcite and smectite. Olivine phenocrysts are completely altered to orange-brown smectite and calcite, and the groundmass is replaced by yellowish green smectite and traces of orange-brown smectite. Vesicles are generally open but lined with clay minerals. Below this level, pillow interiors and breccias are fresher in appearance than those at the top of the sequence, but fresh glass is less abundant. Vesicles are lined with clay minerals and partly filled with calcite and zeolite, and pillow rims are generally altered to smectite. Interpillow spaces are filled with smectite and calcite, with minor umberiferous sediment and zeolites. Where present, olivine phenocrysts are commonly fresh, but may be replaced by orange-brown smectite and calcite. Clinopyroxene is generally fractured and partly altered to colorless or pale green smectite. Interstitial pale brown to orange-brown smectite commonly replaces the groundmass.

Middle zone

The degree of alteration in the aphyric to sparse-olivine- and clinopyroxene-phyric pillow lavas and massive flows of the middle zone is highly variable between, and within, the individual lithologic units. Because the pillows and massive flows have distinct assemblages of zeolites, clays and carbonates, the alteration is discussed for each type of cooling unit.

The *pillow lavas* in the middle zone are greyish green to greyish brown in color. Radial fractures in the pillows are commonly coated with assemblages of smectite, calcite, analcime, natrolite, phillipsite, gmelinite and chabazite in decreasing abundance. Similar assemblages replace glassy pillow-margins, and single zeolite phases, with or without calcite, commonly fill clay-lined vesicles and vugs. Adjacent to massive flows and intrusive bodies, celadonite and rare clinoptilolite may occur on fracture surfaces. Narrow, calcite veins locally cross-cut individual pillows. Late, subvertical, palygorskite – carbonate veins cross-cut or locally bend around the pillow margins in the upper portion of this zone.

Resistant vertical zones, composed of reddish grey basalt fragments and calcite, occur throughout this part of the sequence. These zones are 1–2 m wide and have an oxidation halo that extends into the surrounding rock up to a few metres. Schmincke *et al.* (1983) suggested that they represent syn- to postvolcanic fault-zones.

The primary minerals are relatively fresh in the pillows of this zone. Clinopyroxene phenocrysts may be Fe-stained and clay-rimmed, and plagioclase is commonly cloudy in appearance. Sparse olivine is commonly altered to orange-brown smectite, calcite

and Fe oxides. The groundmass is partly to completely altered to yellowish green and orange-brown smectite. Vesicles are typically rimmed by oxidation halos consisting of orange-brown smectite in a feathery to globular habit. Minor calcite, yellowish green smectite and celadonite are locally associated with these halos.

The degree of alteration within the *massive and sheet flows* is quite variable. Most flows are relatively fresh in appearance, with minor surficial staining of celadonite or hematite. Individual columns of some flows display concentric, clay-rich zones within the outer 1 to 3 cm. Assemblages of smectite, celadonite, calcite, clinoptilolite, mordenite and silica are restricted to flow margins, vesicles, vugs and joint surfaces and are locally concentrated in zones of intense alteration.

Vesicles and vugs are lined with clay minerals and partly filled with silica or calcite. Narrow, clay-lined calcite stringers are present in most units and locally contain assemblages of clinoptilolite, mordenite, silica and celadonite.

Most clinopyroxene and plagioclase phenocrysts are partly altered to smectite and celadonite, although those in the centres of flows are typically fresh. The groundmass alteration in the massive and sheet flows is similar to that in the pillow lavas.

Lower zone

The andesite – dacite – rhyodacite assemblage of the lower zone is composed chiefly of massive and sheet flows accompanied by minor pillow lavas and hyaloclastites. The patterns of alteration and the mineral assemblages in this sequence are similar to those described above for the middle zone. Near the base of this zone in the Malounda area, clear, secondary silica is abundant in vesicles, vugs and narrow, cross-cutting veins. Along the Pedieous River near Kambia, jasper commonly forms along flow tops and in discontinuous, cross-cutting veins. Relatively fresh hyaloclastite layers are abundant in both areas.

Dykes rapidly increase in abundance toward the base of this zone, and the lavas become harder and lighter in color. Minor laumontite and trace aragonite have been identified in vesicles within pillows between the dykes.

DISCUSSION

The assemblages of secondary minerals and their distribution indicate a complex and locally variable history of alteration for the Troodos lavas. However, from this study it has been possible to gain some insight into the styles, controls and timing of the alteration processes in this fragment of oceanic crust. Four types of alteration reported from studies of the oceanic crust have been recognized in the Troodos

lavas: deuteric, hydrothermal, low-temperature interaction of seawater with newly accreted crust, and seafloor weathering.

All alteration that occurs during the cooling of the lava from the temperature of eruption to that of ambient seawater is ascribed to deuteric processes. However, the effects of such alteration are commonly difficult to distinguish from later seawater-rock interaction, as the deuteric minerals may be overprinted by later assemblages. High-temperature deuteric minerals have not been recognized, but we believe that some of the alteration in the centres of massive flows and thick pillows, particularly the formation of low-K, high-Mg smectite, may be ascribed to this process. However, plagioclase in these rocks is commonly replaced by K-feldspar, which suggests at least some penetration by seawater.

Relatively high-temperature, hydrothermal alteration, well known in the Troodos lavas, occurs in narrow stockwork zones and gossans and affects a very small part of the extrusive sequence. This type of alteration has been described previously (*cf.* Constantinou & Govett 1973) and will be discussed in more detail in a series of papers to be published in the ICRDG Initial Reports. Hence it is not covered here.

Most of the alteration observed in the Troodos extrusive sequence is believed to be due to seawater-rock interaction during or after crustal accretion. Distinctive mineral-assemblages formed by this process occur throughout the sequence. Pillow lavas have assemblages that include smectite, calcite, analcime, phillipsite, natrolite, gmelinite and chabazite, whereas massive flows typically contain smectite, calcite, celadonite, clinoptilolite, mordenite, opal-C, opal-CT, chalcedony and quartz. Although exceptions do occur, the constancy of these assemblages throughout the extrusive sequence suggests that the inherent physical properties of each type of cooling unit, particularly grain size and permeability, were important factors that controlled the distribution of the secondary phases.

Isotopic investigations have confirmed that the circulating fluid in the Troodos massif was seawater (Staudigel *et al.* 1984, Heaton & Sheppard 1977, Spooner *et al.* 1977). The zeolite and silica assemblages present in the extrusive sequence are stable at temperatures less than 150°C (Miyashiro & Shido 1970). Many of the zeolites in these assemblages are stable with smectite at temperatures less than 100°C in the geothermal fields of Iceland (Palmason *et al.* 1979). This indicates that low-temperature conditions were dominant during the alteration of the extrusive sequence. The occurrence of laumontite in pillow screens at the top of the Basal Group in the Malounda area indicates that higher temperatures prevailed in these rocks than in the extrusive sequence. Palmason *et al.* (1979) have assigned a temperature range of 100–200°C for the stability of

laumontite in Iceland. Experimental work by Liou (1971) suggests that laumontite is stable in the temperature range of 150–300°C.

The depositional history of the secondary minerals in the volcanic pile is complex and locally variable. The general paragenetic sequence is as follows: smectite → zeolites or celadonite → carbonate. It must be stressed that this order of deposition may be reversed, particularly the relationship between the zeolite and clay minerals, and that more than one cycle of this sequence is commonly present. Many variations in this pattern have been documented, suggesting that the physicochemical conditions changed with time. For example, the accessibility of water to the cooling units was not continuous. Glassy margins and hyaloclastites may be sealed off at an early stage of alteration, preventing exchange of cations between the seawater and basalt. Later, when the alteration is more advanced, these glassy zones break down very quickly, supplying a new source of cations to the system (Honnorez 1981).

Lateral and vertical variations in the intensity of alteration are common within individual stratigraphic units. For example, in units with an abundance of massive flows, the cooling surfaces of one flow may be intensely altered, whereas a few metres beneath it, the margins of flows are only slightly stained with celadonite. This suggests the presence of preferred paths of fluid migration within the extrusive sequence that are largely a function of permeability.

A much more comprehensive study on a regional scale is required to fully understand the role of permeability in bringing seawater to a depth greater than the base of the extrusive sequence. We know that seawater penetrates the Sheeted Dyke Complex and is eventually brought back up to the surface in zones of upwelling (ICRDG 1984, Spooner *et al.* 1977, Heaton & Sheppard 1977). It is not clear, however, if the downward migration of seawater evident in the extrusive sequence is sufficient to supply the zones of upwelling above which the orebodies formed. Other channelways, such as the boundaries between tectonic blocks, may serve as large-scale conduits for the downward flow of water.

The widespread red to reddish green, highly oxidized zone at the top of the extrusive sequence is believed to be the result of prolonged seafloor weathering. The assemblages of secondary minerals in this zone are similar to those recovered from the upper levels of the oceanic crust where similar processes have been invoked (*i.e.*, DSDP Site 417, Donnelly *et al.* 1980). This oxidized zone is absent only where synvolcanic umbers are relatively thick, as in the Kambia-Margi and Kalavassos areas. We suggest that the umbers that were deposited in topographic lows on the seafloor formed an early, impermeable layer that prevented seawater from percolating downward into the upper part of the lava pile. In areas where the umbers are absent, seawater

gained access to the lava pile until the crust was effectively sealed off by the deposition of pelagic sediments of Campanian age.

SUMMARY

Four types of alteration have been recognized in the lavas of the Troodos ophiolite: deuteric, hydrothermal, low-temperature seawater-basalt and seafloor weathering. Relatively high-temperature minerals typical of deuteric alteration have not been identified in the Troodos lavas, but low-K smectite may have formed by this process. Hydrothermal alteration in the lavas is restricted to narrow stockwork zones and is extensive in the Sheeted Dyke Complex. Most of the alteration in the Troodos lavas is the result of low-temperature seawater-basalt interaction during and after crustal accretion. The assemblages of secondary minerals and their distribution were controlled by such factors as: permeability, type of cooling unit, accessibility of water and composition of the host rock. The highly oxidized zone in the upper 20-200 m of the extrusive sequence indicates that there was a period of prolonged seafloor weathering prior to the deposition of the Campanian pelagic sediments. This oxidized zone is absent in areas where synvolcanic unmetamorphosed rock was sufficiently thick to limit the percolation of seawater into the upper portion of the volcanic pile.

The alteration patterns in the extrusive sequence indicate that there is no systematic increase in the degree of alteration with depth and that no consistent stratigraphic or metamorphic boundary can be drawn in the volcanic pile on the basis of distribution of secondary minerals.

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