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HYDROCHEMISTRY OF TRIFYLIA FLYSCH CONGLOMERATE SPRINGWATERS

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ABSTRACT

The fractured Trifylia flysch conglomerates, exhibit distinct double porosity features, through which the rainwater percolates and infiltrates. As a result eight major overflow springs appear at various elevations, due to faulting, from 0.30 up to 700 meters. Piper diagrams show a very good water quality of calcium bicarbonate type, slightly alkaline with low to moderate electrical conductivity values. The Ca/Mg ratios in the seven springs on the western slopes as well as in the only spring (Potamia) on the eastern slopes of the Aegaleon Mountains are very high indicating prevelance of limestone pebbles.

INTRODUCTION

Water samples from eight overflow springs (Plati, Potamia, Christiani, Mouzaki I, Mouzaki II, Chora, Koubes and Tyflomyti) in Trifylia flysch conglomerates of Aegaleon Mountain in southwestern Peloponnesus were taken and analysed chemically for the period 1981-1987. Their elevations range from 700 down to o.30 meters above mean sea level. Sampling was carried out by the Land Reclamation Survey of the Ministry of Agriculture in Kalamata twice a year during the period of 1981 to 1987. Chemical analysis was performed at the laboratories of the Ministry of Agriculture in Athens that included; Ca^{++}, Na^{+}, K^{+}, Mg^{++} cations, and Cl^{-}, $SO_4^{=}$, HCO_3^{-}, $CO_3^{=}$ anions, as well as pH and Electrical Conductivity measurements.

GEOLOGICAL SETTING

The flysch consists of a great thickness of mudstones, siltstones and sandstones in alternating beds, overlain by thick conglomerates. In general, much of the deposition of the flysch is attributed to turbidity currents presumably from uprising regions to the east (Pindus Zone) (B.P. 1971). The Trifylia conglomerates comprise the last stage of flysch sedimentation of the Tripolitsa zone. Their deposition took place in the form of olisthostroms (Mariolakos 1975) in a marine environment during the Oligocene epeirogenic movements in central Peloponnesus. They include a great percentage (up to 90%) of very well rounded pebbles and cobbles mainly of limestone, dolomite, and less sandstone and chert composition fed from the eastern mainland (Tripolitsa and Pindus zones). They are river deposits in a coastal area lacking the clay fraction which was washed way by the sea waves. Thus the cementing agent of these conglomerates is composed entirely of medium-coarse grained sand of predominantly $CaCO_3$ composition. The average rate of sedimentation of these 1000 meter thick Upper Oligocene conglomerates is in the order of one millimeter every five

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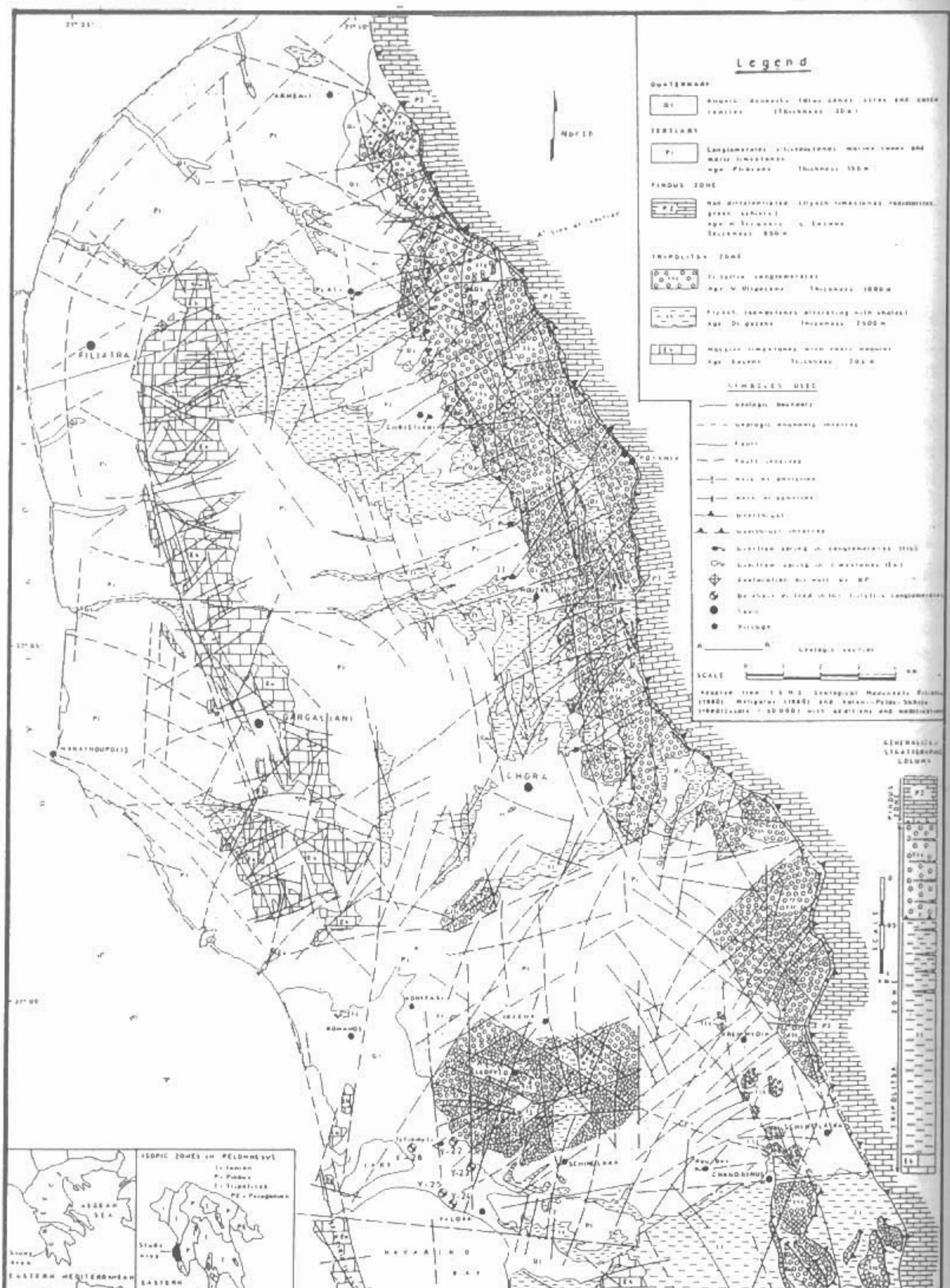
Fig. 1: Geologic map of Trifylia



years. Well sorted, lithologically homogenous conglomerates are typical of widespread basal deposits that mark transgressive seas (Krumbein and Sloss 1963). These flysch conglomeates belong to the "orthoconglomerates" of Pettijohn (1957) which are generally interpreted as originating from deposition under highly turbulant conditions, such as those prevailing in streams and along shores in the zone of breaking waves.

Eastern Trifylia is a region of highly active tectonism. The prevailing movements here are those of compression which cause the continuous vertical movements especially in the land strip between Kyparissia in the north, and Pylos in the south. The differential uplifting of this area by several blocks can be observed from the fault pattern of the Eocene Filiatra limestones, outcroping west of the flysch conglomerates, as well as from the surface hydrographic pattern (Tavitian et al 1993). The general direction of the fold axes in the limestones and the flysch rocks is NNW which is parallel to the major thrust nappes of the Pindus zone in the east of the Aegaleon Mountains. They are overthrusting the clay schists of the Tripolitsa flysch formation (Figure 1). The strong latteral compression of these clay schists and the consequent areal decrease resulted in the folding and fracturing of the mass of these conglomerates together with their uplift over the flysch clay schists. As a result they reach over 1200 meters elevation.

SURFACE HYDROLOGY AND WATER BUDGET

The total areal extent of the northern half of Aegaleon Mountain (mainly composed of flysch rocks) is 46 km^2 and its highest peak reaches 1250 meters. It has an elongated shape with is longer axis trending northwestwards. It is parallel to the main overthrust fault of the Pindus zone over the Tripolitsa zone, lying east of these mountains. The infiltration rate of these conglomerates is in the order of 21% (Kantas and Tiniakos 1988). On average, they receive through infiltration a total of $10x10^6$ m^3/yr of water which drains through the five springs on the western slopes and one spring on the eastern slopes of these mountains.

The southern half of the Aegaleon Mountains (highest peak Manglavas - elevation 720m) together with the Eleofyton Hills (elevation - 220m) has an area equal to 54 km^2 including the area around Kremmydia where the thin layer of calcarenites overly the underlying conglomerates (Kremmydia graben). The amount of water from precipitation received amounts to nearly $38x10^6$ m^3/yr. Out of this $7x10^6$ m^3/yr is partly infiltrated and discharged through the two southwestern major springs, Kubes and Tyflomyti (Figure 1) and partly lost as groundwater flow to the sea.

There are four streams originating from these conglomerates. From north to south they are: Filiatrino, Evangelistria, Langouvardos, and Arapis Poros. They all run in an east-west direction flowing into the Ionian Sea and discharge annually some $11x10^6$ m^3 of water to the sea whereas on average nearly $4x10^6$ m^3 of the runoff water infiltrates as natural recharge into their middle valley channels where these rivers flow through the Eocene Filiatra limestones, west of the flysch rocks (Tavitian et al 1993).

HYDROGEOLOGIC FRAMEWORK

The Aegaleon Mountain can be considered as an isolated hydrogeological unit by itself. It is separated from the limestones of the Pindus zone by the Tripolitsa zone's flysch (Figure 1). Thus it is not in hydrological contact with these limestones and hence it is not latterally recharged from the east (Pindus Zone). The mean annual precipitation of the Aegalen Mountains is in the order

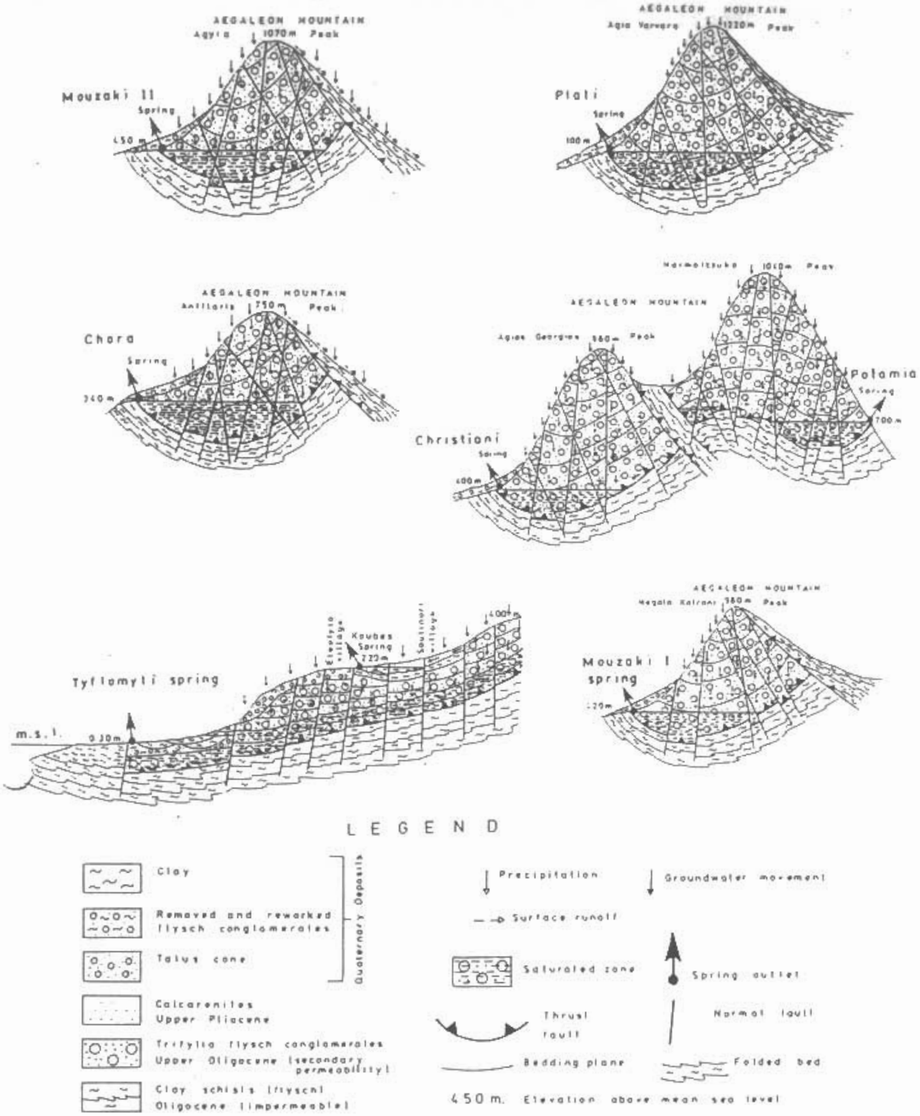


Fig. 2: Schematic east - west hydrogeologic sections across the recharge basin of each spring [not to scale].

of 1000 mm. The high percentage of the carbonate pebbles in connection with the dense network of the intersecting faults and joints facilitates the solution of these conglomerates by the infiltrating rainwater (Figure 2). The faulted and overthrusted conglomerate synclines on the clay schists form the basins in which rain and snow waters are collected and retained mainly in the secondary solution openings. The average hydraulic gradient of these conglomerates is 2.5% (Kantas and Tiniakos 1988).

The double porosity property of all these flysch conglomerates created both by their petrological composition (sandy matrix) and tectonic structure (large and small fractures) is best exhibited by their monthly hydrographs. The depletion graphs of six springs (Figure 3) are composed of two linear segments with different slopes. This property is due to two underground reservoirs draining through the same spring. Such a "two-reservoir model" is often encountered in fissured and karstic rocks where the (highly permeable) wide flow channels drain more quickly than the (less permeable) porous rock matrix (Mandel and Shiftan, 1981).

WATER QUALITY - LITHOLOGY RELATIONSHIP

The extent to which the composition of natural water can be related to the lithology of the area in which it occurs has been studied by many investigators. Ideally, half the carbonate dissolved in water associated with carbonate rocks comes from the rock, and the remainder from soil, air or other similar carbon dioxide sources (Hem, 1970). A general relationship between mineral composition of a natural water and that of the solid minerals with which the water has been in contact is certainly to be expected. This relationship may be comparatively simple and uncomplicated, as in the case of an aquifer receiving direct re-charge by rainfall and eventually from which water is discharged without con-tacting any other aquifer or other water, as in the case of the Trifylia con-glomerate springwaters.

The consolidated resistate sediments, such as these flysch conglomerates, contain cementing material deposited on the pebble surfaces and within the fracture openings and bedding planes. This cementing material is usually deposited from water that has passed through the rock at some past time and can be redissolved. The cementing material in this case deposited from water, is mainly calcium carbonate (in solution as well as in sand size particles) which is one of the most common cementing materials together with silica.

Clay minerals carried to the sea by streams have a given composition and contain certain absorbed ions inherited from the weatherinng site. During transportation some changes may occur in clay mineral composition, but the presence of dissolved salts in ocean waters may produce additional changes during and after deposition on the sea bottom. Common absorbed ions by clays include calcium-ion, sodium-ion and hydrogen-ion (Krumbein and Sloss 1963). Owing to their small particle size, clay minerals (hydrous aluminum silicates) have great surface activity, represented by ionic adsorption, cohesiveness, and other properties (Dunbar and Rodgers 1957). The presence of kaolinite and illite in green shales

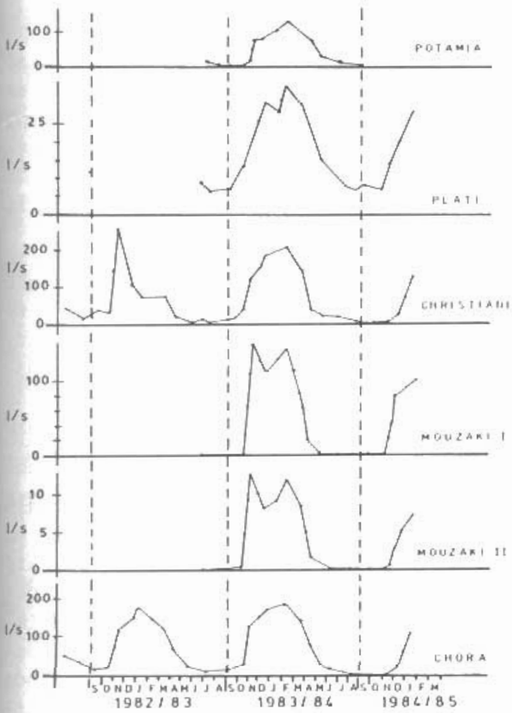


Fig. 3: Hydrographs of six overflow springs in the Trifylia flysch conglomerates. (adapted from Kantas & Tiniakos 1988).

of Albian age, in Lebanon, is mentioned by Tavitian (1993).

The most likely anion-exhange process in natural systems might seem to be the replacement of adsorbed OH^- , and there are sites on kaolinite particles where OH^- is available (Halevy, 1964). Such a source for kaolinite particles in the Aegaleon Mountain area, are probably the underlying green clay schists and shales of the flysch rocks. Ion exchange and membrane effects associated with clays could influence ground and surface water composition (Hem 1970). Hanshaw (1964) showed that when compacted, clays may preferentially adsorb sodium, but when dispersed in water, they may preferentially adsorb calcium. Groundwaters that are in direct contact with clay and shale beds are high in dissolved solids. Kister and Hardt (1961) observed this effect of mixtures of groundwaters from successive beds of sands and clays with unexpected slightly high K and Na ions. Such is the case of the Trifylia springwaters which are relatively high in secondary K and Na ions (Table 1).

The proportion of magnesium to calcium in waters from carbonate rock areas reflects to some extent the composition of the parent rock. This interpretation must be made cautiously, however, because there are many complications that can influence the calcium-to-magnesium ratio of water from limestone (Hem, 1970).

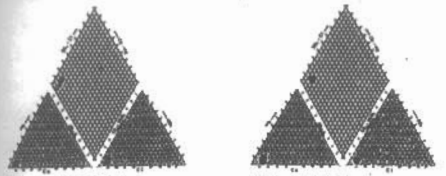
Water analyses data in Table 1 of eight conglomerate springwaters, represent water from a relatively pure limestone. According to the calcite-solublility graph (Figure 18 in Hem 1970), these waters are somewhat below saturation with respect to calcite. The sources are the eight Trifylia conglomerate springs of relatively large discharge (Kantas and Tiniakos, 1988) in a region where water is abundant and probably the circulation is too rapid to permit equilibrium to be reached. The predominance of calcium and bicarbonate ions in these eight analyses, however, is obvious.

HYDROCHEMICAL INTERPRETATION

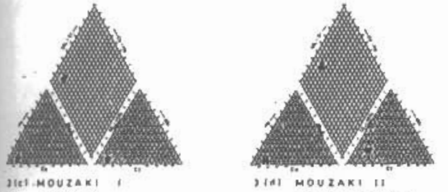
Fresh groundwaters, like these conglomerate springwaters, are undersaturated in all but a few minerals. It is thus generally justified to assume that, as in this case, dissolution from the aquifer is the dominant process. Disregarding the minor mineral content of rainwater, it is here assumed that the major constituents were picked up by dissolution from the Trifylia conglomerates. On the basis of this assumption the chemical composition of these springwaters is thus considered.

Table 1 shows the chemical analysis data of the water samples from the eight springwaters. All pH values are seen to be slightly alkaline (they vary between 7.0 and 7.7). In most natural waters, as in this case, the alkalinity is practically all produced by dissolved carbonate and bicarbonate ions. Alkalinity below a pH value of 8.2, as here, is a measure of bicarbonate ions (Davis and DeWiest, 1966). Alkalinity values of these springwaters vary between 7.0 and 16.3.

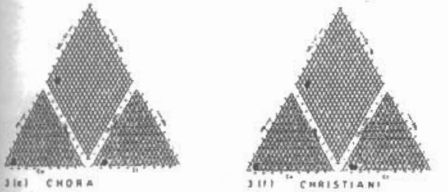
As groundwater percolates in this conglomerate aquifer it is loaded with alkali ions and the carbonic acid is thus totally neutralized. This causes an increase in the values of pH and alkalinity. The dominant anion HCO_3, in this case, identifies the large geochemical group to which these springwaters belong. The principal material in limestones and dolomites are carbonates, chiefly of calcium. The solution of calcium carbonate, with some magnesium carbonate, is therefore the primary action when waters containing carbon dioxiode attack the mineral matter in the limestones and dolomites. The amount of car-



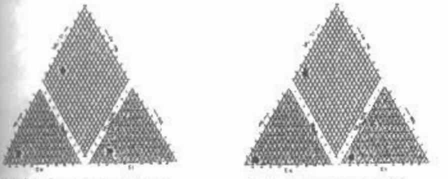
3(a) POTAMIA 3(b) "PLATI"



3(c) MOUZAKI I (MATI) 3(d) MOUZAKI II (PALIOVRYSI)



3(e) CHORA (KEFALOVRYSO) 3(f) "CHRISTIANI"



3(g) TYFLOMYTI-YALOVA 3(h) KOUBES-YALOVA

Fig. 4: Trilinear (Piper) diagrams of the flysch conglomerate springwaters.

bonates that can be dissolved largely depends upon the carbon dioxide content of the groundwater and the calcium and magnesium carbonate content of the rocks. As groundwater percolates downwards and latterally, it continues to dissolve calcium and magnesium carbonate until the carbon dioxide content of the groundwater is exhausted. Thereafter the carbonate hardness of the groundwater tends to remain constant.

In figure 4 the percent composition of the principal cations and anions have been plotted on trilinear graphs (Piper diagram). The springwaters can be classified predominantly as calcium-bicarbonate type waters with low salinity values. This makes obvious the direct relationship of water quality and lithology.

Using a Stiff diagram method (Figure 5) to define individual patterns of chemical character, it is observed that there is one major group of water type describing all the springwaters of these flysch conglomerates.

The sulfate content of Mouzaki II spring is found to be higher than the rest of the springs (Table 1, and Figure 5).

In regions where the country rock was initially well supplied with sulfides, as most shales and fine grained sediments are when lately raised above sea level, like this flysch formation, the natural processes of weathering bring about oxidation from the surface down to or below the water table, and the sulfate thus produced is available for transport away from the area (Hem, 1971). Unlike the carbonate minerals, the amount of sulfates dissolved in groundwater is not dependent on the carbon dioxide content of the water but on dissolving action only (Ibid). Hence the period of contact of the water with sulfate minerals in the aquifer is practically the only governing factor with respect to the dissolved sulfate content of the water. The sulfate content of the water increases continuously as the water flows from the intake area to the discharge area (Walton 1970).

The chemical reduction of sulfur from the fully oxidized S^{6+} state in the form of sulfate ions to the $S^{=}$ or sulfide state commonly occurs in groundwaters (Ibid). The reactions occur in the presence of certain types of bacteria (Hem, 1970). Water is probably required as a medium for the reactions, and the solid products formed would have to be carried away to permit the reactions to go to completion.

According to the chemical analysis data of Table 1, the chloride content of Tyflomyti spring is seen to be higher than those of the other springs. Normally, calcium and magnesium ions from solution replace adsorbed sodium

Table 1: Typical chemical analysis data of Trifylia flysch conglomerate springwaters. (19/03/1985).

Springs	EC mS/cm	pH	meq/l						Revelle coeff $\frac{Cl}{CO_3+HCO_3}$	SAR	Class	Alkalinity	Ca^{++}/Mg	Hardness (ppm)				
			Ca^{+}	Mg^{+}	$Na^{+}+K^{+}$	Cl^{-}	$SO_4^{=}$	$CO_3^{=}+HCO_3^{-}$						Total	Temp	Perm	Calcium	Magn
1 Potamia	380	7.4	3.8	0.2	0.1	0.2	0.1	4.0	0.05	0.2	C_2S_1	7.0	19.0	200	200	0	190	10
2 Plati	480	7.4	4.5	0.3	0.5	0.8	0.4	4.5	0.12	0.2	C_2S_1	9.4	15.0	240	225	15	225	15
3 Mouzaki I	420	7.5	3.5	0.5	0.6	0.6	0.3	3.7	0.16	0.1	C_2S_1	13.0	7.0	200	185	15	175	25
4 Mouzaki II	850	7.0	7.8	0.6	1.1	1.2	2.0	6.1	0.20	0.5	C_3S_1	11.8	12.7	410	305	105	380	30
5 Chora	580	7.1	5.4	0.5	0.5	0.8	0.3	5.5	0.11	0.3	C_2S_1	7.6	10.8	295	275	20	270	25
6 Christiani	550	7.1	5.3	0.2	0.5	0.6	0.1	5.3	0.11	0.3	C_2S_1	8.3	26.0	275	265	10	265	10
7 Tyflomyti	960	7.3	8.8	1.5	1.7	2.0	1.5	6.8	0.29	0.4	C_3S_1	16.3	4.6	420	340	80	345	75
8 Koubes	600	7.3	5.8	0.4	0.7	0.7	0.5	5.5	0.12	0.4	C_2S_1	10.4	14.0	300	275	25	280	20

on the exchange material. The release of calcium and magnesium from exchange position can be observed in some aquifers that become contaminated with sea water (Walton, 1970). The zone of contact of fresh and sea water often contains water that is higher in calcium and magnesium than could be explained by assuming a simple admixture of sea water and fresh water, as in the case of the Tyflomyti spring (Table 1).

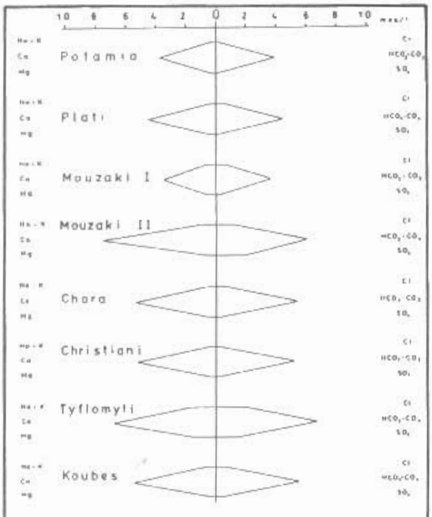


Figure 5

Stiff diagrams showing the water patterns of the eight springs

Fig. 5: Stiff diagrams showing the water patterns of the eight springs.

CONCLUSIONS

1. Petrographically, the one thousand meters thick, extensively faulted and folded Trifylia flysch conglomerates with a total area of over 100 km² in south-western Peloponnesus, are composed of nearly 90% limestone and dolomite well rounded pebbles and cobbles with sand size $CaCO_3$ as their cementing agent. They thus behave as a carbonate unit exposed to water solution.

2. In the Aegaleon Mountain area (northern conglomerates), all the water infiltrated (average 12.5x10⁶ m³/yr) from precipitation is drained through the six major springs whose elevations range between 700 and 300 meters. The depletion segments of their hydrographs display double porosity property, where the wide flow (secondary permeability) channels drain more quickly than the less porous (primary permeability) rock matrix.

3. These conglomerates (northern and southern) forming a separate hydrogeological unit are recharged by direct infiltration and drain through eight springs with an average annual yield of 16.5x10⁶ m³. The elevation of their discharge point of these eight springs varies between 700m, the highest, to 0.30m, the lowest, due to intense normal faulting which has

divided these con-glomerates into several hydrogeologically independant blocks each discharging its groundwater separately.

4. Chemically all these waters are of low salinity (electrochemical values range between 380-960 úS/cm) and calcium-bicarbonate type with very low Revel-le coefficients, indicative of a limestone environment free of sea-water pol-lution. One spring (Tyflomyti) which is topographically the lowest and the closest to the sea has its Cl$^-$ content slightly higher than the rest. This is attributed to slight seawater mixing. A second spring (Mouzaki II) has its SO$_4^=$ ions slightly higher than the rest. This can be attributed to the sulfate content of the underlying clay schists and shales of the flysch formation or to the underlying evaperites.

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