

ASSESSMENT ON HYDROTHERMAL PARTICLE CHEMISTRY FROM A SHALLOW VENTING SYSTEM OFFSHORE KOS, AEGEAN SEA

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Abstract

Shallow submarine hydrothermal vents along Hellenic Volcanic Arc transfer significant quantities of particles enriched in basic metals. Fluids collected by scuba diving from two shallow hydrothermal venting areas on Kos Island in the Aegean Sea in East Mediterranean. Samples were filtrated and membrane filters leached with a mixture of acids. Chemical analysis performed in suspended particles for Fe, Mn, Cu, Pb, Cd, Ca, Ba, Sr, Li, Al and Si. The suspended particulate matter (SPM) flux varied from 0.93 to 8.64 mg/l and between 0.21 and 20.94 mg/l in two sites. Metal/Al ratios also vary significantly within a short distance. The pH of hydrothermal waters was from 5.50 to 5.95 in Kephalos Bay and from 6.09 to 6.53 in Bros Thermi suggesting gases CO₂ and H₂S may control pH values. Particles were dominated by Fe, Ca, Si and Al and strongly enriched in Mn, Cu, Pb and Ba. Three geochemical groups were identified being associated with distinct hydrothermal processes concerning sulphide minerals, carbonate substrate and deeper Al-Silicate rock basement.

Keywords: *particulate matter, basic metals, vents, Hellenic Volcanic Arc.*

Περίληψη

Οι υδροθερμικές πηγές ρηχών περιοχών του Ελληνικού Ηφαιστειακού Τόξου μεταφέρουν σημαντικές ποσότητες σωματιδίων εμπλουτισμένων με βασικά μέταλλα. Υδροθερμικά ρευστά συλλέχθηκαν από δύο ρηχές υδροθερμικές περιοχές Κόλπος Κέφαλος και Μπρος Θέρμη στην Κω στην Ανατολική Μεσόγειο. Τα δείγματα νερού διηθήθηκαν με φίλτρα μεμβράνης και το υλικό που κατακρατήθηκε αφού διαλύθηκε από μίγμα οξέων αναλύθηκε για Fe, Mn, Cu, Pb, Cd, Ca, Ba, Sr, Li, Al και Si. Η εκροή αιωρούμενου υλικού (SPM) ροή κυμάνθηκε από 0,93 έως 8,64 mg/l και μεταξύ 0,21 και 20,94 mg/l στις δύο περιοχές μελέτης, ενώ οι λόγοι Metal/Al διέφεραν με την απόσταση. Το pH των υδροθερμικών νερών ήταν από 5,50 έως 5,95 στον Κόλπο Κέφαλο και 6,09 έως 6,53 στην Μπρος Θέρμη πιθανολογώντας ότι η συγκέντρωση αερίων όπως CO₂ και H₂S ελέγχει τις τιμές του. Το αιωρούμενο υλικό αποτελείται κυρίως από Fe, Ca, Si και Al είναι όμως και εμπλουτισμένο σε Mn, Cu, Pb και Ba. Τρεις γεωχημικές ομάδες εντοπίστηκαν που φαίνεται να συνδέονται με διαφορετικές υδροθερμικές διεργασίες των θειούχων, ανθρακικών και αργιλλοπυριτικών φάσεων του γεωλογικού υποβάθρου.

Λέξεις κλειδιά: *αιωρούμενο υλικό, μέταλλα, πηγές, Ελληνικό Ηφαιστειακό τόξο.*

1. Introduction

The seafloor hydrothermal vent systems influence marine chemistry in every timescale and in large extent (Von Damm, 1990; Parson *et al.*, 1995; Von Damm, 2001). The spatial evolution of magmatic-hydrothermal systems very often presents great extent of several kilometres into the crust and the formation of hydrothermal plumes on sea column (Humphris *et al.*, 1995; Lupton, 1995; Edmonds and German, 2004). The hydrothermal fluid phase such as gases, water, solutes and particulate matter. Particulate matter indeed is an important constituent of hydrothermal fluids and actually it represents sedimentary material in early stage of formation (Whittfield and Turner, 1987). The compositional variability of suspended particulate matter (SPM) depends upon a number of factors such as the nature of chemical reactions taking place in the substrate the prevailing physico-chemical and oceanographic conditions, the amount of dissolved oxygen, other gas content and the rate of mixing of hydrothermal fluids with seawater (Von Damm *et al.*, 1985). Particulate Fe and Mn was found in unusually high concentrations in South Aegean Sea, comparing to other straits of Mediterranean and their origin was attributed to hydrothermal sources (Balopoulos *et al.*, 1999). Furthermore, particulate matter distribution in Aegean Sea seawater is influenced mainly by three factors such as the proximity to the initial sources, the water circulation patterns prevailing and the topography of sea-bottom, while resuspension phenomena affect sediment depositional geochemistry of surface sediments (Karageorgis and Anagnostou, 2001). Moreover, the shallow submarine hydrothermal venting related to the Hellenic Volcanic Arc and its influence on seabed and seawater chemistry has been well investigated (Dando *et al.*, 2000; Price *et al.*, 2013; Yücel *et al.*, 2013), while controls local marine sediment geochemistry have been also attributed (Megalovasilis, 2014, Megalovasilis and Godelitsas, 2015). There are few studies on particle emission in submarine hydrothermal areas in Aegean (Varnavas *et al.*, 1998; Varnavas *et al.*, 2000; Megalovasilis, 2007; Megalovasilis, 2015a; Megalovasilis, 2015b). In this work, statistical data are presented and an assessment on elemental interrelationships between hydrothermal particulates is attempted. Such a research is important because it provides further information on the geochemical influence of hydrothermal fluids along the Hellenic island volcanic arc.

2. Materials and Methods

Sampling was carried out in Kephalos Bay and Bros Thermi. Interactions between hydrothermal fluids and oxygenated seawater result in various precipitates settling to the sea bottom around the venting seeps influence strongly local sediment geochemistry (Megalovasilis and Godelitsas, 2015). Fe oxides and hydroxides are observed both in Kephalos Bay and Bros Thermi. A variety from brown-red Fe oxides to yellowish Sulphur and metal-sulphides phases together with white silica - bacterial mat are observed around the seeps but in lesser extent than those recognised in Milos (Dando *et al.*, 1998; Godelitsas *et al.*, 2015). Samples obtained by scuba diving using fluid samplers consisted of two double plastic bags connected by a Y-shaped selectable plastic connector to a plastic funnel, applied on the top of the venting outlet. All parts were laboratory ultra pure acid cleaned. The first bag was used for collecting primary wastes (sand and seawater) while second bag collection was timed. The volume of gas+water and only water was measured with the Archimedes method of water displacement (Dando *et al.*, 1995). Water samples were transferred in glass bottles. The H₂S was detected in all samples by its characteristic smell. The hydrothermal waters were filtered in the field setup laboratory using a vacuum pump system and with the aid of Millipore Sterifil Aseptic System Holder and Millipore 0.45µm pre-weighted membrane filters while both the ending tube and the top funnel were sealed with plastic covers (Loring and Rantala, 1992). After filtration the sample-filters were then dried in an evacuated desiccator over silica gel and stored in acid-cleaned individual Petri slides. After weighing, the suspended particulate matter on the membrane filters was subjected to chemical leaching (Landing and Lewis, 1991), with the addition of 20 ml of extra high purity 2M HCl-1M HNO₃ mixture, samples left for 4 hours at room temperature. Flasks were put afterwards on a hot plate at 65°C near dryness and after they were cool, 5ml of mixture 0.5M HCl-0.1M HNO₃ were added. All reagents and stock standards for AAS were of extra high purity commercially obtained (Merck), while 3-distilled water

used for preparation of all reagents and working standards, and for rinsing all glassware which previously had been immersed for 2 days in 10% wt HNO₃. Aliquots of the samples were analysed for Fe, Mn, Cu, Pb, Cd, Ca, Ba, Sr, Li, Al and Si, applying Atomic Absorption Spectrometry with Graphite furnace technique (GFFAS) using Perkin Elmer 2100 AAS and 701HGA Graphite Furnace. The operational parameters applied were of these from manufacturer and modified depending on the element (Loring and Rantala, 1992). Accuracy checked with the sensitivity check standards found better than ±5% while analytical precision was checked with replicate analyses and found varied from ±5 to ±10%.

2.1. Geological setting

The Hellenic volcanic arc (HVA) in east Mediterranean region, is part of the pre-Alpine to Quaternary continental crust of the Hellenic subduction zone (Pichon and Angelier, 1979) and is a rather young (5 Ma) volcanic arc in the pre-Alpine to Quaternary continental crust of the Hellenic subduction zone (Royden and Papanikolaou, 2011). It is the result of northward subduction of the last remnant of the oceanic crust of the African plate beneath the southern edge of the active margin of the European plate (Pichon and Angelier, 1979). The volcanoes of the HVA occur onshore the peninsula of Methana, and offshore the islands of Poros in the west, Milos and Santorini in the centre, and on Nisyros and Kos in the east (Fig. 1). Many submarine volcanoes have been discovered recently including Paphsanias near Methana, the volcanic domes to the east of Antimilos near Milos, and the Christiana domes and Kolumbo near Santorini (Nomikou *et al.*, 2013). A great explosion occurred before 161 ka between Nisyros and Kephalos Bay producing >60 km³ of volcanic material which covered half of the island of Kos. Mainly the western part covered with a layer of ash and pumice of about 30 meters in thickness. This formation is unconformably overlying or concordant with older stratified sediment in west Kos basin of thickness more than 100 m. Kos Plateau Tuff (KPT) eruption was the largest eruption in the Pliocene-Quaternary in Hellenic volcanic arc (Pe-Piper *et al.*, 2005). Kos is controlled by WNW-ESE and NE-SW faults systems, which are related to extensional processes and volcanic activity during the Pleistocene and Pliocene (Papanikolaou and Lekkas, 1990; Lagios *et al.*, 1998). The Kos-Nisyros volcanic center is a Plio-Pleistocene magmatic system which characterized by magmas with variable composition of basaltic andesite to high-SiO₂ rhyolite, formed during last 3-4 Ma (Bachmann *et al.*, 2012). Geothermal manifestations on the island are found in various locations such as the hot spring of cape Agios Fokas (Ruffa *et al.*, 1999) in the NE part called Empros Thermes (Bros Thermi in modern Greek), where there is active flow of warm water into the beach of Thermes with temperature of 47 °C (Varnavas *et al.*, 1998) and the hot spring of Agia Irini (Piso Thermes), which is easily accessible by boat, with fluid temperature of 45 °C. Also, there are other hot spring at Kokkinonero found southwest of the Asclepeion archaeological site where water is ferruginous (red in colour) and rich in carbon oxides (CO, CO₂) with a temperature of 22.5°C (Hatzivasileiou, 2013). Finally there is the Volcano hot spring containing muddy mineral water and the hot spring of Kokkinonero nearby (Ruffa *et al.*, 1999). A famous submarine hydrothermal site is the Paradise Beach on Kephalos Bay and together with Bros Thermi they gain a lot of attraction from tourists. Previous research on hydrothermal gas chemistry showed that springs onshore and offshore contain CO₂ (93-99%), H₂S (<0.005%), H₂(<0.001%), CH₄ (0.008-0.362%), N₂ (1.10-4.82%), O₂ and Ar (0.030-0.912%) (Minissale *et al.*, 1997).

The Kos-Nisyros volcanic activity presents great variation with time the last 3 Ma (Bachmann *et al.*, 2012). Although recent and present times are not characterized by any volcanic activity, active onshore fumaroles and shallow submarine hydrothermal fields are found around Nisyros and Yali islands and along the southern coast of Kos (Varnavas and Cronan, 1991), particularly near shore in Kephalos Bay (Paradise bubble beach) in south-west and Bros Thermi in northeast (Megalovasilis and Godelitsas, 2015). At Bros Thermi, seawater moving downwards being modified by water-rock interactions and circulates with Mg and K losses, reaching 110°C close to sea bottom while meteoric water contribution has been found in other geothermal sites in Kos (Ruffa *et al.*, 1999). Details on physiographic characteristics of submarine study areas (i.e bathymetry etc.), can be found in previous research (Megalovasilis and Godelitsas, 2015).

3. Results

3.1. Kephalos Bay

The geochemical data obtained show a significant variability in all parameters (Table 1). The water flux varied from 60 to 122 l/h and the gas flux values varied from 2 to 126 l/h while the gas/water ratio found between 0.03 and 1.30. The hydrothermal suspended particulate matter (SPM) varied from 0.93 - 8.64 mg/l with an average of 4.32 mg/l. The pH in vent waters found between 5.50-5.95 and conductivity was 56.7-57.5 mS/cm. Fe concentrations in SPM were from 8.7-87.2 $\mu\text{g/l}$, Mn 0.14-2.33 $\mu\text{g/l}$, Cu 0.01-0.34 $\mu\text{g/l}$, Pb 0.05-0.52 $\mu\text{g/l}$, and Cd found only in few samples being 0.001-0.015 $\mu\text{g/l}$. Ca varied from 16.9 to 215 $\mu\text{g/l}$, Ba from 0.16 to 1.46 $\mu\text{g/l}$ and Sr 0.12-2.07 $\mu\text{g/l}$. Li varied from 0.01-0.28 $\mu\text{g/l}$, Al 4.83-90.25 $\mu\text{g/l}$ and Si 1.23-112.5 $\mu\text{g/l}$. SPM concentrations are well correlated (correlation coefficient $0.70 < r < 0.98$) with all elements except Cu, Cd and Si. Based on average values of hydrothermal water flux obtained and on the number of vents studied an estimation of annual fluxes can be deduced (i.e. water average discharge/h x hours of year x number of vents). Consequently annual flux of SPM also can be calculated based on annual water discharge. The annual hydrothermal water flux is estimated 819 m^3/y , the annual gas flux 636 m^3/y and annual production of SPM to 24,749 g/y. Actual fluxes should be at least 2 orders of magnitude much more because the total number of observed hot spots is much higher than those studied. Many seeps are not even visible continuously, because gas effluence which gives the visual character of outflow is intermittent.

3.2. Bros Thermi

Significant variability is also observed in this submarine hydrothermal field. The water flux varied from 16.5 to 96 l/h and the gas flux values varied from 4.5 to 60 l/h while the gas/water ratio was between 0.18 and 1.14. The SPM flux varied from 0.21 - 20.94 mg/l with an average of 6.06 mg/l.

The pH in vent waters found between 6.09-6.53. Fe concentrations in SPM were from 6.5-229 $\mu\text{g/l}$, Mn 0.05-2.17 $\mu\text{g/l}$, Cu 0.10-1.01 $\mu\text{g/l}$, Pb 0.08-1.34 $\mu\text{g/l}$, and Cd recorded in most samples being 0.001-0.038 $\mu\text{g/l}$. Ca found between 14.6 and 182 $\mu\text{g/l}$, Ba from 0.09 to 0.91 $\mu\text{g/l}$ and Sr 0.13-1.19 $\mu\text{g/l}$. Finally Li varied from 0.01-0.85 $\mu\text{g/l}$, Al 1.53-192 $\mu\text{g/l}$ and Si 0.56-105 $\mu\text{g/l}$. SPM concentrations are very well positively correlated ($0.70 < r < 0.99$) with all elements studied and moderate positively with Cd ($r=0.54$). Analytical results are presented in Table 1. On the basis of average values and the number of submarine hydrothermal vents studied, annual values can be estimated. Thus, the total hydrothermal water flux is estimated 418 m^3/y , gas flux 216 m^3/y and for SPM 40,540 g/y. For similar reasons as in Kephalos Bay the actual outflow should be two orders of magnitude higher.

3.3. Element to Al ratios

To examine the origin of particulate metals from another view element/Al ratios of their concentrations in SPM were estimated (Table 2). Remarkably, differences on time and space compositional variability of SPM were observed. In Bros Thermi Vent B1 showing higher values for Fe/Al, Cu/Al, Pb/Al, Cd/Al and Ca/Al where Kephalos Bay vents are presenting elevated Mn/Al, Ba/Al and Si/Al ratios considering all analytical data obtained.

The present data strongly suggest that elements are concentrated in different phases in which they are held. The inter-element correlations of particulate elements imply not only a hydrothermal origin, for some particulates (e.g. Ba, Si) but also a biological affiliation of biogenic debris, or calcareous and siliceous tests. A further mineralogical investigation should be performed in order to clarify the above hypothesis. Notably the metal/Al varies significantly from vent to vent within a short distance, both in Kephalos Bay and in Bros Thermi.

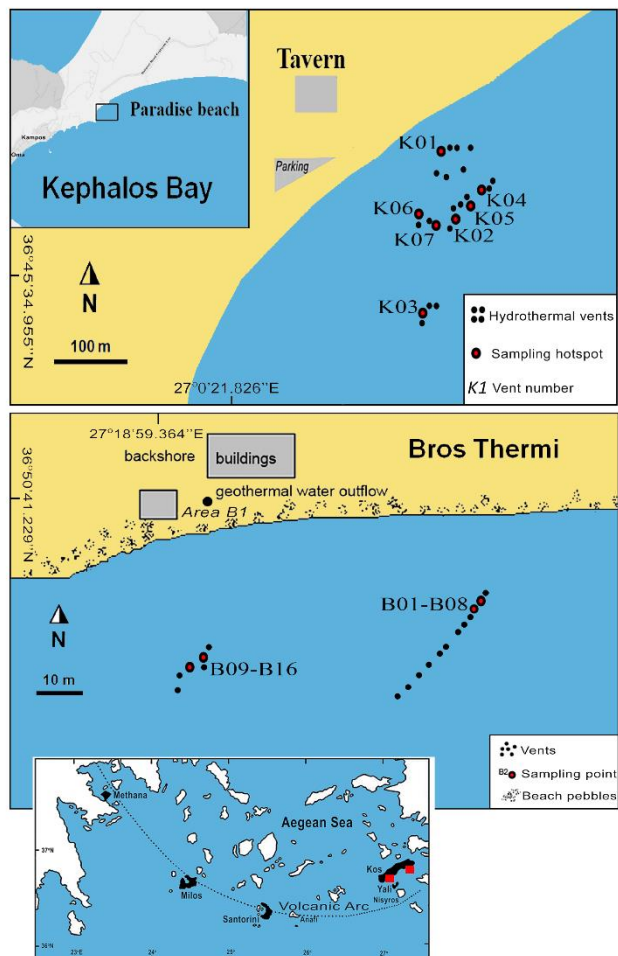


Figure 1 – Study area and sampling sites.

Although Fe/Al and Mn/Al follow different trends between the two hydrothermal fields, the Cu/Al, Pb/Al and Cd/Al are showing quite similar correlation indicating a possible common hydrothermal phase. Moreover, Ca/Al, Ba/Al and Sr/Al are very well and positively correlated. Probably they are concentrated in the same phase, while dissolved Ca derived from the dissolution of carbonates during hydrothermal leaching may form particles of secondary minerals such as anhydrite or clay minerals (Von Damm *et al.*, 1985). Furthermore, particulate Sr should be incorporated in anhydrite as well. Finally, Li/Al and Si/Al are found to be correlated positively only in Kephalos vents. The Fe/(Fe+Mn+Al) ratio and especially that of Al/(Fe+Mn+Al) can be used as an indication of hydrothermal versus detrital sediment inputs. Values being below 0.60 is considered as an indication of hydrothermal versus detrital sediment inputs while values below 10 or even 20 are strongly related to submarine hydrothermalism or volcanism (Bostrom *et al.*, 1969; Edmonds and German, 2004). In Kos hydrothermal particles the Al/(Fe+Mn+Al) ratio varied between 0.16-0.62 and an average 0.29 in Kephalos Bay and from 0.03-0.53 with an average 0.29 in Bros Thermi (Table 2). Furthermore, the fluctuation of Fe/(Fe+Mn+Al) ratio found to be above 0.50 in most samples with only one exception in Bros Thermi and one in Kephalos.

3.4. Factor analysis

R-Mode statistical analysis was performed for SPM elemental data using SPSS 18. In Kephalos Bay

2 factors were account for 73.31 % of total variance and in Bros Thermi 2 factors 87.72%. In Kephalos Bay Factor 1, which described 55.0 % of the total variance, presents high loadings for Mn, Pb, Ca, Ba, Sr Li and Al. The second factor consists from Cu and Si account for 18.3% of the total variance. SPM in this site consist mainly of hydrothermal oxides and hydroxides of Fe, Mn, and Pb but contains also a lithogenic mixture of Ca, Ba and Sr linked with the limestone substrate and also Li-Al fraction which can be attributed to a deeper volcanic rock origin. Cu and Si relationship can be attributed to oxidation of Cu sulphide by exposure to hydrothermal fluids and forming secondary Cu-Si mineral such as Chrysocolla (complex hydrated copper aluminum silicate). Further analysis might need to confirm this. In Bros Thermi Factor 1 described 52.6 % of the total variance presenting high loadings in Fe, Mn, Cu, Pb, Ca, Ba, Al and Si and moderate loadings for Sr and Li. The second factor presents high loadings in SPM, Cd, Li and moderate loadings in Cu, Pb, Ca, Ba, Sr, Al and Si. The different geochemical groups observed within the data from two sites also agree with other recent research on Bros Thermi local sediments and hydrothermal venting additions (Megalovasilis and Godelitsas, 2015).

Table 1 – Summary results of submarine hydrothermal SPM, Kos Aegean Sea.

	Gas	Water	G/W	pH	SPM	Fe	Mn	Cu	Pb	Cd	Ca	Ba	Sr	Li	Al	Si
	l/h	l/h			mg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l
Kephalos Bay																
min	2.00	60.00	0.030	5.50	0.93	8.7	0.14	0.01	0.05	0.001	16.89	0.16	0.12	0.01	4.83	1.23
max	126.00	121.50	1.300	5.95	8.64	87.2	2.33	0.34	0.52	0.015	215.38	1.46	2.07	0.28	90.25	112.50
geomean	48.26	90.55	0.525	5.66	3.43	34.8	0.67	0.10	0.17	0.002	62.05	0.54	0.48	0.04	15.46	10.20
average	72.64	93.46	0.769	5.66	4.32	44.5	0.96	0.14	0.21	0.004	87.57	0.67	0.75	0.08	27.20	29.05
stdev	37.76	23.89	0.432	0.15	2.91	28.9	0.77	0.11	0.15	0.005	69.96	0.44	0.72	0.09	31.23	40.29
Bros Thermi																
min	4.50	16.50	0.180	6.09	0.21	6.5	0.05	0.10	0.08	0.001	14.58	0.09	0.13	0.01	1.53	0.56
max	60.00	96.00	1.140	6.53	20.94	228.8	2.17	1.01	1.34	0.038	181.82	0.91	1.19	0.85	191.95	104.77
geomean	20.62	43.52	0.474	6.23	2.89	55.6	0.43	0.23	0.37	0.006	47.11	0.26	0.37	0.09	18.41	7.98
average	24.71	47.70	0.544	6.23	6.06	80.2	0.66	0.30	0.47	0.011	62.08	0.33	0.48	0.23	53.25	23.15
stdev	14.79	20.20	0.296	0.13	6.88	59.5	0.56	0.25	0.34	0.012	47.79	0.24	0.36	0.28	62.58	29.48

Table 2 – Metal/Al ratios of submarine hydrothermal SPM, Kos Aegean sea.

	Fe/Al	Mn/Al	Cu/Al	Pb/Al	Cd/Al	Ca/Al	Ba/Al	Sr/Al	Li/Al	Si/Al	Fe/Fe+Mn+Al	Al/Fe+Mn+Al
Kephalos Bay												
min	0.58	0.026	0.002	0.005	0.0000	2.39	0.013	0.023	0.002	0.212	0.36	0.16
max	5.03	0.090	0.030	0.029	0.0030	9.45	0.131	0.056	0.006	5.769	0.82	0.62
geomean	2.25	0.043	0.006	0.011	0.0001	4.02	0.035	0.031	0.003	0.660	0.65	0.29
average	2.66	0.048	0.012	0.013	0.0006	4.44	0.046	0.033	0.003	1.384	0.67	0.32
stdev	1.43	0.023	0.012	0.009	0.0011	2.42	0.040	0.012	0.002	2.043	0.15	0.15
Bros Thermi												
min	0.88	0.006	0.002	0.004	0.0001	0.64	0.003	0.005	0.003	0.042	0.47	0.03
max	38.92	0.063	0.122	0.144	0.0202	18.43	0.087	0.122	0.012	2.916	0.97	0.53
geomean	3.02	0.023	0.013	0.020	0.0004	2.56	0.014	0.020	0.004	0.434	0.69	0.23
average	5.56	0.030	0.031	0.039	0.0018	4.39	0.026	0.035	0.005	0.698	0.71	0.29
stdev	9.16	0.019	0.042	0.044	0.0050	4.87	0.028	0.035	0.002	0.813	0.17	0.17

4. Discussion – Conclusions

Different gas content equilibrium, pH and redox conditions of hydrothermal fluids together with different rock basement and water source result in various particulate matter types containing diverse crystal forms and aggregates (Chester and Jickells, 2012). The elemental geochemistry of SPM presents some similarities but also differentiations between study areas were observed. Fe particulate correlates well with Mn, Cu and Pb particles suggesting a common sulphide source. Also Ca, Ba and Sr particulate concentrations are well correlated linked with dissolution of carbonate substrate maybe forming secondary minerals such as anhydrite CaSO₄, BaSO₄ and SrSO₄. Finally the particulate concentrations of Al, Si and Li being also well correlated, forming the “lithogenic” group of hydrothermal particles (Fig. 2).

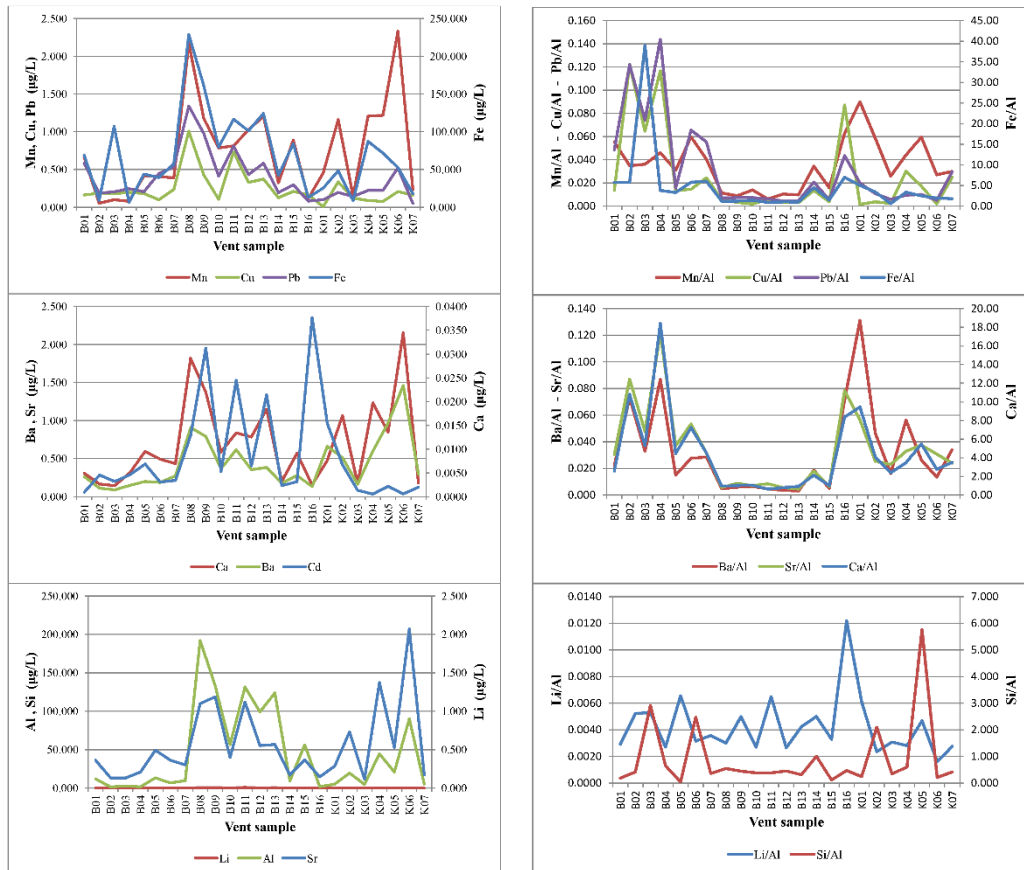


Figure 2 – Elemental concentration variability in hydrothermal SPM, Kos Aegean Sea.

Kephalos Bay hydrothermal site presents higher gas and water flux compared with Bros Thermi but gas/water ratio is similar. Periodicity in sediment temperature caused by tidal and barometric pressure affect pore pressure in sediment and consequently controls flux of nutrients and metals. As a consequence, bacterial mats morphology and expansion around seeps vary with time. (Aliani *et al.*, 2004). The SPM concentration is higher in Bros Thermi than in Kephalos coupled with higher levels of Mn, Cu and Fe. Both fields present same levels of concentrations in Mn, Si and Ca. Higher concentrations are observed in Bros Thermi for Fe, Cu, Cd, Li, Pb and Al, while increased concentrations in Ba and Sr found in Kephalos Bay (Fig. 2). Particulate Fe is associated in a different way with specific elements, such as with Cu on the two hydrothermal areas, presenting no distinct trend in Kephalos while the opposite is observed in Bros Thermi. Furthermore, Fe presents similar positive concentrations trends with Mn and with Pb and Al on both fields. In many environments Ca, Ba and Sr are very well geochemically correlated and coupled because of similarities on their geochemical properties despite possible different sources and biogenic affiliations. In Kos their concentrations are quite similar in both areas indicating a common carbonate substrate beneath the island, leached by the hydrothermal ascending fluids. A barite (BaSO_4), source for Ba is also possible. Lithogenic elements in SPM present different relationships in their concentrations such as between Si and Al while they follow similar interrelationships with Li in both areas studied. Si and Al in Kephalos only show more distinguishable trend (Megalovasilis, 2015b). There are only a few studies for hydrothermal particulate matter along the Hellenic volcanic arc. Comparing with existing literature, Kos submarine hydrothermal SPM levels are below the Milos SPM (Palaeochori Bay) concentrations and similar with other submarine hydrothermal areas in Milos such as Voudia Bay

and Adamas Bay (Varnavas *et al.*, 2000; Megalovasilis, 2007). Notably particulate Fe is exhibiting high concentrations only in Bros Thermi while Mn particulate is high in both fields and both elemental concentrations are comparable with Milos Palaeochori Bay. In addition, the strong influence of sedimentary substrate is imprinted with the very high levels of particulate Ca being the highest observed along the volcanic arc. Elevated particulate Sr is also observed in Kos and remarkably high particulate Al are found in Bros Thermi suggesting strong Al-Silicate mineral assemblages underneath the hydrothermal site. Previous research on sediments deposited near the venting area of Bros Thermi suggested the possible existence of significant metallic sulphide deposits of hydrothermal origin at depth beneath Kos (Megalovasilis and Godelitsas, 2015). It is quite difficult if not impossible to compare fully hydrothermal particulate concentrations of elements in all marine environments such as the shallow vents and hydrothermal fields of open oceans; because of huge differences on sampling procedures and the actual dispersion of plumes in the water column. When scuba diving is involved, sampling results in more condensed and isolated hydrothermal fluid component while niskin bottle sampling (or in situ pumping of seawater), over hydrothermal plumes and submarine volcanoes with hydrothermal activity, contains more diluted hydrothermal component altered by the prevailing oceanographic conditions. Summarising, particle chemistry from the submarine vents studied were dominated by Fe, Ca, Si and Al and strongly enriched in Mn, Cu, Pb and Ba. Data are indicating that hydrothermal vents are major sources for basic metals and trace elements such as Fe, Mn, Cu, Pb and Cd. The different elemental associations in the two study sites are attributed mainly to the different geologic type of substrate petrology rather than in very different hydrothermal processes prevailing. But because the two study sites presented differences in their pH, gas flux, water flux and gas/water ratio a different hydrothermal reactivity between the two sites is assumed. Particulate matter originating from hydrothermal vents plays important role in local marine sediments geochemistry and it seems is ruled by the geochemistry of the geologic basement and the water-rock interactions taking place beneath in the substrate. Long-term or short-term time series or even periodical sampling of hydrothermal fluids are of prime importance in furthering our understanding on shallow-sea hydrothermal systems and strongly suggested. Furthermore, future investigations should incorporate study of both dissolved and particulate species together with mineralogical analysis and SEM images in order to access the geochemistry of these vents in total.

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