Δελτίο Ελληνικής Γεωλογικής Εταιρίας τομ. XXX/3, 225-239, 1994
Πρακτικά 7ου Επιστημονικού Συνεδρίου, Θεσσαλονίκη, Μάιος 1994

Bulletin of the Geological Society of Greece vol. XXX/3, 225-239, 1994
Proceedings of the 7th Congress, Thessaloniki, May 1994

THE ORIGIN OF VOLCANIC-EXHALATIVE DEPOSITS RICH IN Fe, Mn, AND Ba; A COMPARISON OF THE VANI AND THE LÅNGBAN DEPOSITS

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ABSTRACT

The Vani Caldera (on the NW tip of the Island of Milos, Greece) contains a well stratified volcanic-sedimentary sequence, rich in iron, manganese and barium. The general geology and geochemistry of the ores show several similarities with the Precambrian Langban ores in South Central Sweden. Possibly much of the Fe, MN and BA in both deposits were mobilized from marine sediments in a subduction zone at an island arc. Different depths of mobilization of the elements may explain the puzzling compositional differences between the deposits in the Vani caldera and in the Santorini.

INTRODUCTION

Many Precambrian exhalative-sedimentary ores may have an island-arc setting, such as various Fe-MN-oxide deposits (Boström et al., 1979) or sulfide ores (Richard and Zweifel, 1975). However, the metallo-genesis of most old deposits is hard to study due to obscuring tectonic and metamorphic events. Little altered young deposits reveal the metallogenetic processes better, e. g. at spreading centers in the World Ocean (Boström, 1980; Von Damm, 1990). Recent deposits in island arc settings, however, are generally small and poorly developed and have therefore been little studied, but some descriptions (Zelenov, 1972; Waring, 1965) indicate that such deposits may be more numerous than generally realized.

The Vani caldera deposit is an excellent example of a young island arc deposit, which has several logistic advantages compared with other analogous deposits e. g. in the Kuriles (Zelenov, 1972). Furthermore, the Vani and Långban deposits show several similarities, both being rich in Fe, MN and BA and well oxidized with higher oxides of MN and sulfate. Both deposits are probably of an exhalative-sedimentary origin and probably the Långban ores formed at an Island arc as well (Boström et al., 1979).

GEOLOGICAL BACKGROUND AND FIELD RELATION

The Milos group of islands in the SW part of the Cyclades lies almost in the middle of the external volcanic arc of the South Aegean Sea and with the island of Milos and the satellite islets of Kimolos, Antimilos and Polyaigos (Fig. 1) and are located in a large string of volcanic islands in the South Aegean. These volcanic islands formed during the late Pliocene to Quaternary due to

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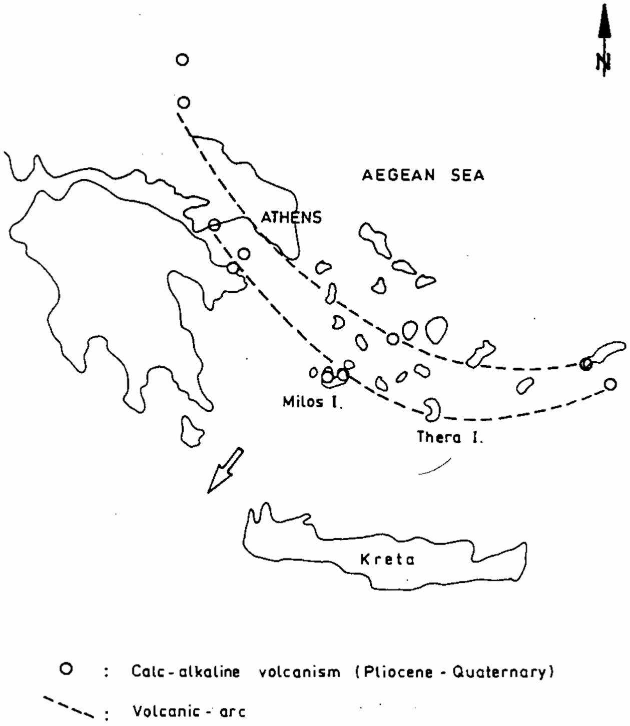

Fig. 1: Map, showing the distribution of volcanic islands and arcs in the South Aegean sea.

volcanic processes at a subduction zone that parallels the volcanic arc, which frequently is referred to as the Helladic Volcanic Arc, HVA. These islands are arranged along twin arc zones, the internal zone including the volcanoes of Antiparos island in the Central Cyclades and Kos Island to the east, and the outer zone the volcanoes of Methana, Aegina, Poros, Milos, Thera and Nisiros islands (Fig 2). The rocks represent a typical calc-alkaline series, ranging from basalt to rhyolite, but the predominating petrology varies fore each island; basalt's, daces and andesites are widely occuring on Thera, whereas rhyolite is the major rocktype on Milos.

The Vani caldera is located on the NW tip of Milos and has a diameter of some 1.5 km, and is restricted by underlying dacitic domes and flows (Fig 2). The dacitic bedrock has a microlitic to porphyritic texture and contains plagioclase, pyroxene, amphibole, biotite, quartz and titano-magnetite (Fytikas, 1977; Liakopoulos, 1987). The exhalative-volcanic sequence of the caldera consists of tuffaceous, clastic and epiclastic deposits, rich in MN, Fe and BA and is Upper Pliocene in age. Late erosional events have formed littoral deposits of sand with crossbedding and conglomerate balls, many some 10 cm in diameter, which occur in the upper part of the sequence. The balls are in many cases covered by later iron-manganese oxides, revealing that the ore forming or remobilizing processes had not fully stopped when the coarse clastics were formed. The tuffs, mainly consisting of K-feldspar, quartz and biotite, alternate with clastic sands, cherts and beds of manganese oxides and barite. The maximum thickness of the sequence is 45 m.

The Vani caldera is hence small compared with that of Thera, but shows a more intense metallogenetic activity (Galanopoulos et al., 1991). To understand these metallo-genetic aspects better four sites (Fig 2) were studied and sampled in detail:

Site 1 is located at the S border of the caldera, and shows intermediary rocks (andecitic lavas and tuffs) that are partly severely brecciated and altered. The clastic and epiclastic siliceous horizons of detrital origin are rich in muscovite and biotite, and are locally impregnated by later mineralisations, consisting of iron, barium and manganese rich layers. The volcanic-exhalative sequence shows a maximum thickness of 35 m.

Site 2 is located near the center of the caldera, where the well stratified deposits with Fe, MN and BA rich beds are best developed. These components are

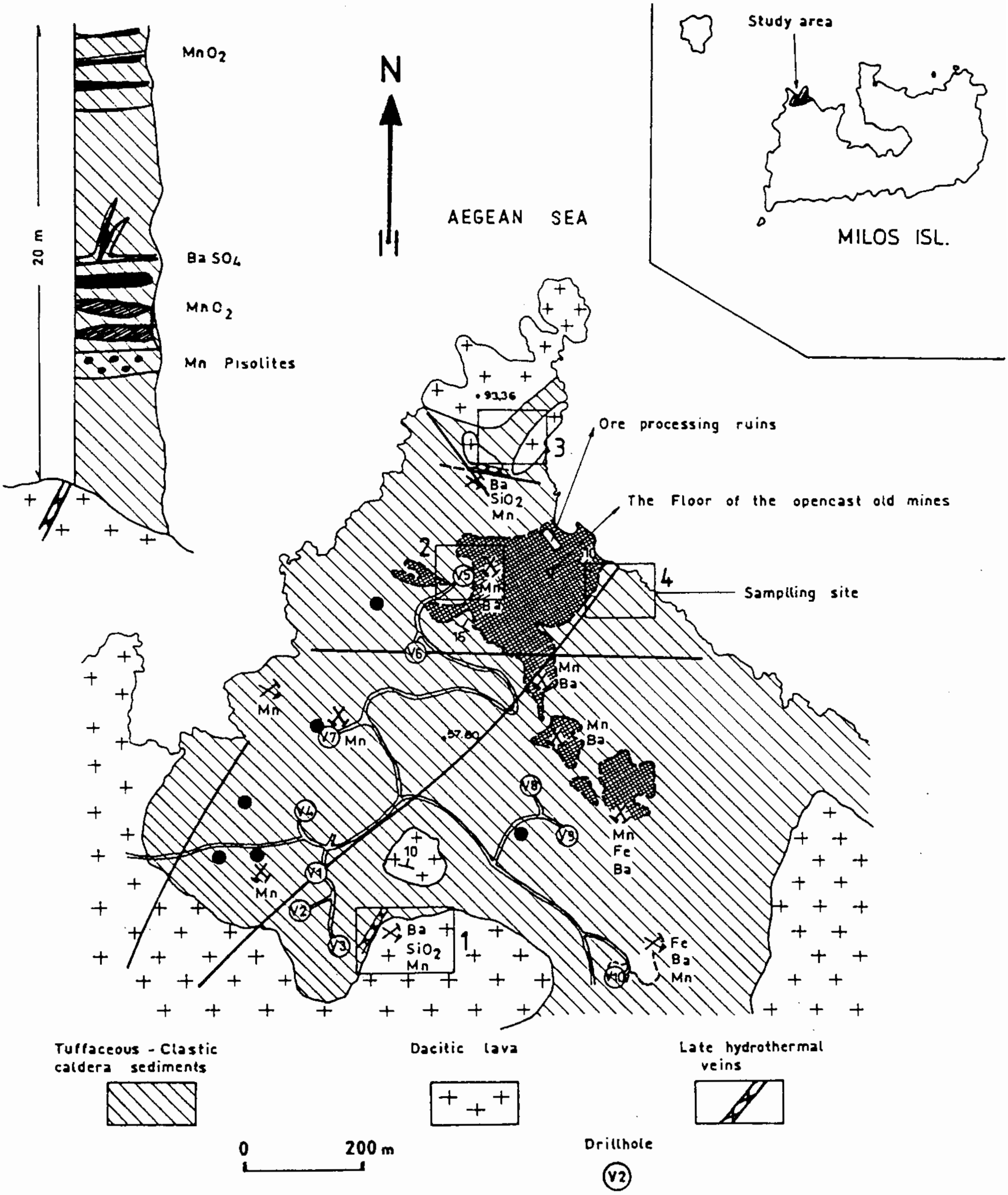

Fig. 2: General geological map and a typical stratigraphic section of the Vani Fe-MN-BA deposit, and its location on the NW tip of the Milos island, see orientation map in upper right corner.

not well mixed, but occur primarily in beds that are either enriched in MN-oxides or in barite, whereas the layers rich in iron primarily formed later, capping the BA- and MN-rich deposits. The maximum thickness of the sequence at this site is 30 m.

Site 3 is located at the northern border of the caldera, and is characterized by extensive secondary remobilizations and introduction of silica-rich solutions. These hydrothermal processes are indicated by a dense veining of manganese, barium and silica-rich minerals such as barite and chert.

Site 4 is located east of the center of the caldera. The top of the sequence contains older tuffaceous rocks that are eroded and reworked, forming sandbeds with crossbedding and conglomerate balls, some 10 cm in diameter The metalliferous sediments below this layer occur as oolithic and pissolitic horizons or as cross-cutting veins with secondary manganese minerals, e. g. coronadite (rich in Pb), crypto-melane (rich in K) and hollandite (rich in BA).

ANALYTICAL METHODS

Several speciments were collected at each site, generally representing very inhomogenous mixtures of ashlayers, barite and MN-oxide impregnations, conglomerate balls etc. Most samples therefore were cut into thin slices using

Table 1: Analyses of Vani rocks, site 1.

Rock	102	112a	112b	112c	132a	132b
SiO_2	61.90	93.74	80.65	79.29	11.15	5.75
Al_2O_3	19.73	0.31	0.15	0.31	1.00	0.53
Fe_2O_3	0.46	1.43	16.09	1.01	74.99	83.85
Fe_2O_3 AL					74.93	83.80
MnO	0.020	0.010	0.010	0.010	0.044	0.051
MgO	0.71	0.040	0.030	0.040	≈0.038	0.021
CaO	0.12	0.070	0.060	0.070	≈0.006	0.004
Na_2O	2.85	0.110	0.040	0.090	-	-
K_2O	1.35	0.040	0.020	0.020	≈0.090	0.042
TiO_2	0.62	0.042	0.080	0.45	≈0.19	0.107
P_2O_5	0.13	<0.02	<0.02	<0.02	-	0.002
Ba	0.013	0.302	0.419	7.45	<0.0005	<0.0002
$BaSO_4$	0.021	0.513	0.712	12.66	-	-
Total-I	87.89	95.79	97.13	81.29	87.50	90.36
Total-II	-	-	-	93.95	-	-
Cr	26	4.7	9	5	-	<3
Zr	72	41	30	60	≈50	31
Sr	2840	43	61	988	≈21	13
S	347	631	985	1070	1160	1250
Ni	6.6	5.7	7.9	<5	31	28
Cu	4.9	2.8	3.1	3.5	33	18
V	34	22	169	50	560	630
Zn	20	6.8	34	14	250	170
La	27	<13	<13	<13	6.5	6.3
Y	4.6	3.0	3.6	4.4	5.4	4.6
Yb	<3	<3	<3	<3	5.4	5.6
ALF (%)					85.53	92.19

Note: All major elements (SiO_2-Total-II) are given in wt.%, all traces (Cr-Yb) in ppm.

Total-I refer to sum of oxides of major ordinary rock components, Total-II to sum of major oxides and barite. Gaps in the columns means that no determination was made. AL indicates amounts of iron and manganese oxides that were leached in dilute acid, and ALF indicates the total acid leached fraction. All data for S-Yb are based on acid leach measurements. Note that barite-S, which is rather insoluble, is not included in the value for S.

a petrographic saw, which made it easier to subsample different rock- and ore-components, producing 5 to 20 g large aliquots for the chemical analysis. All subsamples were then dried at 100^{o}C, crushed and ground.

The samples were analyzed by two methods to avoid severe interferences from the excessive quantities of iron and manganese:

A) Samples poor in Fe-MN oxides were analysed in toto, using a metaborate digestion procedure for the determination of major components, and a hydrofluoric acid digestion for the trace components. The solutions were analysed in a sequential ARL 3250 atomic emission spectrometer, using an inductively coupled argon plasma as excitation source (ICP-AES) (Boström et al., 1990a, b).

B) Samples rich in Fe-MN oxides were treated by a reducing acid leach, using a mixture of 1:3 of concentrated hydrochloric acid and distilled water, spiked with the reducing agent hydroxylaminchloride. This process took place at 50-70oc for about 30-45 min., which removed all oxyhydroxides of Fe and MN, as well as all Cu, Ni, Co etc. that are hosted in these phases, but leaves essentially all silicate phases and barite behind. The solid reminder is treated according to method A discussed above. The solutions were likewise

Table 2: Analyses of Vani rocks, site 2.

Rock	202	212a-1	212a-2	212b	212c	222	232
SiO_2	17.33	24.15	23.10	21.26	18.96	10.96	18.40
Al_2O_3	4.94	6.87	6.72	6.15	5.59	2.75	5.12
Fe_2O_3	1.10	1.21	1.15	1.25	0.83	16.50	1.74
Fe_2O_3 AL	1.02		1.01	1.20	0.83	16.45	1.63
MnO_2	0.554	5.03	4.56	13.89	0.77	47.83	31.36
MnO_2 AL	0.532		4.54	13.88	0.754	47.81	31.34
MgO	0.046	0.19	0.043	<0.04	0.046	0.008	<0.07
CaO	0.037	0.070	0.043	0.059	0.065	0.012	<0.03
Na_2O	-	<0.2	<0.2	<0.2	<0.2	<0.04	<0.15
K_2O	3.61	5.77	5.48	5.05	4.40	2.40	3.96
TiO_2	0.074	0.11	0.078	0.074	0.56	0.029	0.043
P_2O_5	<0.02	<0.02	<0.02	<0.02	<0.02	0.003	0.004
Ba	36.69	31.03	27.73	22.35	34.01	0.012	14.02
$BaSO_4$	62.35	53.11	47.13	37.97	57.79	0.020	23.82
Total-I	27.69	43.40	41.17	47.73	31.22	80.48	60.63
Total-II	90.04	96.51	88.30	85.70	89.01	-	84.45
Cr	<30	16	-	-	<30	<6	<7
Zr	52	44	63	55	50	22	35
Sr	4360	5760	4960	3560	5970	<4	1720
S	460	-	704	235	520	570	360
Ni	2.7	-	5.1	12	<2.5	39	23
Cu	18	-	330	3.5	46	524	560
V	18	-	32	50	13	74	32
Zn	190	-	1930	14	290	5200	1290
La	3.7	-	12	<13	3.6	43	14
Y	2.5	-	4.2	4.4	<1.5	27	13
Yb	0.30	-	0.46	<3	0.17	2.6	1.1
ALF (%)	7.56		13.06	25.76	7.34	83.19	45.03

For explanations, see caption to Table 1.

analysed by ICP-AES. The resulting analyses were combined mathematically to show the in toto composition of the sample. The errors have been discussed in Boström et al., (1990b, 1994a, b), illustrating the accuracy and reproducibility of the data for reference basalt BHVO-1; for further examples, compare samples 212a-1 and 212a-2 in Table 3.

Table 3: Analyses of Vani rocks, site 3

Rock	302	311a	311b	311c	311d	322	334	336
SiO_2	62.97	12.62	54.72	76.20	86.55	92.35	75.71	63.38
Al_2O_3	16.27	<2	<2	<2	<0.5	0.24	0.28	0.18
Fe_2O_3	4.74	0.16	1.67	3.29	2.43	2.44	5.30	0.86
Fe_2O_3 AL	-	0.16	1.67	2.96	-	-	-	-
MnO	0.14	0.005	0.018	0.0022	0.020	0.009	0.028	0.026
MgO	0.69	<0.15	<0.15	<0.15	0.020	0.030	0.020	0.020
CaO	0.38	<0.07	<0.07	0.073	0.030	0.020	0.030	0.030
Na_2O	0.57	<0.3	<0.3	<0.3	<0.2	0.010	0.010	0.010
K_2O	10.26	<0.5	<0.5	<0.5	<0.20	0.040	0.040	0.020
TiO_2	0.44	<0.01	<0.01	0.010	<0.02	<0.02	-	-
P_2O_5	0.070	<0.003	0.005	0.006	0.020	0.010	0.030	0.030
Ba	0.364	42.86	20.70	7.89	5.77	0.33	8.78	18.20
$BaSO_4$	0.588	72.83	35.18	13.41	9.81	0.56	14.92	30.93
Total-I	96.53	-	56.41	79.58	89.07	95.15	81.45	64.56
Total-II	-	85.66	91.59	92.99	98.88	-	96.37	95.49
Cr	8.4	<15	<15	<15	<6	6	<6	<6
Zr	106	<30	<30	<30	-	-	<8	<8
Sr	140	8600	4600	1670	1810	75	2510	3900
S	250	630	590	590	-	760	2560	780
Ni	8.6	0.3	1.3	1.8	-	<5	5.1	<5
Cu	91	3.1	10	10	-	69	90	42
V	109	1.4	19	52	-	-	10	<7
Zn	3260	8.1	21	28	-	600	210	130
La	21	1.8	2.4	3.1	-	<13	11	<13
Y	25	<1.5	<1.5	<1.5	-	<3	6.8	<3
Yb	<3	<0.25	<0.25	0.41	-	<3	<3	<3
ALF (%)		6.01	7.02	8.14				

For explanation, see caption to Table 1.

RESULTS

The results for 25 samples and mean composition of different sample groups are given in Tables 1-5. Recalculated data, see further below, are shown in Table 6, and correction coefficients may be deceptive, but scatter plots show subgroupings with significant covariations.

SiO_2, Al_2O_3, K_2O and Zr. The silica distribution within the Vani caldera varies considerably, as could also be expected in view of the siliceous impregnations observed at for instance site 3. This is clearly demonstrated in Figs 3a and 3b, showing the SiO_2 versus Al_2O_3 and K_2O relations; similarly, K_2O and Zr are well coordinated with Al_2O_3 (Figs 3c-d). These plots show that one population of samples shows a strong correlation between SiO2 and these lithogenic components, whereas another set of silica rich samples show none. The first population has a fairly constant silica-alumina ratio near 3.5 which is normal for the fresh volcanic rocks on the island and hence may represent fairly little altered ash or other rock components that are mixed with other components, that is, diluted to various extent. To test this concept all analyses with normal silica-alumina ratios were recalculated to a barite-MnO_2-Fe_2O_3-free basis (BMFS), leaving a "residue" of remarkably constant composition as indicated by the small standard of errors in Table 6. The same table shows that samples with anomalously high silica-alumina ratios are distinctly different, supporting the impression obtained in field that silica-rich solutions locally have impregnated the rocks on a large scale, particularly at site 3.

Table 4: Analyses of Vani rocks, site 4.

Rock	402a	402b	412a	412b	432
SiO_2	56.58	55.22	60.51	32.71	79.41
Al_2O_3	17.46	15.14	17.35	8.11	2.37
Fe_2O_3	7.45	7.99	2.86	14.17	6.88
Fe_2O_3 AL	-	6.03	-	10.73	6.31
MnO	0.25	-	-	-	-
MnO_2	-	0.734	1.15	22.41	1.64
MnO_2 AL	-	0.622	-	22.32	1.63
MgO	0.48	0.14	0.31	0.19	<0.15
CaO	0.48	0.25	0.38	0.77	<0.07
Na_2O	0.43	0.27	0.72	0.78	<0.3
K_2O	12.00	11.55	12.63	4.23	1.47
TiO_2	0.77	0.47	0.60	0.22	0.019
P_2O_5	0.020	0.011	0.020	0.009	0.011
Ba	0.406	0.336	0.155	0.039	<0.02
$BaSO_4$	-	-	-	-	-
Total-I	95.92	91.78	96.53	83.59	91.80
Total-II	-	-	-	-	-
Cr	18	<15	10	-	<15
Zr	85	62	125	72	56
Sr	215	190	125	72	6.2
S	100	631	105	290	130
Ni	11	7.4	8.1	23	4.7
Cu	11	9.3	3.8	6.9	3.6
V	115	61	100	375	22
Zn	580	460	312	890	210
La	<13	4.6	<13	26	2.7
Y	6.8	2.9	7.1	30	3.7
Yb	<3	0.82	<3	6.3	0.82
ALF (%)	-	12.25	-	43.39	11.74

For explanation, see caption to Table 1.

Plots of these recalculated analyses are given in Figs 3e and f, which reveal that only 3 samples fall outside the distinct groups located at about 67% SiO_2-19% Al_2O_3 and at 97% SiO_2-2% Al_2O_3. It should be recalled, however, that BMGS-data "overextract" Fe; adjusting for a normal iron oxide content of some 4.5% implies that the data in column 1, Table 7, should be corrected with a factor 0.96 to obtain the corresponding fresh rock. Calculations of this type are very common, particularly in maring geochemistry, where the diluting effect from admixed carbonates, siliceous matter and sea salts may conceal the nature of the clay fraction (Chester, 1990).

Table 5: Mean compositions of Vani rocks.

Rocks with:	A. Normal SiO_2/Al_2O_3 ratios				B. Anomalously high SiO_2/Al_2O_3 ratios.					
	A-1		A-2		B-1		B-2		B-3	
	x	s.e.	x	s.e.	x	s.e.	x	s.e.	x	s.e.
SiO_2	59.44	1.5	20.9	2.2	88	3	63.0	9.1	8.5	2.7
Al_2O_3	17.2	0.8	5.8	0.6	0.22	0.04	0.5	0.3	0.8	0.2
Fe_2O_3	4.7	1.4	4.8	2.3	5.6	3.5	2.7	1.0	79.4	4.4
MnO_2	0.5	0.2	15.8	6.0	0.015	0.003	0.3	0.2	0.058	0.004
MgO	0.5	0.1	0.07	0.03	0.030	0.004	0.017	0.004	0.03	0.01
CaO	0.32	0.06	0.13	0.09	0.05	0.01	0.03	0.01	0.005	0.001
Na_2O	0.97	0.48	-	-	0.05	0.03	-	-	-	-
K_2O	9.6	2.1	4.4	0.4	0.030	0.006	0.23	0.21	0.07	0.02
TiO_2	0.58	0.06	0.15	0.06	0.03	0.02	0.07	0.06	0.15	0.04
P_2O_5	0.05	0.02	-	-	-	-	0.016	0.006	-	-
$BaSO_4$	0.4	0.1	35.3	8.8	2.9	2.3	25.7	9.0	0.0002	0.0001
Cr	16	4	-	-	7	1	-	-	-	-
Zr	90	12	49	6	-	-	-	-	40	9
Sr	700	540	3800	800	500	400	3200	1100	17	4
S	200	50	450	60	800	100	900	300	700	600
Ni	8.4	0.8	18	6	-	-	2.6	1.0	30	2
Cu	24	17	230	90	25	22	23	12	26	8
V	66	21	80	50	-	-	26	9	600	30
Zn	930	590	1500	650	220	200	90	35	210	40
La	17	7	15	5	-	-	4.2	1.7	6.4	0.1
Y	9.2	3.9	13	5	-	-	-	-	5.0	0.4
Yb	-	-	1.6	0.8	-	-	-	-	5.5	0.1
n	5		8		4		7			2

For explanations, see caption to Table 1.

The good correlation for aluminum with titanium and zirconium (Fig 3c-d), is a common geochemical feature, since they all are important lithogenic constituents, but the negative correlation between aluminum and iron is obviously a closure effect, since two constituents cannot simultaneously approach 100% concentration.

Fe_2O_3. Iron shows few correlations or subgroupings, except with V and Ni (Table 7), suggesting that some coprecipitation took place.

MnO_2. Manganese shows few good correlation's, except with Cu, Zen, In an La,

Table 6: Mean recalculated silicate fractions in Vani rocks.

Rocks with:	A. Normal SiO_2/Al_2O_3 ratios		B. High SiO_2/Al_2O_3 ratios	
	x	s.e.	x	s.e.
SiO_2	66.60	0.59	97.49	1.07
Al_2O_3	18.78	0.38	1.77	0.81
MgO	0.32	0.08	0.08	0.03
CaO	0.22	0.04	0.05	0.01
Na_2O	-	-	-	-
K_2O	12.87	1.07	0.28	0.14
TiO_2	0.54	0.13	0.31	0.16
P_2O_5	0.04	0.02	-	-
Zr	135	11	-	-
La	27	5	-	-
Y	37	14	20	10
Yb	4.8	2.2	-	-
n	13		13	

For explanations, see caption to Table 1.

Table 7: Correlation coefficients for type A Vani rocks (normal SiO_2/Al_2O_3 ratios)

	SiO_2	Al_2O_3	Fe_2O_3	MnO_2	K_2O	TiO_2	Zr	Sr	Ni	Cu	V	Zn	$BaSO_4$
SiO_2	1.00	**0.99**	-0.03	**-0.57**	**0.66**	**0.81**	**0.82**	**-0.71**	-0.50	**-0.61**	0.03	-0.28	**-0.67**
Al_2O_3		1.00	-0.09	**-0.59**	**0.60**	**0.84**	**0.79**	**-0.64**	-0.52	**-0.61**	0.02	-0.34	**-0.64**
Fe_2O_3			1.00	**0.61**	0.04	-0.07	-0.13	**-0.70**	**0.75**	0.18	**0.60**	**0.57**	**-0.61**
MnO_2				1.00	-0.47	**-0.58**	**-0.59**	-0.14	**0.96**	**0.84**	0.25	**0.69**	-0.21
K_2O					1.00	**0.56**	**0.71**	**-0.61**	-0.38	-0.41	-0.02	-0.16	0.38
TiO_2						1.00	**0.66**	-0.43	-0.42	**-0.67**	-0.03	-0.43	-0.46
Zr							1.00	**-0.63**	-0.48	**-0.63**	0.14	0.27	-0.44
Sr								1.00	-0.41	0.12	-0.50	-0.26	**0.92**
Ni									1.00	**0.73**	0.35	**0.72**	-0.35
Cu										1.00	-0.19	**0.66**	0.03
V											1.00	0.10	-0.44
Zn												1.00	-0.28
$BaSO_4$													1.00

Correlation coefficients, based on 13 analyses of Vani rocks with silica-alumina rations near 3.0.4.0. Correlations with absolute values larger 0.53 are shown in bold face and are significant at least at the 95% level (29 cases), absolute values larger than 0.66 (14 cases) are significant at the 99% level of confidence (Crow et al., 1960). Many correlation coefficients based on all Vani data are much lower and frequently lack real meaning, as the plots in Fig 3 show.

see Fig 4a and Table 7. However, the correlation's with Cu and In are widely observed relations.

$BaSO_4$. Barium is here reported as barite, which is the only form found in BA-rich samples from Vani. Barite shows good positive correlation only with SR, see Fig 4b, and Table 7.

The distribution patterns show that the Vani deposits consist of mixtures of a) volcanic matter, such as ashes and other rock detritus (VM), b) cherty materials, i. e. rich in SiO_2 (SiM), c) manganese rich matter, mostly consisting of higher oxides (MnM), d) iron rich matter, mostly oxides (FeM) and e) barium rich matter, almost exclusively consisting of barite (BaM). Such mixtures can be expressed by the relation:

$$RD = (xVM + ySiM + zMnM + vFeM + wBaM).$$

In which a real deposit RD is a function of the various input phases and in which x, y, z, v and w are input fractions needed to the optimize the fit between the composition of the real deposit and of the mixture. Modelling using real suspected input phases as factors is essentially a form of target factor analyses (Malinowski, 1991) and differs form ordinary factor analysis, which only derives abstract factors that lack physical and chemical meanings. Target factor analysis has proved to be important in the study of many marine geological problems, in environmental research and the study of meteorite compositions (Mason, 1962; Boström et al., 1978, Chester, 1990).

GENETIC MODELS AND DISCUSSIONS

The Vani caldera deposits show remarkable similarities with other Fe-MN deposits in that they are rich in BA and that Cu shows a distinct trend to concentrate in manganese ores. Thus, the Langban ores, and similar deposits in South-Central Sweden (Harstigen, Pajsberg, Sjorguvan) consist of Precambrian stratified ore lenses of either iron oxides or manganese oxides, which chemical are well separated, yet spatially were so closely occurring that both

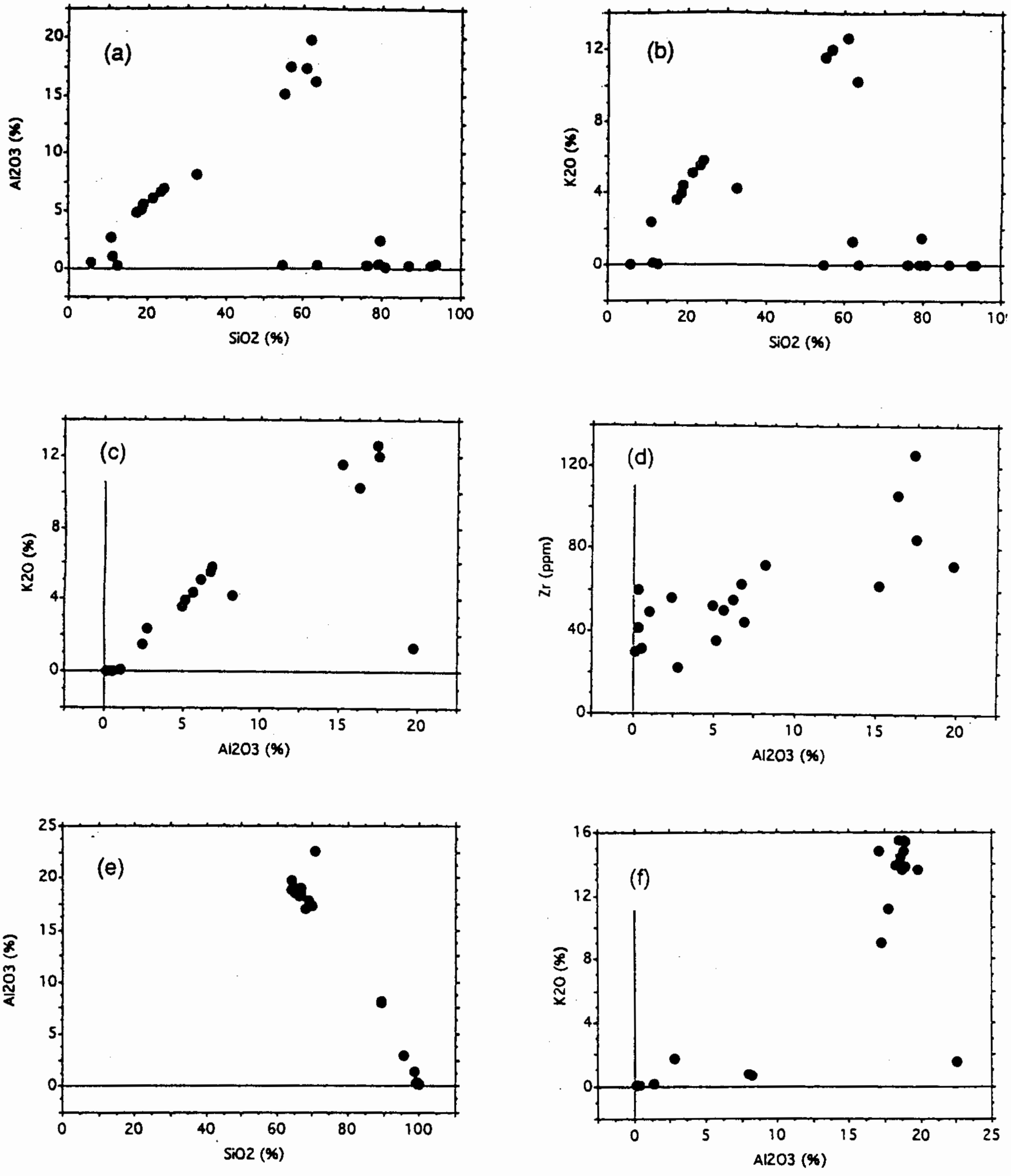

Fig. 3: Interelement variations between the lithogenic components SiO_2, Al_2O_3, K_2O and Zr in rocks from the Vani caldera; for details, see text.

ore types could be recovered in the same gallery in the mine. The ores occur together with silicic tuffaceous volcanites, slightly richer in silica and poorer in alumina than the calcalkaline tuffs on Milos (Magnusson, 1930). Magnusson thought that the ores had formed by emplacement at some depth in the crust, but did not completely rule out an exhalitive-sedimentary origin, Later it was concluded (Boström et al., 1979) that an exhalitive-sedimentary origin was the most likely one, since emplacement of the ores at depth could not explain the high degree of oxidation of the ores, which originally were very rich in Fe_2O_3 and Mn_2O_3, possibly in an environment partly resembling that in the present Atlantis II Deep in the Red Sea (Bischoff, 1969); a related hypothesis was advanced by Frondel and Baum (1974) for the Franklin deposit in New Jersey, which likewise resembles Långban.

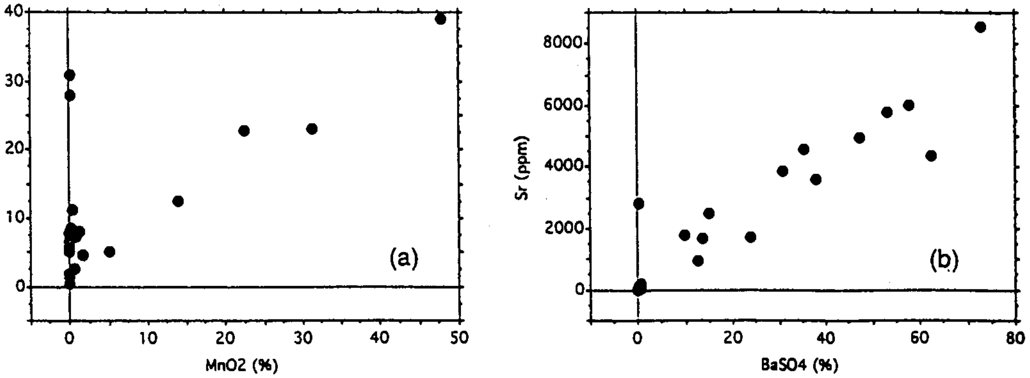

Fig. 4: Interelement variations between MnO_2 and Ni, and between $BaSO_4$ and Sr in rocks from the Vani caldera; for details, see text.

The high concentration of Fe in Vani or Langban is not a major problem to model by leaching of rocks by ascending hot water solutions. Iron is a ubiquitous component in most rocks, and even low leaching efficiencies suffice to model observed iron concentrations. However, the metals MN, BA and to some extent also Cu are harder to explain by leaching. Most volcanic rocks contain only small quantities of manganese, some 0.2% MnO, and contents of BA are generally still lower, that is, the occurrence of MN and BA rich beds requires intense and widely occurring leaching processes. Furthermore, leaching experiments involving hot saline solutions reacting on basalts have been successful in producing Fe-MN-rich hot solutions, but form too low concentrations of Zn and other ore components (Rosenbauer and Bischoff 1983). Likewise, many hot spring systems on the Earth have failed to develop metalliferous deposits, in contrast to what could be expected if water-rock reactions were the sole source (Boström, 1990); particularly in regions with thick continental crusts there is a distinct paucity or total lack of economic deposits even if temperature regimes are high, see references in Boström (1990). Furthermore, those epithermal systems that form precious metals deposits in shallow sections of the Earth's continental crust (Berger and Bethke, 1985) primarily occur in calc-alkaline terranes in e. g. western USA, which have been welded onto the continental shield by plate tectonic processes. Thus, it is wellknown that calc-alkaline magmas are generated at specific depths on subducting oceanic plates (Burnham, 1979).

However, already Coats (1962) had inferred that oceanic crust-components partook in the genesis of the Aleutian arc and Scholl et al., (1977) refined the subduction-related concepts still further.

These observations suggest that extraction of metals from rocks by hot solutions may be a large-scale process only at oceanic spreading centers, where temperature regimes are exceptionally intense, whereas elsewhere the reaction rates may be either too low to support a major metallogenetic process by leaching alone or the crustal thickness may be too big to permit the metallogenetic solutions to migrate high up. Sillitoe (1972) therefore suggested that subducted metalliferous sediments are the primary sources for some ore deposits. Supporting data was shown by Park (1972), who pointed out the parallellism in the occurrence of calk-alkaline rocks and mangetite-apatite ores in an "iron" ring around the Pacific. Tests of subduction models, using thermodynamic data, show that MN, Fe and other constituens can be selectively released from subducted metalliferous sediments and surface as various solutions and magmas, some being rich in magnetite (Boström, 1981). Such magnetite lavas are particularly well known form Chile (Frutos and Oyarzun, 1975).

For deposits of Mesozoic or younger age there are thus compelling reasons to consider subduction zone generated-ore models, but for older deposits the genesis is hard to discuss since little is known about former subduction zones. The big magnetite ores at Kiruna, North Sweden, have been assumed to have a sedimentary origin), although extreme metamorphosis has destroyed all sedimentary features (Landergren, 1948). Parak (1975) considered the ores to be related to volcanic processes like those at Ebeko in the Kuriles, where major iron-rich deposits are forming (Zelenov, 1972). However, both hypotheses are related, since the volcanism at Ebeko may be associated with subducted metalliferous sediments. The major reason Landergren (1948) considered sedimentary deposits as source beds for later formed, magmatic looking ore bodies, was the fact that no other geochemical processes on the Earth can produce such largescale separation of the chemical components, forming resistates, hydrolysates, oxidates, carbonates and evaporates, including many chemical deposits such as phosphorites, laterites and sedimentary iron and manganese ores.

The evidence thus suggests that not only the calc-alkaline rocks but also the ore at Vani have their main source at the subducted plate under HVA, and that the ores represent remobilized metalrich marine sediments; thermodynamic modelling by Boström (1981) suggests that this is a possible process. That per se is no proof, however, but points to a problem that should be further studied.

The small size of the Vani deposit and its different geochemistry compared to that of Santorini (Boström et al., 1990b; 1994b) is a major problem for this model). However, it should be recalled that sediments may vary considerably in composition, that is, the sedimentary source beds under Vani and Santorini may be quite different. A conventional rock-leaching model on the other hand, should rather lead to the development of very similar exhalative-sedimentary deposits.

Mitropoulos (1993) pointed out that the volcanic matter in the central part of HVA, e. g. at Santorini, derives from a deep part of the subduction zone whereas volcanic materials further west, such as Aegina, Methana and Poros, ascend from a shallower section of the subduction zone. At small subduction depths only little material except possibly some volatiles are mobilized from subducted old sediments and crustal matter due to limited heating. With increasing subduction and subsequent increased heating compounds of MN may be selectively lost from the downgoing slab, since MN-compunds are more easily reduced and dissolved, whereas iron compounds are remobilized only at still higher temperatures (Boström, 1981). This sequence of events could therefore explain the differences between the older Vani and the younger Santorini deposits, the former being fed at an early state from a fairly young subduction slab at intermediary depths, which easily could supply much MN, whereas the volcanism at Santorini presently is fed from a deeper and older subduction slab, that now has lost most MN and primarily is supplying iron.

This chemical release sequence is explains the unusual chemical stratigraphy found at Vani, where the Fe-ores form the late capping sections, indicating a separation of Fe and MN already at depth. In other cases, when Fe and MN are discharged simultaneously one would expect Fe to deposit first because of its strong tendency to oxidize easily.

CONCLUSIONS

Much of the Fe, Mn and Ba in the Långban and the Vani deposits may be mobilization products from a subduction zone at an island arc. Different depths of mobilization of the elements may explain the puzzling compositional differences between the deposits in the Vani caldera and in the Santorini caldera.

ACKNOWLEDGEMENTS

The chemical analyses were performed by Mrs Birgitta Boström; this assistance is greatly appreciated. Furthermore, we thank Geological Survey of Greece for kind permission to work on Milos. This work was supported by the Swedish Natural Sciences Research Council; this support is gratefully acknowledged. We furthermore thank our unknown reviewers of the manuscript for valuable comments.

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