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MANGANIFEROUS CHERTS IN SILICEOUS SEDIMENTS OVERLYING THE KOZIAKAS OPHIOLITE, WESTERN THESSALY, GREECE

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ABSTRACT

In the Koziakas range of Greece, manganiferous cherts are hosted within Jurassic siliceous sediments that are spatially associated with ophiolitic basalts. Pyrolusite and minor manganite and barite are found within the manganiferous cherts. The Fe/Mn ratio is very low (0.005). Mn, Ni, Cu and Zn are positively correlated with each other, whereas a negative correlation exists between Si and these metals. A comparison of the chemistry of the manganiferous cherts with ocean-floor metalliferous sediments, Fe–Mn crusts and deep-sea nodules suggests that they were formed as a result of hydrothermal and hydrogenous precipitation of metals. The close association of the siliceous sediments with the ophiolitic basalts and the geochemical features of the manganiferous cherts suggest that the manganese oxides were formed on the flanks of a spreading ridge, away from fields of hydrothermal vents.

Keywords: manganiferous cherts, metalliferous sediments, Jurassic radiolarian cherts, ophiolite, Koziakas range, Greece.

SOMMAIRE

Des cherts manganifères ont été découverts dans la chaîne de Koziakas, en Grèce; ils font partie d'une séquence sédimentaire jurassique associée à des basaltes ophiolitiques. Les cherts contiennent pyrolusite et, comme accessoires, manganite et baryte. Le rapport Fe/Mn est très faible (0.005). Mn, Ni, Cu et Zn font preuve d'une auto-corrélation positive, tandis que Si montre une corrélation négative avec ces éléments. D'après une comparaison de la composition des cherts manganifères avec celle des sédiments métallifères et des nodules des fonds océaniques, et des croûtes à Fe–Mn, ces sédiments résulteraient de la précipitation hydrothermale et hydrogénétique des métaux. L'étroite association de ces sédiments manganifères siliceux et des basaltes ophiolitiques, aussi bien que leurs traits géochimiques, font penser que les oxydes de manganèse ont été précipités sur les flancs d'une ride océanique, à une certaine distance des évents hydrothermaux.

(Traduit par la Rédaction)

Mots-clés: cherts manganifères, sédiments métallifères, cherts à radiolaires jurassiques, ophiolite, chaîne de Koziakas, Grèce.

INTRODUCTION

Occurrences of manganese oxide mineralization genetically associated with ophiolites occur in many localities of continental Greece and the Peloponnesus. Most of these occurrences are of small tonnage and low grade. The mineralization is hosted in cherts and radiolarian cherts and forms pockets or disseminations, mainly of manganese oxides. The geology, mineralogy and geochemistry of the Mn deposits have been studied by various authors (Kiskyras 1957, Spathi 1964, Markopoulos & Skounakis 1980, Panagos & Varnavas 1980, 1984, Skounakis & Markopoulos 1981, Varnavas & Panagos 1983, 1984, Robertson & Varnavas 1990, Varnavas *et al.* 1991). Combined geological, mineralogical and geochemical investigations indicate that the manganese mineralization is a result of hydrothermal processes associated with submarine volcanic activity in small oceanic basins during the Jurassic.

More recently, new geological and petrological findings indicate that parts of a dismembered ophiolite are exposed in the Koziakas range (Capedri *et al.* 1985, Lekkas 1987). Siliceous sediments are associated with the ophiolite. Several outcrops of manganiferous cherts appear in these siliceous rocks, near the villages of Genesi, Mouzaki and Xylopariko (Fig. 1A).

In this paper, geological and geochemical data are discussed in terms of the origin and tectonic setting of the mineralization.

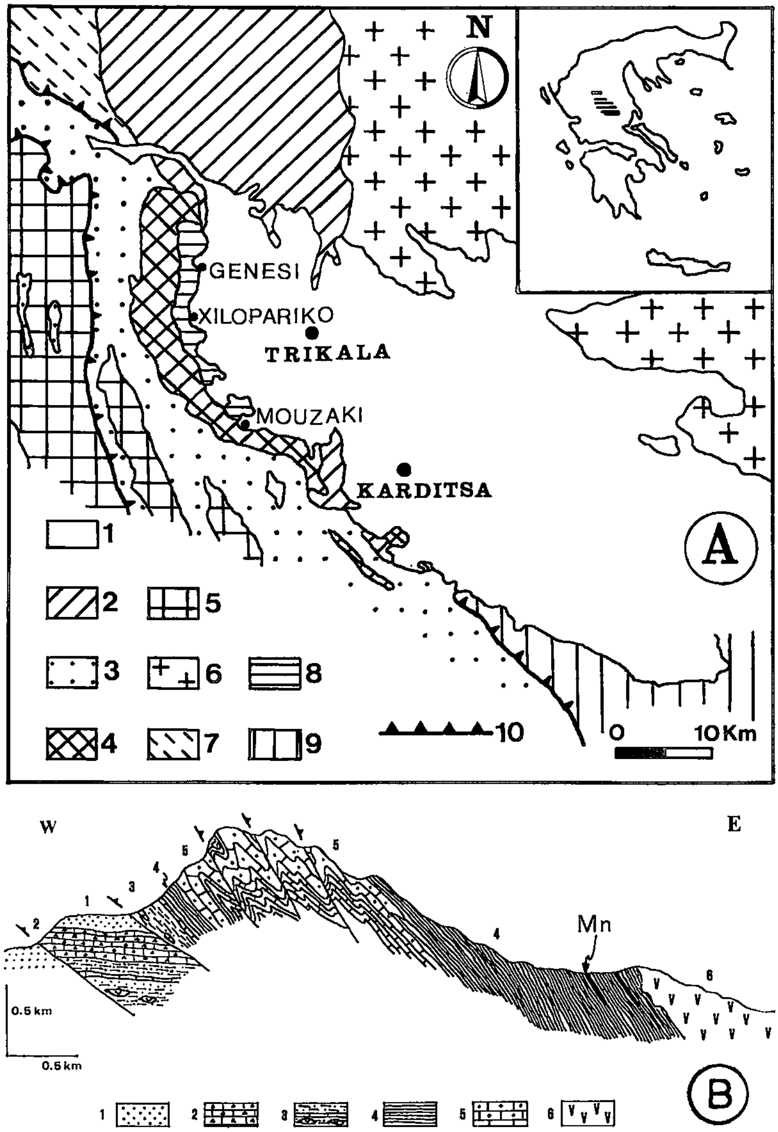

FIG. 1. A. Geological sketch-map of the area of western Thessaly (Capedri *et al.* 1985). 1. Quaternary, 2. Molassic sediments, 3. Tertiary flysch of the Pindos Unit, 4. Western Thessaly Unit, 5. Mesozoic sequence of Pindos Unit, 6. Pelagonian units, 7. Northern Pindos ophiolite, 8. Koziakas ophiolite, 9. Othris ophiolite and transgressive Cretaceous sediments. B. Simplified general section of the Koziakas range (after Capedri *et al.* 1985) showing the setting of manganiferous cherts. 1. Tertiary flysch, 2. Upper Cretaceous limestones, 3. Upper Jurassic - Lower Cretaceous clastic sequence (flysch) rich in ophiolite detritus, 4. Radiolarites and red pelites, 5. Upper Triassic - Jurassic limestones, 6. Ophiolitic rocks of Koziakas range.

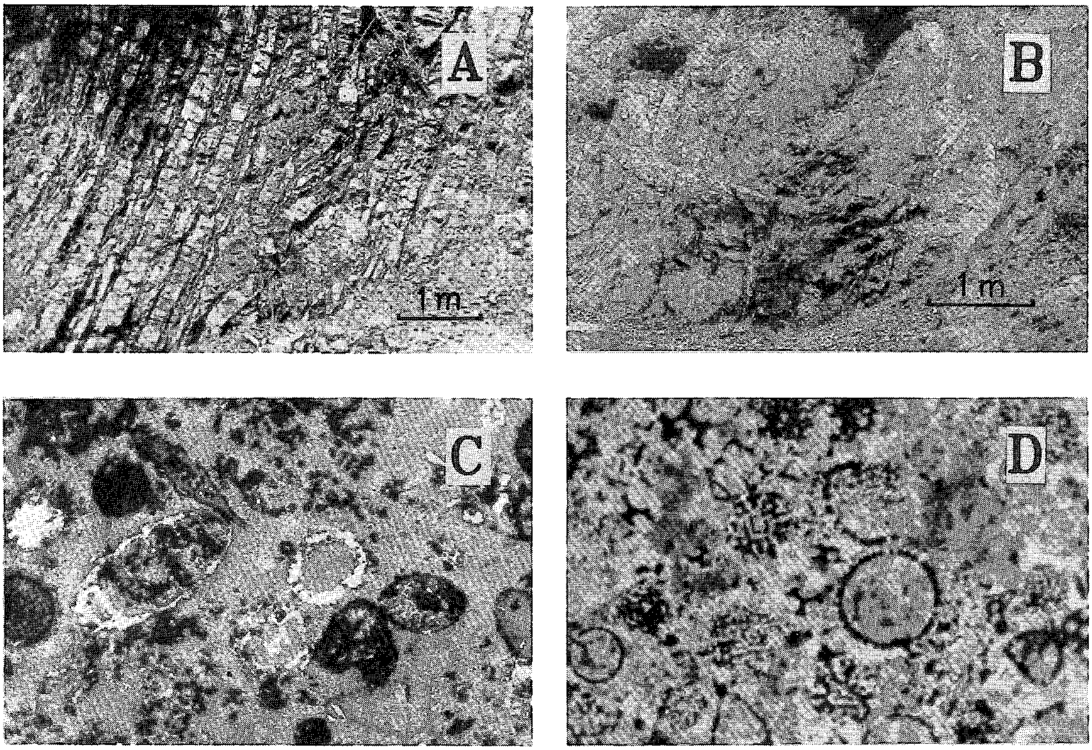

FIG. 2. A. Alternation of parallel-laminated red cherts (light) and pelites (dark) in the Genesi area, Koziakas. B. Manganiferous massive cherts (dark) in bedded cherts and radiolarites (light). C. Skeletons of radiolaria partly replaced by pyrolusite, set in a matrix of fine-grained manganese oxides and quartz, Xylopariko (reflected light). D. Microcrystalline quartz (light) with disseminated grains or aggregates of manganese oxides (dark), and radiolaria replaced by pyrolusite, Genesi (transmitted light).

GEOLOGICAL SETTING

The Koziakas Mountains consist of a sequence of Triassic to Eocene carbonates, cherts, radiolarites and clastic sediments, and Jurassic ophiolitic rocks. The lower part of the sedimentary sequence comprises Triassic to Upper Jurassic carbonate and siliceous rocks, whereas the upper part contains carbonate and clastic rocks of Jurassic to Eocene age. The ophiolitic rocks of Koziakas are thrust over the sedimentary rocks, and the whole Koziakas Unit is thrust over the Pindos Unit (Fig. 1A). These ophiolitic rocks occur along a NW–SE alignment of ophiolite outcrops, with the Othris and Pindos ophiolites to the southeast and northwest, respectively. The general structure of the Koziakas range and the geological setting of the manganiferous cherts are shown in the geological section (Fig. 1B). The ultramafic section of the ophiolite comprises mantle tectonites ranging from spinel harzburgites to plagioclase harzburgites. Pillow lavas interstratified with cherts show a MORB affinity; variable geochemical signatures include normal, transitional and enriched MORB (Capedri *et al.* 1985). Massive gabbros occur in minor amounts to the northeast of Mouzaki; scarce dykes of olivine gabbro cross-cut ultramafic rocks.

Sequences of pillow lava commonly contain interbedded siliceous sediment. Micropalaeontological data indicate an Upper Jurassic age (Lekkas 1987). Sections of siliceous sediment consist of two main alternating lithologies: chert – radiolarian chert and pelite (Fig. 2A). Chert beds are parallel-laminated, reddish brown to beige, and 5 to 30 cm thick. They are composed of quartz and minor amounts of clay minerals, chlorite and hematite. Cherts contain 88–92% SiO_2, $<1\%$ Fe_2O_3, $<1.5\%$ MnO and 2.5–3.0% Al_2O_3 (Skarpelis, unpubl. data). By mode of occurrence, mineralogy and chemistry, the chert beds compare well with the Jurassic bedded cherts overlying ophiolites in the Northern Appennines (Barrett 1981, 1982). Pelitic beds are red to brown and 3 to 5 cm thick. Radiolaria are commonly found in the chert beds. The stratigrafically lower part of the siliceous section contains blocks of ophiolitic basalt, being possibly deposited within the sediments during early stages of siliceous sedimentation.

Mode of Occurrence

The manganiferous cherts at Koziakas occur as massive lenses that lie concordantly within bedded red cherts and radiolarites (Fig. 2B). Maximum thickness of the lenses ranges from 5 cm to 1 m. Commonly, two or more lenses are separated by cherts. Pinch-and-swell structures are rare. Lenses of manganiferous chert gradually pass laterally into barren red cherts, suggesting that the two types of chert were deposited coevally.

Methods

Mineralogy was investigated using optical microscopy, X-ray powder diffractometry and electron-microprobe techniques. Fe$K\alpha$ radiation was used for Mn-rich specimens. Samples of manganiferous cherts taken from various lenses were analyzed using inductively coupled plasma emission spectrometry at the Institute of Geology and Palaeontology, Technical University of Braunschweig. Measurements were carried out on dilute solutions following decomposition with hydrofluoric–perchloric acid. The analytical precision was found to be better than $\pm$ 5%.

Mineralogy and Geochemistry

The main manganese oxide mineral is pyrolusite. Manganite relics and barite are rare. The manganese oxides are commonly disseminated within the microcrystalline siliceous matrix. Radiolaria are preserved within the manganiferous cherts, with their skeletons commonly replaced by pyrolusite (Figs. 2C, D).

The manganiferous cherts have low concentrations of all the major elements except for Si and Mn (Table 1). They contain between 27 and 46 wt% Mn, and between 13.4 and 25.7% Si. The concentration of Fe is extremely low. Extreme fractionation of Fe from Mn is indicated by the very low Fe/Mn value (0.005). The concentrations of Ni, Co and Cu are lower than those of modern oceanic hydrogenous sediments and nodules formed by slow precipitation from normal seawater, and slightly higher than those of typical hydrothermal deposits (Bonnatti *et al.* 1972) (Fig. 3). Co is markedly enriched in the manganiferous cherts relative to typical hydrothermal deposits, and shows a slight positive correlation with Fe, Mn and Cu. The Si/Al ratio is low (Fig. 4), and resembles values in hydrothermal ores like the manganiferous chert deposits of the Franciscan ophiolite in California (Crerar *et al.* 1982). Si is negatively correlated with all elements except Ba, whereas Fe, Mn, Cu, Ni and Zn are positively correlated with each other (Table 2). Ba is depleted in the manganiferous cherts relative to ferromanganese nodules and to manganese oxide crusts from the Galapagos Hydrothermal Mounds Field (Leg 70). Similar levels of Ba concentration have been reported from the Thessaly, Euboea and some Pindos deposits, where it is associated with the Mn-oxide fraction (Varnavas & Panagos 1983, Varnavas *et al.* 1991). Co shows a slight positive correlation with the other metals.

TABLE 1. AVERAGE CHEMICAL COMPOSITION OF KOZIAKAS MANGANIFEROUS CHERTS AND DATA ON RECENT METALLIFEROUS DEPOSITS

	1	2	3	4	5	6	7
Si wt.%	20.96	1.45	–	–	–	16.30	–
Mn	36.20	47.00	41.00	55.00	46.23	48.00	22.20
Fe	0.17	0.66	0.80	0.20	2.22	4.90	19.00
Al	0.11	0.24	–	–	1.61	7.50	–
Ti	0.01	0.03	–	–	–	0.36	–
Ca	0.11	0.98	–	–	0.93	12.50	–
Ni ppm	94	124	310	180	137	4400	5500
Co	204	13	33	39	16	35	1300
Cu	40	80	120	50	22	2000	1480
Zn	57	93	400	2020	74	2200	750
Ba	1407	2400	–	–	–	–	–

1. Koziakas manganiferous cherts (average of 8 analyses). 2. Mean values for manganese oxide crusts from the Galapagos hydrothermal mounds field, DSDP Leg 70 (Moorby & Cronan 1983). 3. Hydrothermal deposit at non–spreading center, southwestern Pacific (Moorby *et al.* 1984). 4. Hydrothermal deposit at spreading center, Galapagos region (Moore & Vogt 1976). 5. Manganese crusts from the hydrothermal mound field near the Galapagos spreading center (Varnavas, unpubl. data, cited in Panagos & Varnavas 1980). 6. Ferromanganese nodules, MANOP site H, Pacific (Dymond *et al.* 1984). 7. Hydrogenous crust (Dymond *et al.* 1984).

The chemical composition of the Koziakas manganiferous cherts is generally comparable with that of Mn deposits described from Othris, Thessaly and Euboea (Panagos & Varnavas 1984, Varnavas *et al.* 1991), and with manganese deposits found at the base of the chert section of the Northern Appennine ophiolites (Bonnatti *et al.* 1976).

Discussion

The mode of occurrence of the manganiferous cherts indicates a synsedimentary deposition, whereas the geochemical data suggest that hydrothermal processes played an important role in their formation. The Koziakas samples are chemically comparable with recent oceanic hydrothermal Mn-rich deposits, and especially with

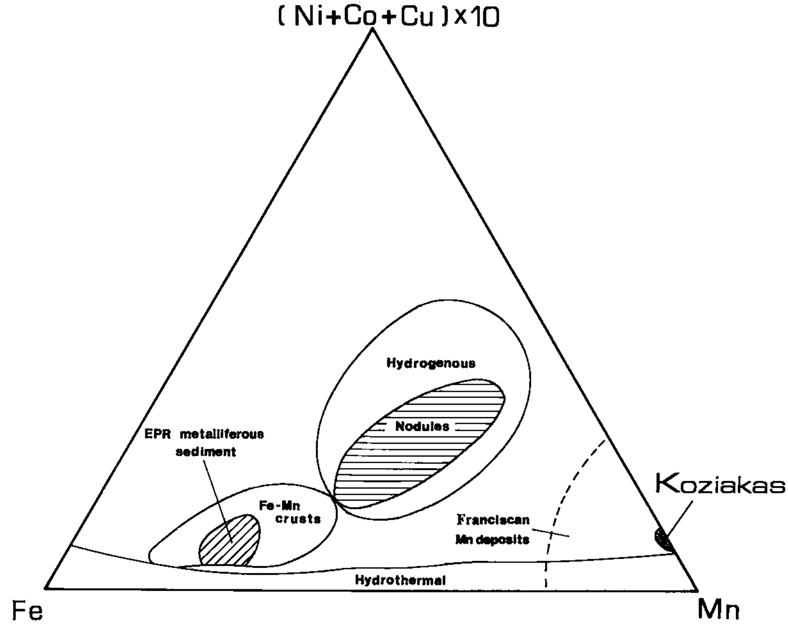

FIG. 3. Triangular diagram showing Mn - Fe - (Ni+Co+Cu) × 10 for the manganiferous cherts of Koziakas. Fields for submarine Fe–Mn deposits are given for comparison: hydrothermal deposits and hydrogenous sediments after Bonnatti *et al.* (1972), Franciscan deposits after Crerar *et al.* (1982), Fe–Mn crusts and ferromanganese nodules after Toth (1980), and East Pacific Rise metalliferous sediments after Corliss & Dymond (1975).

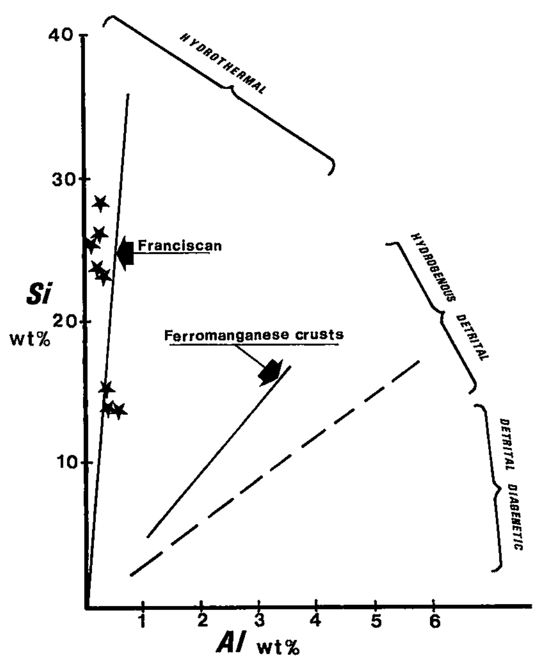

FIG. 4. Si *versus* Al diagram (from Crerar *et al.* 1982) in which compositions of Koziakas manganiferous cherts are compared with fields of typical marine sediments.

manganese crusts from the field of hydrothermal mounds near the Galapagos spreading center (Table 1).

The strong negative correlation between Si and all the metals examined indicates that silica acts as a diluent, as also described for Mn deposits of Thessaly and Euboea (Varnavas *et al.* 1991). The concentration of Ba is negatively correlated with that of Fe, Mn, Cu, Ni and Zn. Although Ba enrichment in hydrothermal sediments is well documented, the positive correlation of Ba with Si and Co suggests that at least some of it is of hydrogenous origin. Since Co shows no evidence of enrichment in hydrothermal deposits (Moore & Vogt 1976, Toth 1980), the higher concentrations detected in the manganiferous cherts suggest a

TABLE 2. CORRELATION COEFFICIENTS BETWEEN ELEMENTS IN THE MANGANIFEROUS CHERTS OF KOZIAKAS

	Si	Fe	Mn	Cu	Ni	Co	Zn	Ba
Si	1							
Fe	–0.48	1						
Mn	–0.99	0.45	1					
Cu	–0.91	0.57	0.89	1				
Ni	–0.88	0.23	0.87	0.89	1			
Co	–0.16	0.38	0.14	0.24	–0.12	1		
Zn	–0.94	0.54	0.94	0.78	0.70	0.20	1	
Ba	0.26	–0.40	–0.25	–0.46	–0.44	0.22	–0.14	1

partial hydrogenous origin. This metal, along with Ni and Cu, may have been coprecipitated or adsorbed onto colloidal Mn hydroxides. Strong hydrogenous inputs are important in areas of slow rates of sedimentation, which favor the slow accumulation of Mn oxides typical of deep-sea manganese nodules. The strong positive correlation of Ni, Cu and Zn with Mn (Table 2) suggests their association with the Mn oxides.

Lalou (1983) considered two models for the formation of hydrothermal and hydrogenous metalliferous deposits. In model I, the two types of deposits had independent sources of elements, the metalliferous crusts having a local hydrothermal source, related to submarine volcanic activity, and Mn nodules from abyssal plains, having a hydrogenous source. In the second model, both the metalliferous crusts and the nodules received an input of hydrothermal Mn and other metals derived from axial or off-axial hydrothermal vents. Most of the exhaled hydrothermal Mn probably accumulates close to the parent vent, whereas a fraction is dispersed in ocean water. Lalou suggested that the hydrothermal fraction of Mn is transported over the abyssal plains in the form of hydroxide particles. As an excellent scavenger for trace metals dissolved in seawater, it becomes enriched in Ni, Cu and Co during its transport, and may represent the main source of Mn in ferromanganese nodules.

In the case of the Koziakas manganiferous cherts, metal deposition may have occurred on the flanks of a spreading ridge, where siliceous sediments were deposited. This conclusion is supported by the following points: a. The geological link of the bedded cherts with MORB-type basalts of the ophiolite. The manganiferous cherts, which lie within siliceous sediments that originally capped the ophiolite, were probably deposited away from the axis of the spreading ridge. b. The geochemical features of the manganiferous cherts indicate that submarine hydrothermal exhalations rich in Mn were responsible for their formation. The hydrogenous input of some trace metals suggests that the Mn oxides accumulated relatively slowly, which is consistent with deposition away from a center of hydrothermal discharge.

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