Iulia (North Dobrogea, Romania): Lower Triassic iron ore of sedimentary-exhalative origin (Sedex)

Albert BALTRES

Geological Institute of Romania, 1, Caransebeş Str., 012271, Bucharest, Romania

Abstract: The iron ore described here is related to Lower Triassic, deep-sea carbonate rocks and consists of a series of isolated lens-like bodies extended in an over one kilometer wide syncline. Maximum normal thickness of an individual lens does not exceed a few meters. The mineralization consists of centimeter-scale shiny bands of hematite, interlayered with green, dull, fine grained garnetiferous bands. The unusual parageneses, particular garnet compositional variation and crystal chemistry, and also the presence of abundant clusters of solid inclusions of halite in lamellar hematite, revealed by SEM, electron microprobe and XRD, were here interpreted as a result of sedimentary-exhalative processes. Certain features, such as load casts and centimeter-scale intrastratal slides and recumbent folds, as proofs of deformation in plastic state, might be attributed to deposition of gravitationally unstable precipitates on the sea floor. Interlayering of hematite and fine grained garnetiferous bands suggest alternate environment changes. The *ore* from Iulia has been formed probably by deposition on the sea floor, in association with some amounts of *chemical sediment*, as a result of hydrothermal activity that accompanied volcanic events at or near the Lower Triassic sea floor. The nature and origin of the associated carbonate rocks help to establish the connection between ore and its environment, because these rocks consist of deep-sea debrites, turbidites and pelagic sediments. Positive evidence of submarine volcanism, such as minor intercalations of spilitized basaltic magma, was also found, although not in close spatial relationships with the mineralisation.

Keywords: Iron ore, Garnet, Grandite, Sedimentary-Exhalative (SedEx), North Dobrogea, Romania

1. Introduction

The iron ore described here occurs at Movila Hill, south-west of Iulia, a small village in the Tulcea County, North Dobrogea (Figs. 1, 2). The iron mineralization from Iulia was first mentioned by Savul (1935). The ore is related to Lower Triassic deep-sea carbonate rocks belonging to the Somova Formation, with a great extent in North Dobrogea (Baltres 1982, 1994), and consists of a series of isolated lens-like bodies filling up an over one kilometer-wide syncline. The ore occurs not far away from the contact with a large fault (Cetăţuia-Consul Fault) to the

Tel: +40213060400; fax: +40213181326
e-mail: alxbal@yahoo.com

west. The orebody fades out within a distance of ca. 2 km towards the north. The exploration of the ore began in 1951 and consisted of open pits, drill holes and underground mining works (adits and shafts). As the exploration evidenced resources that do not exceed three million tons, with a grade of up to 25.5% Fe, the mineralization was considered of no commercial interest, and its investigation was ended in the early '90s. In arriving at an understanding of the ore genesis we produce new bulk rock and mineral analyses (XRD, SEM and electron microprobe), reaching the conclusion that the data obtained argue for the sedimentary-exhalative hypothesis, as previously supposed by Constantinescu and Anton (1979, cited by Constantinescu et al. 1987) and then by Baltres (1984).
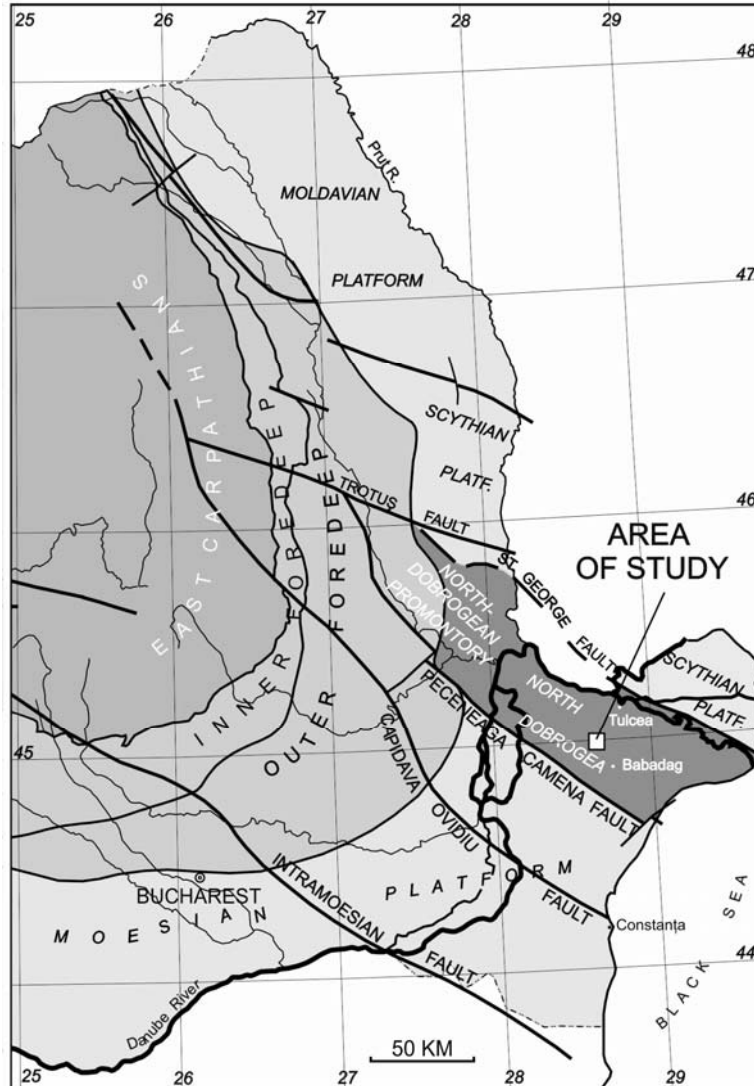
Fig. 1. Structural map of eastern Romania (after Săndulescu and Visarion, 1988, *passim*), showing the location of study area.

2. Geologic setting

The Somova Formation, with a large extent in North Dobrogea and containing in its lower part the mineralization from Iulia, is a geologic body of limestones, more than 750 m thick, associated with minor basalt flows, gabbro intrusions and small stratabound iron, copper and barite deposits. The lower part of the formation is transitional with the underlying Bogza Formation. Somova Formation ends with a rhyolitic member (Consul Rhyolite), up to 200 m thick, and is overlain abruptly by the Nodular and Bioturbated Formation.

Lithologically, Somova formation consists of a sequences of dark limestone beds, 0.5 to 20 cm thick, which are calcarenites grading to micrite, and large intervals with up to ten meters thick beds of limeclast debrites. The limestone layers exhibit sedimentary and biogenic features common in turbidites. The micrites commonly grade vertically into thin, dark shale layers, interpreted as pelagic successions. The depositional model proposed to explain these rocks invoke the emplacement by some type

4

of sediment gravity flow (turbidity and debris flow) (Baltres, 1982, 1994).

The Somova formation has similarities with the Lower Triassic marine sequence of Youjiang sedimentary province in southern China, containing also deep-water clastic and carbonate rocks, including calcirudites and pyroclastic rocks (Luolou and Ziyun formations) formed at the margins of a deep basin, in front of a carbonate platform (Tong and Yin, 2002). Even the macroafaunal and microfaunal content is closely similar with the North Dobrogean formation.

As concerns the paleotectonic setting, in the Early Triassic and later, the North Dobrogean subsiding block, receiving sediments and then volcanics and intrussive gabbro sheets, was situated in the western part of an extensional basin located in the consuming Palaeotethys Ocean. This basin begins to open as a Late Permian-Early Triassic back-arc type marginal oceanic basin, behind the Cimmerian and North Tibet continental slivers[1]. Thus, the geological environment in which the Somova Formation evolved was a fault-controlled setting resulted by extensional tectonics. The back-arc basin was destroyed during the Late Triassic collision of the Cimmerian terrane with the Eurasian Margin (Stampfli et al., 2001). The Lower Triassic sediments, volcanics and ores, recording distinctive signature, resulted somewhere in the mentioned basin, experienced the Late Triassic processes associated with the collision, and reached their present position in the Upper Cretaceous by far-reaching horizontal translations to west. It results that the North Dobrogean block, with its Triassic cover, is a Palaeo-Tethyan remnant resembling a wedge-shaped sliver forced in a gap between the Moesian and Scythian platforms (Fig. 1).

In the Iulia zone, the Somova Formation is confined to a narrow belt between two reverse faults running NNV-SSE: the steep main fracture named Cetăţuia-Consul Fault (also known as Luncaviţa-Consul Fault) in the west and Meidanchioi-Iulia Fault in the east (Fig. 2). Subsequently, cross faults have offset the formation in many places. Southward, the formation is subdued being covered transgressively by an Upper Cretaceous sequence. Between these major faults, the steeply tilted beds were involved in a series of longitudinal tectonic scales oriented parallel to the local structural trends. Striking north, the beds of the Somova Formation dip up to 80 degrees to the east; therefore, the oldest beds crop out in the westernmost outcropping part of the formation. The Lower Triassic (Spathian) age of these rocks can be ascertained on (i) conodont species: *Neospathodus collinsoni*, *Chiosella timorensis*, *N. triangularis*, *N. homeri*, *Gondolella jubata*, *Cypridodella unialata* (Elena Mirăuţă, cited by Baltres, 2003); (ii) benthic foraminifera: *Meandrospira iulia*; (iii) ammonites: *Leiophyllites*. Minor igneous rocks occur as concordant, few meter thick basalt sheets in the Somova limestones, which are cropping out northward from Iulia, for more than 20 km, along the Lozova Valley.

The ore lenses (Fig. 3), localized near the base of the Somova formation, not far from the tectonic contact with the epimetamorphic basement (Boclugea Group), have been tilted up in the west, follow the attitude of the enclosing rocks and are arranged in *en echelon* configuration, reaching as north as the midway between Iulia and Valea Teilor villages, as revealed by old mining works. The iron ore is outcropping in the western part of the Movila Hill, less than 2 km south-west from Iulia. The ore is in close relation with the deep-sea carbonate sequences of the Somova Formation, being folded and faulted together with it.

The upper member of the Somova formation, prominently occurring north-west from Iulia, consists of an up to 200 m thick mass of effusive igneous rocks, which consist of graded rhyolitic tuffite beds, sometimes with abundant limestone clasts, tuffs and massive, porphyritic rhyolite flows (the Consul Rhyolite).

---

[1] The restored image of the Lower Triassic palaeotectonic map are retrievable on: http://jan.ucc.nau.edu/~rcb7/paleogeographic_alps.html (based on Sengor and Natal'in, 1996).
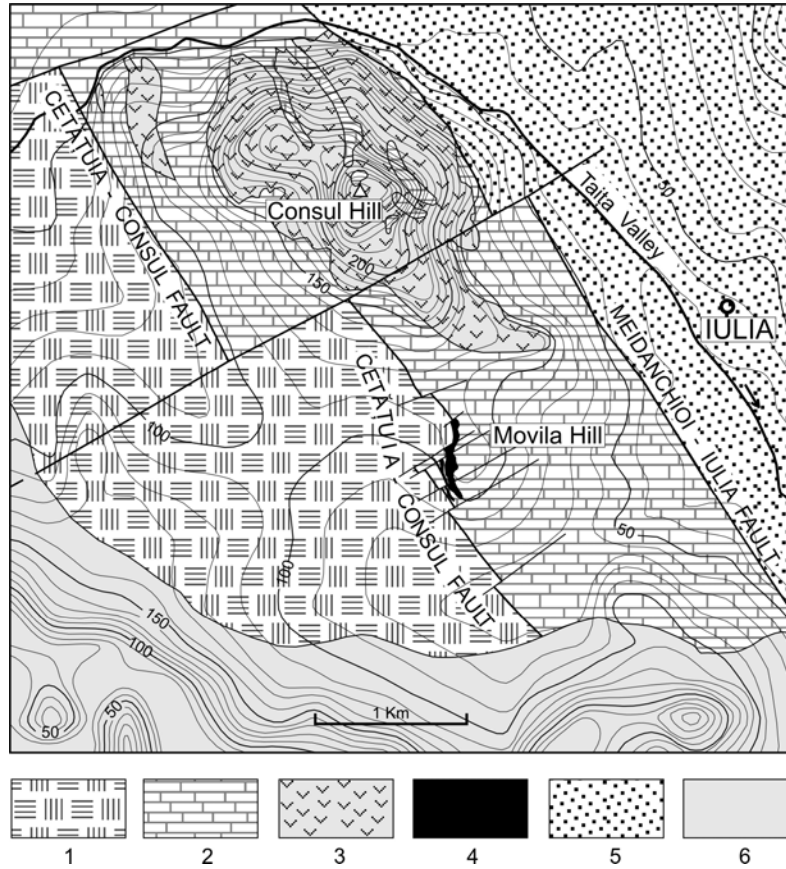
Fig. 2. Geological map of the Iulia zone. Loess cover ignored. 1. Basement (Boclugea Group); 2. Somova Formation (Spathian); 3. Consul Rhyolite (Spathian); 4. Outcropping iron ore (Spathian); 5. Nalbant Formation (Upper Triassic); 6. Dolojman Formation (Upper Cretaceous).
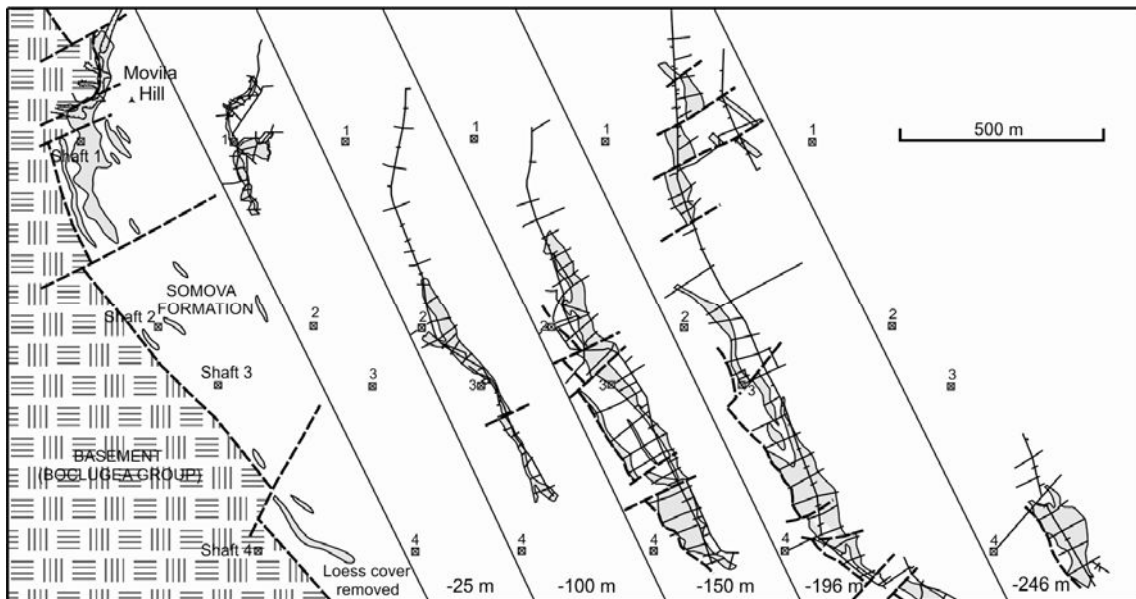

Fig. 3. Map showing the location of iron ore lenses (in gray) at various depths in mining workings undertook at Iulia. Exploration data.

In addition, dark Somova-type limestones, reaching up to 34 m in thicknes, were concordantly intercalated at various levels in the Consul Rhyolite. Along the rhyolite contact with the limestones there is a complete absence of metamorphic phenomena.

3. Previous work

Two different hypotheses have been advanced to account for the origin of the ore from Iulia. Vlad (1978) interpreted the ore as a mineralization of epigenetic origin, which resulted by fluid-rock reaction of ascending, iron-bearing hot fluids, with earlier lithified Triassic limestones. The process acted in the course of Middle Triassic. The mineralizing fluids, originating in the crystalline basement, ascended via Luncaviţa-Consul Fault and permeated the limestones, converting them to metasomatic infiltration skarns, by chemical interactions. Vlad rejected any connection between the ore and the magmatic rocks in the region, based on the lack of evident association with such rocks that might have played a part in their origin.

In contrast, Mârza et al. (1981) asserted that the mineralization is genetically associated with an intrusive center made up of rhyolites. These authors thought that the ore from Iulia was formed at first by pneumatolysis, under the action of hot, mineralized vapours produced by a solidifying deep-seated rhyolitic magma, on a Triassic limestone host. Then, closely related in time, a hydrothermal phase followed. Contact pneumatolysis generated a garnetiferous-vesuvianic microskarn, fine crystalline magnetite, and also hematite that commenced to form in this stage. At somewhat lower temperature and pressure, hydrothermal solutions were fed into the limestone resulting hematite-mushketovite, minor sulphides, and low-temperature gangue minerals (antigorite, sericite, epidote, siderite-calcite, quartz-tridymite). In addition, previously formed garnet was partly or totally transformed into epidote, calcite and chlorite. According to the mentioned authors, the mineralizing solutions, with great ability to accomplish the replacement of carbonate country rocks, rose along the major Luncaviţa-Consul Fault, following branched faults oriented NV-SE.

The field conditions alter significantly the conclusion of Mârza et al. (1981). As it was later evidenced, the fault system was not a forerunner of the rhyolite emplacement and, thus, of the iron ore. Folding and faulting was completed much later so that the Luncaviţa-Consul Fault occurred only in the Lower Jurassic. Both the eruption of the rhyolites and the formation of the ores took place in the Lower Triassic but were also separated in time: whereas the mineralized body is concordantly interbedded in the lower part of the Lower Triassic carbonate pile (Somova Formation), the rhyolites occur in the uppermost part of this formation (Baltres, 1994). In addition, the rhyolites are not intrusive bodies but pyroclastic rocks and submarine flows, with concordant limestone intercalations (Seghedi et al., 1990).

The weak development of the skarn minerals was explained by Mârza et al. (1981) by the presence of dominantly acid solutions, the low content of $CaCO_3$(!) and a high rate of garnet nucleation, whereas the sulfide scarcity was explained as the effect of sulfur-poor oxidant solutions.

Certain new facts revealed by our study appear to be significant in explaining another mode of formation for the ore from Iulia.

4. Analytical methods

Mineral compositions were investigated using a Cambridge Stereoscan 180 scanning electron microscope (SEM) coupled with energy dispersive (EDAX) detectors for elemental analysis. An acceleration potential of 20 kV was used. Bulk rock samples were analyzed for major components by wet chemical analyses carried out using standard methods of quantitative analysis (gravimetry, colorimetry and absorption spectrometry) following techniques recommended by Maxwell (1968) and by Iosof and Neacşu (1980). The Penfield method was used for water determinations. Some minerals were identified by X-ray diffraction, with a Soviet DRON-3 diffractometer using a Cu-Kα radiation.

5. Mineralogy and parageneses

The mineralization, preserving the original bedding, consists of centimeter-scale shiny bands of hematite, interlayered with yellow and green, dull garnetiferous bands (Fig. 4). The lenses maintain characteristic ore-silicate assemblages along their length and the properties of the ore are the same over a wide areal and vertical extent. The hematite bands are more discontinuous and show sometimes small-scale structures as load casts, constrictions, intrastratal slides and folds, sometimes recumbent folds, all of these being proofs for deformation in plastic state of these bands.

The inventory of the minerals in the ore-bearing bands includes hematite, magnetite, mushketovite and subordinately martite. The garnetifeous bands (gangue) consist of finely crystallized garnets (andradite and grandite), large quantities of a regularly mixed-layer mineral (chlorite-swelling chlorite) resembling corrensite, and aluminous chlorite-swelling chlorite, also acicular hematite, magnetite, quartz, calcite, some dolomite, talc and montmorillonite. Mârza et al. (1981) described also antigorite, vesuvianite, sericite and epidote.

5.1. Hematite

Hematite is by far the most important constituent of the ore groundmass. This results also in the larger contribution of Fe_2O_3 (43.28-64.28%) in bulk rock analyses (Table 1), as compared with the FeO content (up to 8.16%; exceptionally 21.67%). As a rule, hematite occurs as millimeter- to centimeter-size, tabular crystals. Rarely, these are associated with skeletal crystals or fine lamellar hematite, resembling the ophitic structure (Ianovici et al., 1977). Often, the large lamellae, grouped in fascicles or wreaths, were bent, folded or broken as a result of compaction that forced the slender, brittle hematite crystals to tighten.

Hematite shows partial transformation to magnetite by pseudomorphic replacement (mushketovite) as was recognized by chalcographic study. The mushketovite contains acicular hematite relics. This magnetite mineral derives from the iron released from hematite, in reducing conditions, and the pseudomorphic replacement occurred probably by diffusive processes instead of solution-precipitation (Matthews, 1976). It is thus, a secondary reaction magnetite.

In the silicate bands, hematite occurs as fine, divergent, acicular crystals embedded in the mixed-layer clay mineral matrix or surrounded by quartz.

Frequently, the large hematite tablets carry minute inclusions of various minerals. Clusters of solid NaCl as inclusions in hematite contain subhedral crystals, up to 3 micrometers across, with typical conical depressions on cube faces (hopper crystals) (Fig. 5). Other NaCl inclusions are hemispherical in shape (amorphous?) reaching only one micrometer in diameter and occur scattered in hematite tablets.

Garnet inclusions in hematite tablets are anhedral in shape. Their very irregular outlines are thought by us to have been formed as they crystallize from solution droplets trapped between growing hematite subcrystals whose endings dictate the ragged appearance of the garnet inclusions. Such inclusions were not found in the spaces interstitial to hematite and are not interconnected. The largest garnet inclusions reach 30 micrometers across and their composition is grandite.

Square shaped, euhedral inclusions of apatite, up to ten micrometers across, occur rarely. Their composition was tested by microprobe. A single Zn sulphide inclusion of 12 micrometers was found in a tabular hematite sample.

Microprobe analysis of single hematite crystals detected the presence of manganese in small amounts, less than in magnetite crystals and in much lower proportion than in garnet. The atomic ratio Mn/Fe, deduced from wet chemical analysis data (Table 1), are small (a mean of 7.25 Mn atoms for each 1000 Fe atoms bound in Fe_2O_3; extreme values between 3.75 and 12.9) while in the garnetiferous bands, the mean value for the same atomic ratio is markedly higher (41).

Table 1. Variation of the chemistry in the silicate and ore bands. Analyst Rosette Ianc. bdl = below detection limit

wt.%	SILICATE BANDS					ORE BANDS				
	#1	#2	#3	#4	#5	#1	#2	#3	#4	#5
SiO_2	43.5	35.7	27.6	30.7	45.8	16.9	35.5	20.4	21.7	19.4
TiO_2	0.7	1.4	0.4	0.5	0.7	0.6	0.7	1.1	1.0	1.1
Al_2O_3	11.2	16.9	3.0	10.4	3.3	2.0	1.5	4.4	1.0	1.2
Fe_2O_3	11.5	14.5	20.6	17.3	11.3	64.3	55.0	63.8	43.3	56.7
FeO	2.1	3.4	1.0	6.6	1.1	1.3	0.0	0.4	21.7	8.2
MnO	0.7	0.5	0.7	0.9	0.1	0.3	0.3	0.2	0.5	0.4
MgO	8.4	9.4	2.6	5.8	9.6	2.0	2.0	4.5	1.5	1.9
CaO	11.8	11.3	38.1	23.9	19.6	6.9	1.8	2.1	7.3	6.0
K_2O	0.4	0.8	bdl	bdl	1.2	bdl	bdl	0.1	0.1	0.1
Na_2O	0.1	bdl	bdl	0.1	0.1	bdl	bdl	bdl	0.2	0.1
P_2O_5	0.2	0.2	0.1	0.2	bdl	0.1	0.1	0.1	0.1	0.1
H_2O	4.6	6.0	0.8	1.5	3.8	0.6	0.7	2.4	0.4	0.8
CO_2	4.5	bdl	5.5	2.5	3.0	4.5	1.8	bdl	1.3	3.5
S	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.2	0.2	0.2
Total	99.5	100.3	100.4	100.2	99.7	99.7	99.5	99.6	100.1	99.6

Both in hematite and in the garnetiferous bands the atomic ratio Mn/Fe to Fe_2O_3 content apparently shows antipathetic relationships. In contrast with the magnetite, hematite does not contain calcium. Table 1 shows comparative analytical data obtained from silicate bands and iron ore bands.

5.2. Magnetite

On polished surfaces examined by SEM, the euhedral to subhedral magnetite crystals, 30 micrometers across, show a zoning evidenced by discontinuities paralleling structural directions (crystal faces), marginal corrosions, pits and small dark inclusions of euhedral garnet. Brittle fracturing in many magnetite grains results in a close-fitting mosaic of irregularly shaped crystal fragments. This may be the response of a directed stress within the ore body.

The hematite replacing magnetite (i.e. martite) occurs along the margins of the crystals forming an amas of minute, skeletal crystals, 5 to 20 micrometers long and 3-5 micrometers thick, proving that the alteration proceeded along the margins of the crystals. Sometimes, martite needles are oriented parallel with the crystal faces of the replaced magnetite, suggesting alteration along predetermined structural directions. The exsolution crystals of martite resulted by a solution-precipitation process, in oxidizing conditions, leaving empty spaces between the skeletal crystals.

Magnetite can occur in narrow bands containing virtually no other mineral, embedded in a garnetiferous groundmass.
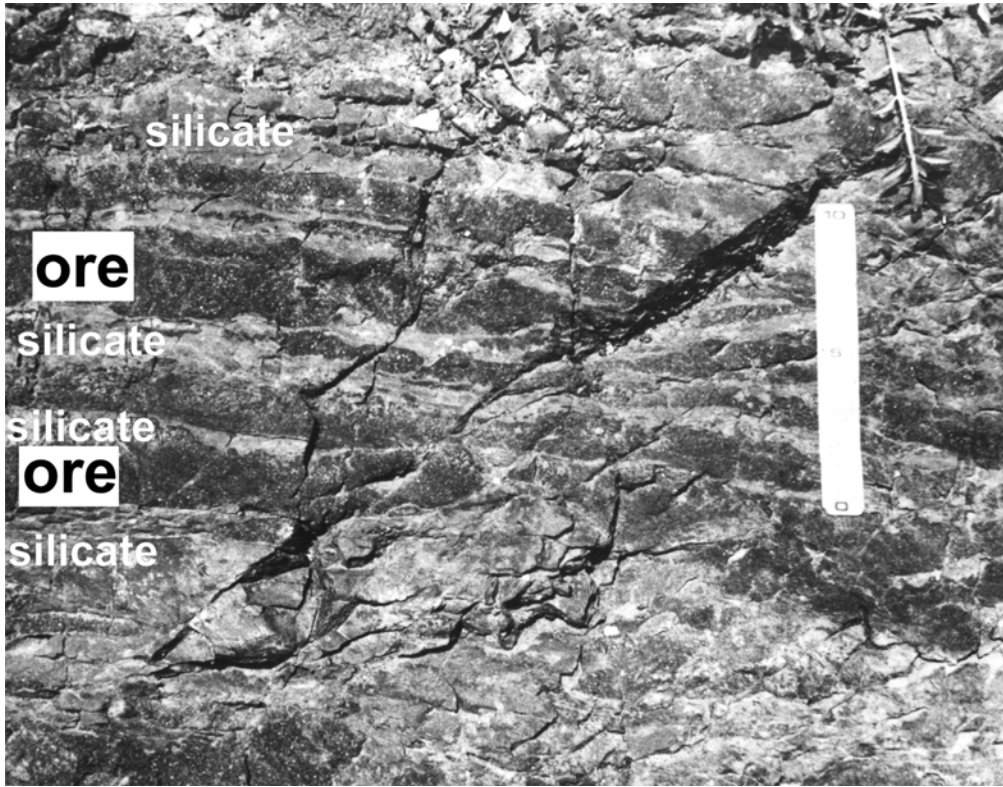
Fig. 4. Typical aspect of the mineralization from Iulia which consists of uneven, centimetric bands and lenses of hematite alternating with green, garnetiferous bands. Scale bar = 10 cm.
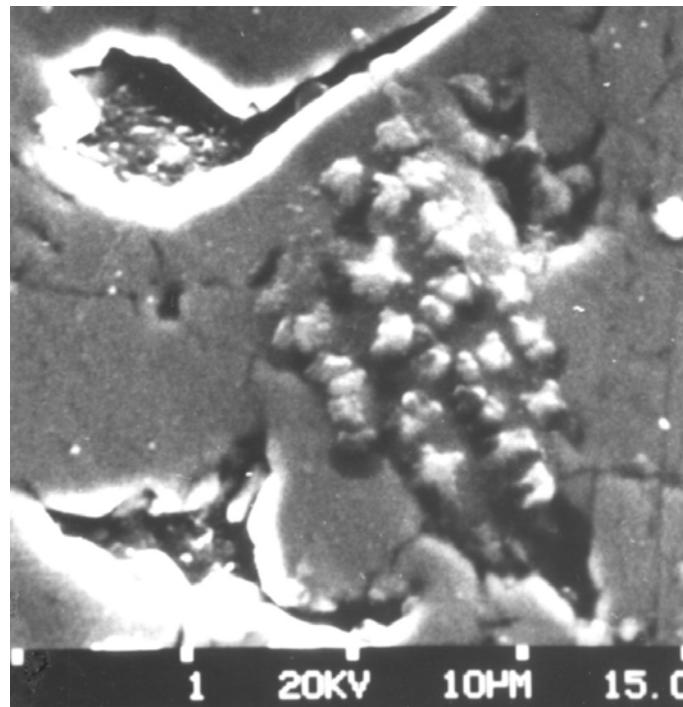

Fig. 5. A cluster of tiny NaCl crystals forming one of many solid inclusions in hematite. Polished surface, SEM image.

Moreover, magnetite occurs in two other parageneses: (i) as inclusions in quartz or calcite which fills the interstitial spaces between large, tabular hematite crystals in the bands of ore, and (ii) as inclusions in irregular calcite patches present in the garnetiferous bands. Magnetite (mushketovite) can also pseudomorphically replace large tabular hematite by a commonly crushed mosaic of crystals containing acicular hematite relics. It might be tentatively suggested that pseudomorphic replacement is the result of the balance between local oxidizing and reducing conditions.

In any paragenesis the magnetite crystals contain small quantities of Si, Ca, Ti, and Mn, as revealed by microprobe. By contrast, in hematite calcium is misssing. The Mn content is always higher in magnetite than in hematite.

5.3. Garnet

Microcrystalline garnet is the main component of the yellow and green bands alternating with hematite bands. It also occurs in low amounts as inclusions in hematite and magnetite.

On polished surfaces, the garnet crystals commonly show hexagonal outlines, and their size ranges between 30 and 60 micrometers across, rarely up to 100 micrometers. On SEM view (Fig. 6) there is an obvious variation in electron absorption between the inner and outer parts of a crystal, caused by compositional inhomogeneity (darker areas in inner parts are depleted in heavy elements, in contrast to outer, lighter areas where heavy elements are present). This inhomogeneity can explain the anomalous anisotropy of the garnets in thin section. Often, the crystals show evidence of chemical corrosion ranging from shallow pits to deeply penetrating irregular hollows. XRD analysis revealed the presence of andradite and grandite, and electron microprobe evidenced the compositional variation of individual crystals, as shown later in this section.

Hemispherical inclusions, up to 5 micrometers in diameter, are probably amorphous and consist of Cl and K. These inclusions are common in garnets and are similar to those signaled in hematite.

The garnet is present in four parageneses:

(i) Paragenesis tabular hematite-grandite (as inclusions) was already described in the Hematite section.

(ii) Paragenesis quartz-grandite (and andradite)-hematite. Here, the garnets occur as inclusions in irregular masses of quartz, interstitial to large hematite tablets of the ore bands. Commonly, garnet occurs in clusters of 2-3 euhedral crystals, each of these 50-60 micrometers across, and showing internal inhomogeneity clearly visible as hues of gray on the compositional images obtain by SEM (Fig. 6). Andradite is rarely present, in contrast with grandite. The occurrence of composite garnet grains embedded in quartz indicates that some garnet commenced to form quite early after hematite crystallization.

(iii) Paragenesis grandite-hematite is essentially composed of tiny grandite crystals and disseminated skeletal hematite that occur in the yellow and green bands.
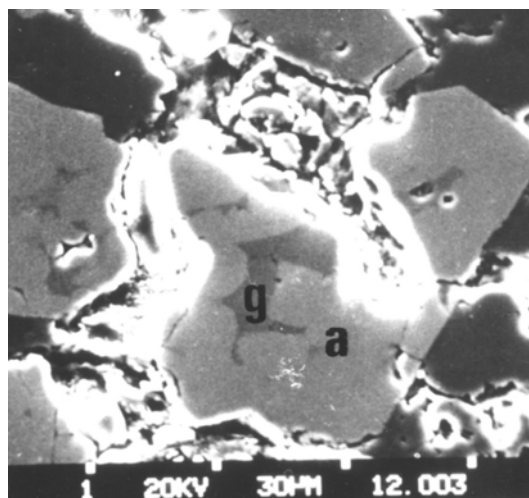

Fig. 6. Polished surface of a grandite crystal with an inner, darker part of near-grossularite composition (g) and a larger outer part with a near-andradite composition (a). SEM image.

(iiii) The paragenesis quartz-grandite-pyrite, forming submillimetric, irregular reflective patches embedded in an apparently crumbled, amorphous matrix with contrasting

polishing hardness, is present in the yellow and green gangue bands.

This matrix will be described in more detail in another paragraph. In the patches of quartz-grandite-pyrite, a loose framework of irregular, ragged grandite crystals was interstitially infilled by quartz containing minute euhedral pyrite cubes, not larger than 5 micrometers.

5.3.1. Garnet chemistry

Electron microprobe analysis of a large number of garnet crystals revealed that andradite, which occur in minor amounts in the garnetiferous bands, is relatively depleted in Fe and Ca and enriched in Si in the core of all crystals. The grandite, with an intermediate composition between grossularite and andradite, is by far the most abundat mineral of the garnetiferous bands and presents invariably a compositional inhomogeneity, with a grossularite-type core and an andradite outer part, reflecting variation in the physical conditions of crystallization. The inner, darker part, with irregular outlines in SEM images (Fig. 6), contains Al, Si, Ca, and some Fe, whereas the outer, andraditic part, that always occupies the largest part of a crystal, consists of Fe, Si, Ca, and some Al. To illustrate this, the composition determined on the inner and outer parts of two grandite crystals are given here. In the inner parts, the oxide contents (wt%) are: 15.98-16.47% Al_2O_3; 40.89-54.32% SiO_2; 31.75-34.77% CaO, and 2.24-4.92% FeO. The outer, andradite parts consist of 0.63-3.24% Al_2O_3; 40.95-46.03% SiO_2; 27.56-28.97% CaO, and 24.99-26.82% FeO.

Typically, the grandite crystals have irregular cores of near-grossularite composition (Fig. 6) and a larger, outer andradite part. The ragged outlines of the cores suggest the mode of crystal nucleation and growth. Probably the early nucleation of a cluster of andradite subcrystals, 5-10 micrometers across, was followed by the growth of an unique, decimicronic andradite crystal. In the inner part, grossularite formation was delayed. Subsequently, grossularite formed from the small quantity of calcium- and alumina-rich silicate solution trapped between the merged, andradite subcrystals, in the core of a final andradite crystal. Early nucleation of andradite caused depletion in Fe in the trapped solution between subcrystals, from which subsequently crystallized the inner, xenomorphic part of the grandite crystal, with a near-grossularite composition. The xenomorphic shape of the grossularite part in the core of the grandite crystals is an effect of moulding between the early andradite subcrystals. An alternative hypothesis is that the compositional inhomogeneity of grandite reflects a variation of the physical conditions of garnet growth, in such a manner that the availability of iron was increased, favouring andradite development at the expense of grossularite.

Compared with the ideal composition of grossularite and andradite, our analyses revealed an excess of SiO_2 whereas other oxides occur in lesser amount. For comparison, are given the compositions of ideal grossularite (22.7% Al_2O_3; 40.0% SiO_2; 37.3% CaO) and andradite (36.1% SiO_2; 32.5% CaO; 31.4% Fe_2O_3). Two analyzed grandite crystals revealed the presence of Ti and Mn. TiO_2 content was 0.02-0.91%, and MnO content was 0.45-0.95%. Manganese is more abundant in garnetiferous bands than in the hematite bearing bands (0.446 and 0.27 wt%, respectively). Also Mn is mainly partitioned in garnet rather than in hematite. The atomic ratio Mn/Fe in garnetiferous bands are significantly higher than in the hematite bands (a mean of 41 Mn atoms for each thousand Fe atoms bound in Fe_2O_3, in contrast with 7.25 Mn atoms in hematite). Possibly, different Eh-pH conditions controlled the uneven extraction of manganese by hematite and garnet. Probably garnet crystallized in oxidizing conditions, favourable for extraction of Mn from solution. By contrast, reducing and slightly acid conditions carried Mn away in solution (Whitehead, 1973). The atomic ratio Ti/Fe × 1000 follows a similar trend as in the case of Mn but the values are much lower (1.2 Ti atoms for each thousand Fe atoms in garnetiferous bands and only 0.45 Ti atoms in iron oxide bands).

5.4. Chlorite-swelling chlorite matrix

A regularly mixed-layer clay mineral, chlorite-swelling chlorite, are always abundant

in the yellow and green bands, especially in their soft, friable parts. On polished surfaces, the apparently crumbling, dull, amorphous or cryptocrystalline matrix occurs receded because of contrasting polishing hardness with the accompanying reflective patches of other minerals (quartz, grandite, minor amounts of pyrite, apatite and hematite) (Fig. 7). XRD analysis carried out on samples of this matrix revealed the presence of a regularly mixed-layer mineral, chlorite-swelling chlorite (C-Cg/R) resembling corrensite, and aluminous chlorite-swelling chlorite (Al/C-Cg/R), and also minor amounts of talc and montmorillonite. Mârza et al. (1981) signaled also the presence of vesuvianite and antigorite in the matrix. Electron microprobe analysis indicates the presence of Ca, Si, Fe, Mg, Al, Mn, Ti, P (in decreasing order of abundance).
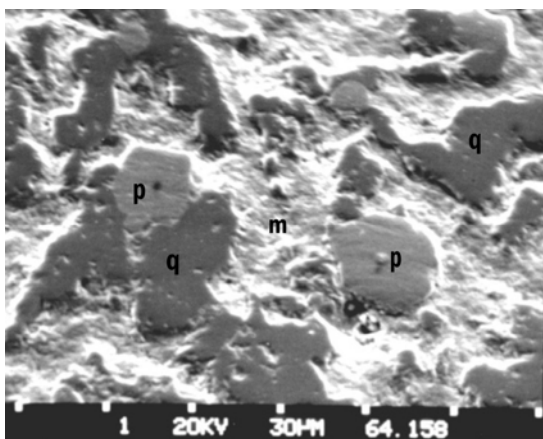

Fig. 7. Polished surface of the amorphous or cryptocrystalline matrix which occurs receded (m), containing irregular patches of quartz (q) and minute pyrite crystals (p). The matrix consists essentially of a regularly mixed-layer chlorite-swelling chlorite clay mineral. SEM image.

5.5. Quartz

Quartz is constantly present both in the hematite and in the garnetiferous groundmass. It occurs in large proportions (15-34%) as infillings in the interstitial spaces of tabular hematite (and mushketovite) and contains inclusions of euhedral magnetite or grandite. Another mode of occurrence is as intercrystalline infillings in garnetiferous bands or as irregular patches in the mixed-layer chlorite-swelling chlorite matrix. The quartz patches include sometimes fine, acicular hematite and tiny, euhedral pyrite crystals.

5.6. Calcite

Calcite occurs in patches in the garnetiferous bands and contains euhedral magnetite crystals. In the interstices of tabular hematite the calcite contains mushketovite inclusions that resulted probably at the expense of hematite. In the garnetiferous bands, the calcite is present in amounts of 5.7% to 12.5%; in the hematite bands the calcite content varies between 2.95% and 10.23%.

5.7. Sulphide minerals

Sparsely disseminated euhedral crystals of pyrite, 3-5 micrometers across (rarely 30 micrometers), occur in the chlorite-swelling chlorite matrix (Fig. 7) but mainly as inclusions in quartz patches embedded in the matrix. Some hematite tablets carry small ZnS crystals. In small, irregularly shaped interstices of the ore groundmass, rare Zn and Cu sulphides sometimes occur intergrown with quartz and calcite in such a manner as to indicate epigenetic infill. Chemical analysis indicates that the S content is lower in the garnetiferous groundmass than in the ore (0.06-0.13wt%, and 0.12-0.18wt% respectively).

6. Discussion on ore genesis

An earlier interpretation of ore genesis at Iulia was proposed by Mârza et al. (1981), who thought that the garnet and magnetite were formed early by pyrometasomatosis whereas the hematite-mushketovite were generated later, as hydrothermal products in the skarns at the contact between rhyolites and limestones. In their interpretation, the authors avoid to explain some facts such as the banded appearance of the ore and the exclusively microcrystalline size of the garnets. However, they noticed that the host limestone shows no signs of thermal recrystallization, that most mineral assemblages are devoid of typical skarn minerals and hydrothermal sulfide minerals, and that evidence of pyrometa-

somatic processes is weak. Also, the intrusive rocks assumed in their interpretation to be responsible for contact metamorphic effects, are in fact alternances of tuffs and graded, green tuffite beds 0.2 m to 3 m thick, with decimetric limestone intercalations, massive perlitic, brecciated and fluidal, green rhyolites, and also massive, porphyritic rhyolite flows (Seghedi et al., 1990). These were formed in a deep marine depositional environment by a combination of gravity-driven processes such as debris flows, turbidity currents and subaqueous emplacement of rhyolitic flows. The stratigraphic position of the rhyolites is at the top succession of the Somova Formation whereas the ore body is located near the base of this formation. Regarding the tectonic factor (the Luncaviţa-Consul Fault) claimed by Mârza et al. (1981), the named fault is subsequent to ore genesis, being involved only in post-Triassic block faulting and horizontal displacements.

A model involving the submarine-exhalative processes is more compatible with the specific features of the mineralization from Iulia. We reached an interpretation different from that of Mârza et al. (1981) because the overall, laterally persistent alternances of centimeter hematite and garnetiferous bands, and certain features as load casts and centimeter-scale intrastratal slides and recumbent folds, as proofs of deformation in plastic state, might be attributed to deposition of gravitationally unstable precipitates on the sea floor. The multiple alternation of the interlayered hematite and garnetiferous bands suggest repeated environment changes. Nonetheless, the deposit suffered minimum post-depositional reconstitution, preserving the original bedding. On the other hand, it shows no signs as being produced by replacing solid rock or filling open spaces in it. In addition, the ore is in sharp contact with the overlying and underlying carbonate rocks, is conformable with the bedding direction of the Lower Triassic carbonate sequence (Somova Formation) and was folded together with this sedimentary sequence. The carbonate rocks adjacent or intercalated with the orebodies show no signs of influence characteristic for the marginal zones of an orebody, being virtually indistinguishable from those away from contact.

As concerns the nature and origin of the associated carbonate rocks, these can help to establish the connection between the ore and its environment. First, the carbonate formation (Somova Formation) consists of deep-sea debrites, turbidites and pelagites. Next, positive evidences of submarine volcanism were found in these rocks, as minor intercalations of spilitized basaltic magma that extend further on strike, where orebodies no longer persist. The degree of continuity between spilitized basalt occurences is low. Elsewhere, the Somova Formation contains some intrusive gabbro sheets, up to 106 m thick, the largest of these showing a narrow zone (2-5 m) of contact metamorphic deposits separating the intrusion from the sediments.

The lack of close spatial relationships of the orebodies from Iulia with basaltic lava do not preclude that these were derived from a deeper seated source, in the form of submarine exhalations. Accordingly, it can be suggested that the characteristics of the ores might be directly attributed to some original hydrothermal processes although the source likely to provide the postulated hydrothermal solutions is apparently absent. Varnavas and Panagos (1983) emphasized that during the interaction between oceanic crust and the sea water near volcanic centers "oxidizing sea water penetrates and circulates, within the fractures of the crust, thus becoming slightly acid and reducing. Such a solution can extract metals from the basalt, such as Fe, Mn, Cu, Zn, etc. The continuous reaction between sea water and basalt, leads to the formation of metal-bearing hydrothermal solutions, which discharge onto the ocean floor".

The ore of Iulia was formed by sedimentary-exhalative processes, while the original sediment of the actual garnetiferous bands was modified in some way by igneous emanations, in a particular geological environment, so that both hematite and garnetiferous bands are cogenetic, being chemical sediments formed by repeated gradual environmental changes. Stratabound ore and gangue mineral interlayering resulted.

The metals of igneous origin were probably carried as chloride complexes whereas the ions necessary for the formation of new silicate minerals, during sedimentation and diagensis, were present at the site of deposition. The buried, semilithified, cohesive interlayers were gravitationally unstable, allowing differential loading that produced deformation structures of the more dense hematite bands. Compaction of hematite produced bending, folding and breaking of brittle hematite fascicles, resulting an uneven, bumpy surface of the iron ore bands.

The different atomic ratio Mn/Fe in hematite and garnet may indicate that the environment was alternatively highly reducing and acid (Mn was reduced and removed in solution from metalliferous sediment), and relatively oxidizing and more alkaline (extracting Mn from solution where the solutions encounter excess silicate and carbonate ions).

The hematite bands were deposited as metal-rich sediments from iron-charged outflowing hot springs rising from the depth or by leaching of extruded basalt. Iron would be generally oxidized, concomitantly with gradual neutralization of the acid bottom water solution, so that uptake of metal by hematite mineral phase takes place in mildly oxidizing and less alkaline conditions. Under these circumstances manganese was incorporated in hematite in lesser amounts, remaining longer in solution, until pH reached the normal value of sea water. Subsequently, excess silicate and carbonate ions, in a reducing and more alkaline environment, favored nucleation of garnet which extracted more efficiently the manganese from solution. The hematite layers require the contribution from a volcanic source as rising hydrothermal pulses of heated solutions carying leached metals, mainly iron, as chloride complexes.

That the solutions carying the iron as chloride complexes were hot and highly saline is proved by the abundant solid NaCl inclusions which occur in intimate association with hematite, as small clusters of tiny, subhedral crystals or as apparently amorphous, spherical inclusions. The sodium and chloride acted as components of a liquid richer in these ions than the ordinary sea water. The poor circulation of sea water at depth prevent contamination, allowing the preservation of a stratum of metal-laden hot brine above the sea floor and the slow precipitation of the elements it contained.

The thin ore bands suggest that the hydrothermal fluids with high concentrations in metal reached the sea floor in small quantities, but in repeated pulses over geologically short periods of time (Ridge, 1973).

When the amount of ore-bearing fluid which entered the sea floor diminished, it reacted with the carbonate mud which was the natural sediment of the basin resulting in silicate minerals, the most interesting of these being the garnet species grandite and the regularly interstratified chlorite-swelling chlorite resembling corrensite. The garnetiferous bands, as immediate lithological associates of the hematite bands, are interpreted as chemical sediments based on their similarity to authigenic garnets of the grandite series occurring in micarb chalk, above basalt at Site 251 from Indian Ocean Ridge, described by Kempe and Easton (1974). As the authors stated "The material introduced for their formation (SiO_2, Al_2O_3, Fe_2O_3) was probably transported from the magma source below the basalt in a highly alkaline hydrothermal fluid, in which silica would be in solution and the trivalent oxides form colloidal gels. Upon introduction into the ooze, a gelatinous Ca-Al (Fe) complex may form, which, by a chemical exchange process, would lead to widespread nucleation of the garnets". In these circumstances, "although the garnets are believed to be metasomatic, they must be considered in the context of authigenesis, in which such an occurrence is extremely rare or even unique". In the case of the garnets described here, which possess several characteristics in common with the microscopic (2-3 micrometers in diameter) garnet grains at Site 251, probably the nucleation proceeded rapidly, in a manner described in the section refering to garnet crystal chemistry. Alternatively, an unstable and reactive initial iron-depleted garnet species, with near-grossularite composition,

rapidly evolved to more stable, near-andradite granet, as the availability of iron increases.

The amorphous matrix occurring in irregular patches in the garnetiferous bands, consisting of regularly interstratified clay minerals chlorite-swelling chlorite and aluminous chlorite-swelling chlorite, represents a stage in the transformation sequence of chlorite through swelling chlorite to smectite, elsewhere known as a transformation product due to hydrothermal actions (Veniale and van der Marel, 1963). Or, the mineral was neoformed from ionic solutions, on the sea floor. The tiny pyrite euhedral crystals which commonly occur in the clay matrix have probably precipitated before reaching the sea floor, carried in the ascending brine, and scattered on the sediment surface. In the garnetiferous and clay mineral bands the iron oxides formed a minor portion so that here only sparse skeletal hematite crystallized.

Particular mention should be made on the numerous inclusions, especially in hematite. In the course of hematite crystallization, garnet occurred sparsely, as shown by grandite inclusions in hematite and by grandite crystals interstitial to hematite lamellae. In the latter case, small clusters of garnet were cemented by quartz while the anhedral grandite inclusions in hematite crystallized from trapped solution droplets adhering on the growing crystal faces that enclosed them in the course of growth. These droplets proceeded from a suspended load of colloidal material.

The presence of tiny NaCl solid inclusions, occurring as crystal clusters in hematite, "implies that the mineralizing fluid was saturated with respect to halite at the time of crystal growth" and resulted "from rapid precipitation of halite from the inclusion fluid as it escapes from the inclusion" (Campbell et al., 2001). It is also possible that, from the saturated fluid, the halite crystals precipitated on a growing crystal surface of hematite, causing the host to grow around the foreign halite crystal, trapping it along with some of the NaCl saturated fluid, as suggested by Becker et al. (2008).

As concerns the depth of the sea receiving the volcanic exhalations, Ridge (1973) predicted the behavior of the saline solutions entering the sea. If the source of the saline solutions is under an overlying 915 m of sea water or more, these reach the sea floor no matter what their temperature is at that time. At shallower depths, the high temperature solutions will boil a short distance beneath the sea floor, causing the sudden precipitation of all constituents of lower vapor pressure than water. To avoid boiling, the volcanic exhalations must reach the sea floor under sufficient confining pressure, at depths exceeding 915 m over the area of deposition. It is highly probable that the carbonate turbidite sequence and the incorporated ore body of Iulia were laid down in a deep sea, as predicted by Ridge.

7. Conclusions

The *ore* by Iulia has been formed by deposition on the sea floor, in association with some amounts of *chemical sediment*, as evidence of hydrothermal activity that accompanied the volcanic events at or near the Lower Triassic sea floor. The minerals that occur now are not in the form in which they were deposited. A primary iron sediment precipitated from hydrothermally derived saline and metal-rich solutions, in response to the convergence with the physical conditions of sea water. The formation of hematite may be attributed to diagenesis at the sea floor, which resulted in the iron sediment progressing toward hematite. Part of the mineralized hot brines that reached the sea floor reacted with the sediments, resulting the occurrence of mineralized carbonate muds and garnetiferous sediments. The ore may have been concentrated preferentially along the general keel direction of a string of small depressions on the sea floor containing hot springs, as the result of volcanic processes. The geological environment where these ores and chemical sediments were ponded, in basin-like depressions, was a deep sea, as suggested by the presence of carbonate debrites, turbidites and pelagic sediments associated with some basaltic volcanics and intrusives (gabbro sheets), in a fault-controlled setting resulted by extensional tectonics.

Acknowledgments

References

Baltres, A., 1982, Sedimentologic study of the Spathian striped limestones in the Mineri-Movila Săpată area (North Dobrogea) (unpublished report, in Romanian).

Baltres, A., 1984, Significance of the mineralization associated with the turbidites of the Consul Formation In: Baltres A., Codarcea V., Boştinescu S., Lithologic and lithostratigraphic study of the calcareous formations from Iulia zone (unpublished report, in Romanian).

Baltres, A., 1994, Somova Formation (North Dobrogea) – Sedimentologic study. (in Romanian) Unpublished PhD Thesis, University of Bucharest, 174 p.

Baltres, A., 2003, The pre-Cenomanian Mesozoic units from North Dobrogea (Part I) (in Romanian). Studii şi Cercetări de Geologie, 48, 49-90, Bucharest.

Becker, S. P., Fall, A., Bodnar, R. J., 2008, Synthetic fluid inclusions. XVII. PVTX properties of high salinity H_2O-NaCl solutions (>30wt % NaCl): Application to fluid inclusions that homogenize by halite disappearance from porphyry copper and other hydrothermal ore deposits. Economic Geology, 103, 3, 539-554.

Bonatti, E., Honnorez, J., Joensuu, O., Rydell,. H., 1972, Submarine iron deposits from the Mediterranean Sea. In: Stanley D. J. (Ed.), The Mediterranean Sea, a natural sedi-mentation laboratory, 701-710, Dowden, Hutchinson & Ross, Stroudsburg, Pennsylvania.

Campbell, A. R., Lundberg, S. A. W., Dunbar, N. W., 2001, Solid inclusions of halite in quartz: evidence for the halite trend. Chemical Geology, 173, 179-191.

Chatterjee, N. D., 1967, Experiments on the phase transition calcite + wollastonite + epidote = grossular-andradite ss + CO_2 + H_2O. Contribution to Mine-ralogy and Petrology, 14, 114-122.

Chukhrov, F. V., 1973, On the genesis problem of thermal sedimentary iron ore deposits. Mineralium Deposita, 8, 138-147.

Cloke, P. L., Kesler, S. E., 1979, The halite trend in hydrothermal solutions. Economic Geology, 74, 8, 1823-1831.

Corliss, J. B., 1971, The origin of metal-bearing submarine hydrothermal solutions. Journal of Geophysical Research, 76, 33, 8128-8138.

Edmond, J. M., 1984, The geochemistry of the ridge crest hot springs. Oceanus, 27, 15-19.

Hosking, K. F. G., 1975, The sulphides of certain deep-sea sediment samples collected on DSDP. Initial Reports of the Deep Sea Drilling Project, 31, 515-517.

Ianovici, V., Stiopol, V., Măldărescu, I., Popescu, G., 1977, Kimmerian metallogenesis in North Dobrogea (in Romanian). Studii şi Cercetări de Geologie, Geofizică şi Geografie, seria Geologie, 22, 11-77, Bucharest.

Iosof, V., Neacşu, V., 1980. Analysis of silicate rocks by atomic absorption spectrometry. Revue Roumaine de Chimie 25, 589–597. Bucharest.

Janecky, D. R., Seyfried, W. E., 1984, Formation of massive sulfide deposits on oceanic ridge crests. Incremental reaction models for mixing between hydrothermal solutions and seawater. Geochimica et Cosmochimica Acta, 48, 2723-2738.

Kempe, D. R. C., 1981, Deep ocean sediments. In: Cocks L.R.M. (Ed.), The Evolving Earth. British Mus. Nat. Hist. & Cambridge Univ. Press, London, Cambridge, pp 103-120.

Kempe, D. R. C.; Easton, A. J., 1974, metasomatic garnets in calcite (micarb) chalk at Site 251, southwest Indian Ocean. Initial Reports of the Deep Sea Drilling Project, 26, 593-601.

Krauskopf, K. B., 1957, Separation of manganese from iron in sedimentary processes. Geochimica et Cosmo-chimica Acta, 12, 61-84.

Lonsdale, P., 1984, Hot vents and hydrocarbon seeps in the Sea of Cortez. Oceanus, 27, 21-24.

Lyle, M. W., Owen, R. M., Leinen, M., 1986, History of hydrothermal sedimentation at the East Pacific Rise, 19° S. Initial Reports of the Deep Sea Drilling Project, 92, 585-596.

Matthews, A., 1976, Magnetite formation by the

reduction of hematite with iron under hydrothermal conditions. Ame-rican Mineralogist, 61, 9-10, 927-932.

Maxwell, J.A. 1968, Rock and Mineral Analysis. Interscience Publishers, London, 584 p.

Maynard, J. B., 1983, Geochemistry of sedimentary ore deposits. Springer, Berlin, 305 p.

Mârza, I., Vladimirov, O., Diaconovici, R., 1981. The pyrometasomatic hydrothermal iron deposit from Iulia (Tulcea County) (in Romanian). Studii şi Cercetări de Geologie, Geofizică şi Geografie, series Geology, 26, 197-211. Bucharest.

Miller, A. R., Densmore, C. D., Degens, E., Hathaway, J. C., Manheim, F. T., McFarlin, P. F., Pocklington, R., Jokela, A., 1966, Hot brines and recent iron deposits in deeps of the Red Sea. Geochimica et Cosmo-chimica Acta, 30, 341-359.

Mitchell, A. H. G., Garson, M. S., 1981, Mi-neral deposits and global tectonic set-tings. Academic Press, London, 405 p.

Rea, D. K., Leinen, M., 1986, Neogene controls on hydrothermal activity and paleoceanography of the Southeast Pacific Ocean. Initial Reports of the Deep Sea Drilling Project, 92, 597-617.

Richards, S. M., 1966, The banded iron for-mation at Broken Hill, Australia, and their relationship to the lead-zinc ore-bodies. Economic Geology, 61, 72-96.

Ridge, F. V., 1973, Volcanic exhalations and ore deposition in the vicinity of the sea floor. Mineralium Deposita, 8, 332-348.

Sangster, D. F., 1976, Carbonate-hosted lead-zinc deposits. In: Wolf K.H. (Ed.), Handbook of stratabound and stratiform ore deposits. Elsevier, Amsterdam VI, 445-456.

Savul, M.M., 1935, Porphyres quartzifères de la région de Meidanchioi-Consul (Dobrogea du nord). Comptes Rendus des Séances Institute Géologique de Roumanie, 20, 164-180, Bucharest.

Săndulescu, M., Visarion, M., 1988. La structure des plate-formes situées dans l'avantpays et au-dessous des nappes du flysch des Carpathes Orientales. Studii tehnice şi economice, Institutul de Geologie şi Geofizică, D/15, 61–68, Bucharest.

Seghedi, I., Szákács, A., Baltres, A., 1990. Relationships between sedimentary deposits and eruptive rocks in the Consul Unit (North Dobrogea) – Implications on tectonic interpretations. Dări de seamă ale şedinţelor Institutului Geologic al României, 74, 125-136. Bucharest.

Stampfli, G.M., Mosar, J., Favre, P., Pillevuit, A., Vannay, J.-C., 2001, Permo-Mesozoic evolution of the western Tethys realm: the Neo-Tethys East Mediterranean Basin connection. Memoirs du Museum National d'Histoire Naturelle 186 (Peri-Tethys Memoir, 6), 51-108.

Şengör, A. M. C. and Natal'in, B. A., 1996, Palaeotectonics of Asia: Fragments of A Synthesis. In Yin, A. and Harrison, M., (Eds.), The Tectonic Evolution of Asia. Rubey Colloquium, Cambridge University Press, Cambridge, 486-640.

Tong, J., Yin, H., 2002, The Lower Triassic of South China. Journal of Asian Earth Sciences, 20, 803-815.

Varnavas, S. P., Cronan, D. S., 1981, Partition geochemistry of sediments from DSDP 424 in the Galapagos Hydrothermal Mound Field. Mineralogical Magazine, 44, 325-331.

Varnavas, S. P., Panagos, A. G., 1983, The use of trace metals in elucidating the genesis of some Greek and Cyprus manganese and ferromanganese depo-sits. In: Augusthitis S., S., (ed.). The significance of trace elements in sol-ving petrogenetic problems & controversies. Theophrastus, Athens, 819-857.

Veniale, F., van der Marel, H. W., 1963, An interstratified saponite swelling chlorite mineral as a weathering product of lizardite rock from St. Margherita Staffora (Pavia Province), Italy. Beiträge zur Mineralogie und Petrologie, 9, 198-245.

Veniale, F., van der Marel, H. W., 1968, A regular talc-saponite mixed-layer mineral from Ferriere, Nure Valley (Piacenza Province, Italy). Contributions to Mineralogy and Petrology, 17, 237-254.

Vlad, S., 1978, Metalogeneza triasică din zona Tulcea (Dobrogea de Nord). Studii şi Cercetări de Geologie, Geofizică şi Geografie, seria Geologie, 23, 249-258. Bucharest.

Whitehead, R.E., 1973, Environment of stratiform sulphide deposition; variation in Mn:Fe ratio in host rocks at Heath Steele mine, New Brunswick, Canada. Mineralium Deposita, 8, 2, 148-160.