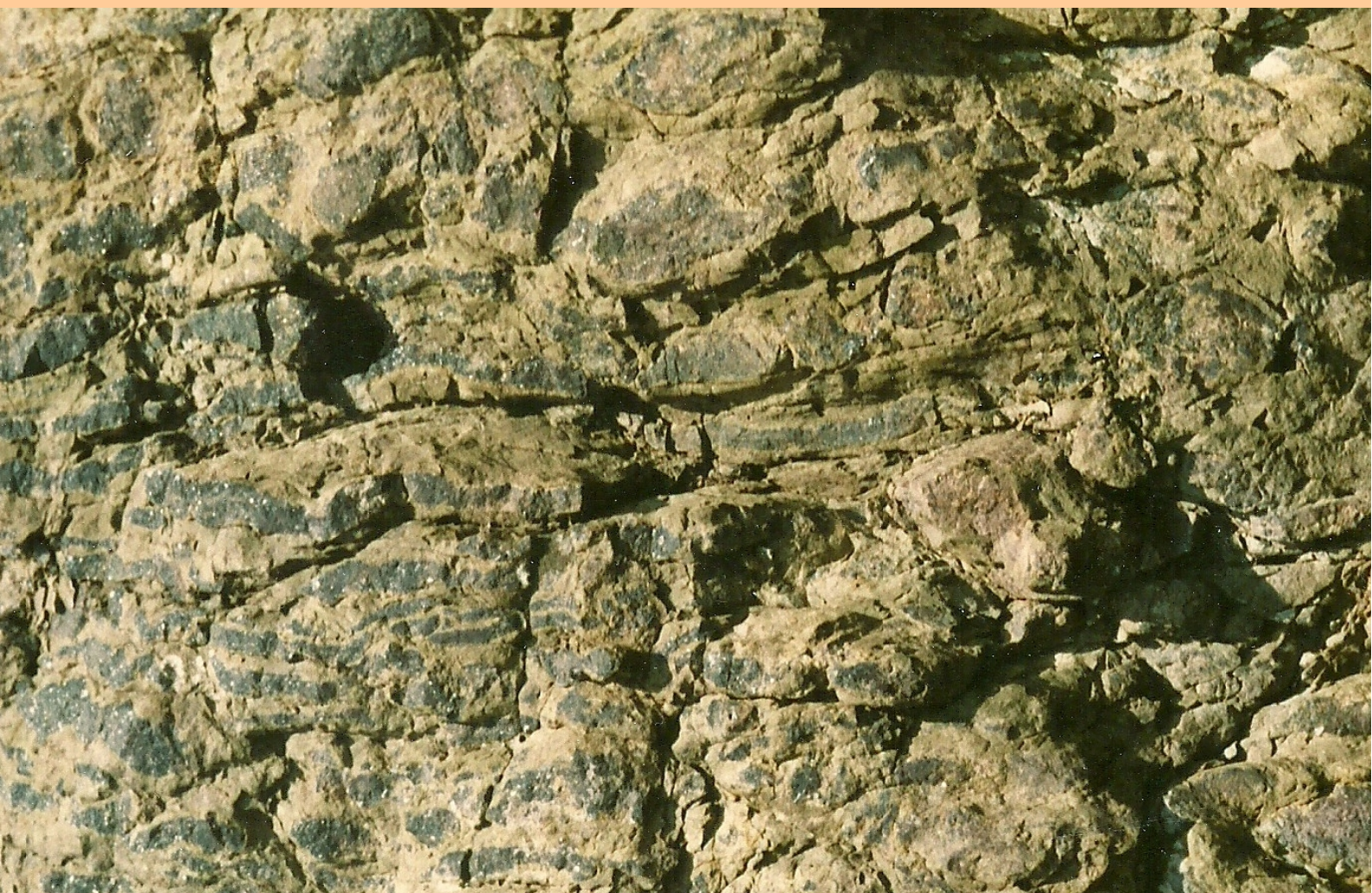


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Cover illustration: outcrop of iron ore at Iulia, with alternating bands of hematite (grey) and garnet-rich gangue (yellowish-greenish). Picture taken by Albert Baltres. The width of the picture is 50 cm.

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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 (Cetățuia-Consul Fault) to the

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).

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

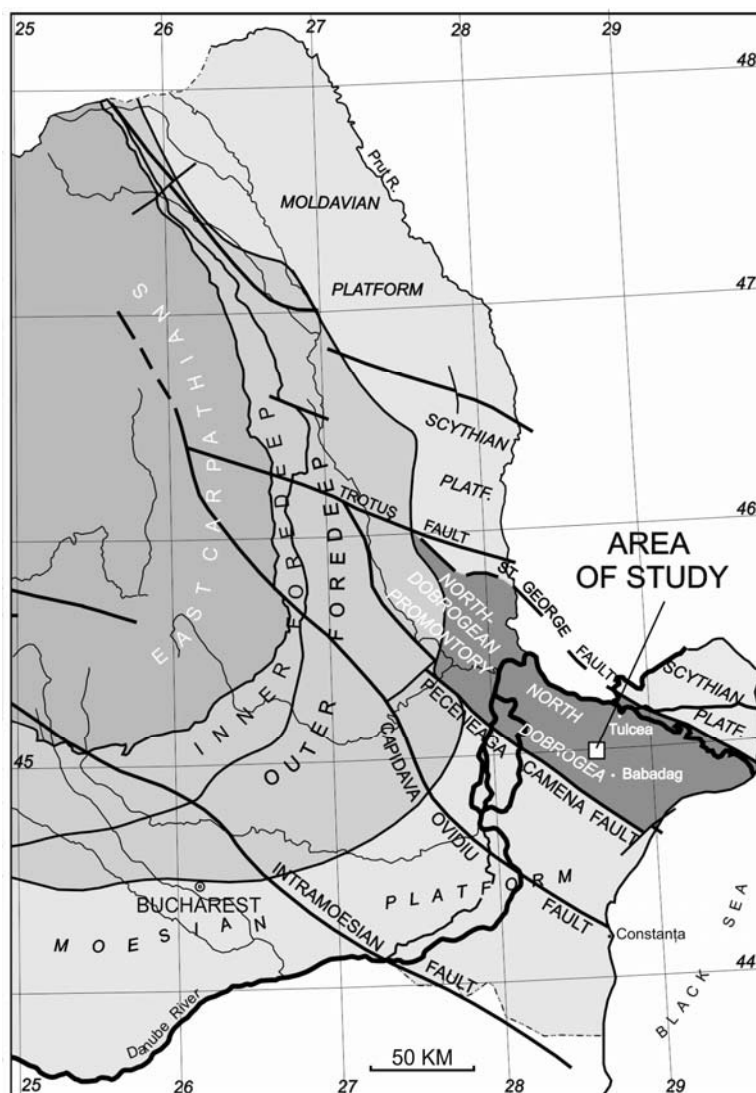


Fig. 1. Structural map of eastern Romania (after Săndulescu and Visarion, 1988, *passim*), showing the location of study area.

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

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 macrofaunal 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 intrusive 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 slivers¹. 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 NNW-

SSE: the steep main fracture named Cetățuia-Consul Fault (also known as Luncavița-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 Mirăuță, cited by Baltres, 2003); (ii) benthic foraminifera: *Meandrosira 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).

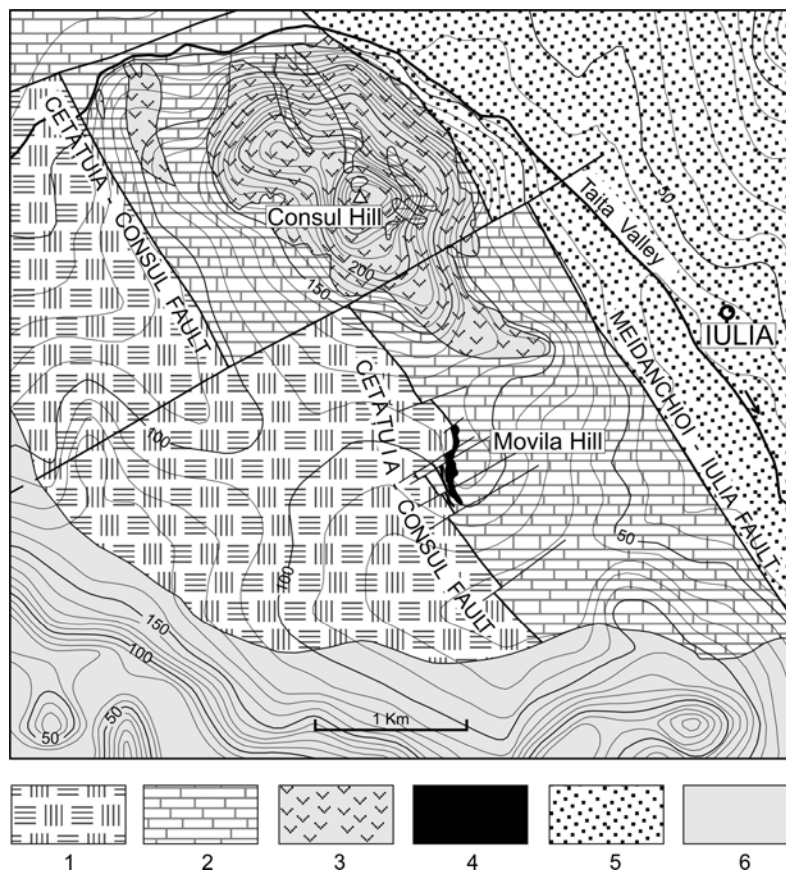


Fig. 2. Geological map of the Iulia zone. Loess cover ignored. 1. Basement (Boclugea Group); 2. Somova Formation (Spathian); 3. Consul Rhyolite (Spathian); 4. Outcropping iron ore (Spathian); 5. Nalbant Formation (Upper Triassic); 6. Dolojman Formation (Upper Cretaceous).

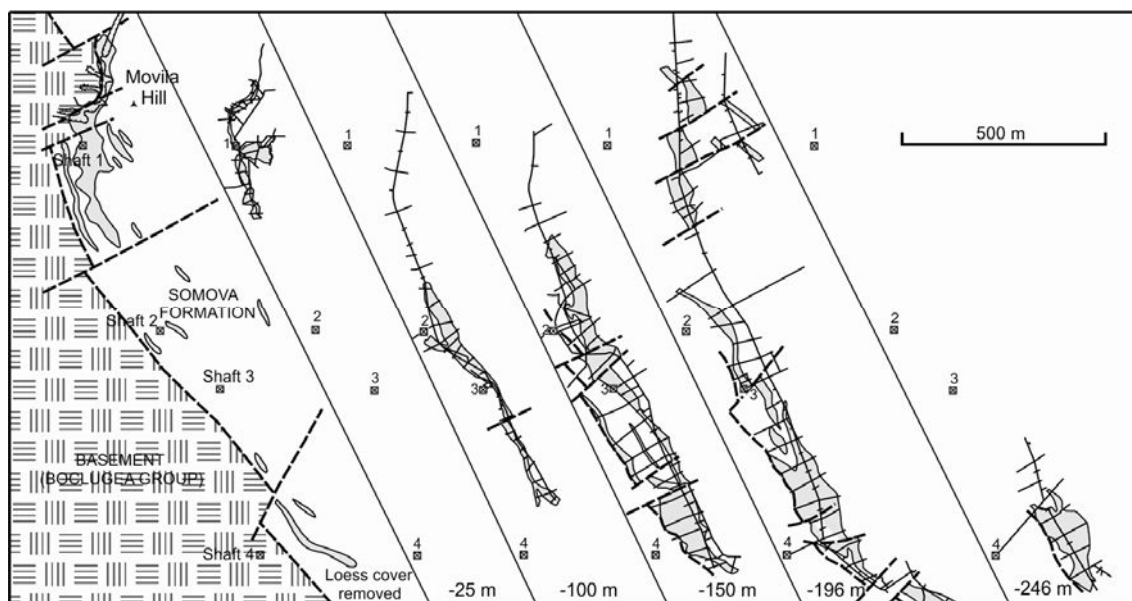


Fig. 3. Map showing the location of iron ore lenses (in gray) at various depths in mining workings undertaken at Iulia. Exploration data.

In addition, dark Somova-type limestones, reaching up to 34 m in thickness, 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 Luncavița-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 Luncavița-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 Luncavița-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 Neacșu (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 $\text{Cu-K}\alpha$ 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 garnetiferous 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 ₂ O ₃	11.2	16.9	3.0	10.4	3.3	2.0	1.5	4.4	1.0	1.2
Fe ₂ O 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 ₂ O	0.4	0.8	bdl	bdl	1.2	bdl	bdl	0.1	0.1	0.1
Na ₂ O	0.1	bdl	bdl	0.1	0.1	bdl	bdl	bdl	0.2	0.1
P ₂ O ₅	0.2	0.2	0.1	0.2	bdl	0.1	0.1	0.1	0.1	0.1
H ₂ O	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 Fe₂O₃ 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 corruptions, 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.

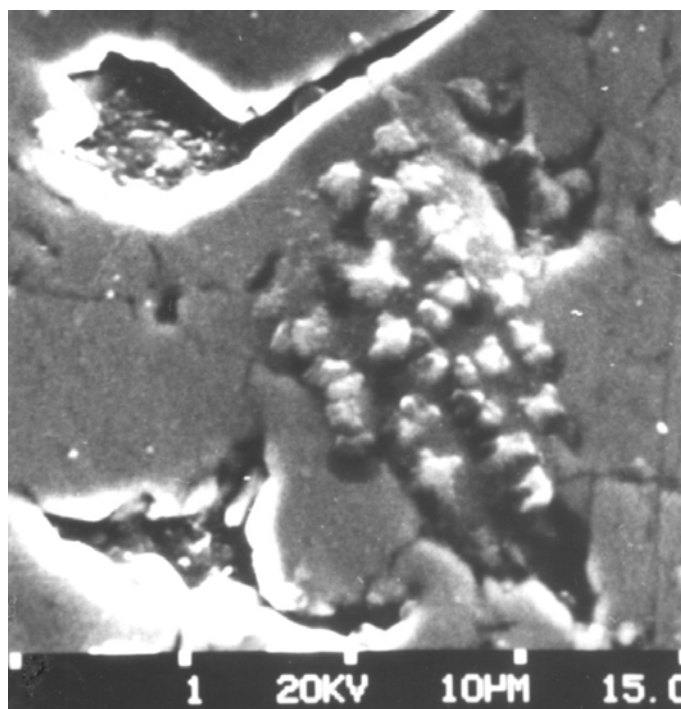


Fig. 5. A cluster of tiny NaCl crystals forming one of many solid inclusions in hematite. Polished surface, SEM image.

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 missing. 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 obtained 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.

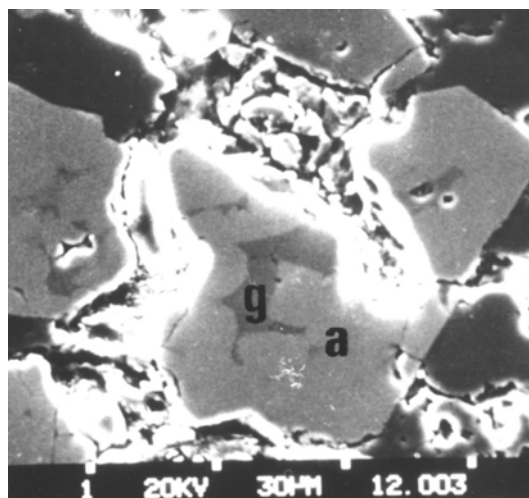


Fig. 6. Polished surface of a grandite crystal with an inner, darker part of near-grossularite composition (g) and a larger outer part with a near-andradite composition (a). SEM image.

(iii) 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 abundant 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, decimetric 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 $\text{Ti/Fe} \times 1000$ 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 recessed 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).

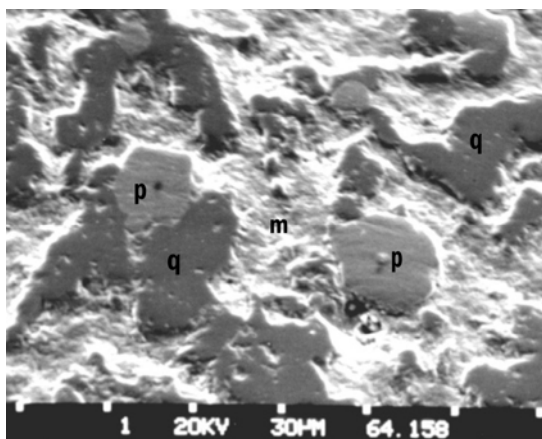


Fig. 7. Polished surface of the amorphous or cryptocrystalline matrix which occurs recessed (m), containing irregular patches of quartz (q) and minute pyrite crystals (p). The matrix consists essentially of a regularly mixed-layer chlorite-swelling chlorite clay mineral. SEM image.

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 pyrometasomatism 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 Luncavița-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 occurrences 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 diagenesis, 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 carrying leached metals, mainly iron, as chloride complexes.

That the solutions carrying 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 referring 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.

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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 H₂O-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 sedimentation 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 + CO₂ + H₂O. *Contribution to Mineralogy 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 Cosmochimica 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. *American 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 pyrometamorphic hydrothermal iron deposit from Iulia (Tulcea County) (in Romanian). *Studii și Cercetări de Geologie, Geofizică și 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 Cosmochimica Acta*, 30, 341-359.
- Mitchell, A. H. G., Garson, M. S., 1981, *Mineral deposits and global tectonic settings*. 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 formation 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 și economice*, Institutul de Geologie și 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 sedințelor 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 deposits. In: Augusthitis S., S., (ed.). *The significance of trace elements in solving 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 și Cercetări de Geologie, Geofizică și 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.

A reconnaissance study on selected intrusive bodies south of Panzhihua, Sichuan Province, South-West China: petrogenetic and metallogenetic significance

Marian MUNTEANU^{1,2,*}, Yong YAO^{1,3}, Mihaela CIOACĂ², Gordon CHUNNETT¹, Yaonan LUO⁴

¹*School of Geosciences, University of the Witwatersrand, Johannesburg, South Africa*, ²*Geological Institute of Romania, Bucharest, Romania*, ³*Department of Geology, Rhodes University, Grahamstown, South Africa*, ⁴*Sichuan Bureau of Geology and Mineral Resources, Chengdu, China*

Abstract: This paper provides petrographic and geochemical data (major and trace elements) on selected Permian intrusions south of Panzhihua municipality: Luobodi (gabbro hosting Fe-Ti-V oxide ore), Jizicheng (dunitic peridotite and olivine pyroxenite $\pm$ gabbro), Gongshanqing (gabbro and peridotite hosting PGE mineralization), one gabbro body and two picrite dikes intruded in the southern part of the Datian Proterozoic complex. These intrusions are genetically related to the Permian Emeishan large igneous province. The attempt to find a geochemical correlation between the investigated intrusions and the high-Ti or low-Ti Emeishan basalts yielded ambiguous results. Most of the rocks have $Ti/Y > 500$, similar to the high-Ti basalts, while Zr/Nb and La/Yb ratios are similar to those of the low-Ti Emeishan basalts. The ultramafic rocks in the Gongshanqing and Jizicheng intrusions have $Cu/Zr \geq 1$ and Cu/Pd ratios within the mantle range (1000-10000), which suggests their genesis from magmas fertile in chalcophile elements. The formation of the Gongshanqing and Jizicheng intrusions in magmatic conduits is inferred.

Keywords: mafic, ultramafic, Emeishan large igneous province, Permian, Panxi rift, China

1. Introduction

The western part of the Yangtze craton is characterized by the presence of a zone of crustal extension, known in the Chinese literature as the Panxi zone or the Panxi rift (Fig. 1A), named from the two municipalities of Panzhihua and Xichang (Fig. 1B). The Panxi rift is located within the Emeishan large igneous province (Xu et al., 2001), made up of the Emeishan basalts, ca. 260 Ma in age (Zhou et al., 2002a), and numerous intrusions cropping out within the Panxi rift. The Emeishan basalts were divided in two geochemical types of low-Ti and high-Ti compositions (Xu et al., 2001; Xiao et al.,

2004; Xu et al., 2004; Ali et al., 2005; Zhou et al., 2008). The low-Ti basalts have $TiO_2 < 2.5\%$ and $Ti/Y < 500$, while high-Ti basalts are characterized by $Ti/Y > 500$ and $TiO_2 > 2.5\%$ (Xu et al., 2001).

Most intrusions of the Emeishan large igneous province crop out within the Panxi rift, and contain various rock types (peridotite, pyroxenite, gabbro, syenite, alkaline granite). The Panxi rift is economically important as it contains several ore deposits hosted in intrusive bodies. These deposits are of two main types: giant-scale Fe-Ti-V oxide deposits (Panzhihua, Hongge, Baima, Taihe) and smaller Ni-Cu(-PGE) sulfide deposits (e.g. Yangliuping, Limahe, Zhubu, Jinbaoshan, Baimazhai). The Fe-Ti-V oxide deposits are hosted in gabbroic intrusions, while the sulfide deposits occur in ultramafic-mafic intrusions. Zhou et al. (2008) argued for a genetic relation between the high-

* Tel: +40213060491; fax: +40213181326;
e-mail address: munteanu.marian@igr.ro

Ti Emeishan basalts and the Fe-Ti-V oxide deposits, on the one hand, and between the low-Ti Emeishan basalts and the sulfide deposits, on the other hand.

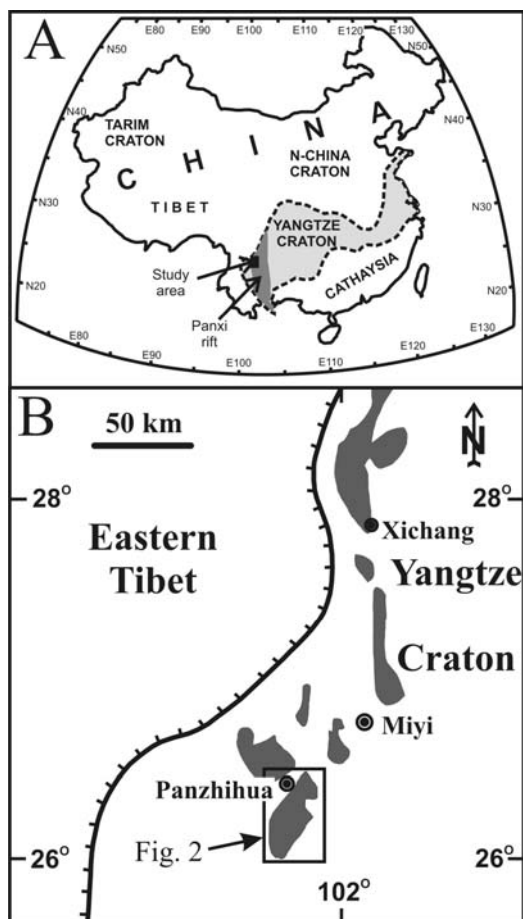


Fig. 1. A. Location of study area in the Panxi rift. B. Tectonic sketch map of the western margin of the Yangtze craton in the south-western part of the Sichuan Province. The Proterozoic intrusions are figured in dark grey.

In this paper we report data resulted from geological observations and geochemical investigations on samples collected during a field trip to several intrusions south of Panzhihua. Based on these data and on the models and hypotheses in the literature, we discuss on the formation of the intrusions and on their Ni-Cu and PGE potential.

2. Geology of the intrusions

The *Datian* intrusive complex is located south-east of the Panzhihua Fe-Ti-V oxide deposit (Fig. 2). It is one of the many batholiths with granitic-dioritic rocks within the late Proterozoic Hannan-Panxi arc (Zhou et al., 2002b); therefore it belongs to the basement of the Panxi rift. Its age is ca. 759 Ma (Li et al., 2003). CGGJC (1986) refer to the Datian complex under the name of Dukou diorite, with an extent of 55 km x 20 km and a petrographic composition dominated by quartz diorite, with variations from hornblende gabbro to granodiorite. Zhao and Zhou (2007a) determined the age of two gabbroic bodies in the north-western margin of the Datian complex to 746 ± 10 Ma and 738 ± 23 Ma. The Datian complex usually displays a gneissic texture and contains enclaves of rocks metamorphosed in the granulite facies (CGGJC, 1986).

Luobodi is a gabbroic intrusion hosting Fe-Ti-V oxide ore. Among the intrusions mineralized with Fe-Ti-V oxides in the Panxi rift, the Luobodi intrusion is located in a western alignment, together with Panzhihua and Malong intrusions (Yao et al., 2001).

Jizicheng is an ultramafic intrusion south of Luobodi. Observations and sampling along a country road that exposes the intrusion almost continuously, showed a spatial zonation, with a marginal zone (ca. 30 m wide) made up of fine-grained peridotite, and a coarser inner zone made up of olivine pyroxenite, the latter showing transitions to more feldspathic compositions (grading to olivine gabbro) in its central part.

Gongshanqing intrusion (ca. 800 m x 500 m) is located at the limit between the dominant Datian quartz diorites (to the east) and the Lixidong granodiorite (to the west). The intrusion is made up of distinct mafic and ultramafic zones. The ultramafic zone is poorly exposed but it was investigated with numerous drill holes and one adit. The exploration conducted during the 1960s indicated Pt+Pd contents up to several g/t and Ni and Cu contents less than 0.5% each.

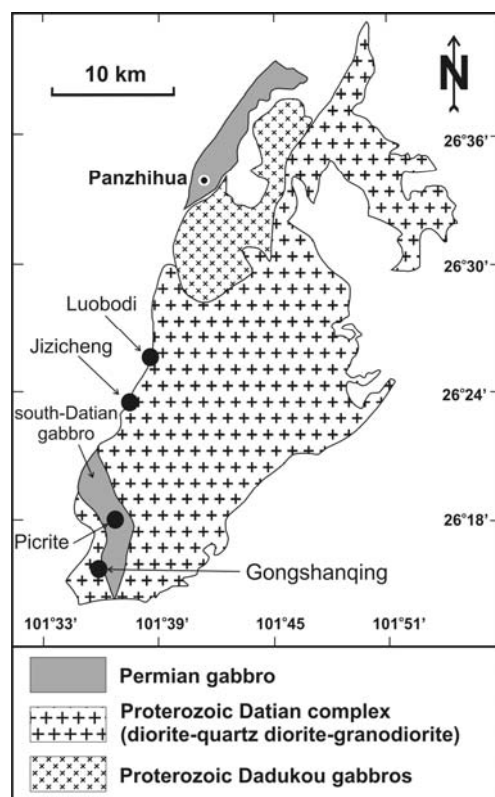


Fig. 2. The Datian intrusive complex and the location of the rocks investigated in this study (geology simplified after Zhao and Zhou, 2007b).

Two *picrite dikes* are figured north-east of the Gongshanqing intrusion on the exploration maps of the Sichuan Bureau for Geology and Mineral Resources. These are limited in their extent (less than 100 m on strike).

The southern part of the Datian Proterozoic complex was intruded by a gabbroic body (Fig. 2) of Permian age (Zhao and Zhou, 2007b, Fig. 2). This intrusion will be referred to hereafter as the *south-Datian gabbros*.

3. Petrography of the Permian intrusions

Luobodi Similar to the rocks in the Panzhihua deposit, the gabbros of the Luobodi intrusion contain olivine. Olivine, pyroxene and plagioclase may be included in Fe-Ti oxides (Fig. 3A,B) but commonly are interstitial to the oxide grains, the latter

exhibiting occasional euhedral shapes (Fig. 3C).

Jizicheng The peridotite from the marginal zones is dunitic (~ 90% olivine). The olivine occurs as euhedral crystals (Fig. 3D), commonly less than 1 mm in size (only exceptionally reaching 2 mm), entirely altered to serpentine. A serpentinized mass occurs between the olivine crystals (presumably dominated by former pyroxene oikocrysts). The peridotite gradually passes to pyroxenite, concomitantly increasing its grain size; the olivine crystals become coarser (3-4 mm in size), being accompanied by smaller pyroxene crystals (1-2 mm). Further away from the margins of the intrusion, the proportion of modal olivine gradually decreases to 20-35% in favor of pyroxene, which generates rare porphyric crystals (ca. 6 mm in size). The increasing frequency of the porphyric pyroxene crystals toward the inner parts of the intrusion leads to the generation of equigranular coarser rocks (Fig. 3E). In the coarse equigranular olivine pyroxenite, the pyroxene can be oikocrystic, embaying olivine crystals (Fig. 3F). Plagioclase occurs as interstitial (anhedral to subeuhedral) crystals (Fig. 3G), with increasing proportions in the coarser rocks, where it can exceed 10% modal. Interstitial brown hornblende (Fig. 3H) occurs as a minor phase (2-5%). In the equigranular coarse pyroxenite, olivine may show interstitial position (Fig. 3E). The gabbros occurring in the central part of the intrusion show mesocratic and leucocratic varieties, made up of plagioclase and green hornblende, without pyroxene and olivine.

Gongshanqing Peridotite is the dominant rock type, showing typical cumulate texture (Fig. 4A). The olivine is cumulus, commonly included in pyroxene oikocrysts (Fig. 4B). Brown hornblende and biotite are also oikocrystic, occurring as skeletal crystals interstitial to olivine and pyroxene (Figs. 4A,C). The peridotite shows transitions to pyroxenite. The outcropping mafic rocks are hornblende gabbros (plagioclase and green hornblende), commonly leucocratic to mesocratic.

The *picrite dikes* show two facies: (a) the fine-grained picrite (Fig. 4D) contains olivine $\pm$ pyroxene phenocrysts in a matrix of unoriented plagioclase laths $\pm$ anhedral plagioclase crystals, with smaller pyroxene and oxide crystals (magnetite and ilmenite) in the interstices; (b) the medium grained picrite (Fig. 4E) is made up of euhedral olivine phenocrysts $\pm$ pyroxene phenocrysts

embedded in a groundmass of anhedral plagioclase and euhedral to subeuhedral pyroxene, hornblende, biotite and Fe-Ti oxides. Our samples of *south-Datian gabbros* show simple mineral assemblages, consisting of plagioclase, green hornblende and Fe-Ti oxides. The hornblende may include small plagioclase crystals and Fe-Ti oxide grains (Fig. 4I).

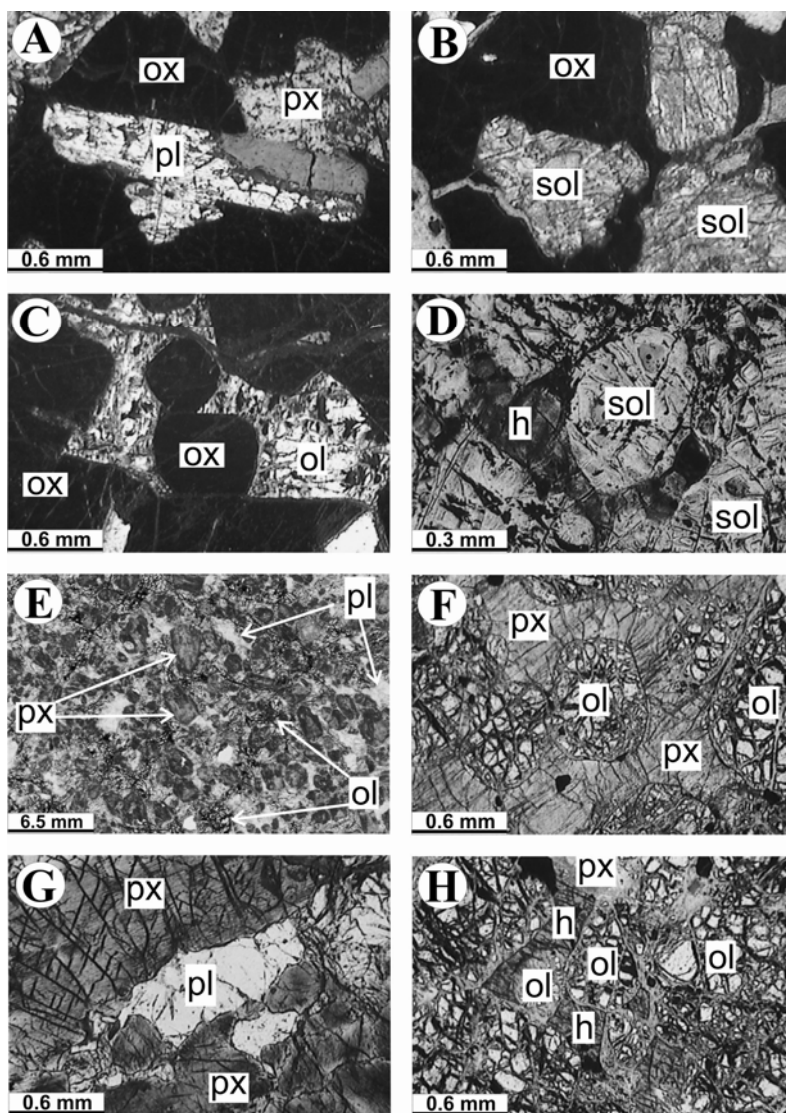


Fig. 3. Mineral relations in the Luobodi (A-C) and Jizicheng (D-H) intrusions. All microscope images (A-E and F-H) were taken in transmitted light, with parallel nicols. Symbols: h= hornblende; ol = olivine; ox = oxide; pl = plagioclase; px = pyroxene; sol = serpentinized olivine. A. Plagioclase crystal included in oxide. B. Serpentinized olivine included in oxide. C. Euhedral oxide grains. D. Dunitic peridotite of the outer zone of the Jizicheng intrusion. Serpentinized olivine crystals and interstitial hornblende. E. Olivine pyroxenite with interstitial anhedral plagioclase. Scanned thin section. F. Pyroxene oikocryst with included olivine crystals. G. Anhedral plagioclase between pyroxene crystals. H. Hornblende oikocrysts with olivine inclusions

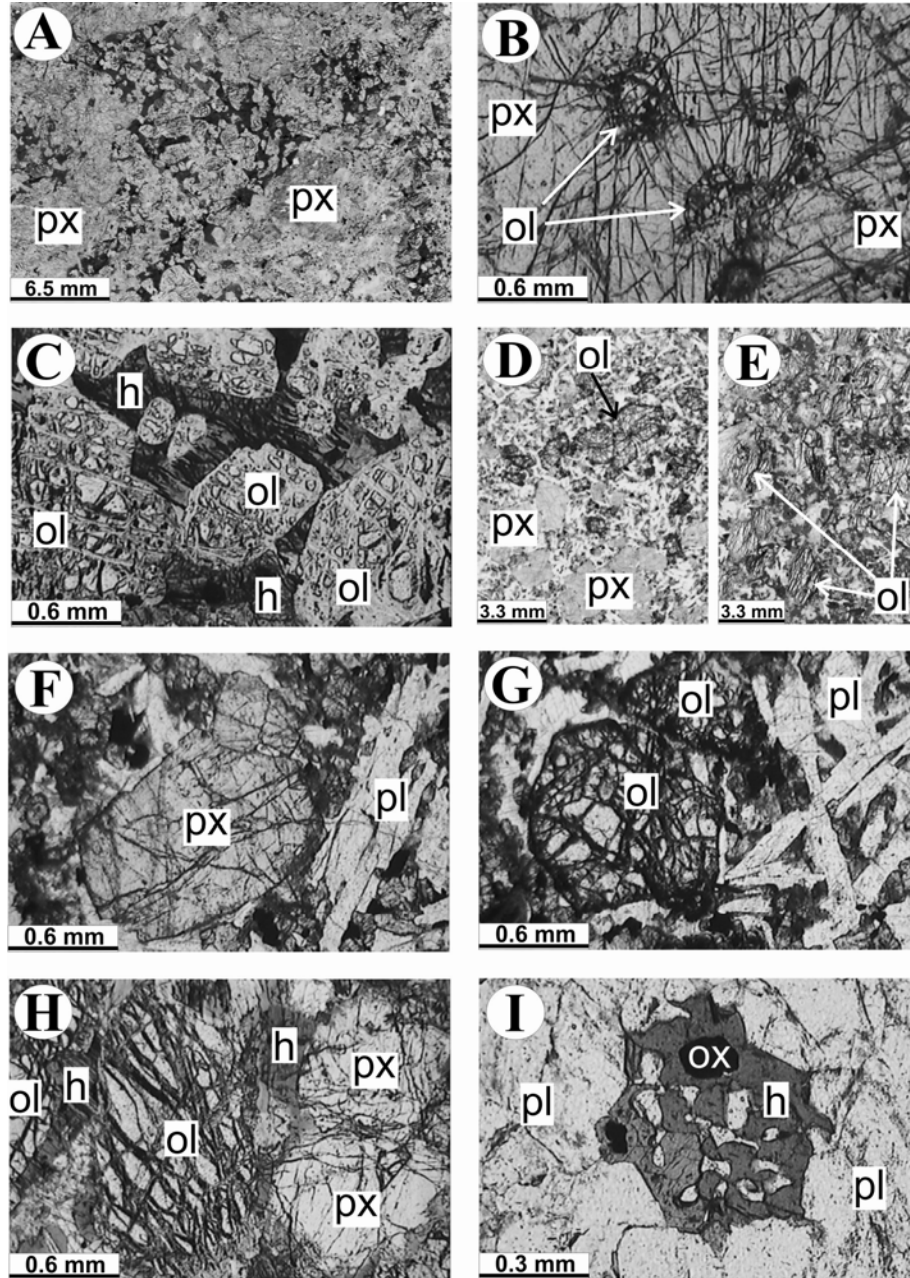


Fig. 4. Mineral relations in the Gongshanqing intrusion (A-C), in the picrite dikes and in the south-Datian gabbros (I). The pictures at the microscope (A-C and F-G) were taken in transmitted light with parallel nicols. Symbols: h= hornblende; ol = olivine; ox = oxide; pl = plagioclase; px = pyroxene. A. Peridotite with hornblende oikocrysts (dark) between pyroxene oikocrysts (px), both including olivine crystals. B. Olivine crystals in pyroxene oikocryst. C. Olivine crystals in hornblende oikocryst. D. Fine-grained facies of picrite, with porphyric olivine and pyroxene in a matrix made up of euhedral plagioclase laths and interstitial pyroxene. Scanned thin section. E. Medium-grained facies of picrite, with olivine crystals in a matrix made up of anhedral plagioclase, pyroxene and hornblende. Scanned thin section. F. Fine-grained facies. Euhedral plagioclase, porphyric pyroxene, surrounded by small euhedral pyroxene, oxide, euhedral to subeuhedral plagioclase, anhedral hornblende. G. Fine-grained facies. Euhedral plagioclase, porphyric olivine and interstitial pyroxene, oxide and hornblende. H. Medium-grained facies. Porphyric pyroxene and olivine with interstitial hornblende and plagioclase. I. South-Datian gabbro. Hornblende with inclusions of plagioclase and oxide.

Table 1. Major and trace element contents of the investigated intrusive rocks. Dt = Datian; gbb = gabbro; Gg = Gongshanqing; Jzc = Jizicheng; Lbd = Luobodi; mgt = Fe-Ti-V oxide ore; per = peridotite; pxt = pyroxenite; qd = quartz diorite; sDg = south-Datian gabbro; bdl = below detection limit.

Sample	Dt1	Dt5	Dt7	Dt7A	Dt8	Dt9	Dt10	Dt11	Dt12
Latitude	26.35968	26.26312	26.26312	26.26438	26.26467	26.26439	26.26378	26.42225	26.42225
Longitude	101.7639	101.6053	101.6053	101.6076	101.6071	101.6071	101.6062	101.6348	101.6348
Lithology	qd	per	gbb	per	per	per	per	pxt	pxt
Intrusion	Dt	Gg	Gg	Gg	Gg	Gg	Gg	Lbd	Lbd
SiO ₂ %	64.78	41.08	56.95	45.19	47.21	40.64	40.38	18.73	19.94
TiO ₂	0.44	0.81	0.54	2.19	0.9	0.76	0.78	11.45	10.46
Al ₂ O ₃	17.02	4.32	18.47	7.59	3.94	3.46	3.63	8.51	9.23
Fe ₂ O ₃	4.17	15.32	5.52	14.7	13.11	15.37	15.25	49.13	47.76
MnO	0.05	0.18	0.1	0.18	0.19	0.18	0.18	0.27	0.27
MgO	2.32	26.85	3.82	19.53	22.38	29.42	28.48	5.76	6.7
CaO	4.17	3.82	5.18	5.91	8.76	2.89	3.1	3.26	2.28
Na ₂ O	3.93	0.51	5.32	1.11	0.51	0.41	0.36	0.53	0.38
K ₂ O	2.32	0.31	1.54	0.24	0.2	0.22	0.23	0.09	0.09
P ₂ O ₅	0.13	0.07	0.16	0.16	0.07	0.08	0.09	0.06	0.03
LOI	0.6	5.8	2.3	2.6	1.9	5.5	6.5	2.1	2.6
S	bdl	0.11	bdl	bdl	0.14	bdl	bdl	0.38	0.33
Total	99.94	99.18	99.92	99.44	99.31	98.99	99.05	100.27	100.07
Sc ppm	7	14	11	22	33	11	13	27	28
V	74	133	104	219	167	113	122	1643	1587
Cr	37	357	28	381	253	292	372	0.5	bdl
Co	11	96	11	62	57	107	102	121	137
Ni	21	1297	31	1029	994	1579	1503	29	33
Cu	3	57	10.5	288	245	44	53	69	63
Ga	19	7.2	19	12.2	7.1	5.6	6.7	28.2	28
Rb	92	7.3	42.2	2.4	5.1	5.1	5.7	2.1	2.1
Sr	476	140	672	240	102	120	106	202	170
Y	5	8.4	11	18.2	10.7	6.5	8	8.1	7.2
Zr	77	49	106	124	47	44	48	34	32
Nb	6.2	6.4	4.5	12.6	4.2	4.7	5.6	6.1	5.7
Ba	494	67	369	78	40	43	48	216	388
Cs	4.1	0.4	0.5	0.8	0.4	0.2	0.3	0.2	0.3
La	10.2	6.1	15.9	12.5	4.9	4.8	5.5	3.1	2.6
Ce	20.3	15.2	34.9	33.2	13	11.8	13.6	8.6	6.9
Pr	2.3	2.0	4.2	4.5	1.8	1.6	1.8	1.4	1.1
Nd	8.6	8.8	17.6	21.5	9.1	7.2	8.5	7.4	6.4
Sm	1.56	1.92	2.83	4.41	2.11	1.58	1.76	1.71	1.49
Eu	0.62	0.62	0.82	1.4	0.72	0.51	0.56	0.91	0.96
Gd	1.28	1.79	2.26	4.1	2.17	1.49	1.69	1.9	1.67
Tb	0.22	0.33	0.39	0.72	0.41	0.26	0.31	0.34	0.29
Dy	0.85	1.51	1.74	3.34	1.97	1.26	1.37	1.56	1.37
Ho	0.15	0.27	0.33	0.61	0.36	0.22	0.25	0.27	0.24
Er	0.38	0.71	0.88	1.53	0.89	0.58	0.64	0.67	0.59
Tm	0.06	0.11	0.15	0.24	0.14	0.09	0.1	0.09	0.08
Yb	0.36	0.64	0.94	1.36	0.77	0.51	0.58	0.53	0.49
Lu	0.05	0.1	0.14	0.2	0.12	0.08	0.08	0.08	0.07

Permian intrusive bodies south of Panzhihua, SW China

Hf	2.2	1.4	3	3.7	1.5	1.4	1.3	1.2	1.3
Ta	0.3	0.4	0.2	0.7	0.2	0.2	0.3	0.3	0.3
Pb	1.08	0.88	5.69	1.04	0.79	0.78	0.9	0.6	0.73
Th	2.5	0.9	2.7	1.8	0.7	0.8	0.7	0.1	0.2
U	0.6	0.2	0.7	0.4	0.2	0.2	0.2	bdl	bdl
Pd ppb	bdl	bdl	bdl	28	36	15	19	bdl	bdl
Pt	bdl	bdl	bdl	19	28	15	19	bdl	bdl
Ti/Y	528	579	295	722	505	702	585	8481	8717
Zr/Nb	15.5	5.8	9.7	6.8	4.4	6.8	6.0	4.2	4.5
La/Yb	28.3	9.5	16.9	9.2	6.4	9.4	9.5	5.8	5.3
Cu/Pd	0	0	0	10298	6794	2957	2769	0	0
Cu/Zr	0.04	1.17	0.10	2.32	5.22	1.00	1.11	2.01	1.94

Table 1 (continued)

Sample	Dt13	Dt15	Dt16	Dt17	Dt18	Dt19	Dt20	Dt22	Dt25
Latitude	26.42225	26.38146	26.38153	26.38135	26.38158	26.38195	26.38195	26.38257	26.38657
Longitude	101.6348	101.6145	101.6148	101.6142	101.6138	101.613	101.613	101.6129	101.6132
Lithology	mgt	pxt	pxt	pxt	pxt	pxt	gbb	pxt	pxt
Intrusion	Lbd	Jzc	Jzc	Jzc	Jzc	Jzc	Jzc	Jzc	Jzc
SiO ₂ %	4.91	38.97	38.94	45.13	43.59	48.36	46.47	44.15	45.68
TiO ₂	15.82	0.28	0.31	0.71	0.75	0.82	0.62	0.61	0.84
Al ₂ O ₃	4.3	1.48	1.74	3.18	3.53	3.37	11.85	2.32	5.83
Fe ₂ O ₃	71.03	12.48	13.35	13.6	15.52	12.03	11.51	14.27	12.36
MnO	0.36	0.14	0.15	0.19	0.21	0.19	0.15	0.19	0.18
MgO	2.84	33.1	32.05	22.58	22.49	19.4	15.65	24.69	18.9
CaO	0.17	0.04	0.07	11.96	10.77	14.88	11.49	10.21	12.99
Na ₂ O	0.01	bdl	bdl	0.3	0.33	0.41	1.5	0.25	0.58
K ₂ O	bdl	bdl	bdl	bdl	bdl	bdl	0.11	bdl	0.06
P ₂ O ₅	0.05	0.01	0.02	0.01	0.01	bdl	0.02	bdl	0.02
LOI	0.3	12.4	12.4	1.7	2.2	0.1	0.4	2.7	2.1
S	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Total	99.82	98.92	99.04	99.37	99.41	99.58	99.78	99.40	99.56
Sc ppm	18	7	8	42	39	57	31	36	43
V	1760	63	61	167	185	241	156	145	184
Cr	37	314	255	223	321	126	347	201	257
Co	11	113	106	78	91	49	64	97	65
Ni	54	2268	1914	934	1071	480	445	1082	699
Cu	31	14	74	56	37	101	10	14	23
Ga	28.1	3.3	3.3	5.2	5.8	5.9	11.7	4.4	8
Rb	0.5	bdl	bdl	0.5	0.6	0.5	1.2	bdl	1.3
Sr	576	3.3	6.6	76	101	104	526	57	210
Y	3.7	3	2.4	9.1	8.1	12.1	7.2	8.5	10.6
Zr	28	11.1	8.3	18.1	15.7	21.9	14.8	15.8	22.8
Nb	5.6	0.6	0.6	0.4	0.3	0.5	0.4	0.2	0.6
Ba	253	bdl	bdl	bdl	5	bdl	45	bdl	18
Cs	0.1	0.1	0.1	bdl	0.1	bdl	0.2	bdl	0.2
La	2.2	0.9	0.8	1.5	1.3	1.7	1.8	1.2	2
Ce	5.5	2.7	2.4	5.4	4.7	6.8	5.3	4.4	6.8
Pr	0.8	0.44	0.38	1.03	0.91	1.34	0.93	0.89	1.25
Nd	3.8	2.4	2	5.7	5.2	8.1	5.4	5.7	7.7

Sm	0.87	0.62	0.48	1.68	1.56	2.33	1.43	1.56	2.07
Eu	0.36	0.2	0.2	0.59	0.55	0.79	0.66	0.54	0.72
Gd	0.89	0.69	0.54	1.92	1.81	2.59	1.65	1.84	2.2
Tb	0.15	0.12	0.09	0.36	0.34	0.49	0.29	0.32	0.41
Dy	0.67	0.52	0.47	1.77	1.59	2.29	1.41	1.6	1.89
Ho	0.12	0.1	0.08	0.3	0.28	0.41	0.26	0.29	0.36
Er	0.3	0.25	0.23	0.75	0.7	1.03	0.6	0.7	0.84
Tm	0.04	0.04	0.03	0.1	0.1	0.15	0.09	0.09	0.13
Yb	0.24	0.23	0.19	0.59	0.58	0.87	0.51	0.58	0.76
Lu	0.04	0.04	0.03	0.09	0.08	0.12	0.07	0.08	0.1
Hf	1	0.4	0.3	0.8	0.8	1.1	0.8	0.7	1.1
Ta	0.3	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Pb	0.08	3.62	0.53	0.05	0.02	0.11	0.06	0.02	0.2
Th	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
U	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Pd ppb	bdl	17	22	15	bdl	17	bdl	bdl	bdl
Pt	bdl	32	17	13	9	17	6	3	2
Ti/Y	25654	560	775	468	556	407	517	431	475
Zr/Nb	7.6	3.7	3.5	2.0	1.9	1.8	2.1	1.9	2.2
La/Yb	9.2	3.9	4.2	2.5	2.2	2.0	3.5	2.1	2.6
Cu/Pd	0	795	3361	3743	0	5963	0	0	0
Cu/Zr	1.12	1.22	8.91	3.10	2.36	4.63	0.71	0.87	1.02

Table 1 (continued)

Sample	Dt27	Dt28	Dt29	Dt30	Dt31	Dt32	Dt33	Dt34	Dt35	Dt36
Latitude	26.38655	26.38654	26.28963	26.28971	26.28958	26.28844	26.28803	26.29106	26.29106	26.29008
Longitude	101.6129	101.6112	101.6369	101.6372	101.6373	101.6391	101.6047	101.622	101.622	101.6129
Lithology	pxt	per	qd	gbb	gbb	gbb	granite	picrite	picrite	picrite
Intrusion	Jzc	Jzc	Dt	sDg	sDg	sDg	Dt	dike 1	dike 1	dike 2
SiO ₂ %	38.54	39.78	59.08	45.04	45.31	45.19	64.39	46.78	43.49	46.57
TiO ₂	0.32	0.36	0.56	2.97	3.27	3.45	0.43	1.52	1.12	2.65
Al ₂ O ₃	2.04	3.44	18.14	13.94	13.94	14.21	15.67	10.36	6.06	9.2
Fe ₂ O ₃	18.14	14.67	5.69	17.72	17.58	16.59	4.75	12.19	12.48	12.46
MnO	0.21	0.18	0.08	0.17	0.17	0.18	0.1	0.17	0.16	0.16
MgO	30.5	31.01	3.47	5.85	5.82	5.68	2.86	13.61	25.81	14.53
CaO	2.57	3.09	6.65	9.23	8.29	9.19	2.48	9.97	5.29	7.73
Na ₂ O	0.07	0.17	4.13	2.44	2.72	2.6	4.53	1.79	1.09	1.59
K ₂ O	bdl	0.05	1.14	0.9	1.09	0.89	2.98	0.56	0.47	1.48
P ₂ O ₅	0.02	0.04	0.17	0.17	0.16	0.16	0.12	0.15	0.12	0.31
LOI	6.8	6.2	0.8	1.5	1.6	1.8	1.6	2.6	3.3	2.9
S	bdl	bdl	bdl	0.35	0.29	0.25	bdl	0.1	0.11	0.17
Total	99.22	99.03	99.92	100.28	100.24	100.19	99.91	99.80	99.50	99.75
Sc ppm	13	10	12	29	29	29	12	33	17	24
V	94	88	112	628	579	503	85	278	169	245

Permian intrusive bodies south of Panzhihua, SW China

Cr	91	141	34	1.4	0.8	1.5	38	116	290	206
Co	117	109	11.0	40	36	31	10	42	80	48
Ni	1940	1659	30	34	11	6	31	386	1548	641
Cu	29.6	45.8	1.5	79	52	44	5.1	94	72	103
Ga	3.5	4.6	18.6	22.6	20.7	21.6	16.6	14.2	8.8	15.2
Rb	0.5	1.1	27.9	21.8	32.1	20.1	83	13.6	11.2	31.5
Sr	24	114	678	394	412	414	455	338	244	618
Y	2.2	3.2	11.5	24	22.3	25.3	21.1	18.8	12.3	23.5
Zr	6.4	15.1	95	111	106	117	114	109	81	244
Nb	0.2	1.1	4.2	18.5	18.8	22.2	7.2	12.3	11.3	35.2
Ba	6	21	365	207	264	219	627	182	147	630
Cs	0.1	0.1	1	0.5	0.5	0.3	2.3	1.1	0.3	2.7
La	0.7	1.5	16.2	17.2	16.4	18.2	16	13.9	12.6	42.5
Ce	1.7	3.8	37	40	38	42	37	34	29	96
Pr	0.29	0.57	4.38	5.14	4.86	5.41	4.84	4.44	3.71	11.89
Nd	1.6	2.7	17.9	22.8	21.8	24.4	21.3	20.4	16.4	50.3
Sm	0.41	0.63	3	4.53	4.25	4.81	4.56	3.95	2.98	7.78
Eu	0.16	0.26	0.94	1.53	1.42	1.58	0.92	1.29	0.93	2.2
Gd	0.54	0.68	2.5	4.59	4.19	4.76	4.18	3.76	2.67	5.91
Tb	0.09	0.12	0.42	0.87	0.81	0.89	0.77	0.69	0.47	1
Dy	0.44	0.54	1.93	4.04	3.89	4.36	3.5	3.2	2.15	4.36
Ho	0.08	0.1	0.36	0.79	0.72	0.81	0.67	0.62	0.4	0.76
Er	0.21	0.29	1	2.09	1.89	2.12	1.76	1.62	1	1.89
Tm	0.03	0.04	0.16	0.32	0.29	0.35	0.27	0.25	0.16	0.28
Yb	0.18	0.29	0.99	1.96	1.81	2.03	1.64	1.53	0.91	1.66
Lu	0.03	0.04	0.16	0.28	0.26	0.29	0.24	0.21	0.13	0.23
Hf	0.3	0.4	2.9	3.3	3.3	3.8	3.7	3.3	2.5	7.2
Ta	bdl	bdl	0.2	0.9	1	1.2	0.3	0.7	0.7	1.8
Pb	5.41	1.22	1.63	2.37	3.02	2.02	8.23	1.54	1.56	2.75
Th	bdl	0.1	4.4	3	2.9	3	4.8	2	1.6	5.4
U	bdl	bdl	0.9	0.6	0.5	0.6	0.5	0.4	0.4	1.2
Pd ppb	bdl	14	bdl	bdl	bdl	bdl	bdl	10	bdl	bdl
Pt	15	8	bdl	bdl	bdl	bdl	bdl	9	5	5
Ti/Y	873	675	292	743	880	818	122	485	546	677
Zr/Nb	2.9	4.7	8.2	4.6	4.8	4.6	5.4	5.8	6.6	10.4
La/Yb	3.9	5.2	16.4	8.8	9.1	9.0	9.8	9.1	13.8	25.6
Cu/Pd	0	3271	0	0	0	0	0	9362	0	0
Cu/Zr	4.63	3.03	0.02	0.71	0.49	0.38	0.04	0.86	0.89	0.42

4. Samples and analytical methods

The coordinates of each sample are given in Table 1. Three samples come from the Datian intrusive complex. Three further samples were collected from the south-Datian gabbros. Three samples were taken from a former exploration site in the Luobodi intrusion. All of them are mineralized with Fe-Ti-V oxides (massive to semi-massive ore). Six samples (one gabbro and five ultramafic rocks) come from the Gongshanqing intrusion (from outcrops, adit and drill cores spread around drill sites). Other three samples were taken from picrite blocks occurring on two creeks downstream from the picrite dikes (one from the fine-grained variety and two from the medium-grained type). We also analyzed ten samples from the Jizicheng intrusion (four from the marginal dunite, five from the inner olivine pyroxenite and one gabbro from the central part of the intrusion).

Bulk rock analyses were performed at the ACME laboratories in Vancouver. The samples were mixed with lithium metaborate/tetraborate and fused in a furnace. The cooled beads were dissolved in ACS grade nitric acid. Loss on ignition was determined by weight difference after ignition at 1000°C. The major elements and Ba were analyzed by ICP-OES (inductively coupled plasma optical emission spectrometry) using a Varian spectrometer. Sulfur was analyzed by combustion, using a LECO CS-200 analyzer. Trace elements were analyzed by ICP-MS (inductively coupled plasma-mass spectrometry), using a Perkin-Elmer instrument, after lithium metaborate fusion and dilute nitric acid digestion (Cs, Hf, Nb, Rb, Sr, Ta, Th, U, V, Zr, Y and REE) or after Aqua Regia digestion (Cu, Pb, Ni, Co, Cr, Pd and Pt). The accuracy and precision of the trace element data were about 5%.

5. Results

The mineralogical and chemical composition of the investigated samples reflect the diversity of the investigated

material (Table 1). In order to characterize the analyzed samples, we used spider diagrams of REE (normalized to chondrite) and of the incompatible elements Cs, Rb, Ba, Th, U, Nb, Ta, K, La, Ce, Pb, Pr, Sr, P, Nd, Zr, Sm, Eu, Ti, Dy, Y, Yb, Lu (normalized to the primitive mantle). The normalizing values for chondrite and primitive mantle were taken from Sun and McDonough (1989). The spider diagrams of the samples from each investigated intrusion are given in Figs. 5 and 6.

Datian. The large ion lithophile elements (K, Rb, Cs, Sr, Ba) are enriched relative to the high field strength elements (Zr, Nb, Hf, Ta), a feature consistent with the formation of the complex by arc magmatism. The Lixidong granite shows incompatible elements patterns similar to those of the quartz diorite. The REE show sloped patterns, with remarkable differentiation between LREE and HREE ($La_N/Lu_N = 7-22$).

Gongshanqing. In general, REE patterns of peridotites show flat patterns of LREE and HREE ($La_N/Sm_N = 1.1-1.8$, $Er_N/Lu_N = 1-1.2$) relative to MREE ($Sm_N/Ho_N = 2.2-2.7$). A saprolitic peridotite from the adit shows similar trend but increased REE contents. A steeper descending pattern is shown by the gabbro ($La_N/Lu_N = 12$). The peridotites display small variations of the normalized values of the incompatible elements. The saprolitic peridotite shows negative anomalies of Rb, K and P. The gabbro exhibits high values of LILE and negative anomalies for HSFE, similar to arc-related/crustal magmas.

Jizicheng. The intrusion has lower contents of incompatible elements, compared with Gongshanqing. REE are lower in the peridotites from the marginal zone of the intrusion than in the pyroxenites of the inner part, all showing flat trends ($La_N/Lu_N = 1.5-3$). The peridotites show steeper slope between the MREE and HREE ($Tb_N/Ho_N = 1.7-1.8$). Pyroxenites show depletion of LREE and HREE relative to MREE. The gabbros have trends similar with those of pyroxenites, showing no Eu anomaly. This suggests the formation of the gabbro by the local increase of the proportion of interstitial melt, without plagioclase fractionation/accumulation,

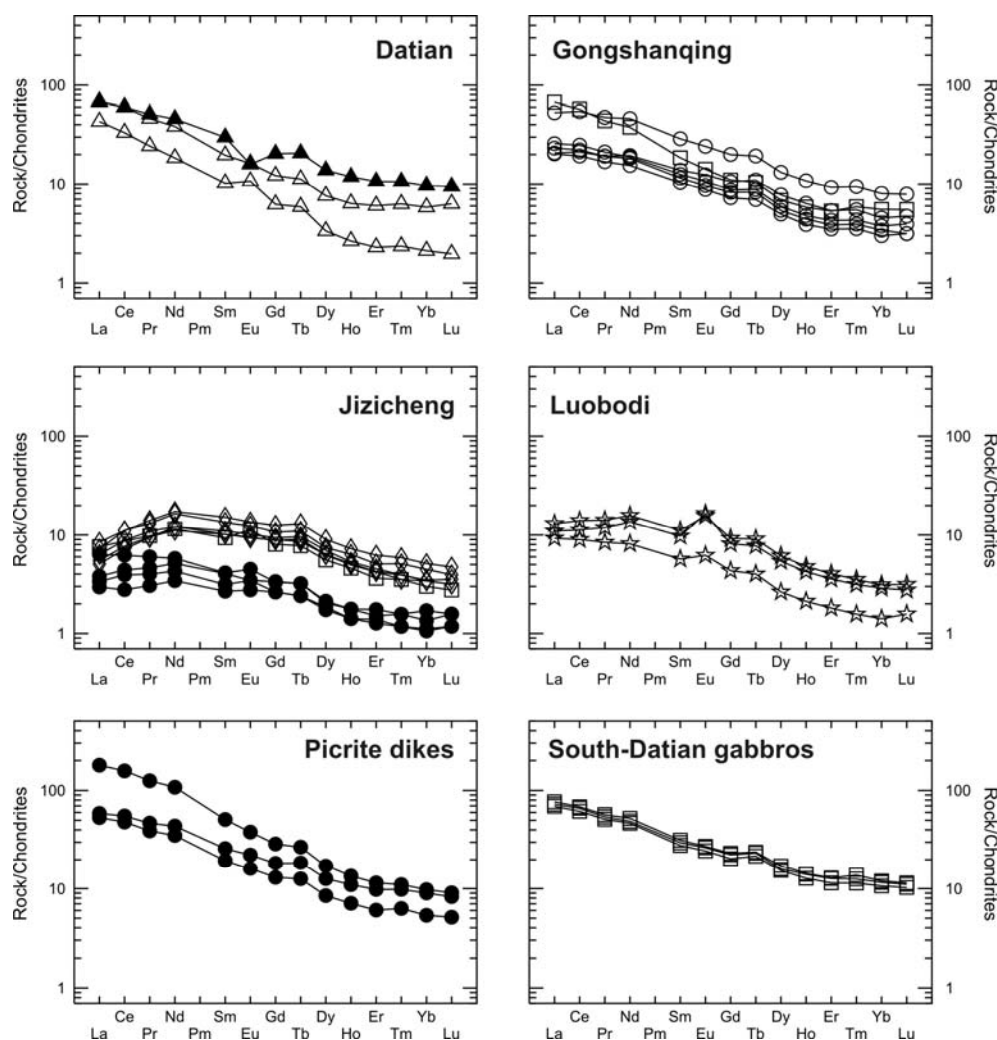


Fig. 5. Chondrite-normalized REE patterns for the investigated intrusions. Chondrite normalization values from Sun and McDonough (1989).

in agreement with the petrographic observations, which indicate plagioclase as an intercumulus phase.

Luobodi. The three ore samples exhibit similar trends of incompatible elements, with marked positive anomalies for Cs, Ba, Sr and Ti, and negative anomalies for Rb, Th and U. The REE patterns exhibit positive Eu anomalies. All samples have high metal contents (33-50% Fe, 6-9.5% Ti, 0.16-0.17% V).

Picrite dikes show descending REE patterns ($La_N/Lu_N = 7-20$) and relatively uniform trends of incompatible elements, only with small negative anomalies for Rb and P.

The three samples of **south-Datian gabbros** show remarkably homogeneous compositions, with incompatible elements and REE patterns similar to those of the picrite dikes, only flatter ($La_N/Lu_N = 6.6-6.8$), suggesting less differentiation of the parental magma.

6. Discussions

Except for the Datian complex, which is Proterozoic, the investigated intrusions are Permian, related to the mantle plume magmatism the other rocks in the intrusion of the Emeishan large igneous province.

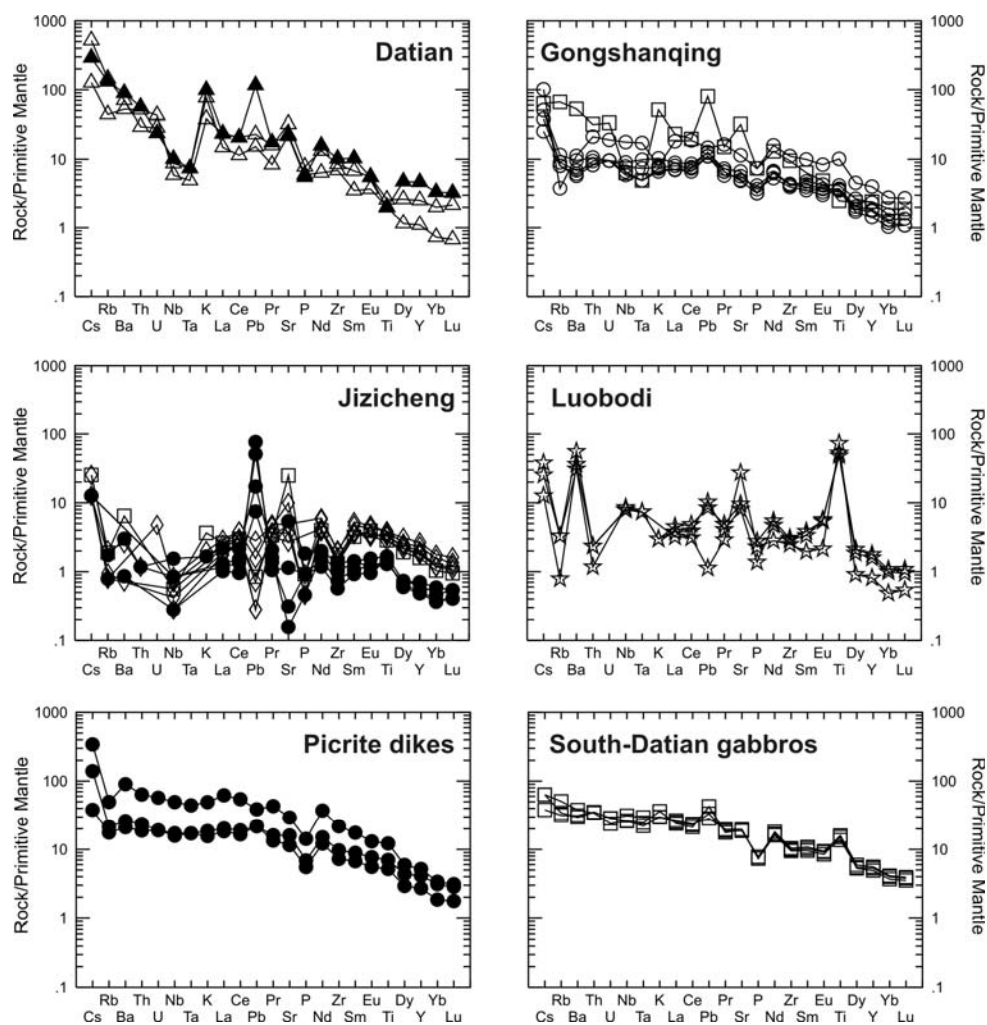


Fig. 6. Primitive mantle-normalized patterns of the incompatible elements in the investigated intrusions. Primitive mantle normalization values from Sun and McDonough (1989).

The anorogenic geotectonic setting is supported by the composition of picrite dikes and south-Datian gabbros, which have contents of incompatible elements close to ocean island basalts, as illustrated in Fig. 7. The relative depletion of LREE in the olivine pyroxenite from Jizicheng (Fig. 5) reflects clinopyroxene accumulation, whereas LREE have smaller partition coefficients in clinopyroxene than those of the other REE (e.g. McKay, 1989; Hack et al., 1994). The patterns of the incompatible elements in the ore from Luobodi (Fig. 6) is similar to the trends of the gabbros in the Panzhihua (Zhou

et al., 2005) and Baima (Shellnutt et al., 2009) Fe-Ti-V deposits. The ore in the Luobodi intrusion displays visible positive Eu anomaly (Fig. 5), suggesting the entrapment of cumulus plagioclase in the oxide ore. One problem recently raised for the intrusions and ore deposits in the Panxi rift is the correspondence (genetic affinity) between different types of rocks/deposits and the two geochemical types of Emeishan basalts (Zhou et al., 2008). Among the studied rocks, only the picrite dikes and south-Datian gabbros show distributions of incompatible elements that suggest the lack of substantial fractionation

processes. The Ti/Y ratio is higher than 500 in most analyzed samples, irrespective of rock types, which would classify all intrusions in the high-Ti geochemical type. Xiao et al. (2004, Fig. 4) show that high-Ti basalts have $\text{La/Yb} > 10$ and $\text{Zr/Nb} < 10$, while low-Ti basalts show $\text{La/Yb} < 10$ and Zr/Nb ratios that overlap the variation field of high-Ti basalts. An examination of our results shows that most samples (including gabbros, oxide ore and ultramafic cumulates) have $\text{La/Yb} < 10$, similar to low-Ti basalts of Xiao et al. (2004). The Zr/Nb ratio is typical for low-Ti basalts (> 10) only in the Jizicheng intrusion, where it can be correlated with the Ti/Y ratio lower than 500 in the samples from the inner zone made up of olivine pyroxenite.

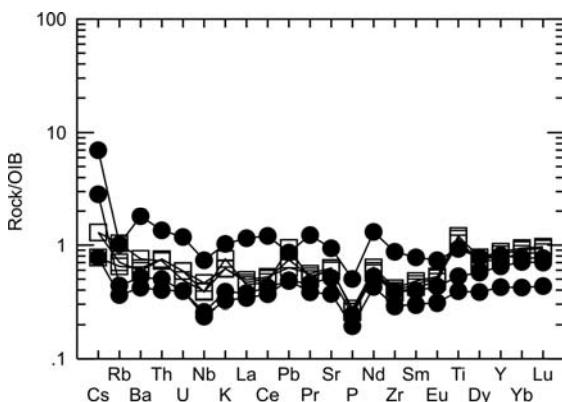


Fig. 7. Spider diagram of the incompatible elements in the picrite dikes (solid circles) and south-Datian gabbros (open squares) normalized to ocean island basalts. Normalization values from Sun and McDonough (1989).

The presence of economic Ni-Cu and PGE mineralization in several mafic-ultramafic intrusions from the Panxi rift is a main reason for the investigation of the economic potential of other intrusions. The genesis of mafic-ultramafic intrusions involves partial melt of the mantle, the ascent of the resulted magmas and their emplacement in the crust. Because of their high affinity for sulfides, the PGE are readily removed from the magma even at low ratios of sulfide exsolution and fractionation. Hence, one critical condition for the occurrence of mineable PGE mineralization is the absence of

any pre-emplacement sulfide fractionation from the parental magma. The PGE contents in most ultramafic rocks at Gongshanqing and Jizicheng (22-64 ppb) are similar to or higher than those of the PGE-undepleted mafic magmas (Greenough and Owen 1992; Barnes and Picard 1993; Brüggmann et al. 1993). Considering the cumulate nature of these rocks and the fact that both Pt and Pd behave incompatible in olivine and pyroxene, it is reasonable to consider that the PGE contents in these rocks indicate the presence of sparsely disseminated PGE-rich sulfide grains. This is consistent with the higher sulfur content in the PGE-rich samples (Table 1).

The Cu/Zr ratio can be used as an indicator of sulfide fractionation before magma emplacement. Both Cu and Zr are strongly incompatible in most silicate phases, but Cu concentrates in sulfides. It is considered that magmas which did not experience sulfide fractionation have Cu/Zr ratios close to 1 (Lightfoot et al., 1994; Li and Naldrett, 1999; Wang et al., 2006), while in the case of a pre-emplacement sulfide fractionation, Cu/Zr ratio would be less than 1, because a significant part of the Cu fractionated with the sulfides. The ultramafic rocks from Gongshanqing (Table 1) display Cu/Zr ratios both close to 1 or higher (2.3-5.2). This suggests the absence of any pre-emplacement sulfide fractionation and the occurrence of zones with sulfide accumulation, which induced the increase of Cu content. A similar situation occurs at Jizicheng, which contains rocks formed from magmas that did not experience sulfide fractionation or sulfide accumulation (Cu/Zr ratios close to 1) and rocks containing accumulated sulfides (Cu/Zr in the range 2.4-8.9). The gabbro from Gongshanqing, with $\text{Cu/Zr} = 0.1$, would suggest sulfide fractionation, in contrast with the other rocks in the intrusion. This feature might indicate a substantial contribution of crustal material to the genesis of the gabbros of the Gongshanqing intrusion. A similar spatial association between ultramafic cumulates and crustal melts was inferred for the Lengshuiqing Ni-Cu deposit in the Proterozoic basement of the Panxi rift (Munteanu et al., 2010). In the case of the south-Datian gabbros, with Cu/Zr ratio be-

tween 0.4 and 0.7, sulfide fractionation probably occurred in the parental magma at greater depth. The picrite dike that shows Cu/Zr ratios slightly lower than 1, probably formed from magmas that did not reach sulfide saturation. The picrite dike having Cu/Zr = 0.4 contains excess Zr compared with the other dike, a feature that probably resulted from assimilation of crustal material. This is consistent with the higher contents of K, P and Rb.

The Cu/Pd ratio in a magma is sensitive to sulfide fractionation since the Pd partition coefficient in sulfide is much higher than Cu partition coefficient. Therefore, in the case of sulfide fractionation, Pd is removed from the magma at much higher rate than Cu, inducing the increase of Cu/Pd above the original ratio, which is supposed to be within the mantle range (Barnes et al., 1993; Barnes et al., 2004; Barnes and Lightfoot, 2005). In this respect, the Cu/Pd ratios of the ultramafic samples in our set (Table 1), with values within the mantle range (1,000-10,000) suggest a parental magma that did not experience sulfide fractionation before the formation of the actual intrusions.

The Gongshanqing and Jizicheng intrusions, dominated by ultramafic cumulates were probably generated in wider zones of magmatic conduits. Similar genesis was inferred for several ultramafic-mafic intrusions in the Panxi rift, such as Zhubu (Zhu et al., 2007), Limahe (Tao et al., 2007a), Jinbaoshan (Wang et al., 2005; Tao et al., 2007b) and Baimazhai (Wang and Zhou, 2006), based on their composition different than the normal compositions of the mafic magmas. In the petrogenetic and metallogenetic models involving magma conduits, mafic crystals $\pm$ immiscible sulfide droplets are transported from a staging chamber to shallower levels in the crust. When the section of a conduit increases, the flow of magma is slowed down and cannot carry the denser mafic crystals $\pm$ sulfide melt, which accumulate, generating ultramafic rocks $\pm$ Ni-Cu or PGE mineralization. Although the association with magma conduits seems to be characteristic for Ni-Cu deposits (Li et al., 2001; Maier et al., 2001), it facilitates the contact of the immiscible sulfides with large quantities of flowing

magma, contributing to their enrichment in PGE. Such a process was invoked to explain the genesis of the Jinbaoshan PGE deposit (Wang et al., 2005; Tao et al., 2007b) and could be applied in the case of the Gongshanqing and Jizicheng intrusions, as well.

7. Conclusions

This work produced and interpreted data on several intrusions of the two main petrographic-metallogenetic associations related to the Emeishan large igneous province: gabbroic intrusions with Fe-Ti-V oxides and ultramafic-mafic intrusions with Ni-Cu(-PGE) sulfide mineralization. The geochemical investigation could not evidence a correlation between the studied intrusions and the high-Ti and low-Ti Emeishan basalts. The Cu/Pd and Cu/Zr ratios of the ultramafic rocks investigated here suggest the genesis from Cu- and PGE-fertile magmas. The Cu/Pd and Cu/Zr ratios are similar in the Gongshanqing and Jizicheng intrusions, suggesting that the Jizicheng intrusion could contain a PGE-rich mineralization like the one discovered in the Gongshanqing intrusion.

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References

- Ali, J.R., Thompson, G.M., Zhou, M.-F., Song, X., 2005. Emeishan large igneous province, SW China. *Lithos*, 79, 475–489.
- Barnes, S.-J. & Lightfoot, P.C., 2005. Formation of magmatic nickel-sulfide ore deposits and

- processes affecting their copper and platinum-group element contents. In *Econ. Geol.* 100th Anniversary Volume (Hedenquist, J.W., Thompson, J.F.H., Goldfarb, R.J. & Richards, J.P., eds.), 179-213.
- Barnes, S.-J., Picard, C.P., 1993. The behaviour of platinum-group elements during partial melting, crystal fractionation and sulfide segregation: an example from the Cape Smith fold belt, northern Quebec. *Geochim Cosmochim Acta*, 57, 79–87.
- Barnes, S.-J., Couture, J.-F., Sawyer, E.W., Bouchaib, C., 1993. Nickel-copper occurrences in the Belletre-Angliers Belt of the Pontiac subprovince and the use of Cu-Pd ratios in interpreting platinum-group element distributions. *Economic Geology*, 88, 1402-1418.
- Barnes, S.-J., Maier, W.D. and Ashwal, L.D., 2004. Platinum-group element distribution in the Main Zone and Upper Zone of the Bushveld Complex, South Africa. *Chemical Geology*, 208, 294-317.
- Brügmann G.E., Naldrett, A.J., Asif, M., Lightfoot, P.C., Gorbachev, N.S., Fedorenko, V.A., 1993. Siderophile and chalcophile metals as tracers of the evolution of the Siberian Trap in the Noril'sk region, Russia. *Geochim Cosmochim Acta*, 57, 2001–2018.
- CGGJC (Co-operative Geological Group of Japan China in the Panxi Region), 1986. *Geology of the Panxi region, Sichuan Province, southwest China*. Yamaguchi University, Japan. 340 pp.
- Greenough, J.D., Owen, J.V., 1992. Platinum-group element geochemistry of continental tholeiites: analysis of the Long Range dyke swarm, Newfoundland, Canada. *Chemical Geology*, 98, 203–219.
- Hack, P.J., Nielsen, R.L., Johnston, A.D., 1994. Experimentally-determined rare-earth element and Y partitioning behaviour between clinopyroxene and basaltic liquids at pressures up to 20 kbar. *Chemical Geology*, 117, 89–105.
- Lightfoot, P.C., Hawkesworth, C.J., Hergt, J., Naldrett, A.J., Gorbachev, N.S., Fedorenko, V.A., Doherty, W., 1994. Chemostratigraphy of Siberian trap lavas, Noril'sk district, Russia: implications for the evolution of flood basalt magmas. In: Lightfoot, P.C., Naldrett, A.J. (Eds.), *Proceedings of the Sudbury-Noril'sk Symposium*. Ontario Geological Survey, Special Publication 5, 283–312.
- Li, C., Naldrett, A.J., 1999. Geology and petrology of the Voisey's Bay intrusion: reaction of olivine with sulfide and silicate liquids. *Lithos*, 47, 1–31.
- Li, C., Maier, W.D., de Waal, S.A., 2001. Magmatic versus PGE deposits: Contrasting genetic controls and exploration implications. *South African Journal of Geology*, 104, 309-318.
- Li, Z.X., Li, X.H., Kinny, P.D., Wang, J., Zhang, S., Zhou, H., 2003. Geochronology of Neoproterozoic syn-rift magmatism in the Yangtze Craton, South China and correlations with other continents: evidence for a mantle superplume that broke up Rodinia. *Precambrian Research*, 122, 85–109.
- Maier, W.D., 2005. Platinum-group element (PGE) deposits and occurrences: mineralization styles, genetic concepts, and exploration criteria. *Journal of African Earth Sciences*, 41, 165–191.
- Maier, W.D., Li, C., De Waal, S.A., 2001. Why are there no major Ni-Cu sulfide deposits in large layered mafic-ultramafic intrusions? *The Canadian Mineralogist*, 39, 547-556.
- McKay, G.A., 1989. Partitioning of rare earth elements between major silicate minerals and basaltic melts. In: Lipin, B.R. and McKay, G.A. (Eds.), *Geochemistry and Mineralogy of Rare Earth Elements*. Reviews in Mineralogy, Mineralogical Society of America, 21, 45-78.
- Munteanu, M., Wilson, A.H., Yao, Y., Jiang, S.Y., Chunnett, G., Luo, Y., Mafurutu, L., Phadagi, R., 2010. A conduit-related genesis of the Lengshuiqing intrusive assemblage (Sichuan, SW China). *Journal of Volcanology and Geothermal Research*, 189, 118-130.
- Shellnutt, J.G., Zhou, M.-F., Zellmer, G., 2009. Formation of peralkaline A-type granitoids: insights from the Permian Fe–Ti-oxide bearing Baima Igneous Complex (China). *Chemical Geology*, 259, 204–217.
- Sun, S.-S., McDonough, W.F., 1989. Chemical and isotopic systematics of oceanic basalts: implications for mantle composition and processes. In: Saunders, A.D., Norry, M.J. (Eds.), *Magmatism in the Ocean Basins*. Geological Society Special Publication no. 42, 313–345.
- Tao, Y., Li, C., Hu, R., Ripley, E.M., Du, A., Zhong, H., 2007a. Petrogenesis of the Pt–Pd mineralized Jinbaoshan ultramafic intrusion in the Permian Emeishan Large Igneous

- Province, SW China. *Contrib. Mineral. Petrol.* 153, 321–337.
- Tao, Y., Li, C., Song, X.Y., Ripley, E.M., Du, A., Zhong, H., 2007b. Mineralogical, petrological, and geochemical studies of the Limahe mafic-ultramafic intrusion and associated Ni–Cu sulfide ores, SW China. *Miner. Depos.* 43, 849–872.
- Wang, C.Y., Zhou, M.-F., 2006. Genesis of the Permian Baimazhai magmatic Ni–Cu–(PGE) sulfide deposit, Yunnan, SW China. *Miner. Depos.* 41, 771–783.
- Wang, C.Y., Zhou, M.-F., Zhao, D.G., 2005. Mineral chemistry of chromite from the Permian Jinbaoshan Pt–Pd-sulphide-bearing ultramafic intrusion in SW China with petrogenetic implications. *Lithos* 83, 47–66.
- Wang, C.Y., Zhou, M.-F., Keays, R.R., 2006. Geochemical constraints on the origin of the Permian Baimazhai mafic-ultramafic intrusion. *Contributions to Mineralogy and Petrology*, 152, 309–321.
- Xiao, L., Xu, Y.G., Mei, H.J., Zheng, Y.F., He, B., Pirajno, F., 2004. Distinct mantle sources of low-Ti and high-Ti basalts from the western Emeishan large igneous province, SW China: implications for plume lithosphere interaction. *Earth and Planetary Science Letters*, 228, 525–546.
- Xu, Y.G., Chung, S.L., Jahn, B.M., Wu, G.Y., 2001. Petrologic and geochemical constraints on the petrogenesis of Permian–Triassic Emeishan flood basalts in southwestern China. *Lithos*, 58, 145–168.
- Xu, Y.G., He, B., Chung, S.L., Menzies, M.A., Frey, F.A., 2004. The geologic, geochemical and geophysical consequences of plume involvement in the Emeishan flood basalt province. *Geology*, 32, 917–920.
- Yao, Y., Viljoen, M.J., Viljoen, R.P., Wilson, A.H., Zhong, H., Liu, B.G., Ying, H.L., Tu, G.Z., Luo, Y.N., 2001. Geological characteristics of PGE-bearing layered intrusions in southwest Sichuan Province, China. Information Circular no. 358. Economic Geology Research Institute, Hugh Allsopp Laboratory, University of the Witwatersrand, Johannesburg, 21 pp.
- Zhao, J.H., Zhou, M.-F., 2007a. Geochemistry of Neoproterozoic mafic intrusions in the Panzhihua district (Sichuan Province, SW China): implications for subduction-related metasomatism in the upper mantle. *Precambrian Research*, 152, 27–47.
- Zhao, J.H., Zhou, M.-F., 2007b. Neoproterozoic adakitic plutons and arc magmatism along the western margin of the Yangtze Block, South China. *Journal of Geology*, 115, 675–689.
- Zhong, H., Zhu, W.G., 2006. Geochronology of layered mafic intrusions from the Panxi area in the Emeishan large igneous province, SW China. *Mineralium Deposita*, 41, 599–606.
- Zhou, M.F., Malpas, J., Song, X., Robinson, P.T., Sun, M., Kennedy, A.K., Leshner, C.M., Keays, R.R., 2002a. A temporal link between the Emeishan large igneous province (SW China) and the end-Guadalupian mass extinction. *Earth and Planetary Science Letters*, 196, 113–122.
- Zhou, M.-F., Yan, D.P., Kennedy, A.K., Li, Y.Q., Ding, J., 2002b. SHRIMP zircon geochronological and geochemical evidence for Neoproterozoic arc-related magmatism along the western margin of the Yangtze Block, South China. *Earth and Planetary Science Letters*, 196, 51–67.
- Zhou, M.-F., Robinson, P.T., Leshner, C.M., Keays, R.R., Zhang, C.-J., Malpas, J., 2005. Geochemistry, petrogenesis, and metallogenesis of the Panzhihua gabbroic layered intrusion and associated Fe–Ti–V-oxide deposits, Sichuan Province, SW China. *Journal of Petrology*, 46, 2253–2280.
- Zhou, M.F., Arndt, N.T., Malpas, J., Wang, C.Y., Kennedy, A.K., 2008. Two magma series and associated ore deposit types in the Permian Emeishan large igneous province, SW China. *Lithos*, 103, 352–368.
- Zhu, D., Xu, Y.G., Luo, T.Y., Song, X.Y., Tao, Y., Huang, Z.L., Zhu, C.M., Cai, E.Z., 2007. Conduit of the Emeishan basalts: the Zhubu mafic-ultramafic intrusion in the Yuanmou area of Yunnan Province, China (in Chinese, with English Abstract). *Acta Mineralogica Sinica*, 27, 273–280.

Preliminary data on two tin-sulfosalts (canfieldite and pirquitasite) from Roșia Montană

Gheorghe C. POPESCU¹ and Antonela NEACȘU¹

Department of Mineralogy, Bucharest University, 1, N. Balcescu Blvd, Bucharest

Abstract: During the re-assessment of the collection of ore minerals “N. Petrulian” from the Department of Mineralogy of the University of Bucharest, one sample from Roșia Montană was investigated by micro-Synchrotron Radiation X-Ray Fluorescence (SR-XRF). The results, correlated with microscope study revealed, for the first time at Roșia Montană, the presence of two tin sulfosalts (canfieldite si pirquitasite), and of two types of gold (Ag-rich and Ag-poor). Such differences in gold composition are related to temperature and sequence of formation, as suggested by mineral relations. The Ag-rich gold formed earlier, at higher temperature, while the Ag-poor gold was generated subsequently, at lower temperature.

Keywords: Roșia Montană, gold, canfieldite, pirquitasite

1. Introduction

Roșia Montană is one of the most famous gold ore deposit in the Neogene Province of the Apuseni Mts., and also one of the oldest historical sources of gold in Romania and in Europe. Archaeological research places the origins of this deposit at least in the times of the Roman Empire if not earlier (Cauuet et al., 2003). Together with Roșia Poieni porphyry copper ore deposit, it forms a real metallogenetic knot (Fig. 1). The fame of this deposit has been reactivated during the last years, mainly due to the mining project of the Canadian Company *Gabriel Resources Ltd.*, developed by its Romanian branch, the *Roșia Montană Gold Corporation*.

2. Previous research

The mineralogy of Roșia Montană ore deposit is comparatively less known with respect to other gold ore deposits in the

Metaliferi Mts. e.g. Săcărâmb, Stănița, Baia de Aries, all of which are type localities for several minerals. Yet, native gold and beautiful, large mineral samples from Roșia Montană are famous exhibits in various mineralogical museums around the world.

The mineralogical investigations carried out during last decade, especially using scanning electron microscopy (SEM) and electron probe microanalysis (EPMA), have revealed numerous metallic minerals in the Roșia Montană ore deposit. Newly described minerals such as *stephanite*, *polyargyrite*, *achantite*, *tennantite* and also *proustite-pirargyrite*, *miargyrite* and *argyrodite* (Tămaș et al., 2004), were added to the minerals already mentioned by Petrulian (1934) e.g. *argentite*, *proustite*, *pearceite*, *polybasite*.

Tămaș et al. (2006) mentioned several new tellurium mineral occurrences from Roșia Montană: *altaite*, *hessite*, *sylvanite*, *cervelleite*, *petzite* which added to the already rich telluride inventory of the Metaliferi Mts.

¹tel: +40721 295833, fax +4021 3112053

e-mails: ghpop@geo.edu.ro, antonela@geo.edu.ro

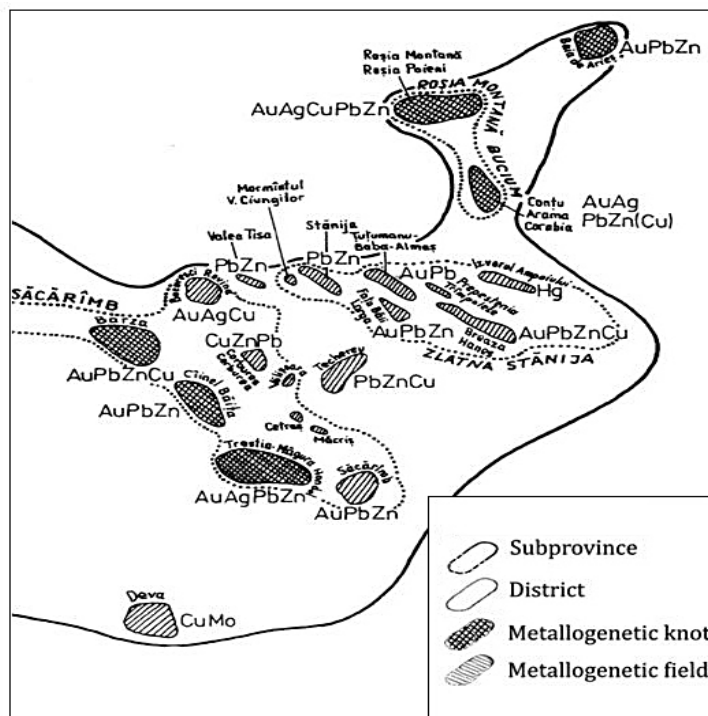


Fig.1. The metallogenic Neogene Subprovince in the South Apuseni Mts. (after Popescu, 1986)

Chemical micro-analyses suggesting the presence of *tellurium-argyrodite* have also been mentioned. During the last two years, a series of new investigations of native gold from classical occurrences in Romania have been carried out in co-operation with physicists from the Nuclear Physics and Engineering Institute in Bucharest, in order to identify the sources of gold used for ancient jewelry artifacts.

The origin of gold in various artifacts was seen as crucial for clarifying some debates among archaeologists and geologists on different possible gold sources within the Romanian territory. For example, Constantinescu et al. (2008) found traces of Sn in several gold bracelets of a Dacian treasure, a feature interpreted as an indicator of an alluvial origin of gold, which was mixed with some cassiterite grains during the panning. Nevertheless, the authors mentioned trace amounts of Sn in the primary gold extracted from Roşia Montană and Valea Morii deposits.

3. Sample description

Following the research mentioned above, a polished section of native gold from Roşia Montană (Petruilian Collection, Department of Mineralogy, Faculty of Geology and Geophysics, University of Bucharest) was chosen for mineralogical and geochemical investigations.

The investigated sample originates from a vein-type ore, which is relatively rare at Roșia Montană, where the gold ore is commonly located in breccias. Most likely, the sample was taken from the Cărnic body, which is the part of the deposit studied by Professor Petrușian in the 1930s. The sample represents a typical example of symmetrical banded texture, where the oldest bands (Fig. 3a - band 1) are disposed in an outer position, while the youngest are located in the center (Fig. 3a - band 4). In the present, similar banded texture can be found at Roșia Montană in the Mn carbonate-rich veinlets that cross the *black breccia*'.

4. Methods

The sample was first investigated by micro-Synchrotron Radiation X-Ray Fluorescence (SR-XRF) at the FLUO-beam and XRF analyze with a XGT-7000 X-ray Analytical Microscope (Simon et al., 2003) at ANKA/ISR in Karlsruhe, we performed 2-dimensional scans with the beam focused to 7-10 μm^2 (Vasilescu et al., 2003). The scan area could be visualized with an optical based on various standards and fundamental parameter calculations.

To clarify the distribution of the chemical elements have been done some more detailed XRF analyze with a XGT-7000 X-ray Analytical Microscope at the University of Bucharest, Faculty of Geology and Geophysics.

The acquisition characteristics set on XGT-7000 were: time - 263 [s], X-ray tube vol. - 30.00 [kV], Current - 1.000 [mA], XGT Diameter - 10 [μm]. The element maps are generated by showing X-ray intensity between a specific energy ranges (corresponding to the particular XRF lines of an element). Each pixel of the element map shows the X-ray intensity at that position.

Subsequently, we have re-examined the sample by means of reflected light microscopy in order to identify the minerals that can accommodate the elements indicated by the XRF results.

5. Results and discussions

The XRF spectrum of the investigated sample revealed the presence of Sn and other less common elements (Fig. 2). Following this indication, we examined the sample with the chalcographic microscope and we identified two tin-sulfosalts intergrown with gold.

A first Sn-phase was the relatively easily recognizable *canfieldite* (Ag_8SnS_6), a member of the isomorphic series with *argyrodite* (Ag_8GeS_6), already identified in Roșia Montană.

Canfieldite is always associated with gold and has a light-gray color with a weak creamy tint, which becomes brown-reddish due to the oxidizing processes and to the

microscope and recorded with a camera. The detector used was an HPGe crystal. The maximum excitation energy of the X-rays at both sites was 32.5 keV. The samples were mounted in air on a dedicated frame, put on a motorized xyz stage and positioned at an angle of 45° to the primary X-ray beam. The identification of the peaks and the off-line data analysis was performed with AXIL software. Relative concentrations of minor and trace elements were determined using a procedure

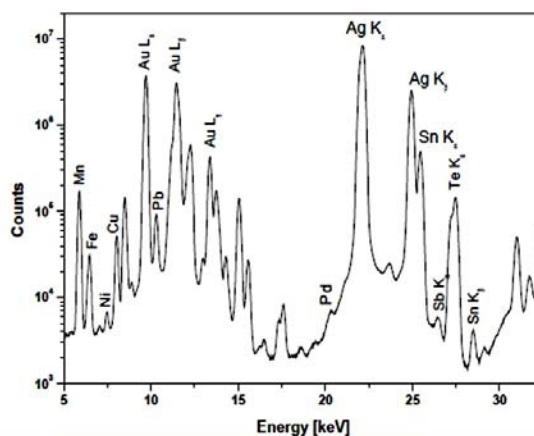


Fig. 2. The XRF surface analysis on an area of approx 1 mm by 1 mm of the investigated polished section from Roșia Montană. Maxima for Au, Ag, Sn, Te, Cu, Pb, Fe are visible in the spectrum (analyzed by Angela Vasilescu, from IFIN-HH Bucharest).

alteration caused by the light. Canfieldite cross-cuts or partially replaces gold grains (Fig. 4, a-d).

The presence of tellurium, identified by the XRF-analysis in the same sample, can indicate the Te-rich composition of canfieldite; this is supported by the absence of any other tellurium-bearing minerals in the polished section and is consistent with the presence of tellurium-argyrodite in Roșia Montană (Tămaș et al. 2004). There are places in the world where tellurium-canfieldite has been identified e.g. Revelstoke - Canada, Belukhinskoe - Russia, Tsumo, Kuga and Nakatatsu - Japan, Zlata Bana - Slovakia, Cirotan - Indonezia, some authors (e.g., Harris & Owens, 1971) indicating $\text{Ag}_8\text{Sn}(\text{S},\text{Te})_6$ as the chemical formula.

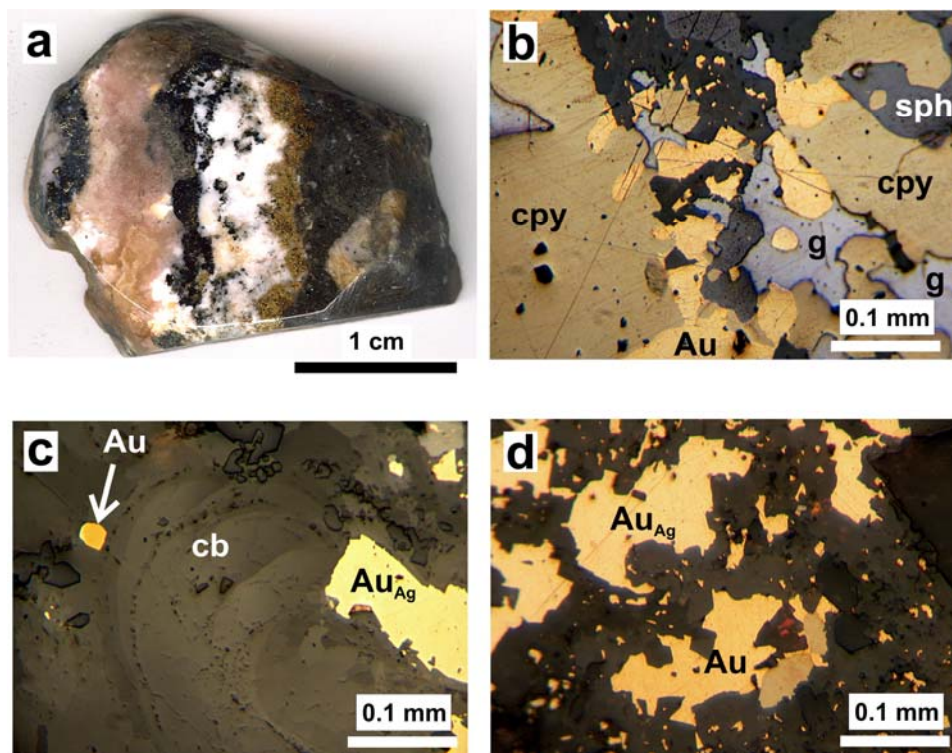


Fig. 3. Gold associations in zoned gold ore, Roșia Montană ore deposit. **a.** Polished section (The „Petrulian Collection”) through the parallel-textured gold ore from Roșia Montană 1. gold zone; 2. quartz and carbonate zone; 3. sulfides and gold zone; 4. manganese carbonate zone. **b.** gold (Au) associated with sulfides: chalcopyrite (cpy) appears yellowish-green in comparison with the bright yellow gold; g = galena (parallel nicols). **c** and **d.** (parallel nicols): Silver-rich gold (Au_{Ag}) is light yellow whereas pure gold is dark yellow; image **c** presents the association between native gold and carbonates with a colloid texture (cb).

Another discovery is an extremely rare mineral found in the intergrowth area between gold and quartz-carbonate gangue. This is a member of *pirquitasite* (Ag_2ZnSnS_4) – *hocartite* (Ag_2FeSnS_4) series. It appears as clear pleochroic grains, with brown-gray tints (Fig. 5a,b), with a strong anisotropy in various colors: brown-reddish-gray to brilliant green (Fig. 5c,d). We believe the optical properties can be assigned to *pirquitasite*, an observation sustained also by the frequent red internal reflections and by the presence of Zn in the XRF spectral analysis.

In the same gold band, closely associated with quartz and carbonate gangue where canfieldite appears, *achantite* (*argentite*) – Ag_2S and *polybasite* (Ag, Cu) $_{16}Sb_2S_{11}$ – *pearceite* (Ag, Cu) $_{16}As_2S_{11}$ were identified. *Argentite* may be distinctly observed, in quasi-euhedral gray-green grains, strongly affected by light and without any

anisotropy (Fig. 4a, d). All observations sustain the occurrence of argentite, signifying a higher temperature phase (179° C). The central parts of argentite grains, have a purple tint, are intensely altered by light, and may represent *jalpaite* (Ag_3CuS_2) – which is also sustained by the presence of copper in the XRF analysis. As far as *polybasite-pearceite* is concerned, the optical characteristics and the presence of Sb in the XRF analyses sustain mainly the first term of the series (Fig. 5a, b). Reflected-light microscopy has revealed another peculiar characteristic, that is the existence of two types of gold in the analyzed polish section (Fig. 3, a): the prevalent gold-type is a light yellow silver-rich variety (Fig. 3, d) which is intergrown with all the minerals of the „gold-related zone”. The second gold type has a clear yellow color, is less frequent, and associated with carbonate minerals (see Fig. 3, d).

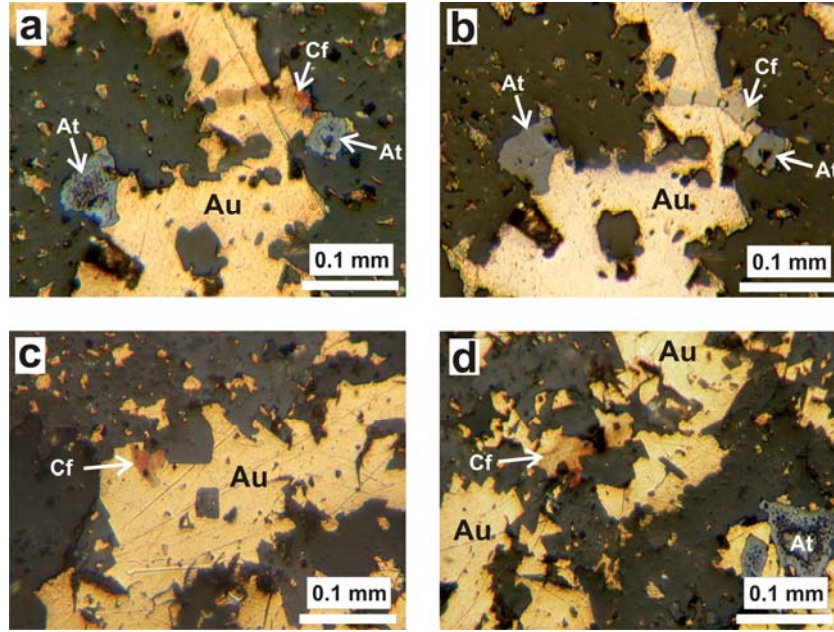


Fig. 4. Silver-rich gold with canfieldite and argentite. Polished section, parallel nicols; **a.** Tarnished polished section. Brownish canfieldite (Cf) is cross-cutting a gold grain; zoned argentite (At) is also present. **b.** The image of the same visual field after the tarnish was polished away. It is of note the light gray color with creamy tints of canfieldite and the white-yellowish color of silver-rich gold. **c** and **d.** Tarnished polished section. Gold grain (Au) including canfieldite (Cf). Zoned argentite (At) occurs in image d.

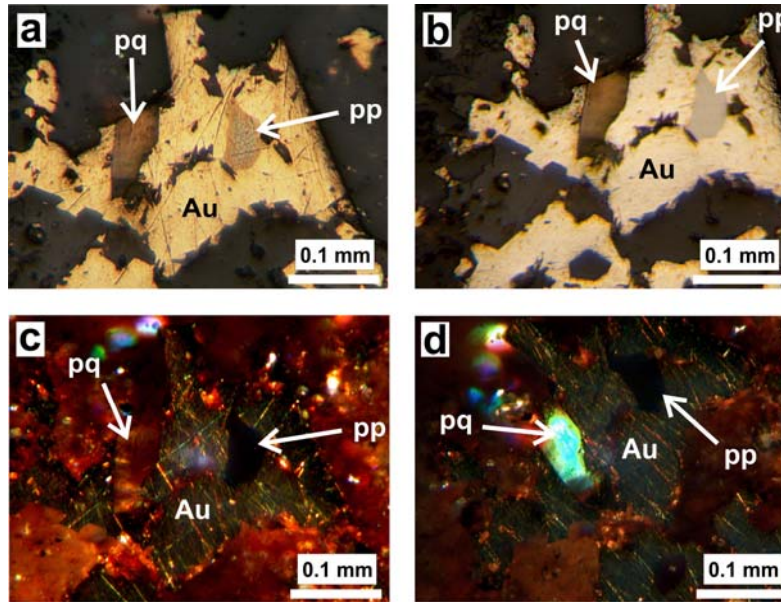


Fig. 5. Silver-rich gold (Au) with pirquitasite (pq) and polybasite-pearceite (pp). Reflected light. **a** and **b:** parallel nicols; **c** and **d:** crossed nicols. Microscopic images of intergrowths between silver-rich gold, pirquitasite and polybasite-pearceite. **a.** brown-gray colored pirquitasite and zoned polybasite-pearceite (more tarnished in the central part of grain); a weak-brownish tint can be seen towards the margins, probably where the pearceitic term occurs. **b.** The same visual field after a fresh polish: the light color of silver-bearing gold and the clear brown color of pirquitasite are visible, polybasite-pearceite are recognized by a standard gray color with a weak creamy tint. **c.** Pirquitasite with brown-reddish color and many internal reflections. **d.** The same view with partially crossed nicols, showing a green color of pirquitasite with local reddish internal reflections.

The paragenetic relationship suggests that the first gold type is of older generation, in association with pyrite, polybasite, argentite, canfieldite, quartz and „adularia” gangue, whereas the second type is younger, associated only with collophorm carbonates (Fig. 3, c).

6. Conclusions

For the time being, the preliminary data referring to the genesis of this association are the following:

- The mineral assemblage of Roșia Montană probably contains two new tin-sulfosalts: *canfieldite* and *pirquitasite*; the later one is now mentioned for the first time in Romania.
- The described minerals occur in parallel-zoned texture, exclusively together with an intergrowth between gold and quartz - „adularia” gangue. These are probably generated in an earlier, higher temperature mineralization phase.
- Gold intergrown with carbonates represents a late phase, the latter being newer than quartz. No tin minerals were found in the sulfide and native gold band of the investigated polished section; only silver-rich gold, galena, chalcopyrite, sphalerite, tetrahedrite and pyrite occur in that band suggesting a distinct phase of mineralization.
- These data may prove useful for the archaeological research, suggesting that the existence of tin may not be an irrefutable evidence for the provenance of gold from placer-type deposits, as inferred by Constantinescu et al. (2008). The presence of canfieldite suggests the primary deposits of the Apuseni Mts. as another possible source. This would imply that the Dacian gold was not necessarily obtained by panning, but also by mining.

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References

- Cauuet, B., Ancel, B., Rico, C., Tamas, C., 2003. Ancient mining networks. The French archaeological missions 1999–2001, In: Damian, P. (Ed.) *Alburnus Maior Monographic series I*, 467–526, Bucharest.
- Constantinescu, B., Bugoi, R., Cojocaru, V., Radtke, M., Calligaro, M., Salomon, J., Pichon, L., Roehrs, S., Ceccato, D., Oberlaender-Târnoveanu, E., 2008. Micro Sr-XRF and micro-PIXE studies for archaeological gold identification—the case of Carpathian (Transylvanian) gold and of Dacian bracelets. *Nuclear Instruments and Methods in Physics Research B* 562, 2325–2328.
- Harris, D., C., Owens, D., R., 1971. A tellurium-bearing canfieldite from Revelstoke, B.C. *Canadian Mineralogist*, 10, 895–898.
- Petruilian, N., 1934. Étude chalcographique du gisement aurifère de Roșia Montană (Transylvanie, Roumanie), *Anuarul Institutului Geologic al României*, XVI, 499–539.
- Picot, P., Johan, Z., 1982. *Atlas of ore minerals*, B.R.G.M.–Orleans & Elsevier Scientific Publishing Co., Amsterdam, 458 pp.
- Popescu, G.C., 1986. *Applied Metallogeny and Geological Prognosis* (in Romanian). Editura of Bucharest University, 316 pp.
- Simon, R., Buth, G., Hagelstein, M., 2003. The X-ray-fluorescence facility at ANKA, Karlsruhe: Minimum detection limits and micro probe capabilities. *Nuclear Instruments and Methods in Physics Research*, section B, 199, 554–558.
- Szakall, S., Udubașă, G., Duda, R., Kvasnytsya, V., Koszowska, E., Novak, M., 2002. *Minerals of the Carpathians*, Editura Granit, Prague, 480 pp.
- Tâmaș, C., G., Baillz L., Cauuet, B., 2004. Breccia structures and Au–Ag mineral assemblages in Roșia Montană ore deposit, Apuseni Mountains, Romania. In: Cook, N.J. and Ciobanu, C.L. (Eds.), *Au–Ag telluride deposits of the Golden Quadrilateral, South Apuseni Mts., Romania* (Guidebook of the

Preliminary data on two tin-sulfosalts from Roșia Montană

- International Field Workshop of IGCP Project 486, Alba Iulia, Romania. IAGOD Guidebook Ser.12, 254-255.
- Tămaș, C., G., Bailly, L., Ghergari, L., O'Connor, G., Minuț, A., 2006. New occurrences of tellurides and argyrodite in Roșia Montană, Apuseni Mountains, Romania and their metallogenetic significance, Canadian Mineralogist, 44, 367-383.
- Vasilescu, A., Constantinescu, B., Bugoi, R., Radtke, M., Reinholz, U., Simon, R., 2010. X-Ray Optics and Microanalysis, Proceedings Book Series: AIP Conference Proceedings, 1221, 139-143.

Geochemistry and origin of two magmatic rock associations from the banatitic magmatic-metallogenetic province in Romania

Haralambie SAVU*

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

Abstract: Within the Laramian (Upper Cretaceous) continental volcano-plutonic arc from the western part of the Romanian territory, the Lăpuşiu Basin and the Vlădeasa Mountains are two areas with distinct associations of banatitic rocks. The first area is located in the northeast of Banat and the second is in the northern part of the Apuseni Mountains. These volcanic associations differ from one another by their general rock composition, since the rocks from the Lăpuşiu Basin are more basic, being represented by andesites, while in the Vlădeasa Mountains the banatitic rocks consists especially of dacites, rhyolites and related plutonic rocks. All these volcanic and the associated plutonic rocks are calc-alkaline in composition, with some alkaline tendency, bearing an obvious continental arc signature. The Lăpuşiu volcanics differ from the Vlădeasa ones by their high Sr, Ba and Zr contents and low Y contents, suggesting an adakitic tendency. The trace elements of the Vlădeasa volcanics are within a range normal for arc-related rocks. The andesitic (dioritic) parental magmas of the Laramian (banatitic) rocks in both areas resulted from the partial melting of a wedge of metasomatic mantle located above the subduction plane, at a depth of about 100 km. The Paleogene basalts, which cut the Laramian volcanics, are of within-plate type and their parental magmas resulted from the partial melting of a lherzolitic plume-source at about 50 km depth. The Lăpuşiu volcanics are associated with Pb-Zn-Cu mineralizations, while uranium deposits are related to the Vlădeasa magmatic rocks.

Key words: Banatitic volcanics; andesites; arc magmatism; felsic rocks; within-plate basalts; Carpathians, Romania

1. Introduction

The Laramian Banatitic Province (Cotta, 1864) extends from the north of Romania through Serbia to the southeast of Bulgaria. Recently, this province was described by Berza et al. (1998) and Ciobanu et al. (2002) as the Banatitic Magmatic and Metallogenetic Belt, with a length of more

than 1,000 km (Ciobanu et al., 2002). On the Romanian territory it includes mostly acid rocks (Giuşcă et al., 1966). However, the rock association from the Lăpuşiu Basin makes an exception from this rule, consisting mostly of intermediate (andesitic) rocks. This review will compare the prevalently intermediate rocks of Lăpuşiu Basin with the dominantly felsic rocks of the Vlădeasa region, as the

* Tel: +40213060491; fax: +40213181326;
e-mail address: office@igr.ro

geology of the two regions is better known compared with other banatitic zones in Romania. Moreover, each of these regions has its specific metallogeny.

2. Occurrences, petrography and metallogensis

The two Laramian volcanic areas (Fig. 1) are situated on the bent zone of the Laramian continental volcano-plutonic arc (see also Rădulescu and Săndulescu, 1973; Savu et al., 1992; Savu, 2005a, Constantina et al., 2009), but occurring in somehow different geological setting. The Lăpugiu volcanics were formed near the Mureș ophiolitic suture, whereas the Vlădeasa volcanics occurred within the northern part of the Apuseni Mountains, formed of old crystalline schists. Necks and dykes of Paleogene hotspot basaltic rocks are crossing the banatitic volcanics in both areas. But these basalts have a different origin than the banatitic rocks.

2.1. The Lăpugiu volcanic rocks

In the Lăpugiu Basin the Laramian volcanics are lining the bottom of the basin, under the Neogene sedimentary deposits, so that they outcrop mostly on its margins (Fig. 1). On the northern margin of the basin these volcanics extend between Groși, Bulza, Gurasada and Vorța Valley. Kadić (1906), Pinkert (1907), Papiu (1954), Gheorghiu and Mareș (1964), Rădulescu and Borcoș (1968), Ianovici et al. (1976), Peltz et al., (1970), Peltz and Urcan (1972), Savu et al. (1992, 1994), Roșu et al. (1993) and, recently, Constantina et al. (2009) studied these volcanics. The Laramian volcanics occurring on the southern margin of the basin, between Pietroasa, Roșcani and Ilia, have been investigated by Dittler and Kirnbauer (1933), Papiu (1956), Savu (1962) and Downes et al. (1995).

It is noteworthy that till 1974, in the absence of any precise dating, the Lăpugiu Laramian volcanics were considered as Neogene rocks. In 1974 a first Rb/Sr dating of 60 Ma was obtained (Herz et al., 1974) on a perlite from the Ilteu area. Later, Savu (1984) presented a K/Ar age of 59.6 Ma, obtained on

a rhyolite tuff from Vica, and Vijdea (unpublished data) determined an age of 70 Ma on a rhyolite from the Căpriorișca Valley. Concomitantly, Popescu (in Borcoș et al., unpublished report) determined the Upper Cretaceous age of these volcanics, studying the microfauna from the associated sedimentary deposits. These values have recently been confirmed by Constantina et al (2009), who obtained ages of 69 to 80 Ma on the Gurasada volcanics.

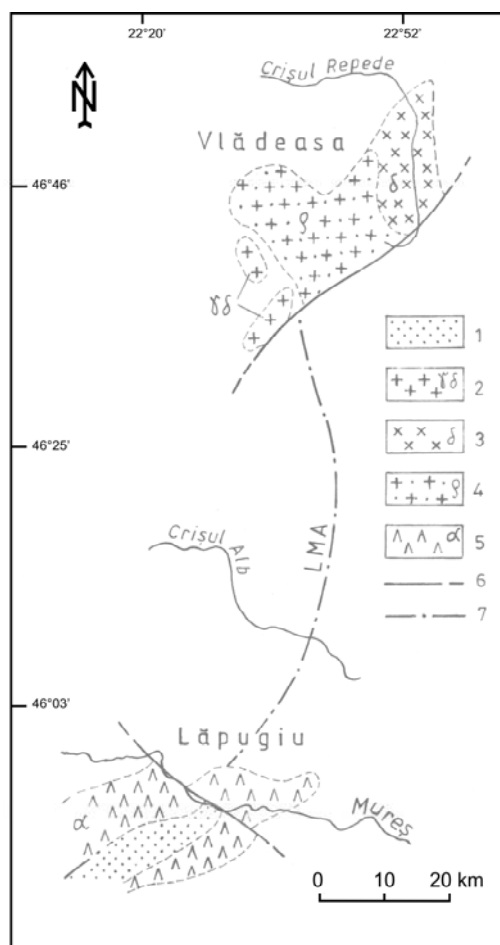


Fig.1. Sketch-map showing the position of the two areas of volcanics on the Laramian continental volcano-plutonic arc from the Romanian territory (after the Geological map of Romania, scale 1:1000000, Geological Institute of Romania, 1966, with the additions of the author). 1, Neogene deposits; 2, granodiorites and granites; 3, rhyolites and rhyodacites; 4, dacites and trachydacites; 5, andesites and trachyandesites; 6, fault; 7, inferred Laramian magmatic arc segment (LMA) of the Banatitic province.

As shown in Figure 2, in the Lăpugiu Basin the Laramian volcanics consist mostly of andesites and trachyandesites; the acid rocks like dacites, trachydacites, trachytes and rhyolites are scarce. Both the andesites and acid rocks occur mostly as pyroclastics, usually stratified. From a lithologic column made by Savu (1962) on the volcanics from the base of the Pietroasa volcanic sequence, in the southern margin of the basin, it results that the Laramian volcanics lie over a basement consisting of the Poiana Ruscă crystalline schists and Upper Cretaceous deposits. On the northern margin they lie on the Coștei Triassic intra-plate basalts and the Jurassic to Upper Cretaceous formations of the Mureș ophiolitic suture. They form an important pile of volcanics consisting of andesitic volcanic breccias, microbreccias, rarely lavas, and fine-grained to psammitic tuffs, which are often bearing plant impressions. The petrographic types include pyroxene andesites, hornblende biotite andesites, augite hornblende biotite andesites, hornblende andesites, hyperstene augite hornblende andesites and hyperstene augite hornblende biotite andesites, which are covered by Neogene gravels. These rock varieties can be found on both margins of the basin (Savu, 1962; Savu et al., 1992; 1994, Constantina et al. 2009). These are often associated with alkaline rocks such as trachyandesites (Fig. 2). The volcanic layers show a thickness of a few centimeters, in case of tuffs, and of up to 50 meters in case of the volcanic breccias.

The acid rocks from the Lăpugiu Basin, although rare, can be found on both margins of the basin, where they are associated with fine layers of sedimentary deposits.

On the northern margin of the basin they occur as layers of rhyolite tuffs intercalated in the lowermost part of the volcanic pile at Vica, on the Căpriorișca Valley and at Ilteu. At the last locality, the acid rocks are represented by perlites. On the Dineș creek, south of Mureș River, a trachyandesite dyke intruded Upper Jurassic limestones. On the southern margin of the basin, rhyolitic rocks occur in a volcanic neck, situated on the Bega Valley (Dittler and Kirnbauer, 1933). The respective rocks

contain corroded quartz, sanidine and rarely albite and biotite phenocrysts. South of Pietroasa, acid pyroclastics are intercalated at the base of the volcanic sequence.

On the northern margin of the Lăpugiu Basin there are basic rocks, as well, such as basalts and basaltic andesites (Fig. 2), among which is the basaltic neck located south of Petrești (see the map in Savu et al., 1992). The latter rocks show some geochemical peculiarities which place them (or at least a part of them), among the rocks of the Paleogene necks from the Mureș Rift (Savu et al., 1996), that originate in the Transylvanian mantle plume (Savu, 2004).

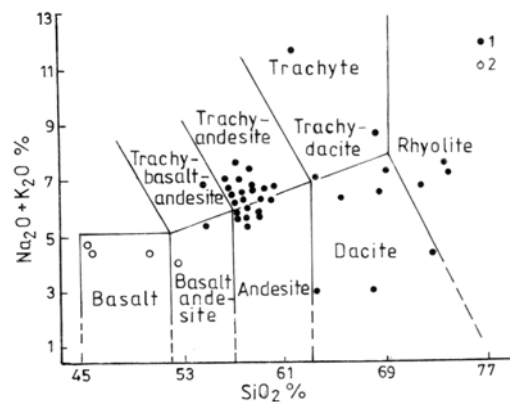


Fig. 2. Plot of the Laramian volcanics from the Lăpugiu Basin on the $\text{Na}_2\text{O}+\text{K}_2\text{O}$ vs. SiO_2 diagram. Fields according to Le Maître et al. (1989). Data from Savu (1962), Savu et al. (1992; 1994) and Downes et al. (1995). 1, Lăpugiu volcanics; 2, Paleogene basalts.

2.2. The Vlădeasa magmatic rocks

As it was mentioned above, the acid rocks are prevalent among the Vlădeasa Laramian volcanics. They are associated with granodiorite and granite intrusions, resulting in a typical volcano-plutonic complex (Giușcă et al., 1969). Geological data concerning these volcanics have been presented in numerous papers, summarized by Istrate (1978) and Ștefan (1980). A more documented paper was published by Ștefan et al. (1992).

The diagram in Figure 3 shows that these volcanics are represented especially by dacites, trachydacites and rhyolites (see also Fig 1). It is of note that Hauer and Stache (1863) introduced in geology the term “dacite”, referring to the rocks from this region. Intermediate rocks like andesites and trachyandesites rarely occur. Giuşcă (1950), Istrate (1978) and Ştefan (1980) distinguished various types of andesites, dacites and rhyolites. At the same time, an ignimbritic formation was evidenced there by Giuşcă et al. (1969), extending over an area of about 400 km². Within the northern part of the Vlădeasa volcanic area, Istrate (1978) described a similar volcano-sedimentary formation.

The K/Ar dating (Bleahu et al., 1984) showed ages of 61 ± 3 Ma and 61.5 ± 5 Ma. These values show that the magmatic activity in the Vlădeasa area started a little later than in the Lăpuşiu Basin.

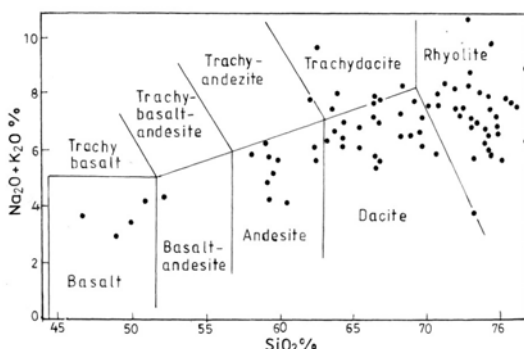


Fig. 3. Plot of the Laramian volcanics from the Vlădeasa area on the Na₂O+K₂O vs. SiO₂ diagram. Fields, according to Le Maître et al. (1989). Data from Giuşcă (1950), Istrate (1978), Ştefan (1980) and Ştefan et al. (1992).

The rocks occurring in the basaltic and basalt-andesite fields in Figure 3 are represented by lamprophyres *sensu stricto* (Ştefan, 1980) and Paleogene basalts (Istrate, 1978). The basaltic rocks occur as NW-SE trending dykes within the western part of the Vlădeasa volcanic area, where they are intruding the ignimbrite formation and the Senonian deposits (Istrate, 1978). They are very similar to the rocks from the Paleogene dyke swarm from the neighboring Bihor

Mountains, which could originate in a Bihor mantle plume (Savu, 2005b), occurred during the extension period that followed the Laramian compression.

The two study areas are associated with different types of mineralization. According to the observations of Ghiţulescu and Socolescu (1941), Savu (1972) and Savu and Nicolae (1975), the Lăpuşiu volcanics are associated with Pb-Zn-Cu hydrothermal mineralizations, occurring in the Căpâlnaş-Vorţa-Nevoiaş metallogenetic district (Savu, 2011).

The mostly acid magmatic rocks of the Vlădeasa area can be related with U mineralizations, occurring in the Băiţa-Avram Iancu (Bihor) metallogenetic district from the Apuseni Mountains uranium metallogenetic province. Based on the geological conditions, in this district there are two types of uranium mineralization. One is represented by the concentrations of uranium occurring in the Upper Paleozoic crystalline schists of the Păiuşeni series, such as the uranium concentrations occurring on the Păiuşeni river and Rănuşa, which are intercalated as lenses in the crystalline schists (Savu, 1993). The second one is related to the postmagmatic solutions released by the Băiţa granitoid pluton (Niţu, 2000). In both cases, the metal assemblage is U-(Co-Ni) of hydrothermal origin, being associated with enrichment in some other elements such as Fe, Pb, Zn, Cu and Mo. After their emplacement, the uranium deposits have been affected by the tectonics of the Apuseni Mountains Neogene rift (Niţu, 2008).

3. Geochemical features and tectonic setting

The average chemical composition of the Laramian volcanics from the two areas was presented in Tables 1 to 3. These data confirm that the Laramian volcanics from the Lăpuşiu Basin, where SiO₂ varies from 50.78 to 68.47%, are more basic than the Vlădeasa rocks, in which this component increases from 49.54 up to 74.50%. The values of FeO_{tot} decrease from 9.26 to 0.16% in the first rock-series and from 8.23 to 2.08% in the second one. MgO varies from 9.76 to 0.66% in the Lăpuşiu volcanics and from 7.02 to 0.52% in

the Vlădeasa rocks. The sum of alkalis increases from 3.48 to 6.74% in the first series and from 4.29 to 7.55% in the second one, showing that the rock alkalinity is relatively higher in the Vlădeasa rock-series. Except for some alkaline and acid rocks, in both areas Na_2O prevails on K_2O .

The diagram in Figure 4 shows that in both volcanic areas rocks with an obvious alkaline tendency already remarked by Giușcă et al. (1966) on the rocks of the banatitic province. The Paleogene basaltic rocks from both regions plot on the diagram in the tholeiitic field showing a different origin.

The trace elements presented in the same tables also show some peculiarities of the Lăpugiu volcanics compared to the Vlădeasa ones. Elements like Ni, Co, Cr, V and Sc have variable contents in both series, but they are higher in the Lăpugiu rocks than in the Vlădeasa ones. Among these elements Cr and V are remarkable, since in the Lăpugiu

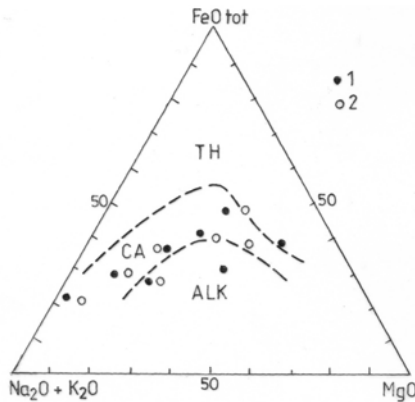


Fig. 4. Plot of the Laramian volcanics on the $\text{FeO}_{\text{tot}}\text{-Na}_2\text{O}+\text{K}_2\text{O-MgO}$ diagram. Fields according to Irvine and Baragar (1971) and Hutchinson (1982). TH, tholeiitic; CA, calc-alkaline; ALK, alkaline. 1, Lăpugiu volcanics; 2, Vlădeasa volcanics, Data from the sources quoted in Tables 1 and 2.

volcanics Cr varies from 260 to 13 ppm and from 350 to 0 ppm in the Vlădeasa rocks. The V contents vary from 310 to 32.66 ppm in the first area and from 190 to 19 ppm in the second one.

The Zr contents in both series are high for calc-alkaline volcanics. The average Zr is

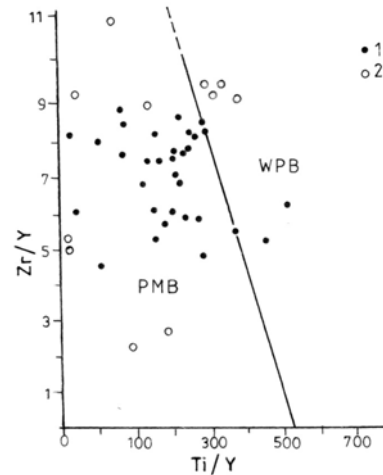


Fig. 5. Plot of the Laramian volcanics and the Paleogene basalts on the Zr/Y vs. Ti/Y diagram. Fields according to Pearce and Gale (1977): PMB, plate margin basalts; WPB, within-plate basalts. Legend as in Figure 4.

in the Lăpugiu rocks of about 125 ppm and of 257.6 ppm in the Vlădeasa ones; it is much higher in the more acid rocks of the second volcanic series. Accordingly, on the Zr/Y vs. Ti/Y diagram (Fig. 5) all the Laramian volcanics plot in the plate margin basalt (PMB) domain, namely, at higher values of the Zr/Y ratio. The basaltic rocks from both areas plot in the WPB field, which supports their affiliation to the Paleogene volcanic province.

The Y and Yb contents are variable, compared with those of the normal island arc volcanics. The average Y is of about 18 ppm in the Lăpugiu rocks and of 27 ppm in the Vlădeasa volcanics. The low Y content from the Lăpugiu rock series is characteristic for the volcanics with the adakitic features (Sajona et al., 2000). It could be supposed that it was determined by the fact that the Lăpugiu volcanics occurred within the Mureș adakitic province area (Savu, 2002), situated between the Southern Carpathians and the Apuseni Mountains.

The Sr and Ba contents are also variable in comparison with those from the normal island arc volcanics. The first element varies from 720 to 247.5 ppm. It has an average of

477 ppm in the Lăpugiu rocks and of only 113 ppm in the Vlădeasa volcanics. Ba presents an average of 478.5 ppm in the Lăpugiu rocks and of 459 ppm in the Vlădeasa ones.

The relationships between Sr and Y determined the plotting of the volcanics from

both regions in the “Typical arc field” of the Sr/Y vs. Y diagram (Fig. 6). Nevertheless, due to their high Sr and low Y contents, some the Lăpugiu rocks plot on the diagram at higher values of the Sr/Y ratio, like those of adakitic rocks.

Table 1. Average chemical composition of the Laramian volcanics from the Lăpugiu Basin. Data from Savu (1962); Savu et al. (1992); 1994) and Downes et al. (1995)*

Element	1	2	3	4	5	6	7	8
SiO ₂ %	50.78	52.90	55.75	58.26	60.33	66.43	66.47	68.47
TiO ₂	1.50	1.04	0.66	0.88	0.75	0.13	0.27	0.33
Al ₂ O ₃	15.24	13.92	17.17	16.45	17.10	14.77	18.05	16.05
Fe ₂ O ₃	4.33	2.63	2.83	3.10	2.53	1.35	0.14	1.70
FeO	5.37	5.67	4.48	2.94	2.30	1.16	0.04	1.0
MnO	0.17	0.15	0.14	0.12	0.11	0.27	1.84	0.52
MgO	8.18	9.76	4.29	3.40	2.74	1.88	0.75	0.66
CaO	9.21	9.78	7.45	6.70	6.60	0.88	3.57	2.04
Na ₂ O	2.43	2.55	3.03	3.13	3.35	2.33	2.82	2.83
K ₂ O	1.53	0.98	2.80	2.55	2.49	2.48	3.92	3.72
P ₂ O ₅	0.23	0.11	0.24	0.18	0.19	0.06	0.10	0.05
H ₂ O ⁺	1.05	0.75	0.64	1.54	1.13	1.52	1.95	4.15
CO ₂	-	-	-56	0.39	0.44	0.31	-	-
S	0.07	0.27	0.20	0.21	0.28	0.4	-	0.18
Total	100.1	100.51	100.24	99.84	100.34	94.01	99.95	100.70
Ni ppm	17	21	46	19	19.24	3.25	7.27	28
Co	34	25	30	16.77	14.26	2	4.7.33	
Cr	100	260	116	52.83	137.2	3.2.5	48.5	13
V	300	100	310	184	161.89	61.50	47	32.66
Sc	44	17	29.66	16.22	17.23	3.50	5.75	5.25
Zr	110	75	216.6	162.2	164	42.50	110	104.16
Y	21	121	27	19.88	25.3	15.50	12	13.16
Yb	2.8	1.3	2.56	2.11	2.48	0.75	1.35	1.71
La	-	-	42.66	32.88	38.73	41.50	41.50	36.83
Ba	280	300	556	494	650	220	650	480
Sr	440	720	496.6	570	642	192.5	470	247.5
Pb	7.5	11	19.66	15.27	35	20.20.5	6.71	
Cu	23	80	28	16	23.3	9.75	17.50	41.08
Zn	-	-	50	65	25.16	30	83.50	32.66
Ga	13	15	18.33	14.88	20	16	17.50	9.91
Sn	2	2	2	1.75	2.2	1	2.5	2
Nb	10	10	10	10	24.	16	10.20	
Mo	-	-	-	-	-	30	-	57

* The analyses in the table represent: 1, one basalt; 2, average of 2 basaltandesites; 3, average of 3 trachybasalt-andesites; 4, average of 9 andesites; 5, average of 15 trachyandesites; 6, average of 2 dacites; 7, average of 2 trachydacites; 8, average of 7 rhyolites.

On the contrary, the Vlădeasa rocks have values of the Sr/Y ratio lower than 10. The position of the Lăpugiu rocks on this diagram at higher values of Sr/Y ratio, as well as the fact that some rocks of this series plot

even in the adakitic rock field (see also Savu, 2002), show their tendency toward rocks with adakitic characteristics. Therefore, it suggests that the Mureş adakitic province includes Upper Cretaceous, Paleogene, Neogene and

Quaternary volcanics. Because of the high Zr and low Y contents, on the Zr/Y vs. Zr diagram (Fig. 7), most rocks from both study areas plot within or near the within-plate basalts field. The high Zr could have been induced by the contamination of the parental magmas and seems to be a characteristic of the rocks erupted along the continental volcanic arcs. The Lăpuşiu and Vlădeasa volcanics could not be within-plate rocks as long as their Ti content is a normal one for the island arc volcanics (Fig. 5). On the Ti vs. Zr diagram (Fig. 8) the studied rocks plot within the IAB field, or near it. However, a difference occurs between the rocks of the two volcanic areas. The more basic Lăpuşiu rocks, which are richer in Ti than those from the Vlădeasa area, plot on the diagram at values higher than 5000 ppm Ti, while most of the Vlădeasa rocks are situated at values lower than 2000 ppm Ti.

The high average contents of Ba and Sr in the rocks with adakitic tendency from the Lăpuşiu Basin show that Ba and Sr usually make a characteristic pair in such rocks (Savu, 2001). Moreover, both the Laramian volcanics from the Lăpuşiu Basin and the Neogene adakitic volcanics from the Mureş adakitic province have been engendered under the control of the fluids derived from oceanic crust slab subducted on the Benioff plane (Savu, 2001). These fluids generated a metasomatic wedge in the mantle, above the subduction plane, which was the source of the Laramian parental magmas. Other trace elements like Pb, Cu, Ga, Be and Li have varied contents in both volcanic series (Tables 1 and 2).

In Table 3, the contents of REE and other trace elements, as well as the values of some characteristic ratios from the Laramian volcanics were presented. The REE show similar average content in the two volcanic series. However, in the Lăpuşiu rocks the REE values, excepting Yb, increase from the basic to the acid rocks. The REE from the Vlădeasa rocks display varied values within the range characteristic for the arc volcanics (Savu et al., 1992).

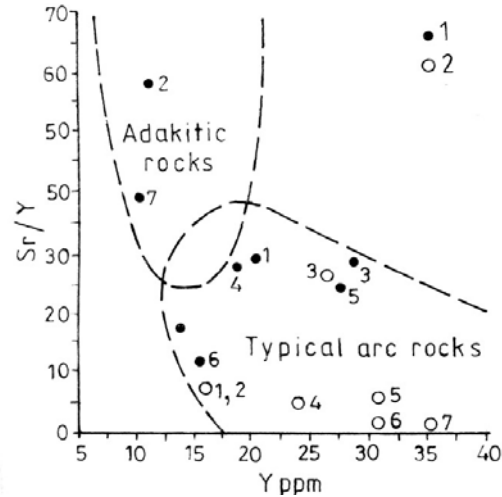


Fig. 6. Plot of the Laramian volcanics from both regions on the Sr/Y vs. Y diagram. Fields according to Drummond and Defant (1990), revised by Sajona et al. (2000). Legend as in Figure 4.

The chondrite-normalized REE patterns (Figs. 9 and 10) show some differences between the two rock series. The pattern of the acid volcanics from the Lăpuşiu

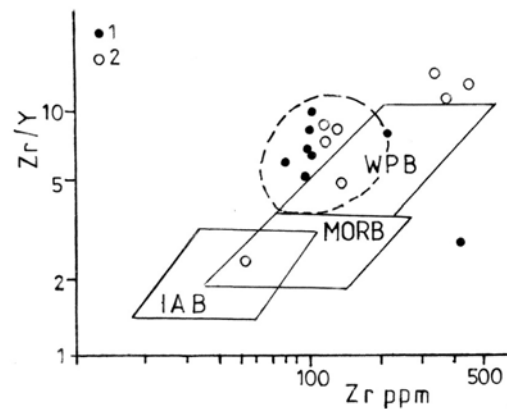


Fig. 7. Plot of the Laramian volcanics on the Zr/Y vs. Zr diagram. Fields according to Pearce and Norry (1979): WPB, within-plate basalts; MORB, mid-ocean ridge basalts; IAB, island arc basalts. Legend as in Figure 4.

Basin shows a weak Ce positive anomaly, as well as a strong Yb depletion (Fig. 9). The pattern of the acid rocks from the Vlădeasa area (Fig. 10) shows a strong Eu negative anomaly that is typical for the island arc rocks.

The pattern of the intermediate rocks has the same significance, but it indicates a Tb negative anomaly, that is more obvious at the Dumbrava hornblende biotite andesite (Ştefan et al., 1992).

Table 2. Average chemical composition of the Laramian volcanics from Vlădeasa. Data from Giuşcă (1950); Istrate (1978); Ştefan (1980) and Ştefan et al. (1992)*.

Element	1	2	3	4	5	6	7
SiO ₂ %	49.56	52.74	59.88	62	65.86	68.63	74.59
TiO ₂	1.31	0.85	0.18	0.7	0.22	0.25	0.13
Al ₂ O ₃	17	15.62	16.72	19.4	15.42	12.51	13.20
Fe ₂ O ₃	3.70	3.28	2.92	2.43	2.30	1.17	1.14
FeO	5.91	3.87	3.39	1.98	1.47	2.71	1
MnO	0.06	0.03	0.06	0.06	0.07	0.24	0.04
MgO	6.81	7.02	4.36	1.60	1.34	2.04	0.53
CaO	7.73	7.88	4.88	3.04	3.16	2.76	1.40
Na ₂ O	2.59	2.77	3.56	4.40	3.58	3.52	3.27
K ₂ O	0.81	1.52	1.46	3.20	2.93	3.42	4.28
P ₂ O ₅	0.34	0.22	0.32	0.17	0.13	0.10	0.15
H ₂ O ⁺	2.58	2.59	1.33	0.88	0.70	0.45	0.53
CO ₂	1.51	1.41	0.91	0.22	0.83	1.42	0.33
S	0.02	0.04	0.11	0.08	0.41	0.22	0.09
Total	100	99.65	100.08	100.18	98.42	99.46	100.74
Ni ppm	45.5	72	15	9	5.60	3	4
Co	32	37	14.5	14	7.75	5	-
Cr	250	350	29.5	-	12.25	-	-
V	205	190	99.5	66	25.80	30	19
Sc	30.5	29	18	17	9.10	-	14
Zr	150	120	54	375	126.6	420	450
Y	18	18	22.5	19	33	33	36
Yb	2.8	1.3	2.56	2.11	2.48	0.75	1.35
Ba	220	220	345	380	540	420	850
Sr	130	130	189	95	182	53	28
Pb	30	30	25	30	29.30	30	30
Cu	30	42	17	12	11.66	-	4
Ga	15.5	13	22.5	18	18.80	16.15	-
Be	1.75	2	2	2	2.66	2	3
Li	-	-	37.5	43	46	-	-

* The analyses in the table represent: 1, average of 4 basalts and lamprophyres; 2, average of 2 basaltic andesites; 3, average of 10 andesites; 4, one trachyandesite; 5, average of 20 dacites; 6, average of 7 trachydacites; 7, average of 32 rhyolites and rhyodacites

For comparison, the pattern of the Paleogene basalts is characteristic for within-plate basic rocks. It is noteworthy that the relationships between the (Dy/Yb)_N and (Ce/Yb)_N ratios determined in a Paleogene basaltic rock from the Vlădeasa area, place it near the plume-source line on the diagram of Haase and Devey (1996), which confirms the supposition that the Paleogene dyke swarm of

basic rocks from the neighboring southern area could originate in an inferred Bihor mantle plume (Savu, 2005b), a rock-series to which the basic dykes from the western part of the Vlădeasa area belong, as well. Other trace elements like Th, U, Rb, Hf and Nb (Table 3) were determined only in the rocks from the Vlădeasa area. It is obvious that the first three elements have the lowest contents in the basic

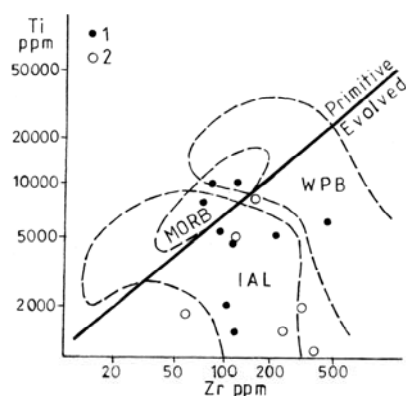


Fig. 8. Plot of the Laramian volcanics from both areas on the Ti vs. Zr diagram. Fields according to Pearce (1980): WPB, within-plate basalts; MORB, mid-ocean ridge basalts; IAL, island arc lavas. Legend as in Figure 4.

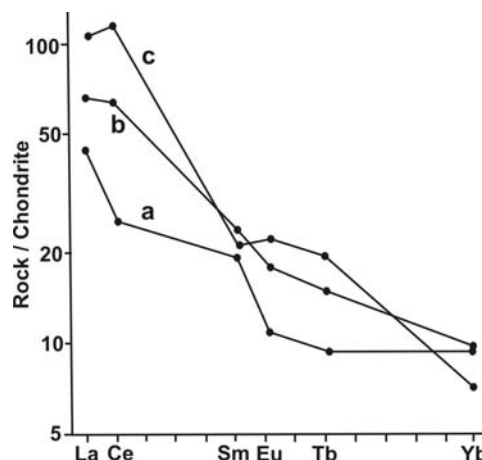


Fig. 9. Chondrite-normalized REE patterns (normalized values from Boynton, 1984) of the Lăpugiu rocks. a, basic; b, intermediate; c, acid. Data from Table 3.

Table 3. The average contents of the REE and of other trace elements from the Laramian magmatic rocks and the values of some of their characteristic ratios. Data from Savu et al., (1992) and Downes et al. (1995)*.

Area	Lăpugiu Basin			Vlădeasa		
	Rock-group	Basic	Inter-Mediate	Acid	Basic	Inter-Mediate
	La	14	22.6	33	27	19.6
	Ce	21	55.8	100	25	30
	Sm	3.85	4.74	4.30	5.6	4.13
	Eu	0.82	1.34	1.70	1.29	1.23
	Tb	2.05	2.06	1.5	3.2	2.3
	Yb	2.05	2.06	1.5	3.2	2.3
	Lu	0.21	0.32	0.58	-	-
	Th	-	9.1	-	6.8	9.04
	U	-	2	-	1.4	2.62
	Rb	-	7.5	-	43.9	68.8
	Hf	-	-	-	2.6	6.76
	Nb	-	7.6	-	23.5	19.28
	Sr/Y	21	29.5	22.38	7.22	6.84
	Rb/Sr	-	1.3	-	0.14	0.21
	Th/U	-	4.5	-	4.85	2.48
	(La/Yb) _N	4.60	7.40	14.83	5.68	5.74
	(La/Ce) _N	-	1.05	0.85	-	1.70

* The data in the table represent the averages of 27 analyses of andesites from the Lăpugiu Basin and 15 analyses on the acid rocks from Vlădeasa.

rocks and increase in the other rock groups. Among the ratios presented in Table 3, the values of Sr/Y ratio from the Lăpugiu rocks are in obvious contrast with those from the Vlădeasa volcanics, which are very low. The

higher values of this ratio in the Lăpugiu rocks are in accordance with their adakitic tendency, as shown above. The Lăpugiu rocks show higher values of (La/Nb)_N ratio than the Vlădeasa volcanics.

4. Origin of the magmatic rocks in the study areas

Referring to the genesis of the Lăpugiu rocks, Savu et al. (1992) and Savu (2005a) showed that these rocks originated in the continental volcano-plutonic arc from the western part of Romania, generated by the westward subduction of the Moesian Plate under the Transylvanian units (Savu, 1983). Indeed, as the diagram in Figure 11 shows, the Laramian volcanics from both volcanic areas plot in the “OROGENIC ANDESITE” domain. Most of these rocks occur in the High-K field, except for two of them that plot in the Medium-K field. The genesis related to subduction processes was also accepted by Ștefan et al. (1992) for the Vlădeasa magmatic rocks and more recently by Constantina et al. (2009) for the volcanics from the Gurasada area.

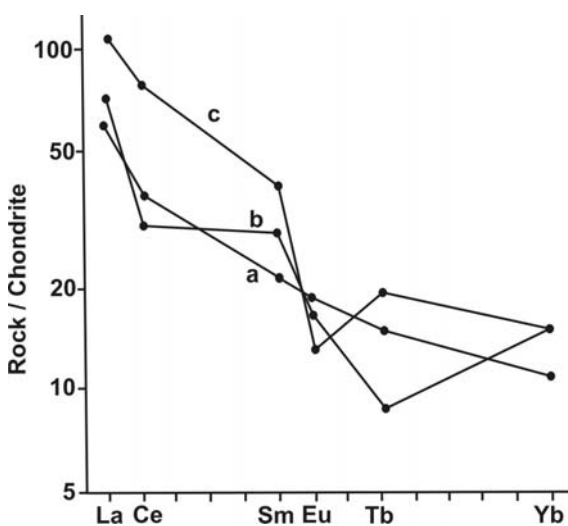


Fig. 10. Chondrite-normalized REE patterns (Boynton normalized values, 1984) of the Vlădeasa rocks. a, basic; b, intermediate; c, acid. Data from Table 3.

The parental calc-alkaline magmas of the Laramian volcanics were intermediate magmas, likely of andesitic (dioritic) composition. They were engendered at great depth in the mantle. According to the Ce/Yb vs. Ce (A) and Ce/Yb vs. Sm/Yb (B) diagrams (Fig. 12), these magmas were formed at a

depth of about 100 km (diagram A) or shallower (diagram B).

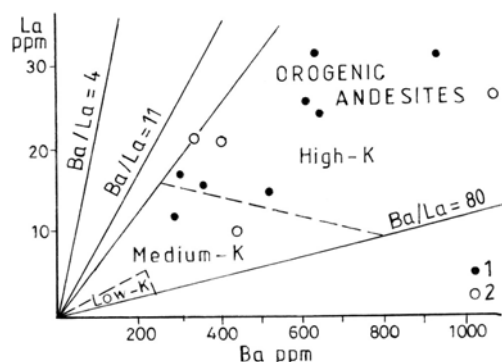


Fig. 11. Plot of the Laramian volcanics from both regions on the La vs. Ba diagram. Fields according to Gill (1981). Legend as in Figure 4.

Accordingly, the fields of the Laramian volcanics occur near the fields of the Réunion Island volcanics or overlap them. The fields of the Paleogene basalts on both diagrams suggest depths shallower than those of the Laramian magmas (ca. 50 km or deeper in Fig. 12A), near the field of the intraplate Deccan traps or partly overlapping it. This is consistent with, although somehow different from the depth of ca. 70 km estimated by Tscheegg et al. (2010), based on geothermometric estimations on mantle xenoliths from the Paleogene mafic rocks. The origin at different depths and the geochemical similarities with the Deccan traps supports the origin of the Paleogene basalts in a geotectonic setting different from the one associated with the banatitic intrusions, and a possible lherzolitic source, as argued by Savu (2004, 2005b).

There are several models concerning the genesis of the calc-alkaline magmas in relation with a subduction plane. Taylor (1968) supposed that such magmas could have resulted from the melting of the subducted ocean crust, an opinion contradicted by Gill (1981). Other authors like Mysen and Boettcher (1975) and Green (1976) showed that the andesitic parental magmas resulted

from the melting of a hydrated peridotite at a pressure of about 10 Kbar. Considering these ideas and those published by Minear and Toksöz (1970), Mysen (1979), Roden and Murthy (1985), Savu et al. (1992) and Kepezhinskas et al. (1995), it is reasonable to assume that the andesitic (dioritic) parental magmas of the Laramian volcanics from the Lăpugiu Basin and Vlădeasa Mountains were

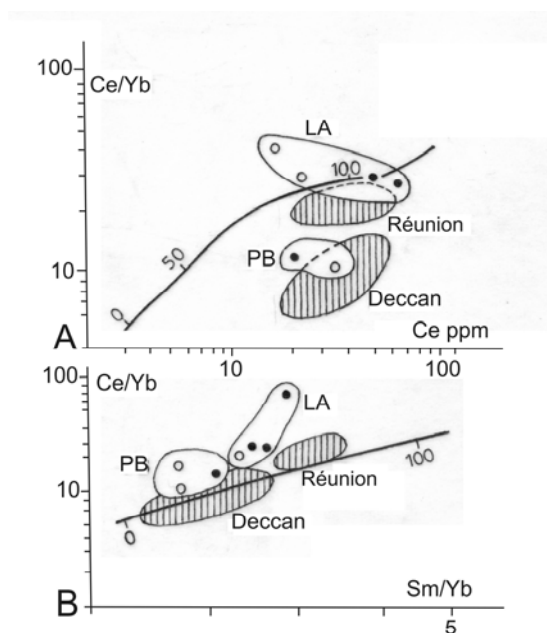


Fig. 12. Plot of the Laramian volcanics on the Ce/Yb vs. Ce (A) and Ce/Yb vs. Sm/Yb (B) diagrams. The depth lines and values, and the Réunion and Deccan rock fields were taken from Ellam (1992). LA, Laramian arc volcanics; PB, Paleogene within-plate basalts. Legend as in Figure 4.

produced by the partial melting of a mantle source. That mantle source should have been previously affected by metasomatism and contamination processes determined by the very hot fluids carrying various elements released by the subducted ocean crust slab in the process of eclogitization. In this respect, it must be emphasized that the subducted ocean crust was not a homogeneous basaltic one, since the Mureș ophiolitic suture contains, beside the ocean basaltic crust, intercalations of red argillites, limestones and sandstones.

Moreover, the magmatic minerals from the ocean floor basalts were in most cases substituted by secondary minerals like uraltite, chlorite, epidote, calcite and iron hydroxides; similarly, the plagioclase laths were altered into argillic minerals, calcite, zeolites and albite, depending on the temperature that controlled the process. Such minerals also occur in the basalt amygdals. All these materials, along with the water from the secondary mineral network and the water from the sediments contributed to the generation of a wedge of metasomatic and contaminated peridotite above the subduction plane, from which the parental magmas of the Laramian rocks derived by partial melting.

It seems that, before its emplacement in the upper crust, the parental magma underwent an intense differentiation. The low contents of Ni and related compatible elements like Cr, V, Mg etc. in the Laramian volcanics from both regions (Tables 1 and 2) indicate extensive fractionation of the mafic minerals during the differentiation of the parental magma. This process led toward the formation of a more basic magma/cumulate by the enrichment in mafic components, and toward a more acid/evolved magma that remained after the loss of a part of the mafic crystals. Concomitantly, an enrichment of the parental magma in alkalis took place, leading to the occurrence of some alkaline magma fractions, from which the alkaline and adakitic rocks resulted (Defant and Drummond, 1990). According to the low value of the $(La/Ce)_N$ ratio (Table 3) the metasomatic mantle source underwent LREE depletion during the mentioned processes.

The average isotope values of the Sr^{87}/Sr^{86} ratio are of 0.70703 - 0.70704 in the Lăpugiu andesites (Downes et al., 1995) and of 0.7059 to 0.7084 in the rocks from the Vlădeasa Mountains (Ștefan et al., 1992). These values show processes of contamination, both by metasomatism and contamination of the mantle source, as indicated by the low values of the $^{206}Pb/^{204}Pb$ ratio (Downes et al., 1995), and assimilation during the ascent of parental magma through the crust.

The parental magmas of the Paleogene tholeiitic basalts resulted from mantle plume sources, which were not affected by metasomatic processes (Savu, 2004; 2005b).

5. Conclusions

Two areas with distinct volcanic products are located along the Romanian segment of the Laramian (Banatitic) continental volcano-plutonic arc, extending from Banat to the Apuseni Mountains. The volcanics from these areas differ by their geochemical composition. The Lăpugiu rocks are mostly intermediate, being represented especially by andesites. The Vlădeasa rocks consist mostly of dacites, rhyolites and related plutonic rocks. All these igneous rocks are calc-alkaline in composition, with an obvious alkaline tendency. The Laramian volcano-plutonic rocks are bearing a remarkable continental arc signature, in contrast with the spatially-associated Paleogene basalts that are WPB rocks. The Lăpugiu volcanics show higher Sr, Ba and Zr and lower Y contents, in comparison with the Vlădeasa volcanics, where these trace elements are normal for island arc rocks. The first rock-series presents a slight adakitic tendency, consistent with their eruption within the Mureș adakitic province. The parental magmas of both Laramian volcanic series resulted from the partial melting of a metasomatic and contaminated mantle source, located at a maximum depth of ca. 100 km. In conclusion, the petrographic and geochemical differences between the two areas of Laramian continental arc rocks have been determined by several control factors, among which the most important could have been the mantle heterogeneity (see also Ringwood, 1979) and the degree of mantle source metasomatism and melting, as well as the magma contamination and differentiation.

The parental magmas of the Paleogene basalts resulted from the partial melting of a non-metasomatic lherzolitic mantle plume source, at a depth of about 50 km, like the magmas of the Deccan traps. The mineral deposits associated with the Lăpugiu volcanics are hydrothermal mineralizations of the Pb-Zn-Cu type, while the Vlădeasa

magmatic rocks are associated with uranium mineralizations.

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References

- Berza, T., Constantinescu, E., Vlad, S.N., 1998. Upper Cretaceous magmatic series and associated mineralizations in the Carpathian-Balkan orogen: Resource Geology, 48, 291-306.
- Bleahu, M., Soroiu, M., Catilina, R., 1984. On the Cretaceous tectono-magmatic evolution of the Apuseni Mountains as revealed by K-Ar datings. *Revue Roumaine de Géophysique*, 20, 123-130, Bucharest.
- Boynnton, W.V., 1984. Cosmochemistry of the earth elements, meteorite studies. In Henderson, P., (Ed.), *Rare Earth Element Geochemistry*, 63-114.
- Ciobanu, C.L., Cook, N.J., Stein H., 2002. Regional setting and geochronology of Late Cretaceous banatitic magmatism and metallogenetic belt. *Mineralium Deposita*, 37, 541-567.
- Constantina, C., Szakács, A., Pécskay, Z., 2009. Petrography, geochemistry and age of volcanic rocks in the Gurasada area, Southern Apuseni Mountains. *Carpathian Journal of Earth and Environmental Sciences*, 4, 31-47.
- Cotta, B.V., 1864. *Erzlagertstätten im Banat und Serbien*. Editure W. Braunmüller, Wien.
- Defant, M.J., Drummond, M.S., 1990. Derivation of some modern arc magmas by melting of the subducted lithosphere. *Nature*, 347, 662-665.
- Dittler, E., Kirnbauer, F., 1933. Das Bentonitvorkommen von Tomești in Rumänien. *Zeitschrift für praktische Geologie*, 41, 121-127. Berlin.
- Downes, H., Vaselli, O., Seghedi, I., Ingram, G., Rex, D., Coradossi, N., Pecskey, Z., Pinarelli, L., 1995. Geochemistry of late Cretaceous – Early Tertiary magmatism in Poiana Ruscă (Romania). *Acta Volcanologica*, 7 (2), 209-217.
- Ellam, R.M., 1992. Lithospheric thickness as a control on basalt geochemistry. *Geology*, 20, 2, 97-112.

- Gheorghiu, C., Mareş, I., 1964. Neogene eruptions from Mureş valley (region Deva-Zam): petrographic characteristics (in Romanian). *Comunicările Societăţii de Ştiinţe Naturale şi Geografie, seria Geologie*, II, 47-72, Bucharest.
- Ghiţulescu, T.P., Socolescu, M., 1941. Étude géologique et minière des Monts Metallifères (Quadrilatère aurifère et régions environnantes). *Anuarul Institutului Geologic al României*, XXI, 181-464, Bucharest.
- Gill, J.E., 1981. Orogenic Andesites and Plate Tectonics, 390 p., Berlin.
- Giuşcă, D., 1950. Le massif éruptif de la Vlădeasa. *Anuarul Comitetului Geologic*, XXIII, 199-251, Bucharest.
- Giuşcă, D., Cioflica, G., Savu, H., 1966. Petrologic characterization of the banatitic province (in Romanian). *Anuarul Comitetului Geologic*, XXXV, 13-45, Bucharest.
- Giuşcă, D., Istrate, G., Ştefan, A., 1969. Le complex volcano-plutonique de la Vlădeasa (Roumanie). *Bulletin of Volcanology*, XXXIII/4, 1118-1127.
- Green, O. H., 1976. Experimental testing of „equilibrium” partial melting of peridotites under water-saturated, high-pressure conditions. *Canadian Mineralogist*, 14, 255-268.
- Haase, K.M., Devey, C.W., 1996. Geochemistry of lavas from the Ahu and Tupa Volcanic fields eastern hotspot, southeast Pacific: implications for intraplate magma genesis near spreading axis. *Earth and Planetary Science Letters*, 137, 129-143.
- Hauer, F., Stache, G., 1863. *Geologie Siebenbürgens*. Wien.
- Herz, N., Jones, D., Savu, H., Walker, R.L., 1974. Strontium isotope composition of ophiolitic and related rocks, Drocea Mountains, Romania. *Bulletin of Volcanology*, XXXVIII/4, 1110-1124.
- Hutchinson, C.S., 1982. Indonesia. In Thorpe R.S., Willey J., (Eds.), *Andesites*, 207-224, Chichester.
- Ianovici, V., Ghiţulescu, T.P., Borcoş, M., Lupu, M., Bleahu, M., Patrulius, D., Dimitrescu, R., Savu, H., 1976. Geology of the Apuseni Mountains (in Romanian). Editura Academiei Române, 631 p.
- Irvine, T.N., Baragar, W.R.A., 1971. A guide to the chemical classification of the common volcanic rocks. *Canadian Journal of Earth Sciences*, 8, 523-548.
- Istrate, G., 1978. Petrologic study of the Vlădeasa Massif (western part). *Anuarul Institutului de Geologie şi Geofizică*, LIII, 177-298, Bucharest.
- Kadić, O., 1906. Die geologischen Verhältnisse des Berglandes am linken Ufer der Maros, in der Umgebung von Czella, Bulza und Pozsoga. *Jahresbericht der kgl. Ung. Geologischen Anstalt für 1904*, 148-165. Budapest.
- Kepezhinskas, P.K., Defant, M.J., Drummond, M.S., 1995. Na metasomatism in the island-arc mantle by slab melt-peridotite interaction: evidence from mantle xenoliths in the North Kamchatka arc, *Journal of Petrology*, 36, 1505-1527.
- Lemaître, R.W., Bateman, P., Dudek, A., Keller, J., Lameyre, R., Le Bass, M. J., Sabine, P.A., Schmid, R., Sörensen, H., Strekeisen, A., Woolley, A.R., Zanettin, B., 1989. A classification of igneous rocks and a glossary of terms. Blackwell, 183 p.
- Minear, J.W., Toksöz, M.N., 1970. Thermal regime of a downgoing slab and new global tectonics. *Journal of Geophysical Research*, 75, 1397-1419.
- Mysen, R.O., 1979. Trace element partition between garnet peridotite minerals and water-rich vapor: experimental data from 5 to 30 kbar. *American Mineralogist*, 64, 274-287.
- Mysen, R.O., Boettcher, A.J., 1975. Melting of a hydrous mantle, II, Geochemistry of crystals and liquids formed by anatexis of mantle peridotite at high pressure and high temperature as a fraction of controlled activities of water, hydrogen and carbon dioxide. *Journal of Petrology*, 16, 459-593.
- Niţu, G., 2000. Origin of the mineral material and the age of the uranium deposits in Romania (in Romanian). *Studii şi cercetări de geologie*, 45, 27-50, Bucharest.
- Niţu, G., 2008. The transcurrent rift of the Apuseni Mountains and the position of the uraniferous knot of the Central Bihor Mountains. *Studii şi cercetări de geologie*. 51-53, 31-58, Bucharest.
- Papiu, V., 1954. Preliminary note on the Valea Mare-Căprioara-Bulza-Pojoga region. *Dări de Seamă ale Comitetului Geologic*, XXXVI, 169-178, Bucharest.
- Papiu, V., 1956. Geological investigations on the north-western slope of Poiana Ruscă massif. *Dări de Seamă ale Comitetului Geologic*, XL, 135-149, Bucharest.
- Pearce, J.A., 1980. Geochemical evidence for the genesis and eruptive setting of lavas from Tethyan ophiolites, In Panayiotou (Ed.) *Ophiolites, Proceedings of the International*

- Ophiolite Symposium, Nicosia, 1979, 261-273.
- Pearce, J.A., Gale, G.H., 1977. Identification of ore deposits environment from trace element geochemistry of associated igneous host rocks. In Jones M.J. (Ed.), *Volcanic Processes in Ore Genesis*, Institute of Mining and Metallurgy and Geological Society of London, Special Publication, 7, 14-24.
- Pearce, J.A., Norry, M.J., 1979. Petrologic implications of Ti, Zr, Y and Nb variations in volcanic rocks. *Contributions to Mineralogy and Petrology*, 69, 33-47.
- Peltz, S., Urcan T., 1972. The Neogene volcanism from the south-western part of the Metaliferi Mountains and associated metallogenesis (in Romanian). *Dări de Seamă ale Institutului Geologic*. LVIII/1, 52-77, Bucharest.
- Peltz, S., Peltz, M., Urcan, T., 1970. Contributions to the knowledge of the Neogene volcanism in the region Groşi-Bulza-Fintoag (in Romanian). *Dări de Seamă ale Institutului Geologic*, LV/1, 109-134, Bucharest.
- Pinkert, E., 1907. Beiträge zur Kenntnis der Eruptivgesteine der Berggruppe von Bulza. *Földrajzi Közlöny*, XXXVII (6-8), 273-300. Budapest.
- Rădulescu, D., Borcoş, M., 1968. Aperçu général sur le déroulement du volcanisme néogène en Roumanie, *Anuarul Comitetului Geologic*, XXXVI, 177-193, Bucharest.
- Rădulescu, D., Săndulescu, M., 1973. The plate tectonics concept and the geological structure of Carpathians. *Tectonophysics*, 16, 155-161.
- Ringwood, A.E., 1979. *Origin of the Earth and Moon*. Springer-Verlag. New York, Heidelberg, Berlin, 295 p.
- Roden, M.F., Murthy, V.R., 1985. Mantle metasomatism. *Annual Review of Earth and Planetary Sciences*, 13, 269-296.
- Roşu, E., Ştefan, A., Vieru, C., Robu, L., Stoian, M., Grabari, G., Udrescu, C., 1993. Petrology of the banatitic magmatites of the Bulza-Coşteiu area, Timiş District, *Romanian Journal of Mineralogy*, 76, Supplement 1, Abstracts, 41-42, Bucharest.
- Sajona, T.G., Maury, R.C., Pubellier, M., Leterrier, J., Bellon, H. Cotton, J., 2000. Magma source enrichment by slab-derived melts in young post-collision setting, Central Mindana (Phillipines). *Lithos*, 54, 173-206.
- Savu, H., 1962. On the Neogene eruptions in the northern part of the Poiana Ruscă massif (in Romanian). *Dări de Seamă ale Comitetului Geologic*, XLIII, 113-130, Bucharest.
- Savu, H., 1972. Metallogenesis associated to the ophiolitic magmatism in Drocea Mountains (in Romanian). *Dări de Seamă ale Institutului Geologic*, LVIII/2, 93-119, Bucharest.
- Savu, H., 1983. Geotectonic and magmatic evolution of the Mureş Zone (Apuseni Mountains), Romania. *Anuarul Institutului de Geologie şi Geofizică*, LXI, 253-262, Bucharest.
- Savu, H., 1984. The Mélange with pyroclastic matrix associated with the southern island arc of the Mureş zone (in Romanian). *Studii şi cercetări de geologie, geofizică, geografie*, (Geologie), 29, 36-43, Bucharest.
- Savu, H., 1993. Uranium mineral occurrences in the crystalline schist area of the Drocea Mountains. *Romanian Journal of Mineralogy*, 76/1, 43-46, Bucharest.
- Savu, H., 2001. Geochemical aspects and origin of the continental adakitic rocks from the South Apuseni Mountains and the Mureş Couloir, Romania. *Proceedings of the Romanian Academy, Series B*, 3/2, 151-157, Bucharest.
- Savu, H., 2002. The Paleogene continental adakites from the Mureş Couloir, Romania. *Proceedings of the Romanian Academy, Series B*, 1, 23-27, Bucharest.
- Savu, H., 2004. The Transylvanian mantle plume and the related hotspot volcanic rocks, Romania. *Proceedings of the Romanian Academy, Series B*, 2004, 1, 33-40, Bucharest.
- Savu, H., 2005a. Tectono-magmatic evolution of the Romanian territory and origin of its bent orogen structures. *Geo-Eco-Marina*, 9/10, 2003-2004, 116-131, Bucharest.
- Savu, H., 2005b. Post-Laramian collision dike-rocks from the Bihor Mountains, North Apuseni, Romania: Geochemistry and origin. *Analele Universităţii Bucureşti, Geologie*, XLIX, 15-27, Bucharest.
- Savu, H., 2011. The Căpâlnaş-Vorţa-Nevoiaş (Pb-Zn-Cu) metallogenetic district of the banatitic province, Romania (in press).
- Savu, H., Nicolae, I., 1975. Metallogenesis of the Vorţa region (Metaliferi Mts) (in Romanian). *Dări de Seamă ale Institutului de Geologie şi Geofizică*, LXI/2, 71-80, Bucharest.
- Savu, H., Udrescu, C., Neacşu, V., Stoian, M., 1992. Petrology, geochemistry and origin of the Laramian volcanics of the Mureş Couloir, between Zam and Gurasada. *Romanian Journal of Petrology*, 75, 117-130.

- Savu, H., Udrescu, C., Neacșu, V., 1994. Neocimmerian island arc volcanics and Laramian (banatitic) continental arc volcanics in the region Groși-Ilteu-Tisa (Mureș Corridor) (in Romanian). *Studii și cercetări de geologie*, 39, 7-19.
- Savu, H., Udrescu, C., Stoian, M., Neacșu, V., 1996. The Brănișca Hill calco-alkaline and the Măgura Sîrbi alkaline Paleogene volcanic rocks (Mureș Corridor). *Romanian Journal of Petrology*, 77, 83-96.
- Ștefan, A., 1980. Petrographic study of the eastern part of the Vlădeasa eruptive massif. *Anuarul Institutului de Geologie și Geofizică*, LV, 207-325.
- Ștefan, A., Roșu, E., Andăr, A., Robu, L., Bratosin, I., Grabari, G., Stoian, M., Vîjdea, E., 1992). Petrological and geochemical features of banatitic magmatites in Northern Apuseni Mountains. *Romanian Journal of Petrology*, 75, 97-115.
- Taylor, S.R., 1968. Geochemistry of andesites. In Ahrens L.H. (Ed) *Origin and Distribution of the Elements*, Oxford, 559-583.
- Tschegg, C., Ntaflos, T., Seghedi, I., Harangi, S., Kosler, J., Coltorti, M. 2010. Paleogene alkaline magmatism in the South Carpathians (Poiana Ruscă, Romania): Asthenospheric melts with geodynamic and lithospheric information. *Lithos*, 120, 393–406.