

Metallogensis and Distribution of Elements Around the Zones of Subduction

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Abstract

According to a new model of plate tectonics most magmatic rocks derive by the partial melting of the sedimentary cover of the subducted plates. The distribution of the minor elements and the magmatic ore formation are controlled by the correlated processes. Geochemical correlation between ore minerals and conjugated rocks indicates that the heavy metallic cations of the hydrothermal veins are supplied mostly by magmatic solutions, while their sulfidic and related quasianions (S, Se, Te, As, Sb, with some volatile cations e. g. Hg) derive mainly from the (meta) clays of continental origin. (Average S content in SO_3 : volcanics 0,03 %, geosynclinal clays and carbonate rocks 0,11 and 0,03 %, continental clays and carbonate rocks 0,43 and 2,36 %.) The investigation of the flow system in the ore veins indicates also that hydrothermal sulfide ore minerals are mostly precipitates of the anion forming elements of descendent-hemiascendent solutions by the heavy metallic ions of ascendent solutions. The pre- and postmetallogenic propylitization and other (clay, silica etc.) wall rock alteration products related to these ore veins are characterized, too, by the volatile elements of sedimentary origin. According to the lower content of sulfur in the oceanic and geosynclinal clays, the hydrothermal ores of the orogenic belts (Lahn-Dill type etc.) form mostly oxydic mineralizations. Both cations and anions of the pegmatitic-pneumatolytic ore formations are of magmatic origin. According to the low sulfur content of the magma they form mostly oxide or silicate and carbonate minerals. They crystallize by the cooling of the magmatic solutions, according to the much higher geothermal gradients during their formation than those of the hydrothermal ores.

The mobilized series of the elements differed considerably for the melts and aqueous solutions — as computed from the ratio of their average contents

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in the granites and the crust, e. g. from that in the clays and the crust — corroborate the above statements, too.

Many transitory types exist between these two extreme types of postmagmatic ore formation, e. g. the tin-boron-mineralization accompanied by sulfidic ores.

Examples of subduction zones were given from the Pannonian area, with special reference to the Carpathian Arch.

Zusammenfassung

„Metallogene und Verteilung von Elementen in Subduktionszonen“

In Übereinstimmung mit neuen Auffassungen über die Plattentektonik entstehen die meisten magmatischen Gesteine durch partielles Schmelzen der Sedimentbedeckung unterschobener Platten. Die Verteilung der Nebenelemente und die magmatische Erzbildung werden durch voneinander abhängige Prozesse gesteuert. Die geochemischen Wechselbeziehungen zwischen Erzmineralen und zugehörigen Gesteinen zeigen, daß die Kationen der Schwermetalle der hydrothermalen Gänge meist aus magmatischen Lösungen stammen, während deren sulfidische und verwandte Quasi-Anionen (S, Se, Te, As, Sb, auch einige flüchtige Kationen wie z. B. Hg) hauptsächlich kontinentaler Herkunft (Tone und Metatone) sind. (Der durchschnittliche S-Gehalt als SO_3 beträgt in Vulkaniten 0,03 %, in geosynklinalen Tönen und Karbonatgesteinen 0,11 und 0,03 % und in kontinentalen Tönen und Karbonatgesteinen 0,43 und 2,35 %.) Die Untersuchung der Fließverhältnisse in den Erzgängen zeigt überdies, daß hydrothermale sulfidische Erzminerale meist durch Schwermetall-Ionen aszendenter Lösungen aus dezenten bis hemi-aszendenten Lösungen, die die Elemente der Anionen enthalten, ausgefällt werden. Propylitisierung vor und nach der Vererzung sowie andere Nebengesteinsveränderungen (Vertonung, Silifizierung, etc.) in Zusammenhang mit der Vererzung werden durch flüchtige Elemente sedimentärer Herkunft charakterisiert. Entsprechend des niedrigen Schwefel-Gehaltes der ozeanischen und geosynklinalen Tone liegen die hydrothermalen Erze der Orogengürtel meist in oxydischer Form vor (Lahn-Dill-Typus u. a.). In den pegmatitisch-pneumatolytischen Erzformationen sind sowohl Kationen als auch Anionen von magmatischer Herkunft. Entsprechend dem niedrigen Schwefel-Gehalt des Magmas werden meist Oxyde oder Silikate und Karbonate gebildet. Infolge des wesentlich höheren geothermalen Gradienten gegenüber den hydrothermalen Erzen kristallisieren sie als Folge der Abkühlung der magmatischen Lösungen aus.

Die Mobilisationsreihen der Elemente unterscheiden sich für Schmelzen und wässrige Lösungen beträchtlich, wodurch die oben gemachten Feststellungen weiter untermauert werden.

Zwischen diesen beiden extremen Arten der postmagmatischen Erzbildung gibt es eine Reihe von Übergängen, wie z. B. die Zinn-Bor-Vererzung, die von sulfidischen Erzen begleitet wird.

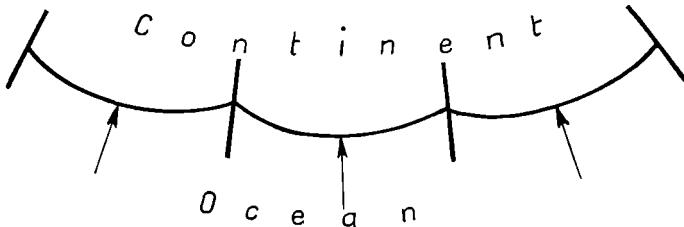
Beispiele von Subduktionszonen werden für das Pannonische Gebiet mit besonderem Hinweis auf den Karpatenbogen gegeben.

1. *Two main types of subduction. Upper Cretaceous-Tertiary plate tectonics of the Carpathian-Pannonian area.*

In the Circumpacific belt mostly broad oceanic plates are drifting either parallel or slightly divergently. Hence they are not hindered in their movements by each other.

The Mediterranean microcontinents generated by the (partly horizontal) confrontation of two continents are drifted often convergently together with the narrow oceanic stripes of relatively short lifetime between them. Thus, the microcontinental plates are mutually hindered in their movements and become dissected into small sections moving with different velocity. Minimum velocities occur at the edges of the main plate sections resulting in a garlande structure (fig. 1). The accreting margins of the small oceanic plates gradually merge by the subduction into the consuming type and the abyssal sediments mostly vanish.

Circumpacific type



Mediterranean type

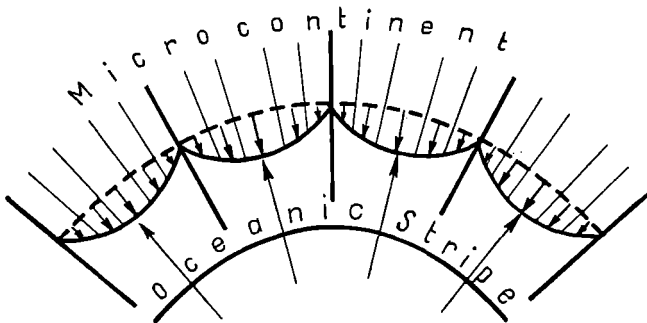


Fig. 1. The Circumpacific and the Mediterranean type of subduction.

Particularities of the mediterranean microcontinents was studied in the Carpathian-Pannonian area. First the sutures of the young Cretaceous and Tertiary subductions (*Author, 1973a*) were traced using more than twenty different methods (*Author 1973b*) and the following system of subductions was found for the Pannonian-Carpathian area (fig. 2 and 3).

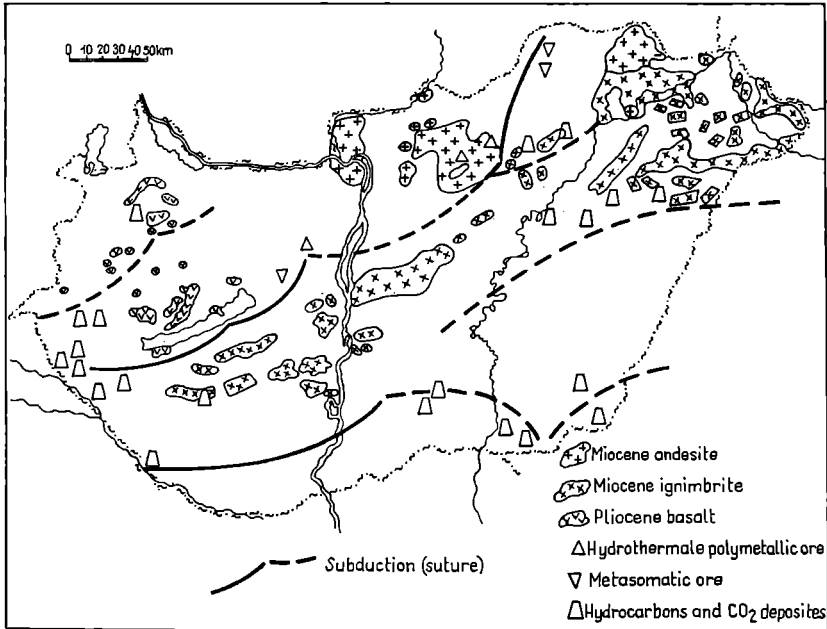


Fig. 2. The suture lines of subductions and their relation with igneous rocks, ores and hydrocarbons in the Pannonian Basin.

1. The Carpathian Klippenzone suture forms on the surface mainly a rock-mélange. It dips convergently towards the Pannonian Basin. The dip angle is mostly flat (about 50°), in the East it is steeper. The continuation of this subduction in the Alps is presumable (also according to *Dewey & Bird*).

2. The marginal subduction of the Hungarian Central Mountains appears on the surface as a mélange ("Darno line"); it is, however, partly covered by the Neogene of the Pannonian Basin. It dips mostly steeply (70—80°) towards the NW. Southwestwards it continues in the Judicaria-Insubria line. Northeastwards it is presumably perpendicularly deflected into the Szamos-Somes-line, described by *Stille*.

3. The subduction at the southern border of Mecsek Mts dipping \pm northwards proceeds eastwards under the Great Hungarian Plain and reaches the surface again in the Maros-Mures-belt of Transylvania forming there a Klippen-belt with mélange.

The presumed continuation of this system in the Alps, Dinarids and Balkans is delineated schematically in fig. 3, mostly according to the volcanic derivatives of the subduction.

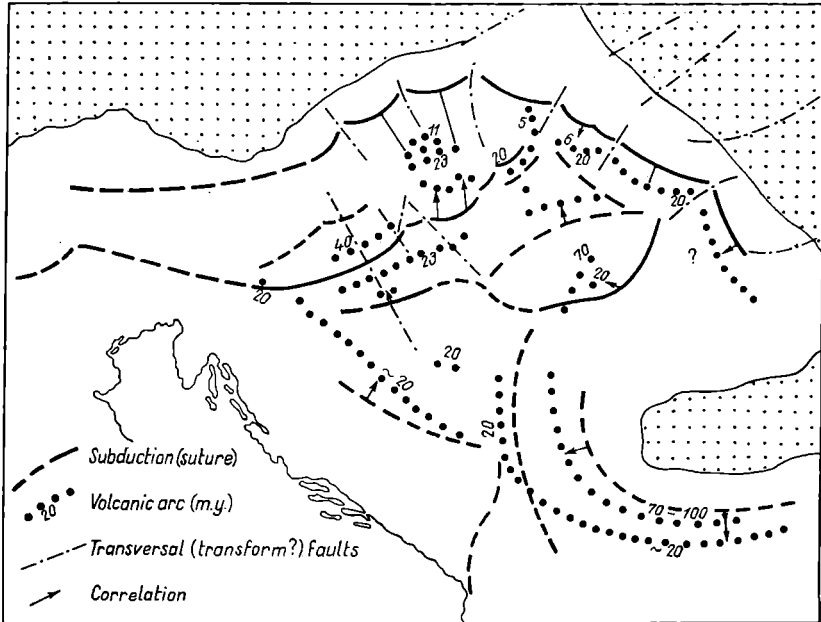


Fig. 3. The suture lines of subductions and the related volcanic arcs in the Alp-Carpathian-Balkan and Dinarid system.

Two further covered sutures occur presumably along the Rába-line under the Little Hungarian Plain and along the covered Upper Cretaceous-Paleogene flysch belt under the Great Hungarian Plain, the latter dipping according to geomagnetic data (fig. 6; Pozsgay, 1966) steeply (about 80°) towards NW and N.

The subducted sediments are transformed within the belt of subduction into metamorphites, granitoides, andesites, and basalts with an end-rest of ultrabasites (fig. 4). Thus subduction zones are accompanied by correlated descendent volcanic arcs, i. e. partial melts of the subducted chiefly sedimentary rocks being younger only by several million years than the beginning of the subduction.* Closer to the suture line the andesitic — or in case of a steeper subduction the ignimbritic belt —, and farther off the basaltic and alkaline volcanoes occur. In case of steep subductions the basalts are slightly alkaline (e. g. only basalts and basanites). The alkaline-basaltic volcanism appears mainly along structurally weakened lines according to the decreased eruptive energy of their magma.

* *Stille* has already supposed such a correlation between the sedimentary sequence and the volcanic arcs of the Carpathians as mentioned kindly by Professor Dr. W. E. *Petráscheck*.

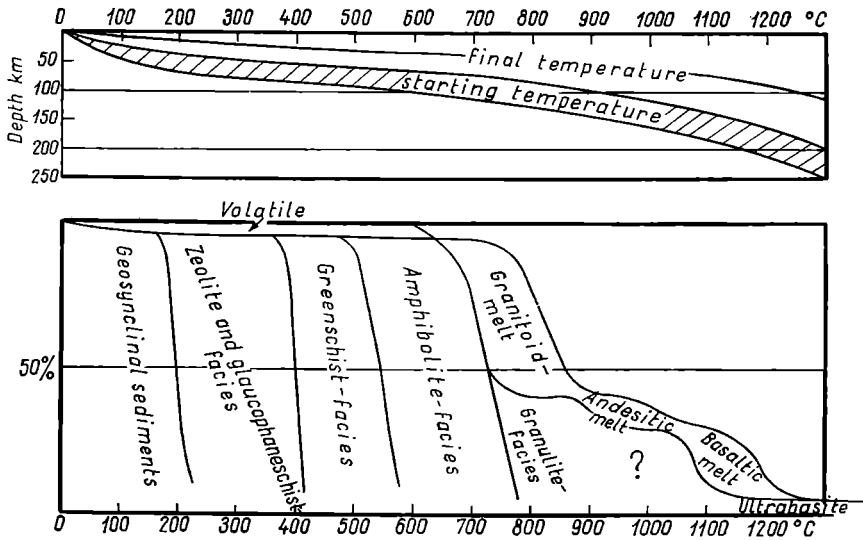


Fig. 4. Products of the subducted geosynclinal sediments as a function of temperature and depth.

In young volcanic areas, e. g. in the mainly Neogene subduction and volcanic system of the Carpathians-Pannonians the volcanic bodies are still mighty. In the high mountains of the Alps subducted earlier (mainly in the Cretaceous) most andesites are eroded. However, andesitic necks are known, e. g. in the Bacher Mts. and tonalite porphyries along the Judicaria (kind personal communication of Prof. Dr. E. *Clar* and Prof. Dr. *Exner*). In the deeper areas the younger basaltic derivatives of the Alp-subduction (E. g. Auvergne, W-Germany, Czechoslovakia, Silesia) are better conserved. Along the deep structural lines some volcanoes may occur also at the opposite side of the suture line (e. g. Euganeen).

The correlated volcanic belt of the Carpathian Klippen-belt subduction being garland-like dissected into seven sections (fig. 3) is represented by the Intra-Carpathian andesitic volcanic arc separated also into six or seven sections. Derivatives of subductions of steeper dip and faster rate form mixed ignimbrites (covered mostly by the Neogene of the Great Hungarian Plain).

On the basis of the K_2O/SiO_2 ratio of the volcanic rock (according to *Dickinson*, *Hatherton*, *Ninkovitch*, *Hays* and others) the depth of the primary "magma-chamber" was calculated* and proved to be 120 to 160 km for the andesitic ones,

* Even a method for the determination of the mass, thickness and breadth of the subducted sediments, including the differential velocities of the subduction from the mass and age relations of the andesites is elaborated (*Author*, 1773 b).

150 to 250 km for the ignimbritic ones and 150 to 260 km for basalts and basanites. Some comparative calculations for other areas resulted similar values. These depths of volcanic magma chambers correspond to those of the low velocity layer of the Gutenberg channel characterized by a portion of partial melt, according to the generally accepted views. These depths are presumably the most suitable for partial melting.

Ignimbrites characterized by greater and variegated depths of magma chamber and by steeper dip of subduction (fig. 2 and fig. 6) occur in the Pannonian Basin between two parallel and synchronous suture lines of subduction. In this case the drift and subduction of the posterior plate are furthered by the parallel movement of the first one above it. The sedimentary cover of the posterior plate is subducted faster, it remains colder and reaches greater depths without melting, then it produces violent ignimbritic eruptions characterized by high vapor contents.

In the front of the subduction mainly at the concave side of curved suture lines there is usually an elevation of imbricate ("wedge") structure (fig. 7), e.g. Central Mts. of Hungary, Slovakian Carpathians. Behind the suture line — especially on the convex side of the inflexion — depressions occur, e.g. Little and Great Hungarian Plain, (fig. 5).

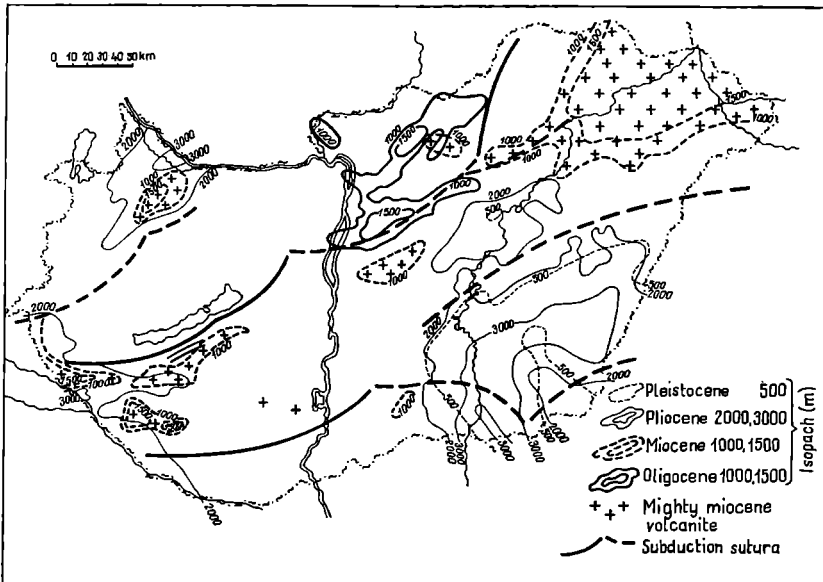


Fig. 5. Correlation between subduction and subsidence in the Pannonian Basin.

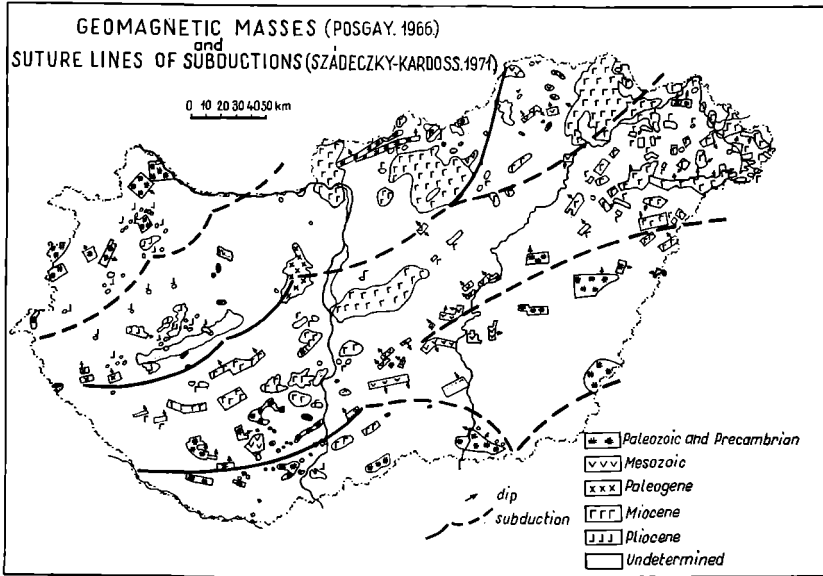


Fig. 6. Correlation between subductions and geomagnetic masses.

In the continental crust, the depression behind the subduction produces a partial transformation of the lower basaltic crust into eclogite facies representing seismically a sub-Moho "mantle" layer (fig. 8). The thin out of the crust of the Pannonian Basin and of other median masses may be partly due to this (*Stegena*), but relates to the higher position of the Gutenberg low velocity layer, too, according to the increased vapor pillow fed by more neighbouring subduction belts. The position of the basalt crust as partial melting product of the ultrabasic mantle and that of the low velocity layer containing also partial melt products are controlled primarily by temperature, thus their positions change as a rule similarly.

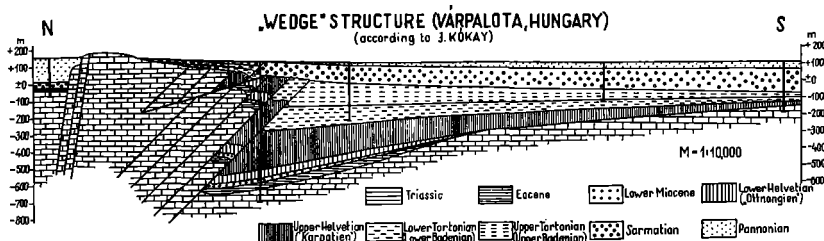


Fig. 7. Profile across the marginal subduction of the Hungarian Central Mts., Várpalota north of the Balaton lake, according to J. Kókay.

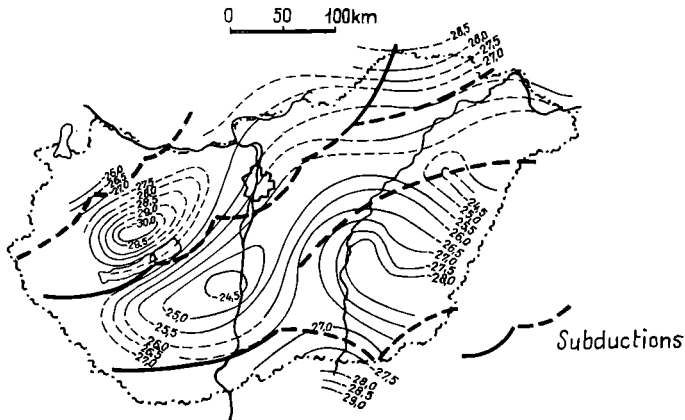


Fig. 8. Depth of the Moho-layer (km) and the positions of the suture lines of subduction in the Pannonian Basin.

2. Ore formations and distribution of trace elements

The oblique belt of subduction and the vertical channels of their volcanic derivatives represent the main transport ways of the ore forming solutions and melts. Thus, the appearance of mineral resources near the surface are mostly connected to these two main transport lines.

Along subduction zones ore forming volatiles are transported mainly as ascending and relatively low temperature aqueous solutions and gases. The main mineral resources correlated to the suture lines are therefore hydrocarbons and metasomatic hydrothermal Fe and Pb-Zn ores (fig. 2). In the vertical igneous channels the ore forming volatiles are connected to ascending magma and to mostly high temperature solutions forming e. g. Au-Ag-Pb-Zn-Cu ores and skarns connected to the subsequent andesites and late-kinematic granitoids. The ignimbritic volcanism is nearly ore-free, the ore-containing fluids escape in this case into the atmosphere.

Due to the reclosing of the narrow oceanic stripes between the microcontinents in median mass older, mostly "eugeosynclinal" ophiolites containing high temperature "liquid magmatic" ores (Cr, Ti-V, Cu, Ni, Co) also occur near and in the subduction planes.

In the frontal elevation belt of the subductions bauxite, sedimentary Mn and Fe ores and coal, in the subsided area behind the suture of the subduction and between two subduction sutures evaporites occur. Massif sulfide ores (Kuroko type etc.) connected to the eugeosynclines in the front side of the sutures (Guild, 1972) are restricted to this type.

Petrologic changes in the belt of subduction are accompanied by changes in the distribution of trace elements. During the *progressive metamorphism* of clayey sediments volatiles produced by the subduction gradually emigrate from these rocks, transporting certain parts of the less volatile elements, too. Since these solutions pass through the whole series of the transforming rocks, the quantities of the element departing upwards and being supplied from the depth are compensating each other, but the quantity of most of the elements suddenly decreases at the lowermost ultrabasic rest of the series (Table I). This approximate dynamic equilibrium of the non volatile elements is expressed by the "isochemical transformation" of metamorphites.

Table I
Distribution of minor elements in the main rocks

| | Maximum content | Minimum content |
|-----------------|---|--|
| Clay | Li, Cs; Al, La, U; Mo, W Hg; Ga, Ge, Sn, Pb; As, Sb; S, Se F, J; B; C | |
| Carbonate rocks | Ca, Sr, Ba; Br | Na, Al, Sc; Si, Zr, Th; V; Fe, Co; Cu, Ag; Cd; Ge, Sn |
| Sand | Si; Y; Zr | Sc, U, Nb; Ni; Zn, Cd; — Cl, P |
| Granite | Na, K, Rb, Cs; Be, Ba; Y; Si, Zr, Th; Ta, Nb; Ga, In, Tl; Pb, Bi; — Cl, F; Ni | Mg, Ca; Cr, Mn, Bi, Se, J |
| Basalt | Al, Sc; Ti; V; Mn Cu, Ag; Zn; — P | Pt; Se |
| Ultrabasite | Mg, Cr, Fe, Co, Ni, Au, Pt | Li, K, Rb, Cs; Be, Sr, Ba; Y, La; Ti, Ta; Mo, W Cd, Hg; Ga, In, Tl; Sn, Pb; As, Bi; S, Te; F, Br, J; B; C; N |

First the heavy sidero- and chalcophile rare elements bound incongruently in the rock-forming minerals are mobilized by the high pressure vapors formed during the metamorphism and partial meltings. During the crystallization of the melts they become camouflaged by the main elements of the new magmatites according to their ionic radii. In the course of the hydrothermal process they — being bound incongruently again — are partly released and concentrated forming independent ore deposits.

Consequently, mainly the trace elements in a given magmatite are relatively concentrated, the ionic radii of which are commensurable to those of the main elements of the magmatite. The same trace elements form also the main ore

deposits in the surroundings of the magmatic suite (fig. 9). According to this model the petrometallogenetic relations described by *Bilibin, Smirnov, Borchert, Abdulaev* and others originate in this way.

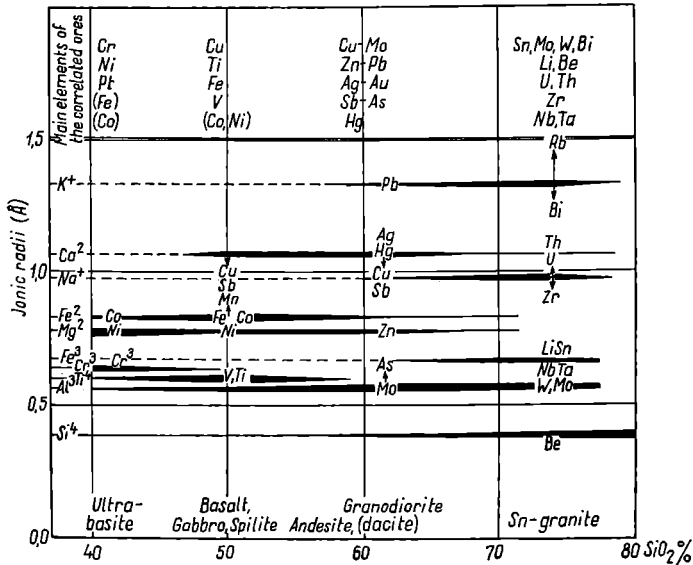


Fig. 9. Correlation between major and camouflaged main minor elements in the magmatic rocks.

The distribution of the trace elements depends mainly on their mobilities. In the belt of subduction and in the volcanic channels differences exist among the average lithospheric melt, solution and gas-mobilities. These mobilities can be determined for different elements by geochemical-statistics. The melt mobility of an element (M_m) can be expressed by the ratio of its average concentration in the final granitic (C_g) melt and in the "molten" crust (C_m). Since $M_m = C_g / C_m$, and the sequence of melt mobility is essentially identical with that of "granitophily". The calculation summarized in Table II and fig. 10 shows that the granitophile elements, i. e. highly mobile in magmatic melts, are first of all the lithophile ones in the broader (*Goldschmidt*) sense, further three chalcophile elements of changing valency (Sn, Pb, Bi) as well as the Cl and F. *De Wijs* (1960) qualified the same elements as granitophile, only Ca, Ti and V was qualified to granitophile instead of granitophob. The term granitophob means actually the terms basaltophile- and ultrabasaltophile together.

Table II

| Element | Concentration (p.p.m.) in the | | | Melt mobility (= 1. : 3.) | Solution mobility (= 2. : 3.) | Complex mobility (= 4. + 5.) $\left(\frac{2}{6.}\right)$ |
|------------------|-------------------------------|---------|-----------------|---------------------------------|-------------------------------------|---|
| | granites | clays | "molten crust" | | | |
| | 1. | 2. | 3. | 4. | 5. | 6. |
| Ag | 0,05 | 0,1 | 0,07 | 0,71 | 1,43 | 1,07 |
| Al | 77,000 | 104,500 | 80,533 | 0,95 | 1,29 | 1,12 |
| As | 1,5 | 6,6 | 1,67 | 0,89 | 3,95 | 2,42 |
| Au | 0,0045 | 0,001 | 0,004 | 0,65 | 0,68 | 0,66 |
| B | 15 | 100 | 11,67 | 1,29 | 8,57 | 4,93 |
| Ba | 830 | 800 | 653,33 | 1,27 | 1,23 | 1,25 |
| Be | 5,5 | 3 | 3,8 | 1,45 | 0,79 | 1,12 |
| Bi | 0,01 | 0,01 | 0,009 | 1,11 | 1,10 | 1,10 |
| Br | 1,7 | 6 | 2,13 | 0,80 | 2,82 | 1,81 |
| C | 0,03 | 2,28 | 0,023 (0,70) | 1,30 (0,04) | 99 (3,25) | 50,15 (2,27) |
| Ca | 15,800 | 25,300 | 32,933 | 0,47 | 0,77 | 0,62 |
| Cd | 0,1 | 0,3 | 0,13 | 0,77 | 2,31 | 1,54 |
| Ce | 100 | 50 | 68,17 | 1,46 | 0,73 | 1,09 |
| Cl | 240 | 160 | 176,67 | 1,36 | 0,91 | 1,13 |
| Co | 5 | 20 | 18,33 | 0,27 | 1,09 | 0,68 |
| Cr | 25 | 100 | 83,33 | 0,30 | 1,20 | 0,75 |
| Cs | 5 | 12 | 3,67 | 1,25 | 3,27 | 2,26 |
| Cu | 20 | 57 | 47 | 0,43 | 1,21 | 0,82 |
| F | 800 | 500 | 656,67 | 1,22 | 0,76 | 0,99 |
| Fe | 27,000 | 33,300 | 46,533 | 0,58 | 0,72 | 0,65 |
| Ga | 20 | 30 | 19,33 | 1,03 | 1,55 | 0,79 |
| Ge | 1,4 | 2 | 1,43 | 0,97 | 1,39 | 1,18 |
| Hg | 0,08 | 0,4 | 0,083 | 0,96 | 4,82 | 2,89 |
| H ₂ O | 0,61 | 4,76 | 0,59 | 1,03 | 4,60 | 2,81 |
| In | 0,26 | 0,05 | 0,25 | 1,04 | 0,20 | 0,62 |
| J | 0,4 | 1 | 0,4 | 1,0 | 2,5 | 1,72 |
| K | 33,400 | 22,800 | 25,033 | 1,33 | 0,91 | 1,12 |
| La | 60 | 40 | 49 | 1,22 | 0,82 | 1,02 |
| Li | 40 | 60 | 31,67 | 1,25 | 1,89 | 1,57 |
| Mg | 5,600 | 13,400 | 18,733 | 0,29 | 0,72 | 0,50 |
| Mn | 600 | 670 | 1,066 | 0,56 | 0,62 | 0,59 |
| Mo | 1 | 2 | 1,13 | 0,88 | 1,77 | 1,32 |
| N | 20 | 600 | 19,3 | 1,04 | 31,1 | 16,07 |
| Na | 27,700 | 6,600 | 24,933 | 1,11 | 0,26 | 0,68 |
| Nb | 20 | 20 | 20 | 1,0 | 1,0 | 1,0 |
| Ni | 8 | 95 | 58,66 | 0,13 | 1,62 | 0,87 |
| P | 700 | 770 | 933,33 | 0,75 | 0,83 | 0,79 |
| Pb | 20 | 20 | 16 | 1,25 | 1,25 | 1,25 |
| Pd | 0,01 | 0,013 | 0,76 | — | — | — |
| Rb | 200 | 200 | 148,33 | 1,35 | 1,35 | 1,35 |
| S | 400 | 3,000 | 366,67 | 1,08 | 8,19 | 4,63 |
| Sb | 0,2 | 1,5 | 0,2 | 1,0 | 7,5 | 2,21 |
| Sc | 3 | 10 | 10 | 0,30 | 1,00 | 0,65 |

| Element | Concentration (p.p.m.) in the | | | Melt mobility (= 1. : 3.) | Solution mobility (= 2. : 3.) | Complex mobility (= 4. + 5.) $\frac{2}{6.}$ |
|---------|-------------------------------|---------|----------------|---------------------------------|-------------------------------------|--|
| | granites | clays | "molten crust" | | | |
| | 1. | 2. | 3. | 4. | 5. | 6. |
| Se | 0,05 | 0,6 | 0,05 | 1,00 | 1,20 | 6,5 |
| Si | 323,000 | 238,000 | 295,333 | 1,09 | 0,80 | 0,94 |
| Sn | 3 | 10 | 2,5 | 1,20 | 4,00 | 2,60 |
| | | (6) | | | | |
| Sr | 300 | 450 | 346,67 | 0,86 | 1,29 | 1,07 |
| Ta | 3,5 | 3,5 | 2,49 | 1,40 | 1,41 | 1,40 |
| Th | 18 | 11 | 13,00 | 1,38 | 0,85 | 1,12 |
| Ti | 2,300 | 4,500 | 4,533 | 0,50 | 0,99 | 0,74 |
| Tl | 1,5 | 1 | 1,07 | 1,40 | 0,96 | 1,18 |
| U | 3,5 | 3,2 | 2,50 | 1,40 | 1,28 | 1,34 |
| V | 40 | 130 | 93 | 0,43 | 1,39 | 0,91 |
| W | 1,5 | 2 | 1,33 | 1,12 | 1,50 | 1,31 |
| Zn | 60 | 80 | 83,33 | 0,72 | 0,96 | 0,84 |
| Zr | 200 | 200 | 166,67 | 1,19 | 1,20 | 1,19 |
| Y | 34 | 30 | 29,33 | 1,16 | 1,02 | 1,09 |

Since diluted solutions of the crust together with the elements dissolved in them originate mainly from the dehydration of the clays and metaclays, the solution mobility (M_s) is determined by the weight-per cent ratio of the average concentration of the element in the clays (C_c) and in the "molten" crust. Hence, $M_s = C_c / C_m$ and the sequence of solution mobilities is essentially that of "argillophily". First of all anion forming sedimentophile and chalcophile elements are argillophile, e. g. N, B, C, halogens, the sulphur- and arsenic group and alkali elements. Thus, the separation of the volatiles from the non-volatiles takes place mostly in the solution phase. The extension of the term "volatile" over the melts is a rather arbitrary extrapolation.

To perform this calculations the data of *Vinogradov* (1962), and of *Turekian* and *Wedepohl* (1960) were used. According to *Vinogradov* the "molten" crust can be approximated by the mixture of two parts of granite and one part of basalt. The composition of the real complex crust determined by *Ronov* and *Yaroshevski* shows somewhat greater contents of (ultra)basic elements, e. g. Fe, Mg, Mn, Ti and Ca (Table III) as the real complex crust contains ultrabasic erosion products, too, and the subduction of the calcium-rocks, limestone and other sedimentary carbonates forming great rigid masses is often hindered (*Author*, 1971).

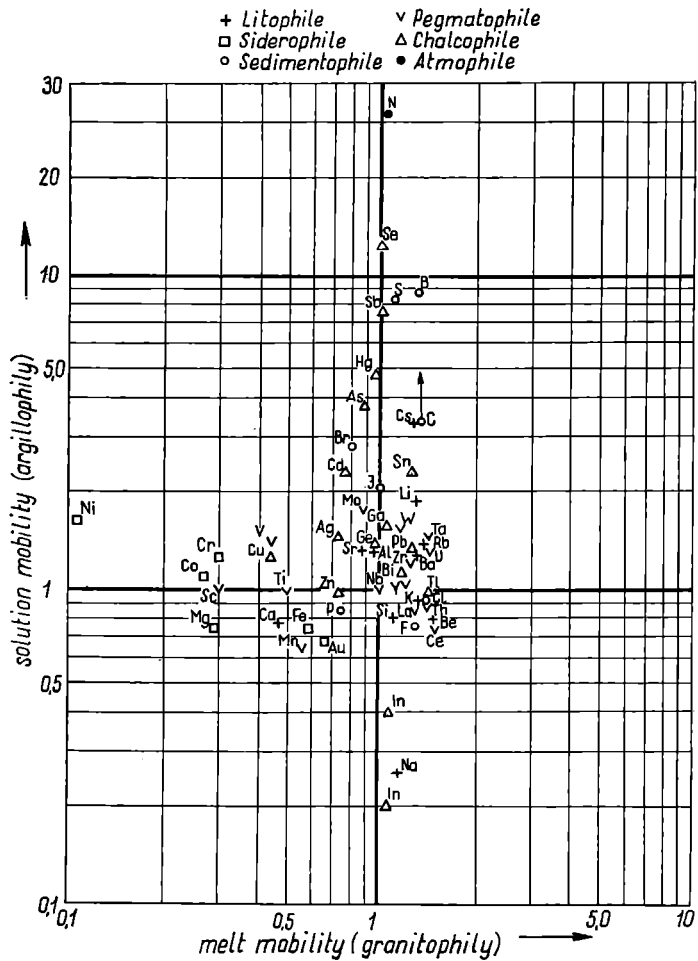


Fig. 10. Geochemical characters of the elements in function of their melt mobilities and solution mobilities.

Table III
Composition of the complex and molten crust

| Oxides | Complex crust % (Ronov-Yaroshevski) | | Cations | | Primary molten crust | Difference between molten and complex crust % |
|--------------------------------|--|-------|---------|-------------|----------------------|---|
| | Oxygen | | | | % | |
| SiO ₂ | 57,64 | 30,74 | Si | 26,90 | 29,53 | +2,63 |
| TiO ₂ | 0,88 | 0,35 | Ti | 0,53 | 0,45 | -0,08 |
| Al ₂ O ₃ | 15,45 | 7,25 | Al | 8,20 | 8,05 | -0,15 |
| Fe ₂ O ₃ | 2,43 | 1,69 | Fe | 5,04 { 1,69 | 4,65 | -0,39 |
| FeO | 4,30 | | | | | |
| MnO | 0,15 | 0,03 | Mn | 0,12 | 0,10 | -0,02 |
| MgO | 3,87 | 1,53 | Mg | 2,34 | 1,87 | -0,47 |
| CaO | 7,01 | 2,01 | Ca | 5,00 | 3,29 | -1,71 |
| Na ₂ O | 2,87 | 0,74 | Na | 2,13 | 2,49 | +0,36 |
| K ₂ O | 2,32 | 0,39 | K | 1,93 | 2,50 | +0,57 |
| P ₂ O ₅ | 0,23 | 0,13 | P | 0,10 | 0,09 | +0,01 |
| C _{org} | 0,13 | 0,94 | C | 0,48 { 0,13 | 0,02 | -0,46 |
| CO ₂ | 1,29 | | | | | |
| S | 0,04 | — | S | 0,04 | 0,04 | ±0,0 |
| Cl | 0,05 | — | Cl | 0,05 | 0,02 | -0,03 |
| H ₂ O | 1,33 | 1,19 | H | 0,14 | 0,00006 | -0,13994 |
| Σ | 99,99 | 46,99 | | 53,00 | 53,10006 | |

In the crust lithospheric melt and solution mobilities control mainly the distribution of the elements. Their mutual relation is shown by fig. 10 demonstrating the distribution of the elements according to the plate-tectonics, too. The field of minimum melt and solution mobility contains the main and the ore elements of the (ultra)basic rocks, i. e. Fe, Mg, Ca, Cr, Ti, Ni, Co, V, Cu. These elements appear next to the plate margins, especially in the depth of the consuming belts along the trenches and of the accreting margins. The elements of the granitoides and of the subsequent andesites — Si, Al, Be, Li, La, Ce, U, Th, Nb, Ta; Sn, Mo, W, Cl, F, Zn, Pb, Ag — characterized by high and medium melt but changing solution mobilities (medium and right side of the diagram) are enriched along the vertically ascending igneous channels derived from the depth of the subduction belt. Elements of high solution mobilities — N, B, C, S, Se, As, Sb, Bi, Hg, Cs, Na, Br, J — appear on the surface in the sedimentary rocks, especially in clays.

The main elements of pegmatitic-pneumatolitic mineralization are of greatest melt mobility, thus they are mostly ascendent and magmatic (fig. 11). According to the values of the melt and solution mobilities hydrothermal ores are controlled by combined magmatic (melt) and solution processes. The telescoping succession of *Emmons-Berg-Schneiderhöhn* for hydrothermal ores in veins corresponds essentially to a complex mobility sequence computed as mean values of the lito-

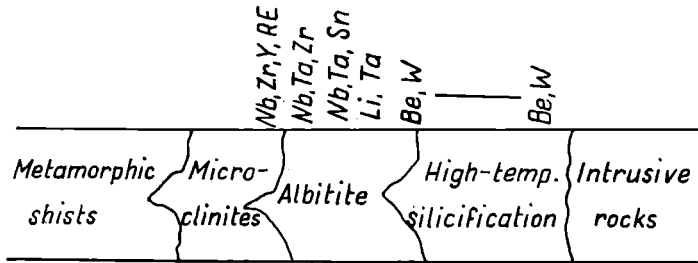


Fig. 11. Generalized sequence of metasomatic rocks and ores in the apical parts of granitoid bodies, according to data of A. A. Bews, 1970.

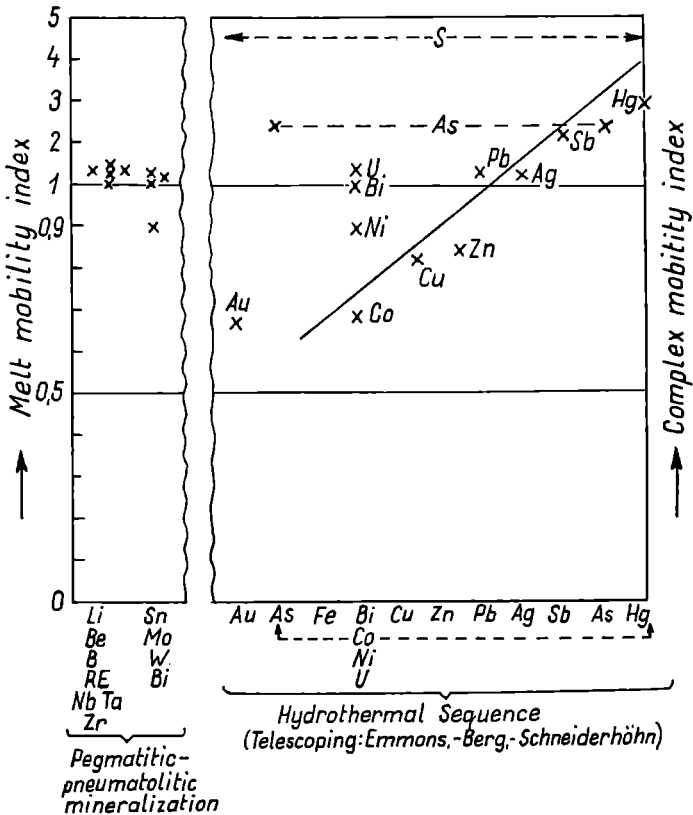


Fig. 12. Sequence of the postmagmatic ore formations in function of the complex mobilities.

spheric melt and solution mobilities (fig. 12). According to their different valencies the anion and cation forming elements, sulphur and arsenic, occur several times in these sequences, at lower places of the mobility than expressed by their total complex mobility indices. The schematic sequence of the horizontal metallogenic zonation supposed e. g. by *Gabelman* and *Krusiewski* (1972) is similar to the telescoping sequence. Therefore, such zonations can be characterized by the complex mobility indices progressing from the melt to the solution mobilities, too.

In the course of metamorphism the distribution of the elements, determined in a first approximation on the basis of several characteristic metamorphic and metasomatic parageneses by *Korshinski* for three temperature ranges, seems to be controlled by the transition of the melt and solution mobilities, i. e. approximately by the complex mobility sequence, as well as the distribution of elements observed e. g. by *Shaw* in the case of the progressive metamorphism of New Hampshire. The quantities of elements of small mobilities (Ni, Cu) decrease, those of high complex and solution mobilities (Li, Sr, Pb) increase towards the depth.

These lithospheric solution mobilities control solutions of the volcanic channels and subduction belts. At the Earth's surface more varying conditions prevail and solution mobilities are more changing. E. g. the mobility of Ca or Na considerably increases in presence of CO₂ (HCO₃) resp. of Cl.

3. Geochemistry of the pegmatite-pneumatolytic and the hydrothermal ores and related rocks

The conspicuously different chemical peculiarities of the pegmatitic-pneumatolytic and hydrothermal ores and related rocks do not follow neither from their plutonic (pegmatites and pneumatolytes) or plutonic and volcanic (hydrothermalites) relations, nor from their similar depth of crystallization mostly in the uppermost level of six km of the Earth's crust, (*Author* 1957, numerous papers of the St. Andrews ore-symposium 1970), nor from the supposed crystallization temperature differences, since these temperatures overlap mostly one another according to many measurements by the derepitation method. The differences between pegmatitic-pneumatolytic and hydrothermal mineralization seem rather to be the consequence of their different rate of cooling, i. e. geothermal gradient (fig. 13).

The pegmatitic-pneumatolytic formation with tin-molybdenum-tungsten ores appears mainly around highly ascending granitic cupolas where the value of geothermal gradient is about 40° C / 100 m to 130° C / 100 m. Thus, the crystallization of the pegmatitic and pneumatolytic ores may be due to the rapid drop of temperature.

In the contrary, the temperature gradient of the hydrothermal ore formation mostly does not exceed the value of 40° C / 100 m. This is, however, obviously

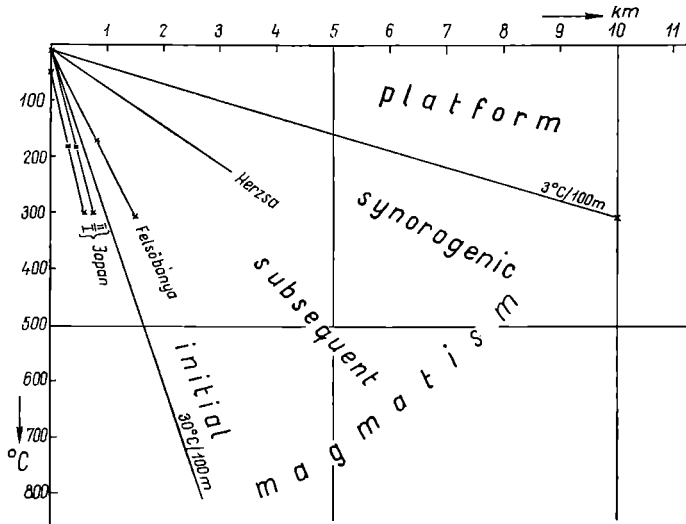


Fig. 13. Changes of the geothermal gradients in the crust of the earth.

insufficient to produce crystallization from the dilute hydrothermal solutions even in the case when the solubility of the metallic ions is increased by the presence of alkali-halogenides. As indicated by the calculated different solubility values hydrothermal ores represent rather chemical precipitates of the ascending solutions relatively rich in metallic heavy cations and of the descending or quasi-lateral-secretional solution relatively rich in anions of the sulphur and arsenic group. In this way hydrothermal ore minerals may form an even almost closed vein system surrounded by clays (metaclays) when they become compacted and dehydrated by hot solutions ascending from the environment of a magma body.

The rhythmic alternation of the hydrothermal vein minerals supports this model. In the course of uniform dilatation of the vein fissure the barren minerals (quartz, carbonates etc.) crystallize relatively rapidly tightening more and more the fissure. When the fracture is almost closed, the ore minerals are precipitated by the interaction of the slower infiltrating quasi-descendent sulphidic and the ascendent heavy-metallic solutions. The further uniform dilatation opens the fissure again and the crystallization of the subsequent rhythm follows.

Hence, most hydrothermal ores are supposed to represent diplogenic products of the quasi-descendent argilogenic anions and of the ascendent magmatogenic heavy-cations.

On the contrary, both the heavy cation and the (oxydic) anion of the pegmatites and pneumatolytes are of igneous origin, i. e. they represent mostly monogenetic formations.

According to this model the main condition of the hydrothermal ore formation is a possibility of exchange between the igneous mass and the level of clays or

metaclays — either directly or by fracture lines. Geological evidences of this original situation, however, often vanish, the clayey roof may be metamorphosed or eroded and only the partly descendent ore vein of the underlying crystalline basement remains. A subsequent recrystallization of the ore may even contraindicate the original situation.

However, there exist other indirect evidences of this new model. According to this model the composition of the country rock may determinate decisively the type of ore. Especially the effect of the changing sulphur content is remarkable. Pegmatitic-pneumatolytic ores are mainly oxidic, according to the anion deriving from the magma poor in sulphur. They occur mostly at the top of highly differentiated, strongly ascendent igneous masses crystallizing in areas of older igneous or strongly metamorphized and carbonated rocks. — The average sulphur content (counted as SO_3) of the continental clays and carbonate rocks is 0,43 resp. 2,36 per cent (Table IV) according to *Ronov* and *Yarosewski*. On the contrary, it is 0,02 to 0,03 per cent in the oceanic sediments and volcanic rocks. Accordingly, the hydrothermal ores of the continental areas are mostly sulphidic, while those of the eugeosynclines at the oceanic margins are rather oxidic (Lahn-Dill type) and only partly sulfidic (e. g. massif sulphide deposits, Kuroko type).

Table IV
Sulphur content of rocks (according to *Ronov* and *Yarosewski* 1969)

| | Continental | Geosyncline SO ₃ - content | Oceanic |
|-----------------|-------------|--|---------|
| Sands | 0,29 | 0,12 | — |
| Clays | 0,43 | 0,11 | — |
| Carbonate rocks | 2,36 | 0,03 | — |
| Volcanites | 0,03 | 0,03 | — |
| Total S | 0,04 | — | 0,02 |

Greisens and albite or microcline belts in connection with pegmatitic-pneumatolytic mineralization (fig. 11) are essentially of pure igneous origin, too. — On the contrary, propylitization preceding and following the hydrothermal ore formation, represents $H_2O - H_2S - CO_2$ metasomatism due to the volatiles deriving from sedimentary rocks. The propylitic chlorite-sericite-carbonate alteration may be accompanied by further metasomatic mineral assemblages, mostly in the following sequence from below upwards: (propylite), kaolinite-sericite-quartz, pyrophyllite-dickite-quartz, diaspore-quartz, pure quartz. This sequence of metasomatic alteration may be several hundred metres thick (*Drovenik, Radonova and Velinov, Skripchenko, Naboko, Romanova & Petrachenko, Takeushi & Abe*). In the Sredno-Gora series of Bulgaria and Yugoslavia this sequence is e. g. about 700 metres thick. The silica zone occurring often in the upper- and lowermost level derives from the surplus of silica released by clay mineralization and chloritization of the primary igneous feldspars and pyroxenes or amphiboles.

These metasomatic series were formed mostly by the sulphuric acid derived from the oxydation of the sedimentary pyritic deposits accompanying them. In other cases sulphuric acid originates from ascendent endogenic H₂S being often an additive factor to the predominant sedimentary process, too.

The endogenic ascendent factor becomes predominant in the areas of intense late-volcanic activity, e. g. in the NE of the Carpathian Basins, where sedimentary rocks are accumulated in the depth by subductions from several directions. In this case a strong potash-metasomatism develops in connection with the hydrothermal ore formation due to the late-igneous alkali-rich solutions. The potash-metasomatics, which can be followed downward farthest in the surface spreads with a mushroom-shape according to the near-surface mobility of these solutions. Potash-metasomatism may form a metamorphic depth-sequence of several mineral assemblages of the zeolite and greenschist facies: chlorite-carbonate-adularia-zeolite assemblage in the uppermost, epidote-chlorite-albite assemblage in the middle and actinolite-epidote-albite assemblage in the lowermost level (Széky-Fux 1965, Vasilevski 1970).

In accordance with the alkaline reaction of the potash solutions the potash-metasomatites show a high oxydation degree with a considerably increasing ratio of Fe₂O₃/FeO. The rich gold-silver ores — exhausted in the Charpathian area mostly during the preceding centuries — appear mainly in these oxydized rocks, separatedly from the wide lower level of the normal polymetallic ore formations.

The formation of potash-metasomatites is analogous to the pegmatitic-pneumatolytic microlinization. Sometimes the sodium-metasomatites, e. g. sodium-rhyolite, corresponding to the pegmatitic-pneumatolytic albitization also occur in connection with the hydrothermal ore formation.

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