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ACID VOLCANISM AND MINERALIZATION IN THE CADOMIAN AND VARISCAN STAGES OF THE BOHEMIAN MASSIF HISTORY

(Figs. 8)

Abstract: Chemistry of the volcanics both in the Cadomian and Variscan orogens of the Bohemian Massif exhibits two trends, the earlier is of tholeiitic and the later of alkalic character. The alkalic character developed by the penetration of magmatic melts into the environment of higher O_2 and water partial pressure. Magma enriched in water and alkalies passed into a hydrothermal phase with Cu, Pb, Zn mineralizations.

Chemistry of acid volcanics — keratophyres derived from the tholeiites of initial magmatism — differs from that of acid calc-alkalic volcanics of the subsequent phase in the ratios of Th/U and of alkalies. The higher U and Th values in subsequent volcanics suggest that these can be derived from the granite layer of the earth's crust, whereas keratophyre volcanics with lower U and Th contents are rather of deeper derivation. Relative to the Proterozoic, the Variscan volcanic cycle is richer in potassium and in alkalies altogether, particularly in the mineralized areas. Stratiform mineralization is generally associated with keratophyres having a higher alkali content, chiefly K_2O.

An important factor in metallogeny was water, which was brought into circulation through the volcanic apparatus, or both volcanism and water circulation resulted from the same tectonically induced cause, which called forth a rise in thermal flow. This interpretation is supported by the coincidence of anomalies in the content of water bound in minerals at places tectonically affected and followed by ore-bearing acid volcanites.

Резюме: Химизм вулканитов Чешского массива проявляется в кадомском и также в варийском орогене в двух химических тенденциях из которых у старшего толеитический характер и у моложего — щелочной.

Щелочная тенденция возникала при проникании магматических выплавок в наводненную среду. Магма обогащена водой и щелочами переходила до гидротермальной фазы с минерализациями Cu, Pb, Zn.

Химизм кислых вулканитов-кератофиров, которые происходят из толеитов первичного магматизма отличается от кислых вулканитов субсеквентной фазы отношением Th/U и щелочей. Качество и T в субсеквентных вулканитах указывает, что эти вулканиты можно вывести из гранитового слоя земской коры, но кератофировые вулканиты скорее из глубших областей. Напротив протерозоика — варийский вулканический цикл главным образом в областях местонахождений богаче калием и все таки щелочами. Стратиформное оруденение как правило связанное с кератофирами имеющими высшее содержание щелочей или обогащенными щелочами, главным образом K_2O.

Значительную роль при металлогенезисе имела вода, которая была приведена в циркуляцию вулканическим апатитом, потому что вулканизм и циркуляция воды являются последствием одинаковой причины вызванной тектоникой и обусловливающей возрастающее тепловое течение. Это подтверждает совпадание аномалий в содержании воды в связном состоянии в минералах в местах под влиянием тектоники и сопутствующих рудоносным кислым вулканитам.

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Introduction

In solving the genesis of stratiform Cu-Pb-Zn ores in the Bohemian Massif much thought has been given to the relationship between mineralization and acid volcanics. A direct association of mineralization with acid members of the keratophyre suite, particularly with quartz keratophyre is presumed for economically important stratiform deposits in the Devonian formations, such as the Zlaté Hory (Cu-Pb-Zn), Horní Benešov (Pb-Zn) and Horní Město (Pb-Zn) deposits, (F o j t, 1962; H a v e l k a — P a l a s — S c h a r m, 1964; P o u b a, 1971; P e r t o l d — P o u b a, 1976 etc.). This assumption is in agreement with the spatial connections of the mineralization maxima with the occurrence of major volcanic bodies of acid to superacid nature in the Vrbno Zone and the Šternberk—Horní Benešov Zone.

These relationships are less defined in minor Cu-Pb-Zn and Pb-Zn ore deposits of the stratiform type in the Orlické hory Mts. (O p l e t a l et al., 1968) and in the Krkonoše Mts. (P e r t o l d — K o p e c k ý, 1979; P e r t o l d — P o u b a, 1981 etc.), which are dated as Proterozoic. The spatial connection of ores with keratophyre occurrence are relatively closer in the Orlické hory Mts., being ill-defined in the Krkonoše Mts.

In the Krušné hory mountain system the only important stratiform Cu deposit occurs at Tisová near Kraslice. It is of Early Palaeozoic age and there are no rocks in its neighbourhood that might belong to acid volcanics except for siliceous rocks, some of which might represent the tuffs (Š k v o r, 1959; P o u b a — R e n é, 1975).

Recently, attention has also been devoted to stratiform deposits in the Proterozoic of central Bohemia, particularly in the Jílové Zone (M o r á v e k, 1970) and in the Lukavice Formation, Vítanov Formation and others in the Železné hory unit (V a c h t l, 1972; H o l u b, 1978). In these cases the mineralization is also associated with the volcanics of the keratophyre or porphyry type.

On the other hand, there are complexes of acid volcanic rocks in the Bohemian Massif, especially Cambrian and Permo-Carboniferous porphyries which lack whatever economic mineralization. These rocks involve Cambrian porphyry complexes of the Křivoklát—Rokycany Zone (W a l d h a u s e r o v á, 1971), Permo-Carboniferous porphyries of the Vraní hory Hills in NE Bohemia (their petrology is described by Fediuk and Schovánek in T á s l e r et al., 1979), and porphyries from Teplice and Žernoseky areas and other less known localities in N Bohemia. All manifestations of mineralization are absent from these rocks or, as is the case of the Teplice porphyry, are obviously associated with young Tertiary volcanism in their proximity.

The questions dealt with in this paper concern the differences in metallogenic manifestations of acid volcanics, and the differences caused by geological age and position of volcanics in metallogenic and tectogenic cycles, as well as the chemical trends of volcanics and the primordial sources of metals. It has not yet been cleared up safely whether the source of mineralization was intramagmatic or, as granitoids show more and more frequently whether the ores concentrated from solutions of non-magmatic source, by the effect of heat-conditioned circulation of waters.

Influence of geological factors

The stratiform mineralization in the Bohemian Massif is associated with volcanic phenomena displayed pricipally by the last members of initial volcanism, as is observable in the Cadomian tectonomagmatic cycle and the Variscan cycle as well. The older Proterozoic volcanic formations, studied in detail by Fiala (1977, 1978 etc.) show that the more acid members, particularly keratophyres and porphyries concentrated into the younger members of volcanic complexes. The earlier members predominating in tholeiites are only responsible for pyrite mineralization (e.g. in the areas of Litý, Dražeň, Kamenec in the Plzeň basin). According to Waldhauserová (1960) and Morávek (1978) the keratophyre rocks of the Jílové Zone bearing polymetallic mineralization are rather younger members of the volcanic complex. Analogous conditions exist evidently also in the Železné hory Hills; the stratiform polymetallic ores are there associated with acid volcanics, which appear to be younger than the Proterozoic complex of tholeiitic basalts. After the Proterozoic volcanic activity had terminated by the emplacement of late acid rocks, the period of flysch sedimentation set in, virtually without any volcanic manifestation. Only in the post-orogenic phase did appear continental volcanics in the Early Cambrian. These members of the subsequent volcanic apparatus are of porphyry chemical composition (volcanics of the Křivoklát—Rokycany Zone, studied petrographically by Waldhauserová, 1971).

A very similar situation was repeated in the Bohemian Variscides, where the major volcanic activity associated with a complete development of a geosyncline is concentrated in the NE part of the Bohemian Massif, in the Jeseníky Mts. The earlier members of initial volcanism are tholeiites with sporadic sulphide mineralization, particularly with pyrite-pyrrhotite ores. The main volcanic phase is represented by subalkalic to alkalic basalts, which were followed by keratophyre volcanism; this was apparently syntectonic in essence. Stratiform mineralization was associated with it and with relevant changes in the history of the entire Variscan marine basin. Similarly as in the Proterozoic, sedimentation of the flysch character followed, and eventually the porphyry volcanism of the subsequent type. This, however, did not develop before the consolidation of the Variscide volcano-sedimentary formations into a continent. The chief representatives of the subsequent volcanism occur in the NE Bohemia, some of them are also known from NW Bohemia, where they are devoid of significant mineralizations. Petránek (1977) assumes justifiably that a large mass of subsequent porphyries also existed in central Bohemia where they gave rise to thick complexes of Permo-Carboniferous arkoses. The granitoids of central Bohemia, the role of which in the metallogenic history of the Bohemian Massif is indisputable, originated in the subvolcanic layer.

On account of the incompleteness of geological formations and extensive metamorphism in the Krušné hory and Krkonoše Mts. it cannot be decided whether or not the geological history of volcanics and associated mineralizations proceeded in the same way in their Proterozoic and Palaeozoic units, but geological extrapolations are suggestive of such a trend. Since only lower layers of the orogens have been preserved in all parts of the Bohemian

Massif, it is necessary to reconstruct the units which succumbed to erosion. This is most difficult to do in the Cadomian cycle; as concerns the Variscides, the molasse sediments of intermontane depressions and particularly Zechstein sediments of the Mansfeld type deposited at the periphery of the Bohemian Variscides provide some clue to the solution of the problem. They indicate that the Variscan volcanics, including the subsequent ones, had to be very rich in mineralization.

The analogies in the Cadomian and Variscan history of the Bohemian Massif suggest a similarity of the principles of metallogeny. The maxima of mineralization will fall in the last phase of initial volcanism, from which the ore occurrences are known, and in the entire phase of subsequent volcanism, the mineralization of which in the today destructed units can only be postulated.

Influence of petrological and geochemical factors

The correlation of the petrology and chemistry of volcanic rocks, both mineralized and barren, is considered to be one of the most promising approaches to the recognition of the relationship between acid volcanism and metallogeny. To answer the question of the chemistry and petrography of the volcanic units of these two types would be probably more simple if they were preserved in completeness and if they had not been affected by Variscan metamorphism. Under the existing conditions we have to be satisfied with approximate results, only some of which are usable for the solution of the problem. Suitable for the expression of the chemistry of vol-

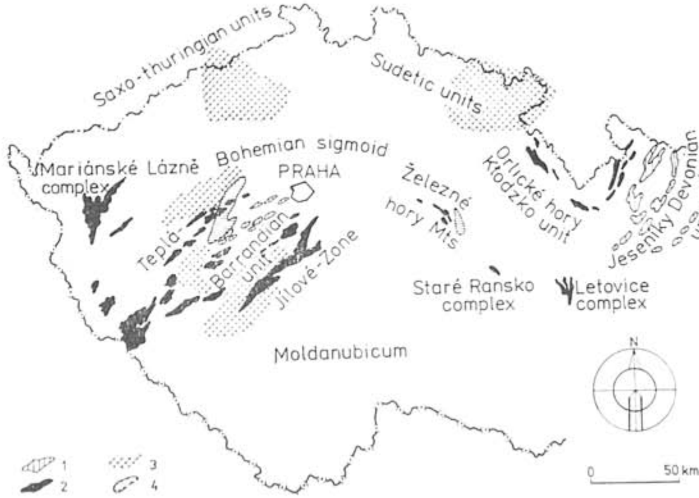

Fig. 1. Schematic map of principal occurrences of Cadomian and Variscan volcanics of the Bohemian Massif (except for areas affected by hygher-grade metamorphism). 1 — Variscan initial volcanics, 2 — Cadomian initial volcanics, 3 — Variscan subsequent volcanics, 4 — Cadomian subsequent volcanics. Major occurrences of stratiform mineralization are marked by symbols Cu, Pb, Zn.

canics proved to be Jensen's diagram, as it respects the relatively stable components $[Al_2O_3]/[FeO + Fe_2O_3 + TiO_2]/[MgO]$. The values plotted in the diagram are given in mol. per cent (J e n s e n, 1976). We have tested with good results the diagram of MgO/total iron (in mass per cent) in studying the evolution of ore-bearing magmas with respect to their development at a certain partial pressure of oxygen (in P o u b a, 1971; P o u b a — in print; P e r t o l d — P o u b a, 1976).

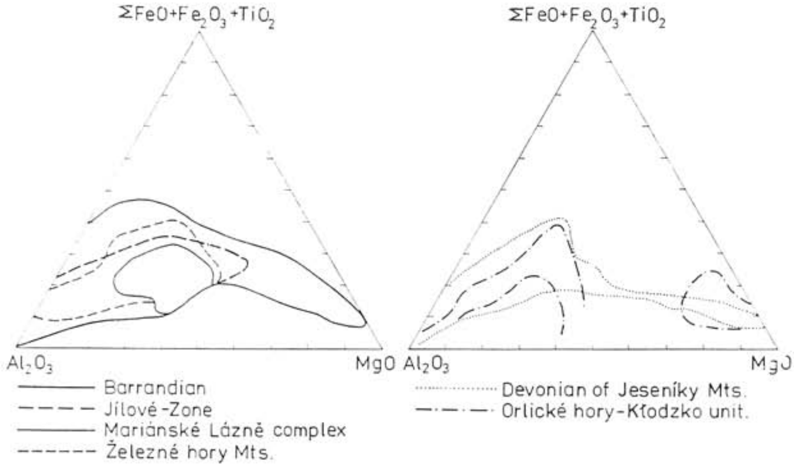

Fig. 2. Proterozoic and Devonian volcanics of the Bohemian Massif in J e n s e n's diagram. (Proterozoic: Barrandian, Jílové Zone, Mariánské Lázně complex, Železné hory Mts., Orlické hory—Kłodzko unit; Devonian: Jeseníky Mts. — After P o u b a in print.)

In Fig. 2 the chemistry of the Proterozoic volcanics of the Teplá-Barrandian region is shown in Jensen's diagram. This summary diagram shows that the set of rocks (characterized petrologically by F i a l a, 1977) involves a combination of several geochemical suites of volcanics. The overall chemical trend, however, reveals that at a certain a reversal of the tholeiitic trend of volcanism into the alkalic trend took place. From the geological literature this reversal is known to have occurred between the volcanic units building up the central part of the Barrandian basin, which K e t t n e r (1918) denoted as the spilitic and post-spilitic units. Polymetallic mineralizations are limited to the more acid rocks of the later unit, especially in the Jílové Zone. The field in which fall the Lower Cambrian barren subsequent volcanics (petrologically studied by W a l d h a u s e r o v á, 1977) coincides with the field of Proterozoic acid volcanics in the $FeO + Fe_2O_3$: Mg diagram.

The diagram in Fig. 3 again shows that the basic members of Proterozoic magmatism follow a tholeiitic trend, turning into the alkalic branch which is represented by keratophyres. With respect to the role of water and O_2 in the evolution of magmas in the region of their passage from water-poor environment into environment rich in water, the reversal of chemistry is likely to be connected with the passage of the mantle magmas into the „water-enriched" part of the earth's crust, and with the formation of a new focus of differentiation.

This chemical reversal is known from the Jeseníky Mts. (Fig. 4). At the place of a sudden increase in partial oxygen pressure it is accompanied by the formation of Fe ores (Fe oxides) and, eventually, by the development of a branch showing a typical Bowen (alkalic) trend, which is terminated by

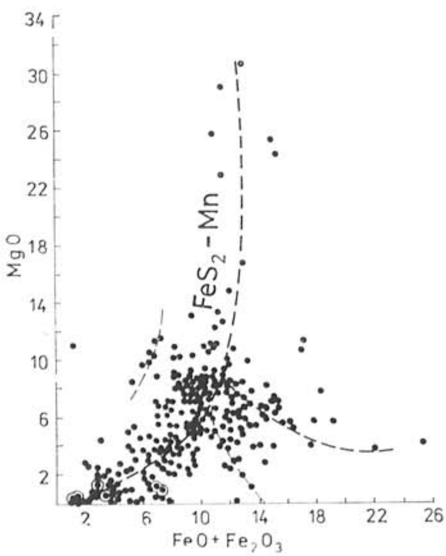

Fig. 3. Cadomian volcanics of the Bohemian Massif in $FeO+Fe_2O_3$:MgO diagram — dots. Circled dots — acid subsequent volcanics of Cambrian age. FeS_2-Mn — the associated ores. (After P o u b a — in print, modified.)

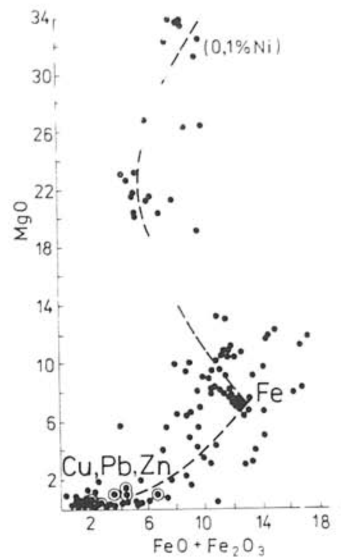

Fig. 4. Devonian volcanics of the Bohemian Massif in Jensen's diagram. Circled dots — acid subsequent volcanics of Permo-Carboniferous age. Fe; Cu Pb, Zn — the associated ores. (After P o u b a — in print, modified.)

strongly quartzose keratophyres to silexites (P o u b a, 1971). At the end of this branch there appear rocks accompanying the Cu-Pb-Zn mineralization. Without this reversal the magma would have probably developed either as in the Lower Palaeozoic of the Barrandian or in the Proterozoic of the Letovice crystalline complex (see the schematic Fig. 5 a, b).

In the Proterozoic of the Teplá—Barrandian unit the tholeiitic rocks are at the place of trend reversal also accompanied by the formation of Fe oxides, which in the last two centuries were mined intensively laying a basic to the local iron industry (in the Mirocite area).

The comparison of the chemistry of acid volcanics of the initial and subsequent phases in the diagrams shows that there are no great differences (except for alkalies) between the rocks of the „granitic" (porphyry) volcanism and the keratophyres (Fig. 6). As the keratophyre volcanism has to be derived from the basic, most probably tholeiitic magmas, the difference between the two types of acid volcanics is more pronounced in the Th/U ratio, the keratophyres being markedly poor in uranium. This difference could be used with advantage in prospecting because in the Bohemian Massif it discriminates between the rocks indicating the granite magmatism (usually tin-tungsten bearing ± Mo ± Li) and those indicating keratophyre volcanism (usually accompanied by Cu-Pb-Zn ± Ba ores). The difference of U and Th contents in acid volcanics are shown in Fig. 7, which is compiled from

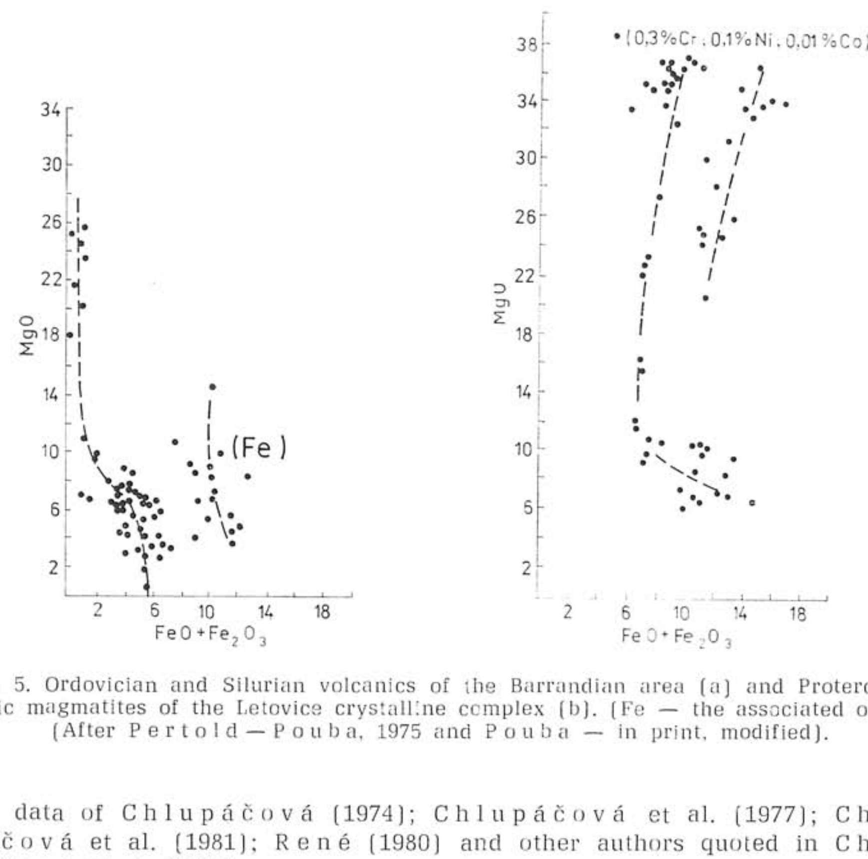

Fig. 5. Ordovician and Silurian volcanics of the Barrandian area (a) and Proterozoic basic magmatites of the Letovice crystalline complex (b). (Fe — the associated ores.) (After P e r t o l d — P o u b a, 1975 and P o u b a — in print, modified).

the data of C h l u p á č o v á (1974); C h l u p á č o v á et al. (1977); C h l u p á č o v á et al. (1981); R e n é (1980) and other authors quoted in C h l u p á č o v á et al. (1980).

The chemical differences between initial keratophyre volcanics and subsequent porphyry volcanics are not very great, if the alkalies are disregarded and only total iron and MgO are taken into consideration (see diagram in Figs. 3,4). The alkalies, if their shifting due to metamorphism is omitted, exhibit greater differences in the Proterozoic and Palaeozoic volcanics. Palaeozoic volcanics of the keratophyre type are richer in potassium and sodium and display therefore an identical chemical pattern in the SiO_2 : Na_2O : K_2O diagram (Fig. 6) with that of continental volcanics of the subsequent phase, which are slightly richer in potassium. The Proterozoic keratophyres are impoverished in alkalies and sodium is the predominant element in them. The

Cambrian subsequent volcanism being markedly richer in potassium differs strikingly enough from the Proterozoic volcanism.

In general, the chemistry of acid volcanics appears to have been one of the decisive factors in ore concentration; it indisputably influenced the metallogeny, particularly in the more alkalic units. The geotectonic history of volcanics together with the role of water had probably equally prominent effects.

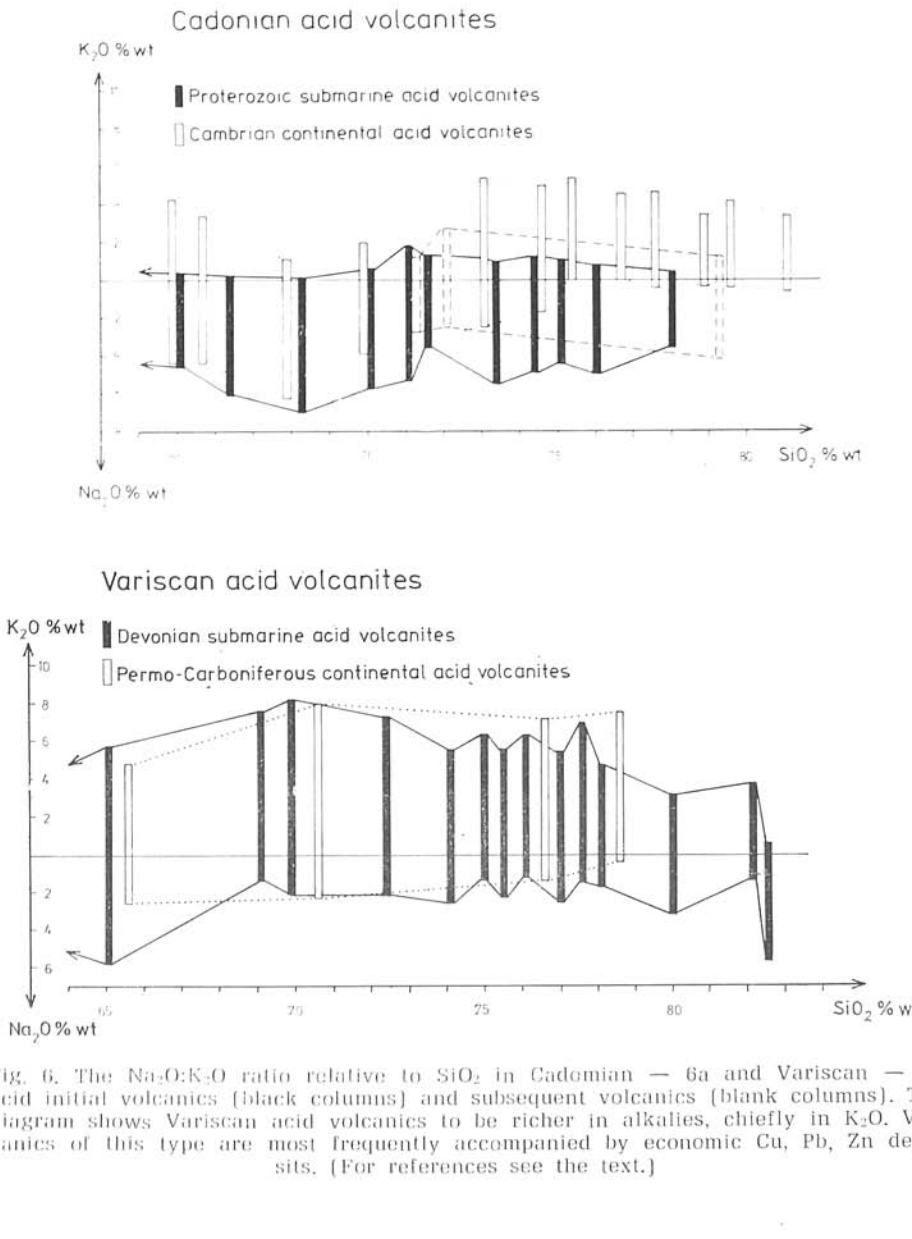

Fig. 6. The $Na_2O:K_2O$ ratio relative to SiO_2 in Cadomian — 6a and Variscan — 6b acid initial volcanics (black columns) and subsequent volcanics (blank columns). The diagram shows Variscan acid volcanics to be richer in alkalies, chiefly in K_2O. Volcanics of this type are most frequently accompanied by economic Cu, Pb, Zn deposits. (For references see the text.)

The influence of water-bearing environment is quite distinct in stratiform deposits. The water-bearing environment was not only under the influence of magma but also of tectonic and metamorphic impacts, which obviously opened the paths for water solutions capable of transferring heavy metals. In the Jeseníky Mts. the bound-water conditions in the country rocks of the stratiform deposits have been studied. It has been assessed that in a geochemical

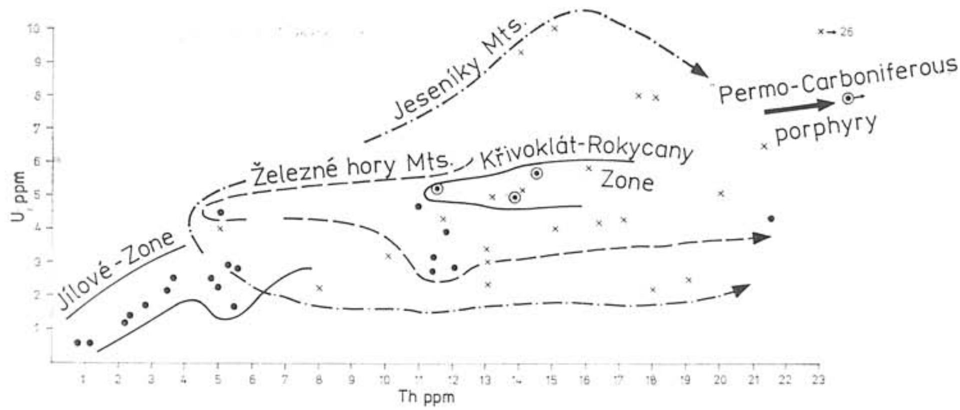

Fig. 7. The U:Th ratio in Cadomian and Variscan acid volcanics (Jílové Zone, Železné hory Mts., Křivoklát—Rokycany Zone). (Jeseníky Mts., Permo-Carboniferous porphyry.) The diagram shows that the two sets have similar ratios of these elements, but their fields in the diagram are separated. The difference in the position of the fields would be partly smoothed out by introducing a correction for radioactive decay depending on the age of rocks (according to the model of Matolín, 1970). Even in this case, however, the acid volcanics of initial and subsequent stage would show differences, as demonstrated by the diagram. (For references see the text.)

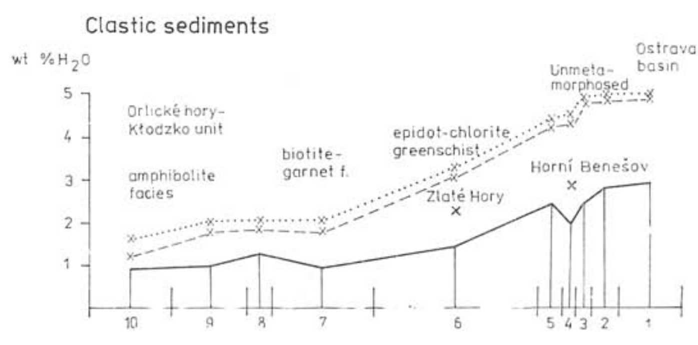

Fig. 8. Bound water content in the country rock of the stratiform deposit Zlaté Hory. The water content is plotted in the diagram showing water contents in individual metamorphic zones of the Variscides in the NE part of the Bohemian Massif (after Peuba — Šichtařová). The curves for thermal gradients of 20°C, 30°C and 50°C are plotted according to Fyfe — Price — Thompson, 1978. (Water content in clastic sediments.) The area with stratiform mineralization — Zlaté Hory and Horní Benešov — associated with acid volcanics shows anomalously higher contents of water bound in rock minerals. Numbers 1—10 — geol. units of analyzed rocks.

section perpendicular to the isogrades of metamorphism the minerals in the vicinity of the Zlaté Hory ore deposits and volcanics have an increased water content (see Fig. 8 a, b). This may represent a relict picture of the primary water-bearing environment heated by volcanic activity. It may also be interpreted as a manifestation of the heat flow, which enabled both the volcanism and hydrothermal activity joined with metallogeny to have been generated (Dvořák, 1973). In any case, the metallogeny is not a product of volcanic activity alone but it is a result of the coincidence of geological factors, among which the chemistry of acid volcanism of the keratophyre type is the principal indicator of a certain type of magmatic history.

Conclusions

1. Acid volcanics of the Cadomian and Variscan tectogeneses in the Bohemian Massif are developed in two separate and metallogenetically different phases. The earlier phase associated with initial volcanism is accompanied by the submarine type of Cu, Pb and Zn mineralization. The later phase of the subsequent type lacks important ore occurrences, but it has been preserved only in relics.

2. The chemistry of volcanics of both the Cadomian and Variscan orogens exhibits two trends, the older of which is of a tholeiitic character and the younger is alkalic. It seems that in the development of magma from which the volcanics and some Cu, Pb and Zn deposits are derived, a reversal of the tholeiitic trend into the alkalic took place when a large amount of magmatic melts had penetrated into the water-bearing environment. Magma enriched in water and alkalies was developing into the ore-bearing hydrothermal phase.

3. The chemistry of acid volcanics derived from the tholeiites of initial magmatism differs from acid volcanics of the subsequent phase in the ratios of Th:U and alkalies. The U and Th amounts in subsequent volcanics suggest that the latter can be derived from the granite layer of the earth's crust, whereas the origin of keratophyres can be rather placed in deeper regions underlying the granite layer. Major differences have further been found in the contents of alkalies. Relative to the Proterozoic cycle, the Variscan volcanic cycle, especially in ore-bearing areas, is richer in alkalies, chiefly in potassium. The differences in ratio of Fe:Mg and other components are immaterial. The stratiform mineralization is generally linked with keratophyres richer or enriched in alkalies — mainly in K_2O.

4. An important factor in metallogeny was water, which was either brought into circulation by the volcanic apparatus, or both the volcanism and water circulation were a result of one and the same tectonically induced cause, which gave rise to an increased heat flow. This assumption is supported by the coincidence of anomalies in the content of water bound in minerals at the sites of tectonic activity and ore-bearing acid volcanics, which are linked up with the intrusions and effusions of basic rocks.

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