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THE PRESENCE OF TIN AND TUNGSTEN IN THERMAL WATERS CONNECTED WITH GRANITES OF SOME SELECTED REGIONS IN EUROPE

(3 Figs.)

Obecność cyny i wolframu w wodach termalnych masywów granitowych w wybranych rejonach Europy

(3 fig.)

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Abstract. The presence of tin, tungsten and also molybdenum and some other trace elements is often detected in thermal waters occurring in close vicinity to granitic massifs. Their origin is still not entirely explained. The existance of greisens with Sn – W paragenese appearing in the acidic magmatic rocks regions is generally known. On the basis of the results of water investigation in the several European Hercynian massifs: Vosges, Pyrenees (France) and the Rila mountains (Bulgaria), and also taking into consideration Sn – W – Mo mineralization in other areas, an attempt has been made to explain the chemical composition of thermal waters and the environment where they are present.

Key words: trace elements, thermal waters, granitic massifs, Hercynides, Europe.

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Treść: W wodach termalnych występujących w bezpośrednim sąsiedztwie masywów granitowych stwierdzana jest obecność jonów cyny i wolframu, a także molibdenu i innych pierwiastków śladowych. Ich pochodzenie nie zostało, jak dotąd, w zadowalający sposób wyjaśnione. W rejonach intruzji kwaśnych skał magmowych powszechne jest występowanie grejzenów, zawierających często paragenezę cynowo-wolframową. Opierając się na wynikach badań wód z hercyńskich masywów: Wogezy, Pireneje (Francja) oraz Riła (Bułgaria), a także biorąc pod uwagę okruszcowanie Sn – W – Mo skał na innych obszarach, podjęto próbę wyjaśnienia zależności między składem chemicznym wód termalnych i środowiskiem, w którym one występują.

INTRODUCTION

The samples of thermal waters have been collected from two geothermal regions of France (Eastern Pyrenees and the Vosges) and one of Bulgaria (Rila – Rhodopes). In the laboratories of Antverp and Gent Universities the samples were examined by the neutron activation analysis (NAA) and spark source mass spectrometry (SSMS).

The results of trace element analysis confirmed the known dependence between occurrence of the raise of tin and tungsten ions concentrations in thermal waters and the presence of greisens and metamorphosed wall rocks in the magma intrusion region. The conditions, where the leaching of mineral substance from deep tectonic fissures takes place, are similar to that, as prevailing during hydrothermal stage. Therefore the genetic analysis of the Sn – W – Mo metallogenese and of the physico – chemical parameters present at that time, might be helpful in solving the problems of mass-transfer in the instance of thermal waters. Especially useful in this case is the thermodynamical treatment of the procceding reactions and of the mineral compounds leaching. It is shown in this work on the basis of molybdenum ions.

THE TECTONO-MAGMATIC ACTIVIZATION AND METALLOGENY

The provinces of tin – tungsten mineralization are most often sought for in the areas of Hercynian or Kimerydian geosynclines. According to Kazanski et al. (1976), the endogenous ore deposits formed during the process of tectono-magmatic activization are connected with large upcast of different age on the folded regions. During the first stage molybdenum – tungsten deposits associated with the fissure type near-surface intrusions of granites and granite-porhyries originate. They are represented by a number of genetic type: greisen, skarn, hydrothermal. They can form during several stages of mineralization and are connected with decreasing of temperature of circulating solutions and with zonal distribution of ores. In the classification of ore deposits Gruszczyk (1972) mentions also albititic deposits, connected with greisen zones. Literature mentions also the "orthomagmatic" porphyry tin deposits as for example the one in Bolivian province, described by Sillitoe et al. (1975). The porphyry' deposits typical for the areas with volcanic activity, are very often surrounded by hydrothermal breccia (Fig. 1). In the initial stages the metasomatic alteration takes place just when the fluid pressure exceeds load pressure. It gives rise to bodies of hydrothermal intrusion breccia. An escape of fluids accumulated in the apical part of magmatic body, starts the hydrothermal mineralization. On the other hand rapid congealing of a further volume of magma, leads to the porphyritic texture (Sillitoe et al., 1975, p. 923).

The review of more important Sn – W ore deposits shows us that they are coming together with granite elevation of batholith. The acidic magmatic rocks undergo albitisation processes, while the surplus of potasium is connected in greisen occurring on the border between the intrusion and wall rocks. The joints and the fissures in the marginal and apical parts of batholith are here of great weight. They essentially favour the localization of Sn–W–Mo greisen deposits, and thus decide about their petrographical species (Schust, 1976). Deep fissures in the rocks are connected here with the change in volume of transformed rocks, solidification of the magmatic body or mechanical displacement in the marginal zone of the intrusion.

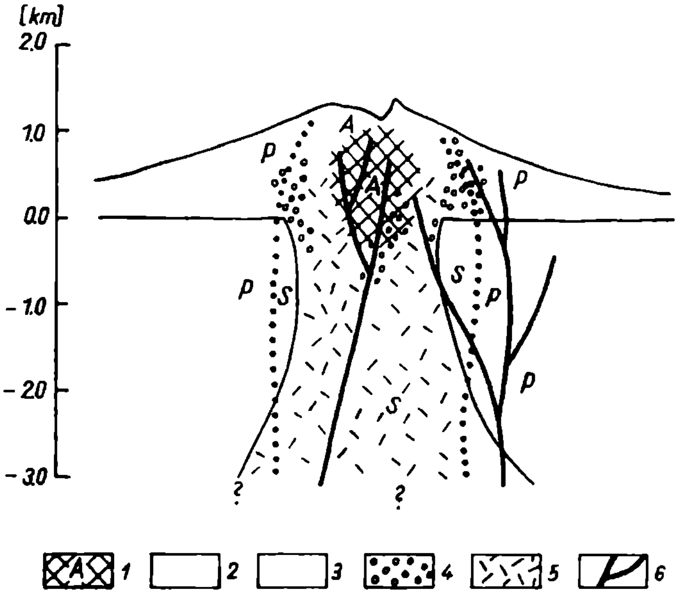

Fig. 1. Schema of a porphyry tin deposit of Bolivian province, according to Sillitoe et al. (1975). *1* – argillic alteration and silification, *2* – propylitic alteration, *3* – sericitic alteration, *4* – hydrothermal breccia, *5* – quartz, latite, porphyry, *6* – late Sn–Ag veins

Fig. 1. Szkic występowania porfirowych złóż cyny w Boliwii, wg Sillitoe i in. (1975). *1* – albityzacja i silifikacja, *2* – propilityzacja, *3* – serycytyzacja, *4* – hydrotermalna brekcja, *5* – kwarc, latyt, porfir, *6* – późniejsze żyły Sn–Ag

The geological-cross section of the magmatic intrusion in Tshechish Massif could be quoted here as a typical example (Fig. 2).

In the processes of acidic magmatic rocks metasomatosis one can mainly focus the interest on the transformation of feldspars and the redistribution of Na and K towards outer zones. Hence, the decomposition of feldspars, the draining off of alkalies and aluminum and supply of fluorine, boron a.o., lead to the formation of greisen. Gruszczyk (1972) mentions the possibility of reactions of potassium feldspars with silica and fluorine which give rise to the aggregates of quartz–topaz and muscovite.

According to Goldschmidt (1954), at the stage of residual crystallization, biotite

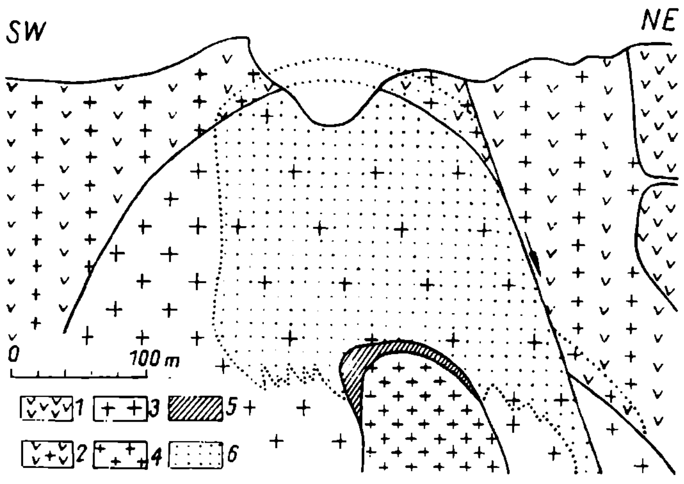

Fig. 2. Geological cross-section illustrating the tin deposit of Altenberg, cited by Schust (1976). *1* – quartz porphyries of Tepliz, *2* – granite porphyries of Altenberg, *3* – exterior granites, *4* – interior granites, *5* – pegmatites, *6* – greisen bodies

Fig. 2. Przekrój geologiczny przez złoża cyny w Altenbergu, cytowany przez Schusta (1976). *1* – porfiry kwarcowe z Teplitz, *2* – granitowe porfiry z Altenbergu, *3* – zewnętrzne granity, *4* – wewnętrzne granity, *5* – pegmatyty, *6* – złoża grejzenowe

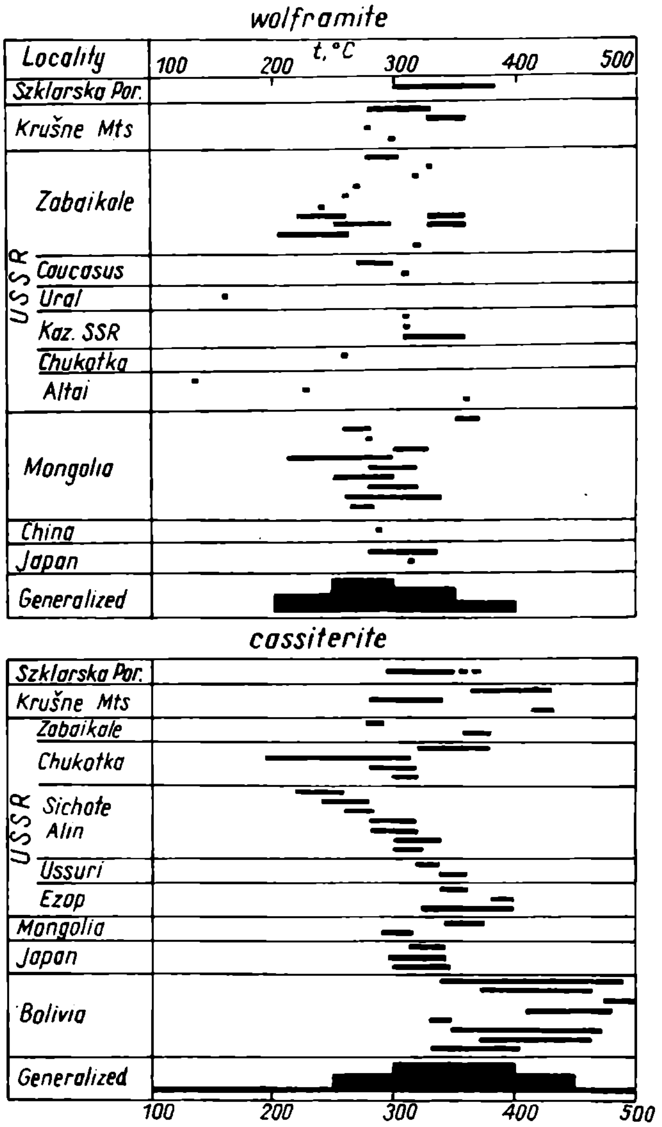

Fig. 3. Crystallization temperatures of wolframite and cassiterite in different ore deposits. Data collected by Kozłowski et al. (1975)

Fig. 3. Temperatura krystalizacji wolframitu i kasyterytu w różnych złożach, wg zestawienia Kozłowskiego i in. (1975)

and sodium-potassium feldspars are formed i.e. the main rock-forming minerals are the richest in tin and tungsten. Sillitoe et al. (1975), Brownlow (1979) and also Kozłowski et al. (1975) claim, that feldspars resolution is the primary source of tin and tungsten compounds. The authors of the last mentioned work maintain that the increasing activity of Ca^{2+} ions in the hydrothermal solutions results from the replacement of Ca by Na in plagioclases. The Ca^{2+} ions react with wolframite forming scheelite and releasing Fe – ions into solution.

On the basis of mineralizing zones of sudetic granites one is given the physical-chemical conditions of forming Sn–W–Mo ore deposits, according to Karwowski (1975) and Kozłowski et al. (1975). Studies of fluid inclusions in limpid minerals of greisens, on the ground of Naumow-Malinin method, confirmed the presence of pneumatolitic stage in the begining of matallogenese. The temperature was decreasing from 500°C to 110°C and less during the hydrothermal stage. In a high temperature, tin forms unstable compounds with boron and halogens while tungsten has the same behaviour against fluorina. Gundlach (1959) mentions the following mobile compounds of tin and tungsten:

- isopoly–acids,
- single–acids,
- colloidal solutions.

Moreover, the migration of these ions is possible in the form of:

$$SnCl_4;\quad H_8[Si(W_2O_7)_6];\quad H_3[P(W_3O_{10})_4];\quad H_3[Sb(W_3O_{10})_4].$$

Whereas in alcaline conditions, (Kozłowski et al., 1975), can coexist ions: WO_4^{2-}; $WO_2S_2^{2-}$; MoS_4^{2-}.

The pressure prevailing during the mineralization in sudetic massifs has been stated on ~800±80 atm (Karwowski, 1975). In the some way the lithostatic pressure in the early stage of Bolivian ore deposits was estimated as equallius from 800 m to 2000 m, while hydrostatic pressure varied between 2100 to 5200 m (Sillitoe et al., 1975). The pH – values oscillated near the neutral and Eh was slightly higher than zero.

In order to compare the temperature of crystallization of minerals in Sn–W–Mo ore deposits are given different examples in Fig. 3. It is evident that during ore deposits formation chiefly the hydrothermal conditions existed. These deposits reveal a strong connection with the parent rocks and they have a similar tectonic and geometry of system: batholith – wall rocks.

Many researchers are of an opinion about periodical activation of regions which might have been of pulsatory nature. It must have favoured the remobilization of selected ions from mineralized parts of the intrusion to the outer zones of granitic massif.

GENERAL CHARACTERISTICS OF THE THERMAL WATERS IN THE INVESTIGATED AREAS

The thermal waters under study are mainly nitrogen-rich alcaline waters typical of granite or granite–gneiss at depth.

Thermal springs of the eastern Pyrenees exhibit a pH of 8 to 9.5 and a temperature from 30° to 75°C. The springs near Thués–les–Bains will be taken as typical example. They are characterized by a rather high sulphur content: $10^{-3.66}$ mol/dm^3 HS$^-$; $10^{-3.86}$ mol/dm^3 SO$_4^{2-}$ and $10^{-4.2}$ mol/dm^3 S$_2$O$_3^{2-}$. The content of HCO$_3^-$ and CO$_3^{2-}$ are $10^{-3.09}$ and $10^{-4.58}$ mol/dm^3, respectively. Other main anions are chloride and fluoride having concentrations of $10^{-3.7}$ and $10^{-3.56}$

Table – Tabela 1

Comparison between thermal waters of Bulgaria (Rila MTS.)
and France (Vosges, Eastern Pyrenees)
Porównanie wód termalnych Bułgarii (Góry Riła) i Francji (Wogezy, Pireneje Wschodnie)

			Rila MTS.	Vosges	East. Pyrenees
TDS° (ogólna mineralizacja)	ppm	low	1.0	0.4	0.3
Temperature at the outflow (temperatura na wypływie)	°C		50–90	58–70	40–78
pH		high	8.0–9.5	8.0–8.1	8.5–9.0
Fluorine (fluor)	mg/dm^3	high	7.0–25.0	16.0	5.0
SiO$_2$	mg/dm^3	high	100.0	100.0	90.0
Gas	(%N$_2$)	high	95.0	90.0	90.0
Tungsten (wolfram)	ppb	high	50.0–300.	225.0	28.0
Rb/Cs ratio			0.8–0.9	0.8	2.3
Li/Cs ratio			5.2	5.7	6.1

° – Total dissolved substance.

mol/dm^3, respectively. Sodium ($10^{-2.55}$ mol/dm^3) is the major cation in these waters.

In the Vosges area (e.g. Plombières – les – Bains), the waters are of a pH of 8.0 to 8.1 and a temperature at the outflow of 68 – 70°C. They are chemically characterized by the predominance of HCO_3^- (approximately $10^{-2.78}$ mol/dm^3) and Na^+ (appr. $10^{-2.37}$ mol/dm^3). The sulphur content (all SO_4^{2-}) is about $10^{-3.1}$ mol/dm^3.

The Bulgarian waters are quite similar to the waters of the two above areas. A comparison between these different areas is given in Tables 1 and 2.

Table – Tabela 2

Concentration levels of some trace elements that might be indicators of tin and tungsten mineralization at depth (concentration in microgram per liter)

Poziomy koncentracji wybranych pierwiastków, które mogą być znacznikami mineralizacji Sn – W (koncentracja w mg/l)

Region	pH	F	W	U	Mo	Sn	Zr	Ta
Plombières-les-Bains	° 8.0 – 8.1	13000.	225.0	0.07	6.0	13.0	26.0	0.01
Bourbonne-les-Bains	° 7.4 – 7.5	3200.	6.0	0.40	3.0	10.0	10.0	0.49
Bains-les-Bains	° 7.1 – 7.4	6600.	50.0	11.00	0.5	6.0	29.0	0.08
Thués-les-Bains	°° 8.5 – 9.0	5200.	28.0	0.01	6.0	0.6	1.0	0.01
Sapareva Banja	°°° 8.8	12000.	260.0	0.01	9.0	0.6	12.0	0.01
Cold spring	° 6.0	550.	0.2	1.60	0.5	0.6	1.0	0.21

° Plombières-les-Bains, Bains-les-Bains, Bourbonne-les-Bains and the cold source are situated in the Vosges.
Miejscowości znajdujące się w Wogezach.

°° Thués-les-Bains is situated in the Eastern Pyrenees.
Miejscowość znajdująca się w Pirenejach.

°°° Sapareva Banja is situated in Bulgaria.
Miejscowość znajdująca się w Bułgarii.

The low Mg and tritium content of the waters shows that there is no mixing with cold superficial water in the mentioned areas except for the Vosges (e.g. Bains – les – Bains) where the portion of cold water reaches 40%.

By means of chemical geothermometers (Na/K, Na/K/Ca, SiO_2), one can calculate the temperature at depth for the sources of the Eastern Pyrenees and the Bulgarian sources is about 120°C while that for the sources of the Vosges is about 140°C.

THE ACTION OF THERMAL WATERS AND THE BEHAVIOUR OF TRACE ELEMENTS

The regions where thermal waters are found can hardly be connected with active post-volcanic processes. The ground water in hot springs is of meteoric origin; the recharge areas for these springs being the highest parts of the granite batholites – the Pyrenees, the Vosges. In most cases, however, the water warmed up in the intrusive rocks is drained off at the border of its outcrop in the river valleys. The depth which the infiltrating water reaches, determined by means of geothermometers is up to about 1500 m below the surface level, and the temperature at that depth reaches 120°C (Blommaert et al., 1981). For the purpose of comparison it is worth mentioning that the greisen zone spreads up to 1000 m from the surface down to the magmatic rocks (Gruszczyk, 1972).

Hence, the thermal water under consideration at the lowest parts of its circulation path in the rock massif may create the conditions similar to those at the hydrothermal stage of residual crystallization. A deep circulation of water (more than 1000 m), in magmatic rocks may take place in fissures and discontinuity zones of tectonic origin. The discontinuity portions either take their origin from the stage of foldings of the area adjacent to the intrusion, or are the results of epeirogeny during later stages (Vosges). These fissures, at the first stage, are the privileged ways of circulation of hydrothermal liquid and of impregnation or partial filling up with minerals of the hydrothermal stage. Renewal and enlargement of the fissures facilitate the infiltrated water to come in contact with the surface. This water may become enriched on its way with oxygen and carbon dioxide due to their diffusion in fissures of the rock massif. The dissolution of minerals contained in fissures is facilitated by a high temperature of the water (above 100°C) as well as the pressure (above 100 bars at a depth of 1 km). In such conditions, the processes of leaching and bringing up to the surface of mineral constituents of rocks can be defined as "hydrothermal erosion".

The extent of this erosion may by evaluated on the example of the hot springs of the axial zone of the Pyrenees.

Evaluated total flow of springs: $Q = 500\ m^3/h$

Mean T.D.S. $M = 0.4\ G/dm^3$

(Total dissolved substance)

Annual amount of transported matter: 2000 kG.

In the geological scale, the transportation of the dissolved matter should be referred to the time unit: 1 mln years. In this case, the result of "hydrothermal erosion" would be the leaching of about 2 mln tons of mineral substances from the area under consideration.

On the basis of work of Andrews–Jones (1968) common geochemical associations of trace elements for the following rocks may be quoted:

1. Granite rocks: Ba, Li, Be, W, Mo, Sn, Nb, Ta, Sc, U, Hf, Zr, Ti, Sr.
2. Pegmatitic rocks: Sn, Mo, Nb, W.
3. Contact metamorphic rocks: W, Sn, Mo, (B, Li, Be).

The same author mentions the association of elements of interest ore:

	Main elements	Trace elements
cassiterite	Sn	Ta, Nb, Fe, Ti, Mn, In, Ag, Pb (Sc).
wolframite	W, Fe, Mn	R.E., Nb, Ta, Sc, Zr, Hf, In, Sn
scheelite	Ca, W	R.E., Nb.

The connections of tin and tungsten with trace elements are the results of diadochia in crystallic nets, e.g. niobium and tantalum in relation to tungsten, and also from chemical affinity or analogical conditions of formation of minerals at the residual crystallization of magma.

In secondary environments, the ions of tin and tungsten have a low mobility or are immobile, practically in all conditions (oxidizing, acidic, neutral). Their concentration in ground water increases in the case of thermal water, in a batholith of acid rocks, through contact with mineralized zones. Therefore, associations of trace elements being typical for pneumatohydrothermal deposits of Sn – W are most often observed in thermal waters.

Thermal waters of the area of granite intrusion are rich in trace elements. It results both from analysis of the migration of post – magmatic liquid in the vicinity of intrusion and from the observations made during the search for deposits.

THERMODYNAMICAL BEHAVIOUR OF TRACE ELEMENTS IN THE WATER IN CONTACT WITH GRANITES

Most of the springs under investigation show a variety of trace elements related to the granites at depth (Li. F, Ge, Rb, Cs, W), Pentsheva (1961), and to a lesser extent: Sn, Mo, Ta, Zr and U.

The differences between the Vosgesian and the Pyrenean springs in the content of W, F, Sn and Zr, can not be simply explained by the differences in water-bearing formation and temperature. The largest difference from the geological point of view between these two areas in France is that the Vosges are situated in an active tectonic zone (near the Rhine graben). The uplift of mountains creates facilities for the deeper circulation of the ground water and the subsequent dissolution of new parts of the mineralized veins.

In order to find out to what these waters are in chemical equilibrium with certain mineral phases there has been calculated the saturation indices Ω for the element with respect to a slightly soluble compound. Ω is then defined by: $\Omega = M_e/M_c$, where: M_e – measured concentration of the element, M_c – calculated concentration of the element in equilibrium with a slightly soluble compound, irrespective of the chemical form of the element, but at a specified pH and temperature and in a given environment.

If Ω is found to be about 1, it indicates that the solution is saturated with respect to the compound being considered. Besides analytical difficulties (especially in the case of trace elements) the uncertainty as to the thermodynamical data may lead to unaccurately calculated indices. When dealing with sulfide compounds, Ω – values have to be calculated at the temperature where the sulfides become oxidized. In the case of the Pyrenees, sulfide species were found to be present at the surface (±75°C). Calculations for the case of the Vosges revealed that oxidation took place at a temperature of around 100°C. This is indeed the temperature for which calculations related to insoluble sulfide compounds have to be carried out since metal-sulfates are more soluble.

As an example we calculated the saturation index in spring water of Plombières – les – Bains for Mo versus the slightly soluble MoS_3 compound. Thermodynamical data for Mo can be found in Table 3.

Table – Tabela 3

Thermodynamical data for molybdenum

Dane termodynamiczne dla związków molibdenu

Log K_{So} or log K	Temperature		Literature
	25°C	100°C	
$MoS_{3(s)}$ — $MoO_4^{2-} + 3HS^- + 5H^+$	−66.3	−56.5	Karapet'yants
$HMoO_4^-$ — $H^- + MoO_4^{2-}$	−3.7	0.7	et al., 1970
$MoO_2S_2^{2-}$ — $2HS^- + 2H^+ + MoO_4^{2-}$	−4.6	−4.5	Sucha et al. 1972
$MoOS_3^{2-}$ — $HS^- + H^- + MoS_2S_2^{2-}$	−3.3	−3.2	,,
MoS_4^{2-} — $HS^- + H^+ + MoOS_3^{2-}$	−5.4	−5.3	,,

Reactions involving other molybdenum species were found to be unimportant in the case under study and thus can be omitted. These data allow to calculate the fraction of total Mo which occurs as the species MoO_4^{2-} (at 100°C at the corresponding pH of 7.9).

$$\alpha MoO_4^{2-} = \left[\frac{MoO_4^{2-}}{Mo_T}\right] = \left[1 + \frac{HMoO_4^-}{MoO_4^{2-}} + \frac{MoO_2S_2^{2-}}{MoO_4^{2-}} + \frac{MoOS_3^{2-}}{MoO_4^{2-}} + \frac{MoS_4^{2-}}{MoO_4^{2-}}\right]^{-1} = 1$$

and the conditional solubility product $P_s = K_{So}/MoO_4^{2-}$. The calculated total molybdenum concentration in equilibrium with MoS_3 at 100°C is as follows:

$$MoO_4^{2-}\ (100°C) = P_s/(HS^-)^3 \cdot (H^+)^5 = 10^{-7.73}\ \mathrm{mol/dm^3}$$

with $(HS^-) = 10^{-3.09}$ and $(H^+) = 10^{-7.9}$ mol/dm³ at 100°C, whereas the experimentally found concentration of Mo is $10^{-7.20}$ mol/dm³. Hence $\Omega_{Mo} = 3.4$, which indicates that Mo is saturated versus MoS_3 in the waters of Plombières – les – Bains.

Similar calculations were carried out for other elements, both for the Pyrenees and the Vosges. The saturation indices are summarized in Table 4. This table also lists the predominant species of the element of interest that occur in that water. For insoluble hydroxy – compounds the calculation has to be done at the temperature of filtration (e.g. 25°C). Indeed, precipitation of these elements could occur before filtration.

For Ta and U, it was not possible to calculate the Ω values due to the lack of appropriate thermodynamical data. It is also very difficult to take into account the kinetics of these reactions. As a matter of fact it is possible that Zr, for instance, appears in the solution as a result of dissolution of $ZrSiO_{4(s)}$ and that its concentration is afterwards controlled by the kinetically slow $ZrO_{2(s)}$ – precipitation reaction. Anyhow, it may be assumed that in the case of the Vosges (a tectonically active zone), most of the elements are saturated versus slightly soluble sulfide – or oxide compounds. The thermodynamical conditions of formation

Table − Tabela 4

Saturation indices − Ω for several elements

Wskaźniki nasycenia − Ω wybranych pierwiastków

Element Pierwiastek	Main species in solution Główne cząsteczki w roztworze	Insoluble compound Nierozpuszczalne związki	Vosges Ω	Pyrenees Ω
W	WO_4^{2-}	$CaWO_{4(s)}$	1.0	0.1
F	F^-	$CaF_{2(s)}$	0.1	0.1
Mo	MoO_4^{2-}	$MoS_{3(s)}$	3.4	0.01
Zr	$Zr(OH)_4^0$	$ZrSiO_{4(s)}$	0.03	
		$ZrO_{2(s)}$	50.0	$\leqslant 13.0$
$Sn_{(IV)}$	$Sn(OH)_4^0$	SnO_2	200.0	$\leqslant 6.0$
		$SnO_{2(ppt)}$	0.08	
		$SnS_{2(s)}$	0.6	

and dissolution of these compounds are quite similar. From Table 2, we can conclude that elements such as F, Sn, W, Mo and to a lesser extent, uranium are enriched in the latest stage (hydrothermal: 100−200°C) of magma cooling. Therefore they are situated near the roof of the batholith and are easily accesible for water.

Most of the springs of the Eastern Pyrenees are situated on the border of a large batholith and no differences in their chemical compositions have been found. In the Vosges area, however, a different situation takes place. Here, Plombières−les−Bains is situated above the batholith, while Bains−les−Bains and certainly Bourbonne−les−Bains lie further away from the central part of the batholith. Water from the latter two areas is expected to be more influenced by greiseneized zones possibly present at the border of the batholith. The high content of Zr, U and Ta in Bains−les−Bains, is to be pointed out.

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STRESZCZENIE

Wody termalne opróbowane w Wogezach, Pirenejach oraz w masywie Riła należą do typu alkalicznego i są bogate w azotany. Średnia zawartość siarczanów wynosi $10^{-3.5}$ mol/dm^3. Ogólna mineralizacja wód wynosi 0,3–1,0 g/dm^3. Temperatura na wypływie waha się od 30 do 70°C. Natomiast obliczona na podstawie geotermometrów temperatura w głębi masywu wzrasta do ~120°C w Pirenejach i masywie Riła oraz do ~140°C w Wogezach.

W źródłach położonych na wychodniach kwaśnych skał magmowych – granitoidów, gdzie nie zachodzi mieszanie się wód szczelinowych (wgłębnych) z porowymi (przypowierzchniowymi), zwraca uwagę wysoka zawartość takich pierwiastków śladowych, jak: wolfram, cyna i molibden. Stężenie jonów wolframu przekracza miejscami 200 ppm.

Jak ustalono na podstawie warunków termicznych badanych masywów, wody podziemne mogą krążyć w spękaniach tektonicznych do głębokości około 1500 m poniżej powierzchni terenu. Badania geometrii intruzji skał magmowych oraz towarzyszących im tektonicznych spękań wskazują na zwiększoną obecność nieciągłości w partiach brzeżnych, a tym samym maksymalną w tej strefie przepuszczalność skał. Istnieje zatem możliwość ługowania przez wody termalne wytrąconych w etapie pneumatolitycznym i hydrotermalnym minerałów, zwłaszcza w strefach stropowych i brzeżnych batolitów. Są to miejsca często spotykanych mineralizacji Sn–W–Mo typu grejzenowego, albitytowego czy też porfirowego (*vide* Sillitoe et al., 1975).

Według współczesnych poglądów dotyczących pochodzenia związków cyny i wolframu, można upatrywać ich pierwotnego źródła w procesie rozpadu skaleni. Badania homogeniczne inkluzji fluidalnych w przezroczystych składnikach grejzenów (Kozłowski et al., 1975) pozwalają określić warunki fizykochemiczne panujące podczas tworzenia się minerałów paragenezy Sn–W.

Spadek temperatury w szerokim zakresie obniżał się od ~500° do ~70°C w etapie hydrotermalnym. Oszacowana wartość Eh była lekko powyżej zera, natomiast pH odpowiadało naturalnemu środowisku skał (Sillitoe et al., 1975).

Obecne ługowanie minerałów przez krążące w głębokich szczelinach wody termalne, wzbogacone w tlen i dwutlenek węgla, zachodzi w temperaturze powyżej 100°C w warunkach wysokiego ciśnienia (ponad 100 barów). Proces wymywania i wynoszenia substancji mineralnych w opisywanych przypadkach może być utożsamiany z „erozją hydrotermalną". Koncentracja pierwiastków śladowych, które mogą być znacznikami paragenezy Sn – W – Mo w badanych wodach, odpowiada asocjacjom traserów złóż cynowo-wolframowych podanym w pracy Andrews-Jonesa (1968). Szczególną zgodność między okruszcowaniem i stwierdzonym podwyższonym stężeniem pierwiastków śladowych w badanych próbkach wód uzyskano w odniesieniu do F, W, U, Sn, Zr oraz Ta.

Tezę o rozpuszczaniu minerałów Sn – W – Mo zawartych w stropowych partiach intruzji skał magmowych potwierdzają również obliczenia termodynamiczne wskaźników nasycenia. Okazuje się, że w wyższych temperaturach, tj. ~100°C, siarczki rozpatrywanych metali stają się rozpuszczalne i mogą przechodzić do roztworu.

Stwierdzono odchylenia od podanych zależności w przypadku mieszania się wód termalnych z wodami podziemnymi poziomów przypowierzchniowych. Dotyczy to zwłaszcza próbek z Bains-les-Bains i Bourbonne-les-Bains w Wogezach, gdzie ilość wód chłodnych dochodzi do 40% wydajności termalnych źródeł.