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Chemical equilibria and zoning of subsurface water from Jáchymov ore deposit, Czechoslovakia

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Abstract—Water samples from the surface and from different levels of the Svornost mine (Jáchymov, Czechoslovakia) were analyzed and Eh and pH were measured in the field. The saturation indices ($I = \log (Q/K) = \Delta F/2{\cdot}303\ RT$) of water–$P_{CO_2}$ in normal earth's atmosphere, water–calcite, water–Fe$(OH)_3$, and water–pyrite are given. The P_{H_2} in water characterizes individual redox zones of water body which are consistent with the secondary zones of sulfide ore deposits. Complexing among the major ions of water and temperature changes were considered in the calculations. Space dependence of individual physico–chemical characteristics of water is discussed in detail.

INTRODUCTION

THIS paper presents the results of a study on the interaction of ground water with two major types of rock associated with the Jáchymov ore deposit. The rocks are a metamorphic complex affected by mining activity and unmined granitic massif. Much work has been done on solution–solid phase interactions at low temperatures and pressures, particularly using Eh and pH data. Studies of natural solutions provide a means of evaluating the applicability of physico–chemical treatments such as those of BACK (1961), BARNES (1965), BARNES and BACK (1964), BARNES and CLARKE (1964), GARRELS (1954, 1960), GARRELS and CHRIST (1965), GARRELS and THOMPSON (1962), GARRELS *et al.* (1960, 1961), HEM (1960a,b,c), HEM and CROPPER (1959), and SATO (1960). Using the theoretical and experimental results of these authors and the field observations and measurements in Jáchymov mining district, the origin of the chemical composition of water can be explained.

REGIONAL AND GEOLOGICAL SETTING

Location

The Jáchymov ore deposit is in the central tract of the Krušné hory mountains near the northwestern boundary of Czechoslovakia. The investigation was concentrated in the Svornost mine, the largest of the district. Water was sampled from surface springs in an area of 12·5 square miles and from the Svornost mine from sources on the 5th level (depth 1120 ft), the 10th level (depth 1490 ft), and the 12th level (depth 1620 ft) within an area of about one square mile.

The region is mountainous. Land surface at the Svornost mine is at an altitude of about 2470 ft above sea-level.

Climate

The mean annual temperature is about 5°C. The hottest month is July (14°C) and the coldest is January (−4°C). The area receives an average annual precipitation of 38 in.

Geology

More than fifty authors have dealt with the geology and mineralogy of the Jáchymov ore deposit. The most complete works of recent time were written by MRŇA (1963), MRNA and PAVLŮ (1963), and SATTRAN (1961).

The general geological features of the region are a granitic massif overlain by metamorphic rocks. The metamorphic rocks, of possible Cambrian age, were originally psamitic and pelitic sediments with interlayers of carbonate rocks. The most common metamorphic rock type is biotite–muscovite mica–schist. The mica–schist complex contains lenses and interlayers of limestones, silicified limestones and skarns. The mica–schist contains pyrite and graphitic substances. Below the metamorphic rock lies the subjacent granitic massif, the main rocks of which are biotite granite and porphyry of Carboniferous or Permian age.

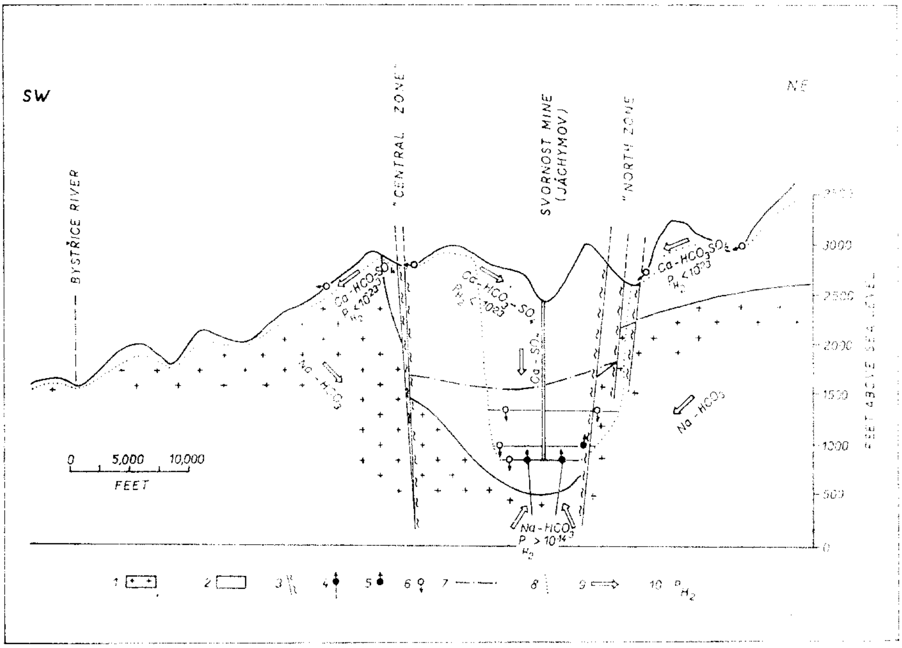

Fig. 1. Cross section through Jáchymov mining district.

(1) Granitic rocks;
(2) Metamorphic complex;
(3) Faults;
(4) Owerflowing drill hole;
(5) Ascendent spring;
(6) Descendent spring;
(7) Piesometric head of water in granitic rocks;
(8) Free O_2 occurs above the line;
(9) Movement of denoted water type;
(10) Hydrogen partial pressure.

The dominant structural trends of both the granitic massif and the metamorphic rocks are NW–SE and E–W. The Jáchymov mining district is limited by the "North Zone" of east–west faults passing 0·6 mile northward and the "Central Zone" of east–west faults passing 1·5 mile south of the Svornost mine. The contact between the granitic massif and the metamorphic complex plunges to a depth of 2200 ft below the earth's surface in the mining district; on the north, the contact passes at the depth of 300 to 1000 ft; on the south the granite crops out (Fig. 1).

The veins of the Jáchymov ore deposit strike northwest and west. In the upper parts of the veins that cut the metamorphic complex there occur arsenides of Co and Ni, native silver, arsenic, and bismuth, the sulfides pyrite, galena, sphalerite, chalcopyrite, and some silver minerals. Dolomite, calcite, and quartz are the most common gangue minerals in the upper parts of the veins. In the lower parts of the veins, especially in granite, the amount of carbonates diminishes and uraninite appears.

Hydrological investigation (LABOUTKA and PAČES, 1966) has proved that water of the Jáchymov mining district during its circulation interacted with air, with minerals of the metamorphic complex and/or the granitic rocks, and with vein minerals. Of particular interest are reactions among carbonate species, mineral, aqueous and gaseous, and oxidation reactions. The abundance of carbonate minerals ranges from very low in the granites (SATTRAN, 1961) to high in skarns with from 2·4 to 33 per cent by weight CO_2. The partial pressure of CO_2 in the earth's atmosphere is taken to be 3×10^{-4} atmospheres (atm.). The extent of oxidation is from negligible, as indicated by the presence of fresh pyrite, to severe oxidation as indicated by the presence of limonite and the absence of pyrite.

METHODS OF INVESTIGATION

Samples of water from about 300 springs, seepages, drill holes and main drains were collected in glass bottles. The water samples were analyzed in the laboratory by the standard methods of the Geological Survey of Czechoslovakia. From the preliminary results, 32 sources of water were chosen for further detailed study. Redox potentials and pH's were measured in these sources by a portable battery-powered pH-meter (Richmond Surrey–England). Accuracy of the meter is ±0·05 pH and ±0·005 V. The apparatus provides for temperature correction according to Nernst's law over the temperature range of 0–100°C. Two electrode systems (saturated calomel reference electrode–glass pH electrode and saturated calomel reference electrode–platinum oxidation electrode) have been equipped with plastic baskets and modified so that they can be dipped directly into the source of water. The redox potential was expressed in terms of the hydrogen scale (Eh) by adding the potential of the saturated calomel electrode at the temperature of the water sample to the potential value which had been read on the apparatus (Er); $\text{Eh} = \text{Er} + [0{\cdot}2444 - 0{\cdot}00066\,(t - 25)]$, where t is the temperature in degrees centigrade. Sources of water for study were chosen and sampled in a manner such that the water was as free as possible from contact with air upstream of the sampling point. The electrodes were immersed to a depth of 2·5 in. into the source. There was no difference between the potential measured by this method and the measured potential of a sample in a container sealed by a rubber stopper. Therefore, the effect of the dissolution of oxygen in the surface layer was probably negligible during the measurement. The streaming potentials, which can be 0·01 to 0·07 V (BARNES and BACK, 1964; BARNES, personal communication) were not measured. However, as the flow velocities were very low, such potentials were probably no larger than the range of other uncertainties in the field measurements.

FIELD RESULTS

Two chemical types of water occur in the Jáchymov district. Waters of the joint system in the underlying granite show a predominance of sodium and bicarbonate. Waters of the metamorphic complex contain dominantly calcium and sulfate. The waters of surface springs from both granitic and metamorphic rocks contain a predominance of calcium with either sulfate or bicarbonate ions. The water of surface springs is low in total dissolved solids, with less than 0·2 g/l. The total dissolved solids (TDS) concentrations of water from the deeper part of the metamorphic complex range from 0·2 to 3·0 g/l but the TDS concentration of water

Table 1. Selected chemical analyses of subsurface water from Jáchymov mining district (Analyses reported in mg/l if not given otherwise)

Sample Group	1 I	4 I	15 II	17 II	20 III	21 III	23 IV	31 V
Sampling in 1964	June 22	June 4	May 4	May 5	May 4	May 4	May 3	Aug. 31, 1962
Type of discharge	Spring	Spring	Seepage	Seepage	Seepage	Seepage	Seepage	Drill hole
Wall rock	Granite		Metamorphic complex					Granite
Depth	Surface		5th level		10th level		12th level	
(ft)			(1120)	(1120)	(1490)	(1490)	(1620)	(2121)
Temperature (°C)	8·1	7·3	15·1	18·3	17·6	20·0	23·4	29·8
Na^+	3·0	0·75	44·0	50·0	22·0	51·0	105·0	140·5
K^+	1·0	trace	10·0	14·5	5·0	4·0	4·5	8·5
Li^+	trace	trace	0·50	0·50	0·10	0·15	0·17	0·15
NH_4^+	0·00	0·00	0·00	0·00	0·00	0·00	0·00	0·00
Mg^{2+}	trace	1·2	110·7	171·5	51·1	71·5	8·5	5·5
Ca^{2+}	8·0	17·0	268·1	531·1	119·8	256·5	38·1	23·6
Mn total	0·00	0·00	0·00	0·00	0·00	0·00	0·00	0·26
Fe total	trace	0·74	0·37	trace	trace	trace	trace	0·37
Cl^-	4·3	3·5	10·6	17·7	16·7	10·6	5·3	12·4
NO_3^-	3	1	3	0	0	0	0	0
HCO_3^-	6·1	39·7	112·9	237·9	143·4	183·1	367·9	441·8
SO_4^{2-}	18·5	12·8	1074·0	1852·6	394·6	862·9	54·3	15·6
HPO_4^{2-}	trace	trace	0·55	trace	0·62	0·29	trace	0·21
H_2SiO_3	13·0	9·6		18·7	20·3	23·9	70·2	56·2
Total	56·9	86·29	1634·42	2894·50	773·62	1463·94	653·97	705·09
Residue at 110°C	67	68	1620	2800	720	1331	454	472
Sr			4·05	6·20	1·94	3·80	0·49	0·11
Ba			0·05	0·08	0·05	0·05	0·08	0·08
As			0·08			0·26	0·052	0·28
HBO_2			0·09	0·14	0·10	0·08	0·09	0·16
F			2·00	1·30	0·94	0·92	3·00	3·00
Be (μg/l)			0·5	0·5	0·5	0·5	0·5	0·7
Zn (μg/l)			439·0	67·8	9·2	40·0	0·8	1·4
U (μg/l)					470	9000	76	17
Rn (10^{-10} Curie)					8·5	9·4		3500
pH (pH units)	5·90	7·15	6·65	6·80	6·55	7·15	7·80	6·75
Eh (mV)	+406	+531	+118	+60	−5	+57	−89	−62

from the underlying granite is nearly constant at 0·65 g/l. Mixed chemical water types which originated by mixing of waters from granite and metamorphic rocks have not been identified. Typical samples of individual chemical groups of waters are represented by the chemical analyses in Table 1; the total dissolved solids and molarites of major ions are summarized in Table 4.

The lowest measured value of pH was 5·5 in a surface spring in mica-schist; the highest value 8·1 was in mine drainage water on the 12th level. Most of the pH values ranged from 6·5 to 7·3. The redox potentials ranged from −0·10 to +0·71 V. The results of Eh–pH measurements are summarized in Table 2.

Table 2. Field data on subsurface water from Jáchymov mining district

Sample measurement in 1964	Depth (ft)	Type of discharge	Depth of hole below level (ft)	Wall rock of source	Discharge (l/min)	Temp. (°C)	Pressure (atm)	pH	Eh (mV)
1 June 19	Surface	Spring (45)		Granite	4	8·1		5·90	+0·406
2 June 18		Spring (128)		Met. cplx.	150	5·6		6·05	+0·713
3 June 18		Spring (127)		Met. cplx.	45	5·6		6·95	+0·483
4 June 18		Spring (132)		Met. cplx.	12	7·3		7·15	+0·547
5 June 19		Spring (91)		Met. cplx.	14	7·5		5·50	+0·441
6 June 19		Spring (57)		Granite	4	6·4		7·05	+0·423
7 June 19		Spring (123)		Granite	32	5·3		5·90	+0·438
8 Apr. 6		Well (Hluboké)		Met. cplx.		12		6·70	+0·377
9 June 18		Spring (96)		Met. cplx.	18	5·9		7·10	+0·433
10 June 16	5th level (1120)	Seepage (5017)		Met. cplx.	0·14	19·8		6·80	+0·172
11 Apr. 8		Drain (5006)			6·5	18·7		6.40	+0·239
12 Apr. 7		Seepage (5003)		Met. cplx.	10	14		7·10	+0·244
13 June 16		Seepage (5018)		Met. cplx.	3	17·8		6·20	+0·279
14 Apr. 7		Seepage (5011)		Met. cplx.	3·1	14·5		6·90	+0·143
15 Apr. 7		Seepage (5008)		Met. cplx.	0·5	15·1		6·65	+0·118
16 June 16		Seepage (5016)		Met. cplx.	0·2	20		6·65	+0·302
17 Apr. 8		Seepage (5001)		Met. cplx.	0·02	18·3		6·80	+0·069
18 June 17	10th level (1490)	Seepage (1017)		Met. cplx.	1·4	22·3		6·95	+0·164
19 Apr. 8		Seepage (1001)		Met. cplx.	0·4	19·8		7·20	+0·112
20 June 17		Seepage (1024)		Met. cplx.	6	17·6		6·55	−0·005
21 Apr. 8		Seepage (1009)		Met. cplx.	7·1	20		7·15	+0·057
22 Apr. 10	12th level (1620)	Drain (XII-16)			2·7	20		8·05	−0·038
23 Apr. 9		Seepage (XII-15)		Met. cplx.	1·1	23·4		7·80	−0·089
24 Apr. 10		Seepage (Hrj-2)		Met. cplx.	0·00	21·2		6·80	−0·031
25 Apr. 9		Drain (XII-03)			3·65	19·8		8·10	−0·012
26 Apr. 9		Drain (XII-13)			3·65	20·8		7·10	−0·095
27 June 17	Drilling on 12th level	Spring (Evangelist)	740	Granite	26	25	6·9	6·75	−0·010
28 *June 16*		Drill hole (C-1)	787	Granite	34·9	29	8·9	6·80	+0·064
29 Apr. 9		Drill hole (HG-2)	728	Granite	8	29·8	20·0	6·80	−0·103
30 Apr. 9		Drill hole (HG-1)	501	Granite	570	29·8	20·0	6·75	+0·063
31 June 16		Shaft sinking (Curie)	114	Granite	25	26	?	6·90	−0·030
32 Apr. 7	5th level	Drill hole (HE 2/5)	1320	Granite	3	20·8		7·55	+0·060

Met. cplx.—Metamorphic complex

COMPUTATIONS

A computer program was written and used to carry out all the computations. The degree of saturation in the water–air, water–calcite, water–ferric hydroxide, and water–pyrite systems can be expressed by the saturation indices (I) defined as log (Q/K), where Q is the proper quotient of a reaction and K is the equilibrium constant of the reaction. The equations used are:

$$I_a = \log[(a_{\mathrm{HCO_3^-}} \times 10^{-\mathrm{pH}}/10^{-3.5})/K_1K_2]$$

$$I_c = \log[(a_{\mathrm{Ca^{2+}}} \times a_{\mathrm{CO_3^{2-}}})/K_4]$$

$$I_h = \log a_{\mathrm{Fe^{2+}}} + 3\,\mathrm{pH} - [(E_{15}{}^0 - \mathrm{Eh})\,\mathscr{F}/2{\cdot}303\,RT]$$

$$I_p = \log a_{\mathrm{Fe^{2+}}} + 2\log a_{\mathrm{SO_4^{2-}}} - 16\,\mathrm{pH} - [(\mathrm{Eh} - \mathrm{E}^{\circ}{}_{16})\,14\,\mathscr{F}/2{\cdot}303\,RT]$$

$$P_{\mathrm{CO_2}} = (K_1K_2 \times 10^{\mathrm{pH}})/a_{\mathrm{HCO_3^-}}$$

$$P_{\mathrm{H_2}} = -2\,\mathrm{pH} - (4{\cdot}606\,\mathscr{F} \times \mathrm{Eh})/RT$$

where R is the gas constant, T is the temperature degrees Kelvin, $\mathscr{F}$ is the Faraday constant. The equilibrium constants and standard potentials are summarized in Table 3. The numerator of the quotient Q is the product of the chemical products each raised to the power of its stoichiometric coefficient and the denominator is the product of the reactants each raised to the power of its stoichiometric coefficient. Since Q is calculated for particular Eh–pH conditions, the saturation indices are linear functions of the free energies of the reactions:

$$I = \Delta F/2{\cdot}303\,RT.$$

If a saturation index is positive the water is supersaturated; if it is negative the water is unsaturated with respect to the compound considered. A saturation index of zero indicates that the water is just saturated (in equilibrium) with respect to this compound. The activities, which were used for the calculation of Q's, were computed by multiplying analytically determined concentrations and activity coefficients. The activity coefficients were obtained from the Debye–Hückel expression (Garrels, 1960, p. 27). Temperature effects on the activity coefficients were considered using regression curves for the terms A and B as:

$$\mathrm{A} = 0{\cdot}4883 + 7{\cdot}380 \times 10^{-4}\,t + 2{\cdot}723 \times 10^{-6}\,t^2,$$

$$\mathrm{B} = 0{\cdot}3241 + 1{\cdot}591 \times 10^{-4}\,t + 4{\cdot}470 \times 10^{-8}\,t^2.$$

Temperatures were also considered in calculating the equilibrium constants and standard potentials (Table 3). The changes in total pressure were neglected and all the calculations are for one atmosphere.

Equations 1 and 2 (Table 3) were used for solving the carbonate equilibria in the water–air system. The carbon dioxide partial pressure of the earth's atmosphere was taken as 3×10^{-4} atm. Utilizing the mass action law the saturation index with respect to the normal earth's atmosphere I_a was calculated. The equilibrium partial pressures of $\mathrm{CO_2}$ also were evaluated.

Equations 3 and 4 (Table 3) express equilibrium in the water–calcite system within pH limits ascertained in the field. The equilibrium activity of $\mathrm{CO_3^{2-}}$ and the saturation index I_c can be calculated using these reactions.

Half-cell 15 (Table 3) corresponds to the water–ferric hydroxide system. Using the Nernst equation for redox potential the saturation index of the system (I_h) was established. Half-cell 16 (Table 3) expresses the reaction of the water and pyrite under Eh–pH conditions where sulfate is a product. Such conditions were found in the field study. $\mathrm{H_2S}$ was not detected in any sample. The saturation index I_p was calculated for this reaction using Nernst's equation. Where the concentration of iron was at the lower limit of analytical accuracy, a value of 0·05 mg/l was input to computer. All the results based on the value are closed in brackets (Table 5) and they are not included in diagrams (Figs. 4 and 5).

Table 3. Equilibrium constants (pK = —log K) and standard potentials (E° in volts) utilized in calculating saturation indices

Equation	Reaction	Temperature dependence or value for 25°C	Source
1	$CO_{2(g)} + H_2O_{(l)} = H_2CO_{3(aq)}$	$pK_1 = 1{\cdot}113 + 1{\cdot}672 \times 10^{-2}\,t - 1{\cdot}051 \times 10^{-4}\,t^2$	HARNED and DAVIS (1943)
2	$H_2CO_{3(aq)} = HCO^-_{3(aq)} + H^+_{(aq)}$	$pK_2 = 6{\cdot}576 - 1{\cdot}250 \times 10^{-2}\,t + 1{\cdot}405 \times 10^{-4}\,t^2$	GARRELS (1960, p. 58)
3	$HCO^-_{3(aq)} = CO^{2-}_{3(aq)} + H^+_{(aq)}$	$pK_3 = 10{\cdot}63 - 1{\cdot}537 \times 10^{-2}\,t + 1{\cdot}335 \times 10^{-4}\,t^4$	
4	$CaCO_{3(c)} = Ca^{2+}_{(aq)} + CO^{2-}_{3(aq)}$	$pK_4 = 8{\cdot}017 + 1{\cdot}402 \times 10^{-2}\,t + 4{\cdot}405 \times 10^{-5}\,t^2$	
5	$CaHCO^+_{3(aq)} = Ca^{2+}_{(aq)} + HCO^-_{3(aq)}$	$pK_5 = 1{\cdot}26$	GARRELS and THOMPSON (1962)
6	$CaCO_{3(aq)} = Ca^{2+}_{(aq)} + CO^{2-}_{3(aq)}$	$pK_6 = 3{\cdot}2$	
7	$CaSO_{4(aq)} = Ca^{2+}_{(aq)} + SO^{2-}_{4(aq)}$	$pK_7 = 2{\cdot}31$	
8	$MgHCO^+_{3(aq)} = Mg^{2+}_{(aq)}\ HCO^-_{3(aq)}$	$pK_8 = 1{\cdot}16$	
9	$MgCO_{3(aq)} = Mg^{2+}_{(aq)} + CO^{2-}_{3(aq)}$	$pK_9 = 3{\cdot}4$	
10	$MgSO_{4(aq)} = Mg^{2+}_{(aq)} + SO^{2-}_{4(aq)}$	$pK_{10} = 2{\cdot}36$	
11	$NaHCO_{3(aq)} = Na^+_{(aq)} + HCO^-_{3(aq)}$	$pK_{11} = -0{\cdot}25$	
12	$NaCO^-_{3(aq)} = Na^+_{(aq)} + CO^{2-}_{3(aq)}$	$pK_{12} = 1{\cdot}27$	
13	$NaSO^-_{4(aq)} = Na^+_{(aq)} + SO^{2-}_{4(aq)}$	$pK_{13} = 0{\cdot}72$	
14	$KSO^-_{4(aq)} = K^+_{(aq)} + SO^{2-}_{4(ap)}$	$pK_{14} = 0{\cdot}96$	
15	$Fe^{2+}_{(aq)} + 3\,H_2O_{(l)} = Fe(OH)_{3(c)} + 3\,H^+_{(aq)} + e^-$	$E^\circ_{15} = (28{\cdot}95 - (t + 273{\cdot}15) \times 0{\cdot}01556)/23{\cdot}062$	Data on ΔH° and S° from LATIMER (1952)
16	$FeS_{2(c)} + 8\,H_2O_{(l)} = 2\,SO^{2-}_{4(aq)} + Fe^{2+}_{(aq)} + 16\,H^+_{(aq)} + 14\,e^-$	$E^\circ_{16} = (134{\cdot}26 - (t + 273{\cdot}15) \times 0{\cdot}05315)/(14 \times 23{\cdot}062)$	
17	$2\,Fe^{2+}_{(aq)} + 3\,H_2O_{(l)} = Fe_2O_{3(c)} + 6\,H^+_{(aq)} + 2\,e^-$	$E^\circ_{17} = 0{\cdot}728$	GARRELS (1960)

The state of substance: c—crystalline, l—liquid, g—gas, aq—in aqueous solution.

Table 4. Some chemical data on subsurface water from Jáchymov mining district

Sample	Ionic strength (Complexing not considered)	Total dissolved solids (mg/l)	Molarities of ions used for equilibrium calculations					
			Na^+	Ca^{2+}	Fe^{2+}	HCO_3^-	CO_3^{2-}	SO_4^{2-}
1	0·00100	44·0	$1{\cdot}30 \times 10^{-4}$	$2{\cdot}00 \times 10^{-4}$	T	$1{\cdot}00 \times 10^{-4}$	$3{\cdot}40 \times 10^{-9}$	$1{\cdot}93 \times 10^{-4}$
2	0·00128	53·8	$8{\cdot}70 \times 10^{-5}$	$1{\cdot}65 \times 10^{-4}$	$5{\cdot}37 \times 10^{-6}$	$3{\cdot}00 \times 10^{-4}$	$1{\cdot}57 \times 10^{-8}$	$1{\cdot}62 \times 10^{-4}$
3	0·00159	71·0	$4{\cdot}35 \times 10^{-5}$	$1{\cdot}50 \times 10^{-4}$	$1{\cdot}45 \times 10^{-5}$	$5{\cdot}51 \times 10^{-4}$	$2{\cdot}64 \times 10^{-7}$	$1{\cdot}33 \times 10^{-4}$
4	0·00163	75·5	$3{\cdot}26 \times 10^{-5}$	$4{\cdot}24 \times 10^{-4}$	$1{\cdot}33 \times 10^{-5}$	$6{\cdot}39 \times 10^{-4}$	$4{\cdot}50 \times 10^{-7}$	$1{\cdot}33 \times 10^{-4}$
5	0·00200	87·8	$2{\cdot}83 \times 10^{-4}$	$3{\cdot}24 \times 10^{-4}$	$2{\cdot}15 \times 10^{-6}$	$2{\cdot}00 \times 10^{-4}$	$3{\cdot}56 \times 10^{-9}$	$1{\cdot}88 \times 10^{-4}$
6	0·00212	81·9	$3{\cdot}70 \times 10^{-4}$	$2{\cdot}74 \times 10^{-4}$	T	$2{\cdot}39 \times 10^{-4}$	$1{\cdot}49 \times 10^{-7}$	$3{\cdot}87 \times 10^{-4}$
7	0·00257	96·7	$1{\cdot}96 \times 10^{-4}$	$2{\cdot}89 \times 10^{-4}$	$3{\cdot}40 \times 10^{-5}$	$3{\cdot}00 \times 10^{-4}$	$1{\cdot}38 \times 10^{-8}$	$4{\cdot}84 \times 10^{-4}$
8	0·00299	146·9	$1{\cdot}09 \times 10^{-4}$	$5{\cdot}24 \times 10^{-4}$	$7{\cdot}88 \times 10^{-5}$	$1{\cdot}40 \times 10^{-3}$	$4{\cdot}66 \times 10^{-7}$	$2{\cdot}06 \times 10^{-4}$
9	0·00311	136·6	$7{\cdot}83 \times 10^{-5}$	$7{\cdot}51 \times 10^{-4}$	T	$1{\cdot}00 \times 10^{-3}$	$8{\cdot}00 \times 10^{-7}$	$3{\cdot}77 \times 10^{-4}$
10	0·00353	195·7	$8{\cdot}26 \times 10^{-4}$	$6{\cdot}26 \times 10^{-4}$	$5{\cdot}91 \times 10^{-6}$	$2{\cdot}10 \times 10^{-3}$	$1{\cdot}26 \times 10^{-6}$	$1{\cdot}58 \times 10^{-4}$
11	0·00467	236·5	$3{\cdot}26 \times 10^{-4}$	$7{\cdot}76 \times 10^{-4}$	T	$2{\cdot}60 \times 10^{-3}$	$1{\cdot}28 \times 10^{-6}$	$1{\cdot}62 \times 10^{-4}$
12	0·0100	397·5	$4{\cdot}35 \times 10^{-4}$	$1{\cdot}65 \times 10^{-3}$	T	$1{\cdot}60 \times 10^{-3}$	$2{\cdot}84 \times 10^{-6}$	$1{\cdot}76 \times 10^{-3}$
13	0·0151	552·5	$4{\cdot}35 \times 10^{-4}$	$2{\cdot}30 \times 10^{-3}$	$1{\cdot}25 \times 10^{-6}$	$1{\cdot}70 \times 10^{-3}$	$5{\cdot}12 \times 10^{-7}$	$3{\cdot}16 \times 10^{-3}$
14	0·0254	924·0	$1{\cdot}02 \times 10^{-3}$	$4{\cdot}10 \times 10^{-3}$	T	$1{\cdot}90 \times 10^{-3}$	$3{\cdot}22 \times 10^{-6}$	$5{\cdot}69 \times 10^{-3}$
15	0·0471	1634	$1{\cdot}91 \times 10^{-3}$	$6{\cdot}69 \times 10^{-3}$	$6{\cdot}63 \times 10^{-6}$	$1{\cdot}85 \times 10^{-3}$	$2{\cdot}48 \times 10^{-6}$	$1{\cdot}12 \times 10^{-2}$
16	0·0610	2230	$3{\cdot}70 \times 10^{-3}$	$1{\cdot}03 \times 10^{-2}$	$5{\cdot}01 \times 10^{-5}$	$4{\cdot}50 \times 10^{-3}$	$7{\cdot}21 \times 10^{-6}$	$1{\cdot}40 \times 10^{-2}$
17	0·0827	2876	$2{\cdot}17 \times 10^{-3}$	$1{\cdot}33 \times 10^{-2}$	T	$3{\cdot}90 \times 10^{-3}$	$1{\cdot}04 \times 10^{-5}$	$1{\cdot}93 \times 10^{-2}$
18	0·00767	521·5	$4{\cdot}35 \times 10^{-3}$	$8{\cdot}11 \times 10^{-4}$	T	$5{\cdot}90 \times 10^{-3}$	$5{\cdot}83 \times 10^{-6}$	$1{\cdot}12 \times 10^{-4}$
19	0·00787	546·8	$4{\cdot}57 \times 10^{-3}$	$8{\cdot}01 \times 10^{-4}$	T	$6{\cdot}20 \times 10^{-3}$	$1{\cdot}03 \times 10^{-5}$	$1{\cdot}58 \times 10^{-4}$
20	0·0204	752·7	$9{\cdot}57 \times 10^{-4}$	$2{\cdot}99 \times 10^{-3}$	T	$2{\cdot}35 \times 10^{-3}$	$1{\cdot}85 \times 10^{-6}$	$4{\cdot}11 \times 10^{-3}$
21	0·0395	1440	$2{\cdot}22 \times 10^{-3}$	$6{\cdot}40 \times 10^{-3}$	T	$3{\cdot}00 \times 10^{-3}$	$1{\cdot}25 \times 10^{-5}$	$8{\cdot}98 \times 10^{-3}$
22	0·00837	551·8	$4{\cdot}78 \times 10^{-3}$	$6{\cdot}51 \times 10^{-4}$	T	$5{\cdot}74 \times 10^{-3}$	$6{\cdot}57 \times 10^{-5}$	$4{\cdot}67 \times 10^{-4}$
23	0·00921	584·3	$4{\cdot}57 \times 10^{-3}$	$9{\cdot}51 \times 10^{-4}$	T	$6{\cdot}03 \times 10^{-3}$	$4{\cdot}61 \times 10^{-5}$	$5{\cdot}65 \times 10^{-4}$
24	0·0102	424·6	$4{\cdot}39 \times 10^{-4}$	$1{\cdot}85 \times 10^{-3}$	T	$2{\cdot}38 \times 10^{-3}$	$2{\cdot}54 \times 10^{-6}$	$1{\cdot}63 \times 10^{-3}$
25	0·0222	933·0	$3{\cdot}61 \times 10^{-3}$	$3{\cdot}28 \times 10^{-3}$	T	$3{\cdot}97 \times 10^{-3}$	$1{\cdot}02 \times 10^{-4}$	$4{\cdot}49 \times 10^{-3}$
26	0·0347	1325	$3{\cdot}83 \times 10^{-3}$	$5{\cdot}42 \times 10^{-3}$	T	$2{\cdot}98 \times 10^{-3}$	$9{\cdot}89 \times 10^{-6}$	$7{\cdot}86 \times 10^{-3}$
27	0·00795	575·7	$5{\cdot}43 \times 10^{-3}$	$5{\cdot}84 \times 10^{-4}$	$2{\cdot}51 \times 10^{-5}$	$6{\cdot}55 \times 10^{-3}$	$3{\cdot}80 \times 10^{-6}$	$8{\cdot}54 \times 10^{-5}$
28	0·00827	612·8	$5{\cdot}67 \times 10^{-3}$	$5{\cdot}84 \times 10^{-4}$	$8{\cdot}42 \times 10^{-6}$	$6{\cdot}92 \times 10^{-3}$	$4{\cdot}61 \times 10^{-6}$	$1{\cdot}24 \times 10^{-4}$
29	0·00855	630·7	$5{\cdot}74 \times 10^{-3}$	$5{\cdot}09 \times 10^{-4}$	$3{\cdot}04 \times 10^{-5}$	$7{\cdot}20 \times 10^{-3}$	$5{\cdot}00 \times 10^{-6}$	$1{\cdot}80 \times 10^{-4}$
30	0·00895	648·7	$6{\cdot}11 \times 10^{-3}$	$5{\cdot}89 \times 10^{-4}$	$6{\cdot}63 \times 10^{-6}$	$7{\cdot}24 \times 10^{-3}$	$4{\cdot}67 \times 10^{-6}$	$1{\cdot}62 \times 10^{-4}$
31	0·00917	663·2	$6{\cdot}09 \times 10^{-3}$	$6{\cdot}66 \times 10^{-4}$	$2{\cdot}08 \times 10^{-5}$	$7{\cdot}49 \times 10^{-3}$	$6{\cdot}61 \times 10^{-6}$	$1{\cdot}42 \times 10^{-4}$
32	0·00409	229·2	$1{\cdot}15 \times 10^{-3}$	$6{\cdot}76 \times 10^{-4}$	$1{\cdot}33 \times 10^{-5}$	$2{\cdot}20 \times 10^{-3}$	$7{\cdot}47 \times 10^{-6}$	$2{\cdot}65 \times 10^{-4}$

T—traces (concentration less than 1×10^{-6} mole).

Molarity of CO_3^{2-} is calculated using molarity of HCO_3^- and pH; complexing is considered.

Table 5. Effect of complexing on ionic strength and molarities of major ions in water

Sample	Ionic strength (Complexes considered)	% uncomplexed ions in water				
		Na^+	Ca^{2+}	HCO_3^-	CO_3^{2-}	SO_4^{2-}
1	0·00098	99·9	97·0	99·7	80·8	97·0
2	0·00125	99·9	97·3	99·6	67·6	95·1
3	0·00155	99·9	97·4	99·4	59·1	93·5
4	0·00158	99·9	97·3	99·3	64·4	93·6
5	0·00195	99·9	97·3	99·3	60·7	93·2
6	0·00202	99·8	94·9	99·4	61·7	93·6
7	0·00242	99·8	93·9	99·3	56·6	92·5
8	0·00289	99·9	95·7	99·0	52·8	90·8
9	0·00293	99·8	94·5	98·8	52·5	90·1
10	0·00342	99·8	95·5	98·9	52·0	90·2
11	0·00449	99·8	95·1	98·4	39·9	85·9
12	0·00865	99·4	86·2	97·5	33·1	81·5
13	0·0122	99·1	81·1	96·7	28·1	78·0
14	0·0193	98·6	75·4	95·5	24·4	74·0
15	0·0326	97·9	68·7	93·4	19·0	68·0
16	0·0418	97·6	66·7	92·2	18·6	66·5
17	0·0529	97·1	64·3	90·4	15·6	62·2
18	0·00747	99·7	92·1	98·6	51·3	89·3
19	0·00766	99·7	91·4	98·7	53·8	90·0
20	0·0161	98·9	79·0	95·9	24·8	75·0
21	0·0285	98·0	70·8	94·0	21·3	70·3
22	0·00807	99·6	88·7	98·8	53·2	90·2
23	0·00879	99·5	88·4	98·4	48·6	88·4
24	0·00887	99·4	86·5	97·3	33·1	81·2
25	0·0180	98·7	76·5	96·3	29·2	77·9
26	0·0261	98·3	71·9	94·8	24·1	73·2
27	0·00780	99·7	91·7	98·9	58·9	91·5
28	0·00812	99·6	91·0	99·0	62·5	92·2
29	0·00837	99·6	90·4	99·0	60·8	92·0
30	0·00875	99·6	90·6	98·9	58·4	91·3
31	0·00896	99·6	90·5	98·8	56·8	90·7
32	0·00395	99·8	94·2	98·9	53·8	90·6

Chemical reactions in the water–rock–air system are affected by the complexing of ions in aqueous solution. Therefore, the distribution of complexes $NaHCO_{3(aq)}$, $NaCO^-_{3(aq)}$, $NaSO^-_{4(aq)}$, $KSO^-_{4(aq)}$, $CaHCO^+_{3(aq)}$, $CaCO_{3(aq)}$, $CaSO_{4(aq)}$, $MgHCO_3^+$, $MgCO_{3(aq)}$, and $MgSO_{4(aq)}$ was calculated for all the water samples from Jachymov district. The program for computation of the distribution was written according to the procedure suggested by GARRELS and THOMPSON (1962, p. 62). Several successive approximations were carried out by computer. The ionic strength of water was calculated after each approximation taking into account the molarities of the complexes. The approximation procedure was terminated by a condition that the ratio of the last ionic strength and the previous ionic strength was within the limits of 0·995 and 1·005. The effect of complexing on activity coefficients was considered. The last value of ionic strength was used for the calculation of activity coefficients from the Debye–Hückel equation. The dissociation constants of the complexes at 25°C are summarized in Table 3. The activity coefficients of uncharged species were assumed to be unity in the solution of low ionic strength. The activity coefficients of singly charged species were considered to be the same as that of HCO_3^-. The chloride complexes of ferric iron can be neglected owing to the low chloride concentrations (BARNES and BACK, 1964, p. 443).

The ionic strength disregarding complexing is reported in Table 2, the ionic strength considering both complexes and the free major ions are summarized in Table 5. The output of the computer gives the saturation indices both including and disregarding complexing (Table 6).

Table 6. Concentration of Na$^+$, log P_{H_2}, P_{CO_2}, and saturation indices of water–air, water–calcite, water–ferric hydroxide, and water–pyrite systems

Sample	Na$^+$ (mg/l)	log P_{H_2}	P_{CO_2} (atm)	Complexes not considered I_a	I_c	I_h	I_p	Complexes considered I_a	I_c	I_p
1	3·0	−26·3	6·47 × 10^{-3}	1·31	−4·26	(−0·24)	(−118·0)	1·31	−4·27	(−118·0)
2	2·0	−37·9	1·33 × 10^{-2}	1·62	−3·79	+6·41	−196·8	1·62	−3·81	−196·9
3	1·0	−31·4	3·06 × 10^{-3}	0·99	−2·68	+5·38	−152·7	0·98	−2·69	−152·7
4	0·75	−34·0	2·28 × 10^{-3}	0·86	−1·91	+7·17	−171·8	0·86	−1·93	−171·9
5	6·5	−26·8	3·19 × 10^{-2}	2·00	−4·19	−0·48	−119·3	2·00	−4·21	−199·3
6	8·5	−29·3	1·06 × 10^{-3}	0·53	−2·67	(+3·41)	(−139·3)	0·52	−2·68	(−139·4)
7	4·5	−27·7	1·85 × 10^{-2}	1·77	−3·74	−1·75	−123·2	1·76	−3·76	−123·2
8	2·5	−26·7	1·47 × 10^{-2}	1·67	−1·85	+3·77	−120·7	1·66	−1·93	−120·8
9	1·8	−29·8	3·89 × 10^{-3}	1·09	−1·60	(+3·70)	(−143·0)	1·09	−1·62	(−143·1)
10	19·0	−19·5	1·91 × 10^{-2}	1·78	−1·32	−0·18	−74·3	1·78	−1·34	−74·3
11	7·5	−21·0	5·81 × 10^{-2}	2·26	−1·58	(−1·13)	(−85·2)	2·26	−1·60	(−85·3)
12	10·0	−22·8	6·54 × 10^{-3}	1·32	−0·93	(+0·73)	(−95·2)	1·31	−0·99	(−95·3)
13	10·0	−22·1	5·66 × 10^{-2}	2·25	−1·61	−1·01	−89·0	2·24	−1·69	−89·2
14	23·5	−18·8	1·18 × 10^{-2}	1·57	−0·74	(−1·68)	(−66·6)	1·56	−0·85	(−66·8)
15	44·0	−17·4	1·97 × 10^{-2}	1·80	−0·86	−2·02	−55·1	1·78	−1·00	−55·4
16	85·0	−23·7	4·99 × 10^{-2}	2·20	−0·21	+2·32	−99·4	2·18	−0·33	−99·7
17	50·0	−16·0	2·92 × 10^{-2}	1·97	−0·10	(−3·14)	(−47·1)	1·94	−0·27	(−47·4)
18	100·0	−19·5	3·82 × 10^{-2}	2·08	−0·61	(−0·56)	(−77·0)	2·08	−0·65	(−77·1)
19	105·0	−18·2	2·18 × 10^{-2}	1·84	−0·40	(−0·87)	(−67·8)	1·83	−0·43	(−67·9)
20	22·0	−12·9	3·43 × 10^{-2}	2·04	−1·04	(−5·07)	(−26·0)	2·02	−1·15	(−26·2)
21	51·0	−16·2	1·09 × 10^{-2}	1·54	−0·03	(−2·09)	(−50·5)	1·52	−0·18	(−50·8)
22	110·0	−14·8	2·86 × 10^{-3}	0·96	+0·33	(−0·90)	(−44·3)	0·95	+0·27	(−44·4)
23	105·0	−12·6	5·56 × 10^{-3}	1·25	+0·33	(−2·25)	(−29·3)	1·24	+0·28	(−29·4)
24	10·0	−12·5	2·12 × 10^{-2}	1·83	−0·84	(−4·45)	(−25·5)	1·82	−0·90	(−25·4)
25	83·0	−16·6	1·67 × 10^{-3}	0·72	+0·82	(+0·03)	(−55·4)	0·71	+0·71	(−55·6)
26	88·0	−10·9	1·24 × 10^{-2}	1·59	−0·12	(−4·77)	(−13·7)	1·58	−0·25	(−13·9)
27	125·0	−13·2	6·96 × 10^{-2}	2·34	−0·85	−2·49	−32·0	2·34	−0·89	−32·1
28	130·5	−15·7	6·92 × 10^{-2}	2·34	−0·70	−1·31	−51·4	2·34	−0·76	−51·5
29	132·0	−10·2	7·28 × 10^{-2}	2·36	−0·74	−3·47	−12·1	2·36	−0·79	−12·2
30	140·5	−15·6	8·19 × 10^{-2}	2·41	−0·72	−1·53	−50·8	2·41	−0·78	−50·8
31	140·0	−12·8	5·68 × 10^{-2}	2·25	−0·58	−2·41	−29·8	2·25	−0·63	−29·9
32	26·5	−17·2	3·59 × 10^{-3}	1·06	−0·50	+0·57	−59·6	1·05	−0·53	−59·7

DISCUSSION

The water samples from the various depths and rock environments differ in their chemical compositions, and in the degrees of saturation and the oxidation–reduction states. The concentration of calcium and sulfate increase as water penetrates through the metamorphic complex that is affected by mining activity. The calcium and sulfate contents are low in water from the unmined granitic substratum. The sodium concentration increases with the depth. The highest concentration was found in water from the granitic substratum. The only linear dependence that is valid for all samples from both the metamorphic complex and the granite was established between sodium concentration and hydrogen partial pressure calculated from the half-cell $H^+ + e^- = \frac{1}{2}H_2$ using Nernst's equation for redox potential. The increase of partial hydrogen pressure versus the increase of analytical concentration of sodium goes in accordance with the regression line $\log P_{H_2} = -30{\cdot}20 + 8{\cdot}06 \log c_{Na^+}$; the coefficient of correlation is $+0{\cdot}960$ (PAČES, 1966, p. 118). It may be supposed that the longer and more completely the water reacted with the sodium feldspars of the metamorphic complex as well as granitic rocks, the higher the concentration of sodium might be expected. Simultaneously, a reduction of the natural aqueous solutions took place according to the half-cell $H^+ + e^+ = \frac{1}{2}H_2$. Therefore, the sodium concentration is chosen as the measure of time and intensity of the physico–chemical interaction in the water–rock system containing sodium feldspars and the hydrogen partial pressure as the measure of the oxidation–reduction state of water.

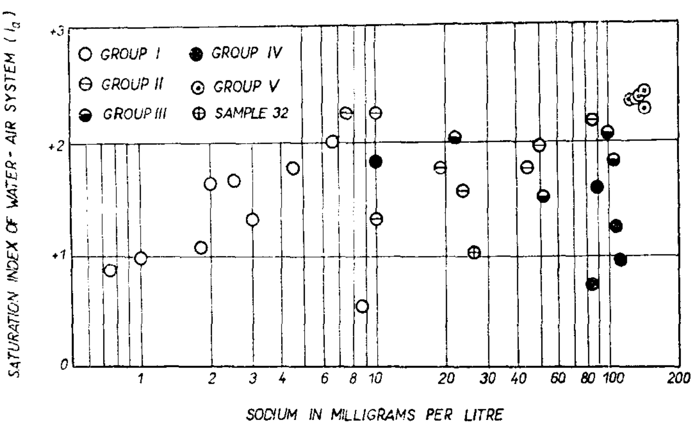

Fig. 2. Relation of saturation indices of water–P_{CO_2} in normal earth's atmosphere to sodium concentration.

Figures 2, 3, 4 and 5 represent the variations of saturation indices with variation of sodium concentrations.

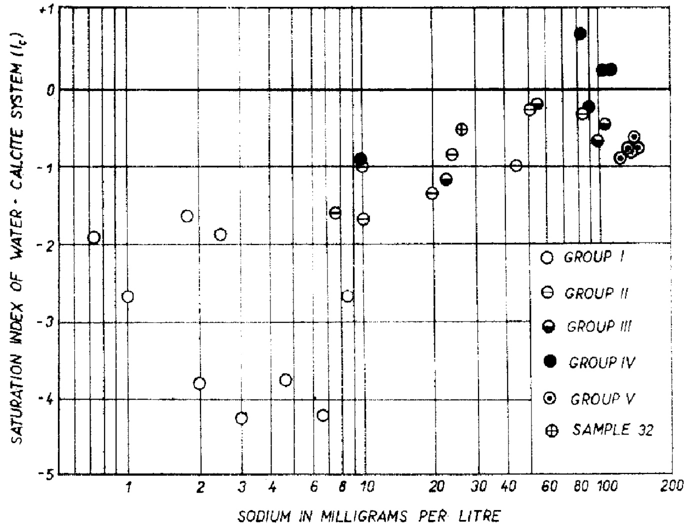

Fig. 3. Relation of saturation indices of water–calcite system to sodium concentration.

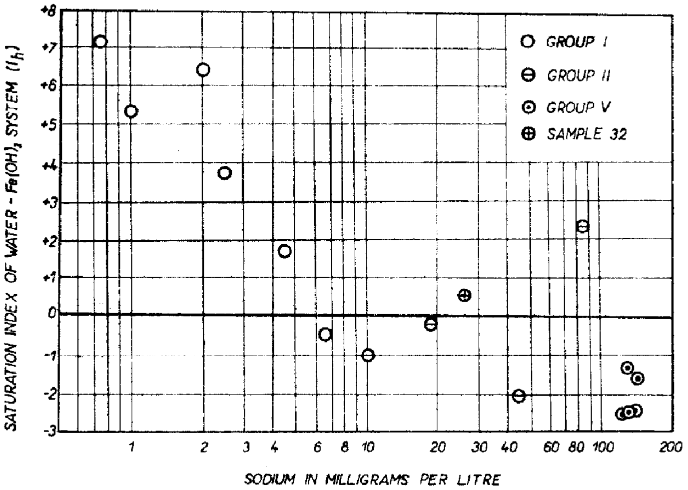

Fig. 4. Relation of saturation indices of water–ferric hydroxide system to sodium concentration.

The water samples can be sorted into five groups according to the depth of discharge, sodium concentration, hydrogen partial pressure, and the degree of saturation with respect to the carbon dioxide partial pressure in air, to calcite, ferric hydroxide and pyrite.

Group I (*Samples* 1 *to* 9)

The surface springs of water from outcrops and screes of the metamorphic complex and granite, and from the soil zone, are included in this group. The water was in contact with soil and rocks for only a short time and was very low in sodium concentration. The water samples were the most unsaturated with respect to calcite and slightly or moderately supersaturated with respect to atmospheric CO_2. The calculated equilibrium P_{CO_2} has limits from $1{\cdot}06 \times 10^{-3}$ to $3{\cdot}19 \times 10^{-2}$ atm. The values are about 10–100 times higher than P_{CO_2} in air which corresponds to the values given for the soil atmosphere (MOHRE, 1938). The great variability of the saturation index of the water–air system may indicate complex controls on the P_{CO_2} of water, or the controls may be only partially effective, being modified by flow relations. The samples which have an iron concentration higher than 0·05 mg/l are the most strongly unsaturated with respect to pyrite and supersaturated with respect to ferric hydroxide. Ferric solids were precipitated from most of the springs in line with the saturation indices. The P_{H_2} was the lowest of all groups and indicated the high oxidizing capability of water. The values of P_{H_2} correspond to the weathering environment of sulfide ore bodies as defined by SATO (1960, p. 957).

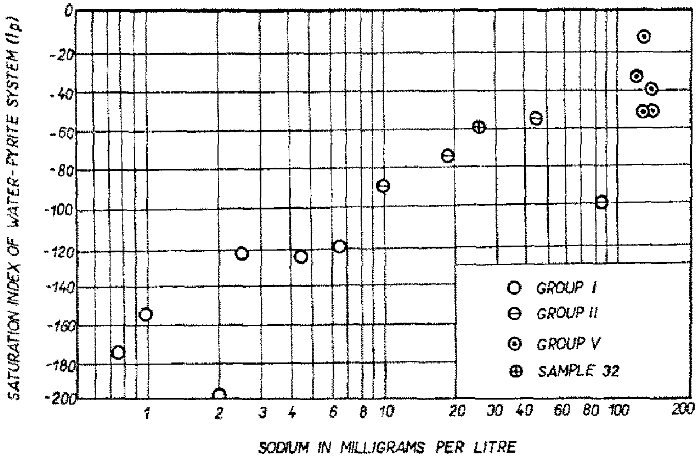

Fig. 5. Relation of saturation indices of water–pyrite system to sodium concentration.

Group II (*Samples* 10 *to* 17)

Water samples of this group were collected on the 5th level of the Svornost mine, in the metamorphic complex. The total dissolved solids range from 0·2 to

3 g/l. The sulfate and calcium predominate especially in the waters with the highest content of dissolved solids. The sodium concentration ranges from 7·5 to 85 mg/l. As the total dissolved solids and sodium concentrations increase, equilibrium with respect to calcite is approached. The supersaturation with respect to P_{CO_2} of the earth's atmosphere is higher and the equilibrium P_{CO_2} is in a narrower range ($6{\cdot}54 \times 10^{-3}$ to $5{\cdot}81 \times 10^{-2}$ atm) as compared to group I. The degree of saturation with respect to $Fe(OH)_3$ is often close to the equilibrium. The precipitation of ferric solids occurred in many underground springs and seepages. The samples were unsaturated with respect to pyrite.

The content of sulfate and P_{H_2} are increased in the waters of group II as compared to the waters of group I. In other words, the oxidizing capability of water decreases as sulfate content increases. The dependence of the sulfate concentration on P_{H_2} in the transitional secondary zone, as defined by SATO (1960), is given by the equation of the regression line $\log c_{SO_4^{2-}} = -4{\cdot}88 + 0{\cdot}124 \log P_{H_2}$; the coefficient of correlation is $+0{\cdot}829$ (PAČES, 1966).

Group III (*Samples* 18 *to* 21)

There are four samples from the 10th level included in this group. Samples 18 and 19 resemble the samples from subjacent granite (group V), samples 20 and 21 resemble the waters from the 5th level (group II) in chemical composition. The water represented by samples 18 and 19 probably penetrated into the metamorphic complex from the subjacent granite. The maximum total pressure (20 atm) that was measured in the drill holes on the 12th level supports this explanation. The saturation indices of the water–air system of all these samples correspond with the waters from the 5th level. The equilibrium P_{CO_2} ranges from $1{\cdot}09 \times 10^{-2}$ to $3{\cdot}82 \times 10^{-2}$ atm. Samples 18, 19, and 20 are unsaturated with respect to calcite; sample 21 is almost saturated. If complexes are considered then sample 21 is also unsaturated. The P_{H_2} of all four samples corresponds to the higher values of group II and differs from the values of P_{H_2} that were calculated for water from the subjacent granite (group V).

Group IV (*Samples* 22 *to* 26)

Water was collected from drains and seepages on the 12th level. Samples 22 and 23 have their origin from the subjacent granite, samples 24, 25 and 26 resemble the water from the metamorphic complex in chemical composition. The water is near the saturation with respect to calcite and slightly supersaturated with respect to P_{CO_2} of the earth's atmosphere. The equilibrium P_{CO_2} is $1{\cdot}67 \times 10^{-3}$ to $2{\cdot}12 \times 10^{-2}$ atm. The extreme values lie within the range of water from surface springs. The hydrogen partial pressure corresponds to the depth environment of sulfide ore bodies as defined by SATO (1960). The saturation with respect to calcite may be influenced by a contact of water with concrete walls of the drains or by the escape of CO_2 from water. The low supersaturation with respect to air may be due to the reactions with concrete or due to a fast equilibration of water with air. In spite of the fact that the water was for a certain time in contact with air its redox potential is negative.

Group V (*Samples* 27 *to* 31)

Water was trapped by several drill holes in the underlying granitic massif below the 12th level. The rock environment has not been affected by mining. The content of total dissolved solids is moderate, sodium and bicarbonate predominating. The degree of supersaturation with respect to P_{CO_2} of the earth's atmosphere is the highest of all the groups. The equilibrium P_{CO_2} is $5{\cdot}68 \times 10^{-2}$ to $8{\cdot}19 \times 10^{-2}$ atm. Water of group V is moderately unsaturated with respect to calcite. The tendency of the saturation indices with respect to pyrite indicates that the samples of this group approach closest to being in equilibrium with pyrite, however, they are still unsaturated. With respect to ferric hydroxide, the water is also unsaturated. In spite of this, ferric solids precipitate in water that overflows from drill hole HG-2 (Sample 29). The saturation index of the water–hematite system was computed for samples of this group according to equation 16 (Table 3). The water is supersaturated with respect to hematite; the indices range from $+1{\cdot}91$ to $+4{\cdot}08$. The measured Eh of these samples is between the calculated equilibrium potentials of the water–ferric hydroxide system and the water–hematite system in agreement with the observations of BARNES and BACK (1964, p. 445). The P_{H_2} is the highest of all groups and corresponds to the water of the depth environment of sulfide ore bodies.

Only sample 32 is not included in the described groups. This water was tapped by the drill hole HE-2/5 on the 5th level drilled into a granitic block behind a fault striking to the northwest. The water has a transitional character. It is nearly saturated with calcite and only a little supersaturated with respect to the P_{CO_2} of air. The equilibrium P_{CO_2} is $3{\cdot}59 \times 10^{-3}$ atm. The sample is saturated with respect to ferric hydroxide. A higher P_{H_2} and a low concentration of sulfate indicate that the water was not in contact with the rocks affected by mining. These properties and the low concentration of sodium (26·5 mg/l) suggest that the water had penetrated comparatively fast along the fault in the deeper part of rock environment where it was tapped.

The dependence on depth of the physico-chemical characteristics of subsurface waters in the Jáchymov mining district is shown in Fig. 6a,b. The water temperatures rise with depth. The temperatures of waters from the surface springs fluctuate with the temperature of the air. The temperature of the water from the subjacent granitic massif is constant. The total dissolved solids are the lowest in the waters of surface springs that circulate in the shallow weathering zone. The highest content of dissolved solids is in the water with the predominance of calcium and sulfate on the 5th level. The samples of the same chemical type on the 10th and 12th levels are also comparatively high in total dissolved solids. The highest of the total dissolved solids is due to the high content of sulfate ion that is produced by oxidation within the mine working. The sodium concentration increases with depth. The mean value of pH increases from the surface to the 12th level. Simultaneously, the degree of unsaturation with respect to calcite lowers. There are no strongly acid waters in the metamorphic complex in spite of the oxidation of sulfides because the pH is raised by reaction of the water with calcite. The water from granite under the 12th level is lower in pH and is more unsaturated with respect to calcite as compared with the water on the 12th level. The redox potential decreases with depth. SATO (1960) defined three secondary environments of sulfidic ore bodies in terms of Eh

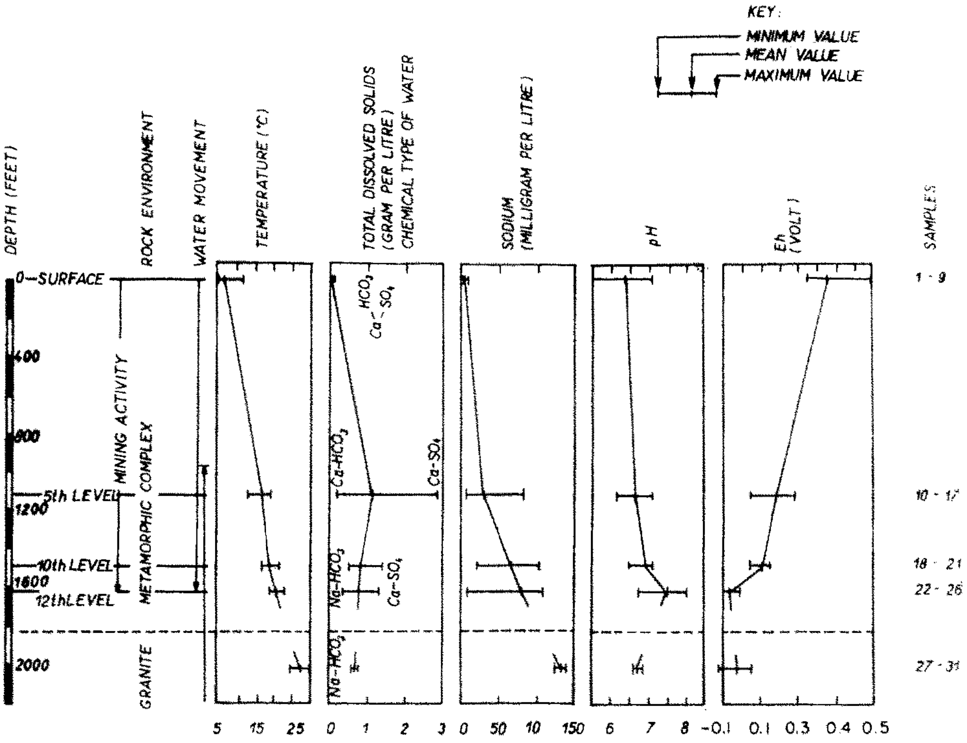

Fig. 6(a)

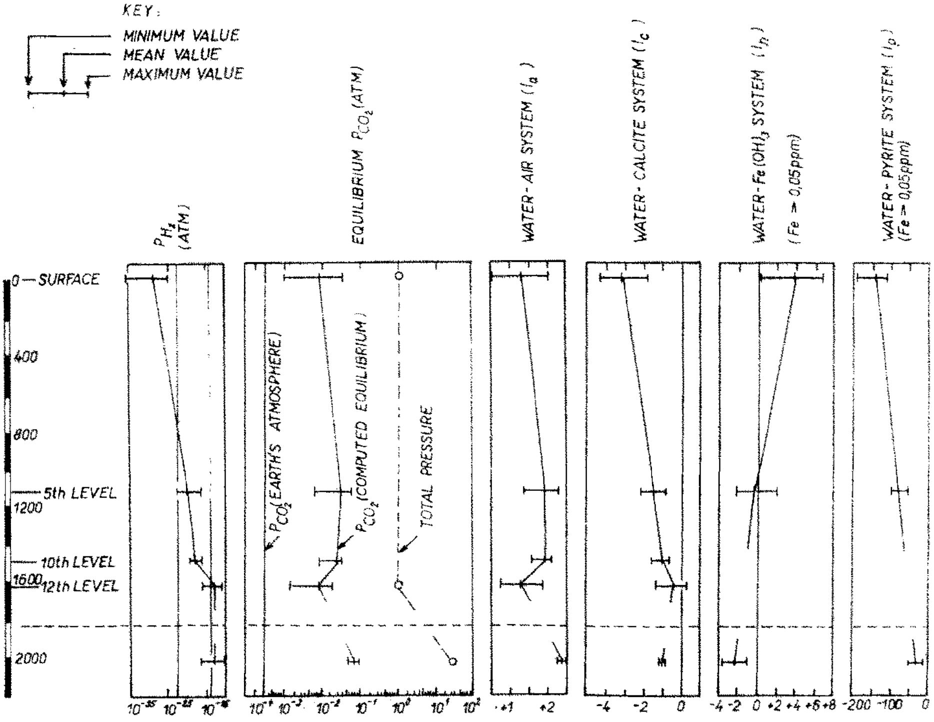

Fig. 6(b)

Fig. 6a, b. Dependence of physico-chemical characteristics of subsurface water in Jáchymov mining district with depth.

and pH. If we express the boundaries between these environments in terms of the hydrogen partial pressure of the water, then the water of weathering environment has a P_{H_2} of 10^{-23} atm or less, the water of the transitional zone is defined by the limits 10^{-23} atm P_{H_2} and 10^{-14} atm P_{H_2}, and the water of the deep environment has a P_{H_2} of 10^{-14} atm or more. Based on the P_{H_2} of water from the Jáchymov mining district, the boundary weathering environment/transitional zone lies between the surface and the 5th level, the boundary transitional zone/deep environment lies at the 12th level, i.e. at the bottom of the mining activity.

The degree of supersaturation with respect to the P_{CO_2} of the earth's atmosphere increases with depth. However, water from the drains on the 12th level is only moderately supersaturated. The equilibrium P_{CO_2} is the lowest in waters both from the surface springs and from the drains on the 12th level. The highest values of equilibrium P_{CO_2} are in water from the underlying granite. With respect to $Fe(OH)_3$ the water has a tendency to be unsaturated as the depth of discharge decreases. The equilibrium of water in the water–$Fe(OH)_3$ system is achieved in the transitional zone. There are some discrepancies between the saturation indices of the system and the precipitation of ferric solids from water (Sample 29). The precipitation from seemingly unsaturated water may be explained by the occurrence of more stable ferric hydroxides and oxides of different structure. The deeper the discharge, the less the water is unsaturated with respect to pyrite. However, the absolute values of the saturation indices are extremely negative even in water from the deep part of granitic massif. This fact suggests that the half-cell 16 is only a hypothetical one and the interaction between water and pyrite involves a more complex mechanism.

The changes of the physico–chemical characteristics with the depth of discharge are discontinuous between water from the metamorphic complex and water from the subjacent granite. Probably the waters from the two environments are of different origin. The two water types do not mix so that the two water bodies are probably hydraulically separated.

SUMMARY

The water samples of the Jáchymov mining district were collected from sources on the surface, the 5th, 10th and 12th levels of the Svornost mine, and from the drill holes drilled from the 12th level into the subjacent granite. There are two chemical types of water in this area: (1) water with a predominance of Ca^{2+} and SO_4^{2-} from the metamorphic cover affected by mining activity, and (2) water with predominance of Na^+ and HCO_3^- from granitic subjacent rocks not affected by mining. Mixing of these types of water was not found and there are in many respects no gradations between the types. Both types are probably hydraulically separated. Not only the chemical composition of the water but also its degree of departure from equilibrium, with respect to P_{CO_2} of the earth's atmosphere, calcite, ferric hydroxide, and pyrite changes with depth of discharge. Generally, the water has a tendency to be supersaturated with respect to P_{CO_2} of air during its penetration through the rock environment. The more intensively or the longer the water reacts with the rocks of the metamorphic complex containing calcite, the closer it approaches equilibrium with respect to calcite. In spite of the longest interaction with granitic rocks, the water is not saturated with calcite probably due to the lack of calcite in the granite. The water slowly approaches equilibrium with respect to pyrite with increasing depth.

Saturation with $Fe(OH)_3$ is attained in the transitional zone; in the weathering zone the water is supersaturated whereas in the deep environment the water is unsaturated. The water body could be zoned according to its redox state as expressed by the partial pressures of hydrogen.

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