Ground water regimes containing country rock minerals in Southern Kuzbass (case study: Narysk-Ostashkin)

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Abstract. The paper describes the calculation results revealing groundwater in equilibrium to carbonates and aluminosilicate minerals of country rocks in Narysk-Ostashkinsk area. It was proved that groundwater is in nonequilibrium to primary (endogenous) minerals in which they dissolve, however are in equilibrium to clays and carbonates which precipitate in the groundwater. The groundwater composition varies.

1. Introduction

There are numerous publications devoted to geochemistry of Kuzbass underground water [1–5]. This issue has been viewed on the basis of the concept proposed by S.L. Shvartsev: water-rock interaction [6]. According to this concept identifying the equilibrium of the groundwater to major minerals is only the beginning in understanding the formation conditions and chemical composition of groundwater. In 2012 and 2014 the investigation embraced Narysk-Ostashkinsk area, Erunakov region, Kemerov Oblast. The research target was to calculate and analyze the thermodynamic equilibrium in the water-rock system based on the data in temperature, pH, chemical composition and country rock composition.

2. Factual information and methods

From 2009 to 2012 41 well were drilled at a depth of 100-1200m within the territory of Narysk-Ostashkinsk area and one well in Chaltok field. All in all, 122 samples from 42 wells were examined. The macro / micro- component compositions of groundwater were analyzed in the Task-Solving Research Hydrogeochemical Laboratory, TPU. The software program HydroGeo, developed by M Bukat [7] was used to calculate the existing water-rock equilibrium, which, in its turn, is based on the equilibrium constant method. Based on hydrogeochemical data saturation value of groundwater relative to the common water-bearing minerals were determined.

3. Groundwater chemical composition

According to previous and new data in hydrogeology and hydrochemistry (2014) the following fact was established within the investigated area: straight vertical hydrodynamic zonality. In accordance to intensive water exchange, two zones were identified- active and moderate water exchange. Groundwater in both zones differs in chemical and gaseous composition and is governed by the straight vertical hydrodynamic zonality [2].

Groundwater in active water exchange zone can be found in the upper cross-section composed of loose Mesozoic-Cenozoic sediments (predominately Quaternary) and in the zone of intensively fractured Jurassic sediments. This fresh water (mineralization from от 0.5 to 1.0 gr/liter), which expands to a depth of approximately 150m., although this is an arbitrary level as it can expand only to 30-50m in some areas and up to 400m, in other areas (Table 1). This is governed by the intensive water exchange and permeability of the sediments. According to its chemical composition the groundwater is calcium hydrocarbonate and calcium-sodium hydrocarbonate, whereas the Na^+ fraction in the water composition increases to the bottom zones of active water exchange. Cl^- and SO_4^{2-} concentrations are not high, not more than 10 mgr/liter in average. In general, groundwater is neutral and weakly alkaline, pH is 7.0-8.6. Gaseous composition includes aerial gases, i.e. N_2 (71–80 %), O_2 (17–22 %) and CO_2 (a fraction of %). CH_4 can also be found in insignificant amounts.

Table 1. Chemical composition (allowable concentration and average value) of underground water in Narysk-Ostashkinsk area; mgr/liter (2012-2014).

Parameters	Active water exchange zone (24 samples)	Moderate water exchange zone	
		Intensively fractured rocks (73)	Fading fracturing (25)
pH	7.0–8.6 (7.7)	7.5–9.8 (8.1)	7.2–9.9 (8.3)
Ca^{2+}	32–120 (77)	3–88 (32)	0.2–61.0 (20.4)
Mg^{2+}	6.1–35.3 (16.7)	0.4–48.6 (10.0)	4.9–79.3 (22.3)
Na^+	8.5–130.0 (47.0)	44–3800 (438)	1996–7230 (3481)
Fe^{2+}	0.05–24.5 (3.9)	0.01–192.0 (10.4)	0.1–29.5 (9.2)
HCO_3^-	321–745 (433)	258–3111 (824)	1399–15494 (7375)
CO_3^{2-}	0.2–6.2 (1.6)	0.3–742.8 (31.1)	18.5–1285.7 (357.8)
Cl^-	0.7–24.0 (5.1)	1.5–182.0 (22.9)	30,0–5494,0 (919)
SO_4^{2-}	0.8–16.9 (5.6)	0.2–185.6 (18.4)	0.21–75.7 (20.3)
SiO_2	7.5–25.3 (14.6)	1.8–42.5 (22.0)	5.9–44.6 (24.6)
Total mineralization	497–1029 (615)	436–4355 (1271)	3999–25139 (12159)

Lower is the moderate water exchange zone which is confined to Mid-Upper Permian sand sediments, partially, within Triassic effusive-sedimentary sediments. This zone is characteristic of not only rather high mineralization (from 1, rarely 0.5–1.2 and 10–25 gr/liter) but also the water composition. The most common water is sodium (HCO_3-Na), typically found throughout Kuzbass with pH from 7.5 to 9.9. Due to complex hydrogeochemical conditions this zone is subdivided into two subzones: upper and lower.

Upper subzone embraces fresh and/or weakly mineralized (0.5–5 gr/liter), calcium-sodium hydrocarbonate and/or sodium-calcium hydrocarbonate water, pH 7.5–9.8. It should be noted Cl^- concentration increases up to 182 mgr/liter, and sometimes, SO_4^{2-} concentration- up to 186 mgr/liter. At the same time, chloride concentration increases to depth, while sulphate-ion decreases. The source of the latter could be sulphates (pyrite), the oxidation of which furthers the emerging sulphate ion. The pattern is reversed in the case of Ca^{2+} concentration – it decreases up to 3mgr/liter. The waster-dissolved gas includes methane (85–95%).

In the lower subzone at a depth of more than 400–500 m saline and weakly saline sodium groundwater (up to 25 gr/liter) can be found. Due to the continuous increase of HCO_3^-, Na^+, Cl^- concentration mineralization also increases. High hydrocarbonate ion concentrations (to 15 gr/liter!) is associated with the coal-bearing Permian sediments, which, in its turn, are sources of carbon. At the same time, SO_4^{2-} concentration is insignificant. In this case the water is hydrocarbonate, rarely chloride-hydrocarbonate, sodium chloride- hydrocarbonate. Methane continues to accumlate in the water dissolved gas (up to 99%).

Analyzed samples (Narysk-Ostashkinsk area, 2014) revealed that groundwater is related to the lower moderate water exchange zone, highly mineralized and increased chloride concentration from 1.0 to 2.3 gr/liter was found in some samples.

**4. Equilibrium calculation results in water-rock system**

Factual data of groundwater chemical composition was imported into the HydroGeo program. The most common minerals in country sediments, basically aluminosilicates (quartz, feldspar, clays, etc.), separate carbonates (calcite, magnesium, dolomite, siderite) and some salts were also selected. Calculation results are depicted in Table 2 and Figures 1 and 2. It was revealed that all water types, if highly mineralized water in the lower water exchange zone are not in equilibrium with source minerals of water-bearing rocks: feldspar, hornblende, amphibole, epidote, pyroxene and others.

Table 2. Value index of saturated groundwater (leading minerals) in (1) active water exchange zone, (2) moderate upper exchange zone and (3) lower zone.

| Mineral	1	2	3	Mineral	1	2	3
Ionic strength	0.008-0.016	0.012-0.054	0.062-0,.24	Aluminosilicates			
Oxides				Albite	-3.3-(-0.3)	-1.7-1.8	0.1-2.2
Hydargillite	1,3-1,8	1,3-2,1	1,4-2,0	Biotite	-23-(-14)	-21-(-13)	-19-(-12)
Carbonates				Anorthite	-5.2-(-2.4)	-5.7-(-1.3)	-7.7-(-0.3)
Calcite	-0.1-**1.3**	**-0.4-1.8**	**0.7-2.7**	K-feldspar	-7.1-(-6.4)	-7.7-(-5.3)	-6.1-(-4.7)
Siderite	-1.2-**2.9**	-0.6-**5**	**0.3-4.1**	Microcline	-5.3-(-0.8)	-4.4-**1.9**	-2.3-**2.1**
Dolomite	-0,5-**2,4**	-0,8-**4,1**	**1.4-5.6**	Moscuvite	-6.4-(-2.5)	-9.2-(-1.3)	-8.3-(-0.8)
Magnesium	-1.7-(-0.3)	-3-(-2.5)	-0,5-**1,6**	Pyroxene	-12-(-9)	-10-(-7)	-9-(-6)
Sodium minerals				Chlorite	-2.0-**0.9**	-2.4-**2.5**	-4.8-**3.1**
Tron	-120	-120-(-100)	-110-(-95)	Ca-Mt	-0.1-**4.9**	**0.1-5.8**	**1.9-9.6**
Natron (soda)	-130-(-120)	-115- (-120)	-110- (-115)	Na-Mt	-1.2-**2.3**	**0.8-5.3**	**2.7-6.1**
Sulphates				Mg-Mt	**0.1-5.5**	**0.4-8.9**	**2.3-10.0**
Gypsum	**1.2–2.4**	-3.4-**0.6**	-5.1-(-0.7)	K-Mt	-2.8-**0.6**	-4.1-**3.1**	-4,7-**2,3**
Anhydrite	-7.3-(-6.1)	-10-(-7.9)	-11.8-(-7.5)	Illite	-0.6-**1.3**	-1.7-**3.0**	-2,3-**3,4**
Chlorides				Kaolinite	**0.1-1.0**	**0.5-1.4**	**0.6-1.2**
	-20-(-19)	-17-(-15)	-13-(-8)	Daphite	-2.4-**2.6**	-2.0-**4.5**	-2.7-**4.5**

Groundwater in active water exchange zone is undersaturated relevant to initial aluminosilicate minerals, due to the low mineralization value and pH. Under such conditions these minerals are unstable and actively dissolve, as a result of which, Ca, Mg, Na, Fe, K, Si, Al and other elements migrate into the solution. Some of the elements migrate out (as the water is oversaturated by these minerals) as secondary formations: oxides and hydrooxides Fe, Mn and Al, clays (kaolonite and different montmorillonites, except potassium), carbonates (calcite, dolomite, often siderite). They are in bold in Table 2.

Water in moderate water exchange zone is more alkaline and mineralized, however, it is undersaturated in endogenous minerals. At the same the groundwater in the upper water exchange zone is highly saturated in secondary aluimnosilicates. (illite appears, montmorillonites, chlorites and even albite and microcline) and carbonates (siderite and magnesium).
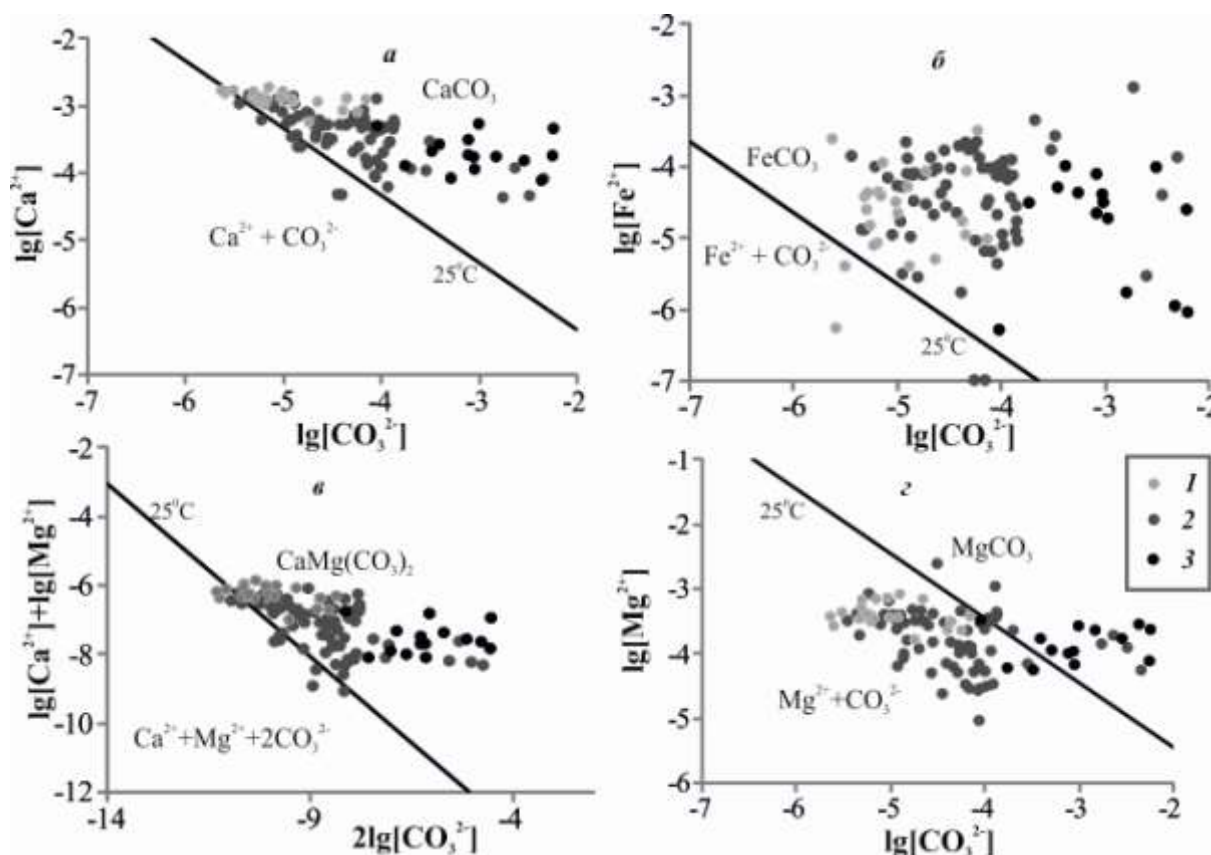
Figure 1. Groundwater equilibrium with (a) calcite, (b) siderite, (c) dolomite, (d) magnesium at standard temperature : 1- groundwater form active water exchange zone; 2- groundwater from moderate water exchange zone (upper) and (3) groundwater from moderate water exchange zone (lower).

According to Shvartsev definition this equilibrium is the so-called "equilibrium-non equilibrium": water is always in non equilibrium with primary aluminosilicates, but under specific geochemical conditions could be in equilibrium with secondary ones. In this case, water composition is determined as the difference between dissolved and precipitated minerals. Thus, at depth water composition alters from HCO_3-Ca to HCO_3-Na. Carbonates are bounded by Ca, Mg, Fe, C, clay minerals- Al, Si, Ca, Mg, Fe, and, partially by Na and K, oxides and hydrooxides- Fe. Na is less bounded to secondary sediments as water remains rather in non equilibrium to sodium minerals (table 2). In this case, Na continues accumulating in water and its composition becomes more sodium saturated. In the upper moderate water exchange zone SO_4^{2} is observed in the water composition which is associated with pyrite oxidation. In the lower zone- there is a significant amount of Cl^-. As there are no salt minerals in this zone, aluminosilicate minerals (in impurities) could be the source of chloride and sodium. In time it accumulates in the solution under conditions of rather moderate water exchange. As the solution is undersaturated in Cl (table 2-halite) such conditions are favorable for its accumulation.
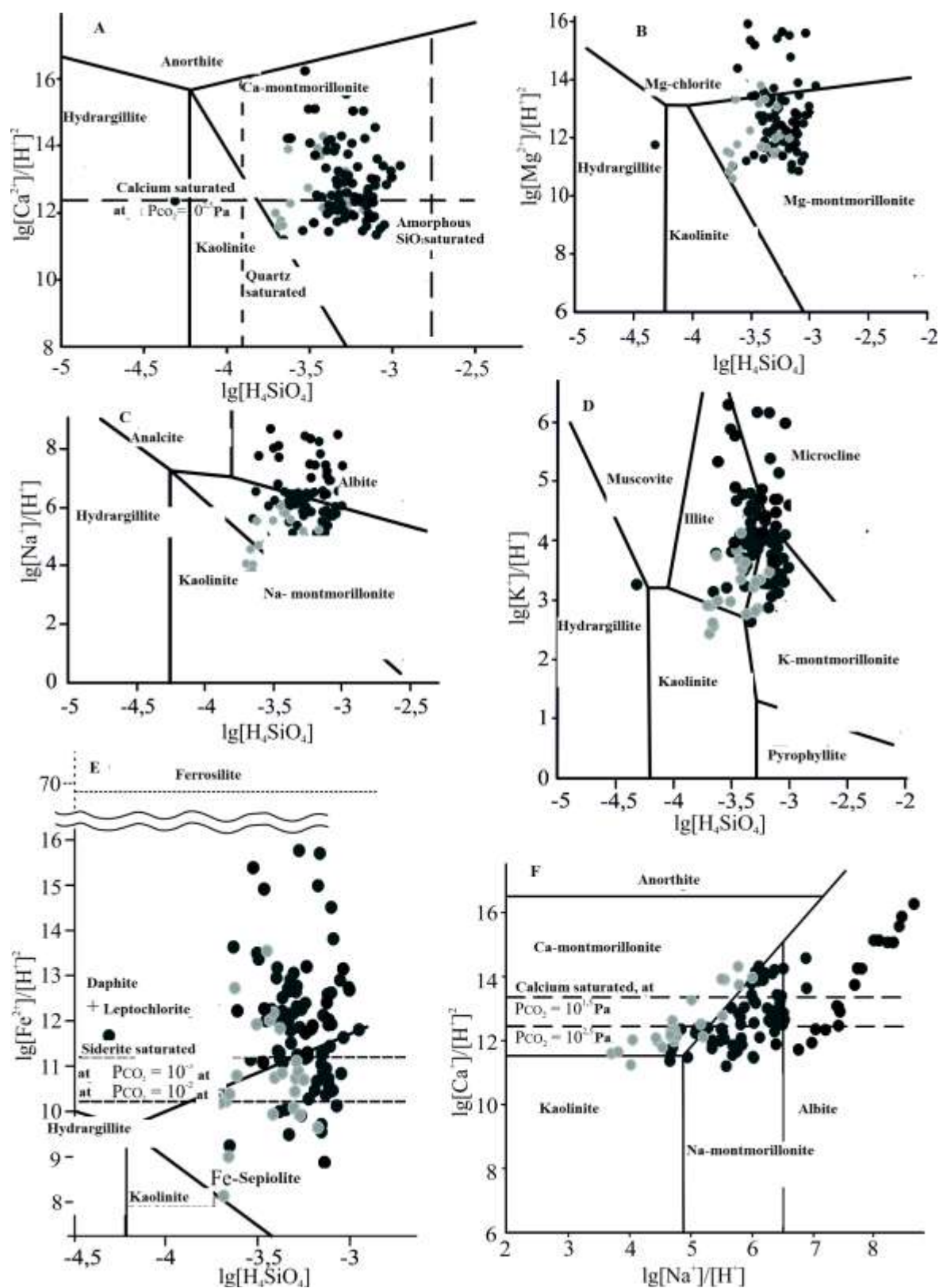
Figure 2. Equilibrium diagrams: (a) calcium, (b) sodium, (c) magnesium, (d) iron-containing, (e) calcium-sodium at $\lg[H_4SiO_4] = -3.25$ and (f) groundwater minerals.

5.Conclusion

According to the recent data it has been revealed that in Narysk-Ostashkinsk area there is straight vertical groundwater zonality: fresh HCO_3-Ca water of active water exchange zone changes to saline (M up to 25 gr/liter) of moderate water exchange zone. Thermodynamic calculations revealed that all groundwater types are in non equilibrium to common aluminosilicate minerals which are the sources Na, Ca, Mg, K, Si, Al and even positive Cl is not an exclusion. Pyrite in the upper level of moderate water exchange zone imports sulphates into the groundwater. A portion of these elements move out of the solution into secondary sediments, where groundwater is in equilibrium with clays (montmorillonite, hydromica, chlorite), carbonates (calcite, dolomite, siderite) and even gypsum. Na is less bounded in the secondary sediments and continues accumulating in the groundwater. Water composition changes from sodium to chloride in depth, as HCO_3^- migrates with carbonates and Cl concentrates in the solution.

Acknowledgments

References

[1]   Domorocheva E 2005 *Gidrogeohimicheskie osobennosti ugol'nyh rajonov Kuzbassa* Dissertation abstract 22

[2]   Shvartsev S L, Khryukin V T, Domrocheva E V, Kuzevanov K I, Rasskazov N M, Popova T S, Lepokurova O E and Shvachko E V 2006 Hydrogeology of the Erunakovo region of the Kuznetsk basin in the context of coal methane formation and mining *Russian Geology and Geophysics* **47** (7) 881–891

[3]   Shvartsev S L 2004 Hydrogeochemical conditions of formation of dawsonite mineralization in the Berezovoyarka area, Kuznetsk Basin *Geochem. Int.* **42** (10) 938–949

[4]   Shvartsev S L 2004 Hydrogeochemistry of processes of dawsonite formation *Doklady Akademii Nauk* **394** (6) 818–821

[5]   Kopylova Y G, Lepokurova O E, Tokarenko O G and Shvartsev S L 2011 Chemical composition and genesis of the carbonic-acid mineral waters of the Tersinskoe deposit (Kuzbass) *Doklady Earth Sciences* **436** (2) 284–289

[6]   Shvartsev S L 2008 Geochemistry of fresh groundwater in the main landscape zones of the earth *Geochem. Int.* **46** (13) 1285–398

[7]   Bukat M B 2002 Razrabotka programmnogo obespechenija dlja reshenija gidrogeologicheskih zadach *Izvestija Tomskogo politehnicheskogo universitet* **305** (6) 348–365