

## Hydrothermal alteration and spring water geochemistry of Sebinkarahisar (Giresun, NE Turkey) volcanic field

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Saplica volcanites crop out in the north part of Sebinkarahisar (Giresun) located in the eastern part of Pontid provenance. The volcanites are in Upper Cretaceous age and comprises of acid to intermediate composition. The volcanic rocks were intruded by same aged acidic plutonic complexes. It comprises granite, syenite, quartz syenite and monzonite. The spring waters are scattered in Saplica volcanites. The volcanites especially around the spring waters have remarkably suffered from hydrothermal alteration as a whole. Various altered rocks such as silicified rock, alunited and white argillized one are distributed inter twinning with each other. Silicification and partly kaolinization were formed by most intense leaching through strongly acid alteration while alunition were occurred by dense sulphuric or sulphuric acid alteration (Celik and Karakaya, 1997).

In the study area spring waters are observed especially near the intruded rocks contact or along the main fractures. The waters are variously coloured and  $\text{SO}_4$  content of waters are too high and it ranges between 360 to 2250 mg/l. They can be classified as acid sulphate water because of high content of  $\text{SO}_4^{2-}$ . Although  $\text{Na}^+$ ,  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$  and K contents are enormously high in some samples, chlorine,  $\text{CO}_3^{2-}$  and Mg content are found to be too low (Table 1). The spring waters covered the rocks black, yellow, brown and white coloured deposits. The deposits contain gypsum, hematite, sulphur, alunite and kaolinite.

Stable isotope investigation  $^{18}\text{O}/^{16}\text{O}$  and D, of spring waters are meteoric in origin and its T (TU) value are between 0.0 to 4.50 (Sheppard, 1986). According to T value the waters were mixed with meteoric water of before or after from 1952 (Mazor, 1991).

The spring waters contains 10 times as much Ca, 100 times as much Mg, 2 to 1400 times Al and Fe, and up to 70 times as much  $\text{SO}_4$  as the deep water. Although the present day spring waters temperature is between 21 to 26°C and pH of the water is between 2.33 to 6.80. pH of the spring waters immediately changes and rises to 11.80 due to carbon dioxide

escape and hydrogen and sulphate ion are produced by oxidation of  $\text{H}_2\text{S}$ . Hydrothermal fluid conceivably rises along major fractures and contact of intruded acid complex. The low pH water percolates downward and reacts with feldspar and micas in the rocks to produce alunite, kaolinite, silica and illite as hydrogen ion is consumed. Reduced sulphur in the rising fluid react with iron bearing minerals to precipitate pyrite.

Molalities, activities, activity coefficients and log activity ratios of ionic species calculates for the thermal water using WATEQF. Activity diagrams represent the major alteration product minerals in the study area. Mineralized water positions plotted on the diagrams of Fig. 3, are consistent with observed alteration mineral assemblages. It is established that generally alunite, kaolinite, quartz, pyrophyllite, gypsum, adularia, anhydrite, goetite, baryte, hematite and celestine are saturated in all spring waters samples. Illite, boehmite, gibbsite, albite, chlorite, anortite and Ca-montmorillonite minerals are determined in some samples while carbonate and klorine minerals were not saturated. The most common alteration mineral products, alunite with opal and/or quartz require a low pH lower than 3.5 and the alunite-kaolinite-quartz assemblages requires a pH below 5.0 (Henley and Ellis, 1985; Pirajno, 1992).

The semi thermal or mineralized spring waters in equilibrium with minerals and gases at depth rises to surface along faults cools by conduction and steam separation and loses carbon dioxide causing a rise in pH. The mineral assemblages produced by interaction with rock are illite, alunite, kaolinite with opal and/or quartz. Reduced sulphur in the rising fluid is oxidised to sulphate activity. Hydrogen ion and sulphate are carried downward by water descending through pyroclastics and fractured rock producing on alteration assemblage stable in low pH solutions superimposed upon that produced by the ascending fluid. Minerals produced by the downward percolating solutions are alunite, kaolinite, illite, and illite-smectite, gypsum, baryte which are produced successively as hydrogen ion and sulphate are consumed.

TABLE 1. Chemical composition (mg/l), isotope value and physical features of spring waters

Samp. num.	1	2	3	4	5	6	7	8	9	10	11
pH	3.56	6.44	4.20	3.28	6.78	6.87	2.92	3.42	3.48	3.73	3.55
T(°C)	23	21	17	20	17	23	20	23	20	18	16
EC(μS/cm)	2450	600	925	1900	3300	1500	2500	900	3800	900	2800
Eh	-213	27	60	213	40	62	210	235	25	170	240
Si	15.10	1.30	31.90	12.15	25.00	26.13	13.4	10.16	11.74	10.06	19.10
Al	66.13	0.96	0.10	54.07	0.75	0.96	57.82	17.20	69.01	1.83	61.70
Fe	56.00	0.25	0.21	0.65	0.35	0.25	17.61	0.32	72.05	0.25	40.90
Na	17.50	13.50	304.0	125.0	60.01	60.00	79.05	10.40	65.00	10.20	37.50
K	22.50	3.00	31.01	12.50	10.05	10.02	20.00	3.00	60.00	9.00	17.50
Ca	100.0	95.50	325.8	160.0	517.5	245.0	298.0	94.00	105.0	162.0	270.0
Mg	87.50	32.00	27.83	47.50	202.5	60.00	33.90	14.00	35.00	25.00	52.50
B	2.50	1.02	2.70	0.50	0.84	0.53	1.33	0.65	0.60	1.15	1.05
Ba	0.03	0.03	0.03	0.01	0.01	0.02	0.02	0.01	0.03	0.05	0.02
Sr	4.71	4.50	4.79	4.82	4.91	0.80	0.70	0.70	0.79	4.82	3.40
Cl	7.09	8.86	7.12	7.09	3.55	3.55	21.27	7.09	14.18	7.09	10.64
SO <sub>4</sub>	1386	391.1	1210	1027	1992	766.9	1241	361.2	2257	378.2	1420
HCO <sub>3</sub>		30.20			259.7	96.63				60.40	
CO <sub>3</sub>						29.70					
Min. acidity											
CaCO <sub>3</sub>	375.0		20.05	40.00			90.00	25.00	360.0		
135.0											
Tot. acidity											
CaCO <sub>3</sub>	1300		125.0	395.5			385.0	145.0	1855		
635.0											
δ <sup>18</sup> O (‰)	-8.52	-9.45	-10.05	-10.19	-10.60	-11.99	-11.42	-5.95	-9.87	-10.62	-10.60
δD (‰)	-47.87	-65.68	-85.19	-88.97	-71.14	-83.57	-89.67	-57.87	-68.77	-71.52	-88.53
T (TU)		9.30	11.20				3.40	4.20			

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