GEOCHEMICAL VARIETIES OF HYDROTHERMAL FLUIDS IN THE AREAS OF RECENT VOLCANISM

V.I. KONONOV

Laboratory of Geoenergetics and Hydrogeochemistry,
Geological Institute, Russian Academy of Sciences, Moscow, Russia

SUMMARY - Several geochemical varieties of hydrothermal fluids are identified in volcanic areas. N_2-CH_4-rich water with moderate content of total dissolved solids (TDS up to **25** 000 ppm) and relatively low temperature (< 50°C) occur outside of the zone of direct influence of volcanic chambers as well as N_2-rich alkaline low-mineralized fluids (TDS< 1500 ppm) with temperature **up** to the boiling point. CO_2-rich thermal water (TDS<10 ,000 ppm, $T \leq 75^oC$) surround the extinct volcanic edifices and indicate the intensive thennometamorphic processes in the interior. Areas of active volcanism are marked by high-temperature fluids (200-350°C) riched in CO_2 (sometimes with N_2). H_2S is the predominant gas in acid fumarolic fluids discharged in the craters or on the slopes of active volcanoes , H_2-rich fluids with temperature up to 400°C distinguish the volcanic areas within oceanic rifts; these fluids associate most closely with the mantle melts discharge and are typical for submarine geothermal fields.

1. INTRODUCTION

Origin of the diverse thermal waters was studied by many researchers (Amorsson, 1979, Arnorsson et al. 1978; D'Amore and Truesdell, 1985; Ellis, Mahon, 1964,1967, 1977; Henley, Ellis, 1983; Giggenbach, 1980; Ivanov, 1976; Kononov, 1983; Kononov, Polak, 1978, 1982; Matsubaya et al., 1973; Naboko, 1959, 1980; Nakamura et al., 1977; Waring G.A., 1965; Whiie, 1957; White et al., 1971). As a result, many data characterizing their distribution, composition and possible genesis were obtained in volcanic areas of Russia, **USA,** New Zealand, Italy, Japan, Island, Mexico, Ethiopia and other countries. Tectonically they are associated with active belts of the Earth crust, comprising island arcs, active continental margins, alpine fold-mountain belt, epiplatform orogenic areas, and mid-oceanic ridges. This data showed the existence of the different types of thermal fluids spread in volcanic areas in depend on their tectonic position. Classification of these varieties is especially important for prospecting of hydrothermal resources for practical use.

2. METHODS

The proposed classification (table 1) is based on the comparative analysis of regional sets of data, characterizing thermal fluids in above areas. Formal criteria of this classification were the following: 1) composition of gas phase of the fluids; 2) composition of predominant anions; 3) content of total dissolved solids and 4) base temperature (maximal temperature of the fluids in the reservoir, estimated by direct measurements or indirect methods like Si-geothermometer etc.). **Based** on the first criterion fluids can be subdivided into six groups rich in CH4 (CH_4+N_2), N_2, CO_2, CO_2+H_2 and CO_2+H_2S, respectively. According to the second criteria each group can be subdivided into three subgroups: HCO_3, SO_4 and Cl. Then these subgroups can be divided in the varieties based on the abundance of dissolved solids (the third criterion): with TDS, in 1.10^3 ppm, 1, 1-5, 5-35, 35-300, >300.

For temperature boundaries we used some specific points (connected with the degree of H_2O dissociation, in particular) and values, reflected the possibility of different applications of hydrothermal resources. Besides that, we considered the phase state of the fluids at their discharge onto the earth surface, since this state reflects the thermodynamic conditions in reservoir and distinguished hydrothermae (hot waters), steam-water mixtures, steam-gas jets. Based on these criteria, each of the studied hydrothermal systems can be localized in definite grid of the proposed classification.

3. RESULTS

The six main geochemical varieties of hydrothermae and five types of steam-water mixtures are identified in the areas of recent volcanism.

3.1. Beyond of active influence of volcanic processes

"N_2 - CH_4" and "CH_4" waters are spread in artesian basins of intermountain areas. These waters contain $CaCl_2$ up to 25 000 ppm; their temperature at a 1 km depth is no higher than 50°C. They are observed in many regions of the Pacific, Mediterranean and East-African provinces. This type incorporates, for instance, well known CH4 and N_2-CH_4 waters concluded in Miocene-Pliocene deposits of the Akito and Kanto depressions on the Honsu Island (Japan) and in Cenozoic sequences that composed the frames of California and Mexican Gulfs.

"N_2" fissure-veined waters are recorded in hydrogeological massifs. They have alkaline reaction

Table 1

THE CLASSIFICATION OF THERMAE OF THE RECENT VOLCANIC AREAS

Gas composition	Predominated anion	TDS $.10^3$ ppm	Hydrothermae			Steam-water mixture			Volcanic emanations			
			20-50°C	50-100°C	100-150°C	150-180°C	180-240°C	240-400°C	100°C	100-180°C	180-700°C	700-1200°C
H_2S CO_2	HCO_3	<1	Pseudofumaroles						Mofettes Solfataras	Solfataras	Fumaroles (Big Donald)	Eruption complikete composition (Niragongo)
		1-5										
		5-35										
		>35										
	SO_4	<1	Dzidzou	Kagamizawa			Matsukawa					
		1-5		Kichpinichevsky								
		5-35		Verchne Yurjevsky								
		>35	Kawah Ijen									
	Cl	<1										
		1-5		Obyki								
		5-35		Deep formation			Tatun (Matsao)					
		35-300		Tikeyama								
		>300			Dallol							
H_2 CO_2-H_2	HCO_3	<1					Nesjavellir				Fumaroles (Krafla)	Eruption (Surtsey)
		1-5										
		5-35										
		>35										
	SO_4	<1					Namafjall-Krafla					
		1-5					Geysers Sonoma					
		5-35										
		>35										
	Cl	<1										
		1-5					Krisuvik					
		5-35					Ahuachapan	Cerro Prieto				
		35-300		Arima			Reykjanes					
		>300										
CO_2	HCO_3	<1				Monte Amiata	Mud Volcano		Mofettes Solfataras	Caucasus, Carpathian, Apennines		
		1-5	Lysuholl	Shala		Tuchung						
		5-35	Ost-African rift									
		>35										
	SO_4	<1		Apapelsky		Stemboat	Kawah Kamojang					
		1-5		Viterbo			Larderello					
		5-35										
		>35					Cesano					
	Cl	<1					Norris					
		1-5	Sagaku	Nalachevsky		Tongonan	Wairakei	Broadlands				
		5-35	Katwe	Mambuga		New Britain	El Tatio	Tiwi				
		35-300	Danakil	Ishibotoke			Afars Issa					
		>300						Solton Sea				
N_2-CO_2	HCO_3	<1	Dieng	Passo		Hveravellir-Beyk.						
		1-5	Awash	Lakes Valley		Great Geysir						
		5-35										
		>35										
	SO_4	<1				Arhver						
		1-5	Karymsky			Bolshe Banny						
		5-35										
		>35										
	Cl	<1	Lake Bali			Zhyrovsky						
		1-5		Afar and Danakil		Allallobeda	Pauzhetsky					
		5-35	Urundaka	Afrera	Wakuro	Goryachy Plyazh	Onikobe					
		35-300										
		>300										
CH_4 N_2-CH_4	HCO_3	-									Submarine eruption near Azores island	
		-										
		-										
		-										
	SO_4	-		Golyzinsky								
		-										
		5-35										
		>35										
	Cl	<1	Karroo	Gavansky								
		1-5		Goryachy Kluch								
		5-35	Morero	Bogachevka	Gulf of California			21° Lat.N109 Long W				
		35-300		Brines of Red Sea			Naivasha					
		>300										
N_2	HCO_3	<1	Karin	Nyamosi (He)	Reykjavik							
		1-5										
		5-35										
		>35										
	SO_4	<1	Paratunsky	Reykir	Varmahlid							
		1-5		Nachiki								
		5-35										
		>35										
	Cl	<1	Tji-Lahar	Dhimbo								
		1-5	Nichenge	Chiveta								
		5-35	Krahol	Atami								
		35-300	Urinza									
		>300										

(pH–8-10) and low content of total dissolved solids (<1500 pprn), main anions are SO_4 or HCO_3, less frequently-Cl, Na is the predominated cation, with temperature below the boiling point in the discharge area, and less than 150°C at a depth. The total outflow of heat by one "N_2" hydrothermal system is of the order of 10^6 cal/sec. The gas saturation of these waters is low, the gas consists almost entirely of nitrogen (95-99 mole %). The thermae have the transitional values of Eh - from 10 to 160 mV. "N_2" thermae are formed in fracture zones of magmatic and metamorphic rocks of various age. For instance, in Iceland these thermae are associated to deep faults in Miocene-lower Pliocene plateau-basalts (springs of Reykjavik region, etc.).

3.2 In regions with attenuating volcanic activity

"CO_2"-waters are associated mostly with large fault zones in regions of present and Early Quaternary volcanism and (or) intense metamorphic processes at a depth. There CO_2 hydrothermae (up to 75°C) have different salt composition. TDS is commonly less than 10,000 ppm. They are characterized by a subneutral reaction (pH 6-8) and Eh values from 0 to 250 mV. The most "CO_2"-thermal waters use to be of $Na\text{-}CO_3$ in the salt composition (Lysuholl springs in Iceland, for example); less typical are sulphate thermae (for instance, Viterbo in Italy) and chloride ones (Nalychev springs on Kamchatka, etc.).

3.3 In the sphere of influence of active volcanic foci

In zones of tectonic faults there occur "$N_2\text{-}CO_2$" and "CO_2" low-mineralized steam-water mixtures (200-350°C) of different salt composition. Depending upon the water and heat recharge ratio, they are subdivided into "hot water systems" or "vapor-dominated systems".

"$N_2\text{-}CO_2$" steam water mixture are formed in faults under reduction conditions, All of them are the "hot water systems", and are discharged on the day surface as boiling springs and geysers with high yield. The gas content in them does not usually exceed 50-100 ml/l. In the rift zones of Iceland the hydrothermae of such type have the $Na\text{-}CO_3$ or $Na\text{-}SO_4$ composition with mineralization less than 2500 ppm and pH=9 (Great Geysir, Arhver). In the region of recent volcanism of island arcs the most typical are $N_2\text{-}CO_2$ hydrothermae of NaCl composition with TDS 1000-6000 ppm (Geyser Valley, Kireunskie and Pauzhetskie springs on Kamchatka, etc.).

"CO_2" steam-water mixtures are from hydrothermal systems with predominance of both the steam and the water. In the "vapor-dominated systems" (Larderello and Monte Amiata in Italy, Kawah-Kamojang in Indonesia, etc.) the mineralization of fluids is usually below 1000 pprn and the condensate of steam is characterized by $Na\text{-}CO_3$ or $Na\text{-}SO_4$ composition and almost a complete lack of Cl-ions. In systems with hot water (Broadlands, Kaverau, Wairakei in New Zealand, etc.) the hydrothermae are, as a rule, of NaCl composition, and their TDS rises up to 5000 ppm. In hypothermal brine with CO_2 from Californian Salton Sea trough, featuring conspicuous evaporite sequences, mineralization may reach 305,000 ppm.

"$H_2S\text{-}CO_2$"-thermae are associated with active volcanic apparatuses. They are formed under oxidation conditions in places of saturation of underground waters by fumarole and solfataric gases (H_2S, CO_2, HCI, HF, SO_2. etc.), and subsequent interaction of strongly acid (pH) solutions with volcanic rocks. The temperature of steam-gas jets in craters of active volcanoes reaches 700°C and higher, and that of fumarole springs is below, or equal to the boiling point. $H_2S\text{-}CO_2$ thermae are subdivided into two peculiar subtypes (Ivanov, 1976):

a) of surface formation - acid (Eh from -300 to 0 mV), sulphate with a complex cation composition and TDS up to 20,000 ppm;

b) of deep formation - acid and ultra-acid (Eh from -350 to 600 mV), chloride ($Cl\text{-}SO_4$) with a complicated cation composition (Fe, Al, H, etc.) and TDS up to 35,000 ppm.

"$CO_2\text{-}H_2$" ("hydrogenous") fluids are formed in volcanic regions related to oceanic rifts, under influence of mantle melts and high-temperature emanations. Their gas composition contains appreciable, and sometimes abundant amounts of H_2 (in addition to, there are in them CO_2, H_2S, N_2 and other gases). "Hydrogenous" thermae incorporated in basalts of the oceanic crust in under-water conditions are mostly heated sea waters. In the subaerial part of the rift in the Icelandic Median volcanic zone these are low-mineralized (TDS 1000 ppm) solutions characterized by a higher content of silica and absence of chlorine in the anion composition. In condensates of these jets the leading role usually belongs to SO_4, HCO_3. Na. While being discharged, the thermae of this type are characterized by low values of Eh (from -300 to 0 mV) and low-alkaline reaction. The hydrothermal systems with gases of such a composition (Nesjavellir, Namafjall, Krafla in Iceland, Geysers in USA, etc.) are known for the highest heat potential (up to 10^8 cal/sec) and temperature up to 400°C at a depth of some hundreds of meters. Therefore, they are discharged on the Earth's surface as powerful jets of a steam-water mixture.

"CH_4"-steam-water mixtures are formed in continental and intercontinental rift zones with a cover of sedimentary rocks containing evaporites. They are formed as a result of introduction of magmatic foci into artesian basins with CH_4-waters. These waters are characterized by mineralization exceeding 200,000 ppm and a higher content of ore components (for instance, some hydrothermal systems of rift zones of the Gulf of California and East Africa).

"Coastal thermae". On coasts of the seas (or mineralized lakes) there are sometimes favorable conditions for supply of recent sea (or lake) waters into the hydrothermal systems located in the coastal zone (Kononov, Tkachenko, 1982). Such thermae differ in their gas composition, on the contrary their salt composition is rather uniform. On the sea coasts it is chlorine sodic-calcic thermae with mineralization usually up to 35,000 ppm or somewhat higher (for instance the hydrothermal systems Reykjanes and Isafjordur in Iceland, Goryachy Plyazh on the Kunashir Island).

3.4 Origin of thermal and chemical features of different hydrothermae

Thermal parameters of "N_2", "CO_2" and "CH_4" hydrothermae conform with a model of these waters heated by the background heat flow within the upper 2-2,5 km of the section of the enclosing hydrogeological structures. In contrast, the thermal potential of hypothermal "CO_2-H_2", "CO_2-H_2S" and "CO_2-N_2" steam-water mixtures cannot be replenished exclusively at the expense of the back-ground conductive heat flow. In this case there must be either a supply of high-enthalpy deep fluid to the system, or its additional conductive heating by shallow magma foci.

The main water source in present hydrothermal systems, as the isotope composition, oxygen, hydrogen and sulfur show, is meteoric water that filters downward, though some systems may have predominant water; of marine genesis. The share of magmatic fluid in the water balance of hydrothermal systems does not exceed 5-10%.

The major proportion of the dissolved components is either from the enclosing rocks or together with sedimentogenic and modern marine waters. Anomalous concentrations of ore elements found in Salton Sea thermal brine and some thermal springs on the oceanic bottom (Red Sea and Galapagos rifts, submarine hydrothermal at N 21°, W 109°) are largely due to the high-temperature leaching of enclosing rocks by high-mineralized Cl-Na-Ca brine or sea water. At the same time, the isotopic features of helium in some thermal manifestations may suggest, together with the high temperature of hydrothermal systems, the influx of the mantle matter to the surface of the Earth (Kononov, Polak, 1978, 1982).

The principal factors responsible for the character and scale of gas-hydrothermal activity are the geological structure and the composition of rocks, as well as the hydrogeology of hydrothermal system, its P-T conditions, the composition, temperature and pressure of deep magmatic exhalations and the intensity of their injection in ground waters.

The composition of thermal fluid is formed due to different processes: the first one is phase transitions of ground waters. This phenomenon is typical of active volcanic regions. It may be observed in the shallow depth in discharge areas where hyperthermal waters start boiling with intense degassing that accompanies it. Then, chemical components of thermal springs are redistributed between' the vapor and liquid phases, with a conspicuous increase of salt concentration in liquids. The steam condensate usually has HCO_3 -Na or SO_4-Na composition with almost total absence of Cl (they stay in the liquid phase). The other processes occur everywhere. Some of them regulate matter's injection into the solution (gas saturation, leaching and dissolution of the enclosing rocks). The ultimate composition of thermal water depends also on processes that remove matter from the solution (degassing and precipitation of solids etc.). Of importance are also oxidizing processes in the rock-solution system, the matter exchange existing between solution and the rock (metasomatosis, ionic exchange, hydration and dehydration of the rock, membrane effect, valency exchanges in the solution), mass transfer (diffusive and diffusive-conductive), and finally the process that leads to the mixture of waters of different genesis, composition and mineralization.

Thus, in areas of recent volcanism the above factors and processes produce thermal fluids that may differ significantly in the composition of gases, dissolved salts, pH and Eh, total content of dissolved solids and thermal parameters. Variations in the natural setting result in the genetically differing types of thermal solutions.

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