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Geochemical Characteristics of Gases from the Wudalianchi Volcanic Area, Northeastern China

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Abstract The origins of gases in springs, pools and wells from the Wudalianchi (WDLC) volcanic area are discussed based upon molecular and isotope compositions of the gases. Nine gas and water samples were collected from bubbles and water of the springs and pools in the WDLC volcanic area, Northeastern China, in August 1997. The molecular components were measured with a MAT-271 mass spectrometer (MS), helium isotope ratios with a VG-5400 MS, and $\delta^{13}C$ with a MAT-251 MS in the Lanzhou Institute of Geology. The gases are enriched in CO_2, and most of the CO_2 concentrations are over 80% (V). The helium and methane concentrations have relatively wide ranges of 0.7 to 380×10^{-6} and 4 to 180×10^{-6}, respectively. The $^3He/^4He$ ratios are between 1.05 Ra and 3.1 Ra (Ra = 1.4×10^{-6}); the $^4He/^{20}Ne$ values are between 0.45 and 1011, larger than the atmospheric value (0.32). The $\delta^{13}C$ (PDB) values of carbon dioxide range from −9.6 to −4.2‰. These geochemical data demonstrate that the spring water is from aquifers at different depths, and that helium and carbon dioxide are derived from the mantle, and are contaminated by crust gases during deep fluid migration. Also, there are larger fluxes of deep-earth matter and energy in the WDLC volcanic area.

Key words: gas geochemistry, spring, volcano, Wudalianchi

1 Introduction

Gas geochemistry has made a great step forward in the last decades. Different molecular and isotopic compositions of gases of various origins have been found (Du et al., 1991; Ozima et al., 1983; Mamyrin et al., 1984; Xu, 1994; Valbracht et al., 1996), which enables us to distinguish the genetic processes of gases. The chemical properties of gases are responsible for their geochemical behaviour. The gases that escape from the interior of the Earth carry a lot of information about the deep geological processes. This paper aims to discuss the origins and migration of gases based on the gas geochemical characteristics.

2 Geological Setting

There are 14 volcanic cones in the WDLC area of more than 800 km^2, located at 48°30′–48°50′N, and 126°00′–126°25′E. The WDLC volcanic area is tectonically situated on the northern edge of the Songliao rift valley, Northeast China, and connected with the Songwu graben and Xiaoxinganling uplift to the north. The volcanic cones were formed during 2.07 Ma to AD 1721 (Lu, 1990). The exposed rocks in the volcanic area are dominanted by alkali basalts and Quaternary sandy gravels. There are two groups of main faults: one consists of NE-trending compression faults, and the other, NW-trending extensional faults (Fig. 1). The Yaoquanshan cone was formed about 0.5 Ma ago, mainly consisting of black basaltic pumice and other volcanic rocks. The youngest cones in this volcanic group are the Laoheishan and Huoshaoshan cones formed by volcanic eruptions during 1717–1721. There are many springs in the volcanic area. The temperatures of the springs are between 3 to 19℃. Most of the springs are enriched in carbon dioxide.

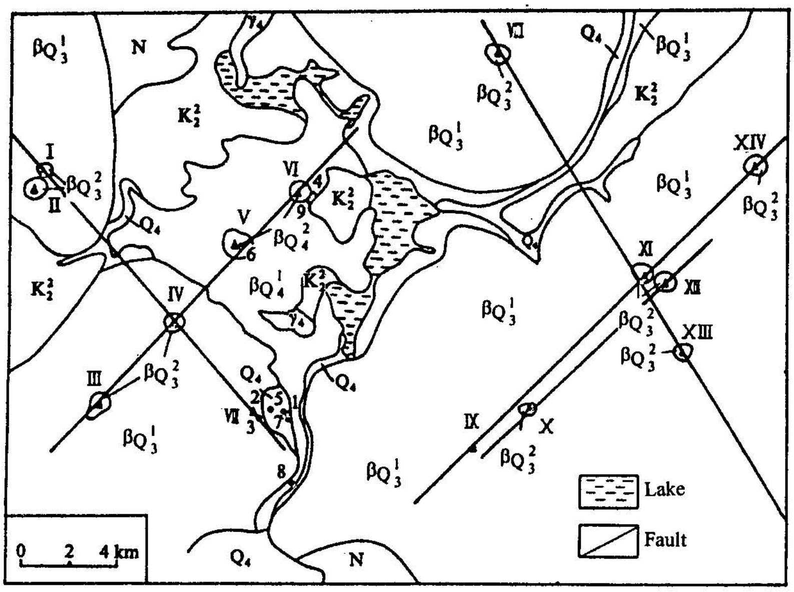

Fig. 1. Map of geology and sampling locations of the Wudalianchi volcanic area (modified after the Heihe Sci. & Tech. Commission, 1974, unpublished).

Q4–Quaternary sand and mud; βQ_4^2 –Holocene new-stage cone lava; βQ_4^1 –Holocene pillow lava; βQ_3^2 –Pleistocene old-stage cone lava; βQ_3^1 –Pleistocene basalt; N–Tertiary sandy gravel; K_2^2 –Cretaceous sandstone and shale, γ_4–Hercynian granite; Δ–volcanic cone and its number; O– sampling site and its number. I–XIV. Volcanic cones: I. North Gelaqiushan, II. South Gelaqiushan, III. Wohushan, IV. Bijashan, V. Laoheishan, VI. Huoshaoshan, VII. Yaoquanshan, VIII. Weishan, IX. West Jiaodebushan, X. East Jiaodebushan, XI. West Longmenshan, XII. East Longmenshan, XIII. Yingbeishan, XIV. Molabushan.

3 Sampling and Analysis

Water and gas samples were collected from the Huoshaoshan, Laoheishan and Yaoquanshan districts in August, 1997 (Fig. 1). Free-gas samples were collected from bubbles in springs and pools. Water samples for analyzing dissolved gases were taken from springs or pools in which large bubbles are not found. The containers of the samples are glass bottles of 500 ml. Helium isotope ratios were measured with the VG-5400 MS, and gaseous molecular compositions were determined with the MAT-271 MS in Lanzhou Institute of Geology, Chinese Academy of Sciences in September, 1997. The $\delta^{13}C$ values were measured with the MAT-251 MS with an analytical error of 0.1 ‰. The data are shown in Table 1.

4 Discussion

The hydrogen and oxygen isotope compositions (Table 1) of the spring water in the study area indicate that it comes from precipitation (Shang Guan et al., 1995). Dissolved air goes deep underground through water convection. Oxygen can be an indicator of water migration because it is exhausted by under-ground che-mical reaction. If the atmospheric water migrates through the deep crust for a long time, the dissolved oxygen tends to be exhausted. The water sample (No. 3) taken from the Erlongyan spring (ELY) contains 17.59% of oxygen in dissolved gas, which indicates that the spring water comes from shallow groundwater. Plenty of surface water penetrates into the shallow aquifer, which causes the concentration of carbon dioxide to decrease to 13.37%. There is a small amount of oxygen in the water samples (Nos. 1, 7 and 2) from the Beiyin spring (BYQ), Nanyin spring (NYQ), and a well at a seismic station (DZT), which indicates that the spring water comes from deep groundwater, but has passed through various strata since the methane concentration in the dissolved gases differs greatly.

Sample No. 8 was collected from the Wenbo pool (WB), which has an average water temperature of about 14℃, and is never frozen in winter although the lowest air temperature reaches −42℃. The compositions and ratios of the dissolved gas (Table 1) are evidently different from the atmospheric values, and its helium isotope ratio of 1.61×10^{-6} is higher than that of the air ($Ra=1.4\times10^{-6}$). Besides, the CO_2 concentration is much higher than that of the air dissolved in water. The differences are caused by additional in-put of gases derived from the deep earth. A large amount of heat energy is carried into the pool during deep-source gas emission, so that it does not freeze in win-

Table 1 Molecular and isotopic compositions of gases from springs in the Wudalianchi volcanic area

No.	1	2	3	4	5	6	7	8	9	10
Sample	BYQ	DZT	ELY	HLQ	FHQ	LHS-1	NYQ	WB	BGL	Air
CO_2 (%)	98.47	96.64	13.37	85.00	84.51	0.51	97.80	2.12		0.0374
N_2 (%)	1.47	2.76	67.51	11.98	10.65	77.87	2.13	88.00		78.08
Ar (%)	0.044	0.050	1.53	0.16	0.24	0.93	0.066	1.49		0.93
O_2 (%)	/	0.53	17.59	2.84	4.55	20.69	0.0027	8.39		20.95
He (10^{-6})	0.7	110.0	5.0	150.0	380.0	4.0	8.0	4.0		5.24
CH_4 (10^{-6})	180.0	74.0	4.0	29.0	150.0	1.0	47.0	4.0		1.4
$^3He/^4He$(10^{-6})	2.17±0.06	3.87±0.10	1.71±0.05	4.55±0.12	4.53±0.12	1.48±0.04	4.52±0.12	1.61±0.05	1.46±0.04	1.4
$^4He/^{20}Ne$	0.85	1011	1.09	103	207	0.35	55.4	1.15	0.45	0.32
O_2/Ar	–	10.6	11.5	17.8	19.0	22.2	0.03	5.6		22.43
N_2/O_2	–	5.6	3.8	4.2	2.3	3.8	788.9	10.5		3.73
N_2/Ar	33.4	55.2	44.1	74.9	44.4	83.7	32.3	59.1		83.60
δD (SMOW)	–88.4	–87.2	–87.8	–77.9			–90.1			
$\delta^{18}O$ (SMOW)	–12.2	–12.5	–12.1	–10.0			–12.2			
$\delta^{13}C$ (PDB)	–6.7*	–7.4*	–9.3*	–4.6*			–5.1*			
		–7.7		–5.5	–4.2	–9.6				

* Data from Shangguan, 1995; others measured in September 1997.

ter.

Free-gas samples of Nos. 4 and 5 were gathered from bubbles in the Hualin bubbling spring (HLQ) near the Huoshaoshan and Fanhua spring (FHQ) near Yaoquanshan, respectively. The gases contain approximately 85% of carbon dioxide, 10% of nitrogen, and minor oxygen. The O_2/Ar, N_2/Ar, and N_2/O_2 ratios are evidently different from those of the air (Table 1). The Ar concentrations in the gases are much (c. an order of magnitude) lower than that in the air but and the N_2/Ar ratios of the former are only slightly lower than the latter. The samples have relatively high helium concentrations, and high helium isotope ratios (c. 3 Ra). Their $^3He/^4He$ values are concordant with those (1–4Ra) of some natural gases derived from the upper mantle in eastern China (Du, 1994), and those (2.0–3.2 Ra) of some volcanic gases in Italy (Tedesco et al., 1990), and are close to the values (1.1–12.7 Ra) of some gases in geothermal systems of Iceland, the Geysers, Raft River and Steamboat Springs (Torgersen et al., 1982). The $\delta^{13}C$ values of CO_2 of the spring gases are concordant with those of the deep-source gases. Some deep-source carbon dioxide reservoirs with similar carbon isotope ratios have been found in the Songliao basin (Du, 1991). The above data indicate that the gases in the HLQ and FHQ springs largely come from the upper mantle.

The DZT free-gas sample was collected from a deep well enriched in gas. The well has a depth of 242 m, and has been monitored for earthquakes since 1984. Water and gases come from Hercynian granite. The N_2 /Ar ratio (55.2) is different from the atmospheric value (83.6). The relatively high concentrations of CO_2 and He, and large $\delta^{13}C$ (CO_2) and $^3He/^4He$ values (Table 1) indicate a deep sources of the gases.

Gas sample No.6 was collected from a vent in a wide fault in the Laoheishan crater. Ice and frost can be seen even in summer on the rock close to the vent from which gas escapes. Based on the molecular and isotopic compositions of the sample (Table 1), it can be concluded that the gases contain the same components as the atmosphere except CO_2. The results show that sample gas has been seriously contaminated by air near the surface.

Dissolved gases in other five water samples (Nos.1, 3, 7, 8 and 9) are also enriched in CO_2; those in spring water of NYQ and BYQ near Yaoquanshan are dominated by CO_2, with a small amount of N_2 (Fig. 1 and Table 1). Sample No. 9 was collected from the Bagualou pool (BGL) close to Huoshaoshan. The gas components could not be analyzed because the sample was contaminated by air after an analysis had been made of the helium isotope ratio. The He isotope composition and the $^4He/^{20}Ne$ ratio of the BGL are similar to the atmospheric values. This indicates that the dissolved gases in the pool may be of an atmospheric origin, or be in an equilibration with air.

All the $^4He/^{20}Ne$ and $^3He/^4He$ values of the gas samples (Table 1) are larger than the atmospheric values. It can be considered that helium and neon in the samples are derived from the crust and mantle instead of the atmospheric noble gases. Kong and Zhao (1993) reported 13 vatios of $^4He/^{20}Ne$ between 0.49 and 196.90, $^{40}Ar/^{36}Ar$ ratios in a range of 267–330, and concluded that He and Ar are partially derived from the deep earth. Based upon the assumption of the isotope ratios of 0.01 Ra and 8 Ra for crustal He and mantle He respectively, it is calculated with a two end-member model that at least 12–37% of helium in the samples is derived from the mantle. It is noteworthy that the samples from DZT, HLQ, and FHQ have relatively high He concentrations (Table 1), and that radioactive elements in Hercynian granite produce a large amount of helium. This indicates that a large flux of mantle helium is still releasing to the crust and atmosphere in the study area.

The $\delta^{13}C$ values of CO_2 in the area range from −9.6 to −4.2‰ (PDB). The mean $\delta^{13}C$ value of CO_2 in the high-temperature (>900℃) eruptive gases from Kilauea Volcano, Hawaii, is −8.82‰ and the $\delta^{13}C$ values of parental magma supplied to the summit chamber are in a range of −4.1 to −3.4‰, but those of melt after summit chamber degassing are between −7 and −8‰ (Gerlach et al., 1990). Similar data have been reported from the East and West Eifel districts, and the Vogelsberg and Kaiserstuhl volcanic sites, Germany, which fall in a range of −10 to −4‰. Carbon dioxide may be the principal carrier phase of the mantle-derived helium to the Earth's surface (Greisshaber et al., 1992). It can be argued that CO_2 in the springs of the WDLC area is of a mantle origin according to the helium and carbon isotopic compositions. The $CO_2/^3He$ ratios of gases from this area are in a range of 5×10^8 to 6×10^{11}, which agrees with those (mean value being 10^9) in basaltic glass from the spreading ridges in the Atlantic, Pacific and Indian oceans (Marty et al., 1987), and those in the CO_2-rich dissolved gases in Germany. The CO_2 and He in the dissolved gases are derived from the mantle (Greisshaber et al., 1992). The wide range of $CO_2/^3He$ ratios in the dissolved gases from the study area is likely attributed to the contamination of crustal He and CO_2 during the underground fluid migration.

5 Conclusions

As revealed by the available gas geochemical data, mantle volatiles in the study area are continuously releasing to the Earth's surface through the crust, and a large flux of mantle-derived gases are still migrating to the shallow crust. At least 13–37% of the helium in dissolved gases are derived from the mantle. The mantle origin of CO_2 in the gases suggests that they are likely occluded gases in the magma chamber after magmatic eruption and degassing, but the contamination of non-mantle gases cannot be excluded. A large amount of deep-source gases migrate into the Wenbo pool, which makes it non-freezing all year round.

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References

Du Jianguo, 1991. Natural gases enriched in carbon dioxide in China. *Geoscience of Natural Gas*, 2(5): 203–208. (in Chinese).

Du Jianguo, 1994. Helium isotope evidence of mantle degassing in rift valley, Eastern China. *Chinese Sci. Bull.*, 39(12): 1021–1024.

Du Jianguo, and Liu Wenhui, 1991. Isotopic geochemistry of nonhydrocarbons in natural gas from Sanshui Basin, Guangdong Province. *Chinese J. Geochem*, 10(4): 318–325.

Gerlach, T.M., and Taylor, B.E., 1990. Carbon isotope constraints on degassing of carbon dioxide from Kilauea Volcano. *Geochim. Cosmochim. Acta*, 54: 2051–2058.

Griesshaber, E., O'Nions, R.K., and Oxburgh, E.R., 1992. Helium and carbon isotope systematics in crustal fluids from the Eifel, the Rhine Graben and Black Forest, F.R.G.

Chem. Geol., 99: 213–235.

Kong Lingchang and Zhao Yi, 1993. Study of isotopic ratios of some inert gases for the Wudalianchi volcanic region. *Seism. Geol.*, 15(1): 88–90 (in Chinese).

Lu Zongwen, 1990. Potential active regions and active characteristics of Cenozoic volcanoes in China. In: Ren J. (ed.), Development and Study of Volcano. Beijing: Seismological Press, 12–48 (In Chinese).

Mamyrin, B.A., and Tolstikhin, L.N., 1984. *Helium Isotopes in Nature*. Amsterdam-Oxford-New York-Tokyo: Elsevier, 75–192.

Marty, B., and Jambon, A., 1987. $C/^{3}He$ in volatile fluxes from the solid Earth: implications for carbon geodynamics. *Earth Planet. Sci. Lett.*, 83: 16–26.

Ozima, M., and Podosek, F.A., 1983. *Noble Gas Geochemistry*. Cambridge: Cambridge Univ. Press, 127–298.

Shangguan Zhiguan, 1995. Study of fluids and their stable isotope compositions from volcanic areas. In: Liu R. (ed.), Human Environment and Volcanic Action. Beijing: Seismological Press, 98–100 (in Chinese).

Tedesco, D., Allard, P., Sano, Y., Wakita, H., and Pece, R., 1990. Helium-3 in subaerial and submarine fumaroles of Campi Flegrei caldera, Italy. *Geochim. Cosmochim. Acta*, 54: 1105–1116.

Torgersen, T., and Jenkins, W.J., 1982. Helium isotopes in geothermal systems: Iceland, The Geysers, Raft River and Steamboat Springs. *Geochim. Cosmochim. Acta*, 46: 739–748.

Valbracht, P. J., Staudigel, H., Honda, M., McDougall, I., and Daveis, G.R., 1996. Isotopic tracing of volcanic source regions from Hawaii: decoupling of gases from lithophile magma components. *Earth Planet Sci. Lett.*, 144: 185–198.

Xu Yongchang, 1994. The Application and Genetic Theory of Natural Gas. Beijing: Science Press, 270–316.

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