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Methane-rich fluid inclusions and their hosting volcanic reservoir rocks of the Songliao Basin, NE China

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Abstract: Methane-rich fluids were recognized to be hosted in the reservoir volcanic rocks as primary inclusions. Samples were collected from core-drillings of volcanic gas reservoirs with reversed $\delta^{13}C$ of alkane in the Xujiaweizi depression of the Songliao Basin. The volcanic rocks are rhyolite dominant being enriched in the more incompatible elements like Cs, Rb, Ba, Th, U and Th with relative high LREE, depleted HREE and negative anomalies of Ti and Nb, suggesting a melt involving both in mantle source and crustal assimilation. Primary fluids hosted in the volcanic rocks should have the same provenance with the magma. The authors concluded that the enclosed CH_4 in the volcanics are mantle/magma-derived alkane and the reversed $\delta^{13}C$ of alkane in the corresponding gas reservoirs is partly resulted from mixture between biogenic and abiogenic gases.

Key words: Songliao Basin; reservoir volcanic rocks; primary fluid inclusion; CH_4 and CO_2; abiogenic origin natural gas

Introduction

Methane-rich fluids in the oceanic crust were detected in basaltic glasses and submarine hydrothermal vents (Kelley, 1996). CO_2 and H_2O are the most abundant volatile species in the fluids outgassing from mid-ocean ridge magma chambers. Similar cases show that CO_2, CH_4 and H_2 are significant components of fluids venting on seafloor (Lilley *et al*., 1993). H_2O-CO_2-CH_4-bearing fluids were found in quartz from ferberite ($Fe_{95}Mn_{05}WO_4$) vein within the low-grade metamorphic aureole of the Borne granite (French Massif Central) (Ramboz *et al*., 1985). In fracture zone environment, carbon-bearing fluids may be of particular importance in chemical and thermal exchanges between the upper mantle and the lithosphere. The reduced nature of carbonic fluids in silica-undersaturated alkalic igneous systems has long been recognized (Konnerup, 1988) and reduced fluids were also found in peralkaline granite (Salvi and Willianms-Jones, 1997). These fluids are dominated by methane, almost invariably contain significant proportions of heavier alkanes (C_2 to C_5 and higher), and less frequently, contain unsaturated aliphatic hydrocarbons. They are also characterized by an unusually high hydrogen content and commonly contain significant nitrogen. Although there is still no clear consensus on the provenance of the carbon, i.e., whether it originated from inorganic gases produced by the magma or represents organic carbon, graphite or carbonate introduced into the magma, the majority of researchers appear to favour the orthomagmatic hypothesis (Kogarko *et al*., 1987).

In this contribution, we report the results of fluid inclusions and the corresponding hosting volcanic rocks that are reservoirs for the commercial natural gases of mainly CO_2/CH_4. Different from the examples above, methane-rich fluid inclusions are hosted in acidic rocks, predominantly rhyolite in the Songliao Basin. Guo *et al*. (1994, 1997) believed that some of natural gases were inorganic origin according to their

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carbon isotopes and comparison to those typical abiogenic gases collected from Yellowstone mud volcano and mid-ridge of the east Pacific (Dai *et al*., 1993, 1995). We provide here in this paper direct evidence for abiogenic gases, the primary fluid inclusions hosted in the volcanic reservoir rocks. And as comparison, we investigate in detail signatures of the volcanic rocks.

1 Geological setting

Songliao Basin is the most important oil and gas productive basin in China. It situates in Northeast China and its present area is ca. 260 000 km^2. The basin is bounded by mountain ranges around and shows NNE orientation with the same strike of the related crustal fault systems (Fig.1). It began its basin filling since Early Jurassic and the overall succession can be stratigraphically separated into two parts. The lower part is characterized by volcanogenic successions including andisite, rhyolite, pyroclastic rocks and epiclastic rocks, lasting from 208 Ma to 113 Ma (Wang *et al*., 2002a). The upper part is characterized by sedimentary sequence. Several petroliferous assemblages have recognized in the basin. The volcanic reservoirs were

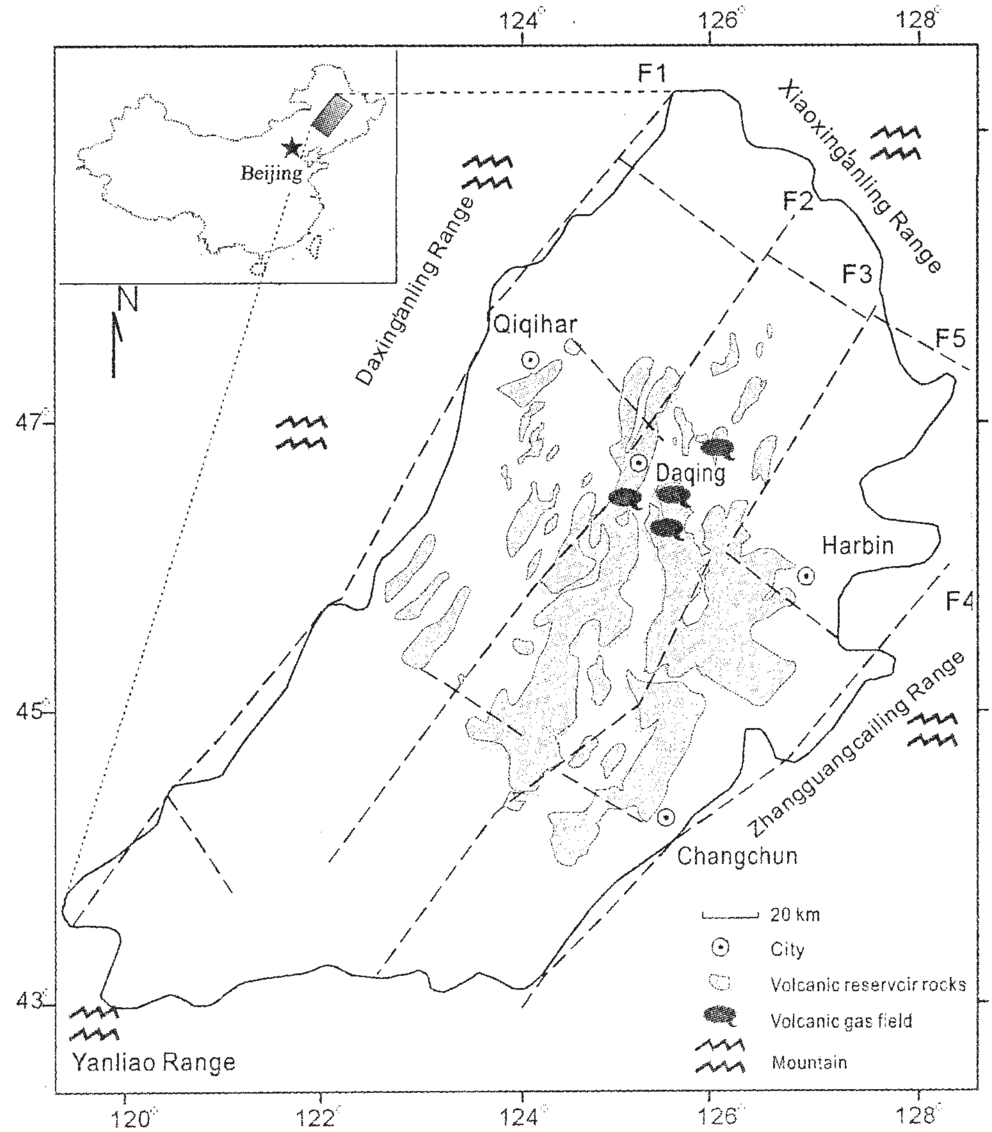
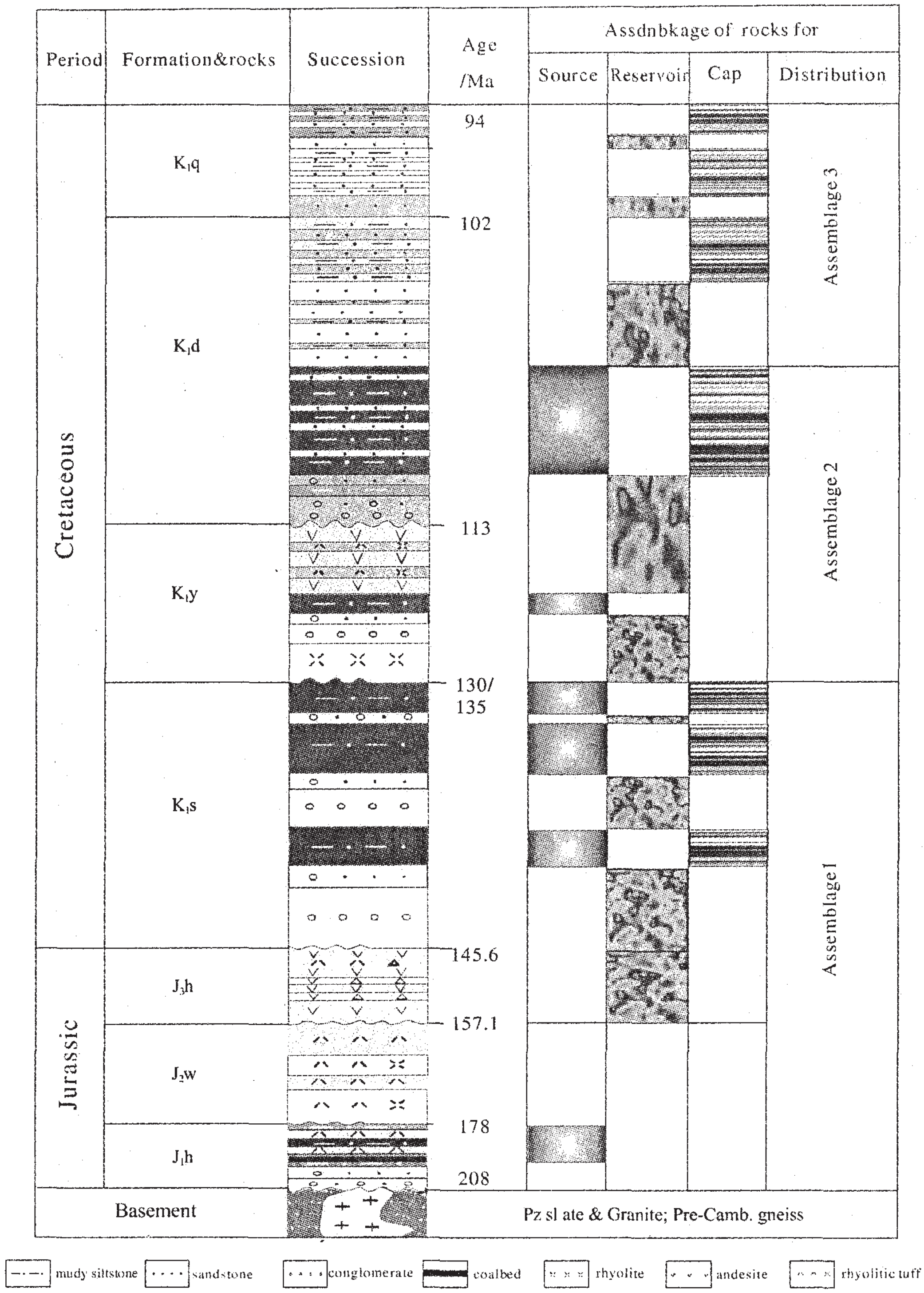


Fig. 1 Schematic map of the Songliao Basin showing major basement faults (F1–F5) and subsurface distribution of the volcanic reservoir rocks (shadows)



K_1q: Quantou Formation K_1d: Denglouku Formation K_1y: Yingcheng Formation K_1s: Shahezi Formation J_3h: Huoshiling Formation J_2w: Wanbao Formation J_1h: Hongqi Formation

Fig. 2 Stratigraphic succession and hydrocarbon trap assemblages of Jurassic-Lower Cretaceous of Songliao Basin

exploited mainly within the Cretaceous Yingcheng Formation correlating to assemblage 2 in Fig. 2.

2 Petrography, geochemistry and genesis of reservoir volcanic rocks

The reservoir volcanic rocks include almost all types from basalt to rhyolite and can be correlated with the surrounding outcrops (Wang *et al.*, 2002b). Because of the frequent occurrence and easy recognition of the inclusions in quartz phenocryst, acidic and intermediate rocks were preferably chosen for this study, involving in rhyolite, andesite, trachyte and ignimbrite. Rhyolites, the most important reservoir rocks, are white to yellowish, vesicle-rich, fluidal structure and porphyritic texture, with complex phenocryst assemblage commonly including quartz, feldspars (sanidine, anorthoclase and plagioclase). Their matrix is commonly with textures of spherulitic, vitreous and cryptocrystal-line. Andesitic rocks are black, brown, dark green, and with pilotaxitic/andesitic textures. Their phenocrysts are quartz, feldspar, biotite and hornblende. Ignimbrites are rich in phenocryst, quartz especially.

Classified with TAS diagram, the volcanic rocks include rhyolite, dacite, trachyte and basaltic trachyandesite (Fig. 3 B). The volcanics are either metaluminous or peraluminous, medium-K or high-K, calc-alkaline series dominant with a few exceptions (Fig. 3 A). The incompatible element data were plotted in order of decreasing incompatibility from left to right (Fig. 3 C and D). The normalized curves slope down from left to right, indicating their enrichment in the more incompatible elements, especially for the LIL elements like Cs, Rb, Ba, Th, U and Th. They also show enriched LREE, depleted HREE and negative anomalies of Ti and Nb. Some of the rhyolites have negative Eu anomalies. Some samples show negative anomalies of Sr and Ba. Half of the volcanic rocks have negative Zr and Hf anomalies.

Based on chronostratigraphy, element geochemistry and isotopes of the volcanic rocks within and around the Songliao Basin, Wang *et al*. (2002a, b) recognized three origins of the acidic-intermediate lavas including crystal fractionation in source region, upper and lower crustal assimilation. Without negative anomalies of Nb, Zr and Hf, a sample shows strong negative anomalies of Sr, Ba and Eu implying a rhyolitic melt derived from source crystal fractionation. Upper crustal assimilation is revealed by both of the negative anomalies of Nb, Zr and Hf and of the enrichment of crustal-elements like Sr, Ba, U, Th and K (Fig. 3 C). Samples with negative Rb anomaly and without anomalies of Nb, Zr and Hf may suggest lower crustal assimilation (Fig. 3 D). Besides, overprinted volcanics in genesis may exist.

3 Fluid inclusion signatures in the reservoir volcanic rocks and their genetic meaning

Three genetic types of inclusions were recognized including melt/glassy-, primary- and secondary ones

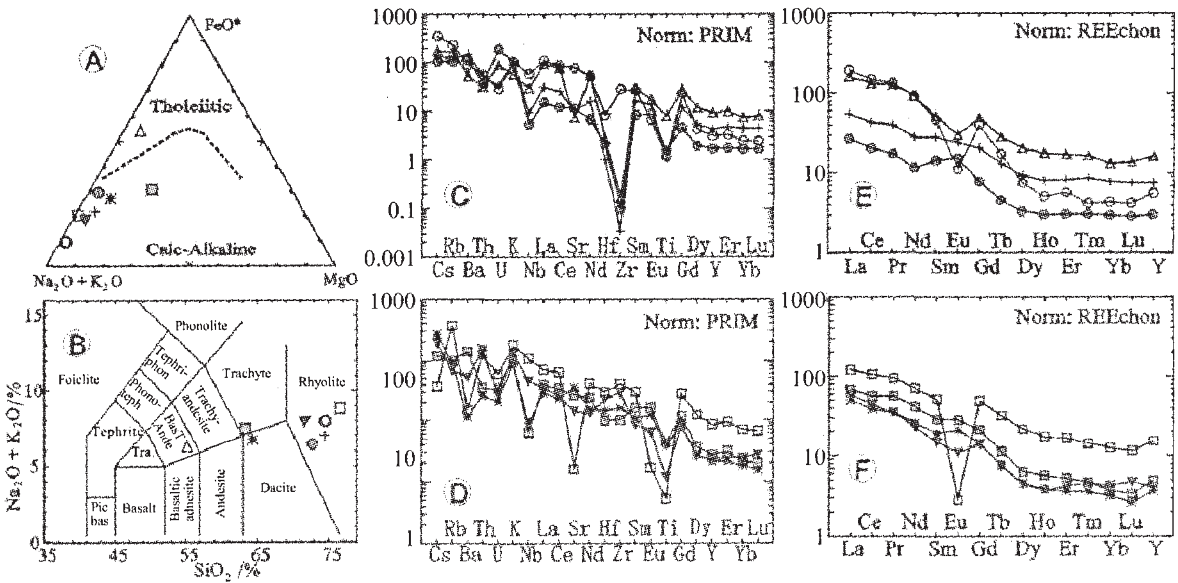


Fig. 3 Geochemical diagrams showing signatures of the reservoir volcanic rocks

A. AFM diagram; B. TAS diagram; C and D. primitive mantle normalized trace element spidergram; E and F. chondrite normalized REE pattern

(Fig. 4). Measured homogenization temperatures for both the primary and secondary inclusions fall in between 120～300℃. But their peak temperatures are a little different. 150～180℃ is for the primary inclusions and 140～160℃ for the secondary ones. Compared with the primary group, the secondary ones have a blank region between 190℃ and 280℃, probably being caused by insufficient samples.

Co-existing liquid and gaseous phases were commonly recognized in the reservoir volcanic rocks of the Songliao Basin. The gaseous phases contain H_2O, H_2, CH_4, C_2H_4, C_6H_6, H_2S, N_2, CO, CO_2, SO_2 and noble gases. The liquid ones have similar components except some salt contents like Cl^-, HCO^-_3, SO^{2-}_4. Water is the predominant component in the inclusions. Over 70% of them contain H_2O more than 90% and the rest are below 10% in mole. About 30% of the inclusions contain high concentration of CH_4 and CO_2, which up to 77% and 95% in mole respectively. A typical example of the fluid inclusions measured by Renishaw System-1 000 Raman Laser Spectrometry is listed in Table 1.

The relationship between concentration of CH_4 and CO_2 in the volcanic fluid inclusion can be summarized as follows: ① CO_2 goes up rapidly with CH_4 at their low concentrat ions; ② the two components increase synchronously when $CH_4>15\%$ or $CO_2>30\%$; ③ CH_4 content correlates negatively to that of CO_2 with a slope about -1 when either is over 50 %.

The former two cases of positive correlation indicate that CH_4 and CO_2 derive from the same origin. The negative lineation of case 3 should be explained by "exclusion principle", that is, a prevailing component must correlate negatively to the rest of the system if there is not any reaction among them.

4 Conclusion and related explanation

Fluids enclosed in the primary vesicles of the volcanic rocks are the synchronous volatiles that are mantle/magma derived. The results of this paper indicate that these volatiles can yield high methane during their cooling process. On the other hand, previously available data have proved that the reservoir gas of CO_2 are typical mantle/magma origin (Xu *et al*., 1996; Li *et al*., 1999) with $CO_2>80\%$、$\delta C_{CO_2}=-0.406\%\sim-0.661\%$、R/Ra $=2.79\sim3.0$. The co-existence and positive correlation between CO_2 and CH_4 suggest that they come from the same source. We therefore concluded that the detected

Table 1 Composition of primary fluid inclusion in the reservoir volcanic rocks

Inclusion No.		1	2	3	4
Vapor phase /%	H_2O	3.98	98.89	94.95	
	H_2		0.18	0.32	
	CH_4	38.25	0.1	0.12	77.77
	C_2H_4	1.09			0.98
	C_2H_6				
	C_6H_6	0.59		0.1	1.06
	H_2S			0.17	0.27
	N_2				2.22
	CO		0.49	1.44	2.25
	CO_2	56.08	0.36	2.92	15.44
Liquid phase /%	H_2O	98.46	97.87	98.27	
	CH_4	0.10	0.10	0.10	
	C_3H_8				
	C_6H_6				
	N_2				
	CO		1.10		
	CO_2	0.51		0.62	
	CL^-	0.60	0.45	0.45	
	HCO^-_3	0.21	0.37	0.34	
	SO^{2-}_4	0.13	0.19	0.26	
	C_2H_4				
PH		6.32		6.45	
Eh		-0.49	0.66	-0.48	0.1

Description of the measured fluid inclusions: 1. Vv/VL=60%～65%, Φ=18 μm; 2. Vv/VL=5%～10%, Φ=20 μm; 3. Vv/VL=10%; Φ=8 μm; 4.Vv/VL=90%～95%, Φ=25 μm.

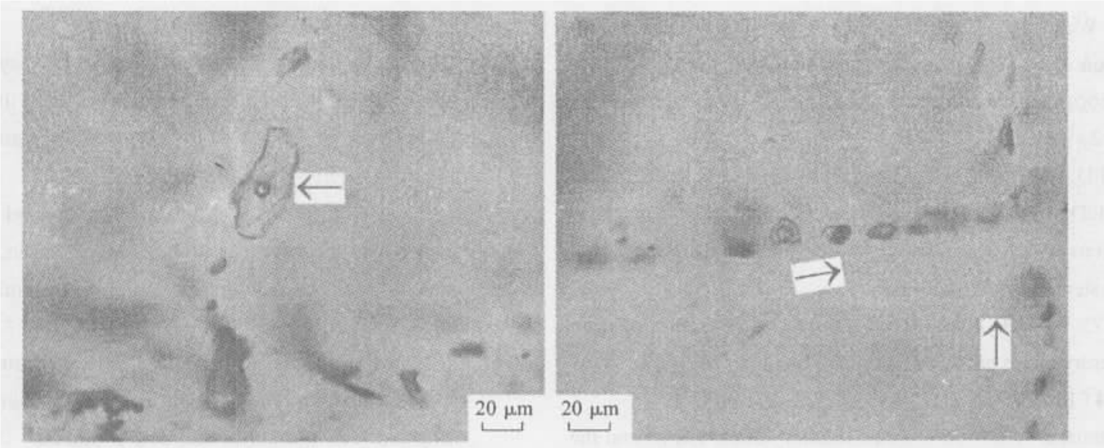


Fig. 4 Pictures of fluid inclusions in reservoir volcanic rocks of Songliao Basin
Left: Primary inclusion (arrow, K_1y); Right: Secondary inclusions (along arrows, K_1y)

CH_4-containing inclusions in the reservoir volcanic rocks should be considered as direct evidence for inorganic origin natural gas.

The proportion of abiogenic origin gases that has contributed to the corresponding gas pools is still a question. Even if there is source of abiogenic origin methane, whether and how can they come into the gas pools is a big problem because volcanic degassing was prior to trap forming. However, our results show that concentration of CH_4 in aqueous inclusion goes up with increasingly reversed order of $\delta^{13}C$ in alkane, suggesting its influence on isotopes of the reservoir gases. Abiogenic alkane must have joined the gas pools significantly.

The volcanic rocks formed during 158～110 Ma (Wang *et al*., 2002a). Since then they have suffered a series of thermal/tectonic events (Hou, 2002; Liu *et al*., 2003) with which the enclosed aqueous could get the chance to escape from volcanic vesicle and come into gas pools. But it is still a question as how many gas the process could provide and how could it change the isotopic compositions of the reservoir gases. Guo *et al*. (1997) proposed that deep abiogenic gases could go up to the basin through crustal faults and natural earthquakes. It is a creative idea though having not been proved.

Aqueous inclusions in the volcanic rocks are heterogeneous on micro-/magro- scales. Even in the same sample they can be very different from each other in their contents, concentrations and homogeneous temperatures. We therefore selected only the inclusions with significant amount of CH_4/CO_2 for our research. The results provided us representative information about inclusion and gases although the inclusions composed mostly of water have been kicked out.

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