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Br/Cl, I/Cl and chlorine isotopic compositions of pore water in shallow sediments: implications for the fluid sources in the Dongsha area, northern South China Sea

LI Yanping[1, 4], JIANG Shaoyong[2, 3]*, YANG Tao[2, 4]

[1] Ministry of Education Key Laboratory for Coast and Island Development, School of Geographic and Oceanographic Sciences, Nanjing University, Nanjing 210093, China

[2] State Key Laboratory for Mineral Deposits Research, Department of Earth Sciences, Nanjing University, Nanjing 210093, China

[3] State Key Laboratory of Geological Processes and Mineral Resources, Faculty of Earth Resources, China University of Geosciences, Wuhan 430074, China

[4] Collaborative Innovation Center of South China Sea Studies, Nanjing 210093, China

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Abstract

The Dongsha area is one of the most promising target areas for gas hydrate exploration in the South China Sea (SCS). The study of pore water geochemistry has played a key role in Chinese gas hydrate exploration. Br/Cl, I/Cl and δ^{37}Cl in pore water were applied here in tracing gas hydrate occurrence, chemical evolution of pore fluids and water/rock interactions in low temperature sediment environments. The samples were collected from Sites HD255PC and HD309PC in the Dongsha area in 2004. At Site HD255PC, we found the elevated Br/Cl, I/Cl and decreased SO_4/Cl at the depth of 4–5 m, suggestive of a laterally migrated fluid probably generated from the gas hydrate occurrence. The range of δ^{37}Cl is –0.54‰ to +0.96‰, and positive δ^{37}Cl at 4–5 m interval should be related with different diffusion rates between ^{35}Cl and ^{37}Cl. At Site HD309PC, a laterally migrated fluid was also found at the depth of 3–4 m, with the Br/Cl two times to that of the seawater and decreased I/Cl, indicating the fluid has no relationship with the gas hydrate. In this site, the chlorine isotopic composition varies from –0.7‰ to +1.9‰. Extra high Br/Cl might relate with the deep generated fluid. At higher temperature and pressure, the Br/Cl of the fluid is elevated during the hydrous silicate formation, while positive δ^{37}Cl is also associated with the same mechanism.

Key words: halogen, chlorine isotope, pore water, Dongsha area

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1 Introduction

The gas hydrate exploration in China began in the last century. Bottom Simulating Reflectors (BSRs) and blanking zones indicate the existence of gas hydrate in the South China Sea (e.g., Song and Geng, 2000; Wu et al., 2005; McDonnell et al., 2000; Shyu et al., 2006; Li et al., 2013). In the Xisha Trough, Shenhu area and Dongsha area, the geochemical anomalies of pore fluids may be related to gas hydrate occurrence (Jiang et al., 2005, 2008; Wu et al., 2007; Yang et al., 2008, 2010, 2013). However, in the Dongsha area, with the complex tectonic background, the deep generated fluids also might migrate along the faults to the shallow sediments (Chao and You, 2006). Different source fluids could be distinguished by geochemistry of pore water (Martin et al., 1993; Spivack et al., 2002; Bagheri et al., 2014; Jiang et al., 2015).

The distributions of halogens (Cl, Br and I) are of special interest in many geochemical systems due to their conservative behavior and unique sources in surface environments. Ratios of Br/Cl and I/Cl can be used as conservative tracers for chemical evolution of pore fluids and water/rock interactions in low temperature sediment alteration (Martin et al., 1993; Martin, 1999) or high temperature hydrothermal systems (Oosting and Von Damm, 1996). Iodine is a very active biophile element, enriched in ocean phytoplankton and algae. The degradation of the organic matter in the sediment would lead to an increase of I/Cl ratio in the interstitial water. Bromine has the similar chemical properties to I, but the enrichment of Br is not as obvious as that of I. During the processes of the organic matter degradation, halite precipitation and hydrous silicate minerals formation, the Br/Cl ratio of the fluid is elevated (Holser, 1970; Martin, 1999).

Chlorine has two stable isotopes, ^{35}Cl and ^{37}Cl. Because of the long residence time, chlorine isotopic composition (δ^{37}Cl) of the modern seawater is constant (Godon et al., 2004). The δ^{37}Cl value of the modern seawater is defined as 0‰. The δ^{37}Cl values in continental environments (i.e., evaporates, ground water, sedimentary basin formation waters, and hydrothermal systems) do not differ from seawater by more than ~2‰. In the sedimentary systems, chlorine stable isotopes (δ^{37}Cl) can define salinity sources, mixing of different fluids and water-rock interaction (Kaufmann et al., 1984; Eastoe and Guilbert, 1992; Eggenkamp et

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*Corresponding author, E-mail: shyjiang@nju.edu.cn

al., 1994; Eastoe et al., 1999, 2001; Zhang et al., 2007a; Li and Jiang, 2013; Bagheri et al., 2014).

In this study, we applied ratios of Br/Cl and I/Cl in the fluids to quantify the influence of the organic matter degradation and hydrous silicate formation in the studied area with possible gas hydrate occurrence and many faults. Based upon the chlorine isotopic composition in pore waters, we discussed the main physical and chemical processes of the pore fluids that may affect the chlorine isotope fractionation.

2 Geological background

The South China Sea (SCS) is one of the largest marginal seas in the West Pacific Ocean, the northern slope of the SCS is covered by thick Mesozoic and Cenozoic sediments, where a number of large and medium-sized sedimentary basins (e.g., the Zhujiangkou, Qiongdongnan, Yinggehai, and Taixinan Basins) are located. The deposition rate was 17.9–19.6 cm/ka and 9.6–14.6 cm/ka for Late Pleistocene and Holocene, respectively, somewhat higher than that for the Pliocene (Gong et al., 2009). The thick sediment layers laid a foundation for the formation of gas source and gas hydrate. The occurrence of gas hydrate in the SCS was known as postulated from the geophysical and geochemical investigations (Ge et al., 2010; Liu et al., 2011). In 2007, natural gas hydrate samples were obtained in the Shenhu area for the first time in China (Zhang et al., 2007b). In 2013, during China's second major expedition, GMGS2, gas hydrates were found in 9 of the 13 sites (shown in Fig. 1). The gas hydrate samples are characterized by shallow burial positions, large thicknesses, multiple types and high concentrations (Zhang et al., 2014; Liu et al., 2015).

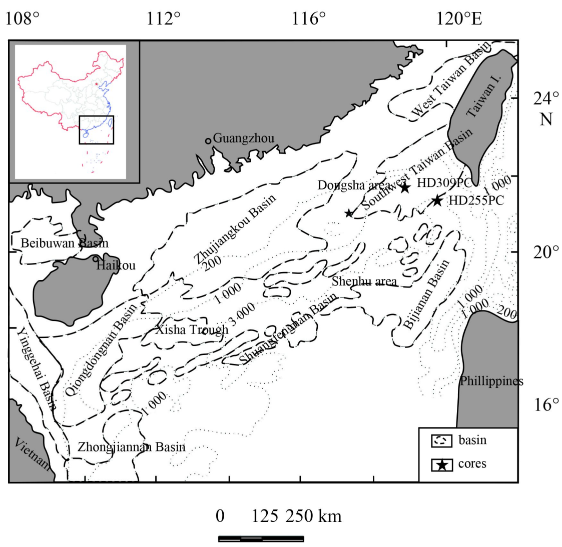

Fig. 1. The basin distribution and location of the sampling sites in the northern South China Sea.

Situated at the southwest of the Taixinan Basin of the passive northern margin, the study area where the topography is complex and the slope varies greatly experienced intensive neotectonic movements, which resulted in complex basement structure and developed complicated fault systems (Wang et al., 2006). The sea water depth in Sites HD255PC and HD309PC (Fig. 1) range from 1 000 m to over 3 000 m. A large number of faults and mud diapirs have been observed in the Dongsha area (Yan et al., 2006; Li et al., 2013), both of which are useful conduits that allow methane gas to migrate upward and link free gas zones beneath BSRs, hydrate zones and seafloor methane seepage. Many faults penetrate the basement of the basins and some active faults can reach the seafloor. The faults and mud diapirs in the Dongsha area provided excellent tectonic environment for the formation of gas hydrate system (Yan et al., 2006; Li et al., 2013).

3 Methods

Core samples (about 6–7 m in length) were collected during a cruise of the onboard R/V *Haiyangsihao* in 2004, using a Gravity Piston. After removal of the bottom 5–10 cm sediments in the gravity piston tube, 15–20 cm sediments were collected at an interval of 100 cm core depth. Pore water was extracted using a vacuum extraction device onboard. All pore water samples were collected and sealed in a PTFE tube, then preserved at a temperature of 4°C. All the geochemical analyses were carried out at the State Key Laboratory for Mineral Deposits Research, Nanjing University.

The anion (Cl, Br, I and SO_4) were measured using the standard method of ion chromatography (790 IC, Metrohm, Switzerland). Repeated measurements of standard sea water showed the analytical reproducibility was better than 2%. The contents of Br and I in the pore water samples were measured by ICP-MS (Element II HR-ICP-MS, ThermoFisher, Germany) and the analytical precisions were estimated to be less than 2%. The determination of Cl-isotopic composition of the pore water was carried out by the negative ion thermal ionization mass spectrometry (Triton TI, ThermoFisher, Germany). The detailed procedure has been reported in Li and Jiang (2013). The Cl isotopic compositions reported here are defined as per mil (‰) deviation from ISL354 standard, which has a measured chlorine isotopic composition of 0.319 130±0.000 29.

4 Results and discussion

Around the study area, two distinctive structural patterns were observed. The passive continental margin of SCS is located in the west and the active imbricate fold and thrust structures are observed in the east (Liu et al., 1997). With a complex tectonic background, deep fluids and gas hydrate were observed in the surface sediment (Chao and You, 2006), resulted in the abnormally large variation of the δ^{37}Cl value and halogen ion ratios. Here the halogen ion ratio characteristics and chlorine isotopic composition are discussed in an attempt to trace the lateral migration fluids at the shallow sediments.

4.1 *Halogen ion ratio*

4.1.1 *Site HD255PC*

The analytical results of the pore water samples are shown in Table 1 and Fig. 2. The Br/Cl ratios in the pore waters at Site HD255PC display a small variation (from 15.2×10^{-4} to 17.1×10^{-4}) from the top to the bottom of the core with a slight increase observed at the depth of 4–5 m. In contrast, the ratios of I/Cl and SO_4/Cl vary significantly, with a remarkable increase of I/Cl and decrease of SO_4/Cl observed between 4–5 m, respectively.

The fact that iodine and methane in the pore water may have the same origin (i.e., the degradation of organic matter) and that iodine flux can substitute the methane flux in methane gas sources (Yang et al., 2013) lead to the expectation of a good correlation between iodine and methane. Indeed, a significantly negative linear correlation is discovered between iodine and sulfate (Fig. 3). The content of iodine could reflect the content of methane primarily and could be used to trace the occurrence of

Table 1. The anion/Cl and chlorine isotopic composition of the pore water in the Dongsha area, the northern South China Sea

Site	Depth/m	δ^{37}Cl/‰	(Br/Cl)/10^{-4}	(I/Cl)/10^{-6}	SO_4/Cl
HD255PC	0.00	−0.54	15.5	7.2	0.047
	1.00	−0.07	15.9	10.6	0.045
	2.00	−0.10	15.2	24.3	0.037
	3.00	−0.17	16.2	34.2	0.032
	4.00	0.59	15.3	43.3	0.027
	5.00	0.96	17.1	84.7	0.011
	6.92	0.86	15.4	98.2	0.008
HD309PC	0.00	1.89	15.94	6.76	0.047
	1.00	0.51	16.53	20.75	0.039
	2.00	−0.74	16.03	35.34	0.033
	3.00	1.17	30.62	28.37	0.036
	4.00	1.10	28.64	39.03	0.032
	5.00	0.51	16.19	45.03	0.029
	6.00	1.26	16.79	56.28	0.019

the gas hydrate. At the depth of 4–5 m, the interstitial water is characterized by elevated amount of methane and ratios of Br/Cl and I/Cl, but depleted sulfate. A similar trend of elevated Br/Cl, I/Cl and depleted SO_4/Cl is also observed at 3–4 m interval from the Qiongdongnan Basin (Yang et al., 2013). The authors attributed the geochemical anomalies of the pore fluids to occurrence of gas hydrate. The characteristic of high iodine content and low sulfate content is similar with the expelled fluids during gas hydrate formation, implying a possibility for gas hydrate occurrence nearby. The observed geochemical anomalies at the depth of 4–5 m at Site HD255PC might also relate with the gas hydrate. A lateral migrated fluid, containing the information on gas hydrate occurrence, may have moved from the deep to shallow sediment.

4.1.2 *Site HD309PC*

The variations of Br/Cl and I/Cl versus depth show similar trend. At the depth of 3–4 m, abnormally increased Br/Cl and decreased I/Cl are observed. The maximum ratio of Br/Cl is about two times to that of the seawater. Additionally, it is different to the increase of Br/Cl and I/Cl at the depth of 4–5 m at Site HD255PC.

Both Cl and Br ions are conservative during most diagenetic reaction, and consequently, their concentrations and Br/Cl ratios commonly remain constant during low temperature alteration of marine sediments (Price et al., 1970). However, some processes, such as evaporation and dilution, are able to alter the

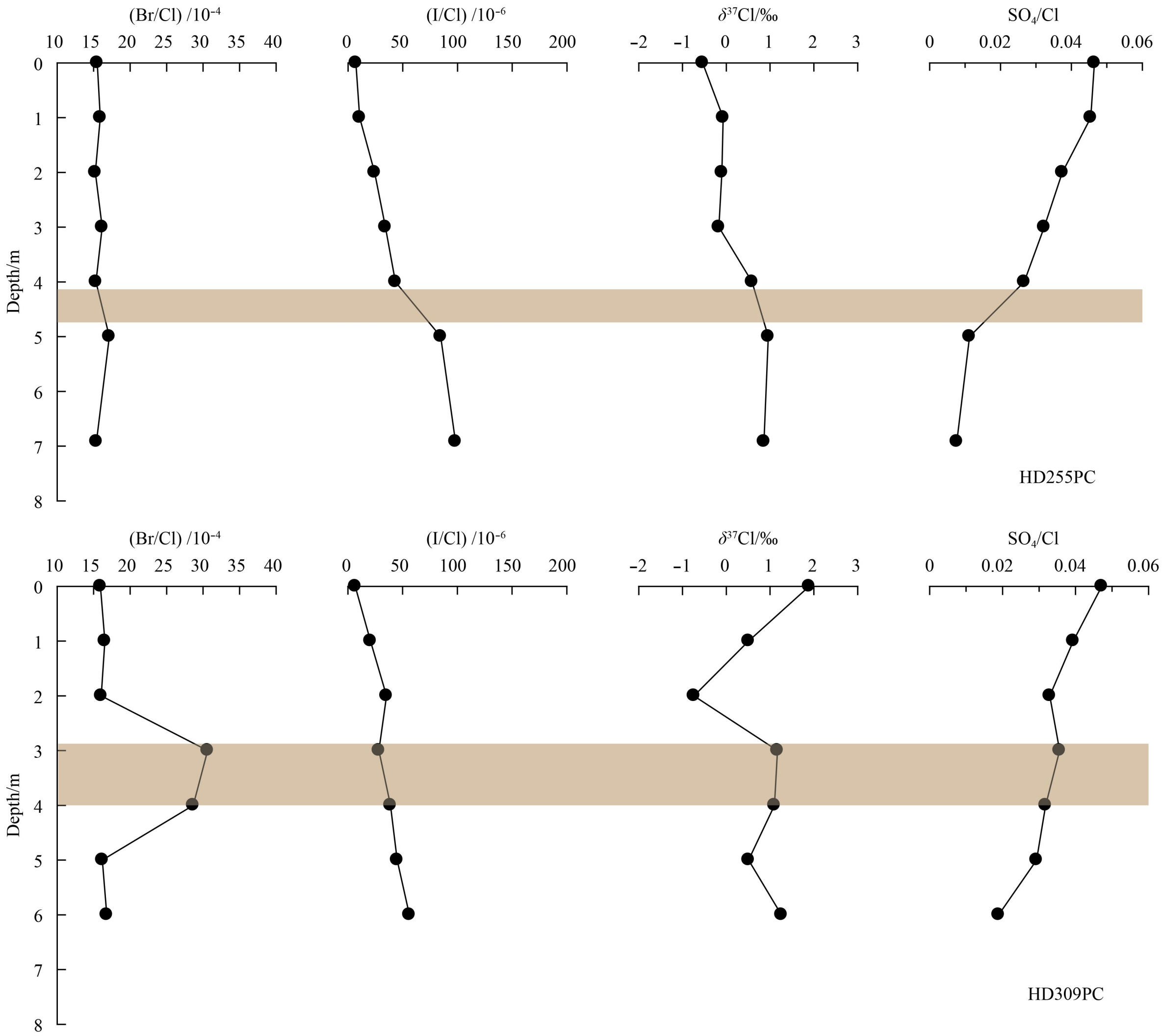

Fig. 2. The Br/Cl, I/Cl, SO_4/Cl and δ^{37}Cl of the pore water at Sites HD255PC and HD309PC. The shaded area shows the anomalous zone.

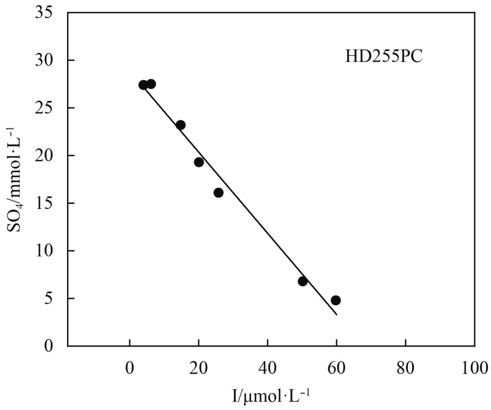

Fig. 3. Sulfate vs. Iodine diagram at Site HD255PC.

concentrations of Cl and Br, but not the ratio of Br/Cl. The degradation of the organic matter is the source of Br to marine pore fluids. Organic matter degradation is supposed to increase the concentration of Br to as much as three times to seawater value (e.g., Price et al., 1970; Pedersen and Price, 1980; Martin et al., 1993), at the same time, iodine is more enriched than Br in the pore fluids. By contrast, the concentrations of Cl are free from this process, as a result, the ratios of Br/Cl and I/Cl are increased with the degradation of organic matter. At Site HD309PC, the extra high Br/Cl ratio along with a lower I/Cl ratio in the pore fluids at the depth of 3–4 m are not derived from the organic matter diagenesis. Halite incorporates trace Br into its structure, Br concentration thus varies slightly with the precipitation and dissolution of halite (Holser, 1970). The difference between distributions of Br and Cl into halite increases the Br/Cl ratio of brines during halite precipitation. Absence of extensive halite in the study area excludes the probability of the halite precipitation. On the other hand, fluid flow can also fractionate Br and Cl in the long distance transportation. In the shallow turbidite section, Br/Cl ratios that are higher than the seawater value are attributed to the organic matter diagenesis rather than the fractionation during transportation (Price and Calvert, 1977).

The formation of hydrous silicate mineral (e.g., smectite and clay) is discovered to elevate the ratio of Br/Cl in the pore fluids (Martin, 1999; Wei et al., 2008). Cl^- substitutes OH^- into the hydrated silicate structures while getting substituted by Br^- into the silicate structure. The size distribution suggests that more Cl^- than Br^- may substitute OH^- into the silicate structure, thereby increasing Br/Cl ratio in the pore fluids. In the study area, the Eurasian plate is subducting eastwards beneath the Philippine Sea Plate at a speed of 7 cm per year along the Luzon Arc-Manila Trench system, contributing to the observation of a large number of faults and mud diapirs (Yan et al., 2006). Many faults penetrate the basement of the basins and some active faults can reach the seafloor. The migration of deep generated fluids along porous sandy layers or the decollement zone has been reported in various accretionary wedges (e.g., Ransom et al., 1995; Spivack et al., 2002). We suggest that the extra high Br/Cl ratio of the pore fluids at the depth of 4–5 m might be related to the laterally migrated fluids, which generates from deep sediment and the formation of hydrous silicate mineral elevates the ratio of Br/Cl in the fluids. During the formation of hydrous silicate mineral, I/Cl ratio of the fluids is elevated similar to the Br/Cl ratio, whereas the I/Cl ratio is observed decreased at the depth of 3–4 m at Site HD309PC. We suggest that the I/Cl ratio is also elevated about one time to the seawater as same as Br/Cl because of the formation of hydrous silicate mineral. Yet, the degradation of the organic matter released more iodine into the fluids at the shallow sediment as a supplementary, so the decreased I/Cl is observed only at the depth of 3–4 m.

4.2 *Chlorine isotopic composition*

The natural δ^{37}Cl variation in the Earth's surface is less than 2‰. There are four prospective mechanisms that may explain the positive δ^{37}Cl in the fluids. First, the difference in diffusion rate between ^{37}Cl and ^{35}Cl in the marine sedimentary column causes ^{35}Cl to become more depleted in depth (Desaulniers et al., 1986; Eggenkamp et al., 1994). Second, the precipitation, dissociation and evaporation of Cl-containing fluids will lead to ^{37}Cl enrichment in solid phases (Magenheim et al., 1995; Eggenkamp et al., 1995). Third, clay membrane filtration may also cause Cl isotopic fractionation (Phillips and Bentley, 1987). Finally, a rather large depletion of δ^{37}Cl, –8‰, observed at the decollement zone at the Nankai Trough, was explained in terms of fluid-rock reactions at depth (Ransom et al., 1995). The degradation of the organic matter will not change the Cl isotopic composition of the fluids.

At Site HD255PC, the down-core Cl isotopic compositions vary from –0.54‰ to +0.96‰. Above 4 m, δ^{37}Cl mostly center about 0‰ except the surface sample. Below 4 m, δ^{37}Cl is more positive than the seawater. As discussed in Section 4.1.1, the laterally migrated fluids, which had moved from deep to shallow sediment, take the message of gas hydrate occurrence. Given no chlorine isotope fractionation occurring during the gas hydrate formation, the enrichment of ^{37}Cl in pore fluids should be caused by other processes. Excluding the halite diagenesis and clay membrane filtration, the different diffusion rate between ^{37}Cl and ^{35}Cl might be an important mechanism in the laterally fluids along the 4–5 m interval at Site HD255PC.

At Site HD309PC, δ^{37}Cl of the pore fluids vary from –0.7‰ to +1.9‰, narrower than that of Site HD255PC. At the depth of 3–4 m, the depleted ^{35}Cl isotopic composition of +1.2‰ is detected in the laterally migrated fluid. As discussed above, the fluid generates from the deep sediment and the formation of hydrous silicate mineral elevates the ratio of Br/Cl in the pore fluids. It appears that under the conditions of high temperature and pressure when hydrous minerals dehydrate, water with positive δ^{37}Cl is also released into the pore fluids. The positive δ^{37}Cl in the pore fluids supports that at many subduction zones, the origin of upwelling pore fluids is the dehydration of the subducting serpentinized crust (e.g., Mottl et al., 2004; Wei et al., 2008; John et al., 2011). To the southwest of Taiwan, the shallow fluid with positive δ^{37}Cl (+3‰) was observed (Chao and You, 2006), and the large variation of δ^{37}Cl was also suggested to be related with the deep generated fluids.

5 Conclusions

We have analyzed pore water samples collected from the potential gas hydrate area in the Dongsha area. Down-core distribution of Br/Cl, I/Cl and δ^{37}Cl show useful information of fluid sources and migration processes. With a complex tectonic background, different source fluids migrate at the shallow sediments. At Site HD255PC, elevated Br/Cl, I/Cl and decreased SO_4/Cl indicate that the fluid generates from the gas hydrate occurrence, and positive δ^{37}Cl at 4–5 m interval should be related with different diffusion rate between ^{35}Cl and ^{37}Cl. At Site HD309PC, two times Br/Cl to the seawater and decreased I/Cl at 3–4 m interval indicate the pore fluids has no relationship with the gas hydrate occurrence. Extra high Br/Cl ratio might relate with the deep generated fluids. At high temperatures and pressures, Br/Cl ratio of the fluids is elevated during the hydrous silicate formation, at the same time, positive δ^{37}Cl also origins from the same mechanism.

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