

Physical and chemical environments of abnormal vitrinite reflectance evolution in the sedimentary basins

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Abstract Based on the tested data of pressure and vitrinite reflectance of some wells in sedimentary basins, abnormal high pressure is regarded as not the only factor to retard the increase of vitrinite reflectance (R_o). Apart from the types of the organic matter, the physical environment (temperature and pressure) and chemical environment (fluid composition and inorganic elements) will result in the abnormal vitrinite reflectance values in the sedimentary basins. This paper tested trace elements and vitrinite reflectance data from the abnormal high pressure and normal pressure strata profiles, respectively, and found that the acidic and lower salinity strata are favorable for the increase of R_o . By discussing the corresponding relationship between the contents of some trace elements in the mudstone and the vitrinite reflectance values, the typical trace elements were found to suppress and/or catalyze the vitrinite reflectance of organic matter, while the elements of Ca, Mn, Sr, B, Ba and P may result in the retardation of R_o . However, elements of Fe, Co, Zn, Ni and Rb may catalyze the organic matter maturation. This study is conducive to the organic maturation correction, oil and gas assessment and thermal history reconstruction by the paleothermometry.

Keywords vitrinite reflectance, trace element, retardation/catalysis, abnormal pressure

1 Introduction

There is usually abnormal low vitrinite reflectance (R_o) in the abnormal high pressure strata profile in many basins, such as Ying-Qiong basin, Junggar basin, Bohai Bay basin, Albert

basin, Mexico Gulf basin, the area of Rocky Mountains and so on (Gentzis and Goodarzi, 1994; Hao et al., 1995, 1998; Waples et al., 1995; Mello and Karner, 1996). Although the retardation of the organic matter evolution is to some extent related to the sedimentary environment in which the organic matter deposited (Petersen and Lerche, 1994; Carr, 2000), it is generally accepted that abnormal high pressure is the fundamental reason for retarding the thermal evolution of organic matter and hydrocarbon generation (Price and Wenger, 1992; Khorasani and Michelsen, 1994; Hao et al., 1995, 1998; Gong et al., 1997; McTavish, 1998). The retardation of pressure is also validated by the analyses of geology and geochemistry and the modeling experiment (Domine and Engnehard, 1992; Dalla et al., 1997; Gong et al., 1997; Jiang et al., 1998). This retardation of the thermal evolution of the organic matter has long been a concern in the petroleum geology field.

The abnormal high pressure seems to not be the only factor to retard the maturation of the organic matter (OM). First, the temperature and pressure are abnormally high in the profile with typical hydrothermal activity, and the abnormal high pressure (AHP) does retard the OM maturation. However, the abnormal high temperature and fluid flow in this system are less discussed in the process of organic maturation. According to the Arrhenius equation for thermal degradation of OM, there is an exponential relationship between the reactive rate of OM and temperature, but the OM maturation is still retarded in the profile with abnormal high temperature. How is the effect of temperature taken to account? Second, if it is true that the high pressure retards the OM maturation, why is the OM maturation retarded in the AHP strata profile and why is it not the case in the deep strata profile where the pressure is higher than that of AHP? Third, the maturation of OM is not retarded in some AHP strata profiles.

The vitrinite reflectance is the most common index to characterize the OM maturation and the thermal evolution history in the sedimentary basins. How to acquire vitrinite

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reflectance data objectively and accurately is the key to evaluate the maturation of source rock in the basins. Meanwhile, the paleotemperature, R_o , is the index of reconstructing thermal history of basins, and its accuracy is important to analyze the tectonothermal evolution objectively. This paper studies the mechanism for the abnormal R_o , based on the relationship between the vitrinite and its surrounding inorganic matter and the physical and chemical environment of R_o (such as temperature, pressure and fluid). This is of great significance to build the model of the hydrocarbon generation of the organic matter, to evaluate the maturation of source rock and to reconstruct the thermal history of the sedimentary basin.

2 Function of pressure

In most cases, the depth with abnormal low R_o is in accordance with the abnormal high pressure strata profile. This is why most scholars agreed with the abnormal pressure retarding R_o . In some profiles, however, the abnormal R_o has nothing to do with the abnormal high pressure; there are even some contradictions, e.g. in the western part of Qaidam basin, when R_o is relatively high in the abnormal high pressure strata profile (Fig. 1) and R_o is normal in some deep intervals. The present day's pressure is 49.1 MPa at the depth of 3898 m in the Well Boshen-4 of the Jiyang depression, which belongs to weak AHP, and the evolution of R_o is normal. The pressure, 41.7 MPa at the depth of 3698 m in the Well Yi-135 belongs to weak AHP, and the evolution of R_o is normal too (Fig. 2). While in some profiles where the pressure is abnormally low, the R_o is still normal, e.g. Well Chang-64 of Changwei depression, the pressure is 19.22 MPa at the depth of 2661 m, 17.22 MPa at the depth of 2990 m, and 21.5 MPa at the depth of 3243 m. These all belong to relatively low pressure, and the evolution of R_o is normal (Fig. 3). Sometimes, the R_o is low in the normal pressure strata profile, e.g. the pressure is 27.83 MPa at the depth of 2849 in the Well Bin-653, a state of normal pressure, and R_o is abnormally low (Fig. 4).

These results of analysis demonstrate that the AHP is not the only factor to affect the abnormal evolution of R_o . Although the strata profile with relatively low R_o is always in accordance with AHP, the high and/or normal R_o is also found in the AHP strata profile. All of these demonstrate that there are other factors to result in the abnormal R_o besides the AHP. The type of the organic matter, the environment in which the organic matter forms (consisting of inorganic geochemical environment), and major and minor elements may catalyze and/or retard the OM evolution. Many papers have been published on the types of organic matter that retard maturation (Hunton and Cook, 1980; Zhao and Wang, 1990; Goodarzi et al., 1994; Petersen and Rosenberg, 1998).

To analyze whether the AHP affects R_o or not, the time that the AHP forms and the mature time of OM must be taken into consideration. Whether the AHP retarding R_o or not

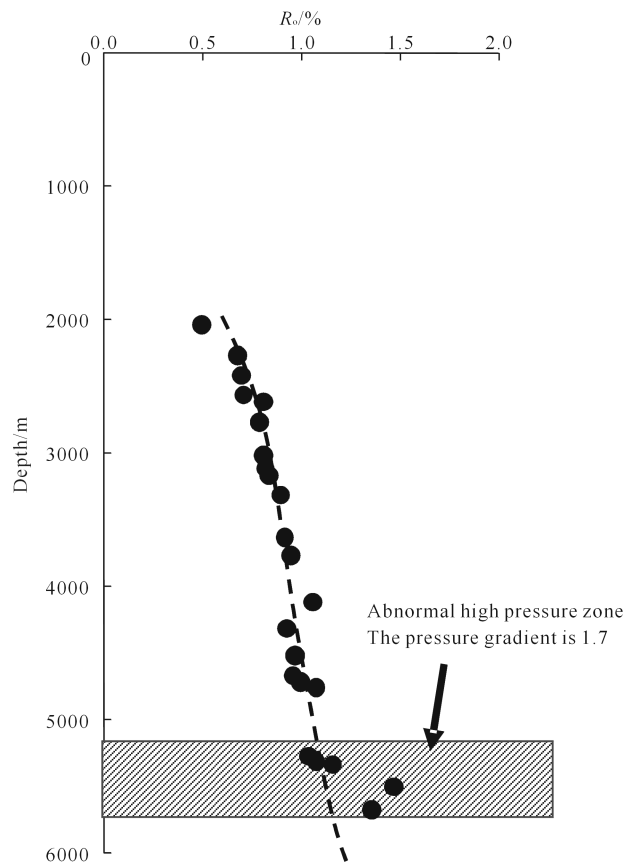


Fig. 1 The relationship between depth and vitrinite reflectance in the Well Shi-23, Qaidam basin
Note: The dashed line is the normal R_o evolution obtained by the thermal gradient of the basin.

depends on the formation time of the AHP and the time of the evolution of OM. Although there are many difficulties to reconstruct the paleopressure, there are still some methods to study the paleopressure evolution history and to get the formation time of the abnormal pressure (Roedder and Bodnor, 1980; Aplin et al., 2000; Chen et al., 2002; Li et al., 2002a; Mi et al., 2003). For example, in terms of the organic matter of some strata, if it underwent the maturation evolution before the formation of the AHP, we can infer that the AHP has no effect on the OM evolution. On the contrary, if the AHP existed before and/or along with the OM evolution, then the effort may be considerable. Therefore, the key point is to determine the formation time of AHP. Nowadays, the AHP always appears in the profile where the OM maturation is retarded, which leads to the viewpoint of the AHP's retardation to OM. In the practical work, we should determine the formation time of the AHP, and then the retardation of OM maturation can be studied objectively (Fig. 5).

3 Function of temperature

The organic matter evolution with the change of the normal subsurface temperature is not discussed here. This paper only

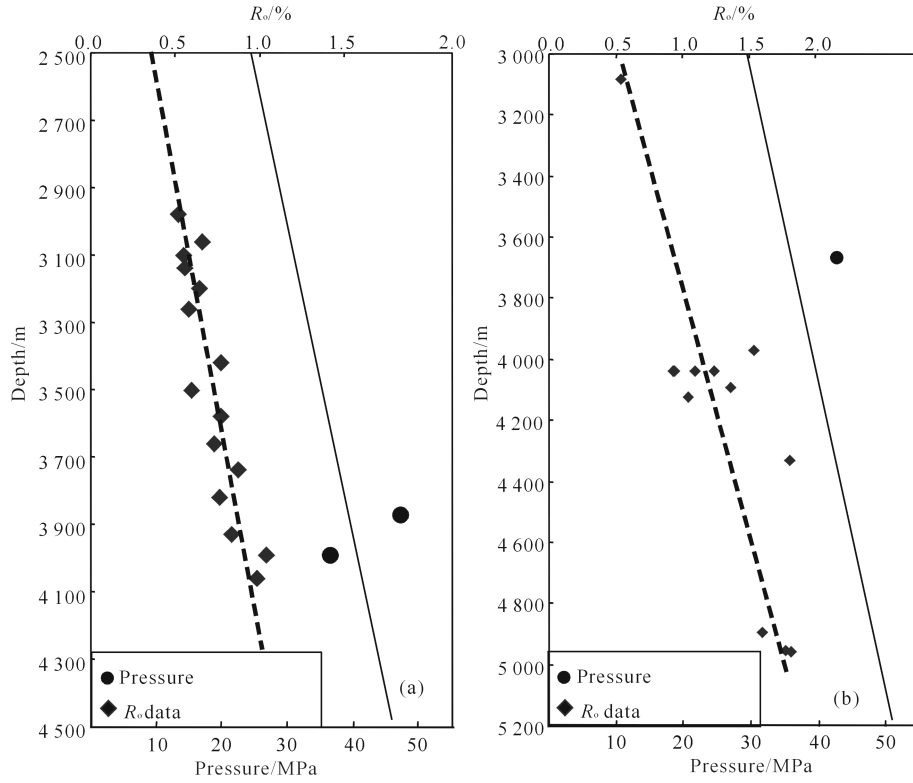


Fig. 2 The vitrinite reflectance and pressure vs. depth in the Well (a) Boshen-4 and (b) Yi-135 in Jiyang depression
 Note: The dashed line is the normal R_o evolution obtained by the thermal gradient of the depression and the line is the hydrostatic pressure.

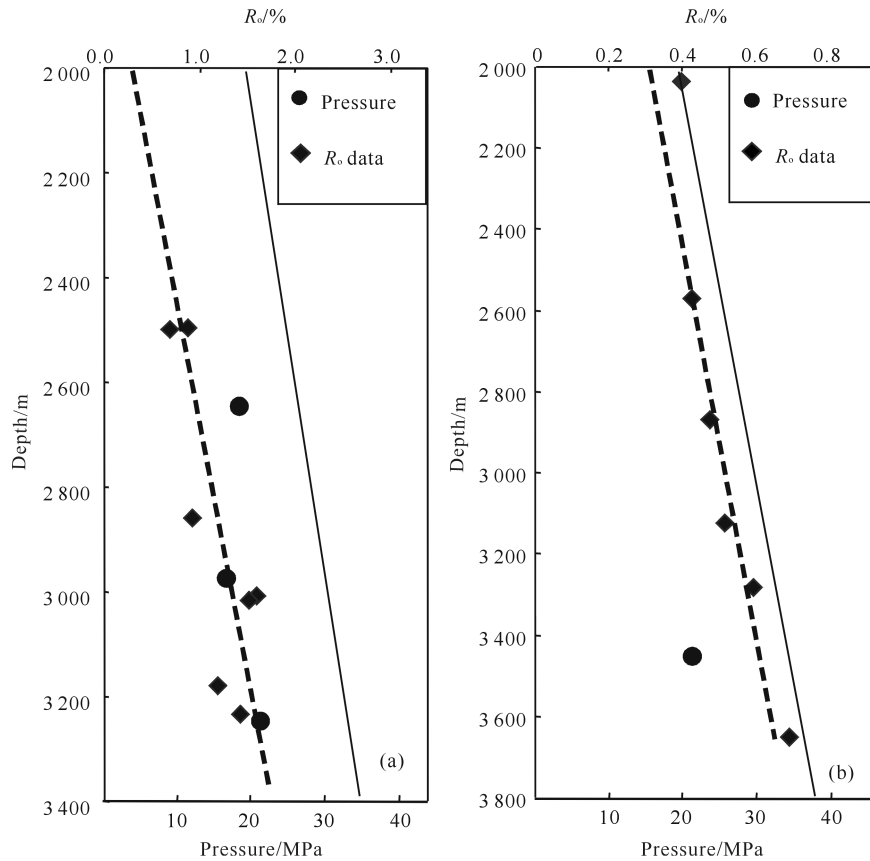


Fig. 3 The vitrinite reflectance and pressure versus depth in the Well (a) Chang-64 and (b) Yi-36
 Note: The legends are the same as those in Fig. 2.

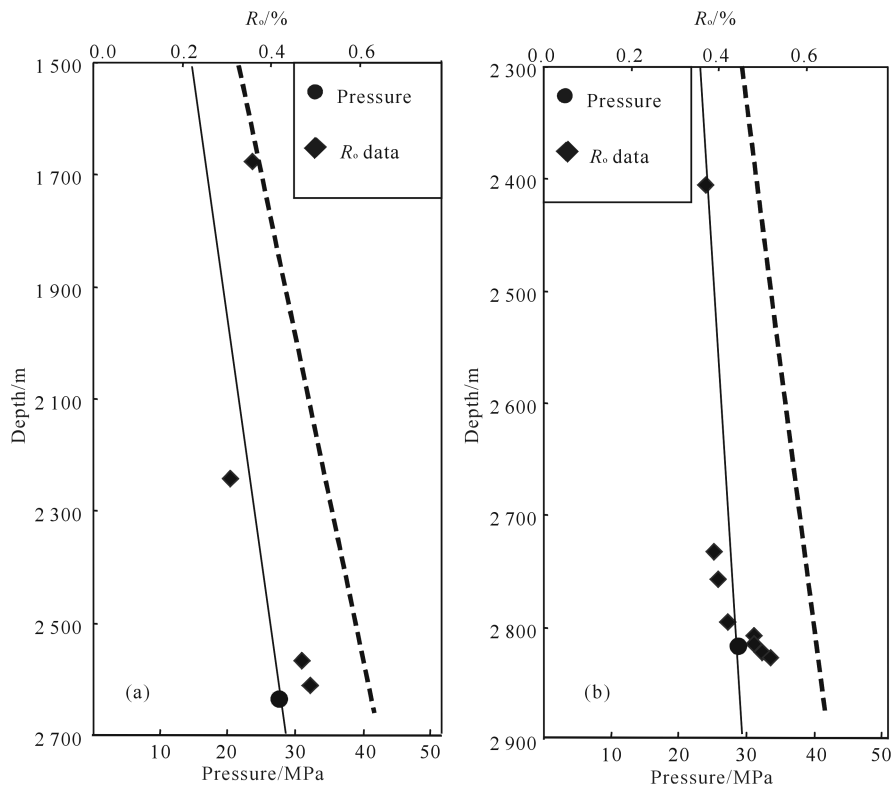


Fig. 4 The vitrinite reflectance and pressure versus depth in the Well (a) Shao-4 and (b) Bin-653 (the legends are the same as those in Fig. 2)

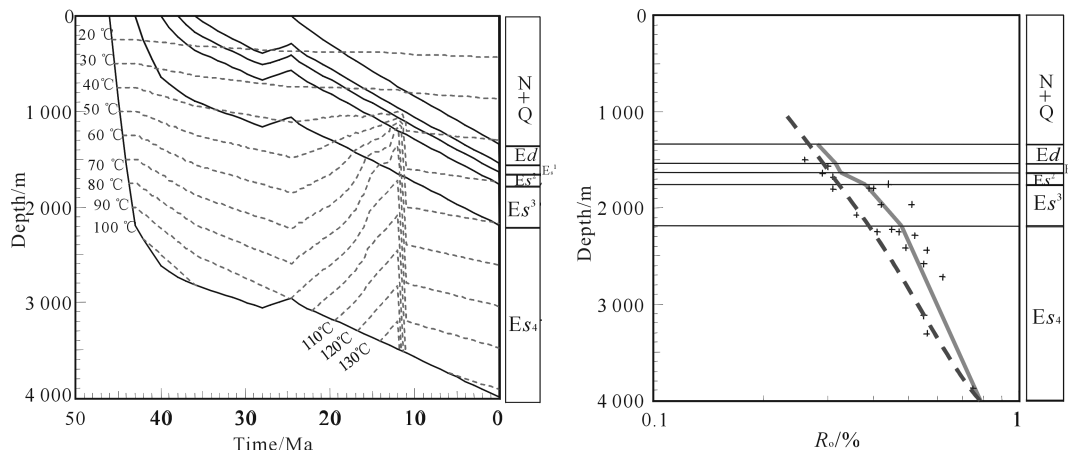


Fig. 5 The thermal modeling result of magma intrusion in the well of Jiyang depression

Note: The dashed line is the modeled R_o evolution obtained by the normal thermal gradient and the line is the modeled R_o evolution by the magma intrusion.

analyzes the abnormal change of R_o because of the abnormal thermal field, e.g. the instrument of igneous rock, the deep thermo-fluid activity, etc. Some studies have been carried out on the abnormal temperature field caused by the instrument of igneous rock (Pettersen and Lerche, 1994; Zhang and Shi, 1997; Fan et al., 1999; Hou et al., 1999; Jin and Zhai, 2003). On one hand, the organic acid generated from the organic matter in the source rock is an effective solvent and migrating medium for the metal element in the volcanic minerals,

particularly for some transitional metal, which is a good catalyzer for the hydrocarbon generation and can improve the hydrocarbon generation ability of source rock. On the other hand, the igneous rock will change the distribution of temperature field, accelerate the evolution of the source rock, and even destroy the generation ability of the source rock due to its abnormal temperature which is much higher than that of surrounding rock. Taking one well of Jiyang depression for example, the R_o is obviously higher in sections Sha3 and Sha4

of Shahejie Formation. The modeling for the igneous rock instrument shows that the temperature rises quickly in a short time, and the source is baked, which results in the abnormal high R_o .

4 Fluid medium and inorganic mineral/element

The evolution of the organic matter in the basin is a complex reactive progress which is the organic-inorganic reaction system under certain temperature, pressure condition and surrounding fluid flow. Therefore, the minerals in the special strata may be another factor to retard or catalyze the OM maturation. In the organic-inorganic reaction system composed by the organic matter and its surrounding inorganic matter, after the reaction between different mineral elements and the organic matter, it may change the condition of chemical reaction and it may also change the structure of the organic matter. Therefore, it may accelerate or retard the evolution of the organic matter. Nowadays, some scholars have noticed such effect caused by the organic-inorganic reaction on pyrolysis of organic matter, including oil. (Liu, 1995; Li et al., 1998, 1999, 2002b; Seewald et al., 2000; Guo et al., 2000). The water and minerals can affect the reaction of organic matter as the reactor or catalyzer, and affect the progress of the thermal evolution of the organic matter (Zhu and Zhou, 1991; Mello et al., 1995; Hetenyi, 1995; Jin, 1998; Li et al., 1999, 2002b; Seewald et al., 2000; Seewald, 2001, 2003; Qin et al., 2002). Clay minerals, carbonate minerals, halogenide, some metal oxide and sulphide (e.g., Fe, Ti, V, Cr, Co, Ni, Mn, Mo, etc.), hydrothermal activity and vulcanite

and inorganic salts can all affect the thermal evolution of OM to some extent, and they affect the reaction in the progress of hydrocarbon generation, such as oxidation, dehydrogenation, dehydration, hydrogenization, polymerization, isomerization, alkylation and skeleton rearrangement of hydrocarbons (Mango et al., 1994; Lei et al., 1997; Ning et al., 2004). Furthermore, the minerals that act with organic matter consist of some metal elements surrounding the source rock and some minor elements in the fluid. The AHP strata profile in the basins, which the fluid generally takes part in, forms a fluid-rock reactive system. The hydrothermal fluid movement often results in the high concentration of some minor elements in certain strata profiles.

Sixty one samples were collected in the Well Niu-38 and Niu-35 of Dongying sag, the inorganic elements and R_o were tested respectively. The inorganic elements consisted of major elements and minor elements, including elements of K, Na, Mg, Li, Ca, Mn, Sr, B, Ba, Cr, Fe, Co, Zn, Ni, Ti, V, Rb, Al, Si, Cu, U, Th, Hg, Pb. Based on the measured pressure data, the strata of the Well Niu-38 were in the background of AHP with pressure coefficient 1.5. The R_o was obviously abnormal low at 3000 to 3400 m, decreasing from 0.6% in the upper part to 0.45% in the lower part (Fig. 6). The Well Wang-35 was in the normal pressure environment with the pressure coefficient about 1.1, and the R_o was obvious abnormal low at 2 140 to 2 180 m. The dashed line in Fig. 6 is the general evolution trend based on the thermal history in the study area (Qiu et al., 2004).

In the geological fluid, calcium (Ca) is concentrated due to its retarded activity in the alkali solvent, but it is dissociated in the acid fluid and its motivate activity improved, the Ca is easy to be lost. Therefore, the concentration of Ca can reflect

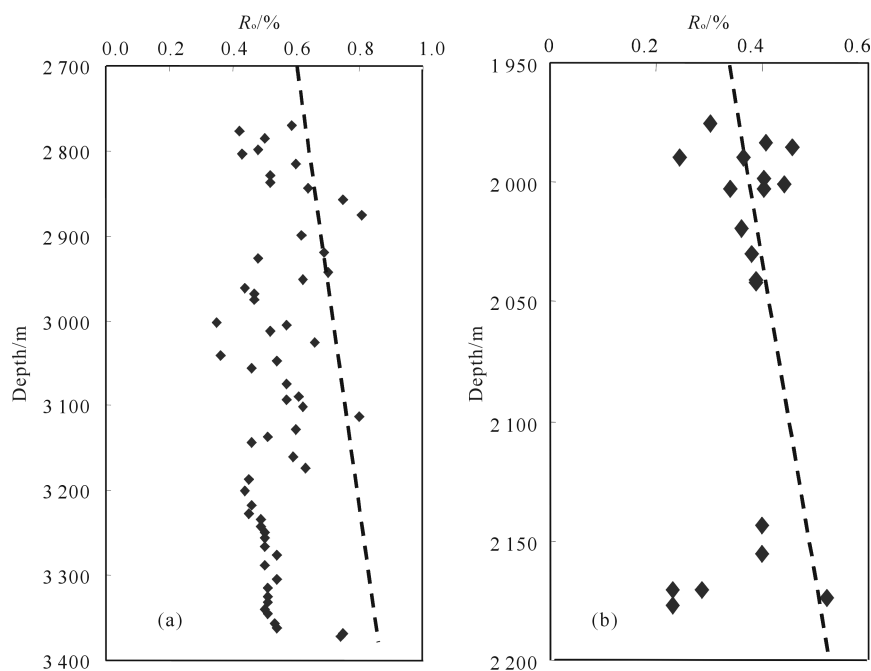


Fig. 6 The vitrinite reflectance versus depth in the (a) Well Niu-38 and (b) Well Wang-35
Note: The dashed line is the normal R_o evolution obtained by the thermal gradient of the depression.

the condition of paleofluid, and the concentration of Sr/Ba can reflect the changes of salt in the paleofluid. The concentration of Ca decreases from lower to upper strata with 18.73% to 0.56% at the 2750 to 3380 m of the Well Nui-38 (Fig. 7), which shows the lake water body transition to acid gradually. The low R_o corresponds to the alkali fluid and Ca has the negative relationship with R_o . In fact, many reactions, especially the broken of C-O bond, have been catalyzed by the acid. We can conclude that limnogeotic environment

facilitates the maturation evolution, based on the fact that the value of Sr/Ba decreases with depth, and the water is desalinated from down to up strata. Because the organic matter is in favor of getting hydrogen in the salt water environment, the R_o is retarded in the progress of maturation. The concentration of Ca changes from acid environment to alkali environment, from at the depth of 1965 to 2010 m in Well Wang-35. The concentration of Sr/Ba decreases with the increasing depth, and the water is desalinated gradually (Fig. 8). This also

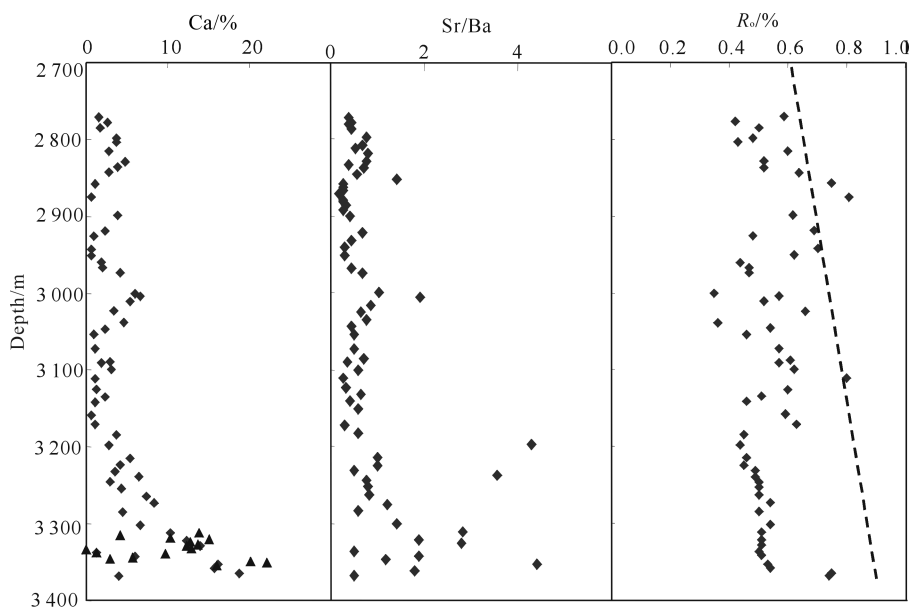


Fig. 7 The contents of element Ca and Sr/B value versus depth in the Well Niu-38 and their relationship with R_o . Note: The dashed line is the normal R_o evolution obtained by the thermal gradient of the depression.

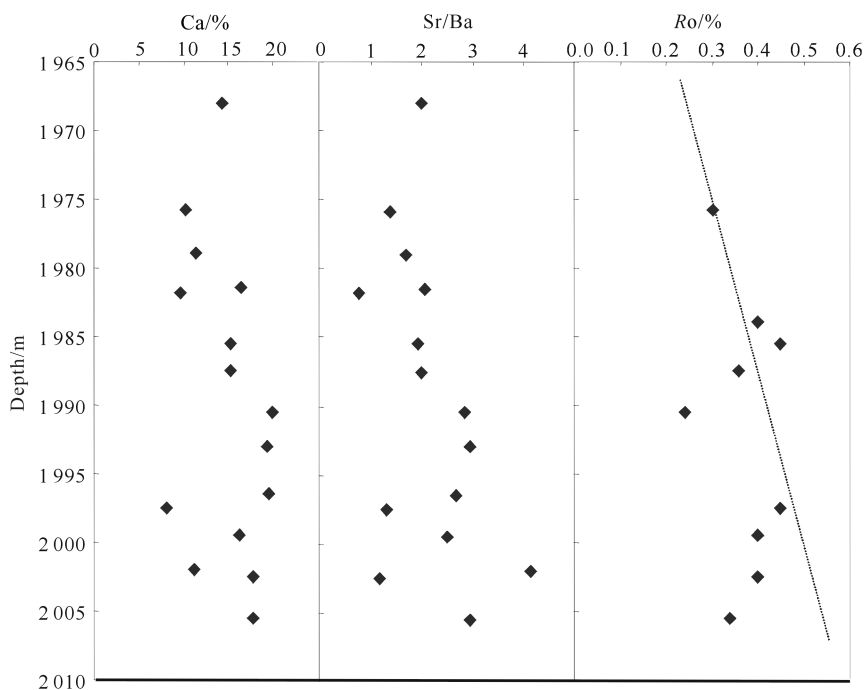


Fig. 8 The contents of element Ca and Sr/B value versus depth in the Well Wang-35 and their relationship with R_o . Note: The dashed line is the normal R_o evolution obtained by the thermal gradient of the depression.

shows that the thermal evolution is retarded in high acid and salty environment. The R_o increases in the fresh water environment.

The elements of Mn, Sr, B, barium (Ba) have some relationship with R_o , based on the concentration of these elements and R_o at the depth intervals of 2750 to 3380 m in the Well Niu-38 (Fig. 9). The average content of Mn is 607 ppm at the lower study strata and 389 ppm at the upper strata, which reflects the transition from alkalinity to acidity. The content of Mn has the negative relationship with R_o in this depth interval. The value of Sr/Ba changes from >1 in the lower part to <1 in the upper part, which demonstrates the water body desalinated gradually. The distribution of Sr is similar to Ca, the concentration of Sr has the positive correlation with R_o . Ba, as a metal element, is similar with Sr and Ca in chemical property, the concentration of Ba increases from lower to upper strata, and it shows that the water is desalinated gradually. The strata profile with the lower concentration of Ba is in accordance with lower R_o , indicating that the limnogeotic environment is in favor of the maturation of the organic matter. The concentration of Ba has the opposite correlation with R_o .

The concentration of Ca is also decreased with depth at the Well Wang-35, and it demonstrates the decreasing pH value. The higher concentration of Ca at the depth interval of lower part is in accordance with lower R_o , showing that the acidic environment is in favor of the thermal evolution of OM. The content of elements Ca, Ba, Mn, Sr, and B increases with the depth and the R_o is abnormally low, which indicates the retardation of OM by the Ca, Ba, Mn, Sr, and B elements (Fig. 10).

Take the Well Niu-38 as an example, the relations between R_o and elements K, Na, Ca, Mg, Li, Fe, Go, Zn, Ni, Rb were analyzed (Fig. 9). Generally, there was the negative correlation between R_o and elements Ca, Mn, Sr and B, and the strata profile with high concentration of these elements was in accordance with R_o retardation, which reflects these elements retarded the increase of R_o .

In the acid environment, the deoxidization of Fe increases and Fe is promoted to go into the fluid with two dyads. However, the oxidization of Fe improves in the alkali environment, and it deposits from the fluid with three dyads. The oxidized environment is in favor of the deposition of Fe, but the deoxidized is in favor of its immigration. The concentration of Fe is high over the studied strata, the center part is middle, and the lower part is low. It means the oxidization increased as the sedimentary environment moved from centre to bank of the lake. The low concentration of Fe is in accordance with the strata where R_o is retarded (Fig. 11). The activity of Ni is not affected by the surrounding condition, but it often forms the sulfide of Ni in the anoxic environment. The element Ni is prone to be dissolved in the acid environment, resulting in the high concentration of Ni in shale enriched OM. However, the sensitivity of Ni is less than that of the elements discussed above. The higher R_o value may be in accordance with the higher concentration of Ni at the upper part of the strata in Well Niu-38 (Fig. 11), which indicates that the maturation of OM is accelerated by the elements Ni, Rb, Zn and Co. The element Zn has the similar character with elements of Cu type ion, and it is a kind of strong chalcophile element and has some oxyphile character. The lower concentration of Zn is in accordance with lower R_o at the strata profile, which demonstrates that Zn may catalyze

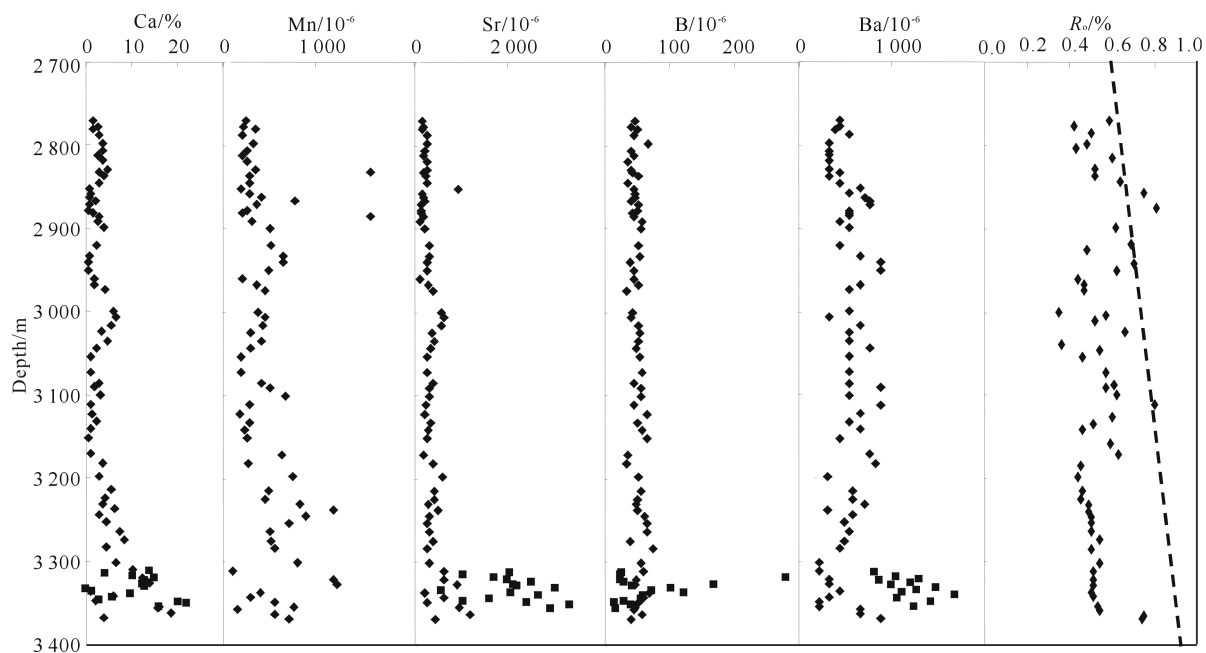


Fig. 9 The contents of elements Ca, Mn, Sr, B and Ba versus depth in the Well Niu-38 and their relationship with R_o . Note: The dashed line is the normal R_o evolution obtained by the thermal gradient of the depression.

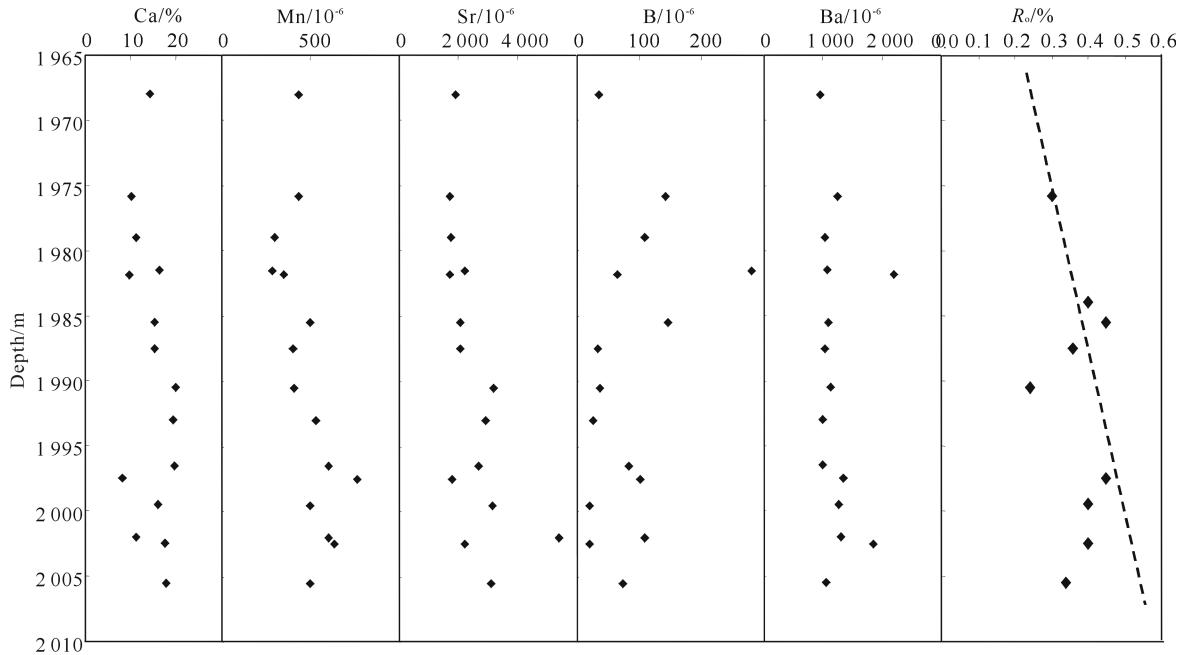


Fig. 10 The contents of elements Ca, Mn, Sr, B and Ba versus depth in the Well Wang-35 and their relationship with R_o . Note: The dashed line is the normal R_o evolution obtained by the thermal gradient of the depression.

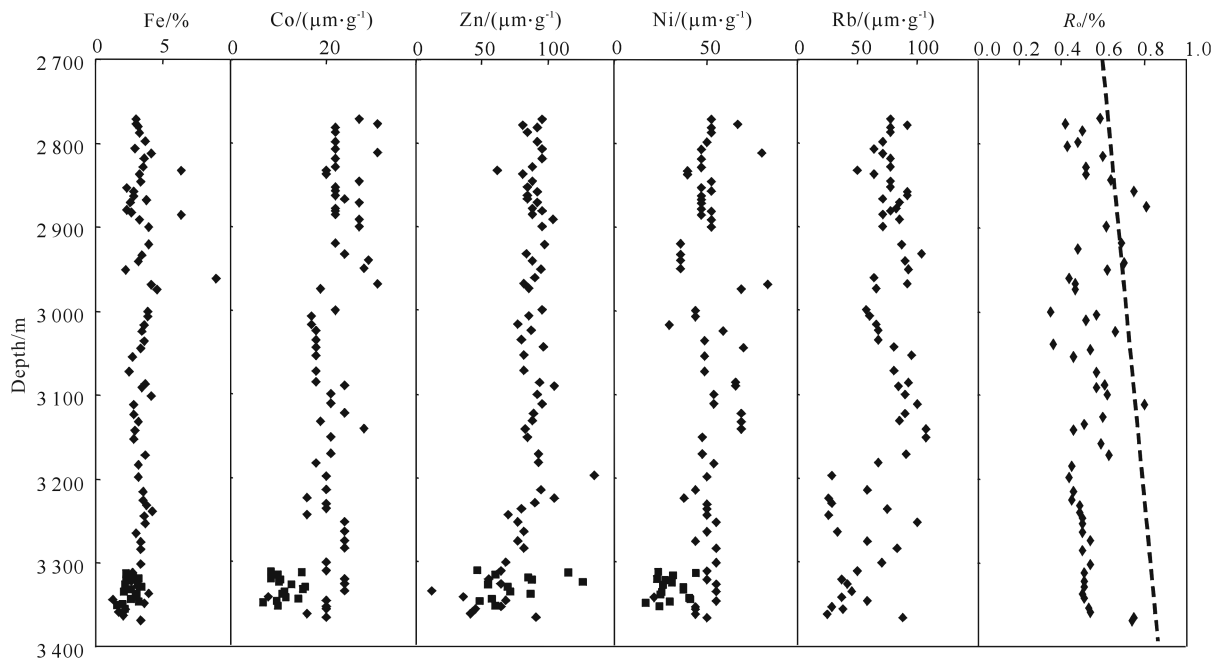


Fig. 11 The contents of elements Fe, Co, Zn, Ni and Rb versus depth in the Well Niu-38 and their relationship with R_o . Note: The dashed line is the normal R_o evolution obtained by the thermal gradient of the depression.

the thermal evolution of the organic matter. The element Co has the property of siderophile and chalcophile affinity, but the chalcophile affinity is stronger. When the pH value is over 5, Co will deposit. The Co increases a little with the depth decrease in the studied depth interval of Well Niu-38, and the lower concentration of Co is in accordance with retarded R_o values. This result demonstrates that Co catalyses the thermal

evolution of OM and increase of R_o , which conforms to the result of Mango et al. (1994). Rb and Zn have the similar trend with Co (Fig. 11). Therefore, it can be said that the elements Fe, Ba, Co, Zn, Ni, Rb have the positive correlation with R_o , and the lower concentration of these elements is in accordance with R_o retardation, which indicates that these elements will accelerate the thermal evolution of OM.

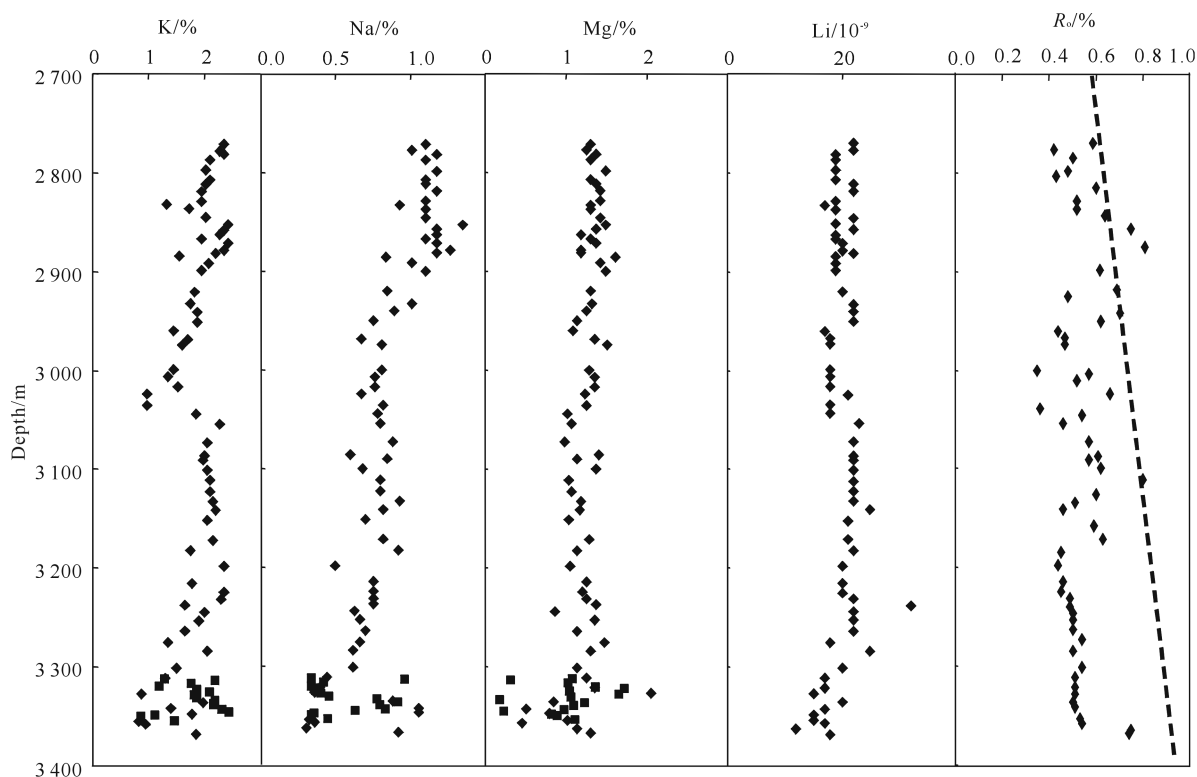


Fig. 12 The contents of elements K, Na, Mg and Li versus depth in the Well Niu-38 and their relationship with R_o . Note: The dashed line is the normal R_o evolution obtained by the thermal gradient of the depression.

The concentrations of K, Na, Mg, Li change little, and have no obvious relationship with R_o in the Well Nui-38 (Fig. 12).

5 Discussion and conclusions

Based on the above results, the physical and chemical environments are the key factors to affect the thermal evolution of the organic matter. (1) The AHP is not the only reason for the R_o retardation, and we must combine the pressure evolution history when discussing whether the AHP retards the OM evolution or not. (2) The abnormal high temperature, including magmatism and deep hydrothermalism, is the important factor to result in the abnormal high R_o . (3) The acidic and high salty fluid medium may be in favor of the increase of R_o . (4) The elements Ca, Mn, Sr, B, Ba and P may retard the evolution of R_o , and the elements Fe, Co, Zn, Ni, Rb may catalyze the evolution of R_o .

The OM evolution is a complex process in the organic-inorganic interaction system in the sedimentary basins, the retardation and/or catalysis of OM maturation is affected by the combination of several factors. How to weight each factor in the retardation and/or catalysis needs further study. One factor's effect can be obtained by the simulation experiment. However, if there is the combination of several factors, the simulation experiment will be extremely complex to carry out. In general, in a certain strata or area of a basin, it may be

only one dominant factor, such as AHP or the type of organic matter. However, as stated above, it is only a kind of phenomenon description for the AHP retardation. We do not know what function is and/or which stage will the AHP play on the retardation to the OM maturation in the geological history. It is difficult to qualitatively study the retardation and/or catalysis of each element on OM during the geological time. Nowadays, most studies are limited to being qualitative. This study focused on the inorganic-organic elements interaction with OM, and it is of great significance to recognize and evaluate the maturation of organic matter better. In the meanwhile, the catalysis and/or retardation of minor elements to the OM maturation will result in the change of depth threshold of liquid hydrocarbon, and the index of OM maturation is the important parameter to reconstruct the paleotemperature of basins. How to recognize and obtain the paleotemperature index will get more objective results in the analysis of paleotemperature field of basins.

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