PROGRESS IN NATURAL AND ARTIFICIAL SOURCE ROCK MATURATION: A NEW INTEGRATED ANALYTICAL APPROACH

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Introduction

The modifications of organic matter and rock matrix during maturation, generation and expulsion of hydrocarbons were studied through an integrated methodological approach employing samples of a specific source rock at different levels of thermal maturity, obtained either naturally or artificially.

The natural samples derive from outcrop and from well. Artificial maturation was performed on the outcrop sample via an experimental device, the "Expulsinator" (Stockhausen et al., 2014 and 2016) pyrolizing rock plugs with intact kerogen and mineral matrix by treatements at near-natural pressure conditions. In the first experiment the temperature was continuously increased from 300° to 360°C at a rate of 0.42°C/h and the lithostatic pressure from 400 to 900 bar at 2.08 bar/h (exp. A). In the second experiment a single sample was subjected to 4 steps of maturation characterized by temperatures of 300, 330, 345 and 360°C and corresponding lithostatic pressures of 600, 750, 825 and 900 bar (exps. B, C, D and E).

The naturally and artificially matured samples for each step of maturation were characterized by geochemical approaches via Rock-Eval analysis, optical microscopy, vibrational spectroscopy and by mineralogical methods via X-Ray powder diffraction (XRD). Thermal maturity was evaluated by means of classical methods including vitrinite reflectance analysis (%Ro), Rock-Eval analysis with determination of T_{max} values and XRD considering the Smectite and/or Illite/Smectite (I/S) illitization. In addition, more advanced methods were applied: Attenuated Total Reflection-Infrared (ATR-IR) with the measurement of the "aliphaticity" via the CH_2/CH_3 ratio and Raman spectroscopy with the measurement of the "Gr-D"spectral distance. Finally, at all maturity levels, nanostructure and porosity of the organic matter were characterized by means of High Resolution Scanning Electron Microscopy (HR-SEM). The results of the artificial maturation series were integrated with those of the natural maturation.

Results

The outcrop sample showed a high Total Organic Carbon (TOC) content of 12.88 weight percent (%wt) and a high total clay amount (about 40%wt, with "illite type" – smectite+I/S+illite - as main component). A good kerogen quality was shown by Hydrogen Index (HI) of 456 mg HC/g TOC. The sample is immature, with a vitrinite reflectance lower than 0.5% and a T_{max} of 419°C, corresponding to 0.38 %Ro equivalents.
In the artificially matured samples the TOC and the HI decreased (up to about 5%wt and 60 mg HC/g TOC) during maturation. Absence of vitrinites in all samples prevented direct %Ro determination, but vitrinite reflectance equivalents deducted from T_{max} values increased in parallel to the artificially induced maturity from 0.55 to 1.17 % Ro. The mineralogy changes were in good agreement with the thermal evolution of the organic matter. In fact, even if the total clays did not vary in quantity, significant modifications in typology were observed: the smectite component disappears completely, the I/S increases, while the illite seems fairly costant but loses the crystallinity. These evidences are in agreement with a progressive

conversion of the smectite into I/S mixed layer. Finally decomposition of carbonates, sulfides and sulphates was also observed.
The naturally matured core sample showed the lowest TOC and HI values (5.3%wt and 11 mg HC/g TOC), the highest maturity (1.91 %Ro and Tmax>500°C) and about 30%wt of total clays.

From immature outcrop sample to intermediate experimental series and to high maturity core sample, the mixed layered I/S phase decreased, while the illite increased showing an evolution of the clays as a function of the maturity degree. The organic matter maturity parameters from spectroscopic techniques showed a linear relation with % Ro equivalents (Bonoldi et al., 2016). In detail, the G-D ratio from Raman spectroscopy increased from about 186 to 222 and the CH_2/CH_3 ratio from ATR-FTIR spectroscopy decreased from 3 to 0.2.

Results of qualitative HRSEM analysis on organic matter are in agreement with literature (Driskill et al., 2013) and revealed that bubble-type pores were present only in low maturity samples (outcrop, exps. B-D); fracture-type porosity appeared upon intermediate maturity (exps. A and E), while spongy type porosity developed only at high maturity step (core sample). In artificially matured samples, spongy porosity started to appear in samples with %Ro equivalents >1 (exps. A and E).

Conclusion

Organic and inorganic maturity parameters acquired with different methodologies recorded an increase of maturation during the artificial experiments coherently with simulated burial depth and with natural analogues. The morphology of the pores, occurring mainly in the organic matter, varied with thermal maturity in agreement with literature data: low maturity samples showed bubble-type porosity; intermediate maturity samples (oil window) showed increasing fracture-type porosity while moving to high maturity samples (gas window) spongy-type porosity became prevalent.

Reference

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