Nitrogen fate during laboratory maturation of two kerogens (type I and type II). Implications for Nitrogen cycle

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Low nitrogen contents, ranging from 0.5 to 3 wt.% of total sedimentary organic matter (SOM), are typically observed (e.g. Tissot and Welte, 1984; Baxby *et al.*, 1994) in immature samples (low-rank coals, oil shales, low maturity kerogens) and oils generally exhibit still weaker values. Nevertheless, the presence of nitrogen-containing compounds in fossil fuels is associated with a number of major problems. For example, (i) nitrogen compounds poison oil-reforming catalysts and generate toxic products, especially oxides, upon combustion (e.g. Schmitter *et al.*, 1980) and (ii) the presence of a large contribution of molecular nitrogen, in a number of natural gas accumulations, represents a serious exploration risk (e.g. Kroos *et al.*, 1993; Boudou and Espitalié, 1995). Accordingly, deriving quantitative and qualitative information on the fate of nitrogen functions, upon SOM maturation, is important both for geochemical purposes and for studies concerned with the nitrogen cycle. However, no complete study on this topic had been previously carried out since establishing nitrogen mass balances and analysing the nitrogen-containing gases generated upon a thermal stress was strongly hampered due to extensive contamination by atmospheric nitrogen.

Purposes and methods

The major aims of the present work were to establish, for the first time, complete nitrogen mass balances through analysis of the different fractions generated upon SOM maturation (gases, soluble compounds, insoluble residue) and to determine the abundance and nature of the nitrogen-containing gases thus generated. To this end (i) a new device for gas analysis, allowing to sharply reduce and to control contamination by atmospheric nitrogen, was designed (Gillaizeau *et al.*, 1997), (ii) closed, isothermal, pyrolyses of two immature kerogens (Oligocene, Turkey, type I and Cenomanian, Italy, type II) were performed in sealed gold tubes, under an argon atmosphere, for various temperature/time conditions so as to simulate natural maturation, (iii) nitrogen distribution and complete gas composition were determined for each of the above conditions and (iv) these observations were extrapolated to geological conditions.

Results and conclusions

The main conclusions of these quantitative and qualitative studies are summarized below: (1) N_2 is the only nitrogen-containing gas generated from both kerogens and it is almost exclusively formed during metagenesis. (2) For the type I kerogen, nitrogen distribution between the different fractions (as wt.% of the total nitrogen in the initial, unheated, kerogen) indicates that:

– A relatively large fraction (up to 35%) is found in the soluble compounds, especially those generated during the catagenetic stage. Under a higher thermal stress, a part of these nitrogen-containing soluble products is transformed into insoluble material via condensation reactions associated with secondary cracking processes. – A large production of N_2 (corresponding to about 50% of the total nitrogen) is only observed under a drastic thermal stress, corresponding to high temperature metagenesis. Moreover, even under such temperature/time conditions, an important fraction of the initial nitrogen (about 25%) is retained in the insoluble pyrolysis residue. This nitrogen with a high thermal stability shall be located in heterocyclic aromatic units with a high degree of condensation. (3) Comparisons of the results obtained from the Cenomanian sample, with the above ones, indicate that the type II kerogen exhibits the following features: – A lower fraction of the total nitrogen (maximum value of about 20% during the early metagenetic stage) is released in the soluble compounds. When the thermal stress increases, these nitrogen-containing products are partly transformed into insoluble material via condensation reactions, as described above for the type I kerogen. However, the secondary cracking of the soluble pyrolysis products also results, in that case, in some production of molecular nitrogen. – Nevertheless, the metagenetic production of molecular nitrogen is much lower (12 %) for the type II sample. Indeed, the bulk of the initial nitrogen (about 80%) is retained in the insoluble residue, even after a drastic thermal stress. The level of highly condensed heterocyclic aromatic units, with a high thermal stability, thus appears much higher in the maturated, residual, type II kerogen than in the type I material.

These pyrolysis experiments also allowed to compare the production of molecular nitrogen with the one of other gases, such as CH_4, CO_2 and H_2S. Information was thus derived on the composition to be expected for the gas fraction generated from kerogens, like the tested Oligocene and Cenomanian samples, during different stages of the maturation process. In addition, when the global nitrogen cycle is considered, it appears that an important part of the total nitrogen of such SOMs will remain sequestered within the insoluble residual fraction, upon maturation, unless they are submitted to a very high thermal stress.

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