Nitrogen gas from sedimentary organic matter: production rates and isotopic compositions

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N_2 occurrence in natural gas accumulations is a world-wide phenomenon. Potential sources for N_2 are of two types: (1) primordial, i.e. derived of deep-crust and mantle; (2) 'recycled', i.e. atmospheric nitrogen incorporated into the lithosphere (a) via dissolution in meteoric water or (b) through biological activity followed by sedimentation of organic matter. Process (2b) leads to sedimentary nitrogen which occurs either as organic nitrogen or as ammonium ions in clays. Released upon maturation of sediments, it generates N_2.

The present study addresses production rates and isotopic signatures of N_2 during maturation of organic matter.

Overmature type I, type II and type III kerogens with nitrogen contents between 1 and 2 wt.% (Table 1) were selected for artificial maturation in open system pyrolysis under non-isothermal conditions from 200 to 900°C at 5°/min. Two different experimental conditions were applied: produced gas was either instantaneously pumped out the pyrolysis device (dynamic) or maintained in the pyrolysis device (static). Some experiments were run in two steps: 1) from 200 to 600°C; 2) from 600 to 900°C.

A specific analytical device in order to have negligible contamination with atmospheric nitrogen was set up. Experimental procedure was developed using organic products chemically and isotopically calibrated in two other laboratories with N contents from 41% to 32000 ppm and $\delta^{15}N$ values ranging from −3 to +10‰.

Gas chromatography monitoring of gas products has shown that N_2, the only nitrogen product, is released between 600 and 900°C. Studied type I and type II kerogens releases respectively 12% and 10% of initial nitrogen under open pyrolysis. Studied type III kerogen releases no nitrogen when produced gas is instantaneously pumped out (dynamic conditions), whereas it released 7% of initial nitrogen in static conditions.

Quantities of produced N_2 range from 24 µmol/gTOC for type II, 30 µmol/gTOC for type I to 42 µmol/gTOC for type III (Table 2). These results suggest that type I kerogens can potentially produce N_2 at a level similar to type III kerogens. Quantities of produced N_2 relative to methane are higher for type I and type II kerogens than for type III. Closed system pyrolysis under isothermal conditions at 550°C/24h, run in our laboratory, on another type I kerogen containing 1.45 wt.% of N yields 175 µmol N_2/g TOC (48% of initial nitrogen), with a $C1/N_2$ molar ratio of 21, difference in production rates being either due to source kerogen or pyrolysis conditions. On the basis of these results, N_2 from organic source is produced conjointly with methane in geologic conditions.

Nitrogen isotopic compositions of all pyrolysis effluents were measured (gas, residue and oil when

TABLE 1. Elemental analysis and Rock Eval parameters of samples

Sample		Elemental analysis								Rock Eval parameters		
	Type	C (%)	H (%)	N (%)	O (%)	S (%)	Fe (%)	Tot (%)	H/C	Tmax	HI	S2
15781 KC	I	61.91	3.43	1.13	16.60	7.71	5.76	96.54	0.66	441	44	27
96541 KC	II	51.26	2.55	1.22	4.76	23.60	16.66	100.05	0.60	453	34	18
157633 KD	III	88.84	4.63	1.83	4.05	0.65	0.00	98.17	0.63	474	120	106

TABLE 2. Pyrolysis yields under different experimental conditions. Cr: conversion rate of initial kerogen defined as the ratio of the pyrolysis solid residue mass by the initial kerogen mass

Type	Conditions	Pyrolysis Cr	µmol/gTOC N_2	CH_4	$C1/N_2$
I	Static, 200–600°C	0.73	0.0	160.2	–
I	Static, 200–900°C	0.68	29.4	335.1	11.4
I	Dyn, 200–900°C	0.70	30.8	273.1	8.9
II	Static, 200–900°C	0.77	23.8	179.0	7.5
III	Static, 200–900°C	0.78	41.7	1761.1	24.1
III	Dyn, 200–900°C	0.79	0.0	2116.0	

produced). Preliminary results based on mass balance isotopic calculations indicate that N_2 gas produced is isotopically lighter than source kerogen, in the present laboratory conditions

Production rates under open systems will be compared to production rates under closed systems together with isotopic compositions for the different types of kerogens. Contribution of organic nitrogen to N_2 accumulations in sedimentary basins will be discussed at conference.