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Systematics of pyrolytic gas (N_2, CH_4) liberation from sedimentary rocks: Contribution of organic and inorganic rock constituents

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ABSTRACT

Open system non-isothermal (programmed) pyrolysis was used to analyse the pyrolytic release of molecular nitrogen (N_2) and methane (CH_4) from sedimentary rocks of different geological age, facies and depositional environments. Pyrogram patterns were compared and classified according to the specific release intensities (peaks) of the two gases as a function of temperature. Selected model substances, such as humic acid and tobelite (ammonium muscovite) were pyrolysed for reference purposes to assess the relative contributions of organic and inorganic species to the pyrolytic liberation of N_2. The peak patterns of the N_2 pyrograms were tentatively attributed to different inorganic or organic precursor components. They could be classified into five groups reflecting the different thermal stabilities of inorganic and organic nitrogen-containing components.

The influence of maturity, sulphur content and depositional environment was investigated by systematic comparison of the N_2 and CH_4 pyrograms. Methane pyrograms provided information on the relative content, composition and maturity of the organic matter of the sedimentary rocks.

For a sample sequence from a stratigraphic Carboniferous shale unit the pyrolytic N_2 and CH_4 generation patterns were recorded over an extended depth interval (791–1750 m) to monitor thermal maturity trends and facies variations and to study their impact on nitrogen geochemistry.

1. Introduction

During the past decades various studies have investigated the geological nitrogen cycle from the atmosphere to the deep underground (Boudou et al., 2008; Boyd, 2001; Jaffe, 1992; Marty and Dauphas, 2003; Rosswall, 1981). Starting from atmospheric N_2, the biochemical nitrogen-fixation via bacteria (Rhizobium) and blue-green algae is the main pathway for the incorporation of nitrogen into the biosphere and hence into sedimentary organic matter. The complexity of the nitrogen cycle is increased by interactions between the bio-, hydro- and geosphere. The biologically fixed organic nitrogen undergoes nitrification, mineralisation and denitrification processes during the degradation of organic matter in soils and groundwater. The inorganic N species nitrate, nitrite and ammonium, formed during the processes are highly reactive and rapidly recycled into the atmosphere (Boudou et al., 2008; Boyd, 2001). Only a small portion of the biologically active nitrogen is sequestered from the biosphere with the organic matter buried in subsiding sedimentary sequences.

In surface and near-surface sediments, the contents of carbon and nitrogen may be highly variable (Boyd, 2001). Mineralization of C and N during early diagenesis is controlled by the quality of biomass, microbial activity, oxygen availability, temperature/thermal stress, sedimentation rate and fluid-rock-interactions. Microbiological decomposition of organic material is followed by thermal and chemical degradation processes leading to further loss of nitrogen as diagenesis and catagenesis proceed. Inorganic nitrogen compounds such as ammonium, formed during these processes and released into pore fluids may be reincorporated into organic matter or react with feldspars, micas and clay minerals (Mingram et al., 2005; Williams et al., 1992). Significant quantities of potassium (K^+) in the silicate interlayer can be substituted by NH_4^+ due to its similar ionic radius.

In the low-grade metamorphic stage most of the ammonium is lost. However, Hall (1999) and other authors cited in this paper note that conditions of oxidation and reduction have a major influence on the equilibrium between the various nitrogen-bearing phases, so that some ammonium can persist up to at high-grade metamorphism or even anatexis. Williams et al. (1989) associate ammonium silicates with organic-rich sedimentary environments. Close genetic connection between NH_4^+-illite and coal seams was also observed by Juster et al. (1987) and Sucha et al. (1994), where the coexisting mineral assemblage of carbonaceous pelitic rocks and the coal rank (semi-anthracite to anthracite) indicate very low-grade metamorphism. This authigenic NH_4^+-rich illite is envisaged to be formed by two reactions in the coal and surrounding

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organic-rich shales during maturation and diagenesis: (1) nitrogen-release from organic matter by devolatilisation processes and (2) the formation of illite from kaolinite (Daniels and Altaner, 1993). Thus, the mineral matter in coals and coal-bearing rocks can contain a significant percentage of NH_4^+-illite.

Another important aspect of the geological nitrogen cycle is the occurrence of natural gas accumulations with high percentages of molecular nitrogen (N_2). In some areas of the Central European Basin System (CEBS) the N_2 percentages reach nearly 100%. Although significant progress has been achieved in the elucidation of the mechanisms of nitrogen uptake and release during thermal maturation and burial of sediments, both the transport/migration as well as the mechanisms that lead to the N_2-enrichment in natural gases and/or dilution of hydrocarbons have not yet been fully explored (Boudou et al., 2008; Kelemen et al., 2006; Krooss et al., 1995, 2005). Previous studies have discussed several possible sources for the nitrogen: sedimentary organic material, mineral matter, radiogenic origin, atmospheric origin, magmatic origin and primordial nitrogen from the deep mantle (e.g. Allègre et al., 1987; Baxby et al., 1994; Beyer, 1955; Gold and Held, 1987; Krooss et al., 1995; Maksimov, 1975; Mingram et al., 2005; Müller et al., 1976; Philipp and Reinicke, 1982; Scholten, 1991; Verweij, 2006).

Currently, two sedimentary nitrogen pools are considered as potential sources of the N_2 gas in these reservoirs: (i) organic nitrogen covalently bonded in pyridinic and pyrrolic nitrogen nitrogen-bearing moities (Boudou et al., 2008; Kelemen et al., 2006) in organic matter, and (ii) ammonium-containing clay minerals in sedimentary rocks (e.g. shales and mudstones) and NH_4^+-illite-bearing interbeds related to coal seams. Coals and dispersed organic matter in clastic and carbonate sedimentary rocks generally have the highest nitrogen concentrations of all sedimentary materials (Jüntgen and Klein, 1975; Krooss et al., 1995; Littke et al., 1995). Average nitrogen (N_{org}) contents of (terrestrial and marine) organic matter reported in the literature are around 1.5%. Nitrogen contents of lignites and coals range from 0.2 to 3% (e.g. for Greek lignites: Mavridou et al., 2008 and Papanicolaou et al., 2004; and coals from the Ruhr area: Littke et al., 1995). In contrast, the content of inorganic nitrogen (N_{inorg} (NH_4^+–N)) in mineral phases from various sedimentary, magmatic or metamorphic rocks is on average in the order of 0.1% (e.g. Hall, 1999; Mingram et al., 2005; Williams et al., 1995). The total nitrogen content (N_{total}) of sedimentary rocks depends on the proportions of organic and inorganic components. Thus, a predominance of organic matter will result in higher nitrogen contents and, in consequence, higher pyrolytic N_2 yields. Metamorphic and magmatic rocks generally have low nitrogen contents, except for pelitic rocks at low grades of metamorphism (Busigny et al., 2003; Littke et al., 1995). Carbonates and sandstones contain only little nitrogen and the role of salt minerals (saltpetre, $NaNO_3$) related to nitrogen-enrichment in natural gases is not well studied yet.

Regardless of the pathway of nitrogen fixation within the investigated sedimentary rocks, the individual pyrolytic nitrogen generation pattern of shales/clay- and siltstones as well as coals/carbonaceous samples can help to determine dominant thermal liberation mechanisms. Different aspects of the data obtained from pyrolysis experiments can be examined with respect to their relation to nitrogen-species/precursor pools and thermal stability.

2. Samples

A list of the samples analysed in this study is given in Table 1. The sedimentary rock samples originate from deep wells, outcrops, opencast and underground mines of different locations worldwide. The primary aim of this selection was to cover a wide range of organic and inorganic nitrogen contents in different proportions. In terms of depositional environment the set comprised samples of lacustrine/continental limnic (L), paralic (P), shallow- (Ms) and deep-marine (Md) environments. Paralic and lacustrine (continental limnic) environments are represented by buddingtonite-containing shales, oil shales, silt- and sandstones as well as various lignites and coals. Samples of deep-marine depositional environments were taken from Lower Carboniferous intervals of the Rhenish Massif (Md5), NW Germany, and Silurian intervals of the Lichtenberg open pit mine (Md3 and Md4), Ronneburg district, Thuringia, Eastern Germany. The shallow marine near-shore environment is represented by the Upper Carboniferous shale samples Ms6 (Rhenish Massif) and Ms5 (RWTH-1 well, Aachen). The Permian Kupferschiefer (Ms-d1) from the Polish Zechstein basin and the Lower Toarcian Posidonia shale (Ms-d2) from the Schwäbische Alb, SW Germany complete the sample set of marine facies.

In addition, two model substances, tobelite (ammonium-containing clay) and humic acid, were pyrolysed in order to elucidate the thermal liberation mechanisms of N_2 from inorganic and organic compounds.

2.1. Classification according to predominance of organic and inorganic precursor moieties

The group of organic-rich sedimentary matter samples consists of lignite and coal of different rank from Carboniferous to Miocene age (paralic and continental limnic; samples L1-4, P5 and P6: Upper Silesian Coal Basin (USCB), Poland and Czech Republic; sample L7: Tarim Basin, China). They represent the TOC- and N_{org}-rich "end-members" as compared to the TOC-lean and N_{inorg}-rich samples. The sample set comprises Pliocene and Miocene lignites from the Servia and Ptolemais Basins (Greece, samples L5 and L6) and a Miocene lignite from the Lower Rhine area (Germany, sample P7). Heim et al. (2011) report the results of a pyrolytic study on a broad spectrum of organic matter of different rank (peat through anthracite). Results on elemental and pyrolysis analyses on several Greek lignite samples were published by Mavridou et al. (2008).

Two Australian oil shales, Condor oil shale (L8) from Hillsborough and torbanite (L12) from the Sydney Basin, NSW, were selected because they contain predominantly lacustrine algae with very minor input of land plants.

The group of samples with predominantly inorganic nitrogen comprises organic-poor siltstones and carbonaceous shales with varying nitrogen contents (Table 1). Two shale samples (L10 and L11) with high contents of ammonium feldspar (buddingtonite; 18.5% in L10, 36.3% in L11) from the Mesozoic-Cenozoic Liaohe Basin (China) and an argillitic andesite – "tobelite" – (ammonium muscovite; Harlov et al., 2001) from the Carpathians, Romania, were selected for the pyrolysis experiments.

2.2. Well Schwalmtal 1001: a representative stratigraphic interval

Well Schwalmtal S1001 in NW Germany (cf. Table 1) provides access to a facies and maturity sequence containing organic-poor and –rich claystones and siltstones with a predominance of inorganic nitrogen (Krooss et al., 2005). The well penetrates Quaternary, Tertiary and Upper Cretaceous sedimentary rocks and then reaches the Carboniferous with several cored intervals down to the final depth of nearly 1800 m (Mathes-Schmidt, 2000). In total, ten representative core samples (P1-4, Ms1-4, Md1 and Md2) were taken and analysed along the entire profile in order to test the reproducibility of, and extend previous measurements by Krooss et al. (2005).

2.3. Model substances and reference materials

Specific model substances and well-characterised reference materials were pyrolysed under the same conditions as the sedimentary rock samples to verify distinct gas liberation patterns of mineral or organic matter. Isolated humic acid (Witte et al., 1998) as a major