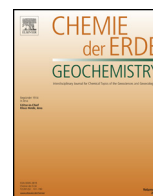




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Formation of solid bituminous matter in pegmatites: Constraints from experimentally formed organic matter on microporous silicate minerals

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ABSTRACT

The formation of solid bituminous matter (SBM) on surfaces of microporous silicates was experimentally studied at pressure and temperature conditions typical of late-stage magmatic and hydrothermal processes. Aliquots of microporous silicate minerals (zorite and kuzmenkoite-Mn, Lovozero Alkaline Massif, Kola Peninsula, Russia) were exposed to solid or liquid organic carbon sources (natural brown coal and liquid 1-hexene for synthesis purposes) in a 0.1 M NaCl-solution for 7 days, at constant pressure (50 MPa), and at three individual temperatures (200, 275, and 300 °C). No thermal decomposition of the solid organic sources happened at 200 °C and only a thin film of brown coal derivatives on the silicates' surfaces and no formation of SBM were observed at 275 °C and 300 °C. But solid bituminous matter on the surfaces of both microporous silicates were detected in experiments with liquid 1-hexene as organic carbon source and at temperatures of 275 °C and 300 °C with a more pronounced formation of SBM at 300 °C compared to 275 °C. The aromatic and aliphatic hydrocarbons, as well as alcoholic compounds of the experimentally produced SBM are similar, if not even partly identical, with natural SBM occurrences of the Khibiny and Lovozero Massifs, Kola Peninsula, Russia, and from the Viitaniemi granitic pegmatite, Finland, as shown by FT-IR and ¹H NMR spectroscopy. This strengthens the hypothesis of formation of natural solid bituminous matter by catalytic reactions between microporous Ti-, Nb- and Zr-silicates and hydrocarbons at postmagmatic hydrothermal conditions.

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1. Introduction

Considerable amounts of abiogenic hydrocarbon gases and reduced forms of carbon (including bituminous substances) are often associated with minerals of alkaline igneous complexes as shown in pioneering studies on rocks from the largest alkaline massifs of the world, i.e., the Khibiny and Lovozero alkaline massifs at the Kola Peninsula in Russia, and the Ilimaussaq alkaline intrusion in South Greenland (Petersilie, 1963, 1964; Petersilie et al., 1965; Ikorskii, 1967; Petersilie and Sørensen, 1970) as well as other studies in the 80s and 90s of the last century (Mathez and Delaney, 1981; Mathez, 1987; Tingle et al., 1990, 1991). A compendium of occurrences of hydrocarbons in igneous rocks as well as on the origin of the abiogenic hydrocarbons is provided by Potter and Konnerup-Madsen (2003), who summarize

three potential origins for abiogenic hydrocarbons: (1) primary mantle origin, (2) late-magmatic origin, and (3) postmagmatic origin (see Potter and Konnerup-Madsen, 2003, for detailed references). While e.g., Potter et al. (1998) question a primary mantle origin of abiogenic hydrocarbons, late-magmatic and postmagmatic origins of abiogenic hydrocarbons are still accepted as possible origins. However, the source of organic carbon and the source of solid bituminous substances have to be considered separately. At the earliest stages of magma evolution, carbon is mainly present as low-molecular volatile components (CO₂, CO, CH₄, and trace amounts of C₂H₆, C₃H₈, and C₄H₁₀), as derived from analysis of primary inclusions in magmatic minerals. The transformation between these volatile components proceeds in reactions like CO + 3H₂ ↔ CH₄ + H₂O, CO₂ + 4H₂ ↔ CH₄ + 2H₂O, or CO + H₂O ↔ CO₂ + H₂ and, in general, the mechanisms of the formation of small organic molecules (CH₄, C₂H₆, C₃H₈, and C₄H₁₀) are well understood. The focus of the present study is therefore on the mechanism of formation of high-molecular organic compounds (i.e., components that assemble solid bituminous matter) from low-molecular species.

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The reduced bituminous substances, also called solid bitumen or solid bituminous matter (SBM), are often enriched in transition elements (see review paper on metal enrichments in solid bitumens by Parnell, 1988). Referring to Parnell (1988) and references therein the origin of the metallic elements might be threefold: (1) the elements are inherited from the hydrocarbon source rock as organometallic complexes, (2) the elements are scavenged by migrating hydrocarbon-bearing fluids, or (3) the elements are from metal-bearing fluids that mix with hydrocarbon-bearing fluids at the site of deposition of SBM. Already in the mid 1970s Saxby (1976) proposed five possible interaction scenarios between organic material and/or organic compound and metal: (1) adsorption of metals into organic materials due to chemical reactions between the organic materials' surface and the metal (chemisorption), (2) physical adsorption of metals onto organic materials (physisorption), (3) formation of organometallic compounds by reaction of metals with organic ligands followed by precipitation of the organometallic compounds, (4) changes in the redox state of the metals due to reduction of metals by organic materials followed by mineral precipitation, and (5) mobilization of metals by the formation of organometallic complexes followed by deposition of ore minerals after destabilization of the complex. In the last decade Chukanov et al. systematically studied the crystal chemistry and properties of microporous silicates in late-magmatic/postmagmatic mineral assemblages of different alkaline igneous complexes (i.e., pegmatites of alkaline plutons) with the main focus on the Khibiny and Lovozero alkaline massifs, Kola Peninsula, Russia, to unravel the possible catalysis role of microporous silicates in the formation of solid bituminous matter from organic compounds (e.g., Chukanov et al., 2004, 2005, 2006, 2008, 2009; Ermolaeva et al., 2007, 2009). The studied microporous silicates contain typically transition elements. All observed solid bituminous substances are associated to the microporous silicates and have elevated contents of transition elements as well. According to the studies by Chukanov and co-workers the microporous silicates might not only act as catalysts of processes that involve reforming (transformation of low-molecular aliphatic hydrocarbons into aromatic hydrocarbons), polymerization of undersaturated hydrocarbons, and selective oxidation of minor carbon-bearing molecules or gases that are present in hydrothermal systems, the microporous silicates might also serve as sorbents of the solid bituminous substances that are formed by the above-mentioned catalytic reactions of organic compounds with the microporous silicates. As an explanation of the elevated concentrations of transition elements in solid bituminous substances, e.g., Ermolaeva et al. (2009) propose that oxygen-bearing aromatic compounds with hydrophilic functional groups form mobile organometallic complexes with transition elements that precipitate solid bituminous substances enriched in transition elements after destabilization of the organometallic complexes.

The unambiguous association of solid bituminous matter with late-magmatic/postmagmatic mineral assemblages let to the assumption that the above-mentioned catalytic reactions between hydrocarbon and microporous silicates take place at late-magmatic/postmagmatic hydrothermal conditions of alkaline intrusions.

The main emphasis of the present work is therefore to experimentally verify the proposed formation scenario of solid bituminous matter at hydrothermal conditions of alkaline intrusions. Experiments are performed to simulate catalytic reactions between organic hydrocarbon sources and natural microporous silicates in the presence of a sodium chloride aqueous solution and at pressure and temperature conditions that correspond to typical hydrothermal conditions. Post-run silicates are optically inspected and spectroscopically analyzed for experimentally formed solid bituminous matter. Finally the experimentally formed

solid bituminous matter is compared with natural occurrences of solid bituminous matter.

2. Experimental and analytical procedures

2.1. Experimental procedures

All experiments were carried out in horizontally oriented Tuttle-type cold seal pressure vessel (CSPV) devices at the Institute of Geosciences, University of Kiel, Germany. Both, run pressure and run duration were constant in all experiments (50 MPa, 7 days), while experimental temperatures varied (200, 275, 300 °C – please note: the experiments at the lowest temperature (200 °C) did not show any evidence for thermal decomposition of the organic source. In the following the focus will be therefore only on experiments at 275 and 300 °C). Gold capsules (50 mm length, 5 mm outer diameter, 4.6 mm inner diameter) were used as sample containers. The samples consisted of natural microporous silicates and an organic solid or liquid hydrocarbon source surrounded by 0.1 M NaCl-solution (see below for a detailed description of the silicates and organic sources and Table 1 for specific weight proportions of starting materials of all experiments with the finally used liquid organic source 1-hexene). The filling operation of the sample containers (Au capsules) was as follows: (1) at first the Au capsule was sealed at one end. (2) Grains of silicate starting material (2–3 mm in size) were placed inside the capsule. (3) Solid organic hydrocarbon source followed by 0.1 M NaCl-solution or 0.1 M NaCl-solution followed by a liquid organic hydrocarbon source were added. In order to assure similar pressures inside and outside of the Au capsule during the experiment, the final fluid pressures inside the capsule at target temperatures and pressures were calculated based on the initial fluid volume inside the capsule. Care was therefore taken by filling in liquid 1-hexene and 0.1 M NaCl-solution into the Au capsules using a syringe to ensure accurately defined fluid volumes. (4) The fully loaded capsule was immediately squeezed at the open end and welded shut. Gold capsules of all runs with solid organic hydrocarbon sources and the first experiment with the liquid organic source 1-hexene were welded shut using an oxy-hydrogen torch. To avoid loss of fluid due to evaporation and to reduce the risk of inflammation of the highly flammable 1-hexene, a modified arc welder (PUK U3, Lampert, Germany) under argon atmosphere was used to weld shut capsules of all later experiments. The Au capsules were then placed into CSPV. The pressure medium was water and the entire CSPV was externally heated. During the experiments pressure and temperature were controlled by pressure gauges and Ni-Cr-thermocouples. The uncertainties in temperature determination are assumed to be less than ± 4 °C due to temperature gradients within the CSPV and sample containers. After termination of the experiment the CSPV was cooled by continuous cold airflow to room temperature within 15 min. Run parameters are given in Table 1.

2.1.1. Silicate starting materials

Natural samples of the two microporous silicates zorite and kuzmenkoite-Mn were used as silicate starting material.

Zorite, a double-chain inosilicate with the idealized formula $\text{Na}_6\text{Ti}(\text{Ti},\text{Nb})_4[(\text{Si},\text{Al})_{12}\text{O}_{34}](\text{O},\text{OH})_5 \cdot 11(\text{H}_2\text{O})$, is a natural analogue of the synthetic microporous material ETS-4. Its crystal structure is based on the heteropolyhedral framework formed by chains of vertex-sharing $(\text{Ti},\text{Nb})\text{O}_6$ -octahedra and xonotlite-type bands $(\text{Si},\text{Al})_6\text{O}_{17}$ (Chukanov and Pekov, 2005). The framework density of zorite is very low: 14.5 knots per 1000 \AA^3 . The sample used for the experiments originates from its type locality, Yubileynaya pegmatite at the Mt. Karnasurt, Lovozero Alkaline Massif, Kola Peninsula, Russia. It occurs as an aggregate of pink acicular crystals

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