

International Journal of COAL GEOLOGY

International Journal of Coal Geology 74 (2008) 114-122

www.elsevier.com/locate/ijcoalgeo

Neo-mineral formation during artificial coalification of low-ash — mineral free-peat material from tropical Malaysia-potential explanation for low ash coals

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> Received 22 July 2007; received in revised form 22 November 2007; accepted 27 November 2007 Available online 4 December 2007

Abstract

Abundant coal deposits have very low inorganic contents (ash yield; <2%) and hence are almost ash-free. Inexplicable to date is that the precursor of coal, modern peat deposits, almost nowhere have such low ash yields as a result of both the inorganic mineral and biogenic phytolith contents. However, despite the common occurrence of phytoliths in modern peats, they are invariably absent in coals. It has thus been hypothesized by some investigators that modern environments are not ideal analogues for the formation of low ash coal deposits. Here we present new evidence to suggest that mineral diagenesis during coalification can transform biogenic inorganics to new minerals and that a substantial component of these new minerals could be removed in solution during expulsion of moisture with coalification resulting in low ash precursors of coal.

This study presents results from artificial coalification experiments of modern tropical forest peat material with ash yields between 2–4.3 wt.%. The inorganic material of the peat consists almost exclusively of Al–Si-and Si-rich phytoliths and other bioliths; no other inorganic mineral matter is present. Compressed pellets of dried peat were deformed in a Griggs constant strain rate apparatus at a constant confining pressure of 5 kb and constant strain rate of 10^{-5} s $^{-1}$ at variable temperatures from 350 °C to 550 °C. The samples, exposed to artificial coalification processes, were then analysed by SEM, EDS, and XRD for semi-quantitative chemical analyses. The deformed material showed a lack of any biogenic silica and Al–Si-phytoliths, but contained neoformed idiomorphic quartz crystals and clays. We conclude that modern peat forming environments that have low-ash peats containing biogenic silica and other biogenic Al–Si-material can represent precursors of very low-ash coal deposits. Our experiments illustrate that during coalification, it is likely all or almost all biogenic material is transformed into new minerals, mainly quartz and clay minerals, such as kaolinite. Because natural systems are not confined to the same degree as our experiments, it is likely that part or all of the inorganic fraction migrates in solutions out of the peat or coal seam with available fluids, resulting in an almost ash-free coal deposit. © 2007 Elsevier B.V. All rights reserved.

Keywords: Peat; Coalification; Biogenic minerals; Authigenic quartz; Clay mineral genesis

1. Introduction

Modern peat deposits are regarded as precursors of coal deposits. Particularly low-ash peat bogs from tropical latitudes are considered model precursors due to their aerial extent, high wood fraction (one of the main precursors of vitrinite in coal) and low ash yields. One of the problems of comparing modern

peat deposits to coals is the difficulty in finding modern peats that contain comparable low mineral matter or ash yield comparative to some coal deposits, some of which have near 0% ash yield, such as the Cretaceous-age coal beds of the Greymouth coalfield in New Zealand (Li et al., 2001; Moore et al., 2006), the Fort Union coals of the Powder River Basin, USA (Crockett et al., 2001), or the Adaro coal in Kalimantan, Indonesia (http://www.energyweb.com). Artificial coalification experiments of modern peat material have demonstrated that the ash content may increase by up to 80% during coalification (similarly to the carbonised material) as a result of the loss of organic volatile

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material (Shearer and Moore, 1996). Modern tropical peat bogs may have inorganic material contents as low as $\sim 1\%$ but often exceed 5% that would result, according to: 1) assumed compaction rates of 10:1 from peat to subbituminous coal, 2) the present inorganic material content, and 3) loss of volatile matter, in ash yields of between 10 and 50 wt.% after coalification and therefore poor quality coals.

The inorganic fraction in coals is comprised mainly of silicate minerals, such as quartz, feldspar, mica, and clays, such as kaolinite, vermiculite, illite, and mixed-layer clay minerals (Diessel, 1992), and carbonate, and sulfide minerals. Several sources have been identified for these minerals in coal, such as detrital, biogenic, diagenetic, or epigenetic (Renton and Cecil, 1979; Davis et al., 1984). The crystalline phases dominate bituminous and anthracite coals; while in brown coals, lignites, and subbituminous coals, inorganic elements in the form of dissolved salts, exchangeable ions and organometallic complexes are also important (Durie, 1961; Kiss and King, 1979).

Mineral matter adversely affects coal properties, and has been the subject of many studies over the last few decades that ranged from descriptive to experimental. Most studies characterize mineral matter in coals and interpreted possible origins; however, few studies have determined changes occurring to modern peat material during artificial coalification experiments. Of these few studies, most focused on characterizing changes in geochemical composition, organic compounds and their concentrations, e.g. increasing aromatic character and C content, decreasing O and H contents (Stach et al., 1982; Orem et al., 1996), as well as petrographic changes (Hayatsu et al., 1984; Rollins et al., 1991; Cohen and Bailey, 1997). Only a few previous studies have documented the chemical changes to the inorganic fraction during artificial coalification (Rollins et al., 1991; Willis et al., 1991; Bailey and Cohen, 1993). Of particular note relative to our study is a paper by Bailey et al. (2000), which documented the abundance of biogenic silica and showed significant changes in the chemical composition of the solutions expelled during artificial coalification tests. Their study demonstrated that cations can be: 1) expelled in solution during compaction; 2) lost as a result of loss of adsorption sites during coalification of organic solids; and 3) lost from inorganic phases due to increased temperature and complexing with organic acids and anions released during coalification.

The inorganic fraction of modern peat deposits may contain different minerals depending on local and regional geology, hydrology, geography, vegetation, and the depositional environment (Andrejko et al., 1983a). These fractions contain a range of different constituents like biogenic material (diatoms, phytoliths, etc) and inorganic minerals (clay minerals, quartz, sulfides, etc) (e.g. Cohen and Spackman, 1977; Andrejko et al., 1983a; Cohen et al., 1984; Wüst et al., 2002). In certain coal-precursor deposits, such as the low-ash ombrotrophic portions of peat deposits of the tropics, the inorganic fraction mainly consists of biogenic silica and Al–Si-structures (Ruppert et al., 1993; Wüst and Bustin, 2003). This kind of deposit has been selected for the present study in order to better understand the alteration of inorganic matter of biogenic origin during coalification. This present study was initiated because certain

coal deposits, with near 0% mineral matter, exist in the rock record whilst almost all modern thick peat deposits have ash content values above 1 wt.% (often between 0.5 and 6 wt.%), which, upon compaction, would result in an even higher weight-percentage of inorganic material. Material from the lowash peats from Malaysia, whose biogenic inorganic matter has been described elsewhere (Wüst et al., 2002) were used as study material. The objectives were to: 1) characterize inorganic constituents of peat after coalification experiments; and 2) evaluate if modern peat depositional environments are potential precursors of coal deposits, or if past peat deposits were significantly different.

2. Sample material and methods

Artificial coalification experiments have been done with different systems (closed, open, geologically open) using different parameters in order to better understand the processes likely involved in the coalification of peat (Orem et al., 1996). The aim of artificial coalification experiments is to simulate natural conditions under which diagenetic changes from peat deposits to coals occur. These conditions are likely to be dominantly controlled by temperature and time, together with loading, resulting from depth of burial (lithostatic pressure) and pore pressure, developed within any fluid phase(s) released during reactions that may occur. Most experimental studies of the past have assumed pressure and temperature conditions as they occur at present in basinal settings believed to be ideal for coal formation (e.g. 70-170 °C and 2-5 km burial depth). However, under such experimental conditions, coalification to a subbituminous rank is difficult to achieve because of a kinetics' shortfall (trade-off with short time). Hence in our experiments, temperatures were of necessity higher (350-550 °C) than those associated with the early onset of natural coalification to accelerate the kinetics of experimental coalification because geologic strain rates cannot be duplicated in the laboratory. This trade-off of strain rate for higher temperature is based on the Arrhenius equation, and has been employed in rock mechanics studies (Heard, 1963; Heard, 1968). Likewise, experimental pressures must be higher than those associated with natural coalification to maximise the amount of ductile strain produced in the samples during deformation, as high pressure and temperature promote ductile strain suppressing brittle phenomena. In our experiment, we have tried to simulate the transformation from peat to a sub-bituminous coal stage, although some of our coalification procedures (such as drying and grinding) have been modified from previous studies of others to facilitate preparation and analysis.

All experiments were conducted in a modified Griggs-type solid pressure-medium apparatus (Green et al., 1970; Tullis and Tullis, 1986) with a mixture of NaCl and KCl as the initial solid confining medium; the proportions of the salts were selected such that, at the constant temperature and confining pressure chosen for the experiment, they comprise a eutectic fluid and thus a perfect hydrostatic medium (a Borcht–Green cell) (Fig. 1).

Runs were performed under "open" conditions because the 0.25-mm thick platinum jackets used to isolate the pellets from

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