A method for rapid analysis of sedimentary environments based on C, N, S, and pyrite content in coals

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C/N ratios and sulfur and pyrite content in coals from separate basins show a good correlation with inferred paleoenvironments. C/N ratios indicate the extent of input by land plants, and the pyrite content implies sea water incursion into the basins. An analysis of C/N ratios and pyrite content in carbonaceous materials can rapidly be used to classify sedimentary environments in coal basins.

Key words: C/N ratios, coal, nitrogen, carbon, pyrite, sedimentary environment, sulfur

INTRODUCTION

An intercalation of coal seams in sedimentary sequences suggests accumulation in a non-marine environment with a high watertable, (e. g. alder swamp, or lacustrine or fluvial setting) and/or in a near-shore marine environment, (e. g. swamp or salt-marsh). Continental basins with low watertables and strong oxidizing conditions such as desert, are characterized by the presence of ferric oxide and the lack of organic matter. Such oxic environments do not allow coal formation, because of a scarcity of vegetation (Berner, 1981, 1984). An open-marine environment is also unsuitable for coal accumulation, owing to dispersion of transported plant debris in wide water areas for one thing, and decomposition of precursor organic matter under oxidizing conditions. Consequently, a geochemical discrimination of non-marine and near-shore paleoenvironments containing coal is geologically important.

Several geochemical parameters have been proposed for characterizing the sedimentary environments of coals (Teichmüller and Teichmüller, 1982). This paper presents a new method for rapid environmental analysis of sedimentary basins using carbon/nitrogen (C/N) ratios and the pyrite content in coal.

MATERIALS AND METHODS

Sixteen coal samples were used in experiments for this study (Table 1, Fig. 1), including eleven from Kyushu, Southwest Japan, two each from Thailand and Poland, and one from Malaysia. They were collected from Tertiary sequences, except one specimen (No. 16) from the Carboniferous in Poland. All samples are clean, homogeneous and unweathered coals. No sulfate minerals were observed in them. Each sample was divided into two subsamples, one for elementary analysis and the other for microscopic observation.

After cleaning and drying at room temperature, the specimens were pulverized in an agate mortar and analyzed for their C, N, and S content. Carbon and nitrogen were analyzed at the Service Centre of Elementary Analysis of Organic Compounds, Kyushu University, using a YANACO MT-2 type CHN corder. Sulfur was analyzed at Chemex Labs Ltd., Canada by the ESCHKA method following the ASTM D3177.

After pulverizing, sieving (with 24-to 100-
Fig. 1 Location map showing the study areas.

Table 1 Chemical composition and paleoenvironments of the analyzed samples.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Coalfields</th>
<th>C (wt.%)</th>
<th>N (wt.%)</th>
<th>S (wt.%)</th>
<th>C/N</th>
<th>Pyrite content (frequency %)</th>
<th>Paleoenvironments geologically deduced</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Chikuho</td>
<td>52.45</td>
<td>0.76</td>
<td>0.87</td>
<td>69</td>
<td>20</td>
<td>non-marine</td>
</tr>
<tr>
<td>2</td>
<td>Chikuho</td>
<td>35.45</td>
<td>0.52</td>
<td>3.77</td>
<td>68</td>
<td>45</td>
<td>brackish to shallow marine</td>
</tr>
<tr>
<td>3</td>
<td>Munakata</td>
<td>71.37</td>
<td>0.73</td>
<td>0.46</td>
<td>98</td>
<td>8</td>
<td>non-marine</td>
</tr>
<tr>
<td>4</td>
<td>Munakata</td>
<td>34.63</td>
<td>0.64</td>
<td>0.31</td>
<td>54</td>
<td>9</td>
<td>non-marine</td>
</tr>
<tr>
<td>5</td>
<td>Karatsu</td>
<td>67.79</td>
<td>1.40</td>
<td>0.80</td>
<td>48</td>
<td>49</td>
<td>non-marine</td>
</tr>
<tr>
<td>6</td>
<td>Miike</td>
<td>76.16</td>
<td>1.15</td>
<td>0.58</td>
<td>66</td>
<td>22</td>
<td>brackish to shallow marine</td>
</tr>
<tr>
<td>7</td>
<td>Takashima</td>
<td>72.70</td>
<td>1.54</td>
<td>0.37</td>
<td>47</td>
<td>0</td>
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</tr>
<tr>
<td>8</td>
<td>Takashima</td>
<td>80.83</td>
<td>1.42</td>
<td>0.22</td>
<td>57</td>
<td>0</td>
<td>non-marine</td>
</tr>
<tr>
<td>9</td>
<td>Takashima</td>
<td>71.15</td>
<td>1.19</td>
<td>2.94</td>
<td>60</td>
<td>54</td>
<td>marine</td>
</tr>
<tr>
<td>10</td>
<td>Amakusa</td>
<td>81.37</td>
<td>1.29</td>
<td>0.93</td>
<td>63</td>
<td>0 - 1</td>
<td>non-marine</td>
</tr>
<tr>
<td>11</td>
<td>Amakusa</td>
<td>86.09</td>
<td>1.69</td>
<td>1.21</td>
<td>51</td>
<td>3</td>
<td>non-marine</td>
</tr>
<tr>
<td>12</td>
<td>Mae Moh</td>
<td>45.34</td>
<td>1.60</td>
<td>7.07</td>
<td>28</td>
<td>72</td>
<td>lacustrine*1</td>
</tr>
<tr>
<td>13</td>
<td>Ban Hong</td>
<td>54.35</td>
<td>0.76</td>
<td>0.48</td>
<td>72</td>
<td>1</td>
<td>fluviatil*2</td>
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<tr>
<td>14</td>
<td>Batu Arang</td>
<td>49.43</td>
<td>0.78</td>
<td>0.65</td>
<td>63</td>
<td>5</td>
<td>lacustrine</td>
</tr>
<tr>
<td>15</td>
<td>Belchatów</td>
<td>52.21</td>
<td>1.41</td>
<td>1.13</td>
<td>37</td>
<td>44</td>
<td>fresh water*3</td>
</tr>
<tr>
<td>16</td>
<td>Up. Silesian</td>
<td>69.75</td>
<td>1.47</td>
<td>0.35</td>
<td>47</td>
<td>3</td>
<td>fresh water*3</td>
</tr>
</tbody>
</table>

*1 Ratanasthien et al. (1992), *2 Ratanasthien (1990), *3 Bojkowski (1983)
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mesh screens) and pelletizing, each coal sample was observed under a reflecting microscope equipped with a 25x oil immersion objective. Coal particles with pyrite were counted, and the pyrite content in frequency percent was calculated.

RESULTS AND DISCUSSION

The carbon content of the analyzed coal samples ranges from 35% to 86%, and is mostly concentrated around 70%. The nitrogen content is divided into two groups: around 0.7% and around 1.4%. C/N ratios vary from 28 to 98. The pyrite content ranges from 0 to 72 in frequency %, and the sulfur content from 0.22% to 7.07%.

Carbon in sediments exists in various forms such as organic, elemental (amorphous or graphite) and carbonate. Coal originates from plant debris, and petrological examination shows that the samples consist mainly of normal vitrinite, indicating their origin from higher land plants. Consequently, the carbon content in the present samples roughly corresponds to the organic carbon content. Organic carbon and nitrogen in sediments and coals are derived mainly from higher land plants and marine plankton, respectively (Müller, 1977). Thus, the C/N ratios indicate the contribution of terrestrial organic matter to the coal depositional sites as well as clastic sedimentary sites (Miki and Aizawa, 1995). C/N ratios greater than about 30 in the samples are consistent with the geological interpretation that the samples formed on or adjacent to land areas (Table 1). These coals suggest a moderate climate with luxuriant vegetation, and exclude the possibility of a desert or low watertable environment.

Sulfur occurs in various forms in coals, (e.g. pyritic, organic, elemental, and sulfate salts), and is chiefly derived from sea water. In the studied areas, sulfur derived from volcanic activity or plant tissues is less prevalent. Otherwise fluvial or lacustrine water contains trace amount of sulfate ions from soil and weathered rock. However, sulfate concentration in non-marine water by evaporation is less important excepting the temperate zone. Coals deposited in brackish to marine environments have a higher sulfur content than those in fresh water environments (Casagrande et al., 1977; Cohen et al., 1984). The same tendency is observed in this study, in which the sulfur content is over 2.94% or below 1.21%, except for samples from Miike (Sample No. 6) and Mae Moh (Sample No. 12). The lower content of sulfur (0.58%) in the Miike coal may have been a cause for an intermittent change in sedimentary environments of the sampling site, as geologically deduced between brackish and marine. Under such condition, diffusion or concentration of sulfate ion is critical with slight change of water chemistry. The high content of nitrogen (1.60%) and sulfur (7.07%) in the Mae Moh coal is thought to result from dead animal matter being deposited in the sedimentary basin (Ratanasthien et al., 1992) or from an incursion of sea water. According to Berner (1970, 1981, 1984), pyrite formation is not only by sulfate ions, but controlled by the amounts of organic matter and reactive iron present. In organic-rich sediments with detrital iron, the amount of pyrite is controlled by the presence of sulfate, which results from incursions of sea water. According to Berner (1970, 1981, 1984), pyrite formation is not only by sulfate ions, but controlled by the amounts of organic matter and reactive iron present. In organic-rich sediments with detrital iron, the amount of pyrite is controlled by the presence of sulfate, which results from incursions of sea water. According to Berner (1970, 1981, 1984), pyrite formation is not only by sulfate ions, but controlled by the amounts of organic matter and reactive iron present. In organic-rich sediments with detrital iron, the amount of pyrite is controlled by the presence of sulfate, which results from incursions of sea water. Figure 2 shows the relationship between total sulfur content analyzed by the ESCHKA method and pyrite content (frequency %) obtained by point-counting using a reflecting microscope. A good correlation (correlation coefficient r = 0.79) is observed between the two parameters. Consequently, the amount of pyrite in coals is adopted herein as an indicator of sulfur content.

There is also a relationship between pyrite content and inferred sedimentary environments (Table 1). Most coal samples related to marine environments are characterized by a combination of lower C/N ratios and higher pyrite content. On the other hand, most non-marine samples show high C/N ratios and low pyrite content, with the exception of sample Nos. 5, 12 and 15. The reason for high sulfur in sample No. 12 (Mae Moh) was already described. High sulfur in sam-
Fig. 2 Relationship between pyrite content (open circle) and total sulfur content (solid circle). Data are in Table 1.

Fig. 3 Plots of pyrite content and C/N ratios. Data are in Table 1.

samples No. 5 (Karatsu, Japan) and No. 15 (Poland) may be attributed to an intermittent marine incursion.

Figure 3 shows the relationship between pyrite content and C/N ratios along with a geological classification of coal-forming environments (Nakanishi et al., 1990; Miki and Aizawa, 1995). The simple vertical line at C/N=10 in the figure is tentative. Although six paleoenvironmental categories are discriminated, three categories with low C/N ratios that suggest a poor terrestrial vegetation are negligible in this study of coals. Samples from sequences inferred to be of marine origin are characterized by high pyrite content and low to moderate C/N ratios. On the other hand, most non-marine samples have low pyrite content and high to moderate C/N ratios, with three exceptions (Sample Nos. 5, 12 and 15). The sedimentary sequences from which the three samples come are considered to be non-marine, although the pyrite content and C/N ratios indicate otherwise. The high-resolution techniques used in this study evidently detect a slight invasion of sea water and/or changes in salinity in supposedly "non-marine" environments.

It should be noted that no sample is plotted in the area of pyrite content between 22% and 44%. According to Curtis and Spears (1968) and Taylor and Curtis (1995), the stability of iron-mineral phases with pyrite is made critical by changes in oxidation-reduction potential and by the activity of bicarbonate ions, especially at low salinities. Thus, the absence of samples showing the intermediate pyrite content in Figure 3 may relate to mineral stability. The experimental results described here indicate that a combination of C/N ratios and pyrite content can be used to analyze sedimentary environments, especially where sedimentary sequences lack appropriate fossils or sedimentary structures.

CONCLUSIONS

A preliminary experimental study of the C, N, S and pyrite content of coals indicates their usefulness as paleoenvironmental indicators. C/N ratios indicate the extent of land plant input to the depositional basins, and generally indicates the distance between the basins and the source areas. The sulfur and pyrite content are basically controlled by sulfate in sea water. Consequently, an analysis of C/N ratios and pyrite content can be used to rapidly assess the sedimentary envi-
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