SELF-HEATING-GENERATED COMPOUNDS RELEASE TO WATER PHASE SIMULATED BY HYDROUS PYROLYSIS

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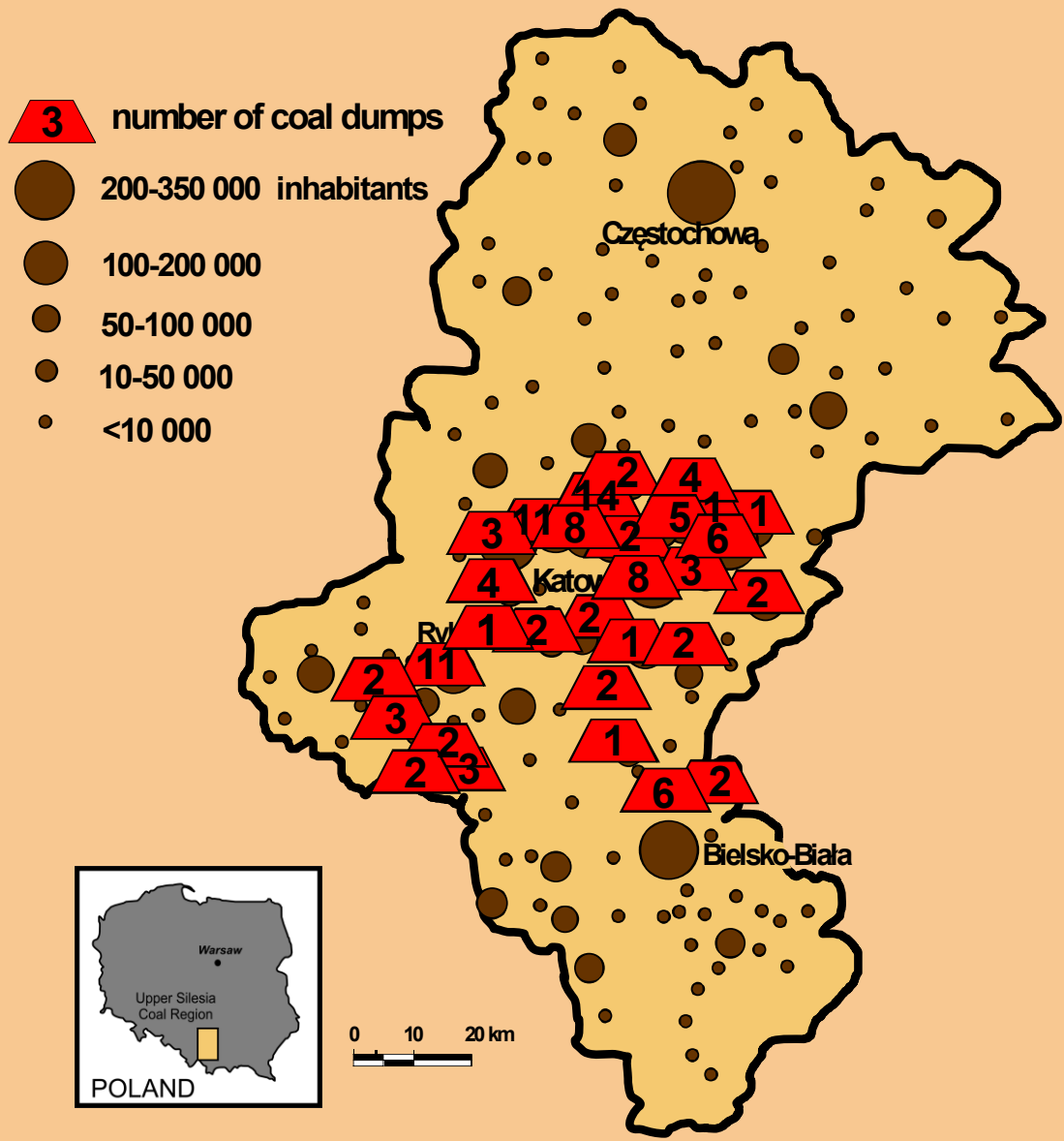
BACKGROUND

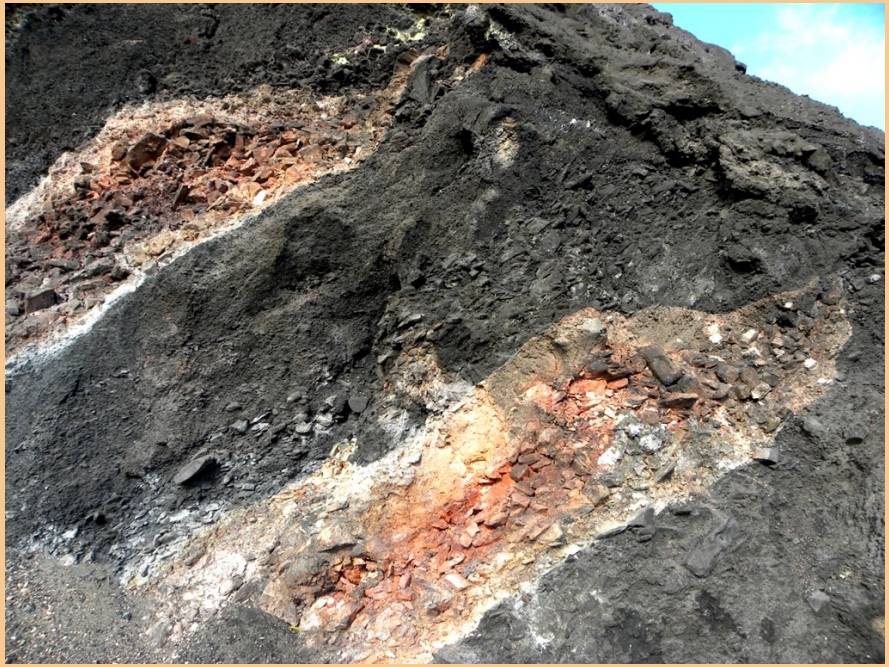
- Coal wastes are a by-product of coal mining, generated in large amounts (~0.7-1.2 ton for every 1 ton of bituminous coal),
- They contain 3-30% of TOC,
- It is estimated that over **762.8 x 10^6** tonnes of coal wastes are stored in Upper and Lower Silesia (Poland, Pennsylvanian) coal waste dumps.



Self-heating-generated compounds release to water phase …

BACKGROUND

- Coal waste re-use is limited due to poor mechanical properties (mudstones and shales predominate),
- During long storage in dumps coal wastes undergo transformations caused by oxidation, leaching, biodegradation, and **self-heating**.



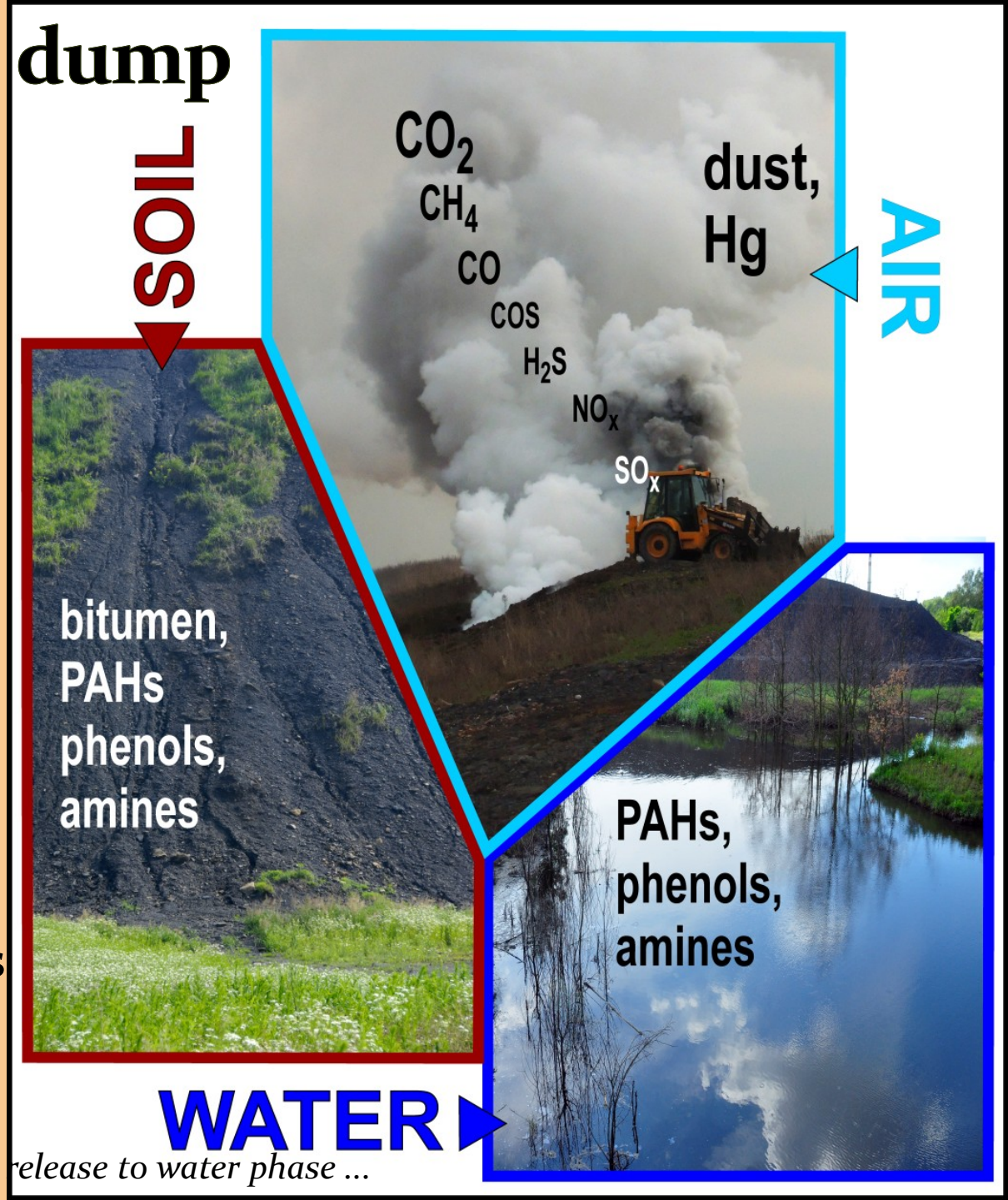
Self-heating-generated compounds release to water phase …

BACKGROUND

- **Oxidation** – a chemical reaction of coal wastes with oxygen; may occur at low temperatures or may accompany the coal waste burning;
- **Biodegradation** – a biological decomposition of coal wastes caused by bacteria and/or lichens; it often leads to formation of better water-soluble compounds;
- **Leaching** – dissolution and removal of coal waste components by rainwater penetrating a dump;
- **Self-heating** – a process of spontaneous temperature increase within a coal waste dump; it may lead to self-ignition and open fire or to slow smoldering of coal wastes.

Environmental impact

- coal waste oxidation, and particularly self-heating, produce compounds hazardous to the environment,
- gases, dust and volatile compounds are emitted to the air,
- leaching and erosion release organic and inorganic contaminants to water and soil.



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PROJECT JUSTIFICATION and AIMS

- Processes within dumps are affected by numerous factors (e.g. weather, dump construction, gangue composition, etc.);
- Organic phase of natural waters is a mixture derived from different sources thus it is difficult to identify contamination from coal waste;
- Thus to research them controlled conditions are required.
- In this project we aimed:
  - to find whether hydrous pyrolysis can be applied as a good method to simulate self-heating within coal waste dumps,
  - to identify types of compounds produced in hydrous pyrolysis that are expelled to the water phase and compare their distributions to those found in natural coal waste leachates,
  - to assess hazards to the aquatic systems caused by coal waste self-heating.

SAMPLING POINTS

Two coal waste dumps were selected. The eastern part of the Upper Silesian Coal Basin (low maturity, Ro ~0.5%, subbituminous coal) is represented by the **Janina** Coal Mine, and south-western (higher maturity, Ro ~0.9%) by the **Marcel** Mine.

Four mudstones (recent production) with high (ca 20%) and low organic matter content (ca 5%) were selected:
two from the Janina Mine and
two from the Marcel Mine.

Katowice
Rybnik
Marcel
Janina
Oświęcim

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METHODS

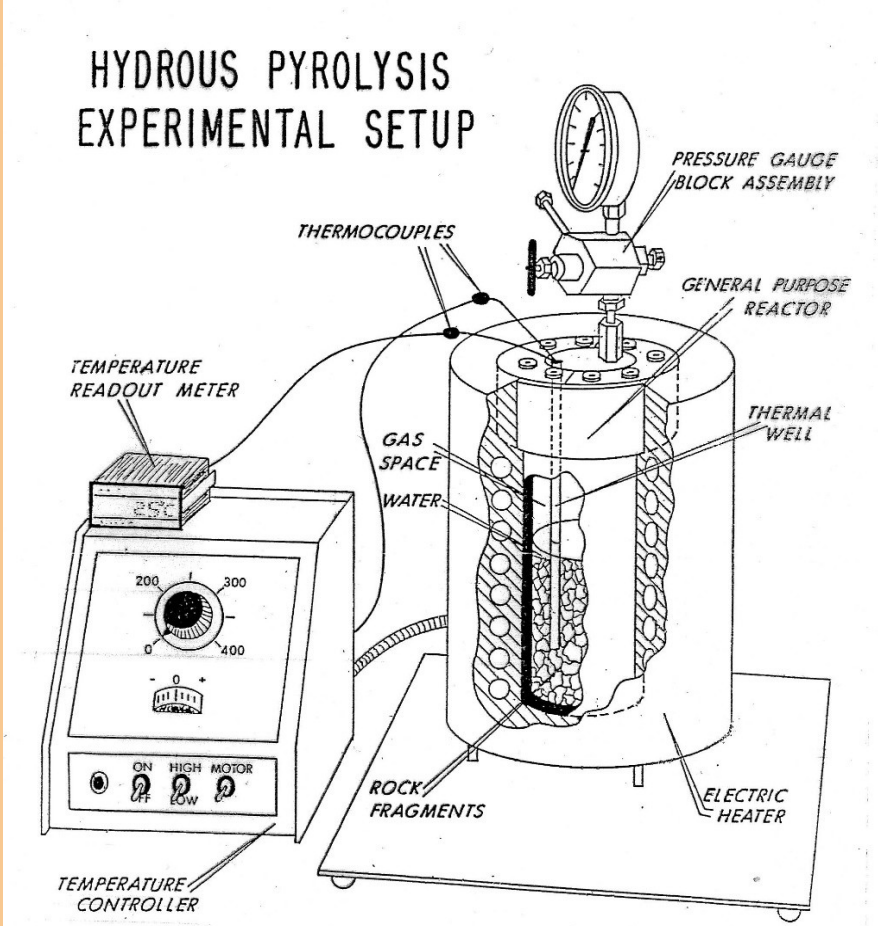
1. **Preparation of mudstone samples**: air drying in ambient temperature for 1 week, crushing to grain size 1-2 cm for hydrous pyrolysis, bulk characterization of the rocks with Rock-Eval Pyrolysis and reflected light microscopy,
2. **Hydrous pyrolysis:** 1-liter reactors (Parr Co.) in temp. 250, 360, and 400°C during 72 h (procedure by Lewan et al.,2008). Amount of water added - 200-380 mL,
3. **Solid Phase Extraction of organic compounds in water**: C18 PolarPlus columns (BAKERBOND, 3g). Compounds were eluted with dichloromethane (HPLC grade),
4. **Gas chromatography-mass spectrometry of SPE extracts:** an Agilent 6890 gas chromatograph coupled with an Agilent Technology 5973 mass spectrometer, EI mode, 70 eV; scan range – 50-650 daltons.

HYDROUS PYROLYSIS

the Hastelloy C-276 1-liter reactor

Photo: T. Kowalski, AGH UST Krakow

Crushed rock were loaded into the reactor and heated isothermally in He atmosphere for 72h. Gas, liquid, and solid products were collected for analyses.



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HYDROUS PYROLYSIS

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The water phase was separated from other products and subjected to further analyses.

Aver. SPE extracts yields [% wt.]:

Janina samples

250°C – 0.001
360°C – 0.011
400°C – 0.001

Marcel samples:

250°C – 0.001
360°C – 0.004
400°C – 0.008

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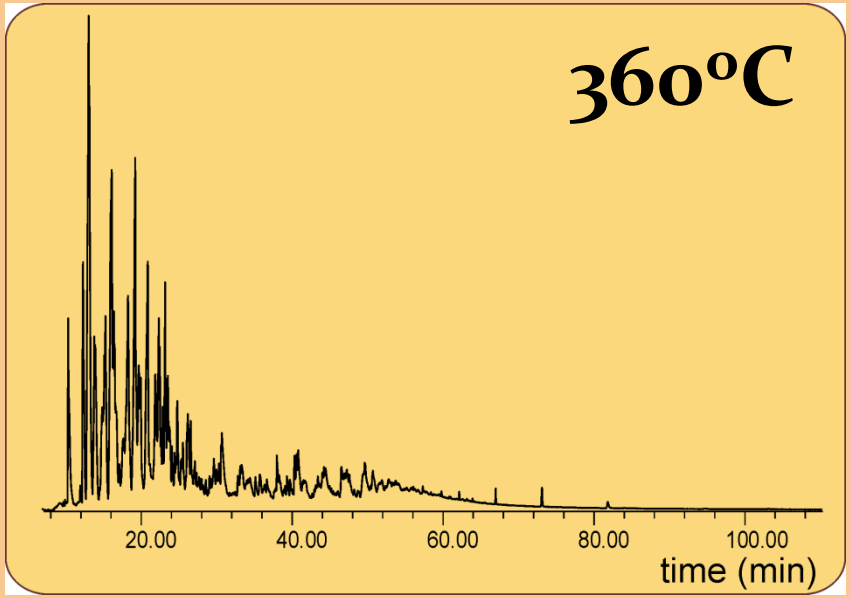
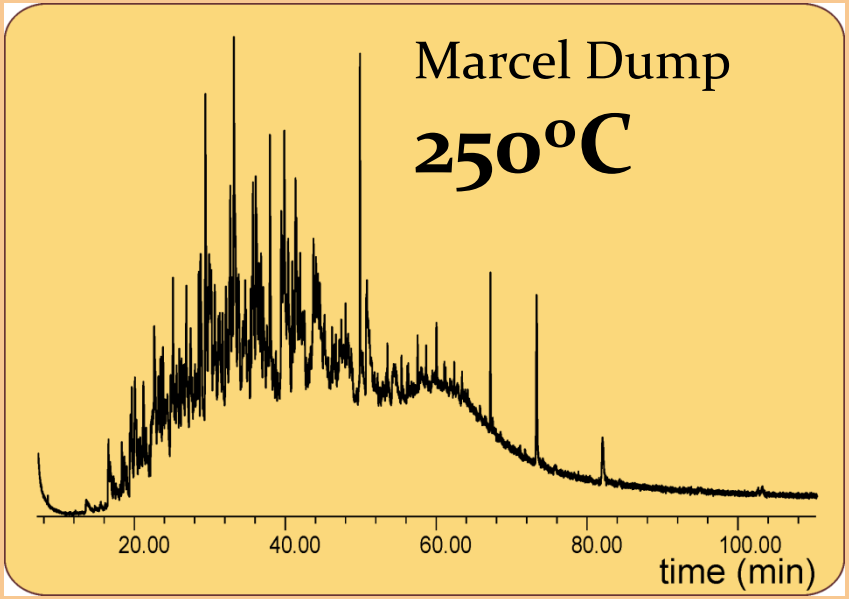
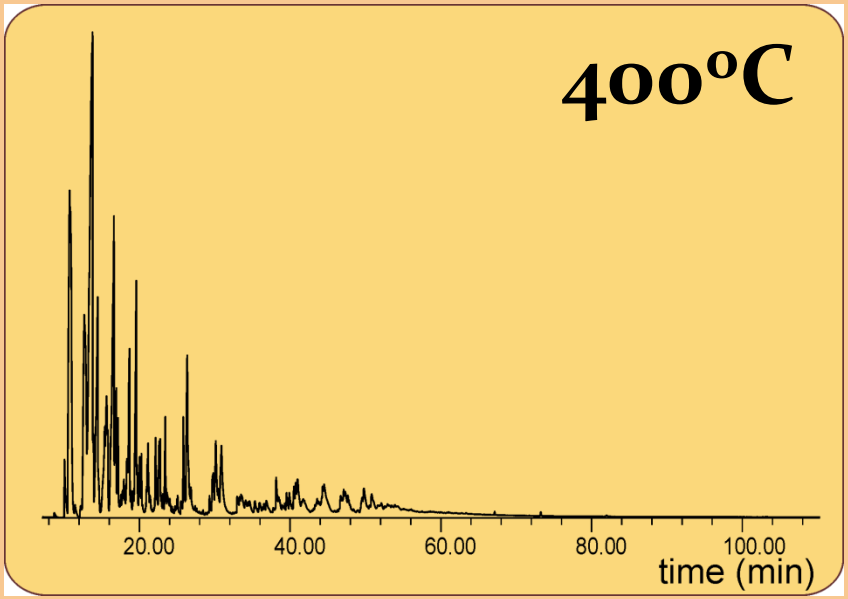
ORGANIC COMPOUNDS IN WATER PHASE

Changes in a general distribution of compounds released to pyrolytical water from pyrolysed coal wastes (TIC).

relative intensity







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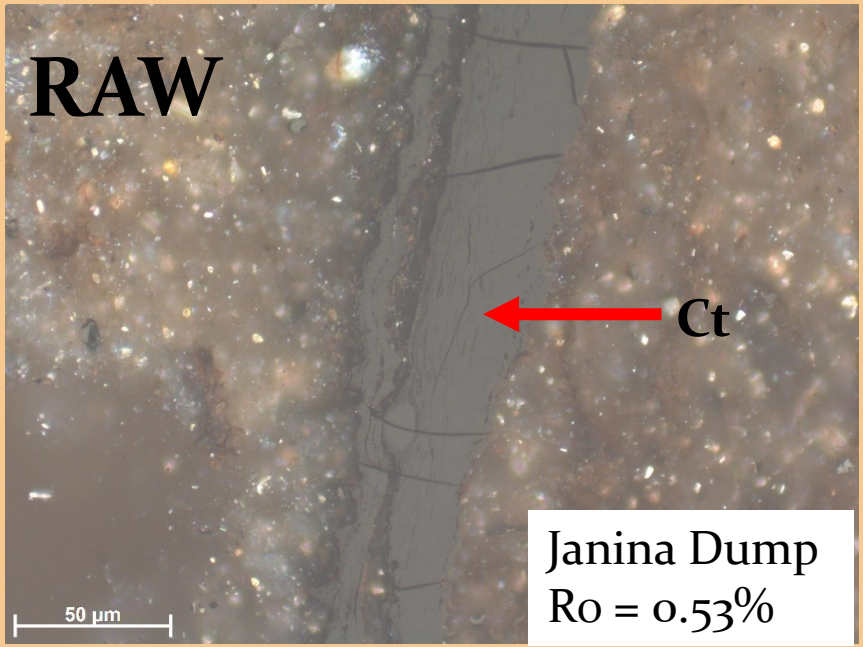
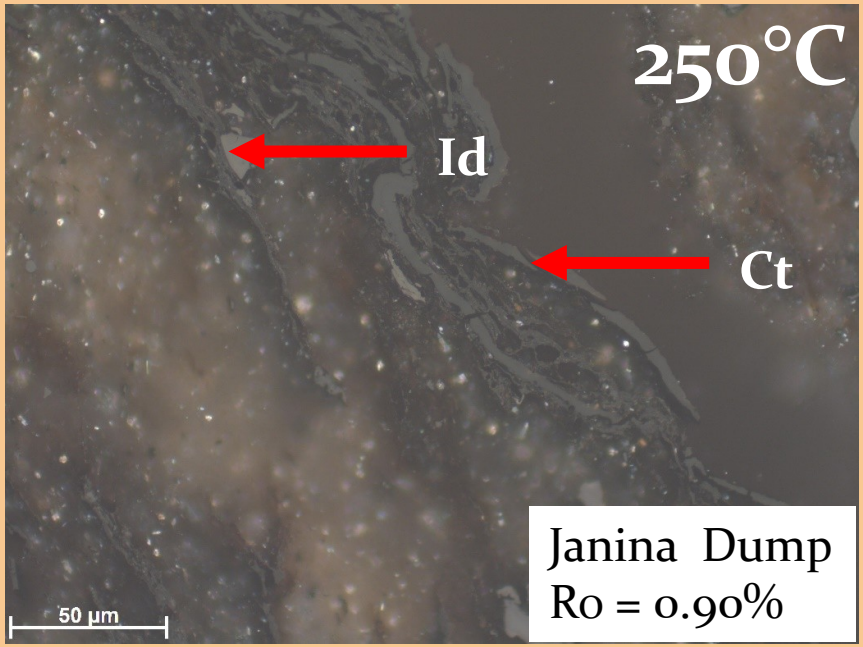
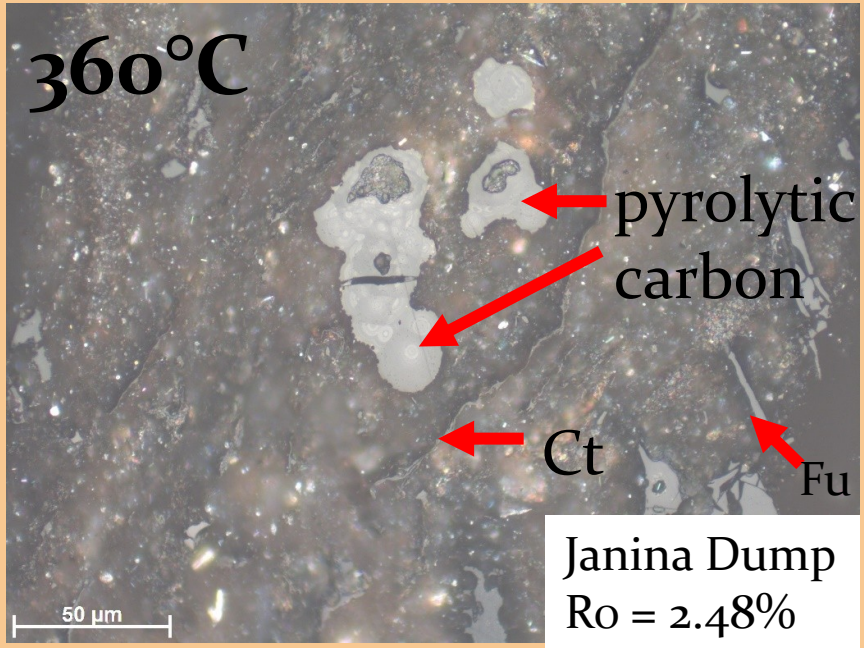
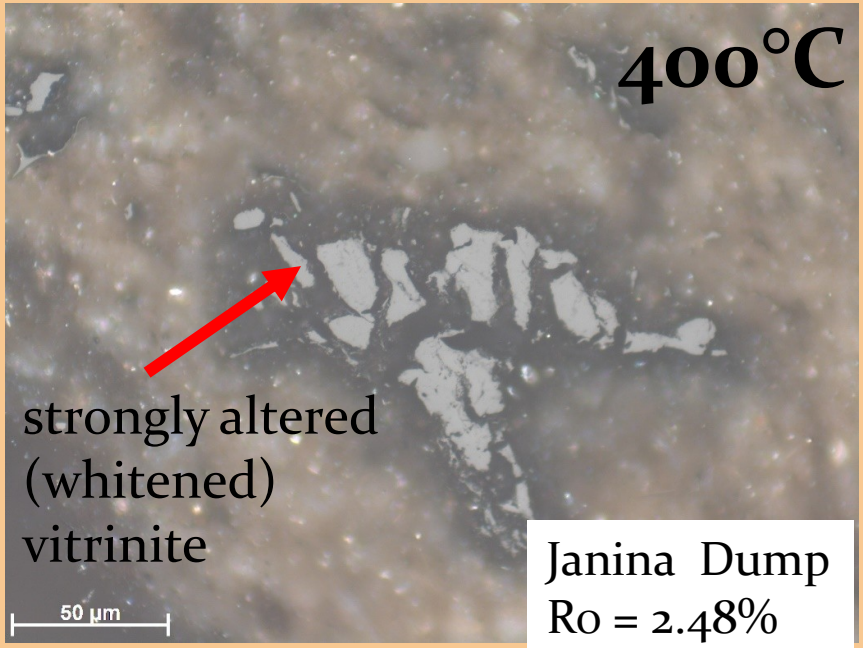
MACERALS TRANSFORMATION









GROUPS OF ORGANIC COMPOUNDS

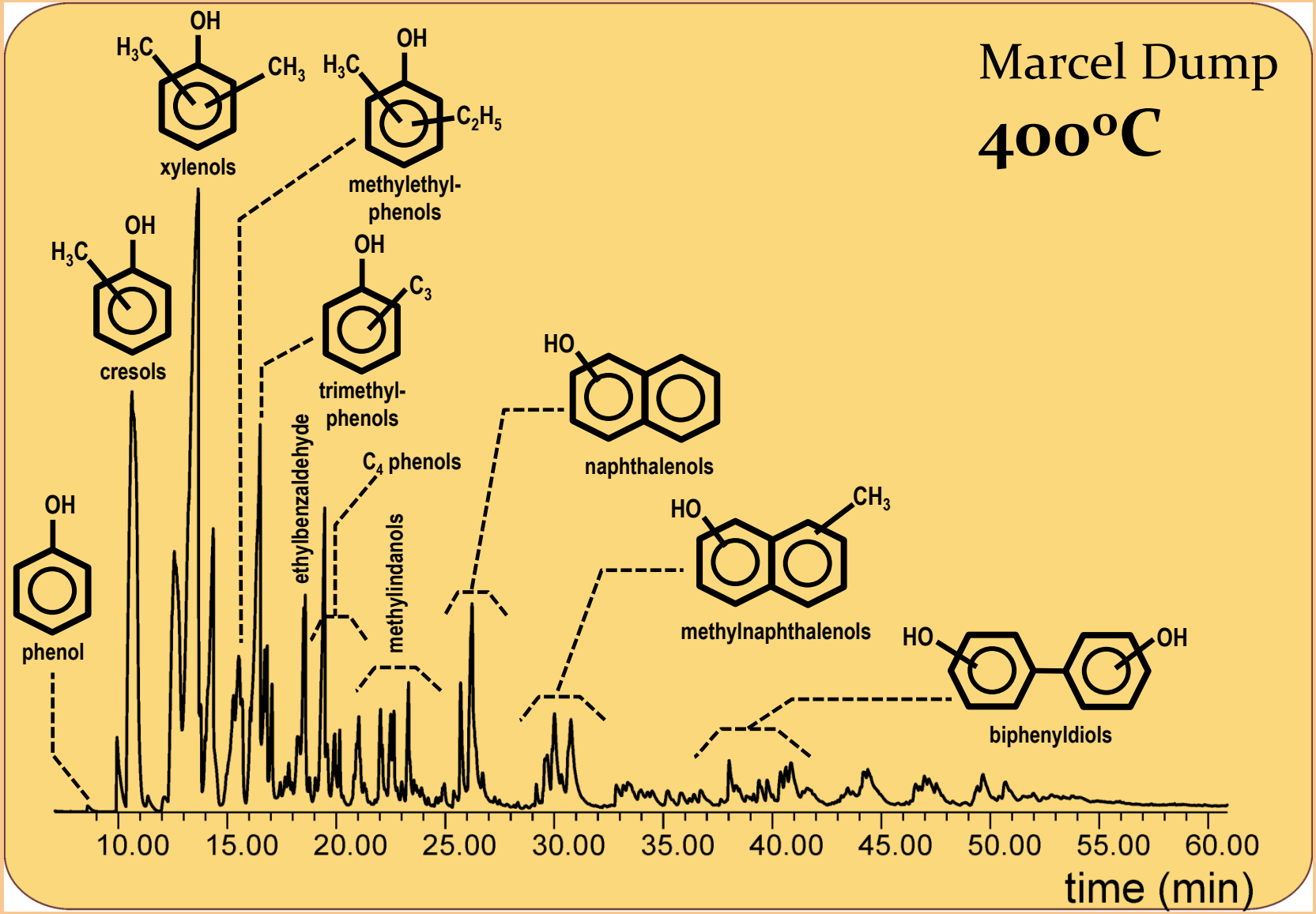
Hydrous pyrolysis released compounds such as:

- phenols, (up to 60% of the total extract composition),
- carboxylic acids,
- aldehydes, and ketones, including numerous aromatic ketones and quinones,
- S-heterocyclic compounds such as dibenzothiophenes.

Phenolic derivatives were perviously found in natural Upper Silesia water bodies (lakes and rivers) located close to coal waste dumps (Nádudvari et al., 2015, Fabiańska et al., 2020).

Due to their adverse impact on the biosphere these compounds were the object of particular interest.

PHENOLIC COMPOUNDS IN PYROLYTIC WATER



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CONCLUSIONS

- Hydrous pyrolysis released to the water phase compounds such as phenols, carboxylic acids, aldehydes, ketones, quinones, and S-heterocyclic compounds such as dibenzothiophenes. Phenolic derivatives predominate in pyrolytic water (up to 60% of the total extract), comprising compounds from phenol (C_0) to C_4 phenols.
- The minimal temperature of phenol release, caused by the macromolecule cracking, was 360°C.
- Water phase from 250°C pyrolysis contained phenols in minor amounts only, and vitrinite, the main source of them, was not changed. The organic phase composition at this temperature corresponds to water leachates of Upper Silesia coal.
- Thus, the major hazard to the aquatic environment are sites in with self-heating temperature >250°C; pollution indicators are phenols with cresols and xylenols domination in the distribution.

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