

Why should we use organic geochemistry in studying mineral deposits?

Krzysztof Foltyn¹, Benedikt Steiner^{2,3} and James Barnett^{2,3}

1. AGH University of Science and Technology, Kraków, Poland

2. Camborne School of Mines, University of Exeter, UK

3. XPLORE GLOBAL LTD., Maidenhead, UK

It is common practice for geologists to use an array of organic geochemical techniques as part of source rock evaluations in the hydrocarbon and coal industries. However, we argue that geochemical analysis of organic matter can be an equally useful tool for studying mineral deposits, especially those which are sedimentary-hosted.

Analytical methods

Rock-Eval pyrolysis is a fundamental and popular organic geochemical method commonly employed by petroleum geologists to determine the quality, kerogen type (i.e. oil- or gas-prone) and thermal maturity of a potential source rock for hydrocarbons. The process can be simply described as the thermal decomposition of organic matter by heating in the absence of oxygen. A sample (usually up to 150 mg, depending on the organic matter content) is put into an oven and heated to 300°C in an inert atmosphere. Detectors collect hydrocarbons and carbon dioxide, which are recorded as peaks on a graph. The first peak, S₁, records the volume of free hydrocarbons present in the sample before the analysis. The sample is then gradually heated to 550°C at 25°C/min, which leads to thermal decomposition (cracking) of the kerogen and produces hydrocarbons recorded as the S₂ peak. CO₂ generated from cracking of the kerogen is recorded as the S₃ peak and is only trapped and collected at temperatures of up to 400°C, due to the potential for CO₂ generation from the burning of any carbonate present within the sample at higher temperatures. Residual organic carbon is also measured by combusting the sample in the presence of oxygen and recording generated CO₂ as the S₄ peak. The measured peaks are used to estimate TOC (Total Organic Carbon, unit weight %), HI (“Hydrogen Index” $\frac{S_2 \cdot 100}{TOC}$, unit mg hydrocarbons per gram TOC), OI (“Oxygen Index” $\frac{S_3 \cdot 100}{TOC}$, unit mg CO₂ per gram TOC), amongst others. As well as being widely used to assess the potential of a sample to generate hydrocarbons, these analyses can also be used to give clues on the oxidation state of the organic matter present. This latter factor is regarded as the most interesting application in terms of economic geology, as it could be used as an indicator for redox processes.

Example: Polish Kupferschiefer

A good case study to showcase the application of organic geochemistry to a sedimentary-hosted mineral deposit is the Kupferschiefer Cu-Ag deposit, located on the Fore-Sudetic Monocline in Poland. The Kupferschiefer (copper-bearing shale), a stratiform horizon rich in organic matter, acted as a reducing agent during metal precipitation and played a crucial role in the genesis of the Cu-Ag body. This process resulted in a large Cu-Ag body deposited in footwall shales and sandstones, along with hangingwall carbonates. At a later stage, highly oxidising metalliferous fluids were responsible for Au-Pt-Pd mineralisation in areas adjacent to the Lubin-Sieroszowice copper deposits. The development and movement of the oxidation front largely removed the early diagenetic base metal mineralisation from altered units as the

process continued. As a result, three different zones can be observed within the deposit (Figure 1): *reduced* (with a high base metal content but low precious metal content at geochemical background level), *oxidised* (with a low base metal content but a precious metal content 2-3 orders of magnitude higher than in the reduced zone), and a *transitional zone* (with a high base metal content and Au-Pt-Pd content of up to 10 ppm).

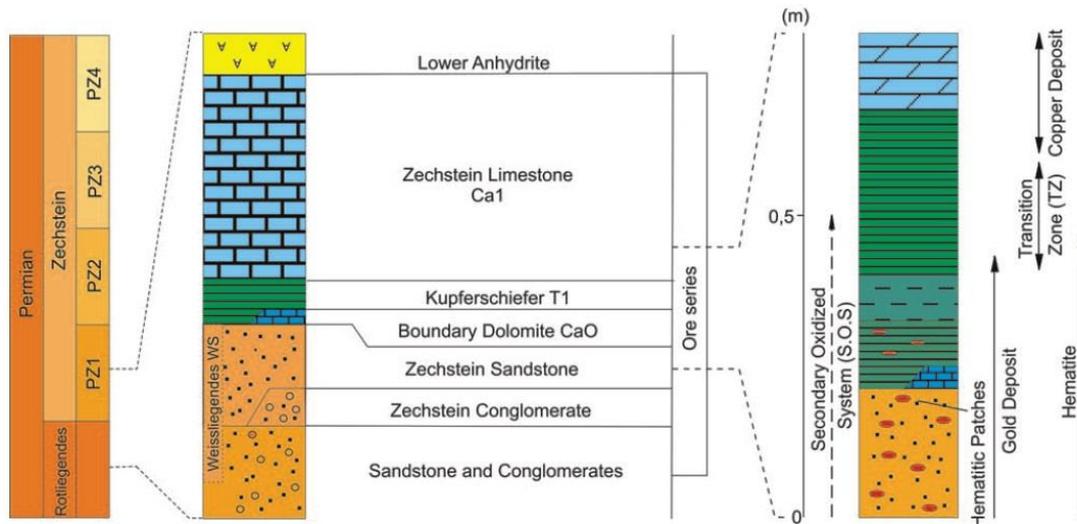
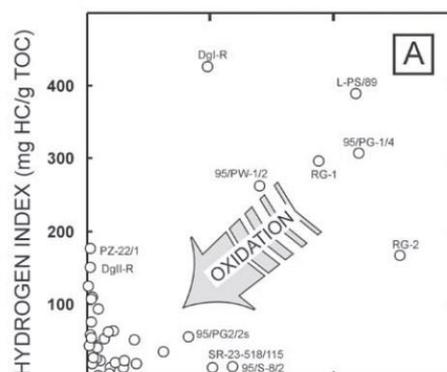


Fig. 2. Lithostratigraphic column through copper deposit (modified after Oszczepalski, 1999), gold deposit after Piestrzyński *et al.* (2002)

Figure 1. Lithostratigraphy and ore deposits associated with the Polish Kupferschiefer (Pieczonka *et al.*, 2008).

Więclaw *et al.* (2007) describe new methods of identifying the distribution of reduced, oxidised and transitional zones in Kupferschiefer strata based on the geochemical analysis of organic matter. The main indicators used for the transitional zone are: S_2/S_3 ratio (HI/OI), TOC and OI, all obtained from *Rock-Eval* pyrolysis. In general, the *reduced zone* is rich in organic matter with high HI and low OI indices which can be used because Cu, Ag, Zn, Pb, Co concentrations usually exhibit a general positive correlation to TOC content and S_2/S_3 index. Organic matter in the *oxidised zone* is minimal. Published results show that samples from the *transitional zone* fulfill one of the following criteria:

- S_2/S_3 index range from 1 to 3 or
- $S_2/S_3 < 1$ and TOC content $> 1\%$ or
- $S_2/S_3 > 3$ and $OI > 30 \text{ mg CO}_2/\text{g TOC}$.



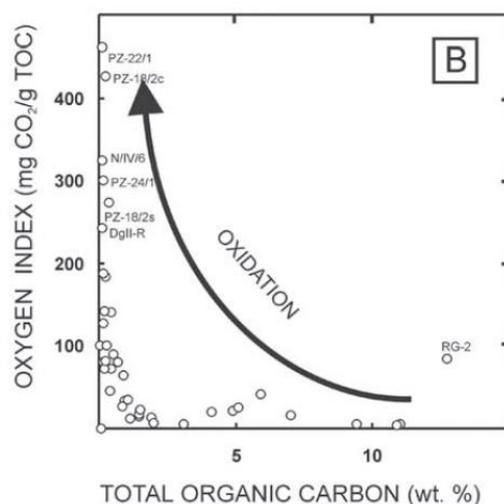


Figure 2. Effects of oxidation on HI and OI (Pieczonka et al., 2008)

Alternative analytical methods

Rock-Eval pyrolysis is a relatively cheap and fast process which requires only a small amount of sample, proving to be a source of useful information for planning efficient exploration programmes. On the other hand, this method has some disadvantages. Most significantly, the low TOC content in oxidised samples increases the potential for analytical error. An analytical accuracy of 0.01% is adequate for a reduced sample with 1-2 % TOC, but becomes more problematic for highly oxidised samples with a TOC of <0.05 %.

Additional information acquired by more sophisticated geochemical methods can provide further criteria for defining reduced, oxidised and transitional zones within a mineral deposit. These rather time-consuming methods are based on the identification of particular hydrocarbons within the sample. Firstly, bitumen have to be washed from the sample using a *Soxhlet extractor* and subsequently separated into saturated hydrocarbons, aromatic hydrocarbons, asphaltenes and resins. Hydrocarbons in each group can be precisely identified by a gas chromatography-mass spectrometer (GC-MS), but how the results can be “translated” into geological context is key for further interpretations.

For example, some particles are easier to destroy, whilst others are more resistant. Oxidised rocks are often characterized by low saturated hydrocarbon, n-alkane, isoprenoid and porphyrin contents, and high concentrations of heavy aromatic hydrocarbons, asphaltenes and resins. Most gas chromatograms of oxidised samples show degraded bimodal n-alkane distribution patterns and elevated percentages of PAH (Polycyclic aromatic hydrocarbons) such as dibenzofuran, dibenzothiophene and phenanthrene. The most widely used criteria to distinguish oxidised rocks is a high Ph/MPh ratio (phenanthrene/sum of methylphenanthrene). This is because the oxidation resulted in an increase of phenanthrene and a decrease of methylphenanthrenes. Reactions and relations between oxidation and many different organic compounds are not fully understood and still need further investigating.

Conclusion and Relevance for Mining

Organic matter is present in many sedimentary-hosted ore deposits and played an important role during ore genesis. Therefore, an understanding of the quantity and type of organic matter is key to reconstructing redox processes in the host-rock. Although not yet common practice, mining companies exploring for sedimentary-hosted ore deposits are encouraged to fund academic studies to better outline key processes related to the precipitation of metals from metalliferous fluids. This could indeed lead to the identification of further targets along identical or similar regional geological trends.

References

- Pieczonka, J., Piestrzyński, A., Mucha, J., Głuszek, A., Kotarba, M. J., & Więclaw, D., 2008. The red-bed-type precious metal deposit in the Sieroszowice-Polkowice copper mining district, SW Poland. In *Annales Societatis Geologorum Poloniae*, 78, 151-280.
- Püttmann, W., Merz, C., & Speczik, S., 1989. The secondary oxidation of organic material and its influence on Kupferschiefer mineralization of southwest Poland. *Applied Geochemistry*, 4(2), 151-161.
- Speczik, S., Oszczepalski, S., Nowak, G. J., Grotek, I., & Strengel-Martinez, M., 2005. Alteration of organic matter as a new exploration guide for Kupferschiefer-type Cu-Ag and Au-Pt-Pd deposits. In *Mineral Deposit Research: Meeting the Global Challenge*, 1065-1068. Springer Berlin Heidelberg.
- Więclaw, D., Kotarba, M. J., Pieczonka, J., Piestrzyński, A., Oszczepalski, S., & Marynowski, L., 2007. Rozmieszczenie strefy redukcyjnej, przejściowej i utlenionej w łupku miedzionośnym na monoklinie przedsudeckiej na podstawie wskaźników materii organicznej. *Biuletyn Państwowego Instytutu Geologicznego*, 423, 125-138.