Organic Geochemical and Petrographic Signatures of Hydrocarbons in Igneous Systems*

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Abstract

The interactions between igneous events and hydrocarbon systems are varied. For example, earlier igneous events can result in nutrient leaching which may simulate phytoplankton growth in an overlying water column, or can rapidly mature source rocks. Igneous systems can, however, have their own organic processes independent of significant hydrocarbon charges. The objective of this article is to present organic geochemical and petrographic data from a range of igneous environments. There is great variability in the tectonic setting of volcanic activity, including "hot spot", extensional and subduction regimes, sub-aerial and submarine. The magmatic composition can comprise a range of silica concentrations, intrusives ranging from granites to gabbros, extrusives ranging from acid tuffs to basalts, as well as kimberlites and carbonatites. The available literature is too extensive to be covered in this here. Selected literature highlights are used, for the reader to find further pertinent publications.

Organic Geochemistry

The schematic cross-section of a subaerial system (Figure 1) makes 3 relevant points: First, a thermal gradient exists, from up to 1200° C in the magma chamber and crater, through geothermal systems at ≈350-100° C, to "hot springs" at ≈70° C, down to ambient climatic conditions. Second, water is dominant, as gas or liquid, is available to react with and transport organic compounds. Third, host rock alteration is a frequent process, providing information on the chemistry of the hydrothermal fluids.

At higher temperatures, volatile hydrocarbons may be abiogenically synthesised. Schwandner et al. (2004) identified and quantified a range of volatile hydrocarbons, including CH_3Br, CH_3Cl, CH_3I, C_2H_5Br, CCl_3F and chlorinated benzenes, in the subduction-related Vulcano (Italy) fumaroles, at pptv-ppmv levels.

Subaerial (and submarine) geothermal systems support a range of "extremophiles" living under T and pH extremes (≈70° C, 1). In the Taupo Volcanic Zone (NZ), Kaur et al., (2015) identified lipids preserved in siliceous sinters and concluded "correlation between lipid distributions

and geothermal conditions is observed. The ratio of archaeol (2,3-di-O-phytanylglycerol) to bacterial diether abundance, bacterial diether average chain length, degree of GDGT (glycerol dialkyl glycerol tetraethers) cyclisation and C_{31} and C_{32} hopanoic acid indices typically increase with temperature. At lower pH, the ratio of archaeol to bacterial diethers, degree of GDGT cyclisation and C_{31} and C_{32} hopanoic acid indices are typically higher." (p. 327).

The organic compounds detected vary with geological location and magma. Teague et al. (2011), using the same techniques as Schwandner et al. (2004), reported far fewer halocarbons in aqueous fumaroles in the Oldoinyo Lengai (Tanzania) carbonatite than those detected at Vulcano. Giże and Macdonald (1993) reported bitumen seepages from a trachyte flow on the Suswa Volcano (East African Rift) to be anomalously enriched in O and N heteroatomic organic compounds and depleted in aliphatics. Compositional and geologic data suggest that the biogenically derived bitumens were partly extracted and/or transported by liquid or supercritical CO_2, rather than H_2O, possibly from caldera-lake sediments. Compositionally atypical hydrocarbons and reduced carbon associated with other alkaline-peralkaline igneous complexes, as well as Hg and Au deposits, may also reflect CO_2-rich fluids. The atypical hydrocarbon compositions were postulated to reflect the partial absence of a H-donor during cracking (Giże and MacDonald. 1993).

Characteristic of organic matter in submarine hydrothermal systems is the complete range of biomarkers, from immature to mature (e.g. stanols to sterenes). Simoneit et al. (1990, p.115) summarised that "This organic matter is primarily of a sedimentary origin with trace components from ambient organic detritus and viable organisms, e.g. bacteria and possibly from deeper source (magmatic, e.g. Wheland and Lupion, 1987). The ambient organic matter, which is suspended and dissolved in the waters around the vents, may become entrained into the fluid discharges by turbulent mixing, resulting in instantaneous hydrous pyrolysis, generating petroleum-like products." In this case, H_2O is the H-donor during cracking (Hoering, 1982; Siskin and Katritzky, 1991).

Organic Petrography

Organic petrography is suggested to be a more reliable technique for recognising hydrocarbons influenced by igneous events (Newman et al.), for three reasons. Once formed, a bitumen is immobile, except when physically entrained (e.g. in faults). A solid bitumen is unlikely to be markedly influenced at a molecular level by diffusion from a later petroleum charge, except at the margins. Maturity is irreversible, and so any T-time increases from the later petroleum event will add to the pre-petroleum charge maturity.

The following interpretations of bitumen textures observed in hydrothermal systems unrelated to significant petroleum charges are based primarily on Franklin (1951). Upon heating, a carbonaceous material relatively poor in heteroatoms (e.g. N, S, O) can eventually develop the long-range ordering of planar polycyclic aromatic hydrocarbon (PAH)-graphene precursors to form graphite. Brooks and Taylor (1965) described optically the formation of anisotropic aromatic domains in an isotropic pitch during heating. A carbonaceous precursor rich in heteroatoms when heated, will have the long-range order of linking PAHs blocked by heteroatoms. The former carbonaceous material is termed a "graphitising" carbon, whereas the latter is a "non-graphitising" carbon. Broader terms for the textures include "coke", "pyrobitumen" or "thermal mesophase".

Figure 2 shows the development of a graphitising carbon formed through contact metamorphism by a dolerite dyke on a bitumen (Nanisivik, Canada: Giże and Rimmer, 1983). The development of aromatic immiscible domains optically follows the Brooks and Taylor (1965) model, with geopetal coalescence to form an optically long-range ordered pre-graphitic texture. A non-graphitizing carbon, with optical domains <1 μm, from a coked anticline reservoir (Carlin, Nevada) shows multiple generations (Figure 3). Both graphitising and non-graphitizing carbons can occur in the same system (Roberts et al., 1993). Hydrogen disproportionation (Horsfield, 1984) results in later pyrolysates, immiscible in water, characteristically showing optical anisotropy (Figure 4). When a pyrobitumen surface is in contact with a hydrothermal water (as preserved in a vein), the optical anisotropy becomes aligned perpendicular to the bitumen-water contact (Figure 5), but never at the pyrobitumen-host rock contact. This texture is interpreted as developing during cooling of the hydrothermal fluid, with heat flow from the host rock and bitumen to the water causing alignment of PAH layers according to thermal conductivity. In an aqueous fluid-poor situation, or when quenching occurs, no such alignment is seen in the pyrobitumen contact (Ixer at al., 2015; Figure 6). As expected, deformation is initially plastic (Figure 7), becoming increasingly brittle (Figure 8) with maturity. Superimposed on the textures developed by hydrothermal systems, are additional processes such as reorientation of optical anisotropy by stress (Figure 7). It is speculated that the surface of a bitumen can be compositionally and optically affected by diffusion from a later petroleum charge. This is based on interpretation of the surface colouration of ambers by hydration, and increased reflectance caused by oxidation inferred from the associated mineralogy (Figure 9).

Summary

Organic compounds are integral to sub-aerial to submarine systems. The limited data indicates abiogenic synthesis at high temperatures (e.g. fumaroles). Extensive data exists on the biogenic extremophiles which live in cooler geothermal systems, with diagnoxtic lipids adapted to the relatively extreme pH-T ranges. In submarine hydrothermal systems, petroleum maturity biomarkers occur intermixed with dominant immature biomarkers. H_2O is the dominant H-donor, although CO_2 systems may yield H-depleted aromatics. Although the organic compounds integral to volcanic systems are specific and readily identifiable, their concentrations may be too low to be detected within a later volumetrically larger petroleum charge due to molecular diffusion, except when preserved by isolation (e.g. sinters, fluid inclusions).

In contrast, organic petrography of bitumens associated with the hydrothermal fluid processes before a petroleum charge is introduced may be more reliable. Such hydrothermal fluids develop and precipitate in the higher temperature regimes shown in Figure 1 (e.g. >150° C). The bitumen thermal maturity is therefore probably higher than that of a later petroleum charge. As maturity as indicated optically is additive, the hydrothermal bitumens should show reflectances higher than those associated with later petroleum charges. The only evidence for thermal cooling of hydrothermal fluids is the reorientation of optical anisotropy perpendicular to the bitumen-water contact. Interpretations of the margins of bitumens should be careful, however, given the evidence for oxidation and diffusion into the margins of amber by water.

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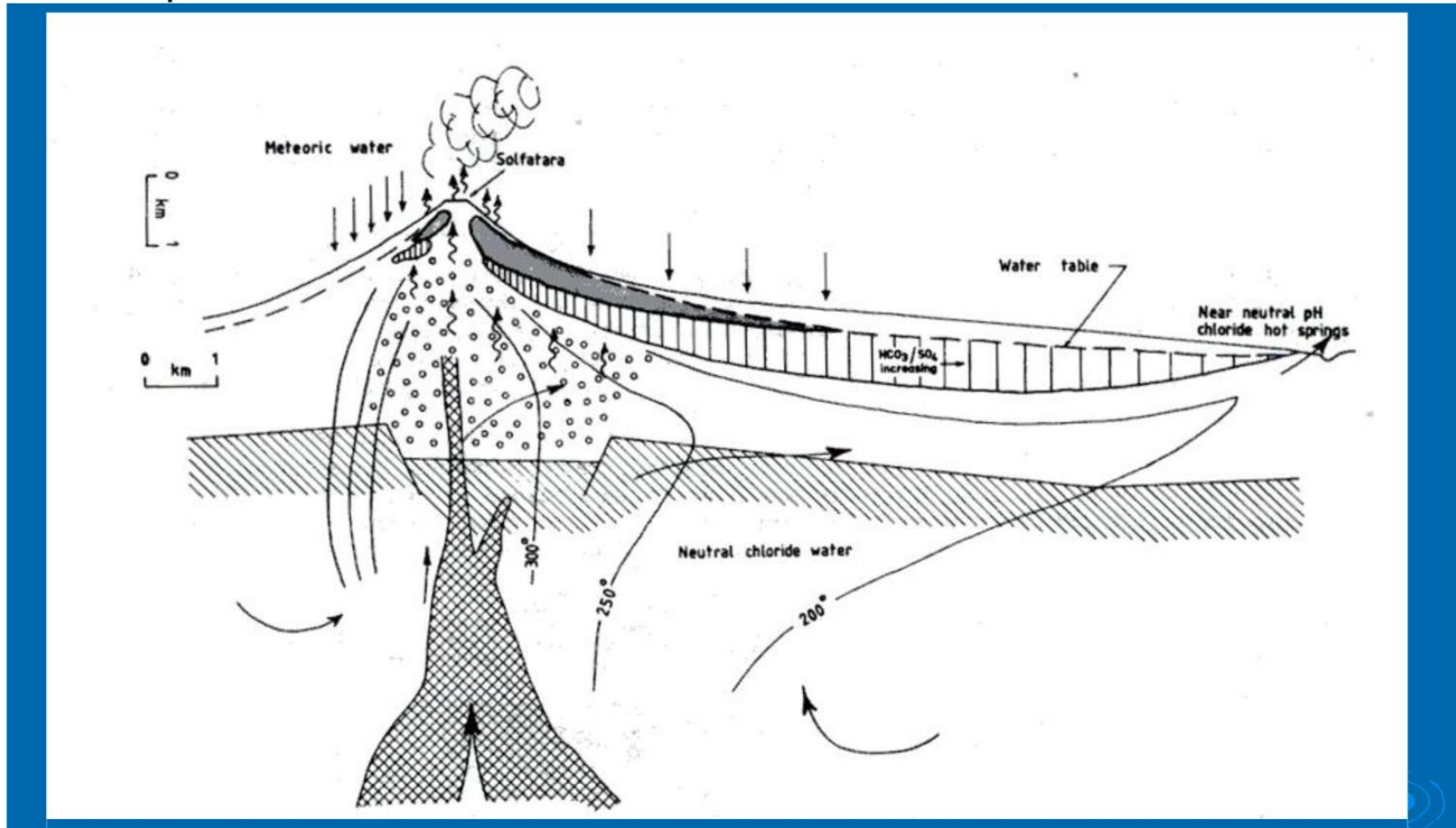
Figure 1. Schematic section of a geothermal system (reproduced from Henley, 1984, p. 14).

1a Nanisivik, air, X-polars, w 900μm:1b w1800 μm
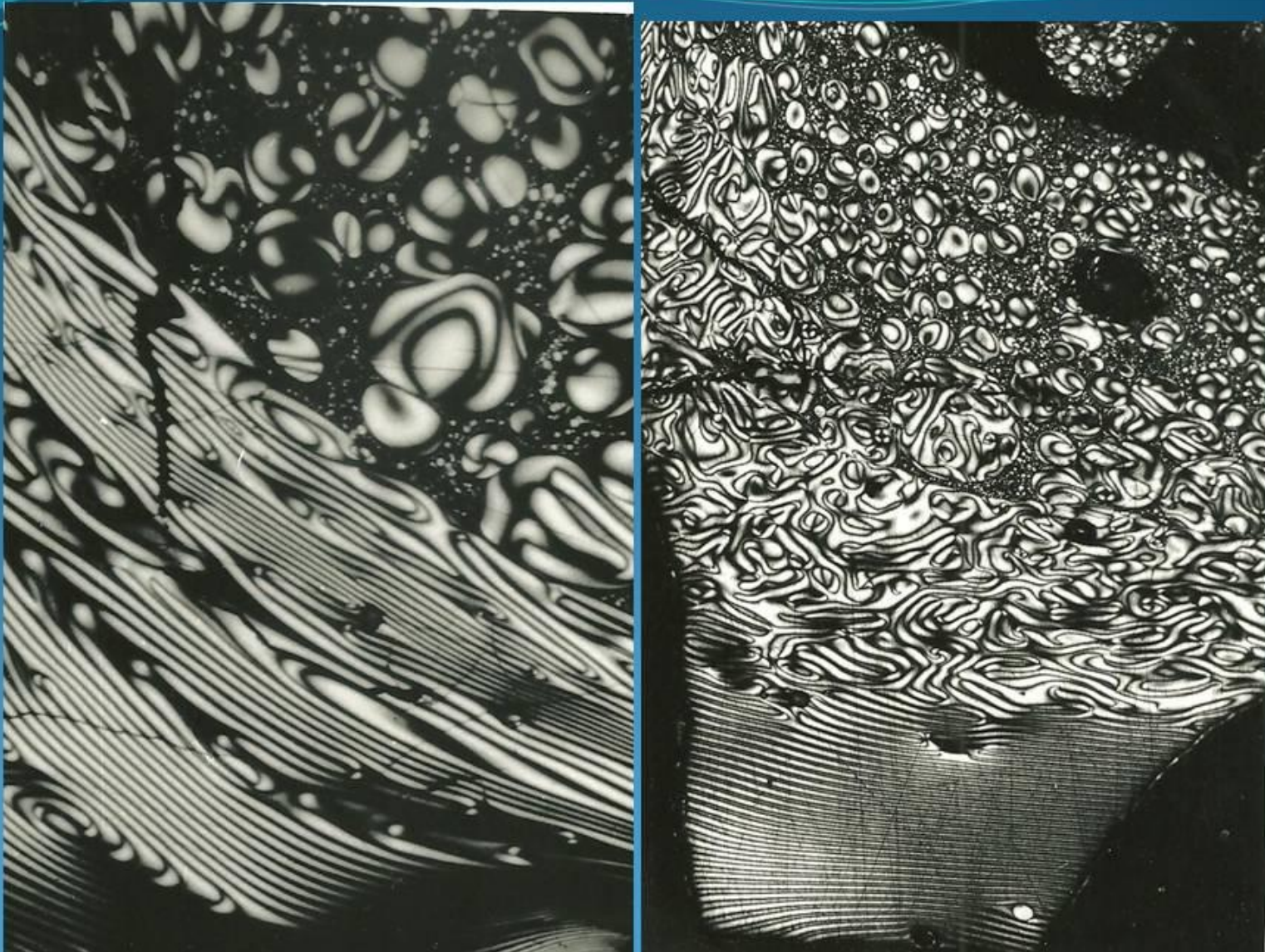
Figure 2. Graphitising bitumen.
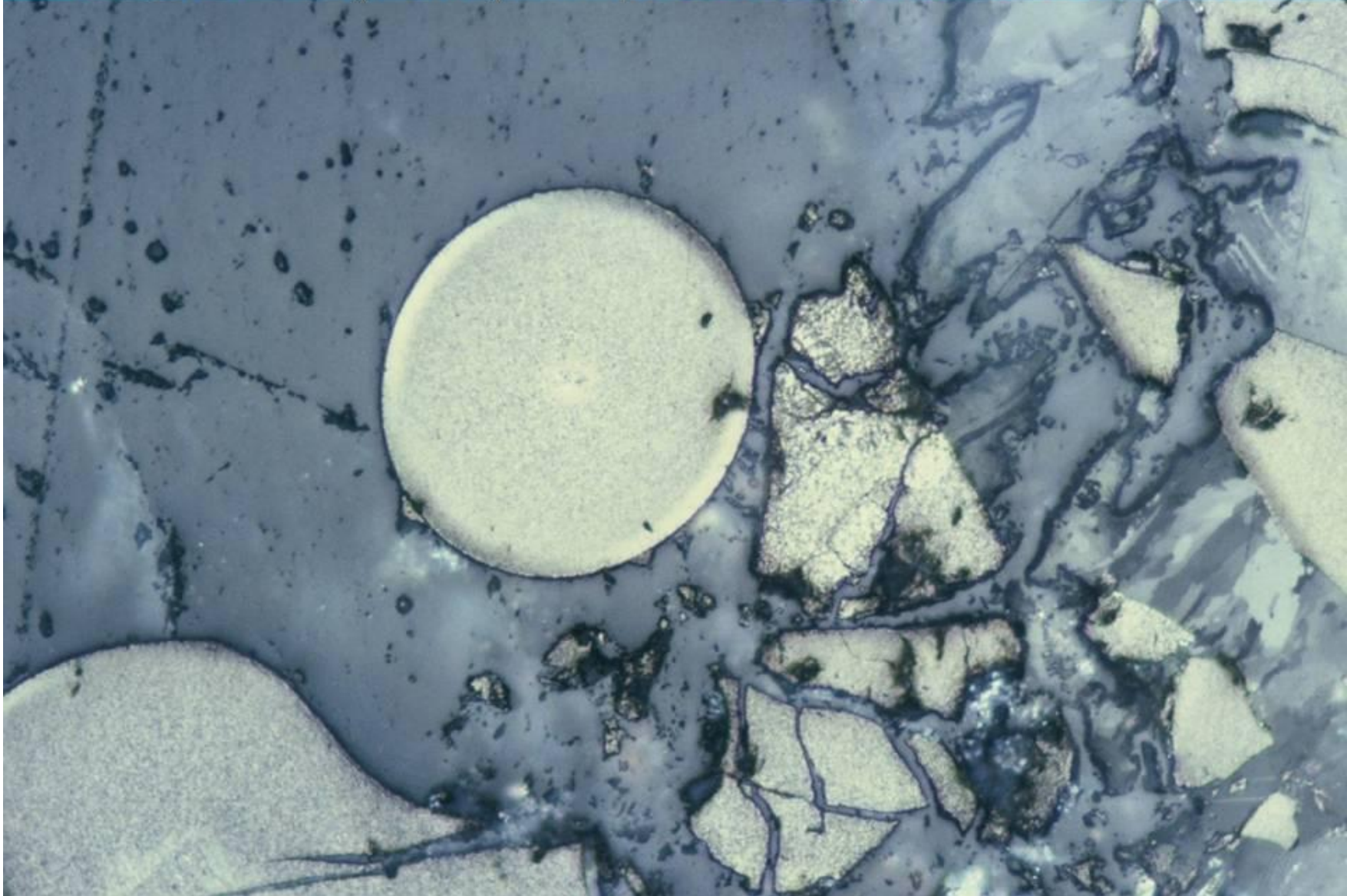
Figure 3. Non-graphitising bitumen.
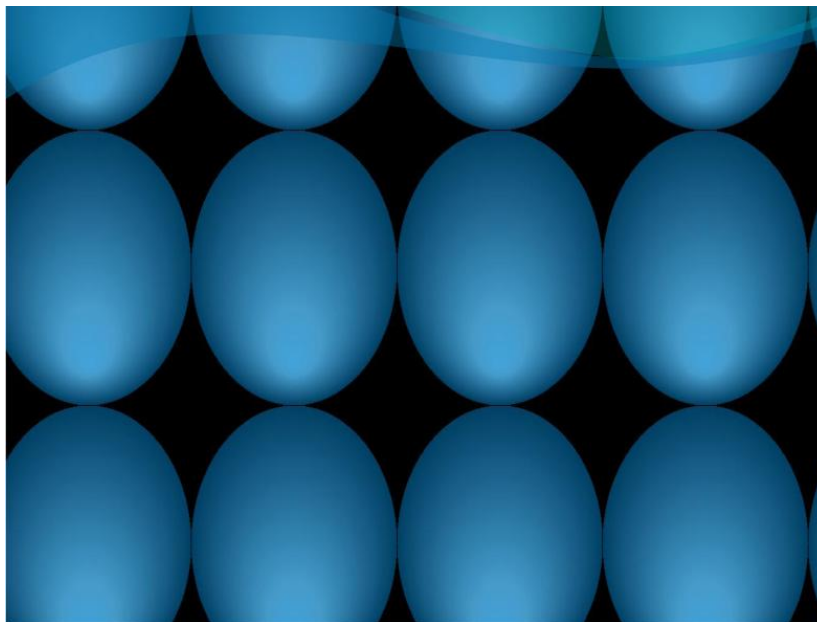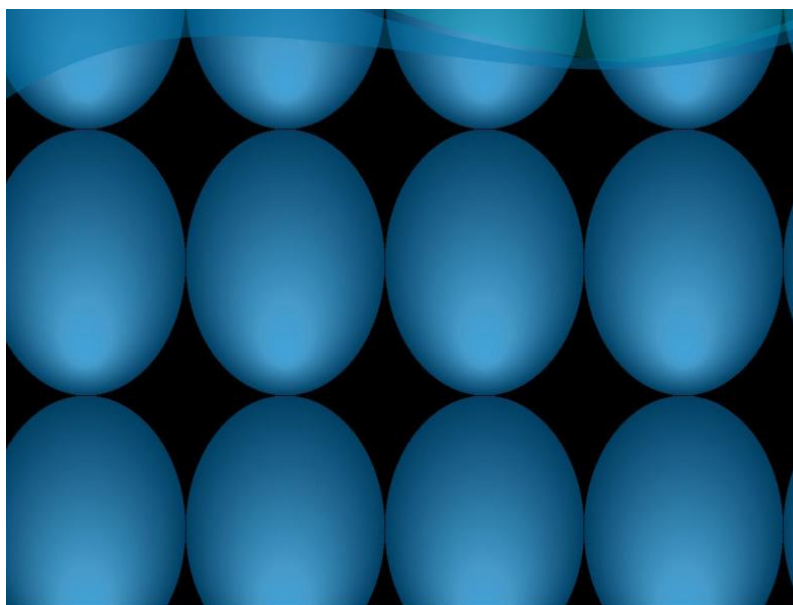
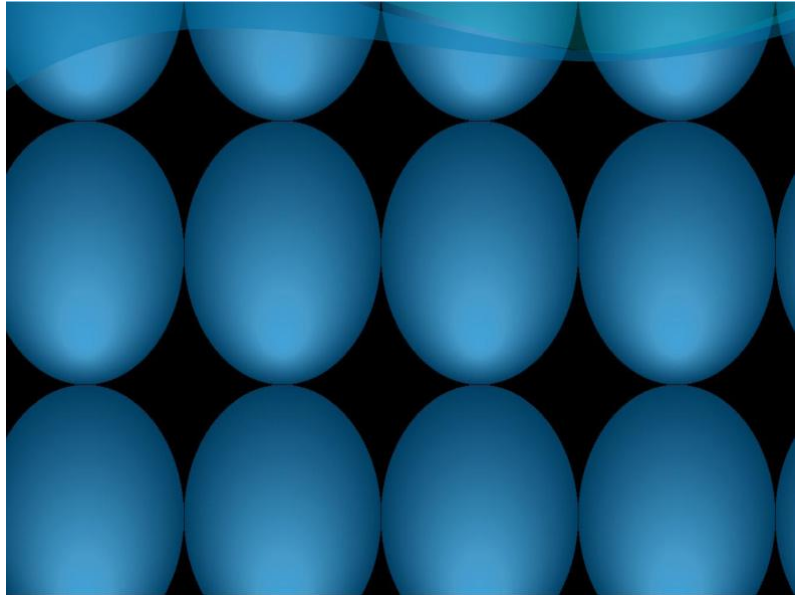Figure 4. Late pyrolysates.

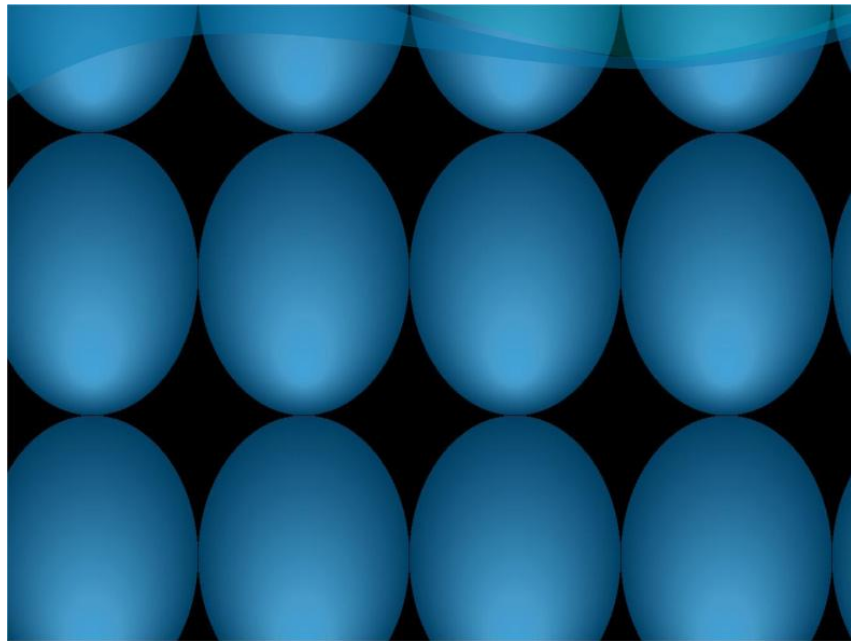Figure 5. Thermal anisotropy.

Figure 6. Quenched texture.
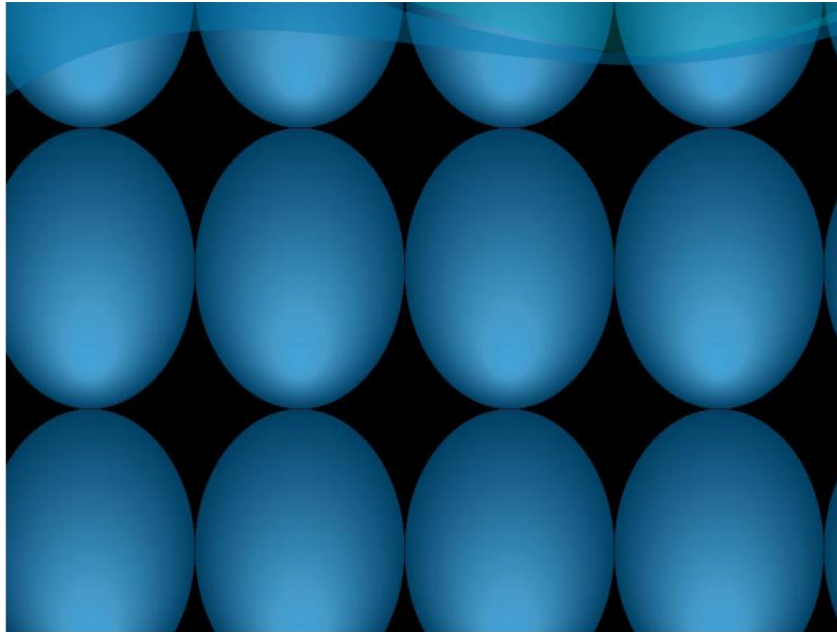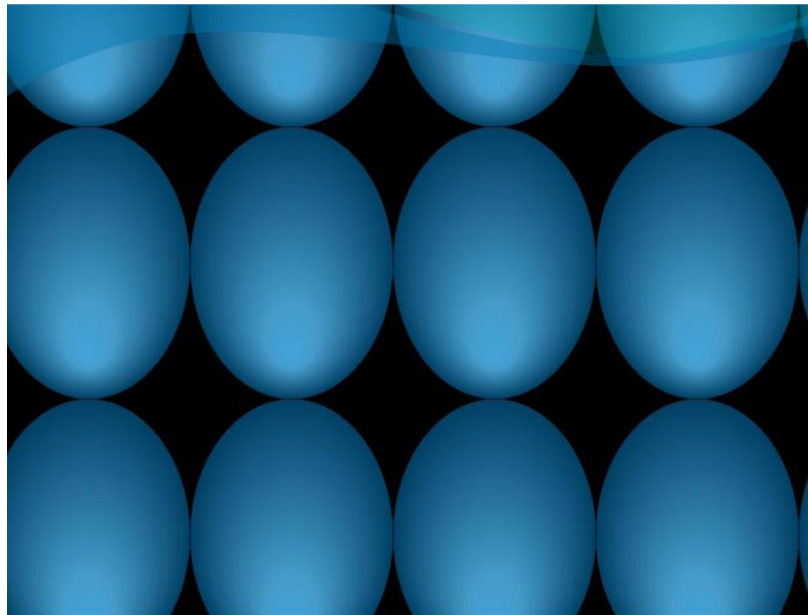

Figure 7. Plastic deformation. X-polars.

Figure 8. Brittle deformation.

Figure 9. Alteration (e.g. oxidation).