KUPFERSCHIEFER MYTHS DEBUNKED

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Myth 1. The Kupferschiefer shales contain one of the great copper concentrations on Earth and occur throughout the base of the Zechstein basin in northern Europe.

The Kupferschiefer as the principal ore carrier for copper in the Zechstein sequence is perhaps the biggest myth of all. Whereas the Kupferschiefer has been the subject of persistent mining since about 1200 A.D., the Kupferschiefer (*sensu stricto*) actually contains only a very small part of the copper (silver) endowment. The recent large scale mining operations in the mid-1950's greater Lubin District in Poland have clearly shown that more than 90% of the copper endowment is actually hosted in the underlying Weissliegende silica sandstones. In the greater Lubin district Kupferschiefer shales have been shown to be a basinward facies deposited in shallow depressions between larger sand mound highs that are on the same timeline as the 'boundary dolomite' facies deposited at the top of the Weissliegende sand mounds.

Reconsideration of the 'sedimentology' of the Kupferschiefer-Weissliegende sequence allows the alternative interpretation that these rocks are part of a metalliferous episode of deep-sourced mud slurry volcanism that appeared at the end of Permian time beginning about 265 Ma. In any case, the fact that the Weissliegende is the main economic host for copper mineralization places renewed emphasis on other parts of the regionally distributed Kupferschiefer shales (especially the German ones). In the German Kupferschiefer, mining has mainly been focused on high-grade copper concentrations near its base (for example the legendary T1 unit at the base of the Kupferschiefer black shale). In light of the Polish mining experience, the historic emphasis on the Kupferschiefer in Germany may have missed or under-evaluated the real economics, which may reside in the underlying Weissliegende. The under-estimated copper potential would reside in the sand mound facies, which may represent the top of potentially copper-rich and silver-gold rich pipe environments. These pipes represent deep-seated conduits that lead to the source of metalliferous brines derived from dehydrated serpentinite near the base of the Zechstein-Kupferschiefer crust. To date, the potential pipe mud slurry feeder environments have gone completely un-assessed.

Myth 2. The Kupferschiefer is a black shale derived from surface continental detrital sources deposited under low temperature, normal sedimentological conditions.

The unusual highly anomalous metal (PGE,Au,Cu,Ag,Co,Ni,V,Se,Sb,Pb,Zn,Mo, and others) and highly elevated hydrocarbon content is not easily derived from northern European, surface continental sources and upgraded by microbial reduction. The Kupferschiefer carbonaceous black muds and related silica sands contain a variable assemblage of hydrocarbons, sulfides, and selenides that can be demonstrated to have formed at higher temperatures (circa 350^{o}C) and lower temperatures (25 to 100^{o}C). These facts falsify the surface sedimentological-microbial reduction model. A deep-sourced, mud-brine volcanism model derived from dehydration of ultramafic serpentinite in an incipient rift setting satisfactorily explains the above compositional and temperature features.

In effect, the sand and mud volcanism was erupted as a sequence of slurries that contained a significant volume of exotic clasts derived from mineral and rock formation events at various depths, temperatures, and times within the mud volcanic system. These events could have occurred deep in the crust in the serpentinite 'kitchen', in the deep dehydration to talc reaction chamber, in shallower mud chambers at various levels in the crust, or at surface temperature-pressure conditions at the eruptive site. In this way, minerals or rocks formed at various times, pressures, and temperatures can all be juxtaposed in the same slurry. Thus, it is no surprise that various viewpoints and interpretations have arisen from what would be a confounding array of differing observation; each with their own set of anomalies.

Myth 3. The overlying Zechstein salt succession accumulated in a shallow salt depression with the chemistry for the extensive volumes of salines derived from local continental sources adjacent to the basin and concentrated by an evaporation process not related to the underlying Kupferschiefer.

The evaporation model does not account for the unusual magnesium-rich muds within the saline succession that contain magnesium-rich minerals like clinochlore chlorite, talc, and serpentine. It does not explain the extensive occurrences of magnesium salts like kieserite, tachydrite, epsomite, polyhalite, dolomite, and others that should not form from a conventional marine evaporation model. These mineral anomalies are readily explained by a deep-sourced, saline brine model whereby low density sodium-, magnesium-, and potash-rich brines are fractionated from a deep-sourced, higher density brine derived from salt-loaded serpentinite. This serpentinite-sourced brine originally formed from seawater brine hydration of mantle peridotite beneath ocean basins, was then underthrust beneath continents by flat subduction. Subsequently, the underplated serpentinite layer (Moho) was dehydrated by mantle heating during incipient rifting to release copious metalliferous mud volcanism.

Myth 4. The age of emplacement is enigmatic. Depending on what mineral is examined, ages from 265 to 135 Ma have been obtained and there is no consensus for the age of formation. The only consensus is based on stratigraphy where the maximum age of formation is established as late Permian circa 265 Ma, which is the age of the youngest rocks affected by Kupferschiefer-related processes.

Re-examination of paragenetic data for the ore minerals, relative age relationships from the stratigraphy, and the presence of the so-called 'Rücken' veins demonstrates the Kupferschiefer was formed during a number of episodic events. It is a mistake to argue for a single age of Kupferschiefer; there is not one age. Greater than ninety-five percent of what can be grouped into the greater Zechstein sequence formed in late Permian-early Triassic time between about 265 and 235 Ma. Based on reconsideration of the paragenetic ordering, Re-Os dates, the K-Ar illite dates (which reflect hydrothermal and not sediment burial diagenesis), and paleomagnetic dates, the greater Zechstein – Kupferschiefer-Weissliegende metallogenic event in any given area can be separated into three main sequential episodes:

1) A late Permian Weissliegende -Kupferschiefer event featured mainly sand volcanism and associated chalcocite-digenite slurry mud volcanism that ranges from 265 to 256 Ma (based on single mineral Re-Os dates on chalcocite and bornite samples and K-Ar dates on high K, crystalline illite [muscovite]). The Permo-Triassic boundary occurs at the top of this event.

2) An early Triassic, early Zechstein age dolomite-hosted chalcopyrite-bornite-galena transitioning to a sphalerite-galena event transitions to a calcite carbonate-hosted late pyrite event that dates between about 249-240, based on Re-Os single mineral ages on chalcopyrite and pyrite and high K crystalline illite (muscovite) ages.

3) A late oxidative hematite-stable noble metal-(uranium) chlorine-enriched Rote Fäule event transgresses the earlier events and based on K-Ar illite ages. The Rote Fäule event in turn may provide a bridge to the first cycle of the Zechstein salt sequence.

4) The Zechstein salt sequence contains at least 4 major cycles of carbonate-salt deposition that become more potash -rich upward.

The entire Weissliegende to Kupferschiefer to Zechstein saline sequence is genetically related to the same ongoing process, which is related to Permo-Triassic, incipient rifting of the northern European portion of the Pangea supercontinent. The earlier events have a greater bulk density than the later saline events and may represent a long-term, density- and viscosity-driven fractionation of a brine-mud system that had about a 30 million year residence time in the crust. The fractionations may have been driven by structurally driven kinematic events that forced separations of the above four stages. This four stage process may have initiated at slightly different times in any given area of the greater Zechstein basin.

With completion of the Zechstein fourth stage saline deposition, at least 95% of the Zechstein-Kupferschiefer-Weissliegende was in place. However, minor failed rifting events recurred in Triassic-Jurassic and Jura-Cretaceous time. Each of these superimposed events is associated with hydrothermalism, both of which have been referred to as the late Rücken veining event. While it is locally impressive at a mine face scale, on a regional scale the Rücken veins are only of minor importance. However, they have complicated the age picture by introducing age resetting and overprinted age effects. Indeed, to this day the region is still a location for thermal anomalism at Spremberg and in the greater Lubin area.

Myth 5. The extremely high hydrocarbon content was derived from surface biological sources and makes the Kupferschiefer carbonaceous black shales a source rock for subsequent oil generation in the conventional oil model. The kerogen hydrocarbons were partially synthesized during the oxidation event associated with Rote Fäule emplacement.

The coincidence of high temperature mineral phases, such as muscovite and copper selenides, make a persuasive case for kerogen existence and synthesis under hot (350°C) hydrothermal conditions. In addition, hydrothermal synthesis of oil has been achieved on Kupferschiefer kerogenous shale at 350°C. The muscovite locked in its radiogenic argon at 350°C. The oil was ultimately produced by the progressive hydrogenation of an initial polyaromatic (PAH) kerogen at depth during the formation of oxygen rich silicates and carbonates (especially muscovite and dolomite, which released hydrogen from the co-existing chloride brine). Hydrogen fugacity was additionally enhanced by sulfide precipitation released hydrogen from the co-traveling hydrogen sulfide gas in the chloride brines. Water was the principal donor of the hydrogen. Eventually, the kerogen became so hydrogen rich that it expelled oil as the S1 component of Rock-Eval literature familiar to the petroleum community. The entire process occurred under hot hydrothermal conditions: hence the term 'Hydrothermal Oil'.

The abundant hydrocarbon literature for the Kupferschiefer can be entirely resynthesized according to hydrothermal oil logic to the point where the Kupferschiefer can be considered one of the first case histories for documentation of hydrothermal oil. Hydrogenation of the deep-sourced kerogen component was reductive in nature and not oxidative. Chromatograms of kerogen that are similar to oil appear in the zinc horizon, which suggests that oil may have been expelled in late Kupferschiefer time circa 252 Ma. This oil generation may explain the oil and gas deposits in the underlying Rotliegend sands and in the overlying main dolomite horizon of the 2nd Zechstein saline cycle.

Myth 6. The hematitic Rote Fäule process is the source of the high grade copper in the Kupferschiefer, which was upgraded and remobilized into the Kupferschiefer metal anomaly from a black shale of normal composition by oxidative leaching and redistribution during the epigenetic emplacement of the Rote Fäule at low temperatures of less than 120°C. As such, the Rote Fäule is a metallogenic low, is not of exploration interest, and should be avoided during mining.

In the context of a deep-sourced, multi-phased, hydrothermal mud-brine volcanism model, the Rote Fäule is viewed as a late stage, epigenetic, oxidized, highly saline brine plume that was emplaced between about 245 and 235 Ma after the Kupferschiefer was already in place. This emplacement coincided in part with the Zechstein saline succession (the lower Werra anhydrite-salt unit). Re-examination of textural information in the robust literature shows that the hematitic Rote-Fäule consumes clasts of Kupferschiefer and is associated with an epigenetic gold overprint. The gold is also associated with a carbonaceous uranium-PGE event that is probably a fringe of the Rote Fäule, which has been described as a transition zone between the Rote Fäule and the Weissliegende-Kupferschiefer-Zechstein succession. This re-examination then leads to the observation that the Rote Fäule is not a barren event to be avoided, but is a potential noble metal-uranium anomaly that may be economic in its own right.

KUPFERSCHIEFER IN ITS GLOBAL CONTEXT

Whereas the Kupferschiefer copper shale has previously been regarded as a geologic 'one off', the process that made the Weissliegende-Kupferschiefer-Zechstein salt basin is not unique. The Zechstein basin was only one of a number of similar features that appeared at the end of Permian time that signaled the beginning of the breakup of the Pangea supercontinent. Similar processes related to hot spots and failed rifting were happening in the Meishan Basin of northern China, the Permian and Holbrook Basins in the U.S.A, the Barents Sea in northern Norway, and the Tunguska Basin in eastern Siberia. In all of these areas, regional-scale, hydrothermal, metalliferous-saline brines were evulsed into the earth's oceans and atmosphere. The enormous volumes withdrawn from the underlying mud 'magma' chambers might have 'single handedly' produced significant basin subsidence.

The toxicity associated with this worldwide Permo-Triassic hydrothermalism overwhelmed the planet's biospheric system to collectively produce the great Permian extinction event. Mud volcanism and associated saline brines reached a volume that was probably the highest in the Phanerozoic and perhaps the most robust in Earth history. In this context, it is amazing the biosphere even survived. But as the well known aphorism made famous in the movie, 'Jurassic Park' states: 'Life finds a way!'

In its global geologic context, the volume of sedimentation that formed through the agency of ultramafic-sourced mud volcanism was magnificently enormous and probably provided the majority of late Permian-early Triassic sedimentation. The scale of the mud volcanism process at the end of the Permian has appeared consistently through time and is consistently associated with changeover between Wilson cycles (i.e. continental breakups). Indeed, the volume of rock produced by this process could be part of a fourth new class of rock type: 'hydrothermalite'. The importance of hydrothermalism as a first order process on this water planet has been much underestimated by the geologic community and it needs to be installed as a fourth pillar in the rock type pantheon; sedimentary-igneous-metamorphic-hydrothermal. Kupferschiefer is only a hydrothermal mud whisper of a process that goes back to the beginning of geologic time.

For details and references that document the above, see: Stanley B. Keith, Volker Spieth and Jan C. Rasmussen (2018). Zechstein-Kupferschiefer Mineralization Reconsidered as a Product of Ultra-Deep Hydrothermal, Mud-Brine Volcanism: Contributions to Mineralization, Prof. Ali Al-Juboury (Ed.), InTech, DOI: 10.5772/intechopen.72560. Available from: https://www.intechopen.com/books/contributions-to-mineralization/