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Life of the Rheic Ocean: Scrolling through the shale record

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ABSTRACT

The isotopic and geochemical compositions of Neoproterozoic to Palaeozoic shales of the Saxo-Thuringian (Gondwana) margin of the Rheic Ocean systematically change as the geotectonic setting of the deposition area evolved. Distinct variations in the Thuringian shales (Schwarzburg Anticline, Teuschnitz–Ziegenrück–Syncline, and Thuringian Slate Belt) through time closely reflect changes in sediment provenance, weathering history in the sediment source, and depositional conditions. With the rifting of the Gondwana margin and the separation of Avalonia in the early Ordovician, this sediment source disappeared and the West African Craton became the dominant sediment source until the late Palaeozoic Variscan Orogeny. The separation of Avalonia is recorded in the sediments by a shift in the Nd isotopic composition to less radiogenic values (lower εNd(T) values), a marked depletion in Na, Ca, and Sr, and an enrichment in K, Rb, and Tl. This geochemical signature reflects the deeply weathered sedimentary cover of the West African Craton, which became increasingly eroded and was deposited in Tremadocian graben systems and the developing continental shelf at the southern margin of the Rheic Ocean. This weathering signature became less important through time and disappeared in the shelf sediments on Saxo-Thuringia with the Hirnantian glaciation. Variations in the composition of Silurian and most Late Devonian shales are dominated by variable input of mafic volcanic material (higher εNd(T) values and increased contents of Cr, Ti, Ni, Co), euxinic events (higher contents of V, Ni, Cu, Mo, Sb, Pb, U), and repeated changes in relative sea level, with uncoupling of geochemical signatures bound to chemically stable and unstable minerals, respectively. With the initiation of the Variscan Orogeny, the sediment source changed from the West African Craton to the Variscan nappes, which predominantly consist of Palaeozoic shelf sediments that had been derived from the West African Craton. This recycling is characterized by an undisturbed Nd isotopic evolution and the reappearance of early Palaeozoic geochemical fingerprints such as high contents of K, Rb, and Ba and high initial $^{87}Sr/^{86}Sr$, $^{206}Pb/^{204}Pb$, and $^{208}Pb/^{204}Pb$ ratios. Only with the deposition of post-orogenic early Permian claystones in fluvial and lacustrine environments, does a new sediment source (i.e., Permian volcanic rocks) begin to dominate the sediment composition.

1. Introduction

The chemical composition of shale varies within relatively narrow ranges, at least for the high field strength (HFSE) and rare earth (REE) elements (cf. McLennan, 1989; Barth et al., 2000). Since shales represent the mechanical mixture of fine-grained material derived from a large source area, they are widely considered as a representative average of the source area and are widely used: (i) to estimate the average composition of continental crust by averaging regionally and super-regionally sampled shales, (ii) to trace temporal variation in the average composition of continental masses, and (iii) to demonstrate subtle compositional differences on a super-regional scale (e.g., Wedepohl, 1991; Condie, 1993; Ronov and Migdisov, 1996; Gao et al., 1998; Yaroshevsky, 2006; Rollinson, 2008; Ranjan and Banerjee, 2009). Shale composition, however, is more variable for elements that are readily scavenged or released from mineral surfaces depending on the depositional environment (cf. McLennan et al., 1990; Cullers, 2002; Schulz, 2004; Lev and Filer, 2004; Wedepohl and Rentzsch, 2006). Averaging large data sets of several thousand samples on a super-regional scale and over large time windows provides a very representative average value, as illustrated by the small variation among the various shale standards (PAAS, NASC; e.g., Gromet et al., 1984; Taylor and McLennan, 1985). This averaging, however, camouflages small, but systematic differences that would be observed for smaller subsets sampled on a smaller geographic scale and in a narrower time window.

There are small regional and temporal variations in the composition of shale (i.e., among different basins and within the sediment column of an individual basin), which reflect the contrasting or changing character of the source for the detrital material contained in the shale. The most obvious example of such source effects is the compositional contrast between Archaean and Proterozoic shales (e.g., Wronkiewicz and Condie, 1990; Gao and Wedepohl, 1995). Similar variations, although less prominent in magnitude, are also present in Phanerozoic shales (e.g., Cox et al., 1995; Bauluz et al., 2000). These reflect the regional variability

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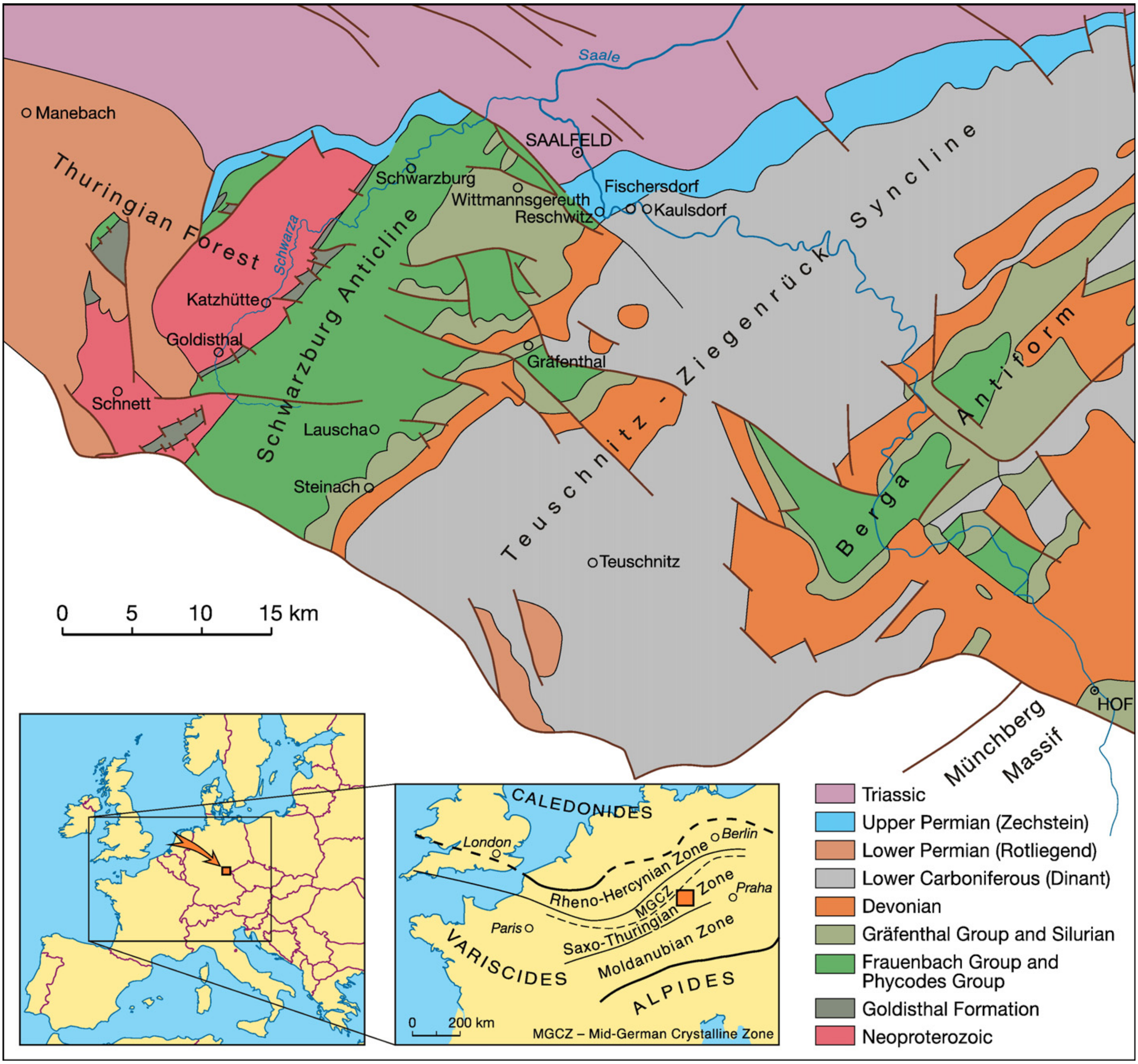

Fig. 1. Simplified geological map of the sampling area in the Schwarzburg Anticline, the Teuschnitz–Ziegenrück Syncline, and the Berga Antiform (Saxo-Thuringian Zone) (modified from Falk et al., 2000). Note that biostratigraphically dated Cambrian sediments (Heinersdorf Group) are not exposed in the Schwarzburg Anticline, but occur in a drill hole in the Berga Antiform (cf. Heuse et al., 2010). Inset map shows the location of the sampling area in relation to the Variscan Orogen. The distribution of the Variscan Zones is according to Kossmat (1927) and Scholtz (1930). The Rheno-Hercynian Zone represents rocks derived from the northern margin of the Rheic Ocean, whereas rocks of the Saxo-Thuringian and Moldanubian zones were derived from the southern margin of the Rheic Ocean. The Saxo-Thuringian Zone basically represents former Gondwana shelf.

of the hinterland with respect to lithology, topography, and climate (e.g., Harnois, 1988; Wilson, 2004), and may occur among different basins or within different segments of the same basin. Sedimentation, erosion, and tectonic instability in the hinterland, as well as eustatic and tectonic sea level changes, may affect the balance among the various sediment sources in the hinterland by making a particular source available or unavailable or by allowing for erosion and redeposition of older deposits. All these processes eventually result in temporal variations in the composition of shales. Processes acting during transport from the source to the deposition area and during deposition and diagenesis may additionally modify the geochemical and isotopic fingerprint of the source (e.g., McLennan, 1989; Cox et al., 1995; Cavalcante et al., 2003; Le Heron et al., 2008; Cai et al., 2008; Schettler et al., 2009).

The Thuringian Slate Belt, in particular the Schwarzburg Anticline, contains the most complete Palaeozoic lithostratigraphic section in Germany (Figs. 1 and 2). The sedimentary record starts before the opening of the Rheic Ocean and ends well after the Variscan Orogeny, i.e., after the Rheic Ocean had closed. The overall evolution of the deposition area is well-known from lithostratigraphy, sediment petrology, the geochemistry of sandstones, arkoses and greywackes, palaeontology, and U–Pb geochronology and Hf-isotope systematics on detrital zircon (e.g., Lützner et al., 1985; Deutsche Stratigraphische Kommission, 1997, 2006, 2008; Linnemann et al., 2000, 2004, 2008, 2010; Linnemann and Romer, 2002; Seidel, 2003; Gehmlich, 2003; Zeh and Brätz, 2004; Kroner et al., 2007; Linnemann, 2007; Zeh and Gerdes, 2010-this issue). This stratigraphic section consequently provides a unique opportunity to trace geochemical variations in shale as a response to changes in the hinterland and the depositional environment. Furthermore, the onset and disappearance of a geochemical signature linked to a particular process provides indirect time constraints for this process and its