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Assessment and application of Hg speciation changes in sedimentary rocks from thermal desorption characteristics

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Sedimentary mercury (Hg) has become a widely used proxy for paleo-volcanic activity. Scavenging and drawdown of Hg by organic-matter (OM) and sulfides are important non-volcanic factors determining variability in sedimentary records. Most studies, therefore, normalize total Hg (Hg_T) to a Hg "host-phase" proxy (e.g., Hg_T/TOC for OM, Hg_T/TS for sulfides), with the dominant host-phase determined based on the strongest observed (linear) correlations. This approach suffers from various non-linearities in Hg-host-phase behavior and does not account for succession-level, let alone sample-level, Hg speciation changes. Thermal desorption characteristics or 'profiles' (TDPs) for many Hg species during pyrolysis analysis are well-established with applications including distinguishing between OM-bound Hg and different Hg sulfides and oxides in (sub-)recent sediments. We explore the use of TDPs for geological sediment (rock) samples and illustrate the presence of multiple release phases (Hg species) – correlated to geochemical host-phase – in (almost) all the 65 analyzed Tithonian (146 – 145 Ma) silt and mudrock samples. By quantifying the Hg in each release phase for every sample, we find TOC concentration may determine ~60% of the variability in the first (lower temperature) Hg TDP release phase: a stark difference with the total Hg released from these samples, where ~20% of variation is explained by TOC variability. TDPs provide insight on sample-level Hg speciation and demonstrate that, while the common assumption of single-phase Hg speciation in sedimentary rocks is problematic, differences in Hg speciation can be detected and quantified with this simple routine.

In addition to the abovementioned application to sedimentary successions, we demonstrate that the use of TDPs may also help understand Hg behavior in contact metamorphic sediments. We generated TDPs for shale samples above a Jurassic sill intrusion in the Ecca Group shales (Karoo Basin, South Africa) previously studied for Hg_T. Our new data show that Hg speciation in these sediments was completely reset above temperatures of ~350ºC though an appreciable amount of Hg remains in strata that have been exposed to such temperatures. The changes in TDPs are used to broadly assess the relative fractions of volatilized and expelled Hg, further constraining Hg emission dynamics around sill intrusions.