The role of metamorphism in vanadium enrichment of organic-rich shales

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Shales and mudstones are common sedimentary rocks forming in marine basins throughout Earth's history. Besides being important record holders of Earth's paleoclimate, they are also a target for mineral deposit exploration since they can hold economic resources of critical minerals such as vanadium (V), which is an essential component of redox-flux batteries. Many Paleozoic shales are, however, metamorphosed and deformed. This commonly obscures primary features including V-bearing host phases and the original composition of organic material.

Here we present geochemical and mineralogical data on the Paleozoic Van prospect, Northwest Territories, Canada, to show that V can be released from organic matter during metamorphism and incorporated in clay phases such as illite. The siliceous argillites at the Van Property host up to 0.69% V_2O_5 and are metamorphosed to (sub-)greenschist facies. Its mineralogy is dominated by quartz with minor graphite, illite, muscovite, pyrite, sphalerite, rutile, and carbonates. Microprobe analyses show that two inorganic phases, illite and rutile, host elevated V concentrations. Based on V content, two illite sub-types are identified: (1) low-V illite that has on average 0.8 wt% V_2O_3, and is of illite endmember composition, deformed (e.g., kinked) and occurs close to quartz and carbonaceous matter, and (2) high-V illite that has on average 10.8 wt% V_2O_3, and is of illite/smectite composition, shows no deformation and occurs adjacent to carbonaceous matter. Rutile has up to 4.4 wt% V_2O_3, shows no deformation or alignment parallel to bedding, occurs with sphalerite and pyrite, and adjacent to carbonaceous matter. However, the inorganic V hosts cannot account for the bulk rock V concentration using simple bass balance calculations. The third V-host is here inferred to be carbonaceous matter in which V was incorporated upon sedimentation and early diagenesis due to metalation and formation of geoporphyrins. During metamorphism, maturated carbonaceous matter degraded resulting in the demetallation of V-bearing geoporphyrins and release of vanadyl ion. Some vanadyl ion was incorporated into high-V illite. Vanadium-enriched rutile also formed during metamorphism. This process of V enrichment highlights the role of carbonaceous matter in scavenging V and importance of metamorphism on subsequent V release and its incorporation into inorganic phases. Furthermore, the geochemistry of siliceous, V-rich argillites at the Van Property is compared to other V-enriched shale and mudstone deposits highlighting the diverse composition of host-rocks in shale-hosted V deposits.