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Metalliferous (Mo-Ni-V-Zn +/-Au-PGE) black shales in Guizhou, Hunan, Hubei, and Jiangxi provinces, South China, with comparison to global occurrences

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Compared to common black shales, many oil- and gas-bearing or organic-rich shale units are highly enriched in a suite of metals that include Ag, Co, Cr, Mo, Ni, Se, U, V, and Zn ± Au and PGE. In some localities, these enrichments approach ore grades. Lower Cambrian shales in the Zunyi and Zhangjiajie regions within the Guizhou, Hunan, and Hubei provinces of South China contain 3-5 cm thick polymetallic sulfide layers that were historically mined, with average Mo grades of 4 wt % and up to 4 wt % Ni, 2 wt % Zn, and high Au, Pt, Pd, and Ir concentrations. Shales in these regions also contain hyper-enrichments in vanadium. More than 800 km to the north-northeast, age-equivalent shales host up to 2% V_2O_5 in prospects in the Xiushui area of Jiangxi province, illustrating the extreme regional extent of the metalliferous intervals.

A geologic and geochemical database of more than 30 globally distributed metalliferous black shale units, compiled recently by the USGS, allows comparison of their geologic and geochemical characteristics, and analyses of their distribution through time and space. In nearly all cases, the metalliferous intervals are a few tens of centimeters to a few meters thick within thicker packages of regionally extensive, continental margin or intra-continental marine shales. Phosphorite, coal, barite, and/or gypsum beds are common within the same stratigraphic package. Deposition of metalliferous shales is restricted almost entirely to the Phanerozoic. Exceptions include the Paleoproterozoic Talvivarra deposit (Co-Cu-Ni-Zn) and time-equivalent units in Finland. The main time periods for deposition of metalliferous shales are Late Neoproterozoic to Early Cambrian, Middle Cambrian to Early Ordovician, Middle or Late Devonian to Early Mississippian, Late Mississippian, Middle to Late Pennsylvanian, Early Permian, Late Jurassic to Early Cretaceous, and Middle Cretaceous. The transition from generally metal-poor Proterozoic black shales to metal-rich Phanerozoic black shales is coincident with widespread oxygenation of the oceans and atmosphere in the Late Neoproterozoic. Previous workers similarly relate the secular distribution of metalliferous shales in the Phanerozoic to cycles of increasing atmospheric oxygen.

Sulfides (bravoite, vaisite, gersdorffite, or jordisite) that host metals in the Chinese black shale deposits are unknown in other occurrences. Pyrite is common in many occurrences and may host As, Ni, Mo, Sb, and Se, although organic matter may be a secondary source. Vanadium is commonly deposited with organic matter and mobilized into clays during diagenesis. The source of metals in metalliferous black shales has been a debate for decades, with most workers proposing derivation mainly from seawater, although syndepositional hydrothermal processes and/or metamorphic remobilization of metals (i.e., Talvivarra deposit) may have attributed to metal enrichments. Trace and rare earth element geochemical signatures and Mo isotopic data for host rocks and polymetallic sulfides in the Chinese deposits suggest that metals were scavenged mostly from seawater. The trigger that produces hyper-enrichment remains enigmatic, but it is unlikely that local conditions (e.g., basin geometry, hydrothermal venting of metals) are

responsible. Some workers have recently suggested a link between trace element hyper-enrichment and hyper-sulfidic conditions.