

A C/MoS₂ mixed-layer phase (MoSC) occurring in metalliferous black shales from southern China, and new data on jordisite

LI-SHUN KAO,^{*,1} DONALD R. PEACOR,¹ RAYMOND M. COVENEY JR.,² GENGMEI ZHAO,¹ KEENAN E. DUNGEY,³ M. DAVID CURTIS,³ AND JAMES E. PENNER-HAHN³

¹Department of Geological Sciences, University of Michigan, Ann Arbor, Michigan 48109-1063, U.S.A.

²Department of Geosciences, University of Missouri, Kansas City, Missouri 64110-2499, U.S.A.

³Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109-1055, U.S.A.

ABSTRACT

A new phase composed mainly of Mo, S, and C and referred to herein as MoSC occurs widely in organic-rich, metalliferous Cambrian black shales in south China. MoSC, which has previously been referred to as jordisite, has been studied by scanning electron microscopy (SEM), electron microprobe analysis (EMPA), transmission electron microscopy (TEM), powder X-ray diffraction, (XRD), extended X-ray absorption fine structure (EXAFS), and catalytic activity. TEM data show MoSC to have a layered structure, with packets resembling molybdenite and graphite-like carbon that average five layers in thickness. Analytical data are consistent with an idealized formula of Mo₃S₆C₁₀ but it commonly contains 1–3 wt% each of Fe, Ni, and As so that its composition may be better approximated by the formula (Mo,Fe,Ni)₃(S,As)₆C₁₀. Selected area electron diffraction (SAED) patterns show a small number of broad, inhomogeneous rings corresponding to randomly oriented layers arranged in subspherical cells. A single broad, weak peak corresponds to a 10–11 Å layer spacing in powder XRD diffraction patterns. Pseudomorphism after fossil bacteria implies an origin by replacement of sedimentary organic material. In its chemical properties and structure, MoSC resembles synthetic compounds used as catalysts for hydrodesulfurization (HDS) in the petrochemical industry. The large surface-to-volume ratio for MoSC may be an important factor in its relatively strong HDS catalytic activity.

Cotype samples of jordisite from Germany, previously thought to be amorphous MoS₂, were also studied by SEM and TEM. Jordisite occurs as sequences of a few curved layers that form subspherical units, with an appearance remarkably like that of MoSC. However, the layer spacing is ~6 Å, like that of molybdenite. The ratio of Mo:S is ~1:2, and no carbon was detected, although it coexists with kerogen. Jordisite is thus confirmed to be a form of MoS₂, but because powder diffraction-like SAED patterns were obtained, it is not amorphous.