

Geochemical anomaly pattern in the Haojiahe sandstone-type copper deposit, Yunnan, China

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Haojiahe deposit controlled by the Upper Cretaceous (K_2mx_2) is the typical one of sandstone-type copper deposits in the Chuxiong Basin. Ore-bodies (average grade: Cu 1.5%) are located in the interface between purple bed and grey bed. From purple bed to grey bed, the ore mineral zonality is hematite, chalcocite, bornite, chalcopyrite and pyrite.

Ore-forming elements association is Cu, Ag, As, Hg. The average contents of copper ores $\Sigma REE=119.19 \times 10^{-6}$, LREE/HREE=8.93, $\delta Eu=0.74$, $\delta Ce=0.95$. Chondrite-normalized REE distribution patterns show oblique to the HREE side with the poor Eu and enrichment in LREE. From oxidized zone to transitional zone (purple bed \rightarrow copper ore \rightarrow grey bed), ΣREE and δCe decrease gradually with the increase of δEu . The geochemical characteristics well indicate the change of oxidation and reducing environment [1, 2]. These are probably related to the water-rock interaction or infiltration metasomatism.

The vertical zonation of indicator elements in K_2mx_2 from the top to the bottom is Zn, Cs \rightarrow Pb, Tl, Mo \rightarrow Cu, Ag, As \rightarrow Sb, Hg, Co and the transversal zonation from grey belt to purple belt is Mo, Pb \rightarrow Cu, Hg, Ag \rightarrow Cu, Ag, As, Sb, Hg.

Geochemical anomaly pattern has been established, that is, the anomaly of Zn, Pb, Mo appears above the orebodies (average distance: Zn 30m, Mo 10m), and the anomaly of Sb, Hg, Co under the orebodies. The anomaly of Cu, Ag and the ratio of $Cu/Ag > 170$, $Cu/(Pb+Zn) > 10$, $Cu/(As+Sb+Hg) > 180$ are concomitant with rich orebodies; the anomaly of Pb, Zn, Co, (Ni) and $Cu/Ag < 128$, $Cu/(Pb+Zn) < 9$, $Cu/(As+Sb+Hg) < 8$ implies barren. The contents of Cu, Ag, As, Hg and the ratio of dual elements increase longitudinally, and it shows that the copper mineralization is enhanced gradually. This pattern provides an important basis for the depth ore-forming prognosis.

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Origins and sources of CO₂ in natural gas in Eastern Sichuan Basin, China

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The eastern Sichuan Basin in China is well-known for the development of H₂S-bearing gas fields such as Puguang, and the natural gas generally contains CO₂. High-content CO₂ was thought to accompany high-content H₂S, and this might be one of the proofs of TSR (Thermochemical Sulfate Reduction) [1]. The CO₂ contents of natural gas from eastern Sichuan Basin vary from 0% to 32.04%, and gas samples with low-content (<2%) and 6%-10% CO₂ account for 61.6% and 20.0% of the total respectively.

The $\delta^{13}C_{CO_2}$ values vary from -23.4‰ to 3.3‰, and 34.4% of the samples have low $\delta^{13}C_{CO_2}$ values (<-12‰) which are in accordance with those of typical organic CO₂ [2], and they are mainly with low contents of CO₂ (<3%). The corresponding H₂S contents are very low or zero. This type of CO₂ was derived from the oxidation of organic matters. However, the other type of CO₂ displays large $\delta^{13}C$ values (>-8.3‰) and shares similar carbon isotopic characteristics with inorganic CO₂ [2] and reservoir carbonates [1], and differs dramatically from that of TSR origin [3]. In this case, no obvious relation exists between the CO₂ and H₂S contents, so it does between the CO₂ and TSR as study by Huang *et al.* [4]. Under the precipitation in the deep-burial period, CO₂ generated during the TSR was mainly transformed into secondary calcite, which demonstrated low $\delta^{13}C$ values (-18.2‰~-10.3‰) [1].

Inorganic CO₂ can be divided into mantle-derived origin and decomposition or dissolution of carbonates [2]. The helium in the natural gas was crustal derived due to the low R/Ra ratios (<0.036) without significant contribution from the mantle. The temperature required for decomposition of carbonates was too high to reach for the deep-buried carbonate reservoirs. In consideration of substantial uplift in late Jurassic, CO₂ with large $\delta^{13}C$ values was mainly derived from the dissolution of reservoir carbonates under the effect of acidic fluid.

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