

## 铼元素赋存状态综述

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**摘要:** 铼是地壳中最稀有的元素之一, 铼主要产自斑岩铜矿(80%)和沉积岩中的层状铜矿(包括砂岩铜矿和铜页岩型铜矿), 少量来自砂岩铀矿。然而, 我国的铼资源回收主要集中在斑岩铜矿和砂岩铀矿中。目前铀矿床中铼的研究缺乏系统、全面的资料, 导致砂岩铀矿矿床中铼的赋存状态和分布规律无法查明。本文探讨了铼元素在各类型矿床中的赋存状态, 并总结了前人针对砂岩铀矿中铀、铼元素赋存状态的研究成果, 为未来查明砂岩型铀矿中铼元素赋存状态奠定了研究基础。

**关键词:** 砂岩铀矿; 铼元素; 赋存状态

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分散金属为我国,乃至世界急需、紧缺矿种<sup>[1-2]</sup>, 全球各国当前都在积极研究分散元素成矿机制, 同时也在努力寻找矿产资源<sup>[3-5]</sup>。因地壳中分散元素丰度极低, 且高度分散于岩石中, 使得地学工作者一直以来都认为分散元素在自然界中是以分散状态存在, 成矿难度非常大, 要成为独立矿床更是难上加难<sup>[6-7]</sup>。涂光炽在“九五”期间提出“分散元素是能够富集的, 且可独立成矿, 意味着我国在分散元素成矿方面的研究已获取极大进展<sup>[8]</sup>”。

在地壳当中, 铼元素也是极为稀有的, 地壳平均丰度不足十亿分之一, 约0.2 ppb<sup>[9]</sup>。世界上80%以上的铼被用于高温合金—特别是用于制造喷气式飞机发动机涡轮叶片的高温合金, 而铼的另一个主要用途是铂铼炼油催化剂。

### 1 铼的赋存状态

铼在自然界很少作为自然元素或硫化物产出,

仅在乌克兰的超镁铁质岩石中发现了微量的自然铼(ReO)<sup>[10]</sup>, 辉铼矿发现于日本乌苏山的火山喷气孔<sup>[11]</sup>、俄罗斯Kudryavyy的火山喷气孔<sup>[12]</sup>和希腊北部Pagoni-Rachi斑岩铜钼矿床<sup>[13]</sup>。此外, 在芬兰尼瓦拉的Hitura镍-铜-铂矿的硫化物精矿中发现了富铼钼铁矿((Cu, Fe)(Re, Mo)<sub>4</sub>S<sub>8</sub>)的显微晶体(≤ μm)<sup>[14]</sup>。

铼对硫化物相有亲和力, 但在大多数硫化物矿物中的浓度相对较低。Re<sup>4+</sup>的离子半径非常接近Mo<sup>4+</sup>的离子半径, 这使得在辉钼矿和其他钼矿物(如CuMo<sub>2</sub>S<sub>5</sub>)中, 铼可以有限地取代钼。此外, 铼的地球化学性质与钼相似, 通常伴随着岩浆和相关热液过程, 集中在与各种花岗岩相关的矿床, 特别是斑岩矿床相关的辉钼矿中铼的含量最多。

#### 1.1 斑岩矿床中铼的赋存状态

铼资源主要包含在斑岩铜钼金矿床中, 该矿约占采矿生产铼的80%<sup>[15]</sup>。斑岩铜矿床中的铼主

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要以  $\text{ReS}_2$  的形式存在于辉钼矿的固溶体中<sup>[16]</sup>。

辉钼矿中铼的含量变化很大,从小于  $1 \times 10^{-6}$  到几个重量百分比不等,但斑岩铜矿床中的辉钼矿通常含有约  $(100 \sim 3000) \times 10^{-6}$ <sup>[16-21]</sup>。相比之下,斑岩型钼矿床中辉钼矿的铼含量通常要低得多,在许多情况下低于  $20 \times 10^{-6}$ 。其他类型斑岩矿床和石英脉中辉钼矿的铼含量通常也较低 ( $<10$  至约  $200 \times 10^{-6}$ )<sup>[22-26]</sup>。

### 1.2 梅林矿——脉状沉积矿床中铼的赋存状态

澳大利亚昆士兰西北部伊萨内利尔山的梅林钼矿床是一个特殊的脉型矿床,该矿床是高品质铼资源,其铼和钼是主要矿产,只有少量铜存在<sup>[27-28]</sup>。梅林钼矿化与硅钠长石蚀变和间隙粘土有关,后者沿裂缝和剪切带形成,并取代结构控制角砾岩的基质,初步认为铼赋存在钼矿中。2012年,探明和推断的矿产资源量为690万t,钼品位为1.38%,铼品位  $22.7 \times 10^{-6}$ <sup>[28]</sup>。

### 1.3 沉积岩中的层状铜矿中铼的赋存状态

沉积岩中的层控铜矿是铼的另一个主要来源。在哈萨克斯坦的砂岩型铜矿床 (Dzhezkazgan 和 Zhaman Aybat 矿床) 和波兰的还原型铜银矿床 (Kupferschiefer) 中,铼是在铜矿石生产过程中被回收的。

沉积岩型层控铜矿化由硅质碎屑岩或白云质沉积岩中层状浸染层中的细粒铜和铜铁硫化物矿物组成<sup>[29-31]</sup>。然而哈萨克斯坦矿床砂岩型 (红层) 铜矿床中铼的产状和赋存状态尚不确定。Zhezkazgan 矿床两个样品中铜矿矿物的分析表明,黄铜矿和斑铜矿中的铼含量范围为  $(3.3 \sim 10.1) \times 10^{-6}$ <sup>[32]</sup>,这是非钼矿样品中铼的极高浓度<sup>[33-34]</sup>。

研究表明 Dzhezkazgan 矿床中,尽管铜和铼之间的质量平衡关系使得大部分铼存在于铼的新矿物 Dzhezkazganite 中<sup>[35]</sup>,但铜-铁硫化物矿物中仍可能赋存了大量铼。

波兰的还原型铜银矿床 (Kupferschiefer) 中

铼与富铜页岩矿石中的钼有关<sup>[36-37]</sup>,铜、铅和钾钙矾土 (铜钼矿) 的钼铼比为 70:1<sup>[38]</sup>, Jankowski (1995) 指出 Mansfeld-Sangerhausen 矿的矿石的钼铼比为 7:1。与哈萨克斯坦层控铜矿床一样,这些钼铼比表明铼相对于钼富集显著。Kupferschiefer 矿石中的铼可能来自黑色页岩,并在局部被重新活化到富铜区<sup>[40]</sup>。

尽管前人做了大量的相关研究,然而沉积型铜矿中铼的赋存状态仍未查明,也无法为砂岩铀矿中铼的赋存状态研究提供有效的对比。

## 2 砂岩铀矿中铼的赋存状态

1969 ~ 1974年,美国德克萨斯州的砂岩铀矿中发现了少量的铼<sup>[41]</sup>,目前铼一般作为前卷型砂岩铀矿的副产品被回收——例如乌兹别克斯坦和哈萨克斯坦在砂岩型铀矿中回收铼<sup>[42-44]</sup>。

砂岩型铀矿层间氧化型矿床主要是在大型自流水盆地形成的,正常情况下盆地构造面积为几万平方公里,有巨大的铀矿床规模,大型或者超大型矿床都可形成。层间氧化带种类共有三种,一是氧化带、二是还原带、三是氧化-还原过渡带。砂岩铀矿体主要形态是卷状与似卷状,其产于氧化-还原过渡带;含矿主岩的类型包含含砾粗砂岩 (灰色、暗灰色) 以及中-粗砂岩;铀元素 (少量铀石和沥青铀矿) 的存在形式通常都为显微粒状、超显微粒状和吸附形式,和炭屑、乳滴状,星点状黄铁矿等往往可以共生<sup>[45-46]</sup>。

砂岩型铀矿层间氧化带和对应的砂岩型铀矿是通过不断供给的含氧地表水,使层间承压水形成于适宜的砂体中,接着在砂岩中承压水进行渗透、径流以及迁移,促使承压水和岩石不断的形成物理化学反应,循环进行平衡、破坏以及恢复平衡、再次破坏的过程,这是其的发育历程<sup>[46-49]</sup>。Re、Se、U 等元素的表生地球化学性质极为相似,在氧化条件下活动性都相对较强,极易形成易溶化合

物, 进而和含氧地表水相溶<sup>[50-52]</sup>。包含这些成矿元素的层间水遇见砂岩当中的还原剂时, 就会还原 Re、Se、U 等元素, Re、Se、U 将会由高价态变成低价态, 失去活动性, 同时也会富集于氧化还原过渡带。其间由于元素化学性质差异, 造成元素离子获取电子的能力以及元素还原的电子供体不同, 如 Se 还原仅需弱还原环境, Fe<sup>2+</sup> 即可成为其电子供体<sup>[50-52]</sup>; Re 还原的条件以及所需的还原剂都相对较强, 且和有机质间的关系非常密切<sup>[51,53-54]</sup>。

### 2.1 砂岩铀矿氧化带、过渡带以及还原带中的矿物组合以及蚀变作用

对于砂岩铀矿的矿物组合、蚀变作用等方面, 已有诸多学者开展了细致的研究工作, 也取得了极为不错的成绩<sup>[55-66]</sup>。

(1) 氧化带: 矿物组合为水针铁矿、褐铁矿、赤铁矿、高岭石、伊利石、蒙脱石、绿泥石等。菱铁矿与黄铁矿会被富氧地下水氧化, 进而反应为水针铁矿 (FeOOHnH<sub>2</sub>O), 且有 H<sup>+</sup> 被释放而出, 脱水之后的水针铁矿将成为针铁矿和赤铁矿<sup>[67]</sup>。在富 H<sup>+</sup> 环境之下, 钾长石、斜长石会出现高岭石化的现象, 进而成为高岭石, 且 K<sup>+</sup>、Ca<sup>2+</sup>、Na<sup>+</sup> 也会在此过程中析出<sup>[67]</sup>。

(2) 过渡带: 矿物组合包含了绿泥石、黄铁矿、伊利石、高岭石、玉髓等。还原带中渗入地下水之后, 会完全消耗水中游离氧, 而富含有机质、植物碎屑的还原带促使其的还原性大大增强。经相关研究得出, 在溶液当中, 黄铁矿的沉淀速度要比铀石、沥青铀矿更快<sup>[68]</sup>。溶液中的 Fe<sup>3+</sup> 在该过程当中被还原为黄铁矿及白铁矿, 且呈现草莓状<sup>[69-70]</sup>。

(3) 原生带: 矿物组合包含了高岭石、方解石、绿泥石、黄铁矿等。原生带中流过的地下水, 通常都包含 K<sup>+</sup>、Na<sup>+</sup>、Fe<sup>2+</sup>、Ca<sup>+</sup>、Mg<sup>+</sup> 等, 几乎是不携带游离氧的。由于原生带中包含了诸多还原物质, 所以溶液性质为酸性。在酸性条件下, 钾

长石也可形成高岭石。Fe<sup>2+</sup> 和 H<sub>2</sub>S 能够形成黄铁矿, 且能够和 Mg<sup>2+</sup> 在高岭石当中变成绿泥石。在重结晶作用之下, Ca<sup>2+</sup> 能够成为亮晶方解石。而黄铁矿、黑云母等在此环境之下无蚀变现象出现<sup>[72]</sup>。

### 2.2 我国砂岩铀矿研究现状

统计了全球砂岩型铀矿, 尤其是中亚地区近 20 个砂岩型铀矿床, 约一半的矿床不同程度地存在富集铼, 其中大部分矿床当中铀与铼几乎都是重叠富集位置, 两者关系为同消长<sup>[72]</sup>。目前, 虽然针对砂岩型铀矿的研究都将重点集中在铀矿物的赋存状态和分布规律, 而铼的赋存状态仍然未知, 但是由于铀和铼的富集位置大体重叠, 可以将砂岩铀矿中铀矿物的赋存状态研究成果作为铼元素赋存状态的参考性资料。

砂岩型铀矿床在我国主要位于伊犁、吐哈、鄂尔多斯、松辽等盆地, 集中在北方的含油气盆地<sup>[73-74]</sup>。

鄂尔多斯盆地中, 铀矿物的存在形式主要为铀石微粒 (UO<sub>2</sub>), 存在具体是以 -1 m 的微粒吸附形式。正常情况下, 铀石微粒是在钾长石、解理缝、微斜长石中富集, 分析数据显示氧化铀的含量可达 1% ~ 3.46%, 在石英和方解石颗粒裂隙或解理缝中比较低<sup>[75]</sup>。

新疆伊犁盆地砂岩型铀矿, 各赋存形态铀含量由高到低依次为: 碳酸盐结合态、铁锰氧化物结合态、可交换离子态、残渣态、硫化物和有机物结合态, 这些铀矿的形态铀含量具体分别为 44.58%、28.46%、12.51%、7.90%、6.52%<sup>[76]</sup>。并且铀矿床层间氧化带中的粘土矿物与铀成矿有相关关系—粘土矿物的存在导致在近地表含氧含铀水在经过砂岩孔隙时被具有较强吸附能力和巨大表面自由能的粘土矿物所吸附, 形成了铀含量较高的片状, 团块状的粘土矿物, 其在铀成矿作用中起到了吸附和界面的作用, 有利于赋矿空间的形成及定位<sup>[77]</sup>。

吐哈盆地西南部层间氧化带型砂岩铀矿，高品位砂岩铀矿石整体来说含有较多的 Se、Re、Mo，三个元素有显著的富集现象，Re 元素量已符合综合利用指标。Mo、Re 富集的位置主要是前锋线位置。成矿元素是以 Se、U、Re、Mo 的顺序成矿的，而四个元素的含砂岩性分别是浅黄色、灰色、浅灰色、灰色及深灰色的砂岩。在还原环境之下，Se、Mo 与 U 的地球化学性质是非常相似的，但在氧化环境之下，三者的地球化学行为是具有一定差异性的；在氧化还原时，Re 与 U 的地球化学特征极为相似，在强氧化、还原的环境下状态分别为易淋失、易沉淀<sup>[78]</sup>。

钱家店砂岩型铀矿是辽河油田在我国东北松辽盆地发现的大型铀矿床。松辽盆地是在晚中生代形成的。盆地为东泛西超、南隆北沉的构造演化状态，盆地砂岩型铀矿床主要位于钱家店凹陷的北段<sup>[79]</sup>。钱家店成矿凹陷长宽大约为 100 km，9 ~ 12 km，可依据其的沉降特征更为深入的划分为 4 个凹陷，分别是衙门子、宝龙山、喜伯子、胡力海，铀矿则是在胡力海中形成的。

钱家店矿床矿体的形态为透镜状、似层状，矿床矿物主要有三种组合：草莓状黄铁矿、胶黄铁矿沥青铀矿、方解石石英沥青铀矿；矿床蚀变类型主要有两种，分别是高岭石、蒙脱石化、伊利石，黄铁矿化、硅化、碳酸盐化、赤铁矿化<sup>[80]</sup>；U<sup>6+</sup> 和 U<sup>4+</sup> 在矿石中的比值是 0.30 ~ 2.07 之间，表明是在偏还原性环境之下成矿的，通过电子探针分析结合野外岩心观察明确本区是具有固体和油气两种还原作用的<sup>[81]</sup>。U 元素和 Pb、S、Re、Mo、Ni、Zn、Co、Ba 等元素为正相关关系，且相关系数都高于 0.241，其中 U 与 Pb、Re、Mo 相关性密切<sup>[81]</sup>。

### 3 结 语

全球范围内，铼主要产自斑岩铜矿（80%）和

沉积岩中的层状铜矿（包括砂岩铜矿和铜页岩型铜矿），少量来自砂岩铀矿。然而，我国的铼资源回收主要集中在斑岩铜矿和砂岩铀矿中。砂岩型铀矿床中铼的超常富集现象，是一种极具找矿潜力的分散元素成矿新类型——其是分散元素在低温环境下受层间氧化作用而出现超常富集现象的成矿种类，而探讨和查明砂岩铀矿层间氧化带中铼元素的赋存状态和分布规律，将是相关领域地学工作者下一步的工作重心。

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## Study on Process Mineralogy of a Rare Earth-bearing Phosphate Ore in Zhijin, Guizhou

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**Abstract:** By means of MLA, EDS, SEM and ICP-MS, the technological mineralogy of a rare earth-bearing phosphate ore in Zhijin, Guizhou province was studied. The ore properties, distribution characteristics of main minerals and occurrence characteristics of rare earth elements have been investigated. The results show that the raw ore belongs to low and middle grade calcium siliceous colophonite, and the grade of  $P_2O_5$  is 20.18%. Apatite is the main useful mineral with a content of 40.86%. It is often closely associated with dolomite, quartz, pyrite and other gangue minerals. La, Ce, Nd and Y are the main rare earth elements, of which Y is mainly detected in apatite, La, Ce and Nd are mainly detected in dolomite, and no independent rare earth minerals are found.

**Keywords:** Phosphate rock; Rare earth element; Process mineralogy; MLA

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## Overview of the Occurrence State of the Rhenium Element

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**Abstract:** Rhenium is one of the rarest elements in the crust of the earth. Rhenium mainly comes from porphyry copper ore (80%) and layered copper ore in sedimentary rocks (including sandstone copper ore and copper shale type copper ore), and a little from sandstone uranium ore. However, the recovery of rhenium resources in China is mainly concentrated in porphyry copper ore and sandstone uranium ore. At present, there is a lack of systematic and comprehensive materials on the study of rhenium in uranium deposits, which leads that the occurrence and distribution of rhenium in uranium sandstone deposits cannot be ascertained. In this paper, the occurrence state of rhenium in various types of uranium deposits is discussed, and the previous research results about the occurrence state of uranium and rhenium in sandstone uranium deposits are summarized, which lays the research foundation for the future identification of the occurrence state of rhenium in sandstone-type uranium deposits.

**Keywords:** Sandstone uranium ore; Rhenium elements; Occurrence state