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纳米矿物与纳米矿物资源

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摘要: 为促进对纳米矿物及纳米矿物资源的认识、深入研究及开发应用, 阐述了矿物纳米颗粒、纳米矿物狭义和广义概念、纳米矿物形貌分类和主要类型, 并从晶体结构和晶体化学理论讨论纳米矿物形成和稳定的本质, 即纳米矿物和矿物纳米颗粒形成分别受内因和外因控制。阐明了纳米矿物学研究内容及其在关键带研究的重要性, 提出了纳米矿物资源的概念、属性及其开发利用的方向。

关键词: 纳米矿物; 矿物纳米颗粒; 纳米矿物资源; 纳米效应; 纳米矿物材料; 纳米矿物学。

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Nano-Minerals and Nano-Mineral Resources

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Abstract: To promote the understanding, further research, and exploration and application of nano-minerals and nano-mineral resources, the narrow and broad conception of mineral nano-particle and nano-mineral as well as the types of nano-minerals and their morphological types are elaborated in this paper. Then, the nature of the formation and stability of nano-minerals in terms of crystal structure and crystal chemistry are discussed. It is found that formation of nano-minerals and mineral nano-particles are controlled by intrinsic factors and extrinsic factors. In addition, this paper presents the research field of nano-mineralogy and its importance in the research of critical zone. Finally, it proposes the conception and properties of nano-mineral resources and its potential applications.

Key words: nano-mineral; mineral nano-particle; nano-mineral resources; nanometer effect; nano-mineral material; nano-mineralogy.

1 纳米矿物及其形成机制

狭义的纳米矿物是指某种矿物的晶体大小在一维、或者二维、或者三维尺度上总是小于 100 nm (Hochella *et al.*, 2008), 与之维度对应的是棒状(纤维状)纳米矿物、片状纳米矿物、粒状纳米矿物。纳米矿物呈现什么样的形貌特征, 与普通矿物一样受到晶体结构和晶体化学特性制约。矿物总是沿着

化学键力强的方向优先生长。

一维纳米矿物呈现棒状、针状、纤维状, 主要包括粘土矿物和氢氧化物(图 1), 根据结构和晶体化学特性可以划分为若干类。第 1 类是具有链层状结构富镁的硅酸盐矿物, 其晶体结构中为了满足硅氧四面体片与镁氧八面体片尺度匹配, 结构中硅氧四面体自由氧的朝向周期性反转, 2 个典型的矿物是坡缕石、海泡石, 晶体形态总是呈现为直径 20~60 nm 的棒状, 而

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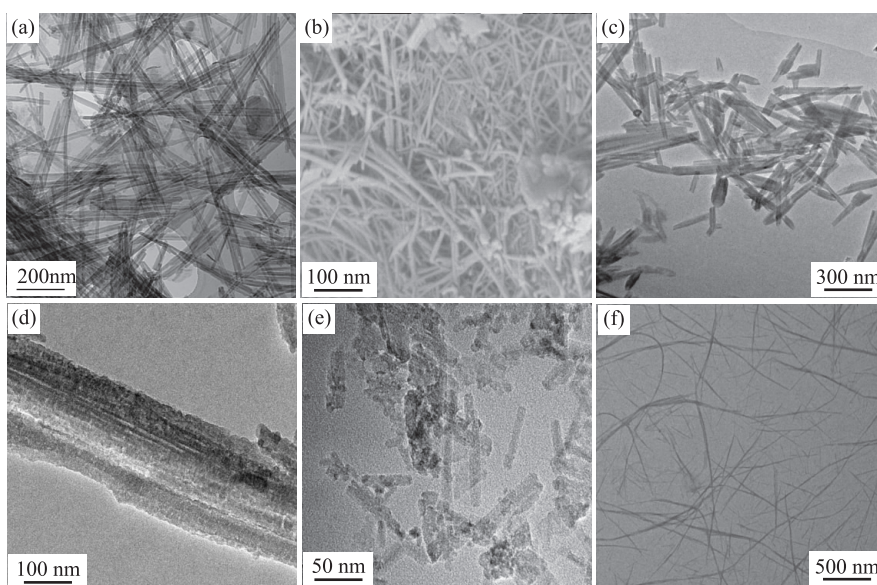


图 1 主要一维纳米矿物电镜图像

Fig.1 Electron microscope images of main one-dimension nano-minerals

a.凹凸棒石;b.锰氧化物;c.埃洛石;d.纤蛇纹石:e.针铁矿:f.伊毛缟石

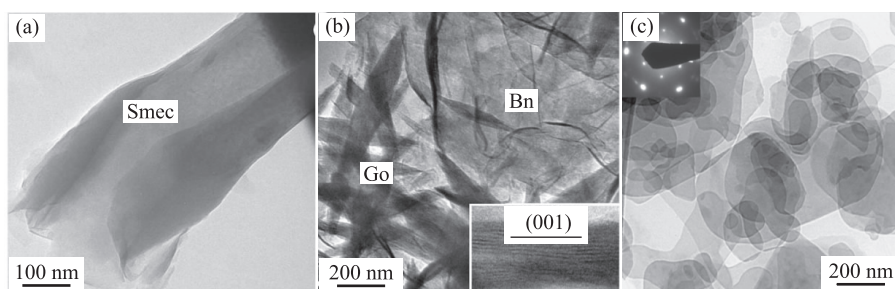


图 2 二维纳米矿物透射电镜图像

Fig.2 TEM images of two-dimension nano-minerals

Smec.蒙脱石;Bn.水钠锰矿;Go.层状双氢氧化物

且这 2 种矿物都具有直径几个埃、蜂窝状排布的一维微孔孔道(叶瑛等, 2002; 陈天虎等, 2004a; Guggenheim and Krekeler, 2011).第 2 类是若干种层状结构的硅酸盐矿物, 同样为了满足硅氧四面体片与镁、铝氧八面体片尺度的匹配片层发生卷曲(Lafay *et al.*, 2016; Thill *et al.*, 2017), 如伊毛缟石($\text{Al}_2\text{SiO}_5(\text{OH})_4$, imogolite)、埃洛石、纤蛇纹石总是呈现不同直径的中空管形态.第 3 类是若干种锰氧化物矿物, 如锰钾矿(cryptomelane)、锰钡矿(hollandite)、钙锰矿(todorokite), 锰氧八面体公棱连接成为截面具有 1×1 、 1×2 、 2×2 、 2×3 、 3×3 的一维孔道(Post, 1999), 总是呈现纳米直径的棒状晶体形态.由于其中存在二价、三价锰替代四价锰, 带有结构负电荷, 各种阳离子存在于晶体表面或者孔道内, 不仅导致孔道结构的锰氧化物具有很复杂

的成分, 而且表现出很强的阳离子交换特性和孔径制约的分子筛分作用.为了与硅氧四面体骨架的硅酸盐矿物、沸石矿物分子筛相区别, 特别地称之为八面体分子筛矿物.第 4 类是铁的氢氧化物, 针铁矿主要呈现针状、棒状形态, 晶体直径为 $10 \sim 100$ nm, 长径比受到其形成时微环境影响(Liu *et al.*, 2012a).

片状纳米矿物中最典型的是层状结构粘土矿物、氢氧化物、层状双氢氧化物(图 2), 如蒙脱石、水钠锰矿等都呈现纳米厚度片状形态(Xu *et al.*, 2010), 而且由于结构中类质同象替代(蒙脱石中主要铝替代硅, 水钠锰矿中主要是二价、三价锰替代四价锰)产生结构负电荷, 表现出阳离子交换特性.层状双氢氧化物具有类似水镁石的结构, 铝离子替代其中的镁离子而在层间出现平衡结构电荷的阴离子, 因而又称阴离子粘土, 在自然界很少聚集成矿,

通常呈现纳米厚度的片状颗粒作为次要矿物存在于风化壳和土壤中(Chen *et al.*, 2006),由于识别和发现困难较少受到关注,但层状双氢氧化物是在实验室条件下非常容易合成的纳米矿物。

粒状纳米矿物中比较常见的是水铝英石(allophane)、施氏矿和水铁矿(Cornell and Schwertmann, 1997; Nishikiori *et al.*, 2017; Paikaray *et al.*, 2017)。水铝英石是硅酸盐矿物,火山灰地表风化早期的产物,也是土壤中最常见的粘土矿物之一。施氏矿是一种发现于矿山废石中的矿物,通常出现在矿山酸性排水环境中,在 pH=3~4 酸性富硫酸盐环境中稳定。水铁矿是地表氧化环境中普遍存在的高活性铁氢氧化物矿物。粒状纳米矿物在高分辨扫描电镜下常常表现为几个纳米不规则粒状,在扫描电镜下常常呈现球型集合体形态。

纳米矿物的共同特点是都形成于地表沉积或者风化环境,只在表生环境下稳定。纳米矿物之所以至少有某一维方向维持在纳米尺度,主要受到其晶体结构和晶体化学制约,属于内因控制。若从晶体能量角度考虑,由于晶体结构的原因,纳米矿物的体系内能随晶体直径变大不是降低而是增大,其体系能量变化不符合经典矿物生长理论。

结晶学经典理论认为,结晶体系总能量变化: $\Delta G = -\Delta G_1 + \Delta G_2$ 。其中: $-\Delta G_1 = f(r^3)$ 为内能与晶核粒径的函数关系; $\Delta G_2 = f(r^2)$ 为表面能与晶核粒径的函数关系。一般情况下, $-\Delta G_1 = f(r^3)$ 随晶核粒径增大晶体的内能降低, $\Delta G_2 = f(r^2)$ 随晶核粒径增大晶体的表面能升高(图3)。结晶体系能量在晶核初始阶段是升高的,但是粒径超过某一尺度时体系能量开始降低,对应的粒径称为晶体成核的临界半径(r_c)。如果某种矿物晶体成核的临界半径在纳米尺度,特别是若晶体成核半径与内能的关系不符合上述函数($-\Delta G_1 = f(r^3)$),体系总的能量不是随着晶体的生长降低而是升高,晶体就难以长大,稳定在纳米尺度。

例如在蛇纹石族矿物中,八面体片为 $Mg-(O,OH)_6$,它的 $b_0 = 0.936$ nm;对应于六角硅氧网孔, $Si-O = 0.1618$ nm,导致层状硅酸盐晶格参数 $b_0 = 0.915$ nm。由于 $Mg-(O,OH)_6$ 八面体片尺寸大于 $Si-O_4$ 四面体片,为了达到二者尺寸匹配,就出现了纤蛇纹石结构单元层卷曲和叶蛇纹石中一定周期后 $Si-O_4$ 四面体片自由氧原子面反向(图4)。纤蛇纹石结构单元层卷曲的曲率半径在纳米范围内四面体片和八面体片是匹配的,超过一定值后就不

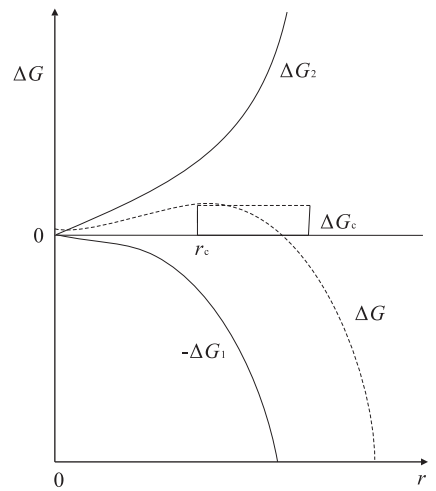


图3 晶体生长体系能量变化

Fig.3 The variation of system energy in the process of crystal growth

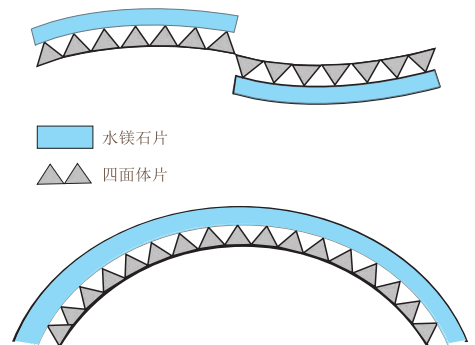


图4 蛇纹石族矿物硅氧四面体匹配方式

Fig.4 The matching mode of Si-O tetrahedron in serpentine group minerals

能匹配,必然导致体系能量升高,所以纤蛇纹石晶体的直径始终维持在纳米尺度。同样,埃洛石结构中 $Al-(O,OH)_6$ 八面体片和 $Si-O_4$ 四面体片大小不匹配,为了相互适应,自发地卷曲成为纳米管状。埃洛石结构单元层间存在水分子,减弱了结构单元层间的作用力,使埃洛石结构单元层卷曲成为可能。

2 矿物纳米颗粒及其形成机制

矿物纳米颗粒是指一些情况下形成大颗粒的矿物,在某些条件下呈现纳米粒级状态。绝大多数矿物都具有呈现纳米粒级的可能(Hochella *et al.*, 2008)。特别是在表生环境下受到矿物界面作用、有机质诱导(图5a)(陈天虎等,2012)、生物大分子调控(图5b)(陈天虎等,2005)、溶解度和生长速度、传质速度的制约(图5c)(陈天虎等,2004a),较多的

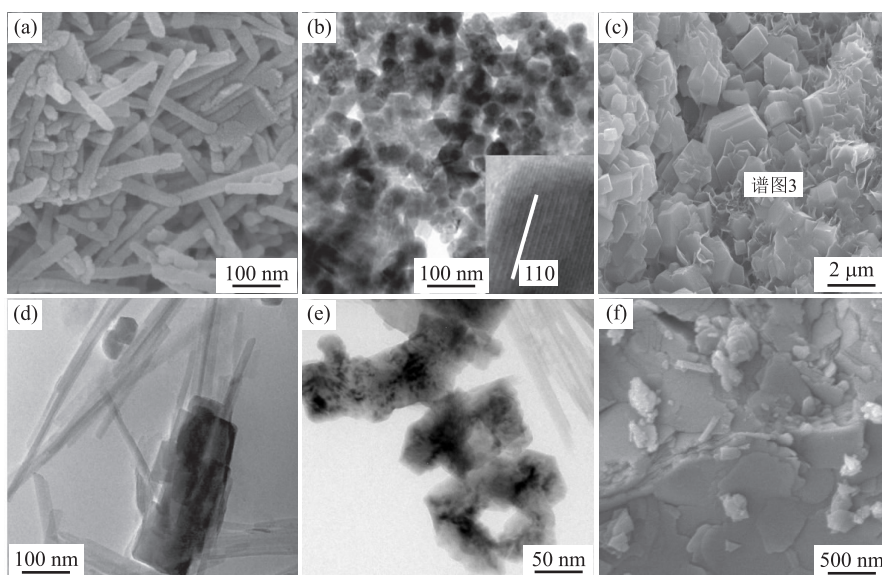


图 5 矿物纳米颗粒电镜图像

Fig.5 Electron microscope images of mineral nano-particles

a.中国黄土中的纳米棒状方解石;b.中国黄土中趋磁菌矿化纳米磁铁矿;c.大洋富钴结壳表面磷灰石;d.凹凸棒石粘土中磷灰石;e.明光凹凸棒石矿;f.鲕状赤铁矿

矿物呈现纳米粒级.成壤过程及土壤环境中、大洋沉积物中、水体中、大气中等都普遍存在各种各样的纳米矿物颗粒.矿物纳米颗粒形成机制主要受外因控制,可以分为以下几种主要机制:

(1)矿物纳米晶核被包裹在矿物内部.其广泛地出现在岩浆、变质、热液等高温环境下形成的矿物中.按照矿物纳米颗粒与主晶矿物形成的先后顺序不同又可以分为几种不同类型.其一是先结晶形成的纳米晶核被另外一种矿物捕获包裹在主晶矿物内部,例如黄铁矿等硫化物中超微细金、银实际上很多都是包裹的纳米自然金、自然银(Wu *et al.*, 2016).其二是已经形成的固溶体矿物由于温度、压力、氧逸度等条件改变发生固溶体出溶形成纳米的客晶(Xu *et al.*, 2014a; Tan *et al.*, 2016).其三是矿物生长时捕获流体包裹体,包括以岩浆、气体、液体状态捕获的包裹体,由于冷却降温等原因在空间和组分受限条件下结晶出纳米晶体.包裹在矿物中的矿物纳米颗粒之所以稳定是由于受到空间和组分物源的制约不能继续长大.随着地球科学研究技术的进步,越来越向微观世界深入,对包裹在矿物中的纳米颗粒认识也在不断深化,成为解读矿物记录地质信息的重要窗口(孙振亚和刘世荣, 1995).

(2)海水雾化液滴中结晶纳米颗粒.全球海岸带海浪与海岸、礁石等撞击产生巨量细微飞沫,在大气中水分蒸发后其中的溶解盐结晶,广泛呈现纳米颗

粒(Buseck and Pósfai, 1999),这是海水中盐类物质对外输送的重要途径.

(3)大气化学反应形成纳米结晶固体.大气中存在气-气反应、气-固反应、液-固反应.由于大气中固体结晶受到组分传质的制约,大气化学反应形成的固体颗粒大部分是纳米颗粒(陈天虎等, 2003; Hochella *et al.*, 2012),即现在受到高度关注的二次气溶胶颗粒物.发生大气化学反应的化合物既包括自然来源,也包括人类活动排放的化合物.自然来源的气体包括火山活动、地震等地球内部气体向大气释放,部分气体因大气化学反应形成纳米颗粒.自然过程和人类活动都向大气释放巨量的 SO_2 、 NO_x 和氨气等,酸性的 SO_2 、 NO_x 气体与碱性的氨气反应形成硫酸盐、亚硫酸盐、硝酸盐、亚硝酸盐纳米颗粒,是形成雾霾的重要贡献者.大气中的碳酸盐纳米颗粒物滞留时间较长,与 SO_2 、 NO_x 反应形成相应的钙、镁、钠、钾盐,又可以中和酸性气体,减弱酸雨的危害.

(4)有机质诱导、生物大分子调控.在矿物生长晶面附着、结合有机分子,改变了晶面性质,阻止了无机离子的堆积,使矿物晶体稳定(段勇等, 2017; 李启来等, 2017).粗大的方解石晶体十分常见,即使是泥晶灰岩中的方解石,其粒径也在微米尺度,常温下无机合成的方解石也稳定在微米尺度,这是因为方解石晶核的临界半径大约在 $1\sim 2$ nm.然而高

分辨电镜研究发现在黄土高原的黄土层中却存在丰富的40~50 nm棒状方解石(大约8%,图5a)(陈天虎和谢巧勤,2005).纳米棒状方解石形成、保存与黄土干旱一半干旱的环境及其中有机大分子的诱导作用有关(陈天虎等,2012).磁铁矿是各类岩石中的最常见铁氧化物副矿物,热液过程可以形成磁铁矿巨晶,岩浆过程可以形成层状堆晶.磁铁矿的粒径一般都在微米一毫米尺度,然而生物作用形成的磁铁矿,特别是趋磁细菌体内矿化形成的磁铁矿,一般是50~80 nm的粒径,近于均匀晶体(图5b)(Buseck *et al.*, 2001; 陈天虎等, 2005),受生物大分子(蛋白质)的调控形成(Komeili, 2012; Siponen *et al.*, 2013).

(5)在地表水环境下矿物结晶成为纳米颗粒.由于结晶矿物的组分在水中溶解度很低,质点迁移很慢,传质速率受到很大制约,矿物生长速度十分缓慢,或者受到杂质离子的影响,晶体稳定在纳米粒级,这是土壤环境、沉积物以及水体中大量存在矿物纳米颗粒的主要机制(Chen *et al.*, 2017; Xu *et al.*, 2017).例如,磷灰石在岩浆和热液中常常形成粗大晶体,但是在沉积物中磷灰石通常表现为纳米颗粒.胶磷矿是沉积纳米磷灰石构成的最重要磷矿石,一些化石中也存在纳米磷灰石.大洋富钴结壳在锰氧化物沉积间断期沉积纳米磷灰石(图5c).苏皖地区与玄武岩风化有关的凹凸棒石黏土中普遍存在少量的纳米磷灰石(图5d)(陈天虎等,2004a),与凹凸棒石共生的白云石也呈现纳米颗粒(图5e)(Xie *et al.*, 2016).热液成因的赤铁矿常常呈现大鳞片状,又称为镜铁矿或云母铁矿,但是沉积成因的赤铁矿一般呈现纳米片状.鲕状赤铁矿是重要的沉积型铁矿石类型,其中的赤铁矿就属于纳米片状晶体(图5f),与黏土矿物、磷灰石、菱铁矿等共生.鲕状赤铁矿矿石属于高磷低品位铁矿石,其中纳米矿物互相紧密嵌生.

从上述可以看出狭义的纳米矿物是受控于某种矿物晶体结构、晶体化学始终保持纳米粒级的矿物,矿物纳米颗粒是受控于外部因素在一些特定条件下形成了纳米粒级的矿物.虽然纳米矿物和矿物纳米颗粒分别受内因和外因控制,但是都属于纳米粒级的固体物质,都会表现出纳米物质所呈现出的特殊性质.不区分形成机制和受控因素,若把纳米粒级的矿物统称为纳米矿物,这即是广义纳米矿物的概念.

3 纳米矿物资源及其应用

纳米矿物很多情况下都表现出纳米颗粒、纳米

材料特性,在声、光、电、磁、热性能方面表现出与宏观矿物不同的特性(陈天虎和徐惠芳,2003),例如纳米矿物具有巨大的比表面积、高吸附和离子交换容量、高化学反应活性、高热分解活性等.这就决定着纳米矿物的加工利用与传统资源的利用有所不同,更多着眼于发挥和利用纳米矿物的纳米特性加工功能性材料.这类主要由某种纳米矿物构成的矿产资源就称为纳米矿物资源.

成为纳米矿物资源应该具备如下几个属性:(1)主要由纳米矿物构成,某种功能性矿物含量达到工业利用所要求的品位;(2)大量聚集达到一定的规模或者可长期开发利用的储量;(3)具有纳米效应和特性,具有纳米矿物材料开发应用价值.纳米矿物资源开发利用是基于矿物的纳米属性,而不是利用矿物的成分,属于非传统的矿产资源.从这角度来说,必须从矿物材料角度重新认识一些传统资源.

凹凸棒石粘土、海泡石粘土就属于非常典型的纳米矿物资源,也是我国的特色非金属矿产资源.苏皖地区凹凸棒石纳米矿物资源的属性在近10余年来得到高度重视和认识(Chen *et al.*, 2011; Liu *et al.*, 2012b, 2013a; 谢晶晶等,2013, 2014),凹凸棒石特有的吸附性能、胶体性能、载体性能、补强性能、高反应活性等纳米属性,在凹凸棒石晶束解聚加工、新型功能材料开发和利用方面都得到很好的体现(Cai *et al.*, 2009, 2014; Huo and Yang, 2010; Yang *et al.*, 2010; Xu and Wang, 2013; He *et al.*, 2014; Mu *et al.*, 2014; Wang *et al.*, 2014; Xu *et al.*, 2014b; Wang and Wang, 2016; Zhang *et al.*, 2016),依托凹凸棒石粘土纳米矿产资源已经开发了系列纳米功能材料产品,诞生了一批高新技术企业,整个凹凸棒石粘土加工和利用产业链已经形成百亿元产值,并成为若干县市的支柱产业.

褐铁矿是纳米矿物针铁矿为主要矿物成分的纳米矿物资源,在长江中下游地区分布十分广泛.最新调查研究表明,仅铜陵地区的褐铁矿成因就有3种类型,分别为硫铁矿矿体风化、菱铁矿透镜体风化、黑柱石砂卡岩风化形成,它们各自具有不同的元素和矿物组成特征(Komeili, 2012; 刘诗贝等,2016).褐铁矿在传统矿产资源类型中一直被当作铁矿石类型之一,含金时当作金矿石利用,但在浸出法提取其中微量金后,矿石的主要组成基本没有变.褐铁矿用于炼铁品位太低,很多情况下作为水泥的铁质配料进行利用,显然没有很好地体现褐铁矿纳米矿物资源的价值.近年来本课题组深化了对针铁矿表面物

理化学性质、晶体化学与晶体形貌、热化学反应活性、热处理气氛与结构演化的认识(Liu *et al.*, 2012b, 2012c, 2013b, 2013d, 2013e, 2013f; 邹雪华等, 2013), 围绕铜陵地区褐铁矿纳米矿物资源特性、矿物环境材料加工与应用开展一系列探索性研究工作(Liu *et al.*, 2013c, 2017c; Zou *et al.*, 2016; Li *et al.*, 2017).

鲕状赤铁矿是以纳米赤铁矿为主要矿物的纳米矿物资源(图 6), 在我国鄂西、湖南、贵州等地分布广泛, 储量超百亿吨, 在传统的矿产资源类型中一直作为铁矿石进行勘探、评价、加工实验. 由于成因和沉积环境制约, 鲕状赤铁矿矿石普遍高磷、高硅、铁品位低, 不同种类的纳米矿物颗粒交互嵌生(Song *et al.*, 2013), 导致难选、难利用. 尽管近十年来在我国铁矿石资源严重短缺的压力驱动下, 鲕状赤铁矿矿石选冶加工开展了大量研究, 主要探索还原焙烧、磁选工艺, 但是到目前为止仍然没有取得实质性的开发利用技术突破(Sun *et al.*, 2016).

硬锰矿、软锰矿常常由多种纳米锰氧化物、氢氧化物矿物构成, 多由富锰碳酸盐风化氧化形成, 也属于纳米矿物资源(Wang *et al.*, 2017). 但在传统工业领域仅作为冶金和生产锰化合物的化工原料. 虽然锰砂作为地下水除锰、铁的滤料已经广泛应用很多年, 对锰砂除锰、铁作用的机理和影响因素也有所探讨和认识, 但是对其纳米矿物材料的属性仍然缺少了解和认识.

纳米矿物资源的重要特点是: 主要由一种或多种纳米矿物或者矿物纳米颗粒组成, 一般都含有非纳米矿物颗粒. 矿物组成复杂、化学组成变化大, 选矿提纯比较困难. 因此, 纳米矿物资源的开发利用有其独特的方面, 必须扬长避短. 充分利用纳米矿物和矿物纳米颗粒比表面积大、化学活性高以及其他功能特异性, 制备功能性纳米矿物环保材料是一个非常

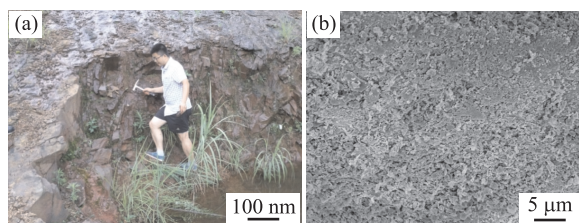


图 6 湖北黑石板鲕状赤铁矿矿层剖面照片(a)和微结构扫描电镜图像(b)

Fig.6 Ore bed section photograph (a) and SEM image (b) of oolitic hematite from Heishi, Hubei Province

前景的研究方向和应用领域, 并已经取得了一些进展(Chen *et al.*, 2009, 2010, 2014; Bao *et al.*, 2014; Liu *et al.*, 2017a, 2017b, 2017c; Wang *et al.*, 2017).

基于纳米矿物资源的环保材料具有如下特点: 资源丰富, 原料廉价, 生态环保; 具有天然的多孔结构, 容易实现纳米结构化, 加工工艺简单; 含有变价元素, 可以转化为多种价态和结构状态的功能材料, 去除污染物的机理多种多样, 具有吸附、沉淀、催化、化学氧化、化学还原、微生物电子供体或电子受体; 应用广泛, 可用作包括水处理、大气污染控制、生态修复各种领域的功能性材料.

4 纳米矿物学及其研究内容

纳米矿物学是矿物学与纳米科学技术交叉形成的一个矿物学新分支学科(陈天虎等, 2004b), 不仅研究与广义纳米矿物有关的基础科学问题, 而且从纳米尺度研究非纳米矿物的有关问题(Nieto and Livi, 2013), 特别是矿物表面纳米层成分、结构、特性的变化以及其演变过程和反应机制(Brown *et al.*, 1999; Hochella, 2002; 陈天虎等, 2004b; 陈天虎和谢巧勤, 2005). 着眼于从纳米尺度揭示矿物超微观结构、形貌、界面关系、形成机理和纳米效应; 纳米尺度认识矿物生长、溶解、转变、演化过程、生物矿化、生物与矿物互相作用; 揭示矿物界面化学过程本质, 从而深化表生地球化学过程、机理及元素迁移规律. 纳米矿物学研究还涉及矿物纳米化有关的科学技术问题及纳米矿物材料、基于矿物的纳米结构化材料加工和应用问题(Chen *et al.*, 2015; Liao *et al.*, 2016; Liu *et al.*, 2017a; Xing *et al.*, 2017; Yang *et al.*, 2017).

由于矿物学比较关注于固体物质结构、晶体化学、物理化学特性、微观形貌的研究, 在相关理论、方法上与凝聚态物理学有着紧密的联系, 使得矿物学家最早关注和从事纳米尺度研究工作(Banfield and Barker, 1994, Banfield *et al.*, 2000, 2001; 陈天虎等, 2004b, 2012; Hochella *et al.*, 2008; Navrotsky *et al.*, 2008), 并对纳米科学发展做出了巨大的贡献(McHale *et al.*, 1997; Penn and Banfield, 1998, 1999).

矿物学作为隶属于地球科学的一个基础学科, 从服务于地球科学发展的角度, 纳米矿物学的研究内容主要包括以下几个方面:

(1) 纳米矿物成因和分布. 研究纳米矿物形成与

结构、晶体化学、环境条件的关系,纳米矿物形貌控制因素和稳定机制,发现和鉴别各类地质体中出现的纳米矿物,调查纳米矿物形成和分布的规律。例如,在中国黄土中发现大量纳米棒状方解石(Buseck *et al.*, 2001; Sheng *et al.*, 2008);在树枝状假化石中发现大量伊利石等纳米矿物以及微体化石(Xu *et al.*, 2014b);在苏皖交界处凹凸棒石矿床发现蒙脱石转化为凹凸棒石的直接证据(陈天虎等,2004b)。

(2)纳米矿物特性及纳米效应。其包括纳米矿物晶体结构、晶体化学、表面特性(比表面积、表面电荷、离子交换容量、表面酸碱位点等),纳米矿物反应途径、活性、机制及其对环境地球化学制约,纳米颗粒团聚效应(Sheng *et al.*, 2008; 王焰新等, 2011),以及纳米矿物热活性、生物活性(Chen *et al.*, 2011, 2014; 邹雪华等, 2013; 董发勤等, 2014; Liu *et al.*, 2017c; Xu *et al.*, 2017)。开发纳米矿物资源提纯、改性、活化加工及应用新技术,矿物纳米化技术及材料应用技术。

(3)纳米矿物信息记录。认识地质体中纳米矿物和纳米尺度地质现象及其地质学意义,从纳米尺度解读矿物记录的信息(陈天虎等,2004b,2012; 谢巧勤等,2014)。例如,黄土中纳米矿物研究揭示了磁铁矿的形貌、结构、成分特征、成因及其在成壤过程的变化规律(陈天虎等, 2003, 2005; 谢巧勤等, 2008);揭示赤铁矿的微观特征、形成与土壤风化的内在联系(Chen *et al.*, 2010);查明凹凸棒石在黄土—古土壤序列剖面中的分布规律及其古气候指示意义(岳统波等,2010; Xie *et al.*, 2013)。

5 小结

在地表环境温度下矿物的风化、转化是关键带中最重要的过程(图7),存在矿物—气、矿物—水、矿物—微生物等多种多样的复杂界面反应。矿物在短时间内发生的变化是纳米尺度的,如硫化物表面氧化、长石表面风化差异淋滤,皆在矿物表面形成硫、铁氢氧化物、或无定型二氧化硅纳米膜。硅酸盐矿物、碳酸盐矿物和硫化物矿物等地表风化产生各种各样的纳米矿物,主要是铁、锰、铝氧化物、氢氧化物以及粘土矿物,因而纳米矿物在土壤、沉积物、水体和空气中广泛存在。纳米颗粒团聚、定向附生已成为一种新的晶体生长方式,且存在的缺陷、纳米孔隙对矿物的物理化学行为和元素循环有重要的影响(Echigo *et al.*, 2013)。这些纳米矿物溶解和沉淀不

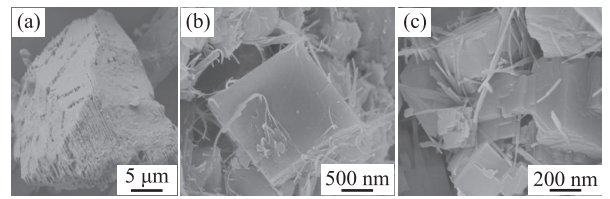


图7 各类纳米矿物转变关系电镜图像

Fig.7 Electron microscope images of various nano-minerals in the process of transformation

a.长石沿010解理面溶解风化;b.自生白云石表面细小叶片状蒙脱石消耗转变为凹凸棒石生长机制;c.白云石溶蚀及凹凸棒石在溶蚀空洞中结晶

仅制约铁、锰、铝、硅等元素的循环,而且还通过吸附、离子交换和氧化还原作用控制有机质、营养元素和重金属等的转化迁移行为,纳米矿物在关键带生物地球化学循环中扮演着重要角色。然而在很多情况下纳米矿物是体系中的次要组分,而且颗粒十分细小,传统的地质学研究方法通常无能为力,需要借用先进的纳米科学技术手段进行研究,更加深入全面地认识表生地球化学过程。

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