

稀有气体同位素测试技术及其在矿床学研究中的应用

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内容提要:稀有气体包含 He、Ne、Ar、Kr、Xe、Rn 六种元素,由于其化学性质十分的稳定,一般不参与各种化学反应过程。其在地球不同圈层及地外物质中的丰度和同位素组成差别巨大,是地球科学研究的重要示踪剂。稀有气体同位素组成的测试方法主要有分阶段加热熔融、真空压碎、激光微区熔蚀等气体采集方式,获得的气体经多级纯化后在静态稀有气体同位素质谱中进行测试。在矿床学研究中,作为灵敏示踪剂的稀有气体同位素大多用于判别成矿物质、成矿流体的来源,特别是幔源物质的贡献大小及壳幔相互作用与成矿的关系,用于揭示矿床在成矿各阶段(期)中的物质和流体源区差异,用以追踪和揭示成矿流体的演化、反演成矿过程并在一定程度上指示成矿流体在成矿过程中的行为。稀有气体同位素为精细成矿作用研究、不同矿种成矿作用差异分析、探寻大规模成矿作用提供了重要的科研手段。

关键词:稀有气体同位素,测试技术,物质来源,成矿过程,矿床学

稀有气体元素是指化学元素周期表中的零族元素,以化学性质不活泼和在地球中含量稀少为特征,包含氦、氖、氩、氪、氙、氡六个元素。因其由稳定的单原子构成,难以与其他物质反应生成化合物,故又称为惰性气体。但事实上,这种不活泼的性质是相对的,1991 年在全国自然科学名词审定委员会公布的《化学名词》中正式将惰性气体改为稀有气体。最初发现的稀有气体是氦,1868 年在日蚀期间,英国的 Lockyer 和法国的 Janssen 分别从太阳光谱中发现了未知光谱,谱线属于新元素“氦”。随后其他稀有气体元素也在 19 世纪末至 20 世纪初被陆续发现和命名(Wang Xianbin,1989)。稀有气体同位素在地球不同储库中的赋存状态、丰度和比值等特征受地质体演化中经历的地质地球化学过程的制约,在不同储库中的特征差异巨大。从上个世纪中叶至今,伴随着测试技术和基础科学研究的不断发展,地质体储库端元的数据得到了不断积累,稀有气体同位素也被越来越多的应用于地球科学研究的各个领域之中(Wang Xianbin,1989;Porcelli et al.,2002;Burnard,2013;):用于阐明地球的形成、热演化史和构造演化史;揭示壳幔相互作用及演化、地壳脱气、岩浆活动;作为示踪剂应用于矿床学、石油一天然气

地球化学、水文和地热资源;进行地震检测和预报以及地质年代学研究等(Fang Zhong,1996;Wang Denghong et al.,1996;Hu Ruizhong,1997;Ye Xianren et al.,1997;Li Yanhe et al.,2000,2002;Li Yanhe,1998,2000;Ma Jinlong et al.,2009)。稀有气体同位素对壳幔源区的高灵敏度识别,使得其在矿床学研究中得以广泛的应用于判别成矿物质、成矿流体的来源,特别是壳幔相互作用与成矿的关系,根据不同储库端元计算获得不同地质圈层中物质的加入信息。但成矿过程中流体的演化所导致的测试样品具有多期叠加的特征并极易发生气体混合提取而使得测试结果趋同性或离散性极高,从而失去了示踪的价值。然而,在精细样品处理和合理测试方法选择的基础上,以上问题可以得到克服,并应用于揭示矿床在成矿各阶段(期)中的物质和流体源区差异,追踪和揭示成矿流体的演化,反演成矿过程的研究中,在一定程度上能够反映成矿过程中的流体行为(沸腾作用,Kendrick et al.,2001)。

本文详细的介绍了稀有气体测试技术,并综述了其在矿床学中应用的有效方面,期望能增强稀有气体同位素的有效使用,为探寻大规模成矿作用的地幔信息、不同矿种成矿作用差异、成矿流体演化、

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成矿物质来源和成矿作用等研究提供重要的科研手段。

1 稀有气体同位素测试技术

1913 年, Thomson 和 Aston 利用质谱仪首次将 ^{20}Ne 从 ^{22}Ne 中分离出来, 开启了稀有气体同位素研究的大门 (Burnard, 2013)。1918 年, Dempster (1918) 在芝加哥大学利用质谱仪发现了多种稀有气体同位素, 建立了磁式同位素质谱仪设计的基本构架。20 世纪 40 年代以来, 稀有气体同位素测试技术及应用有了长足的发展, Daunt 在 1947 年 (Daunt, 1947) 首次测试出了大气中氦同位素的准确组成, Aldrich et al. , (1948a) 利用相同的仪器精确测定了含钾矿物中 Ar 同位素的组成, 为 K-Ar (Ar-Ar) 法地质年代测定奠定了基础。1956 年, Reynolds (1956) 发明的静态真空质谱计, 开创了现代稀有气体同位素测定与研究的先河, 为稀有气体同位素的准确测量提供了有力的技术支撑。Kong Lingchang et al. (1998) 在 1990 年及 1995 年分别成功研制了 NG-2 型稀有气体质谱计和 NG-1000 型 $^3\text{He}/^4\text{He}$ 比值质谱计, 填补了我国稀有气体同位素质谱研制的空白 (Li Zhaoli et al. , 2006a)。伴随着近 60 多年来的迅速发展, 稀有气体同位素测试准确度和精确度得到了大幅度的提高 (图 1), 科学家们依次获得了行星及地球各圈层中不同源区稀有气体同位素的基础性数据, 同时获得了部分干扰同位素测试的化合物种类 (表 1) 为地球科学的深入解剖建立了另一个阶梯。

稀有气体同位素质谱有许多的类型, 基本构成都分为三个主要的部分: 进样系统、纯化系统和测试系统。稀有气体一般以分子游离态的形式存在于岩石矿物的裂隙、矿物分子间和晶格中, 也存在于流体包裹体中, 分析测定其同位素组成, 首先需要将稀有气体从测试样品中提取出来, 取样方式有三种: 压碎法、加热熔融法和激光熔蚀法。①压碎法是在高真空中通过机械物理压碎的方式, 将靶池中的样品破碎, 获得样品包裹体和矿物 (岩石) 裂隙中的气体。压碎法是矿床学研究中获取矿物包裹体中稀有气体的主要方式, 压碎程度和压碎比例越高越大, 释放出的稀有气体相对就越多, 因而在测试后会通过“过筛”来测量压碎量。②加热熔融法可以使固体样品中除了包裹体的和岩石矿物裂隙的气体被释放出来之外, 矿物分子间和晶格间就位的放射性成因稀有气体也会游离释放出来。分阶段加热熔融法取出

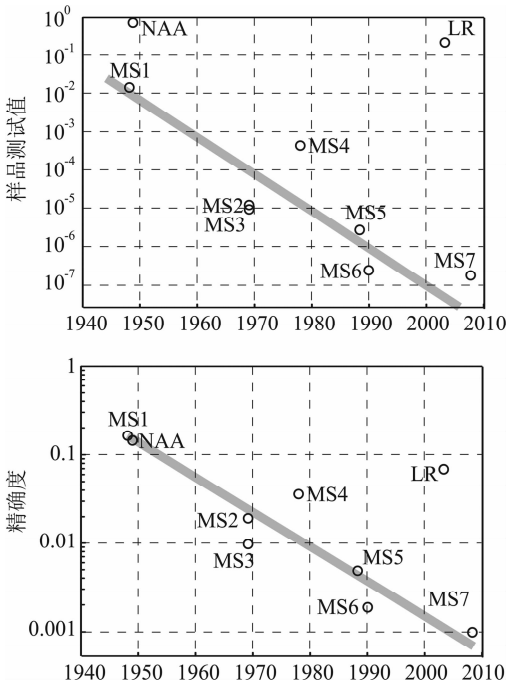


图 1 He 不同时代同位素测试仪器对 He 同位素测试的准确度和精确度 (据 Burnard et al. , 2013)

Fig. 1 Technical advances in helium isotope measurements with time (after Burnard et al. , 2013)

MS1—Aldrich et al. (1948b); MS2—Clarke et al. (1969); MS3—Mamyrin et al. (1969); MS4—Nagao et al. (1981); MS5—Sano et al. (1988); MS6—Lupton (1990); MS7—Sano et al. (2008); NAA—Coon (1949); LR; Wang et al. (2003)

的气体是某一温度阶段中均一化的混合气, 通过设定温度可以分别获得前期捕获和后期就位放射性成因的气体。事实上, 压碎法取样的前期也需要通过对样品加热到一定的温度 (120~150℃) 来去除后期次生包裹体中的气体干扰。③激光熔蚀取样可以有针对地精确释放所选微区的气体, 该方法因有非常高的空间分辨率而得到迅速应用。三种样品提取方式各有优劣, Ye Xianren et al. (2003) 总结认为, 在现有技术和应用中压碎法较高效, 分析的主要是矿物流体包裹体中的稀有气体组成, 可将后期放射性成因稀有气体的影响降至最低, 但受到提取率不高的影响 (<80%) 需要进行多次压碎; 分段加热取样容易受到杂质气体的干扰, 对样品纯净度要求高; 激光熔蚀法每次提取的样品量很有限, 对有限的样品进行含量很低的稀有气体的测试就要求较高灵敏度的纯化和测试系统的配合, 比较适合丰度较高的 Ar 同位素的测量。在分阶段加热获取测试气体时, 矿物包裹体在什么温度下破裂释放气体并非完全由捕获温度控制, 其也受到包裹体大小的制约 (Bodnar et al. , 1989)。Kendrick et al. (2013) 总

表 1 稀有气体同位素测试中干扰气体及化合物
(据 Burnard et al. , 2013)

Table 1 Common interferences found in the region of the noble gases (after Burnard et al. , 2013)

干扰项	质量数	稀有气体	分辨率要求 *	说明
$^1\text{H}^2\text{D}^+$	3. 0215	^3He	509	存在于所有质谱仪中
$^3\text{H}^+$	3. 0161	^3He	150000	
$^1\text{H}^1\text{H}^1\text{H}^+$	3. 0238	^3He	384	
$^{12}\text{C}^{++}$	4. 0000	^4He	1538	
$^1\text{H}_2^{18}\text{O}^+$	20. 015	^{20}Ne	894	Ne 测试中的液氮冷阱纯化阶段
$^1\text{H}^{19}\text{F}^+$	20. 006	^{20}Ne	1406	
$^{40}\text{Ar}^{++}$	19. 981	^{20}Ne	1778	
$^{20}\text{NeH}^+$	21. 000	^{21}Ne	3276	
$^{12}\text{C}_3^1\text{H}_6^{++}$	21. 023	^{21}Ne	709	Ne 测试中的液氮冷阱和锆铝泵纯化阶段
$^{63}\text{Cu}^{+++}$	20. 976	^{21}Ne	1202	
CO_2^{++}	21. 995	^{22}Ne	6232	
$^{66}\text{Zn}^{+++}$	21. 975	^{22}Ne	1405	
$^{12}\text{C}_3^+$	36. 000	^{36}Ar	1109	
$^1\text{H}^{35}\text{Cl}^+$	35. 977	^{36}Ar	3947	
$^1\text{H}^{37}\text{Cl}^+$	37. 974	^{38}Ar	3458	
$^{12}\text{C}_3^1\text{H}_2^+$	38. 016	^{38}Ar	699	
$^{12}\text{C}_3^1\text{H}_4^+$	40. 031	^{40}Ar	580	
$^{12}\text{C}_6^1\text{H}_6-^{12}^+$	78~86	Kr 同位素	~600	
$^{12}\text{C}_{10}^1\text{H}_4-^{16}^+$	124~136	Xe 同位素	~550	普通泵油或油脂碎片

注: * 要求的分辨率是将于干扰项与邻近稀有气体同位素区分出来时的分辨率数值。

结认为,水成流体包裹体直径大于 5 微米时一般于~200~700℃破裂,而石英中小于 1~2 微米的流体包裹体的破裂释气则需要更高的温度(>1200℃);大部分的矿物释放包裹体和晶格中的稀有气体会在~700~1600℃。因此,测试气体的获取需要根据不同的测试对象和研究目的来进行针对性的方法选择和物理条件设计。

现有稀有气体同位素质谱的纯化系统至少有两级(纯度逐级递增),纯化部件包括海绵钛炉、锆铝泵、液氮温度下的活性炭阱以及可精确控温的活性炭冷阱等(Nier,1990;Sun Mingliang et al. ,1997;Li Yanhe et al. ,2000;Li Yanhe,2000;Li Zhaoli et al. ,2006a;Li Junjie et al. ,2015)。海绵钛炉主要吸附烃类、N₂、O₂、H₂、CO₂等活性气体,锆铝泵在常温主要吸收 H₂、在 400℃吸收 N₂、O₂、H₂、CO₂和碳氢化合物等气体,液氮温度下的活性炭冷阱吸收 Ar、Kr、Xe,可精确控温的活性炭冷阱可用于 He-Ne 分离。纯化后的气体进入离子源离子化,加速进入磁场,由于荷质比的不同而产生不同偏转角,最后被法拉第杯或离子倍增器接收。为了提高测试的精度,

目前的稀有气体同位素质谱均属静态质谱,大多采用超高真空度、多接收杯等技术,另有采用双飞行管道(分叉的飞行管道),使得在紧凑的体积内实现优越的离子光学和双聚焦及高色散性能(Ott,2008;Li Junjie et al. ,2015)。

2 稀有气体同位素在矿床学研究中的应用

稀有气体同位素质谱测试技术的逐渐成熟和发展使得其广泛应用于地球科学和行星科学的研究中。近 20 年来,稀有气体同位素在矿床学研究中的应用逐步增多,多用于判别成矿物质、成矿流体的来源,根据不同储库端元计算获得不同地质圈层中物质的加入信息,追踪和揭示成矿流体的演化,反演成矿过程,并用以揭示成矿流体在成矿过程中的行为。稀有气体同位素为成岩成矿作用研究、区域成矿规律探寻,精细成矿作用研究提供了重要的科研手段。

2.1 成矿流体和成矿物质源区判别

稀有气体同位素组成在地球不同圈层不同地质储库中的差异巨大(表 2),在矿床学研究中被广泛应用于斑岩型铜矿床(Irwin et al. ,1995;Kendrick et al. ,2001;Hu Ruizhong et al. ,1997,1998a,2004)、矽卡岩型矿床(Wang Yanbin et al. ,2004;Zhou Taofa et al. ,2001;Samson et al. ,2008;Xie Guiqing et al. ,2016)、VMS 型矿床(Turner et al. ,1992;Lueders et al. ,2010;Zhang Zhixin et al. ,2014)、MVT 型矿床(Böhlke et al. ,1992;Kendrick et al. ,2002,2005)、IOCG 型矿床(Kendrick et al. ,2007)、金矿床(Hu Ruizhong et al. ,1998b,1999;Mao Jingwen et al. ,1997,2001,2002,2003;Burnard et al. ,1999;Sun Xiaoming et al. ,1999,2006,2009;Zhang Lianchang et al. ,2002;Feng Chengyou et al. ,2006;Yang Fuquan et al. ,2006)、铜镍硫化物矿床(Hu Peiqing et al. ,2010;Zhang Mingjie et al. ,2013)、三稀(稀有、稀散和稀土)金属矿床(Stuart et al. ,1995;Burnard et al. ,2004;Li Zhaoli et al. ,2006b;Cai Minghai et al. ,2007;Wu Liyan et al. ,2011)、铀矿床(Hu Ruizhong et al. ,2009;Richarda et al. ,2014;Yan Bing et al. ,2014)等矿床类型的研究中,以判断成矿流体和成矿物质的源区并探讨矿床成因。其中,⁴He-³He, ⁴⁰Ar^{*}/⁴He-R/Ra, ⁴⁰Ar/³⁶Ar-R/Ra, ²¹Ne/²²Ne-²⁰Ne/²²Ne, ¹²⁹Xe/¹³⁰Xe-¹³⁴Xe/¹³⁰Xe, ¹²⁹Xe/¹³⁰Xe-¹³⁶Xe/¹³⁰Xe 等示踪判别图解(图 2)被广泛使用。

表 2 稀有气体同位素在不同地质储库中的组成(据 Ballentine et al. , 2002a; Moreira et al. , 2013 及其参考文献)

Table 2 Elemental and isotopic ratios in MORB, OIB, Continental crust and Air sources

(after Ballentine et al. , 2002a; Moreira et al. , 2013 and its references)

储库	⁴ He/ ³ He	R/Ra	²⁰ Ne/ ²² Ne	²¹ Ne/ ²² Ne	⁴⁰ Ar/ ³⁶ Ar	¹²⁹ Xe/ ¹³⁰ Xe	³ He/ ²² Ne	³ He/ ³⁶ Ar	³ He/ ¹³⁰ Xe	⁴ He/ ⁴⁰ Ar*
空气	722000	1	9.8	0.029	295.5	6496	~0	~0	~0.002	
大陆地壳		0.02	0.08~0.1	0.4~0.52	3000					
洋中脊玄武岩	90000	8	12.6	0.060	~30000	7.7	5.1	0.45	600	1.5
洋岛玄武岩(加拉帕戈斯群岛)		23	12.6	0.033	~3000	6.7	2.3±0.5	0.35	~1000	4.3±0.4
洋岛玄武岩(冰岛)		17.5	12.6	0.035	~5000	6.8	2.3±0.3	0.4	~1200	3.0±0.6

2.1.1 成矿流体来源的示踪以及矿床成因的判别

成矿流体来源的判别、端元的区分以及流体混合比例的计算是稀有气体同位素示踪技术在矿床学研究应用中最为广泛的方面。我国科学家们自 20 世纪 60~70 年代即关注到氦含量和氦同位素组成与铀矿床的形成具有密切的联系,其可用以追踪寻找铀矿床。在 20 世纪 90 年代,应用稀有气体的矿床学研究成果开始涌现,进入 21 世纪此类科研成果大量报道;Li Bin et al. (1994)对日本 Kuroko 矿床进行了 Ar、Ne 和 Xe 同位素的测试研究,模拟计算出成矿过程中有 75%来自岩浆源区和 25%来自大洋水的流体参与;Mao Jingwen et al. (1997,2002)对湖南万古金矿床石英中流体包裹体 He 同位素研究得出富³He 流体参与成矿作用,流体形成于地幔岩石减压引起的部分脱气;Hu Ruizhong et al. (1998a)对马厂箐斑岩型铜矿床黄铁矿中包裹体 He、Ar 同位素分析测试,得出成矿流体为岩浆源区流体与大气成因地下水的混合;Li Yanhe et al. (1997,1999)对东太平洋海盆 C-C 区海底多金属结核及西太平洋马绍尔地区富钴结壳的 He 同位素组成进行了对比研究,发现结核的³He/⁴He 比值普遍较高,认为海底多金属结核和富钴结壳的 He 同位素异常均是由宇宙尘注入引起的;Zhao Kuidong et al. (2007)通过对大厂锡多金属矿床黄铁矿流体包裹体中 He 同位素的研究判断,成矿流体可能为海水与地幔流体的混合;Sun Xiaoming et al. (2009)通过对云南大坪金矿床中白钨矿 He、Ne、Ar、Xe 同位素组成的研究,认为该金矿床成矿流体形成于地幔岩浆上涌和去气作用形成的深源地幔流体与下地壳在上涌地幔烘烤下形成的富含 CO₂、³He、²⁰Ne 和 ¹³⁰Xe 的地壳流体的混合,混合后的成矿流体沿韧性剪切带上升,水岩反应和沸腾作用导致矿质沉淀,大坪金矿属于剪切带控制的深源热液型金矿;Hu Ruizhong et al. (2009)通过对相山铀矿床黄铁矿中流体包裹体 He、Ar 同位素测试,认为成矿流体的为壳幔两端元的混合;Hu Peiqing et al. (2010)对金川

Cu-Ni-PEG 硫化物矿床中硫化物和岩浆岩硅酸盐矿物 He、Ne、Ar 同位素的研究得出成矿岩浆具有地幔—地壳—饱和大气水三个源区端元,硫化物熔体的分离发生在岩浆结晶分异的早期;Geng Xinxia et al. (2014)对新疆准噶尔北缘索尔库都克铜钼矿床黄铁矿中 He、Ar 同位素研究,得出成矿流体来源于壳幔相互作用的岩浆水和大气降水,推断该矿床为矽卡岩型矿床;Deng Biping et al. (2014)通过对滇西富碱斑岩型多金属矿区中黄铁矿和石英流体包裹体的 He、Ne、Ar、Xe 同位素组成的分析测试,探讨了壳幔混染对斑岩型矿床的作用;Zhang Zhixin et al. (2014)对新疆阿舍勒海相火山岩块状硫化物(VMS)铜锌矿床黄铁矿中流体包裹体 He、Ar 同位素的研究确定了成矿流体来源于海水和幔源岩浆。

2.1.2 区域成矿规律的推断

区域成矿规律是对一定时期、一定区域中的矿床类型、成矿环境、成矿条件、成矿过程和成矿演化的研究,以阐明矿床时空分布规律(Zhai Yusheng et al. ,1999)。大规模成矿或大爆发式成矿是在一定特殊地球动力学环境中的产物(Mao Jingwen et al. ,1999;Hua Renmin et al. ,1999),伴随着一定的构造活动、壳幔作用以及大量的水岩反应。在同一成矿带或矿集区中,相似类型的矿床经历着相似的成岩成矿热事件过程,然而单一矿床相互之间的差异以及同一地区不同矿种之间的差异使得这种规律的寻找需要建立在稳定的对比参考特征上。稀有气体同位素相对于 C、H、O、S 等同位素原始源区信息能够得到相对有效的保存。同时,作为一种非常有效的地幔过程示踪剂(Moreira et al. , 2013),稀有气体在揭示成矿作用背景中也发挥着重要的作用。

MaoJingwen et al. (2001,2003)对河北东坪碲化物金矿床流体包裹体的稀有气体同位素研究认为,东坪金矿床并非是浅成热液矿床,成矿流体含有幔源信息与华北克拉通中生代岩石圈减薄所导致的地幔流体上侵有关。Wang Denghong et al. (2002)对我国新生代不同类型主要矿种的稀有气体同位素

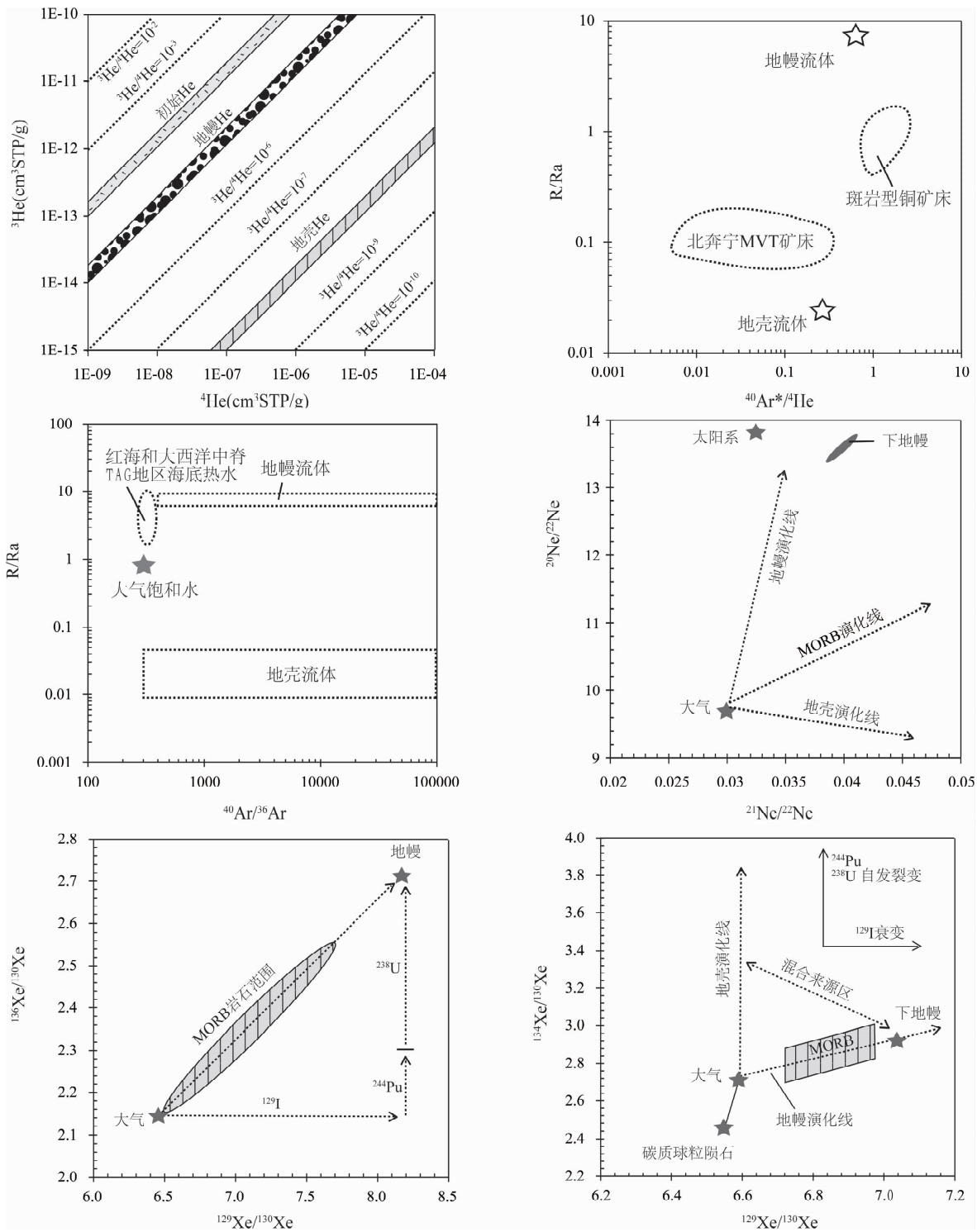


图 2 常用稀有气体同位素示踪图谱(据 Thomas et al. , 1982;Mamyrin et al. ,1984;Zeng Zhigang et al. , 2001;Winckler et al. , 2001; Ballentine et al. , 2002b; Hilton et al. , 2002; Graham, 2002)

Fig. 2 Commonly used noble gas isotopic tracer diagram (AfterThomas et al. , 1982;Mamyrin et al. ,1984;Zeng Zhigang et al. , 2001;Winckler et al. , 2001; Ballentine et al. , 2002b; Hilton et al. , 2002; Graham, 2002)

组成研究,发现地幔流体参与了不同的类型的成矿作用,壳幔相互作用在一定程度上控制了成矿作用的发生,同时在 25Ma 存在着一个地幔脱气作用显著增加的拐点,响应于东部大陆大地构造的改变;

Xue Chunji et al. (2003)通过对金顶、白秧坪铅锌矿床中主要金属矿物和主成矿阶段脉石矿物流体包裹体 He、Ne、Xe 同位素组成的测试,确定了成矿流体为地幔流体与大气成因盆地卤水的混合,认为这种

壳幔流体的混合作用是兰坪地区大规模成矿的基本方式;Cai Minghai et al. (2012)获得荷花坪锡多金属矿床发育有印支期和燕山期 2 期成岩—成矿作用,后一期携带有更多的地幔信息; Hou Tong et al. , (2011)对攀西地区钒钛磁铁矿赋矿侵入岩中橄榄石和单斜辉石 He-Ar 同位素测试获得了与俯冲板片有关的流体或熔体长时间贮存于岩石圈地幔的信息,推测岩石圈地幔富含榴辉岩相物质,很可能是产生富铁原始岩浆的关键性因素之一;长江中下游多金属成矿带是我国东部最重要的成矿带之一,在中生代发育有两期成矿作用(斑岩型—矽卡岩型 Cu-Au-Fe 矿床和与陆相火山岩有关的铁多金属矿床),Xie Guiqing et al. (2016)通过对鄂东矿集区矽卡岩型铜—铁矿床和矽卡岩型铁矿床中的硫化物流体包裹体中 He-Ar 同位素组成的分析研究,得出矽卡岩型铜—铁矿床与铁矿床的成矿流体均具有含幔源信息的岩浆流体和含壳源信息的饱和大气水两个组分端元,差别在于前者幔源(岩浆)流体的含量较多,从而也揭示出成矿带内两期成岩成矿作用的差异。

2.2 成矿过程演化研究

现阶段我国在矿床学研究中稀有气体同位素的应用大多仅仅是用于判断流体或成矿物质的源区,有限数量的源区判别投点大多获得了壳幔混源的结论。这使得稀有气体同位素的示踪作用失效并未未能得到更广发的利用。通过测试与总结,我们发现,稀有气体同位素测试体系本身的误差是可控的,而真正导致示踪信息模糊的原因很可能是测试样品的混合。

稀有气体同位素具有较高的灵敏度,测试结果极易受到样品混合的干扰(同一手标本含有不同期

次相同矿物造成单矿物挑选时不同成矿阶段样品的混合,单一矿物颗粒经历多期热事件携带有多世代演化叠加之后的信息)。样品的混合所导致的结果即为测试值混合趋同或无序离散,处于两个或多个端元的中间而使源区证据盈弱且飘曳,从而模糊了对源区的指示意义。因此,我们需要特别注意存在于矿物的晶格、裂隙和包裹体中的稀有气体在结晶过程中受到他源流体的加入、混合、蚀变改造等作用的影响。在复杂的地质过程中,矿物同位素组成会发生较大的改变,通过对成矿不同阶段或不同世代矿物进行分段加温,有区别的(压碎/分阶段加温)进行大量精确测试并逐步“剥离”源区信息,能够追踪成矿过程中的水岩反应、流体混合,详尽的揭示出成矿流体的演化和矿物的形成过程。

目前,应用稀有气体同位素进行的精细成矿过程的研究很少。Hu Ruizhong et al. (1998b,1999)和 Burnard et al. (1999)对哀牢山地区金矿带各金矿床的成矿流体的 He-Ar 同位素的分析得出,金矿床成矿流体具有壳源岩浆水、相似于地下水并含放射性成因⁴He 的饱和大气水及地下水三个端元,是富硫的深源高温流体与贫硫的大气成因低温地下水二端元混合的产物;金矿的富集是通过富硫深源流体上升加入地壳浅层贫硫流体,使这种贫硫的流体转化成富含足够硫,从而有能力大规模浸取金的成矿流体来实现的(图 3); Zhang Mingjie et al (2013)对金川铜镍硫化物矿床中硫化物和岩浆岩硅酸盐矿物进行了分阶段加温的稀有气体同位素测试和模拟计算,揭示出与成矿有关的侵入岩携带有地幔—地壳—饱和大气水三个源区端元信息;成矿母岩源自大陆岩石圈地幔,岩浆侵位和结晶的过程中受到了来自壳源流体(20%)的混染,进而使得氧逸

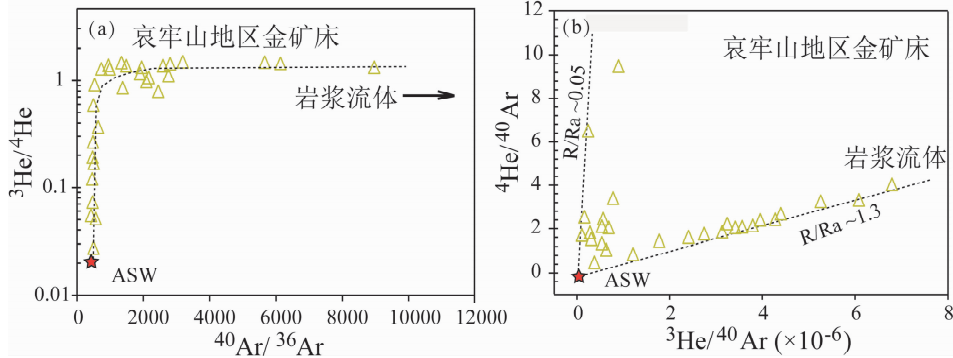


图 3 哀牢山金矿床矿物流体包裹体 He-Ar 同位素特征及成矿流体演化
(据 Hu Ruizhong et al. ,1998b,1999;Burnard et al. 1999)

Fig. 3 He-Ar isotopic characteristics of fluid inclusions in Ailaoshan gold belt and its evolution
(after Hu Ruizhong et al. , 1998b, 1999; Burnard et al. 1999)

度升高、岩浆中硫的溶解度降低,导致硫化物分离;整个过程中有 63% 的饱和大气水加入(图 4)。

此外,在流体演化过程中,流体的物理特征也能够通过流体包裹体中稀有气体组成的差异得以表征。稀有气体在流体发生沸腾作用的过程中进入到气相时流失的比例不尽相同。Kendrick et al (2001)在对斑岩型铜矿的研究中证实伴随着沸腾或者气化作用稀有气体的丢失量具有 $Ar>Kr>Xe$ 的特征,导致了沸腾作用后流体包裹体中稀有气体的含量出现 Xe/Ar 和 Kr/Ar 的升高, Cl 优先保留于液相而使得 $^{40}Ar^*/Cl$ 的值降低(图 5)。稀有气体的这一性质也可在流体包裹体研究中联合判别沸腾作用。

3 结语与展望

稀有气体同位素测试技术与其在地球科学中的应用是相辅相成、相互促进发展的。最近几年大量科研成果的涌现也正是由于测试技术的突破而呈现的结果。随着激光技术的发展,微区原位取样得以成熟应用,而稀有气体同位素质谱的测试准确度和精确度亦在逐步提高,这使得科学家们可以在微米级尺度分析矿物的化学组分,从微观尺度获取连续的成矿过程的精细特征。精确控温技术与高灵敏度质谱测试技术的应用,也使得科学家可以逐层的揭示地质作用的演化。

在矿床学研究中,揭示成矿物质和成矿流体的

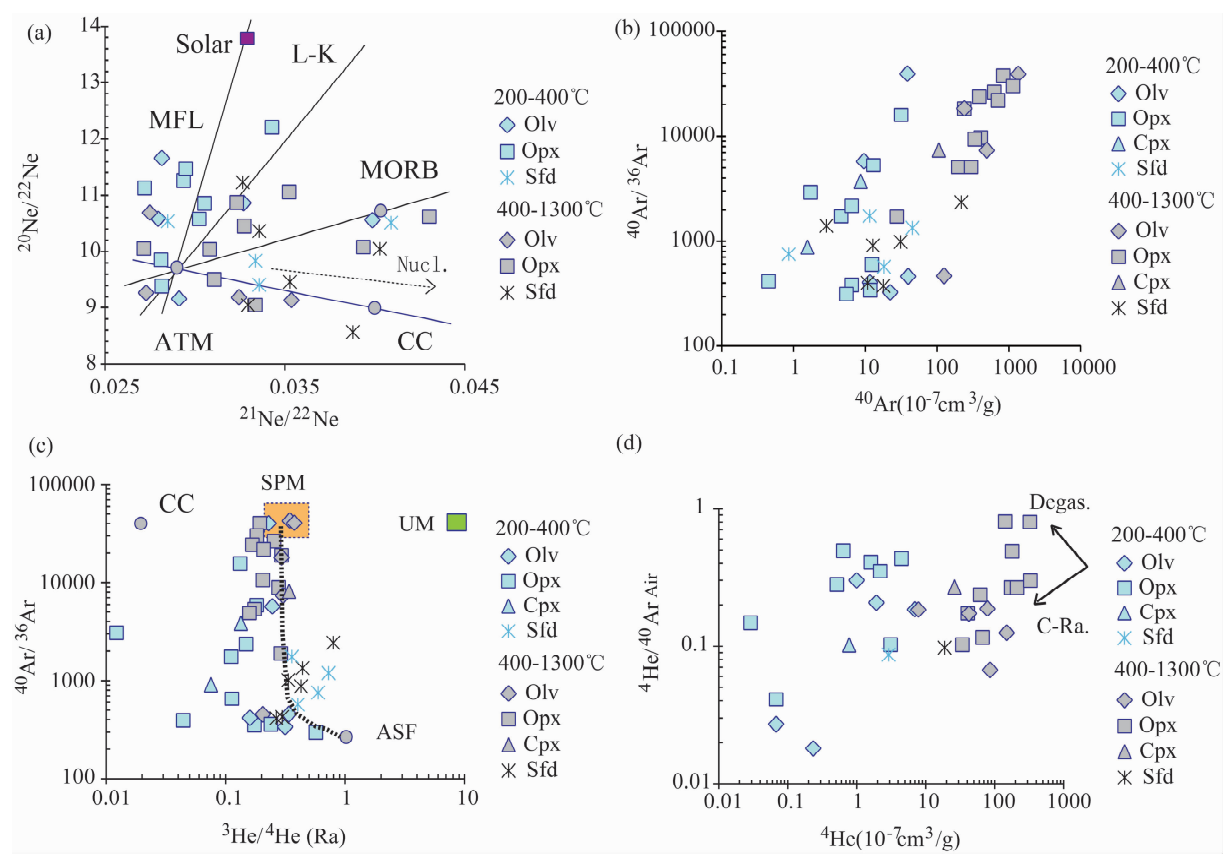


图 4 金川铜镍硫化物矿床中硫化物、橄榄石、单斜辉石、斜方辉石在成矿过程中稀有气体同位素组成特征及其演化(据 Zhang Mingjie et al., 2013)

Fig. 4 He-Ar isotopic characteristics of olivine, orthopyroxene, clinopyroxene and sulfide in the Jinchuan Ni-Cu-(PGE) sulfide deposit and their evolutions (after Zhang Mingjie et al., 2013)

MFL—大气氖质量分馏线; Solar—太阳风; L-K—Loihi-Kilauea 演化线; ATM—大气; MORB—洋中脊玄武岩; CC—大陆地壳演化线; Nucl—放射性成因组分; SPM—原始岩浆; UM—上地幔; ASF—饱和大气流体; Degas—岩浆去气; C-Ra—放射性成因供给; Olv—橄榄石; Opx—斜方辉石; Cpx—单斜辉石; Sfd—硫化物

MFL—Linear mass frac-tionation line of air neon; Solar—solar wind; L-K—Loihi-Kilauea trend; ATM—atmosphere; MORB—mid-ocean ridge basalts; CC—continental crust line; Nucl—nucleogenic component; SPM—the source of primary magma; UM—upper mantle; ASF—air saturated fluid; Degas—magma degassing; C-Ra—contributions of radiogenic; Olv—olivine; Opx—orthopyroxene; Cpx—clinopyroxene; Sfd—sulfide

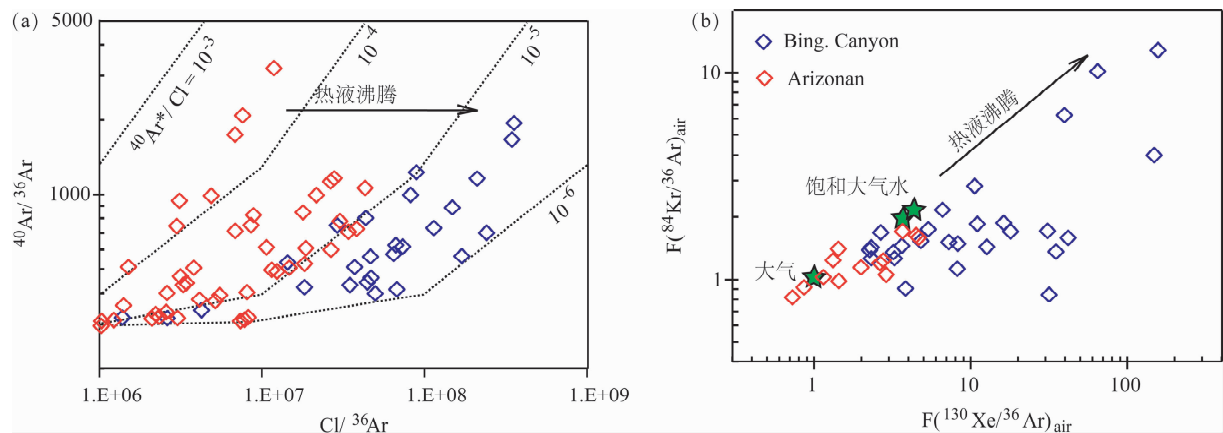


图 5 斑岩型铜矿稀有气体在热液沸腾作用中的分馏(据 Kendrick et al. , 2001)

Fig. 5 Noble gas fractionation during hydrothermal boiling of porphyry copper deposit ore fluids (after Kendrick et al. , 2001)

(a)— $\text{Cl}/^{36}\text{Ar}$ - $^{40}\text{Ar}/^{36}\text{Ar}$ 图解, 沸腾之后残余液相较原始流体具有更高的 $\text{Cl}/^{36}\text{Ar}$ 比值; (b)— $F(^{130}\text{Xe}/^{36}\text{Ar})_{\text{air}}-F(^{84}\text{Kr}/^{36}\text{Ar})_{\text{air}}$ 图解, 沸腾之后残余液相较原始流体具有更高的 $^{130}\text{Xe}/^{36}\text{Ar}$ 和 $^{84}\text{Kr}/^{36}\text{Ar}$ 比值

(a)— $\text{Cl}/^{36}\text{Ar}$ - $^{40}\text{Ar}/^{36}\text{Ar}$ diagram, residual liquid phase has higher $\text{Cl}/^{36}\text{Ar}$ ratio; (b)— $F(^{130}\text{Xe}/^{36}\text{Ar})_{\text{air}}-F(^{84}\text{Kr}/^{36}\text{Ar})_{\text{air}}$ diagram, the residual liquid phase acquires higher $^{130}\text{Xe}/^{36}\text{Ar}$ and $^{84}\text{Kr}/^{36}\text{Ar}$ ratios than the parent fluid

来源与演化以及区域成矿作用对比是稀有气体同位素应用的主要方面。成矿过程的演化是一个非常复杂的地质过程,是在一个巨大的开放系统中物理和化学反应的过程。详细的地质特征的勘察与解剖是进行任何测试工作的基础。对于稀有气体同位素测试,根据被测矿物的特征以及被测矿物在成矿过程中所代表的阶段和地质意义,选择和设定适合的气体提取(阶段加温/压碎/激光熔蚀)与测试方法是应用的关键。同时,这也是一个难点。在选择样品气体提取方法时也需要参考样品生成的物理化学条件。例如:在对多阶段成矿作用中形成的矿物,在区分成矿期次的基础上分别对同种矿物进行测试;在避免混合样产生的同时,测试样品(矿物)形成的温度也是一个重要的参考因素,测试时需要去除次生包裹体的影响,也需要根据矿物形成温度进行分阶段的提取测试气体。

任何一种同位素示踪方法都具有他的优点和缺点,稀有气体同位素在具有高灵敏度的同时,极低的含量使得对他的获取与成功测试的难度较大,并也存在多解性的问题。为降低多解性,在未来的矿床学研究过程中,稀有气体同位素与其他同位素联合示踪成为了发展的必然趋势。例如稀有气体同位素与传统稳定同位素(C、H、O、S)、放射性同位素(Sr、Nd、Pb)以及与流体源区特征元素(卤族元素)的联合应用(Wu Liyan et al. , 2007)。其中,流体包裹体中稀有气体与卤族元素的联合示踪得到了较为成熟的应用(Kendrick et al. , 2013),但在我国这方面

的研究工作仍然未有较多的开展。

稀有气体同位素在矿床学中的应用目前仍处于相对基础的阶段,测试样品精细提取与测试是获得准确信息的关键,其与其他同位素联合示踪是未来发展的方向。伴随着矿床学研究的进步,稀有气体同位素示踪在矿床学、矿床地球化学、区域成矿学等领域的应用也将走向成熟,成为矿床学精细研究的有力阶梯。

谨以此文向中国地质科学院建院 60 周年致敬!

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**Noble Gas Isotope Analytical Techniques and Its Application in
Economic Geology Researches**

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Abstract

The noble gas contains six elements He, Ne, Ar, Kr, Xe, Rn, because of its chemical properties is very stable, generally do not participate in chemical reaction process. The noble gas in different earth spheres and extraterrestrial materials has a huge different abundance and isotope characteristic, and is one important tracer in earth science researches. Analytical techniques of noble gas isotopic composition has three methods for the gas collection, i. e. stepped heating, in vacuo crushing and laser micro zone ablation. The obtained gases will go through multi-stage purify system, and finally are tested by static noble gas isotope mass spectrometry. As the sensitive tracer, noble gas isotope can be used to identify the source of ore-forming materials and fluids, especially for the mantle original contribution, crust-mantle interaction and metallogenic relationship, in economic geological researches. It can be used to trace and reveal the differences among the ore-forming stages and the evolution of fluids and mineralizations. In addition, noble gas isotope also can indicate the behavior of fluid in ore-forming processes. Noble gas isotope provides an important scientific research tool for detailed mineralization study, metallogenic difference research and large-scale mineralization exploring.

Key words: noble gas isotope; analytical technique; material sources; ore-forming; economic geology