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中国地质标准物质研制进展

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摘要: 地质标准物质是保障地质样品分析结果准确性的重要基准。目前，一级地质标准物质数量居十三大类首位，形成了具有国际影响力的地质标准物质体系。本文依据基体类型和定值特性，将一级地质标准物质划分为基础、矿石、海洋、环境、能源和特殊用途等六类，总结了各类标准物质的研制数量、特点、定值指标、应用范围及意义。针对现阶段数量众多的地质标准物质在应用中还存在研制数量少、系列化不足、基体类型单一、定值指标少等问题，本文分析了不同类型存在的具体问题及产生的原因，探究研制技术成熟的地质标准物质中仍有多种成分难定值以及定值方法单一的可能原因，重点讨论了标准物质研制技术中影响定值水平的细节问题：①阐述了均匀性检验测量方法的优缺点，XRF 法以其高精密度的优势应用于均匀性检验值得关注和研究；②提出了考虑元素性质、含量级次兼顾测试技术评定均匀性未检元素的不确定度评定方法；③分析了稳定性不确定度在总不确定度构成中成为主要贡献量的原因是当前的计算方法造成的，有待于进一步研究合理的评定方法；④建议针对不同类型标准物质，制定相对扩展不确定度控制限以获得准确可靠的标准值。结合当前地质标准物质存在的不足和工作需求，本文提出了研制关键金属矿石标准物质、符合“一带一路”沿线国家地质背景的土壤和水系沉积物标准物质、海洋沉积物和海洋矿产与海产品标准物质、生物元素标准物质与有机污染物标准物质的建议。

关键词: 地质标准物质；均匀性；稳定性；不确定度；相对扩展不确定度

要点:
(1)X 射线荧光光谱法以其高精密度的优势应用于标准物质的均匀性检验值得深入研究。
(2)提出一种兼顾元素性质、含量、测试技术的均匀性未检元素不确定度评定的方法。
(3)分析了趋势分析法的监测时长导致计算的稳定性不确定度对总不确定度的贡献过大。
(4)建议针对不同样品类型制定合理的相对扩展不确定度控制限，以提高地质标准物质定值水平。

中图分类号: F407.1；TQ421.3　　**文献标识码:** A

地质标准物质是指具有准确量值的地质物料化学成分和物理特性的测试标准，是评价地质分析结果可靠性与可比性的计量器具。其原料一般以岩石、矿石、矿物等天然地质物料为主，还包括一些土壤、水、生物等，也有采用人工合成的方式研制。地质样品分析数据可以为地质调查研究、矿产资源勘查与环境评价等地球科学问题提供重要信息[1-2]，在分析测试过程中使用标准物质，尤其是与待测样品基体匹配的标准物质，是获得准确可靠测量数据的技术保障。随着中国经济社会转向高质量发展和国际单位制量子化变革的挑战，标准物质在经济社会发展中的基础性和战略性地位更加突出，标准物质需求日益增加。

历经四十余年的发展，中国研制了覆盖岩石、矿石、土壤、沉积物、生物、水等不同介质类型、数以千计的地质标准物质。由国家标准物质资源共享平

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台(www.ncrm.org.cn)查询可见,至十三五末,经国家市场监管总局批准的地质标准物质总数为 1013 个,其中一级标准物质 718 个、二级标准物质 295 个,一级数量居十三大类首位(图 1),在数量、品种类型和系列性等方面可谓处于世界领先地位。作为测量标尺,保证了地质样品测试数据的可靠性和一致性,显著提高了相关资料的可比性和科学价值,有效地支撑了多个全国性乃至全球性具有影响力的重大地质调查和科研计划的实施。此外,还在仪器校准、方法评定、考核认证等方面发挥了重要作用[3]。近年来,随着国家对检测质量的重视和相关工作的需要,地质标准物质数量显著增加[4],“十三五”期间研制的数量是以往每个五年计划的 3 倍左右(以一级标准物质计,见图 2)。目前已基本构建了种类比较齐全、具有一定数量和影响力的地质标准物质体系,成为世界标准物质体系的重要组成部分。地质标准物质被广泛应用于相关领域的生产、科研和教学,产生了巨大的经济社会效益,但面向国家现代化建设仍然存在个别种类数量稀少、系列性不足、个别指标未定值等问题。本文依据文献资料及国家标准物质资源共享平台发布信息,全面梳理了地质一级标准物质研制成果,分类总结了数量、特点、定值指标等研制情况,在总结成果的基础上分析了上述问题产生的原因。除上述需求方面的问题外,还有一些研制技术会影响定值水平,本文对均匀性测量方法、均匀性未检元素不确定度评定方法、稳定性不确定度评定方法、相对扩展不确定度控制限的制定等细节技术进行讨论。

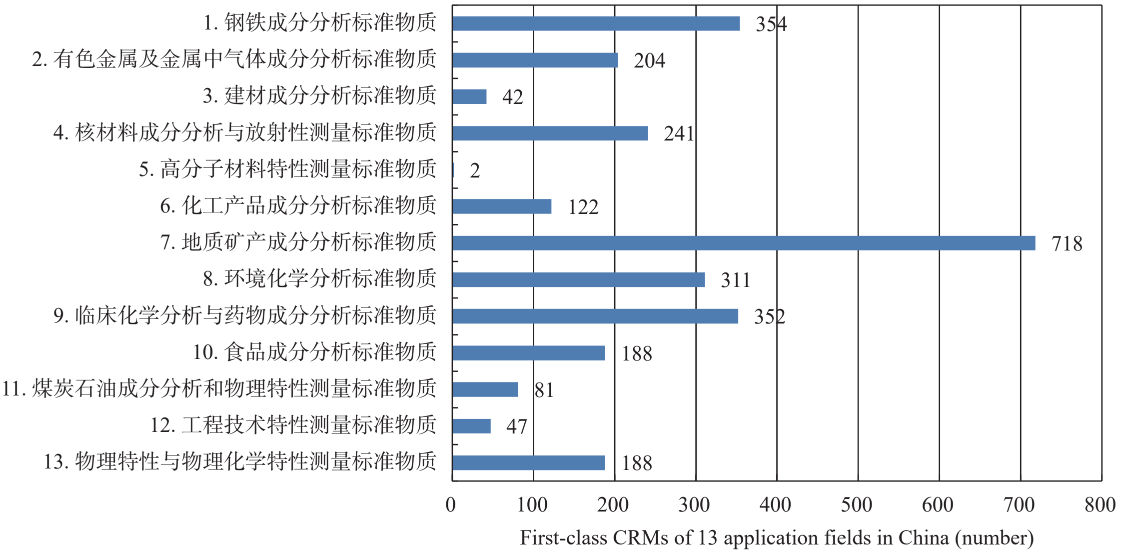

图1　中国十三大类一级标准物质数量

Fig. 1　The numbers of certified reference materials developed in 13 application fields in China.

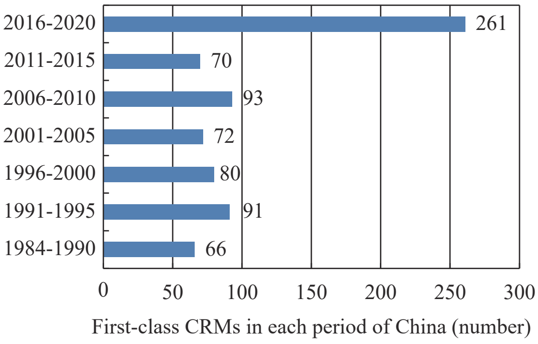

图2　中国各时期国家一级地质标准物质研制数量

Fig. 2　The numbers of geological certified reference materials in each period of China.

1　中国地质标准物质研制现状

地质材料是人类社会发展中最重要、最基本的原材料,其种类繁多、成分复杂、组分含量差异大,正是由于地质材料的复杂性和可靠定量分析的需求[5],造成了如今数以千计的地质标准物质的研制。国家计量管理部门将有证标准物质按定级水平划分为两个级别:一级标准物质 GBW 和二级标准物质 GBW(E)。一级标准物质定值准确度高,均匀性、稳定性、溯源性等属性要求高,研制难度大、成本高,可用于量值的传递、测量仪器的校准、分析方法的评定、实验室认证以及对二级标准物质定值等;二级标准

物质常用于工作标准，用于实验室日常质量控制。中国有证标准物质按属性和应用领域划分为十三大类[6-7]，地质标准物质归属于第七类（GBW07）。地质样品介质类型丰富，还有一些地质行业单位研制的标准物质在分类管理时划归到其他大类，如同位素标准物质归属第四类（GBW04），生物成分标准物质归属于第十类（GBW10），煤炭标准物质归属于第十一类（GBW11），这些标准物质普遍应用于相关地质工作中。地质标准物质在研制时通常设计为多个基体匹配样品构成一个系列，各系列标准物质的适用对象与应用范围各具特色。基于地质标准物质服务对象、基体材料类型、定值成分特性，结合地质工作特色，考虑重要程度，本文将一级地质标准物质分成基础地质、矿石地质、海洋地质、环境地质、能源地质和特殊用途等六类，总结其研制数量、基体特性、定值指标、适用范围等，详见表 1。

表 1　一级地质标准物质种类、数量和基体特性

Table 1　The type, number and matrix of geological certified reference materials in China.

标准物质种类 Types of CRMs	标准物质名称 Name of CRMs	标准物质国家编号（GBW） Country number (GBW) of CRMs	数量 Quantity	样品基体特性 Sample matrix characteristics	十三五期间研制数量 Quantity developed during the 13th Five-Year Plan period
基础地质类 Basic geology	岩石 Rock	GBW07101 ~ GBW07114, GBW07120 ~ GBW07136, GBW07725 ~ GBW07732, GBW07835 ~ GBW07837, GBW07870 ~ GBW07874, GBW07397 ~ GBW07400	51	超基性岩、花岗岩、安山岩、玄武岩、石英砂岩、页岩、石灰岩、花岗质片麻岩、斜长角闪岩、霓霞正长岩、粗面岩、花岗闪长岩、辉长岩、流纹岩、白云岩、辉绿岩、金伯利岩、伟晶岩、蛇纹岩、石英岩、含铀砂岩、二辉斜长麻粒岩、峨眉山玄武岩、辉石橄榄岩、炭硅质页岩、炭质硅质岩、富硒岩石、南极玄武岩、南极凝灰岩、碳酸盐岩 Ultrabasic rocks, granite, andesite, basalt, quartz sandstone, shale, limestone, granitic gneiss, plagioamphibolite, aegirine syenite, trachyte, granodiorite, gabbro, rhyolite, dolomite, diabase, kimberlite, pegmatite, serpentine, quartzite, uraniferous sandstone, diplagioclase granulite, Emei Mountain basalt, pyroxene peridotite, carbonaceous siliceous shale, carbonaceous siliceous rocks, selenium-rich rocks, Antarctic basalts, Antarctic tuff, carbonate rocks	17
	水系沉积物 Stream sediment	GBW07301 ~ GBW07312, GBW07317 ~ GBW07332, GBW07343 ~ GBW07351, GBW07358 ~ GBW07366 GBW07482 ~ GBW07492, GBW07375 ~ GBW07384	67	包括不同地质背景和景观区、成矿区带的水系沉积物及黄河三角洲沉积物 Including different geological background and landscape areas, metallogenic belt drainage sediment and Yellow River delta sediment	10
	土壤 Soil	GBW07401 ~ GBW07411, GBW07418 ~ GBW07435, GBW07439, GBW07440, GBW07446 ~ GBW07457, GBW07475 ~ GBW07480, GBW07385 ~ GBW07391, GBW07913 ~ GBW07942, GBW07536 ~ GBW07573, GBW07900 ~ GBW07904, GBW07978 ~ GBW07986, GBW07965 ~ GBW07968	142	取自不同地质背景的不同土壤类型，包括丘陵山区、平原区、干旱荒漠区、半干旱草原区、黄土地区、三江源地区，及沿海地区滩涂沉积物与河流沉积物、大流域河口泛滥平原沉积物、底泥，农用地土壤等 Different soil types were obtained from different geological backgrounds, including hills and mountains, plain area, arid desert area, semi-arid grassland area, loess area, three-river headwaters area, coastal tidal flat sediment and river sediment, large basin estuary flood plain sediment, bottom mud, and agricultural land soil	93

（续表 1）

标准物质种类 Types of CRMs	标准物质名称 Name of CRMs	标准物质国家编号（GBW）Country number (GBW) of CRMs	数量 Quantity	样品基体特性 Sample matrix characteristics	十三五期间研制数量 Quantity developed during the 13th Five-Year Plan period
矿石地质类 Ore geology	金属矿石 Metallic ore	GBW07201, GBW07202, GBW07213, GBW07218 ~ GBW07227, GBW07261 ~ GBW07266, GBW07818 ~ GBW07830, GBW07838 ~ GBW07842, GBW07846 ~ GBW07853, GBW07875 ~ GBW07878, GBW07139 ~ GBW07140, GBW07896 ~ GBW07899	55	铁、铬、锰、钒、钛等各种黑色金属矿石 Iron, chromium, manganese, vanadium, titanium and other black metal ores	10
		GBW07231 ~ GBW07241, GBW07279 ~ GBW07287, GBW07162 ~ GBW07176, GBW07141 ~ GBW07149 GBW07367 ~ GBW07374, GBW07894 ~ GBW07895, GBW07199	55	铜、铅、锌、镍（钴）、钨、锡、钼（铋）、锑等有色金属矿石 Copper, lead, zinc, nickel (cobalt), tungsten, tin, molybdenum (bismuth), antimony and other non-ferrous metal ores	2
		GBW07177 ~ GBW07182	6	铝土矿 Bauxite	-
		GBW07150 ~ GBW07161, GBW07183 ~ GBW07188, GBW07392 ~ GBW07396, GBW07733 ~ GBW07735, GBW07890 ~ GBW07893	30	铍、锂、钽、锆、锶等稀有稀土矿石 Beryllium, lithium, tantalum, zirconium, strontium and other rare earth ores	12
		GBW07831 ~ GBW07834	4	锗、镓、铟、铊稀散元素矿石 germanium, gallium, indium, thallium ores	-
	贵金属矿石 Precious metal ore	GBW07203 ~ GBW07209, GBW07228 ~ GBW07230, GBW07242 ~ GBW07248, GBW07297 ~ GBW07300, GBW07801 ~ GBW07810, GBW07854 ~ GBW07864, GBW07255 ~ GBW07260, GBW07288 ~ GBW07294 GBW07340 ~ GBW07342, GBW07194 ~ GBW07198, GBW07736 ~ GBW07737	65	金、银、铂族金属矿石 Gold, silver, platinum group metal ores	13
	硫化物单矿物 Sulfide monomineral	GBW07267 ~ GBW07270	4	黄铁矿、黄铜矿、方铅矿和闪锌矿 Pyrite, chalcopyrite, galena and sphalerite	-
	非金属矿石 Non-metallic ore	GBW07137, GBW07318, GBW07210 ~ GBW07212, GBW07214 ~ GBW07217, GBW07250 ~ GBW07254, GBW07277, GBW07278, GBW07811 ~ GBW07817, GBW07843 ~ GBW07845, GBW07865 ~ GBW07869, GBW07879 ~ GBW07889, GBW07742 ~ GBW07744, GBW07905 ~ GBW07912	53	珍珠岩、海泡石、磷矿石、石灰石、白云石、萤石、砷矿石、重晶石、矽线石、菱镁矿、电气石、透辉石、硅藻土、高岭土、膨润土、凹凸棒 Perlite, sepiolite, phosphate ore, limestone, dolomite, fluorite, arsenic ore, barite, sillimanite, magnesite, tourmaline, diopside, diatomite, kaolin, bentonite, attapulgite	29

（**续表** 1）

标准物质种类 Types of CRMs	标准物质名称 Name of CRMs	标准物质国家编号（GBW） Country number (GBW) of CRMs	数量 Quantity	样品基体特性 Sample matrix characteristics	十三五期间研制数量 Quantity developed during the 13th Five-Year Plan period
海洋地质类 Marine geology	海洋沉积物 Marine sediment	GBW07313 ~ GBW07316, GBW07357, GBW07333 ~ GBW07336, GBW07481	10	黄海、南海、东海、近海、太平洋深海、南极、北极海洋沉积物 Sediment of Yellow Sea, South China Sea, East China Sea, near sea, Pacific, Antarctic Ocean and Arctic Ocean	-
	海洋矿产 Marine minerals	GBW07249, GBW07295, GBW07296, GBW07337 ~ GBW07339	6	多金属结核、富钴结壳 Polymetallic nodules and cobalt-enriched crusts	-
环境地质类 Environmental geology	生物无机元素 Bioinorganic element	GBW07601 ~ GBW07605, GBW10010 ~ GBW10028, GBW10043 ~ GBW10052	34	大米、小麦、玉米、黄豆、圆白菜、菠菜、芹菜、胡萝卜、豆角、大葱、蒜粉、紫菜、大虾、扇贝、鸡肉、猪肝、奶粉、花粉、螺旋藻、人参、黄芪、苹果、灌木枝叶、杨树叶、柑橘叶、茶叶、人发 Rice, wheat, corn, soybeans, cabbage, spinach, celery, carrots, beans, green onions, garlic powder, seaweed, prawns, scallops, chicken, pig liver, milk powder, pollen, spirulina, ginseng, Astragalus, apple, shrub branches and leaves, poplar leaves, citrus leaves, tea leaves, and human hair	-
	土壤元素有效态 Effective state of soil elements	GBW07412 ~ GBW07417, GBW07458 ~ GBW07461, GBW07493 ~ GBW07498	16	黑龙江黑土、辽宁棕壤、河南黄潮土、新疆灰钙土、陕西黄绵土、四川紫色土、安徽黄棕壤、湖北水稻土、江西红壤、广东赤红壤、陕西塿土、陕西黑垆土、青海栗钙土、宁夏灌淤土、甘肃灌漠土、新疆棕漠土 Heilongjiang black soil, Liaoning brown soil, Henan yellow tide soil, Xinjiang gray calcareous soil, Shaanxi leossial soil, Sichuan purple soil, Anhui yellow brown soil, Hubei paddy soil, Jiangxi red soil, Guangdong laterite soil, Shaanxi Lou soil, Shaanxi dark loessial soil, Qinghai chestnut soil, Ningxia irrigated silt soil, Gansu irrigated desert soil, and Xinjiang brown desert soil	6
	元素形态 Element form	GBW07436 ~ GBW07438, GBW07441 ~ GBW07445, GBW07462, GBW07463, GBW07974 ~ GBW07977, GBW07464 ~ GBW07468	19	土壤和沉积物元素形态、湖泊沉积物中磷形态、土壤碳形态、地下水砷价态 Elemental morphology in soil and sediment, phosphorus morphology in lake sediment, soil carbon morphology, arsenic valence state in groundwater	4
	元素可提取态 Element extractable state	GBW07943 ~ GBW07964	22	土壤重金属元素可提取态 Extractable state of heavy metal elements in soil	22
	有机成分 Organic ingredients	GBW07469 ~ GBW07474, GBW07352 ~ GBW07355	10	土壤中有机氯农药和多氯联苯与沉积物中多环芳烃 Organochlorine pesticides and polychlorinated biphenyls in soil and polycyclic aromatic hydrocarbons in sediment	4
能源地质类 Energy geology	生油岩 Oil source rock	GBW07115 ~ GBW07119	5	灰色泥岩、黑灰色泥岩、深灰色页岩、深灰绿色泥岩、紫红色致密页岩 Gray mudstone, black gray mudstone, dark gray shale, dark gray green mudstone, purple tight shale	-
	煤 Coal	GBW11139 ~ GBW11154	16	肥煤、气煤、1/3 焦煤、弱黏煤、焦煤、贫瘦煤、无烟煤、长焰煤、气煤、气肥煤 Fat coal, gas coal, 1/3 coking coal, weak viscous coal, coking coal, lean coal, anthracite, long flame coal, gas coal, gas fertilizer coal	-
	页岩气 Shale gas	GBW07499 ~ GBW07500	2	碳质泥岩、煤 Carbonaceous mudstone, coal	2

（续表 1）

标准物质种类 Types of CRMs	标准物质名称 Name of CRMs	标准物质国家编号(GBW) Country number (GBW) of CRMs	数量 Quantity	样品基体特性 Sample matrix characteristics	十三五期间研制数量 Quantity developed during the 13th Five-Year Plan period
特殊地质类 Special geology	人工合成 Artificial synthesis	GBW07701 ~ GBW07724	24	合成硅酸盐、灰岩、X 射线荧光光谱 Synthetic silicates, limestone, X-ray fluorescence spectra	-
	同位素 Isotope	GBW04409 ~ GBW04419, GBW04421, GBW04422, GBW04435, GBW04436, GBW04439, GBW04458 ~ GBW04461, GBW04476, GBW04477, GBW04494 ~ GBW04497, GBW04507 ~ GBW04510, GBW04701 ~ GBW04703, GBW04137 ~ GBW04141	38	地质年龄标准物质包括铷-锶、钐-钕、铀-铅、铀系、钾-氩、氩-氩法、铼-锇等;稳定同位素标准物质包括硫化银硫同位素、硅酸盐氧同位素、碳酸盐碳氧稳定同位素、海洋沉积物碳氮稳定同位素、有机化学物质碳氮稳定同位素、石英砂岩和纯试剂硅同位素、富钴结壳锇同位素、水中氢氧同位素、单体碳同位素 The reference materials for geological age include rubidium-strontium, samarium-neodymium, uranium-lead, uranium series, potassium-argon, argon-argon process, and rhenium-osmium; stable isotope reference materials include silver sulfide sulfur isotope, silicate oxygen isotope, carbonates carbon oxygen isotope, marine sediments carbon nitrogen stable isotope, organic chemicals carbon nitrogen stable isotope, quartz sandstone and pure reagent silicon isotope, cobalt-rich crust osmium isotope, hydrogen and oxygen isotope in water, and monomer carbon isotope	16
	电子探针 Electronic probe	GBW07501 ~ GBW07535	35	方铅矿、闪铅矿、辰矿、重晶石、白铅矿、白钨矿、铌锰矿、碲化镉、硒化锌、砷化镓、硒化锌、锑化铟、磷化铟、砷化铟、氧化锌、铌酸钾、铅玻璃、硼玻璃、蓝晶石、黄铁矿、橄榄石、歪长石、铬铁矿、石英、锰铁榴石、五磷酸钪、五磷酸镧、五磷酸铈、五磷酸镨、五磷酸钕、五磷酸钐、五磷酸钆、五磷酸钬、五磷酸镱、五磷酸镥 Galena, amphibolite, chenite, barite, cerussite, scheelite, mangancolumbite, cadmium telluride, zinc selenide, gallium arsenide, zinc selenide, indium antimonide, indium phosphates, indium arsenide, zinc oxide, potassium niobate, lead glass, boron glass, cyanite, pyrite, olivine, anorthoclase, chromite, quartz, ployadelphite, scandium pentaphosphate, lanthanum pentaphosphate, cerium pentaphosphate, praseodymium pentaphosphate, neodymium pentaphosphate, samarium pentaphosphate, gadolinium pentaphosphate, holmium pentaphosphate, ytterbium pentaphosphate, lutecium pentaphosphate	-
	物相分析 Phase analysis	GBW07189 ~ GBW07193, GBW07271 ~ GBW07276, GBW07738 ~ GBW07741	15	金矿石、铁矿石、铋矿石 Gold ore, iron ore, and bismuth ore	4
	土壤特定用途 Soil specific use	GBW07969 ~ GBW07973	5	土壤界限含水率 Soil limit water cnotent	5
		GBW07987 ~ GBW07998	12	土壤酸碱度 Soil pH	12

1.1　基础地质类

岩石、土壤、水系沉积物是地质工作中最常见的采样介质,是基础地质调查研究的主要对象。用这三种介质所研制的标准物质是定值元素最多、研制量和应用消耗量最大的一类地质标准物质。目前已研制有 260 个,包括岩浆岩、沉积岩和变质岩三大岩类的主要类型岩石,不同地质背景和不同景观条件的水系沉积物,以及不同地质背景、不同区带的不

同类型土壤。定值指标包含主次量成分及除惰性气体、不稳定元素和贵金属元素外的绝大部分微量和痕量元素，一般为 70 种左右，最多达 74 种。这类标准物质主要以服务国家和部门地质调查计划的实施而研制，为中国区域地球化学调查取得系列重要成果提供了坚实保障。

1.2　矿石地质类

矿石地质类标准物质是品种类型最丰富的一类地质标准物质。目前已研制有 272 个，包括：贵金属矿石、金属矿石、单矿物、非金属矿石等，具体包括：金矿、银矿、铂族金属矿、铁矿、锰矿、铬铁矿、钒矿、钛矿、铝土矿、铜矿、铅矿、锌矿、钨矿、锡矿、钨铋矿、镍矿、镍钴矿、钼矿、铼钼矿、锑矿、稀土矿、钽矿、锆矿、锂矿、铍矿、锶矿、稀散元素矿、磷矿、砷矿、石灰石、白云石、萤石、重晶石、矽线石、菱镁矿、电气石、透辉石、硅藻土、珍珠岩、海泡石、高岭土、膨润土、凹凸棒等主要矿种的主要矿床成因类型和工业类型。定值指标包含主要成矿元素、可综合利用元素、具有找矿和评价意义的微量元素以及脉石主成分等，一般为 20 种左右。多数矿石标准物质呈系列化，主要成矿元素含量涵盖矿石边界品位→工业品位→富矿→精矿，主要用于地质勘查、矿产选冶、综合利用、商检贸易等不同领域检测的监控标准。

1.3　海洋地质类

海洋地质类标准物质是海洋沉积物测量和海洋矿产资源调查与研究必备的化学成分计量标准，可以为海洋物质来源、沉积环境、全球变化等海洋科学研究提供科学依据，对于海洋环境综合管理、资源开发利用、海域划界等具有重要意义。海洋地质类标准物质样品采集最为困难。目前研制数量较少，共计 16 个，分别为 1 个近海、1 个黄海、2 个南海、1 个东海、3 个太平洋深海、1 个南极海洋、1 个北极海洋等 10 个海洋沉积物标准物质，与 3 个多金属结核、3 个大洋富钴结壳等 6 个海洋矿产标准物质。定值指标与基础地质类标准物质相同，包含主次量成分与微量和痕量元素，定值元素数 51 ~ 71 种。

1.4　环境地质类

环境地质类标准物质是为服务生态环境地球化学调查评价以及农业、环保等相关工作所需，而发展研制的一类地质标准物质。目前已研制有 101 个，包括土壤元素有效态、土壤和沉积物元素形态、地下水元素价态、土壤元素可提取态、生物无机元素及土壤和沉积物中有机污染物成分标准物质。研制种类主要与服务对象有关，特性指标指向性明确。定值指标主要是生物样品中的无机元素全量，水中元素的价态，土壤和沉积物中元素的有效态、形态及有机氯农药、多氯联苯、多环芳烃等成分。这一类标准物质为土地质量地球化学调查评价、区域生态地球化学评价、多目标地球化学调查及土壤污染状况详查等工作提供了基础技术支撑。

1.5　能源地质类

中国能源矿产资源种类丰富，主要有煤、石油、天然气、页岩气、油页岩、铀、地热等。能源矿产资源勘查、评价与合理利用同样离不开标准物质作为技术支撑，目前地质行业单位研制的能源矿产类标准物质有 23 个，包括：生油岩标准物质，定值指标为有机碳、热解烃 S_2、热解峰温 $T_{\max}$、氯仿沥青“A”；煤炭标准物质，定值指标为热值、灰分、挥发份、全硫、碳、氢、氮、真相对密度及磷、氯、氟、砷；高演化烃源岩标准物质，定值指标为热解烃 S_2、热解峰温 $T_{\max}$、总有机碳 TOC。

1.6　特殊用途类

一定时期内专项地质调查、地质研究或特殊用途的地质标准物质计 129 个。包括人工合成标准物质、同位素标准物质、电子探针标准物质、物相分析标准物质及土壤界限含水率标准物质和土壤酸碱度标准物质等土壤特定用途标准物质。

1.6.1　人工合成标准物质

固体进样分析仪器需要固体粉末标准物质制作工作曲线，而天然地质体的基体组成复杂，在元素组合、含量范围、空白元素、干扰校正等方面无法满足实际工作需要，采用天然物质添加化学试剂的方式制备人工合成的标准物质可满足需求。目前已研制有 20 个合成发射光谱和 4 个 X 射线荧光光谱分析用人工标准物质，定值指标为 28 ~ 29 种无机化学元素。

1.6.2　同位素标准物质

同位素组成被广泛应用于地质年代学和物源示踪研究[8]，同位素分析技术的快速发展迫切需要建立同位素标准物质[9]。目前由地质行业单位研制的同位素标准物质包括 13 个地质年龄标准物质和 25 个稳定同位素标准物质，定值指标包括同位素丰度、同位素丰度比。

1.6.3　电子探针标准物质

电子探针分析是现代矿物学和岩石学研究的重要技术手段，可用来研究微区成分及其变化[10-11]，其定量分析是在相同条件下标准物质 X 射线强度相比较确定元素含量，更加需要标准物质控制准确度。

电子探针标准物质要求微米尺度范围是均匀的[12-13]，许多情况下采用合成矿物，或者人工配制的玻璃代替天然矿物。目前研制的电子探针标准物质包含有矿物、化合物、人工晶体 35 种，定值指标一般为 2 种矿物主成分。

1.6.4　物相分析标准物质

物相分析在地质勘探、矿床评价以及资源利用等方面具有重要作用，但由于矿床、矿物类型复杂，方法针对性又较强，应用受到限制，因而标准物质也较少，目前仅有 6 种铁矿石、5 种金矿石和 4 种铋矿石化学物相标准物质。铁矿石物相分析标准物质定值指标为：磁性铁中铁（MFe）、碳酸铁中铁（CFe）、硫化铁中铁（SFe）、赤褐铁中铁（OFe）、硅酸铁中铁（SiFe）和总铁（TFe）；金矿石化学物相分析标准物质定值指标为：游离自然金（F_{Au}）、连生体金（L_{Au}）、硫化物中金（S_{Au}）、其他矿物中金（A_{Au}）和总金（T_{Au}）；铋矿石化学物相分析标准物质定值指标为：铋（Bi）、氧化矿铋（OBi）、辉铋矿铋（SBi）。

1.6.5　土壤特定用途标准物质

土壤是重要的地质样品介质类型，目前除常见的土壤地球化学标准物质外，还有一些其他理化指标的土壤标准物质，包括土壤界限含水率标准物质和土壤酸碱度标准物质。土壤界限含水率标准物质定值指标为 10mm 液限、塑限、塑性指数[14]，是划分土质类别、评价土的工程性质的重要依据，也是黏土矿勘查和工业利用中重要的评价指标；土壤酸碱度标准物质定值指标为 pH，是土壤质量的重要指标，研制不同土壤类型、具有酸碱梯度的系列土壤酸碱度标准物质，对评估土壤酸碱程度和制定合理的土壤培肥措施具有重要意义。

2　中国地质标准物质现阶段问题与分析

2.1　部分品种数量少、系列化程度不足、基质类型单一、特性量种类少

中国研制了覆盖各种地质样品类型、种类丰富、数量众多的地质标准物质，但现阶段应用中在研制数量、特性量系列化、基体类型等方面存在以下问题。

（1）研制数量少、样品代表性不足。如战略地位凸显的海洋地质类、微观地学研究的微区分析、支撑国家安全的能源矿产类等领域标准物质研制数量较少，相关样品分析测量结果的准确性和可靠性难以保证，制约地质调查、科学研究和分析技术发展。

（2）特性指标量值分布梯度系列化程度不足。如当前备受关注的战略性金属矿产钨、钴、铌钽、铍、锆、铪、锗、镓、铟、铊、稀土等标准物质，主要成矿元素多为低端含量，缺乏作为国际贸易主体的富矿品位和选矿产品的含量品级，而钾盐、硼矿、石墨等非金属矿产标准物质空白，不利于分析测试的质量控制和结果的量值溯源。

（3）基质类型单一、特性量种类少。如日渐重视的生态环境检测中的有机污染物标准物质，样品基质类型仅有土壤和湖泊沉积物，定值特性也只包含有机氯农药、多氯联苯、多环芳烃等目标化合物，种类众多的目标物的检测质量控制主要依靠于进口标准物质，无法满足国家生态文明建设、健康地质调查等新时期地质科技创新和调查工作的需求。

这些问题产生的原因主要有：①样品获得困难，天然样品采集难、成本高，或符合要求的样品筛选复杂；②相关工作研究薄弱、总体部署少，市场需求不足，研制积极性不高；③样品制备和保存技术限制，均匀、稳定特性难以保证；④分析检测手段少，测试误差大，准确定值难。

2.2　现有成熟标准物质仍有多种成分难定值

目前，基础地质类标准物质研制技术成熟、定值指标全面，环境地质类标准物质研制数量日渐增多、种类逐渐丰富，被广泛应用于地质调查、生态地质、农业地质等领域。这些标准物质中，仍有许多调查、评价和研究所需的重要指标未能定值或仅给出了参考值，本文仅探讨元素含量低、测试中的干扰两个主要问题。

（1）元素含量低、准确测试难。定值成分多的岩石、土壤、沉积物等地质标准物质，因基体复杂，各成分在不同样品中含量差异较大，一些元素含量较低，处于研制时分析方法检出限附近甚至检出限以下水平，如 N、Br、Cl、Hg、I、S、Te 等元素，缺乏充足数据未能定值或者仅给出参考值。这种因元素含量低而难定值的情况在生物元素成分标准物质、元素地球化学形态成分标准物质、有效态成分标准物质中更为多见。

（2）测试干扰、定值数据分散。水系沉积物标准物质 GBW07379 的 Se，协作定值的 10 组实验室平均值数据从 0.22μg/g 到 2.33μg/g，其含量远大于原子荧光光谱法（AFS）检出限 0.01μg/g，但数据分散未能定值。后经分析发现，原子荧光光谱仪的激发光源中含有 Pb，当样品中 Pb 含量高时会导致 Se 测试结果偏高[15-16]，GBW07379 为铅锌矿区样品，Pb 含量高达 2690μg/g，AFS 法测定 Se 时受到了 Pb 的正干扰。

有学者[17]采用提高溶液酸度消除干扰，实际工作中也有采用焙烧半熔法[18]分解样品消除干扰。干扰现象在光谱测试中，谱线重叠和质谱测试中双电荷离子干扰尤为常见。在土壤标准物质研制过程中就曾发现，电感耦合等离子体质谱法(ICP-MS)测试元素Ga时存在双电荷干扰现象，定值实验室报出的数据明显呈两个含量段分布，无法定值。经分析研究，ICP-MS方法测试时$^{138}Ba^{2+}$对$^{69}Ga^{+}$存在双电荷干扰[19-20]，样品中Ba的含量超过500μg/g时正干扰较为明显，后请相关实验室选择同位素$^{71}Ga^{+}$重新测试，数据一致，使得Ga得以定值。这种情况也可在溶样时增加H_2SO_4，使之形成$BaSO_4$沉淀以消除干扰。

2.3　定值方法单一

岩石、土壤、水系沉积物等标准物质中的F、Hg、Se、U、Tl及多数稀土元素，目前检测方法单一，缺少不同原理方法相互核验，通常采用增加定值实验室数量，获得尽量多的有效测量组数，以弥补方法单一的不足。随着分析测试技术向快速高效、多元素同时测试的方向发展，一些元素的分析方法逐步被现代化大型仪器分析方法取代，如土壤样品检测中，测试Br和Cl的离子色谱法，测试W、Mo的极谱法，测试Cd、In的石墨炉原子吸收光谱法等方法正逐渐被ICP-MS法取代，土壤标准物质中这些元素的定值方法也将趋于固定。再如中子活化分析法，具有灵敏、准确、基体效应小以及无试剂空白影响等优点，特别适合痕量和超痕量元素分析[21-22]，曾被广泛应用于含量很低的生物元素标准物质的定值，经统计，50%以上的定值元素都使用该方法[23]，但因反应堆逐渐关闭，新近研制的生物成分标准物质未能使用中子活化法，致定值元素中一半以上的元素主要使用ICP-MS法测试。

3　地质标准物质研制细节技术探讨

目前地质标准物质除存在上述应用需求方面的问题外，在研制技术中也存在一些技术问题。中国标准物质是依法管理的计量器具，计量部门参照ISO国际指南制定了统一的技术规范来指导并规范化研制和准确定值，其中《标准物质研制 (生产) 机构通用要求》(JJF 1342)、《标准物质定值的通用原则及统计学原理》(JJF 1343)、《地质分析标准物质的研制》(JJF 1646)、《标准物质计量溯源性的建立、评估与表达计量技术规范》(JJF 1854)等规范是目前地质标准物质研制执行的标准。系列规范明确了研制过程的各项共性技术要求，然而由于地质样品基体的复杂性，均匀性、稳定性与定值环节中的一些细节技术会影响定值水平，包括均匀性检验测量方法、均匀性未检元素不确定度的评定方法、稳定性不确定度的评定方法及相对扩展不确定度的控制限等，有的是申报审批时关注的热点，有的则不被关注、公开资料又鲜有着墨。本文梳理以下四方面展开讨论。

3.1　均匀性检验测量方法

X射线荧光光谱法(XRF)曾是地质标准物质均匀性检验广泛采用的测量方法。然而，由于最小取样量问题，XRF在均匀性检验中的适用性成为争论焦点。JJF 1343—2012要求，均匀性评估后应给出最小取样量，通常将均匀性检验时的称样量作为最小取样量。XRF称样量一般为4g，远大于当前地质标准物质常见的最小取样量0.1g，也远大于当前广泛使用的ICP-MS法和电感耦合等离子体发射光谱法(ICP-OES)等方法的称样量。JJF 1343—2012发布实施后研制的系列一级标准物质[24-30]多采用ICP-MS和ICP-OES法在0.1g称样量下开展均匀性检验。ICP-MS和ICP-OES作为现代分析的支柱方法，在标准物质研制中已成为主体定值方法。初步统计近五年来一级标准物质研制所使用的定值测试方法，在常见的73种无机元素中约有50余种元素的主要定值方法是这两种方法，占全部定值方法50%以上。以这两种方法开展均匀性研究的测量精密度等同于定值方法精密度，从统计结果来看，测试精密度总体低于XRF，个别元素精度相对较差，可能造成总不确定度中引入偏大的均匀性不确定度分量。

针对XRF称样量问题，早有学者[31-33]计算了理论上的有效样品量，一部分元素的有效样品量小于0.1g，但还有一些元素的有效样品量大于0.1g，具有随着元素的原子序数增加而增大的趋势，且这一数据是理论计算值，不满足实验研究确定的要求。近年来，又有学者[34-35]改进XRF制样装置，研究了0.1g称样量下方法的准确度和精密度，并验证了用于均匀性检验的应用效果，但该项研究只实验了土壤和水系沉积物标准物质中10个主量成分，其他基体类型标准物质、微量和痕量元素，特别是重元素还没有开展研究实验。因此，0.1g取样量的方法可行性还有待于进一步验证。

均匀性检验要求测量方法精密度越高越好，这样才可忽略方法误差，使测量结果真实地反映样品均匀状况。XRF是非破坏测量技术，减少了样品分解过程引入的其他误差，对主次量元素具有较高测量精密度，又可同时测定多种元素，是高效、绿色的

现代化分析的良好选择。XRF应用于标准物质均匀性检验还有赖于不同领域的专家学者们，从物理学、光谱学和化学计量学等多学科方向进行共同的深入研究和探讨，方可获得既符合科学原理又满足实际需求的理想答案。

3.2　均匀性检验未检元素不确定度评定方法

JJF 1343—2012规定，均匀性检验合格后，将方差分析结果S_{bb}作为均匀性不确定度分量u_{bb}，计入总不确定度。但地质材料组成复杂、化学成分多、含量跨度大，一般难以做到对所有定值元素都进行均匀性检验。JJF 1646—2017规定，此时应根据待测特性的浓度范围和元素的地球化学分类，选择具有代表性和不易均匀的特性作均匀性评估，未检特性可依据其浓度和元素性质参照已检特性引入的不确定度进行评估，但u_{bb}的具体计算方法和元素的地球化学分类未作规定。本文建议采用一种兼顾元素性质、含量、测试技术的均匀性未检元素不确定度三要素评定方法。

①按元素性质分类。一般岩矿物料的地质标准物质中主要涉及76种元素，按地球化学性质分成9类（表2）；②按元素含量级次分类，分为%、μg/g、ng/g三个等级；③按定值主体测试方法分类（全部定值方法中占比最大的方法为该元素的主体测试方法）。前两点是规范JJF 1646—2017要求的必备条件，第三点非必备条件却很重要，因相同测试方法的误差来源一致，引入的不确定度相关性更强。在引入计算时，若第三点满足，则筛选三要素都符合的已检元素作为引入评定的依据；若第三点不满足，则筛选符合前两个条件的已检元素参照引入。具体计算方法是，以已检元素的均匀性相对不确定度U_r，即已检元素的均匀性不确定度$u_{bb(已检)}$与标准值$\mu_{(已检)}$之比，乘以未检元素的标准值$\mu_{(未检)}$，作为未检元素的不确定度分量$u_{bb(未检)}$。这种计算方法进一步考虑了元素的含量水平差异，例如同为μg/g级含量的元素，量值可能为几百、几十、几个μg/g，以相对量计算的方式消除绝对量的粗大影响。总的想法就是未检元素参照已检元素引入计算u_{bb}时，考虑元素分类和含量级次的同时，兼顾测试方法。

还有一些成分如FeO、H_2O^+、CO_2、Corg、LOI等，不在元素的地球化学性质分类表中，通常又

表2　未检元素均匀性实验不确定度的计算依据参照已检元素

Table 2　Calculation basis for the uncertainty of elements without homogeneity test.

序号 No.	要素 Factor	分类选择的依据 Basis for classification
1	按元素的地球化学性质分类 Classification by geochemical properties of elements	造岩元素 Rock forming elements（SiO_2, Al_2O_3, MgO, CaO, Na_2O, K_2O） 铁族元素 Iron group elements（Ti, V, Cr, Mn, Fe, Co, Ni） 稀有稀土元素 Rare earth elements（Li, Be, Rb, Cs, Nb, Ta, Zr, Hf, Sc, Ym, REE） 放射性元素 Radioactive elements（U, Th） 钨钼族元素 Tungsten-molybdenum group elements（W, Sn, Mo, Bi） 亲铜成矿元素 Chalcophile metallogenic elements（Cu, Pb, Zn, Au, Ag, As, Sb, Hg） 分散元素 Disperse elements（Sr, Ba, Cd, Ga, In, Tl, Ge, Se, Te, Re） 矿化剂及卤族元素 Mineralizer and halogen elements（B, C, N, P, S, F, Cl, Br, I） 铂族元素 Platinum group elements（Pt, Pd, Os, Ir, Ru, Rh）
2	按元素含量进行量级分类 Classification of magnitude by element content	%, μg/g, ng/g
3	按元素测量方法分类 Classification by element measurement method	筛选定值元素的全部测试方法中占比最大的方法作为该元素的主体测试方法，将均匀性已检元素和未检元素按主体测试方法分类。 The method with the largest proportion among all the test methods for screening the element with a fixed value is used as the subject test method of the element. The elements tested and untested for uniformity are classified according to the subject test method.

难以开展均匀性检验，这些成分在岩石、土壤、沉积物、矿石等常见样品类型中一般均为百分含量，可以参考同含量级次的造岩元素计算引入 u_{bb}。

3.3　稳定性不确定度评定方法

天然地质物料在自然条件下经过百万年尺度的形成和稳定过程，大多数岩石矿物都不易变质，稳定性较易达到[36-37]，从已有系列地质标准物质多年使用的情况来看，量值稳定。JJF 1343—2012 规定稳定性评估后应引入稳定性不确定度u_s。

JJF 1343—2012 给出了两种计算稳定性不确定度的方法：趋势分析法和方差分析法。趋势分析法是目前绝大多数地质标准物质评价稳定性所采用的方法，该法是将监测时长内各监测时间点的观测值建立直线方程，计算拟合直线的斜率 b_1 和斜率的标准偏差$s(b_1)$，用 t 检验判断斜率是否显著从而评价稳定性。当判定稳定性良好时，$|b_1| < t_{0.05} \times s(b_1)$，用公式$u_s = s(b_1)\cdot t$计算稳定性引入的不确定度，$t$ 是稳定性的监测时长。通常地质标准物质稳定性监测时长超过一年，即 $t \geqslant 12$，u_s 相比$s(b_1)$放大了至少 12 倍，由此可见，稳定性监测时间越长则u_s越大，在构成标准物质总不确定度（U）的三大部分中甚至可能成为主要贡献量，从公开发表且列有不确定度分量的文章中的数据对比可见一斑。目前列有不确定度分量的文章比较有限，文献 [26-27] 和文献 [38-41] 列出了 u_s 和 u_{bb}，文献 [38] 和 [40] 还列出了定值过程引入的不确定度 u_{char}。通过文中数据对比可见，绝大多数指标的 u_s 大于 u_{bb}；对文献 [38] 的数据进一步分析，发现多数指标的 u_s 不仅大于 u_{bb}，还大于 u_{char}，对 U 起主要贡献。将文献 [39] 所报道的泛滥平原沉积物标准物质（GBW07385 ~ GBW07391）研制时的各不确定度分量数据进行对比，也发现绝大多数元素的 u_s 既大于 u_{bb}，也大于 u_{char}，同样对 U 起主要贡献。但若将 u_s 除以 t，则所有元素的 u_s 与 U 相比其贡献量可忽略（远小于 1/3），对文献 [38] 数据作此处理同样也可忽略稳定性的贡献量。可见，趋势分析法计算的稳定性不确定度受监测时长影响，造成其对总不确定度的贡献过大，这与长期以来地质标准物质量值稳定的观测不相适应。

孟凡敏等[42] 建议用趋势分析法判断标准物质是否稳定，用方差分析法计算 u_s。本文作者在研制 GBW07385 ~ GBW07391 时对比了趋势分析法的 $u_{s(趋)}$和方差分析法的 $u_{s(F)}$，发现多数元素的 $u_{s(F)}$小于 $u_{s(趋)}$，也有个别元素的 $u_{s(F)}$大于 $u_{s(趋)}$，且以 $u_{s(F)}$参与计算其对 U 仍是主要贡献。汪斌等[43] 采用质量控制图作为稳定性评估的手段，用极差法计算 u_s，该方式在地质标准物质中应用还有待于验证。综上所述，对测试误差源较多的基体类标准物质其稳定性不确定度的合理评定有待于进一步研究探讨。

3.4　相对扩展不确定度的控制限

地质标准物质特性量值的确定，除定值方式和数据组数等需符合规范要求外，相对扩展不确定度（U_{rel}）还需满足一定控制要求，这是地质标准物质研制的一种习用方案。然而这一控制限在标准物质的公开资料中鲜见介绍，仅在几篇文章中列出了其研制时采用的 U_{rel} 控制范围，《地质分析标准物质的研制》（JJF 1646—2017）对 U_{rel} 作出了原则性要求。这些 U_{rel} 的控制限均根据标准值含量划分不同范围制定，对比发现控制要求大体一致，一些差异体现在对含量级次更细致的划分和更严格的控制。U_{rel} 是定值数据质量的体现，本文根据前人制定的控制范围，以及对不同类型地质标准物质研制的实际情况进行分析，在 JJF 1646—2017 原则性要求的基础上，提出表 3 的 U_{rel} 控制限，在研制过程中还需综合考虑样品的基体情况、定值指标、元素含量及结合当前的分析技术水平制定合理的不确定度 U_{rel} 控制限，以获得准确合理的标准值与不确定度。

4　结语和展望

中国地质标准物质经过 40 余年发展，已基本建立种类丰富、数量众多、指标齐全、量值准确、系列性好、适用性强、国际领先的地质标准物质体系。本文一方面在分类总结地质标准物质研制成果的基础上，分析探究了现阶段存在的主要问题和原因；一方面在国家标准物质研制规范框架下，围绕研制过程的关键环节，对一些技术细节问题进行探讨，包括均匀性检验测量方法、均匀性未检元素不确定度计算方法、稳定性不确定度评定方法、相对扩展不确定度控制限等，以期引起各方重视，不断提升地质标准物质定值水平。

当前，面向国家战略发展和满足地质工作需求，解决现阶段存在的部分品种类型稀少、系列性不足、基体类型单一、特性量种类少等问题，标准物质的研制可从四个方面系列化地开展。服务国家资源安全保障和找矿突破战略，研制三稀金属矿石、大宗优势矿产和紧缺矿产等矿石标准物质；服务“一带一路”地学国际合作，研制符合沿线国家地质背景的、用于基础性调查工作的土壤和水系沉积物等标准物质；服务海洋强国战略，研制海洋沉积物、海洋矿产和海产品等标准物质；服务生态文明建设、健康地质和食

表3　相对扩展不确定度(U_{rel})的控制条件

Table 3　Control conditions of relative extended uncertainty.

含量范围 Content range	控制限 Control limits				
	JJF1646—2017	岩石、土壤、各类沉积物 Rock, soil, sediment	矿石 Ore	生物[23] Biota[23]	有效态、形态、价态 Effective state, form, valence state
>30%	/	⩽1%	⩽2%	/	/
>10%	⩽2%	⩽2%	⩽5%	/	/
>1%	⩽5%	⩽5%		⩽8%	⩽10%
0.1%~1%	⩽10%	⩽10%	⩽10%	⩽10%	⩽15%
100~1000μg/g	⩽15%	⩽15%		⩽15%	⩽20%
10~100μg/g			⩽15%	⩽20%	⩽25%
1~10μg/g	⩽20%	⩽20%	⩽20%		
0.1~1μg/g	⩽25%	⩽25%	⩽30%	⩽25%	⩽30%
<0.1μg/g	⩽30%	⩽30%	⩽35%	⩽30%	⩽35%
<0.01μg/g	⩽35%	/	/	⩽35%	/

注：为表格统一，没有对应含量级次控制限的以“/”表示。

品安全评价，研制基体类型丰富、指标多样的高质量生物元素标准物质与有机污染物标准物质。

随着地质科技与地质调查工作转型升级，地球系统科学理论研究、自然资源综合调查、深海深地科技攻坚、战略性关键矿产勘查评价、健康地质调查、国土空间规划和用途管控等成为新时期地质工作的重要任务。作为重要技术支撑的地质标准物质要发挥基础性作用，还需做好前瞻性、战略性、综合性预判，面向基础研究、资源环境、生态文明、科技创新等热点领域，研制山水林田湖草沙冰等自然资源多要素新介质不同类型标准物质，满足各类地质工作与调查任务样品分析质量监控需求，以服务自然资源调查、评价、监测技术体系。

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Research Progress of Geological Reference Materials in China

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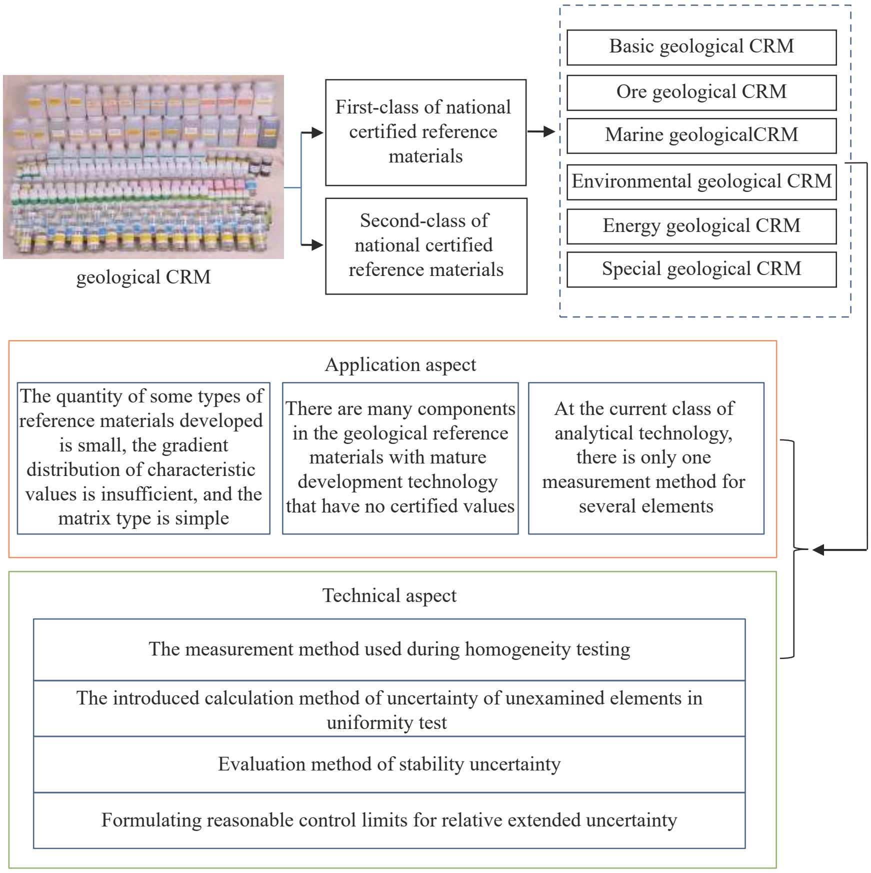
HIGHLIGHTS

(1) The application of X-ray fluorescence spectrometry to the homogeneity test of reference materials is worthy of further study due to its advantages of high precision.

(2) A method is proposed to evaluate the uncertainty of unchecked elements in homogeneity by considering the nature, content and testing technology of elements.

(3) The monitoring time of the trend analysis method is analyzed, which leads to the excessive contribution of the stability uncertainty to the total uncertainty and is not suitable for calculating the stability uncertainty of geological reference materials.

(4) It is suggested to establish reasonable relative extended uncertainty control limits for different sample types to improve the characterization level of geological reference materials.



ABSTRACT: Geological reference material is a primary standard to ensure the accuracy of geological sample analysis results. After more than 40 years of development, China has developed and certified thousands of geological reference materials covering different media such as rock, ore, soil, sediment, organism, and water. China's metrological management department divides the certified reference material into two classes according to the classification class, the first-class reference material (GBW) and the second-class reference material [GBW(E)]. According to their attributes and application fields, they are divided into 13 categories[6-7], and the geological reference materials belong to the seventh category [GBW07 and GBW(E)07]. It can be seen from the National Sharing Platform for Reference Materials (https://www.ncrm.org.cn) that by the end of the 13th Five-Year Plan, the total number of geological reference materials approved by the State Administration for Market Regulation is 1013, including 718 first-class certified reference materials, and the amount of first-class certified reference materials ranks first in the 13 categories (Fig.1). Geological materials are the most important and basic raw materials in the development of human society, with various types, complex components, and large differences in component content. It is because of the complexity of geological materials and the demand for reliable quantitative analysis that thousands of geological reference materials have been developed. Some reference materials developed by some industrial geological agencies are classified into other categories in classification management, such as isotope reference materials belonging to the fourth category, biological composition reference materials belonging to the tenth category, coal reference materials belonging to the eleventh category, these reference materials are widely used in related geological work, and in this paper they will be classified as geological reference materials. To systematically grasp the development status of geological reference materials in China, the first-class geological certified reference materials are comprehensively sorted, and are divided into six categories according to the type of matrix, property value and application scope: basic, ore, marine, environment, energy and special purpose (Table 1),

and the development situation of each type, matrix characteristics and fixed value index respectively are summarized. On the basis of summarizing the results, on one hand, the main problems existing in the application of geological reference materials and the causes of these problems are analyzed. On the other hand, the detailed technical problems that may affect the uncertainty in the process of homogeneity, stability and characterization are discussed, and the views and suggestions are expounded.

In this paper, the first-class geological certified reference materials are divided into the following six categories to summarize the development of each type:

(1) 260 basic geological reference materials have been developed, the type of matrix including rock, soil and river sediments. The characteristic components of the certified value are generally 70 elements and compounds, which are mainly used as monitoring standards for sample analysis in basic geological surveys and research.

(2) 272 ore geological reference materials have been developed, including precious metal ore, metal ore, single mineral, and non-metallic ore. The specific mineral types are shown in Table 1. There are generally 20 property values, which are the main technical indicators in mineral exploration. They are mainly used as a monitoring standard for geological exploration, mineral processing and smelting, comprehensive utilization, commodity inspection and trade amongst other fields.

(3) 16 marine geological reference materials have been developed, including marine sediments and marine minerals. The specific samples include 10 marine sediment reference materials namely, 1 near sea, 1 Yellow Sea, 2 South China Sea, 1 East China Sea, 3 deep Pacific Ocean, 1 Antarctic Ocean and 1 Arctic Ocean. Six marine mineral reference materials are three polymetallic nodules and three ocean cobalt-enriched crusts. The characteristic composition of the certification value is the same as that of the basic geological reference material, but slightly less, generally 51-71 kinds. This is a necessary chemical composition measurement standard for marine sediment measurement and marine mineral resource survey and research.

(4) 101 standard materials for environmental geology have been developed, including the available state of soil elements, the form of soil and sediment elements, the valence state of groundwater elements, the extractable state of soil elements, biological inorganic elements, organic pollutants in soil and sediment and other reference materials. The characteristic components of the matrix and certified values are the total amount of inorganic elements in biological samples, the available states, and forms of elements in soil and sediment, the valence states of elements in water and organochlorine pesticides, polychlorinated biphenyls, and polycyclic aromatic hydrocarbons in soil and sediment. This kind of reference material provides analytical quality monitoring standards for land quality geochemical surveys and evaluation, regional ecological geochemical evaluations, multi-objective geochemical surveys and detailed surveys of soil pollution.

(5) 23 energy geological reference materials have been developed. The property values of oil-generating rock reference materials are organic carbon, pyrolysis hydrocarbon S_2, pyrolysis peak temperature $T_{\max}$, and chloroform asphalt “A”. The property values of coal reference material are calorific value, ash, volatile matter, total sulfur, carbon, hydrogen, nitrogen, true relative density and phosphorus, chlorine, fluorine, and arsenic. The property values of the reference materials of highly evolved hydrocarbon source rock are pyrolysis hydrocarbon S_2, pyrolysis peak temperature $T_{\max}$, and total organic carbon TOC. This is the monitoring standard for the exploration, evaluation and rational utilization of energy and mineral resources.

(6) 129 reference materials for special purposes have been developed, including 20 synthetic reference materials for emission spectroscopy and 4 synthetic reference materials for X-ray fluorescence spectroscopy analysis. The property values are 28-29 inorganic chemical elements. There are 38 isotope reference materials, and the property values of those include isotope abundance and abundance ratio. There are 35 electron probe reference materials, and the property values are generally two principal components of their minerals. There are 15 reference

materials for phase analysis, and the property values are the corresponding main phase. There are 5 soil limit water content reference materials, and the property values are 10mm liquid limit, plastic limit, and plastic index. There are 12 soil pH reference materials, and the property values are pH. It can be seen from the classification and summary that the geological reference material matrix in China is rich in types and quantities, which establishes an influential quality monitoring system for geological sample analysis, ensures the reliability and consistency of geological sample test data, and significantly improves the comparability and scientific value of relevant data.

At present, there are still some problems in the application and development technology of a large number of geological reference materials. The problems are discussed and analyzed, hoping to draw attention to improving the value determination class of geological reference materials. In the aspect of application, the specific problems existing in different types of geological reference materials and their causes at the present stage are analyzed and development suggestions are proposed, according to the work needs of current mineral resources, international cooperation, marine strategy, ecological civilization and other fields. In the aspect of development technology, some detail technologies which may affect the value determination class in the process of homogeneity, stability and characterization are analyzed. In the aspect of development technology, some detail technologies which may affect the setting in the process of homogeneity, stability and value setting are analyzed. The test method of homogeneity and the evaluation method of stability uncertainty are discussed. Suggestions are made for the uncertainty evaluation method of unexamined elements for homogeneity test and control limit of relative extended uncertainty.

1. Three problems existing in the current application of geological reference materials are analyzed:

(1) The quantity of some types of reference materials developed is small, the gradient distribution of characteristic values is insufficient, and the matrix type is simple. For example, the amount of marine geology, micro-area analysis, energy and mineral resource reference material development is small. The ore-forming elements of key metal ore reference materials are mainly low content, lacking rich ore grade or higher content grade. The matrix types of the samples of organic pollutant reference materials are only soil and sediment, and the property values are only organochlorine pesticides, polychlorinated biphenyls, polycyclic aromatic hydrocarbons and other compounds, and the matrix types and target compounds are few. The main reasons for these problems are difficulty in obtaining samples, little working demand, difficulty in ensuring the uniformity and stability of the sample preparation technology, large error of analysis technology unable to determine the value.

(2) There are many components in the geological reference materials with mature development technology that have no certified values. The reasons of low element content and test interference are mainly analyzed.

(3) At the current class of analytical technology, there is only one measurement method for several elements, and for some elements, with the widespread application of modern instrumental analysis technology, the optional measurement method is gradually becoming singular.

2. The detail technology of four aspects in the development of reference material is discussed:

(1) Uniformity testing method. XRF is a widely used measurement method for the uniformity test of geological standard materials due to its high testing precision. However, due to its large sample size, XRF cannot meet the requirements of minimum sample size. Since the release and implementation of China National Technical Specification for Measurement “General and Statistical Principles for Characterization of Reference Materials” (JJF1343) in 2012, the uniformity of reference materials was tested by ICP-MS and ICP-OES under 0.1g weighing sample[24-30]. The measurement precision of these two methods is not as good overall as that of XRF, and the accuracy of individual elements is poor, which may cause the numerical value to be too large when calculating the uncertainty introduced by uniformity, thus affecting the reasonable evaluation of the uncertainty of property value. For this reason, some scholars[34-35] improved the XRF sample preparation device, studied the accuracy and precision

of the method under 0.1g weighing sample, and verified the application effect for uniformity testing. However, only 10 major components in the reference materials of soil and stream sediments were tested under 0.1g weighing sample, while the reference materials of other matrix types and other trace elements, especially heavy elements, have not been studied and tested. Therefore, the feasibility of the XRF method with a sample size of 0.1g still needs to be verified.

(2) Uncertainty calculation method for elements without uniformity test. The composition of geological materials is complex, and its reference substances generally have multiple attribute values, and the content of each component is greatly different, so it is usually difficult to test the uniformity of all attribute values. According to the provisions of JJF1646—2017, the characteristic of representative and less homogeneous should be selected for uniformity evaluation. The uncertainty of the untested elements can be evaluated according to the concentration and geochemical properties with reference to the uncertainty introduced by the tested elements. However, the exact calculation method was not specified. An evaluation method that considers both element properties, content and test methods (Table 2) is presented here. The specific calculation method is to multiply the relative uncertainty (U_r) of the uniformity of the detected element by the standard value μ of the undetected element and take it as the uncertainty component u_{bb} of the undetected element.

(3) Evaluation method of stability uncertainty. At present, trend analysis method is generally used to evaluate the stability uncertainty (u_s) of geological reference materials, and the calculation formula is $u_s=s(b_1)\cdot t$. It can be seen from the formula that the longer the stability monitoring time, the greater the stability uncertainty introduced. The stability uncertainty data of several reference materials were compared and determined to be the main contribution to the total uncertainty, which is inconsistent with the long-term observation of the stability of the geological reference materials. Therefore, this calculation method is not suitable to evaluate the uncertainty introduced into the stability of geological reference material. Meng et al.[42] suggested using the analysis of variance to calculate, and the comparative analysis showed that u_s was still the main contribution to the total uncertainty. Wang et al.[43] used range method to calculate u_s, but the application of this method in geological reference materials has yet to be verified. In conclusion, the reasonable evaluation of stability uncertainty of matrix reference materials with more test error sources needs to be studied further.

(4) Control limits for relative extended uncertainty. The determination of the property value of geological reference materials usually has certain control requirements for relative extended uncertainty (U_{rel}), but these control limits are rarely introduced in the public information of the reference material. It was not until the specification JJF1646 published in 2017 that U_{rel} was required in principle. U_{rel} is the embodiment of the quality of property value data. U_{rel} control limits in Table 3 are proposed on the basis of the principle requirements of JJF1646—2017 by referring to the control limits in the development of existing reference materials and the analysis of different types of geological reference materials. In the process of development, the developer also needs to comprehensively consider the matrix condition, setting index, element content of the sample and formulate reasonable U_{rel} control limits of uncertainty in combination with the current analysis technology class, to obtain accurate and reasonable property value and uncertainty.

KEY WORDS: geological reference material; homogeneity; stability; uncertainty; relative expanding uncertainty

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