

基于蒙乃尔合金溶解度新方法对金属在含氟热液流体中地球化学行为的实验研究

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摘要: 含氟热液流体在热液成矿系统中普遍发育, 且能主导金属的迁移、富集和沉淀成矿过程。溶解度实验可以明确金属在含氟热液流体中的溶解度、迁移形式及其热力学参数, 是研究金属在含氟热液成矿过程的有效手段。然而, 由于传统特氟龙内衬溶解度实验方法材料运行温度($t \leq 250$ °C) 的缺陷, 制约了中高温成矿过程中金属在含氟流体的地球化学行为研究。本文首次将蒙乃尔合金应用于溶解度实验体系, 通过测试蒙乃尔合金耐氟能力实验, 初步确定蒙乃尔合金溶解度新方法在350 °C高温条件具有良好的稳定性, 并且初步开展锡在350 °C条件下含氟流体中的溶解度实验, 证实该方法是研究各类金属在中高温含氟流体中溶解度的有效手段。最后, 对该方法的应用前景做了初步的展望, 期望在与高温含氟热液流体相关的成矿金属地球化学行为研究中得到广泛的应用。

关键词: 蒙乃尔合金; 高温含氟流体; 溶解度实验; 地球化学行为; 成矿过程

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An new experimental study on the geochemical behaviors of metals in fluorine-bearing hydrothermal fluids based on the Monel alloy solubility method

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Abstract: Fluorine-rich hydrothermal fluids are ubiquitous in the ore-forming hydrothermal systems, playing a pivotal role in the ore-forming process including transportation, enrichment, and precipitation of metals. The solubility experiment can be used to determine the solubilities, migration patterns, and thermodynamic parameters of metals within these fluorine-rich hydrothermal fluids. It is effective means for investigating the metallogenic processes of metals associated with the fluorine-bearing hydrothermal fluid. However, the operational temperature limitations of materials ($t \leq 250$ °C) in the traditional Teflon-lined solubility experimental methods had hampered the investigation of the geochemical behaviors of metals in the metallogenic process within the fluorine-bearing fluids at medium-high temperature. In this study, we have firstly applied Monel alloy to the solubility experiment system. Based on experiments for testing the fluorine resistance of Monel alloy, it is basically confirmed that Monel alloy applied in the new solubility experimental method has excellent stability at temperature of 350 °C. Additionally, we have conducted the preliminary solubility experiments of tin in the fluorine-bearing fluid at 350 °C, and have confirmed that this new method is an

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effective means for studying the solubilities of various metals in the fluorine-bearing fluid at medium-high temperature. Finally, a preliminary prospect of the application of this method has been outlined. It is expected that this method will be widely applied to study the geochemical behaviors of ore-forming metals associated with the high-temperature fluorine-bearing hydrothermal fluids.

Key words: Monel alloy; high-temperature fluorine-bearing fluids; solubility experiment; geochemical behavior; metallogenic process

0 引言

氟在多数热液成矿系统中均有富集,如高温的云英岩化W矿床、斑岩型Mo矿床、磁铁矿型IOCG矿床和铁氧化物-磷灰石矿床;中低温的赤铁矿型IOCG矿床,稀土矿床、矽卡岩型矿床和MVT型矿床(Hitzman, 1992; Aksyuk, 2000; Smith and Henderson, 2000; Sillitoe, 2003; Audétat et al., 2011; Chen et al., 2014; Montreuil et al., 2016; Wang et al., 2021)。

前人基于萤石与矿石矿物的空间关系认为氟可以与U、W、Mo、Sn、Be、REE、Ta、Nb等金属元素形成稳定的络合物在热液流体中迁移这些金属元素(Bailey, 1977; Manning, 1981; Eugster, 1985; Keppler and Wylle, 1991; Zhu and Sverjensky, 1991; Williams et al., 1995; Wood and Samson, 1998),然而对于这些成矿金属在含氟热液流体中的地球化学行为仍不清楚。近年来随着钛合金特氟龙内衬反应釜在溶解度实验的应用,前人对金属元素在中低温含氟热液流体中的地球化学行为进行研究并取得重要成果。

然而由于特氟龙稳定工作的温度区间为-180~250℃(郁伟石, 1985),导致特氟龙内衬溶解度实验方法局限于成矿金属在中低温含氟热液流体中地球化学行为的研究。传统的溶解度实验方法无法研究成矿金属在中高温含氟流体中的地球化学行为,如与云英岩化相关的W、Sn矿床,与U矿化相关的IOCG矿床(Xie et al., 2009; Xing et al., 2018)。在一定程度上限制了与高温含氟热液相关金属矿床成矿机制的深入研究。

近年来随着合金材料的不断发展,蒙乃尔合金以优良的耐氢氟酸和酸碱特性为研究金属在高温含氟流体中的地球化学行为提供技术保障。由于本研究首次将蒙乃尔合金应用于溶解度实验室体系,为评估蒙乃尔合金在溶解度实验应用的可行性,进行蒙乃尔合金在高温(350℃)条件下不同氟浓度实验。实验结果表明蒙乃尔合金溶解度新方法在高温条件下耐氟能力与特氟龙内衬实验方法极限温度在30 mmol/kg氟离子条件下的耐氟能力相当,证实了应用蒙乃尔合金开展金属在含氟热液流体中溶解度实验的可行性。在此基础上初步开展锡在含氟高温流体中的溶解度实验,评估蒙乃尔合金溶解

度实验新方法在获得溶解度实验数据的可重复性,并探讨该方法在热液成矿理论研究中的应用。

1 含氟热液流体性质及其热液成矿过程中的作用

氟原子序数9,原子量18.998,位于元素周期表第二周期VIIA组,是卤族元素中最轻、最活泼的元素。由于氟化学性质活泼、氧化性强,几乎能与所有元素化合,自然界中氟通常以离子的形式存在于萤石(CaF_2)和冰晶石($\text{Na}_3[\text{AlF}_6]$)中(刘俊和胡金波, 2019)。根据软硬酸碱理论,氟是硬碱可以与 REE^{3+} 、U(IV/VI)等硬酸离子形成稳定的络合物(Pearson, 1963; Williams-Jones et al., 2000; Bastrakov et al., 2010)。前人通过大量的流体包裹体研究表明,含氟热液流体具有极低的pH,如Hansonburg矿床含氟流体pH为1~2.4; Illinois-Kentuck矿床富氟流体pH为0~1.4(Kenderes and Appold, 2017; Smith-Schmitz and Appold, 2021)。含氟流体的温度为120~240℃,密度为0.8~1.0 g/cm³(刘道荣和商朋强, 2024)。

含氟热液流体与成矿关系密切,如在IOCG矿床中富氟的长英质岩浆与矿体具有密切的空间关系(Hitzman, 1992; Williams et al., 2005; Chen and Zhou, 2012; Chen and Zhou, 2015),在REE矿床中稀土矿物富含大量的氟,如氟碳铈矿和氟碳铈钙矿,并且流体包裹体中氟碳铈钍子晶发育(Fan et al., 2004; Zheng et al., 2021)。目前认为含氟热液流体在成矿过程中主要发挥以下作用:①氟可以与金属形成稳定的络合物在热液流体中运载金属。Nb、Ta、W在 $t \leq 250^\circ\text{C}$,水饱和和蒸汽压条件下,随着氟浓度的升高分别以 $\text{Nb}(\text{OH})_4^+$ 和 $\text{NbF}_2(\text{OH})_3$ 、 $\text{Ta}(\text{OH})_5$ 、 $\text{TaF}_3(\text{OH})_3$ 和 TaF_5 、 H_2WO_4 和 $\text{H}_3\text{WO}_4\text{F}_2$ 的形式迁移富集;REE和Sc在含氟流体中主要以 REEF_2^{2+} 和 ScF_2^+ 和 ScF_3 的形式迁移富集(Migdisov and Williams-Jones, 2007; Migdisov et al., 2009; Loges et al., 2013; Timofeev et al., 2015, 2017; Wang et al., 2021; Wang et al., 2022)。②含氟热液流体在成矿系统中可以为成矿流体开辟通道。酸性的含氟流体通过破坏硅酸盐和氧化物的硅氧键和金属与氧原子的共价键,促使硅酸盐和氧化物的溶解,为流体运移创造通

道(Kline and Fogler, 1981; Keppler and Wyllie, 1991)。③含氟流体具有成矿专属性。在云英岩化成矿系统中, 氟的活度决定着白钨矿和黑钨矿的稳定性, 在低HF活度形成白钨矿, 随着HF活度增高白钨矿转变为黑钨矿和萤石(Pollard et al., 1987; Pirajno, 2012)。

2 蒙乃尔合金性质及其应用

蒙乃尔合金是镍基耐腐蚀的Cu-Ni合金, 以70%的镍和30%的铜组成, Ni主要提供合金的钝化能力而Cu则提高合金在还原介质中的耐腐蚀性(薛慧涛等, 2023)。蒙乃尔合金颜色呈白色, 硬度比钢强, 在盐类及碱类溶液中具有有良好的耐腐蚀性(徐晓刚和郑建国, 2005; Shoemaker and Smith, 2006; Krelling et al., 2019)。由于Ni与S和O容易发生反应形成 Ni_3S_2 和 NiO , 因此, 蒙乃尔合金不抗含硫介质和氧化性介质的腐蚀, 在非氧化性酸(硫酸、盐酸、磷酸、氢氟酸)具有良好的抗腐蚀性(陆钰珍, 2020)。

蒙乃尔合金具有优良的抗氢氟酸性能, 可以在各种浓度的氢氟酸中使用, 甚至在10%氢氟酸沸点下依然可以使用。因蒙乃尔合金具有优良的抗氢氟酸性能在工业中通常作为输送氢氟酸的设备和阀门(陆钰珍, 2020)。

3 实验方法及流程

3.1 蒙乃尔合金的耐氟性实验

蒙乃尔合金具有优良的耐氢氟酸腐蚀性, 在工业上常用于输送氢氟酸的管道以及耐氢氟酸的阀门(陆钰珍, 2020)。蒙乃尔合金的耐氢氟酸性与温度和氢氟酸的水含量相关。当氢氟酸中含有质量分数为0.5%的水时, 蒙乃尔合金表面会生成一层致密的氧化膜阻止氢氟酸对合金的腐蚀, 当 $t \leq 149\text{ }^\circ\text{C}$ 时温度与氧化膜的厚度呈正相关, 温度超过 $149\text{ }^\circ\text{C}$ 氧化膜的致密度下降(赵鹏和张茂, 2021)。对于高温条件下, 蒙乃尔合金能否在溶解度实验中应用有待量化研究。为探究蒙乃尔合金在溶解度实验应用的可行性, 对蒙乃尔合金反应釜进行耐氟性测试。将 $\text{pH}=3$ 、氟浓度为 $4.8\sim 237.6\text{ mmol/kg}$ 的溶液放置在蒙乃尔合金釜中在 $350\text{ }^\circ\text{C}$ 条件下运行5 d(图1)。

实验前笔者使用5% HCl将蒙乃尔釜酸浸7 h, 目的是洗去反应釜中可能存在的金属离子。接着用超纯水浸泡24 h洗去反应釜中可能残留的HCl, 待浸泡完成之后放入干燥箱中烘干备用。此后将蒙乃尔反应釜螺帽使用石墨润滑喷雾剂进行润滑处理备用。

通过在去离子超纯水中溶解定量纯度为99.99%的NaF粉末和质量分数为36%的浓盐酸分别控制实验

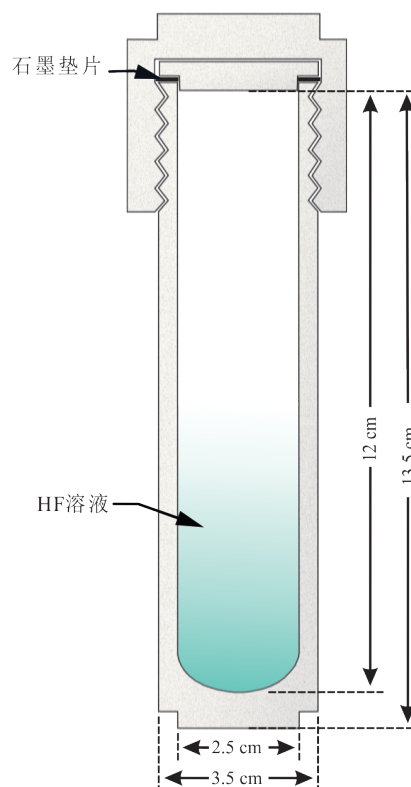


图1 蒙乃尔合金釜示意图(修改自 Wang et al., 2023)

Fig.1 Schematic diagram of the Monel alloy autoclave
(modified from Wang et al., 2023)

溶液的氟离子浓度和 pH 。实验开始前用移液枪量取15 mL的实验溶液放入蒙乃尔釜内, 盖上蒙乃尔金属盖用扳手拧紧螺帽使反应体系密闭。将密闭的反应釜放入已调至目标温度的反应炉中, 待运行设定的天数后, 将其取出置于流动的冷水中淬火至室温。打开反应釜取出3 mL实验溶液, 测试其在室温条件下的氟离子浓度以及 pH 值。在整个实验过程中, 对涉及物质加入或取出的步骤进行称量记录, 以备数据处理分析阶段进行质量平衡计算。

溶液中的氟离子浓度采用氟离子选择电极法测试, 该测试在中国地质大学(北京)成矿模拟实验室完成, 所用设备为氟离子选择电极(perfectION™)。该电极测试的型号范围为 $-2000\sim 2000\text{ mV}$, 精度为 $\pm 0.1\text{ mV}$, 氟离子测试的极限为 10^{-6} mol/L 。配置氟离子浓度为 0.001 、 0.005 、 0.01 、 0.05 、 0.1 、 0.5 mol/L 的6份标准溶液校准氟离子测试电极。在测试过程中, 标准溶液和实验测试溶液需要以1:1比例添加TISAB II溶液(去离子水 $>84\%$, 醋酸钠 $=8\%$, 氯化钠 6% , 醋酸 1% , 环己二胺四乙酸 $<1\%$, Thermo Fisher Scientific)调节控制离子强度。测试结果见表1。

3.2 蒙乃尔合金溶解度新方法可行性研究

该组实验探究蒙乃尔合金溶解度新方法在溶解度

表 1 蒙乃尔合金耐氟实验反应前后氟离子浓度变化表
Table 1 A table for change of fluorine ion concentrations before and after experimental reactions for testing the fluorine resistance of Monel alloy

编号	温度/℃	反应前lg mF ⁻	反应后lg mF ⁻	运行天数
Monel-1	350	-0.624	-0.731	5
Monel-2	350	-0.902	-0.990	5
Monel-3	350	-1.162	-1.243	5
Monel-4	350	-1.465	-1.510	5
Monel-5	350	-1.735	-1.808	5
Monel-6	350	-1.886	-1.984	5
Monel-7	350	-2.317	-2.353	5

注:m=mol/kg。

实验应用的可行性,将过量的纯度为99.99%的SnO₂粉末放置在pH=3、温度为350 ℃和320 ℃的水饱和蒸汽压条件下运行5 d。实验前的准备工作与3.1操作步骤相同。

前期准备工作完成后,将一端封口且盛放SnO₂固体粉末的蒙乃尔合金小管放入蒙乃尔合金反应釜中,用移液枪量取15 mL的实验溶液沿反应釜内壁缓慢加入反应釜中。将反应釜密闭后放入已设置目标温度的反应炉中,待反应釜各组分达到反应平衡后将其取出置于冷水中淬火至室温。打开蒙乃尔合金反应釜,取出装有SnO₂粉末的蒙乃尔小管,用去离子水冲洗浸泡48 h备用。用移液枪从反应釜中取出3 mL实验溶液测试反应后溶液的pH值和氟离子浓度。完成上述步骤后,取5 mL的质量分数为36%的浓盐酸沿蒙乃尔合金内壁缓慢加入,确保将淬火阶段可能结晶在反应釜壁上的沉淀物质全部溶解在溶液内,待其静止2 h后取出5 mL的溶液用于ICP-MS测试分析。上述过程中,从反应釜淬火至室温到取出盛放SnO₂粉末的小管总计时控制在40分钟内。将反应后的溶液进行电感耦合等离子质谱仪(ICP-MS)分析溶液中Sn的含量,ICP-MS分析测试在中国地质科学院进行。测试结果见表2。

表 2 不同温度SnO₂溶解度实验数据
Table 2 Experimental data of SnO₂ solubilities at different temperatures

编号	温度/℃	反应后lg mF ⁻	lg mSn	运行天数
SnM-1	350	-1.777	-4.965	5
SnM-2	350	-1.808	-4.920	5
SnM-3	320	-2.280	-6.000	5
SnM-4	320	-2.305	-5.934	5

注:m = mol/kg。

4 实验结果及分析

实验结果由图2可知,蒙乃尔合金在浓度为4.8~

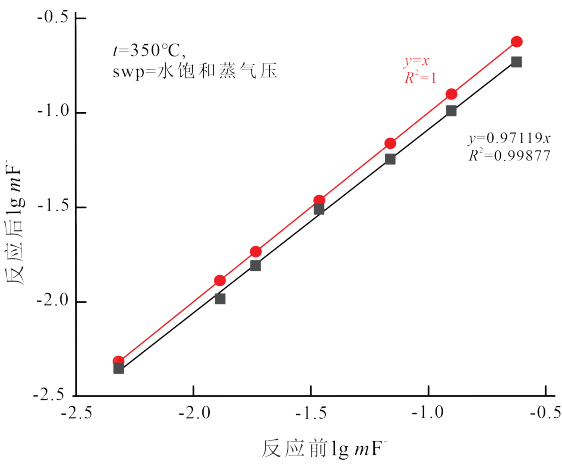


图2 反应前lg mF⁻和反应后lg mF⁻关系
Fig.2 The logarithm of fluorine ion molalities before and after the reaction experiment

237.6 mmol/kg的含氟溶液中,在350 ℃的条件下运行5 d,反应前、后F⁻浓度具有明显的线性关系,斜率为0.97119,R²=0.99877,表明蒙乃尔合金在高温含氟热液具有良好的耐氟性。然而,随着F⁻浓度的增加,反应前后F⁻差值也逐渐增大,暗示蒙乃尔合金的耐腐蚀性与F⁻浓度呈反比。

此外,分别进行SnO₂在350 ℃和320 ℃,lg mF⁻浓度分别为-1.808 ~ -1.777和 -2.305 ~ -2.280溶解度实验。SnO₂在不同温度相似氟浓度条件下溶解度具有较高的重复性(图3),表明蒙乃尔合金溶解度新方法在含氟体系溶解度实验的应用中具有高度的可行性。

为了评估蒙乃尔合金溶解度新方法研究不同金属在含氟流体中地球化学行为的应用,我们对蒙乃尔合金在含氟流体中的背景元素进行检测,检测结果见表3。溶液中REE的含量总体范围为0~1.3×10⁻⁹,除Lu含量

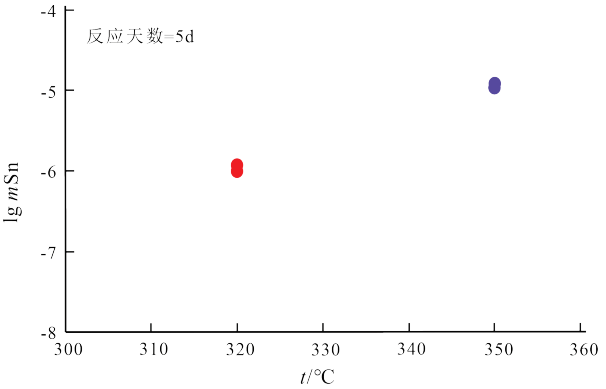


图3 不同温度含氟体系下SnO₂溶解度的重复性实验
Fig. 3 Repeated experiments on the solubilities of SnO₂ in fluorine-bearing fluids at different temperatures

表3 蒙乃尔合金含氟溶液中金属背景元素测试结果

Table 3	Results of background elements in the fluorine-bearing fluid within Monel alloy container												(×10 ⁻⁹)		
	Ti	V	Cr	Mn	Co	Ni	Cu	Y	Mo	REES	Ta	W	Th	U	Sn
SnM-1-0	69.0	10.9	551.7	3725.1	188.4	129856.0	68034.0	8.5	62.0	0-1.3	0.1	4.8	0	0	0.1

注：检测限为0.1×10⁻⁹。

相对较高(1.3×10⁻⁹)其他稀土元素几乎为0。Ta、Th和U含量相对较低,分别为0.1×10⁻⁹, 0.1×10⁻⁹和0.1×10⁻⁹。W、Y、V的含量分别为4.8×10⁻⁶, 8.5×10⁻⁹和10.9×10⁻⁹。Ti、Mo、Co的含量相对较高为69.2×10⁻⁹, 62.04×10⁻⁹和188.4×10⁻⁹。背景元素中含量相对高的为Ni、Cu、Cr和Mn, Ni和Cu含量分别为129.9×10⁻⁶和68.0×10⁻⁶, Cr和Mn分别为551.7×10⁻⁹和3725.1×10⁻⁹。因此,蒙乃尔合金溶解度新方法研究REE、Ta、U、Th、W在含氟体系的地球化学行为是可行的。

5 新的溶解度实验方法对成矿金属在含氟热液流体中地球化学行为研究的应用前景

本文开展在高温不同氟浓度的溶液中蒙乃尔合金的耐氟性以及蒙乃尔合金在溶解度应用的实验,结果表明蒙乃尔合金溶解度新方法在溶解度实验中应用具有高度可行性。蒙乃尔合金溶解度实验新方法可以解决传统溶解度实验特氟龙工作温区低(-180~250℃)的问题,是一种研究金属在高温含氟流体地球化学行为的有效方法。该方法有望在与U、REE相关的IOCG矿床和W、Sn相关的云英岩化矿床中研究U、REE、W和Sn金属元素在高温含氟流体中的地球化学行为。此外,U和Sn是变价元素,可以通过添加氧逸度缓冲剂控制体系氧逸度的方式研究在不同氧逸度高温含氟热液流体中元素的地球化学行为。近年来大量的地质证据表明高温的火山蒸汽对金属的运输可能存在重要的作用。大量的黄铜矿、辉钼矿、锡石、黑钨矿、白钨矿和自然金等矿物在火山蒸汽中凝结沉淀(Naboko, 1964; Stoiber and Rose, 1974; Symonds et al., 1987; Quisefit et al., 1989; Bernard et al., 1990; Taran et al., 2000)。安山质火山蒸汽中相对玄武岩蒸汽具有相似的Cu、Zn、Pb、As含量,但是具有更高的Mo和Hg,含量分别为3×10⁻⁶和340×10⁻⁹(Symonds et al., 1987; Taran et al., 1995)。其次,在日本的Usu和Satsuma Iwojima火山中分别可见7×10⁻⁶的Sn和1×10⁻⁶的Mo(Giggenbach and Matsuo, 1991; Hedenquist et al., 1994)。火山蒸汽主要为H₂O、CO₂、SO₂和HCl,还含有少量H₂、HF、H₂S等挥发分(Symonds et al., 1994; Taran et al., 1995, 2000)。Migdisov和Williams-Jones

(2005)研究了SnO₂在300~350℃, 15000 KPa条件下气相HCl的溶解度,在实验条件下溶解了0.32×10⁻¹²~288.43×10⁻¹²的Sn,远低于地质事实(7×10⁻⁶),暗示HCl并非是主导Sn在气相溶解富集的主要因素。根据软硬酸碱理论,F是硬碱离子Sn⁴⁺是硬酸离子可以形成稳定的配合物,因此HF可能对SnO₂在气相条件下的溶解度发挥重要作用。然而,传统的钛合金反应釜易与HF反应,不利于研究金属在气相HF的溶解度,蒙乃尔合金釜具有高的耐HF的特点,是研究金属在气相含氟条件下溶解度的有效手段。

6 结论

(1)不同氟浓度的溶液在350℃条件下,蒙乃尔合金中运行5 d,反应前后lg mF浓度具有明显的线性关系,且斜率为0.97119, R²=0.99877,表明蒙乃尔合金具有良好的耐氟性能。

(2)SnO₂在蒙乃尔合金溶解度实验不同温度,相似氟浓度条件下具有可重复的溶解度,表明蒙乃尔合金溶解度新方法在研究金属地球化学行为的应用是可靠的。

(3)采用蒙乃尔合金溶解度实验新方法能有效克服传统特氟龙内衬方法在中低温研究金属地球化学行为的瓶颈,是研究金属在高温含氟流体中地球化学行为的有效手段。

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