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碳酸盐矿物阴极发光影响因素研究 ——以鄂尔多斯盆地南缘奥陶系中下统为例

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摘要 【目的】碳酸盐矿物阴极发光特征与其主微量元素及稀土元素含量之间具有密切关系, 现有研究主要关注 Mn 和 Fe 对阴极发光的影响, 忽视了稀土元素的作用。通过探讨主微量元素和稀土元素对碳酸盐矿物阴极发光特征的影响, 旨在为推断矿物成因、沉积环境及成岩过程提供地质依据。【方法】采用阴极发光和激光剥蚀电感耦合等离子体质谱(Laser Ablation Inductively Coupled Plasma Mass Spectrometry, LA-ICP-MS)技术对鄂尔多斯盆地南缘奥陶系中下统的碳酸盐岩样本进行测试, 并结合数理统计和分类算法对测试数据进行分析, 使用稀土元素常用指标分析成岩流体性质。【结果】基质白云石在阴极射线下发弱—中红色光, 具环带发光和均匀发光现象, 胶结物白云石 Mn 和 Fe 含量高, 常为环带发光或不发光; 经方差分析(Analysis of Variance, ANOVA)和 Tukey 的诚实显著差异检验(Tukey's Honestly Significant Difference Test, Tukey's HSD)事后检验得到 Mn、Fe、La、Ce、Pr、Nd、Sm、Eu、Gd、Tb 含量和 Fe/Mn 对碳酸盐矿物阴极发光影响程度较大; 不发光组和强发光组较易区分, 不发光组一般为碳酸盐矿物的 Fe 含量大于 $10\ 000\times 10^{-6}$ 或 Mn 含量小于 40×10^{-6} , 同时 Fe 含量大于 $10\ 000\times 10^{-6}$ 的不发光组碳酸盐矿物稀土元素配分曲线富中稀土元素(Middle Rare Earth Element, MREE), 而强发光组稀土元素配分常表现为轻稀土元素(Light Rare Earth Elements, LREE)亏损, Fe/Mn 比值小的特征, 利用主微量和稀土元素降维的综合参数与 Mn 含量的关系可有效地将极弱发光组、弱发光组和中发光组区分; 成岩阶段的成岩流体性质影响碳酸盐沉积物组成和矿物成分以及主微量稀土元素含量的变化, 对碳酸盐矿物阴极发光有直接影响。【结论】结合原位主微量元素测试和多种数据处理方法, 可以更好地量化主微量元素和稀土元素含量对阴极发光强度的影响, 对于研究阴极发光影响因素具有重要借鉴意义。

关键词 碳酸盐矿物; 阴极发光; LA-ICP-MS; 成岩阶段; 奥陶系

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0 引言

碳酸盐岩沉积范围广泛, 约占全球沉积岩面积的 20%, 其中, 海相碳酸盐岩储层蕴藏丰富的油气资源, 约占全球油气储量的 46.8%, 目前国内外多数盆地已经发现了以海相碳酸盐岩为主的油气田(汪泽成等, 2013; 王大鹏等, 2016; 马永生等, 2017; 沈安江等, 2019; 孙斌等, 2022; 熊加贝和何登发, 2022)。以古生界为主的海相碳酸盐岩是我国陆上油气勘探的重要

领域, 塔里木台地盆地地区奥陶系(陈叔阳等, 2024; 杨德彬等, 2024), 四川盆地川北地区二叠系和川中地区震旦系—寒武系(马慧等, 2021; 苏桂萍, 2021; 魏国齐等, 2022), 鄂尔多斯盆地奥陶系(岳小娟, 2017; 陈强等, 2022; 兰书琪等, 2024; 单俊峰等, 2024; 苏文杰等, 2024; 熊加贝等, 2024)等, 均发现了一批大型碳酸盐岩油气田, 具有良好的油气勘探前景。阴极发光技术(Cathodoluminescence, CL)是研究识别碳酸盐岩矿物类型并揭示其形成环境条件的重要手段之一(黄思

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静, 1990; Yacobi and Holt, 1990; Pagel *et al.*, 2000; Toffolo *et al.*, 2020), 其通过发射高能电子束与岩石样品相互作用, 导致样品中的电子吸收能量并跃迁至更高的能级, 电子在返回较低能态时以光的形式释放能量, 光的波长和强度依赖于矿物内部主微量元素、晶格缺陷及束流密度等因素, 尤其是 Mn 和 Fe 的影响。对于碳酸盐矿物, Mn^{2+} 为矿物阴极发光的激活剂, 会使纯方解石阴极发光颜色为黄色, 镁方解石为橙色, 白云石为红色, 文石为绿色, 而 Fe^{2+} 是猝灭剂, 抑制矿物阴极发光(黄思静, 1992; 刘洁和皇甫红英, 2000; 徐惠芬等, 2006; 刘丽红等, 2010; Schertl 和李旭平, 2022)。目前针对碳酸盐矿物阴极发光特征研究多体现在 Fe 和 Mn 含量对阴极发光的影响上, 忽略了稀土元素对碳酸盐矿物的影响, 同时主微量元素测试方法一般使用电子探针、原子吸收光谱或高温高压密闭溶样法(刘大卫等, 2022), 这些测试方法在测试精度、测试选区及多元素分析等方面均不如激光剥蚀电感耦合等离子体质谱的原位测试结果(Wang *et al.*, 2021; 张世华等, 2022; Paul *et al.*, 2023; 支太云, 2023; 李晨星等, 2025)。阴极发光技术与 LA-ICP-MS 技术结合使用, 可以有效地分析储层的物源、成岩作用序列、胶结作用类型、孔隙演化及沉积成岩环境, 已经在地学中广泛应用(黄思静, 1990; 刘金连等, 2010; 兰叶芳等, 2015, 2017; Sobolev *et al.*, 2017)。

本文针对鄂尔多斯盆地南缘奥陶系中下统的冶里组—亮甲山组和马家沟组中不同类型碳酸盐矿物在阴极射线下的发光特征, 结合 LA-ICP-MS 测试数据, 使用数理统计分析及分类算法研究数据内在联系, 综合分析碳酸盐矿物阴极发光特征与主微量元素和稀土元素之间的关系, 并且系统分析碳酸盐流体成岩作用对碳酸盐矿物阴极发光的影响。

1 区域地质概况

研究区位于鄂尔多斯盆地南缘, 北起甘肃省庆阳市, 南到陕西省麟游县, 西至陕西省陇县, 东抵陕西省铜川市, 地跨甘、陕两省, 包含伊陕斜坡、渭北隆起以及天环凹陷三个构造单元(包洪平等, 2020; 张晓星等, 2020; 师平平, 2021; 丁超等, 2024; 赵航等, 2024)。研究区奥陶系发育完整, 主要有下奥陶统冶里组、亮甲山组、马家沟组马一段、马二段和马三段, 中奥陶统马家沟组马四段、马五段和马六段, 上奥陶统平凉组和背锅山组。南缘奥陶系与下伏寒武系连

续沉积, 而与上覆石炭系呈不整合接触关系, 盆地不同区域对于奥陶系划分以及命名具有一定区别, 整体上冶里组—亮甲山组、马家沟组与平凉组—背锅山组的分层界限是一致的(苏中堂, 2011; 熊斌, 2014; 高春云和周立发, 2019; 陈强等, 2022; 王香增等, 2022; 张军涛等, 2022; 兰书琪等, 2024; 熊加贝等, 2024)(图1)。

2 研究方法 with 结果

2.1 样品制备与测试方法

选取河津西磴口剖面($110^{\circ}43'13.62''$ E, $35^{\circ}43'21.60''$ N)、岐山崛山沟剖面($107^{\circ}43'11.30''$ E, $34^{\circ}31'55.97''$ N)以及岐山曹家沟剖面($107^{\circ}45'03.50''$ E, $34^{\circ}30'35.67''$ N)中具有代表性的碳酸盐岩样品磨成多用片(16片), 用于阴极发光和 LA-ICP-MS 原位测试分析, 相关样品分析在西南石油大学油气藏地质及开发工程全国重点实验室完成。阴极发光由 CL8200 MK5 阴极发光显微镜拍照分析, 电压为 15 kV, 束流电流为 400 μ A, 温度为 20 $^{\circ}$ C, 相对湿度为 60%。碳酸盐矿物 LA-ICP-MS 原位测试在装备有 ASI Resolution LR 193 nm 激光剥蚀系统的 iCap-TQ 的 ICP-MS 上进行, 测试过程采用 SQ 模式, 测试前利用 NIST 612 的线扫方式对 ICPMS 进行调谐, 光斑为 50 μ m, 频率和能量分别为 10 Hz 和 3 J/cm², 调整 ICP-MS 的灵敏度, 同时保证氧化物产率小于 1%。激光剥蚀过程中采用 300 mL/min 的氦气作载气、0.87 L/min 氩气为雾化器流速, 同时设置 5 mL/min 的高纯氮以调节灵敏度。激光束斑和频率分别为 67 μ m 和 8 Hz, 激光能量密度为 3 J/cm², 以 MACS-3 为外标, ⁴³Ca 为内标, 利用 iolite 软件完成数据处理(Woodhead *et al.*, 2007; Paton *et al.*, 2011)。

2.2 碳酸盐岩阴极发光特征

鄂尔多斯盆地南缘奥陶系中下统以发育白云岩为主, 白云岩一般发育在局限台地的潮上带和潮间带, 若海水蒸发程度强烈(蒸发台地), 白云岩可与膏岩共生, 冶里组—亮甲山组白云石晶体普遍较大, 而马家沟组白云石晶体一般较小, 灰岩一般以泥晶为主。根据朱筱敏(2020)碳酸盐岩粒级的划分方案, 将研究区白云岩划分为泥晶—粉晶碳酸盐岩(碳酸盐矿物粒径小于 0.1 mm)和砂晶碳酸盐岩(碳酸盐矿物粒径 0.1~2.0 mm)两大类, 按产状可以划分为基质碳酸盐矿物和胶结物碳酸盐矿物(马慧等, 2021)。

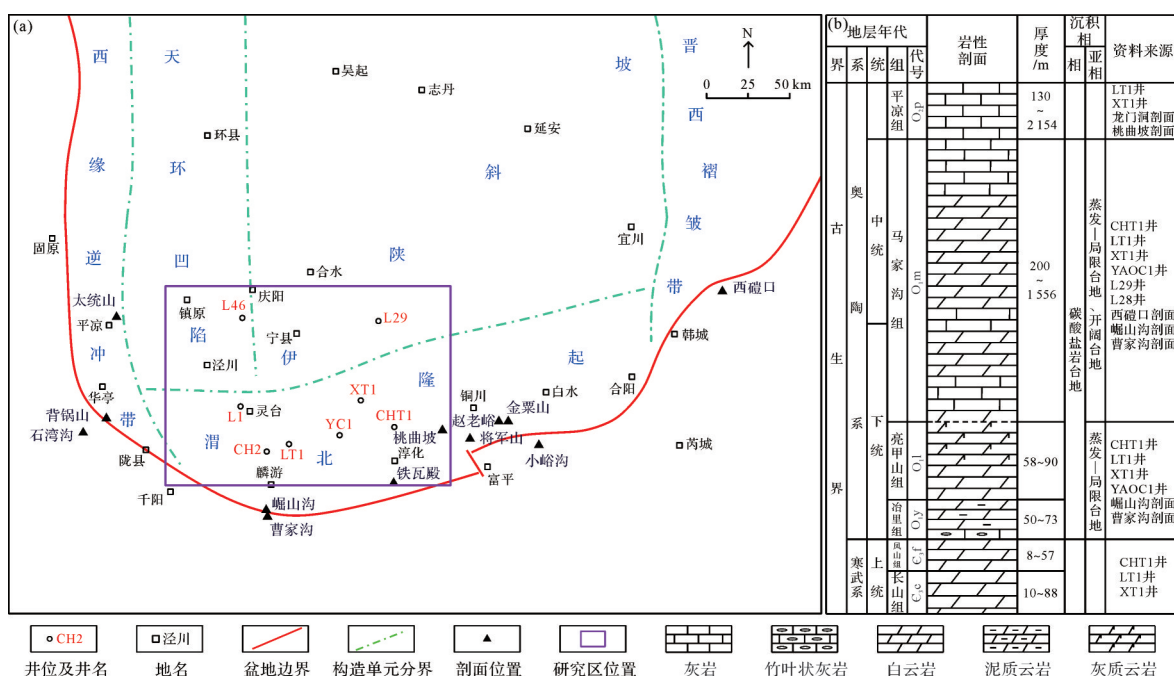


图1 研究区综合地质背景图

(a)构造图及研究区位置;(b)奥陶系中下统综合柱状图

Fig.1 Integrated geological background map of the study area

(a) structural map and location of the study area; (b) comprehensive stratigraphic column of the Lower and Middle Ordovician

泥晶—粉晶白云岩在阴极射线下发弱—中红色光,以基质白云石为主(图2a~d,g~j),其中图2b中的X35-1为马家沟组上部的细粉晶云岩,发中红色光,阴极发光中可见裂缝充填具环带结构的晶簇状方解石发强橘黄色光。X30-1样品中泥晶白云岩呈褐黄色结核状产出,发弱红色光,围岩泥晶灰岩不发光,可见裂缝充填的亮晶方解石发弱橘黄红色光,亦可见粉晶—细晶方解石具有核心不发光但边缘发橘黄红色光(图2c~f)。J13-1样品为粉晶—细晶云岩,在阴极发光下见白云石晶体的环带发光构造,具从白云石中心至白云石边缘依次为小范围明亮—暗淡—明亮的发光特征(图2g,h)。

砂晶白云岩(细晶、中晶、粗晶和极粗晶),阴极射线主要表现为不发光—强红色光,偏光显微镜下发现砂晶白云岩孔隙中常发育晶粒大的白云石,常为粗晶或极粗晶(图2i~t)。基质白云石晶体单偏光下雾心亮边构造常见,一般发弱—中红色光,环带发光现象常见,多表现为明亮—暗淡—明亮的发光特征(图2g~n),也可见在阴极发光下表现出均匀发弱红色光现象(图2q,r)。x5-2胶结物白云石见环带构造,同时阴极射线环带发光特征较为明显,白云石从中心至晶体边缘依次发暗红色—弱暗红色—不发光—亮红色光(图2o,p),亦见x6-4胶结物白云石

在阴极射线不发光(图2s,t)。

2.3 LA-ICP-MS测试结果及碳酸盐矿物微量元素和稀土元素特征

结合阴极发光以及薄片显微镜下特征,针对性地对16块样品磨制的多用片使用LA-ICP-MS进行测试,共测试62组数据,其中包括Al、Sc、Ti、V、Cr、Mn、Fe等33种元素,通过对异常数据的整理以及去除未打在碳酸盐矿物的数据点,共保留57组数据,包括Al、Mn、Fe、Co、Ni、Cu、Zn等24个元素,其中9个主微量元素和15个稀土元素(附表1)。稀土元素分为三部分:(1)轻稀土元素(LREE),包括La、Ce、Pr和Nd;(2)中稀土元素(MREE),包括Sm、Eu、Gd、Tb、Dy和Ho;(3)重稀土元素(HREE),包括Er、Tm、Yb和Lu,碳酸盐岩的REE研究通常包括元素Y,在配分图解上插在Dy和Ho之间。Ce异常(Ce/Ce^*)使用 $2Ce_N/(La_N+Pr_N)$ 计算,Gd异常(Gd/Gd^*)使用 $2Gd_N/(Eu_N+Tb_N)$ 计算,Eu异常(Eu/Eu^*)使用 $2Eu_N/(Sm_N+Gd_N)$ 计算,N代表使用后太古宙澳大利亚页岩(Post-Archean Australian Shale, PAAS)标准化后REE+Y的值(Webb and Kamber, 2000; Kamber and Webb, 2001; van Kranendonk *et al.*, 2003; Bolhar *et al.*, 2004; Hohl *et al.*, 2015; 王宇航等, 2018; 赵彦彦等, 2019; 朱士波, 2024)。

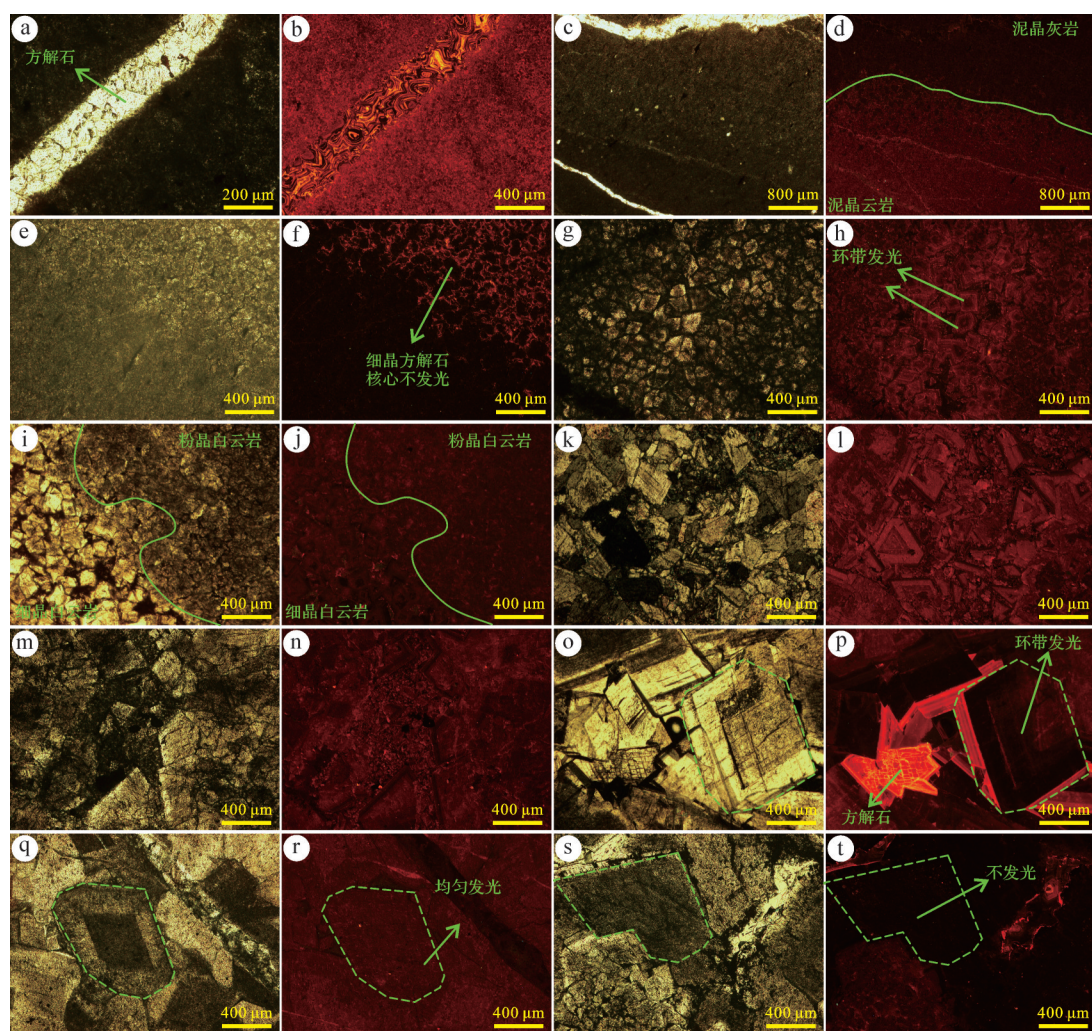


图2 碳酸盐岩阴极发光特征

(a)灰质细晶白云岩,裂缝被方解石充填,西磴口X35-1,马家沟组,多用片,(-);(b)灰质细晶白云岩,细晶白云岩发中红色光,裂缝方解石见明亮环带(强橘黄色光),西磴口X35-1,马家沟组,阴极发光;(-);(c)泥晶白云岩,裂缝被方解石充填,西磴口X30-1,马家沟组,多用片,(-);(d)泥晶白云岩,白云石发弱红色光,围岩泥晶灰岩不发光,西磴口X30-1,马家沟组,阴极发光;(-);(e)泥晶细晶白云岩,方解石重结晶,西磴口X30-1,马家沟组,多用片,(-);(f)泥晶细晶白云岩,泥晶方解石不发光,细晶方解石核心不发光,边缘发橘黄色光,西磴口X30-1,马家沟组,阴极发光;(-);(g)粉晶细晶白云岩,雾心亮边,峨山沟J13-1,马六段,多用片,(-);(h)粉晶细晶白云岩,环带发光,峨山沟J13-1,马六段,阴极发光;(-);(i)粉晶细晶白云岩,西磴口X6-4,马家沟组,多用片,(-);(j)粉晶细晶白云岩,细晶白云石与粉晶白云石发光程度一致,西磴口X6-4,马家沟组,阴极发光;(-);(k)中晶白云岩,曹家沟C10,冶里—亮甲山组,多用片,(-);(l)中晶白云岩,环带发光,曹家沟C10,冶里—亮甲山组,阴极发光;(-);(m)中晶粗晶白云岩,曹家沟C12,冶里—亮甲山组,多用片,(-);(n)中晶粗晶白云岩,环带发光,曹家沟C12,冶里—亮甲山组,阴极发光;(-);(o)中晶极粗晶白云岩,白云石具环带结构,西磴口X5-2,马家沟组,多用片,(-);(p)中晶极粗晶白云岩,极粗晶白云石具暗红色—弱暗红色—不发光—亮红色光交替出现的环带发光,方解石发强橘黄色光,西磴口X5-2,马家沟组,阴极发光;(-);(q)粗晶极粗晶白云岩,雾心亮边,曹家沟C07,冶里—亮甲山组,多用片,(-);(r)粗晶极粗晶白云岩,白云石发光均匀,曹家沟C07,冶里—亮甲山组,阴极发光;(-);(s)细晶白云岩,溶蚀孔充填的极粗晶白云石,西磴口X6-4,马家沟组,多用片,(-);(t)细晶白云岩,溶蚀孔充填的极粗晶白云石不发光,西磴口X6-4,马家沟组,阴极发光

Fig.2 Cathodoluminescence characteristics of carbonate rocks

从主微量元素箱型图中可以发现,胶结物白云石与基质白云石Al、Mn和Fe元素含量存在较大差别,胶结物白云石含量较低的Al元素和含量较高的Mn和Fe元素,其Ni、Cu、Sr和Ba元素含量低于基质白云石(图3)。对不同类型碳酸盐矿物的稀土元素常用指标进行了统计,发现基质白云石稀土元素总量(ΣREE)介于 $3.99 \times 10^{-6} \sim 47.52 \times 10^{-6}$,平均为 11.07×10^{-6} ,配分曲线以平坦型为主(图4a),不同晶粒

大小的白云石之间配分曲线形态差距较小(图4c),Gd元素多表现为正异常,HREE微弱右倾,Ce/Ce*介于0.91~1.32,平均值为1.02, Eu/Eu*介于0.57~1.08,平均值为0.79,Ce异常不明显,而Eu具负异常。胶结物白云石 ΣREE 介于 $3.62 \times 10^{-6} \sim 159.48 \times 10^{-6}$,平均值为 76.60×10^{-6} ,配分曲线具明显的MREE富集的“帽型结构”(图4b),Ce/Ce*介于0.89~1.10,平均值为0.97, Eu/Eu*介于0.70~1.27,平均值为1.01,Ce和Eu

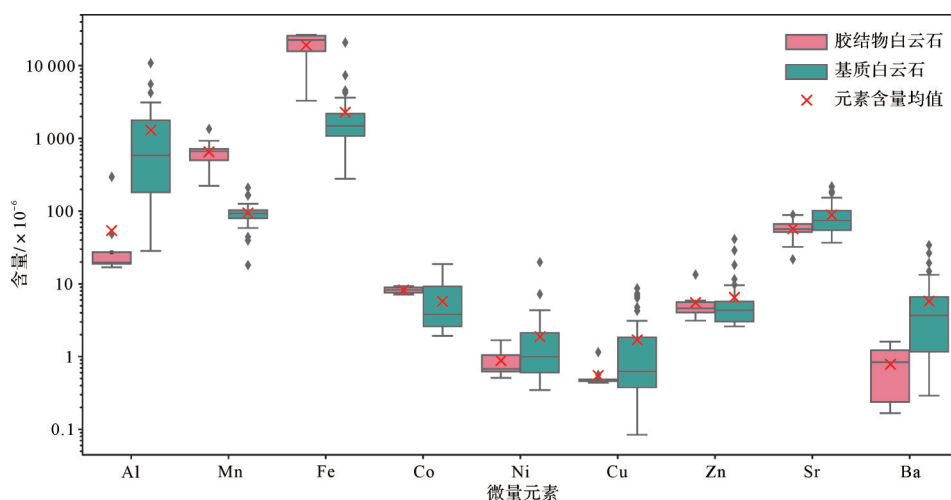


图3 基质白云石与胶结物白云石主微量元素箱型图

Fig.3 Box plot of major and trace elements in matrix and cement dolomites

异常不明显。此外,从方解石的配分曲线中可以发现x35-1-1裂缝方解石和x4-3-3孔隙方解石具明显的Ce异常,具自生碳酸盐岩的稀土配分特征,其他方解石样品配分曲线较为平坦且Gd异常不明显(图4d)。

3 讨论

3.1 碳酸盐岩矿物阴极发光特征与主微量、稀土元素之间的关系

早在20世纪80—90年代,国内外学者就开始研究碳酸盐矿物阴极发光特征与微量元素之间关系,并普遍认为碳酸盐矿物的阴极发光特征主要受其晶格中的Fe、Mn含量以及Fe/Mn控制,同时Fe³⁺为淬灭剂,Mn²⁺为激活剂(Pierson, 1981; Frank *et al.*, 1982; Fairchild, 1983; 黄思静, 1990, 1992)。黄思静(1992)根据测试的84个碳酸盐岩样品的Fe、Mn含量以及阴极发光强度测定结果,以定量化的方式确定了碳酸盐岩样品的Fe、Mn含量与其阴极发光性的关系,并绘制了二者综合关系图。稀土元素对碳酸盐矿物的阴极发光亦有一定的影响,尤其是Sm³⁺、Dy³⁺、Tb³⁺、Eu²⁺/Eu³⁺等元素,同样它们替代碳酸盐矿物晶格中的钙镁离子进入矿物结构作为发光的激活剂,Sm³⁺发射出橙色或红色的发光,Tb³⁺发射绿色光,Dy³⁺发射乳白色或淡黄色的光,Eu³⁺会导致红色发光,而Eu²⁺发射蓝光(Machel *et al.*, 1991; Götze, 2000; Romppanen *et al.*, 2021)。

本次在进行LA-ICP-MS测试前先对样品进行阴极发光分析,LA-ICP-MS测试后在偏光显微镜下找到LA-ICP-MS测试点,然后将阴极发光照片与偏光显微

照片进行叠合,确定阴极发光照片上的LA-ICP-MS测试点。在获取准确测试点的基础上,通过观察分析不同测试点碳酸盐岩矿物阴极发光强度,可分为5组,分别为不发光组、极弱发光组、弱发光组、中发光组和强发光组。结合分组信息,对主微量元素和稀土元素的含量及Fe/Mn比值进行了单因素方差分析(ANOVA)(肖明魁, 2019; 孙丽环, 2020)和Tukey的诚实显著差异检验(Tukey's HSD)(Abdi and Williams, 2010; Nanda *et al.*, 2021),发现Mn、Fe、Ce、Pr、Nd、Sm、Eu、Gd、Tb元素和Fe/Mn在不同组之间的均值存在显著性差异($p < 0.05$)。值得注意的是,不发光组在多个元素(Mn、Fe、Ce、Pr、Nd、Sm、Eu、Gd、Tb)和Fe/Mn比值中均显示出与其他组的显著差异,表明不发光组在这些元素的含量和Fe/Mn比值与其他组存在较大差异,即这些元素以及Fe/Mn比值对于碳酸盐矿物阴极发光性有不同程度的影响(表1)。

主微量元素和稀土元素的含量及Fe/Mn比值的箱型图展示了不同组之间在各元素含量上的差异,可以发现不发光组的Mn、Fe、La、Ce、Pr、Nd、Sm、Eu、Gd、Tb元素含量均值普遍偏大,分布较为分散且具显著差异,进一步支持了ANOVA和Tukey's HSD检验得出的结论。随着发光程度的增强,Mn元素含量逐渐增加趋势明显(除了不发光组),Fe、Sr、La、Ce、Pr、Nd元素含量以及Fe/Mn比值均具有下降的趋势;同时,也可发现不发光组的稀土元素由LREE到HREE含量分布逐渐集中,而强发光组的稀土元素由LREE到HREE含量分布逐渐分散且MREE至HREE(Tb~Lu)含量升高(图5)。

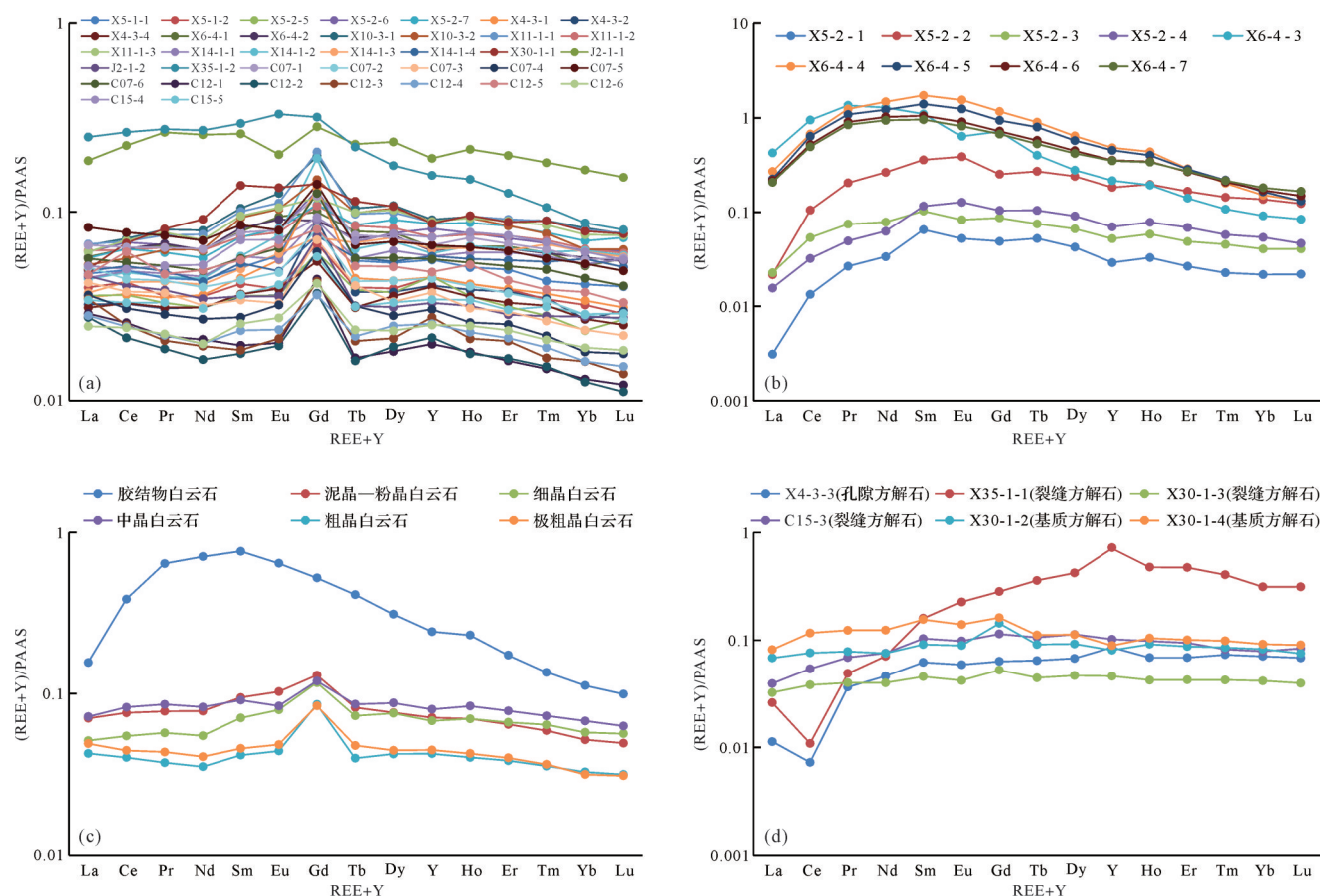


图4 碳酸盐矿物 REE+Y PAAS 标准化后的配分型式图解
(a)基质白云石;(b)胶结白云石;(c)不同类型白云石(均值);(d)方解石

Fig.4 Distribution pattern of rare earth elements and yttrium (REE+Y) in carbonate minerals normalized to major/trace Post-Archaeon Australian Shale (PAAS)
(a) matrix dolomite; (b) cement dolomite; (c) different types of dolomite (mean values); (d) calcite

表1 主微量元素和稀土元素的含量及Fe/Mn 的 ANOVA 统计检验指标

Table 1 Analysis of variation (ANOVA) test results for major/trace elements, REEs, and Fe/Mn contents

统计检验指标	主微量元素和Fe/Mn														
	Al	Mn	Fe	Co	Ni	Cu	Zn	Sr	Ba	Fe/Mn					
F-value	0.814 7	5.713 9	11.450 6	1.447 0	0.595 3	0.985 5	0.968 7	1.529 9	0.726 1	4.424 5					
p-value	0.521 6	0.000 7	0	0.231 8	0.667 6	0.423 7	0.432 6	0.207 2	0.578 1	0.003 7					
统计检验指标	稀土元素+Y														
	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Y	Ho	Er	Tm	Yb	Lu
F-value	0.852 9	3.550 5	5.292 9	5.713 1	5.437 7	3.760 6	2.797 1	3.110 0	1.830 4	1.683 1	1.153 7	0.766 5	0.548 7	0.441 5	0.446 2
p-value	0.498 4	0.012 3	0.001 2	0.000 7	0.001 0	0.009 2	0.035 3	0.022 8	0.137 0	0.167 9	0.342 0	0.551 9	0.700 8	0.778 0	0.774 7

从不同分组稀土元素的配分型式图解中可以发现,不发光组($Fe>10\ 000\times10^6$)配分曲线具明显的MREE富集的“帽型结构”,而强发光组LREE具明显的左倾,相对MREE和HREE亏损严重,极弱发光组、弱发光组和中发光组稀土元素配分曲线较为平坦,不发光组($Mn<40\times10^6$)稀土元素配分曲线与极弱发光组、弱发光组和中发光组相似,为平坦型(图6)。

将本次测试的57组数据投在黄思静(1992)绘制的Fe、Mn含量与其阴极发光性的关系图中可以发现,不发光和强发光的数据点与此图版吻合程度较好,其中碳酸盐矿物不发光的原因与过高的Fe含量($Fe>10\ 000\times10^6$)和过低的Mn含量($Mn<40\times10^6$)有关。极弱发光组、弱发光组 and 中等发光组有较多重复的区域,也进一步说明极弱发光组、弱发光组和中

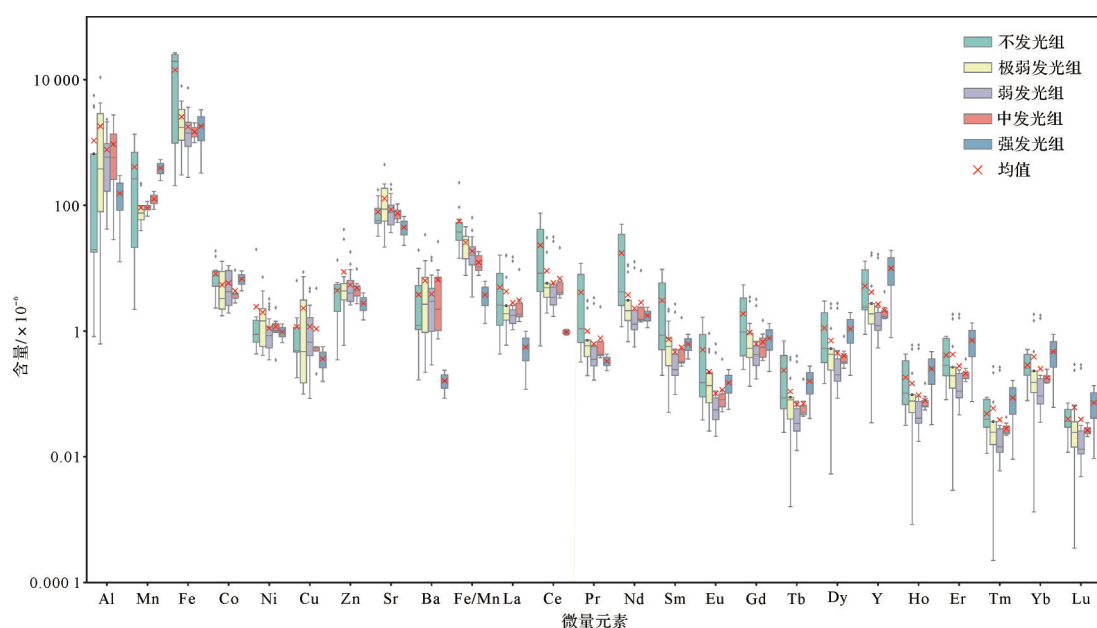


图5 不同发光组的主微量元素和稀土元素的含量及Fe/Mn箱型图

Fig.5 Box plot of major/trace elements and REE contents, and Fe/Mn across different luminescence groups

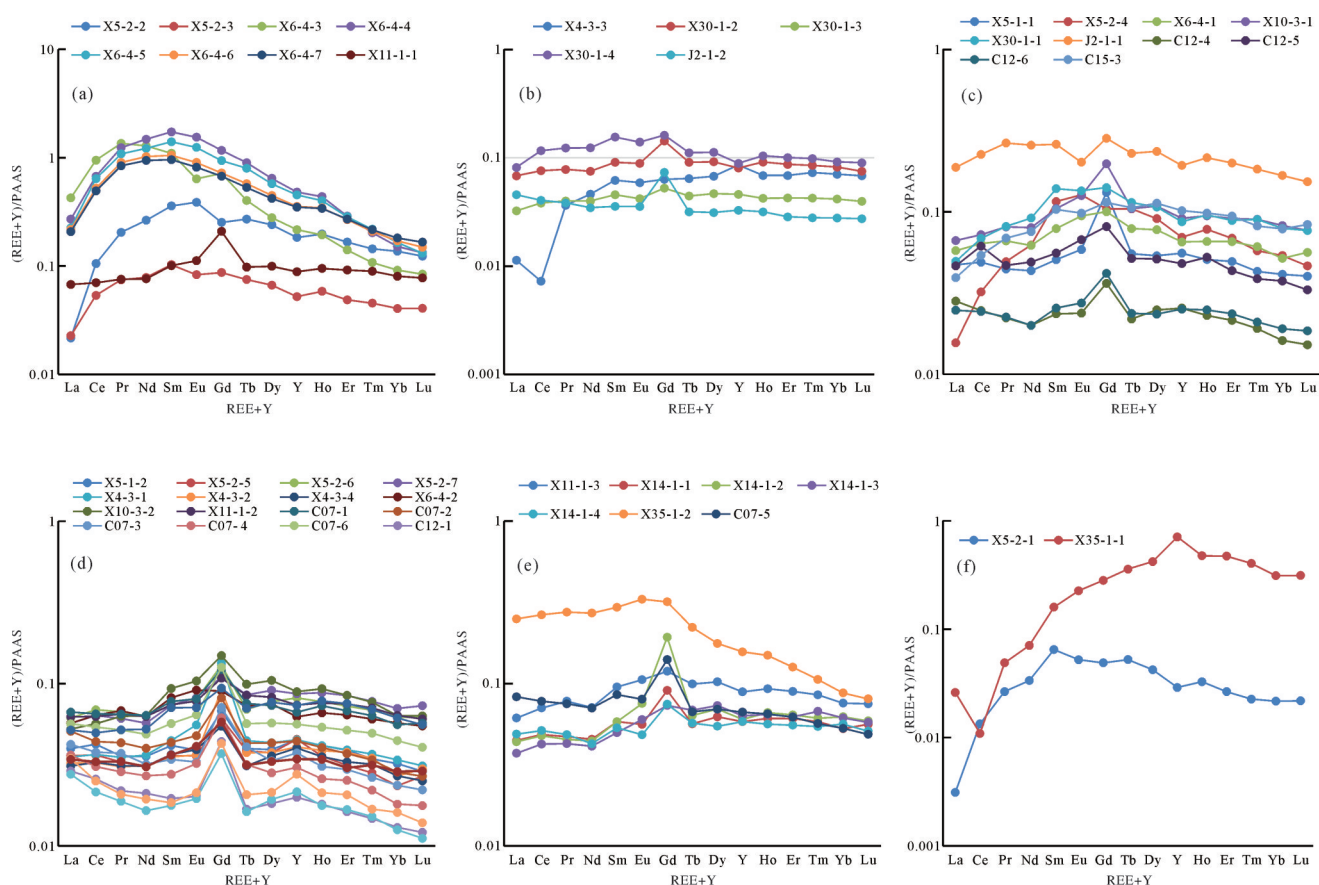


图6 不同发光组 REE+Y PAAS 标准化后的配分型式图解

(a) 不发光($\text{Fe} > 10\,000 \times 10^{-6}$); (b) 不发光($\text{Mn} < 40 \times 10^{-6}$); (c) 极弱发光组; (d) 弱发光组; (e) 中发光组; (f) 强发光组

Fig.6 Distribution pattern of REE+Y normalized to PAAS across different luminescence groups

(a) non-luminescent ($\text{Fe} > 10\,000 \times 10^{-6}$); (b) non-luminescent ($\text{Mn} < 40 \times 10^{-6}$); (c) extremely weak luminescent group; (d) weak luminescent group; (e) moderate luminescent group; (f) strong luminescent group

发光组中各种元素含量接近,不易区分(图7)。为了解决这个问题,笔者尝试使用了多种机器学习中的分类算法(支持向量机、决策树、随机森林和朴素贝叶斯)对极弱发光组、弱发光组和中发光组中的数据进行分类,但这些分类算法如同黑盒一般,并不具备较好的可视化效果。通过尝试,使用线性判别分析分别对主微量元素及稀土元素进行降维处理(Xanthopoulos *et al.*, 2013; Tharwat *et al.*, 2017),形成

$$\text{LDA}_{\text{主微量元素+稀土元素}} = 0.002 \times \text{Al} - 0.219 \times \text{Mn} + 0.006 \times \text{Fe} - 2.071 \times \text{Co} + 0.361 \times \text{Ni} + 1.089 \times \text{Cu} + 0.436 \times \text{Zn} - 0.151 \times \text{Sr} + 9.661 \times \text{Y} + 0.609 \times \text{Ba} - 9.414 \times \text{La} + 4.710 \times \text{Ce} - 1.895 \times \text{Pr} + 2.183 \times \text{Nd} - 29.666 \times \text{Sm} + 78.757 \times \text{Eu} - 52.105 \times \text{Gd} + 52.142 \times \text{Tb} + 44.906 \times \text{Dy} - 784.458 \times \text{Ho} + 610.293 \times \text{Er} - 4\,241.861 \times \text{Tm} + 131.588 \times \text{Yb} + 391.661 \times \text{Lu} + 21.982 \quad (1)$$

在以上的研究中可以发现 Mn^{2+} 似乎是碳酸盐矿物中最重要的发光激活剂,尤其是在低 Fe 含量的条件下, Mn^{2+} 能够在低浓度下产生明显的发光(Roeder *et al.*, 1987; Mason and Mariano, 1990; 黄思静, 1992; Götze, 2000)。本次实验中测试的稀土元素含量多数小于 10×10^{-6} , 肉眼不易观察稀土元素对碳酸盐矿物在阴极射线下的发光特征,然而稀土元素(尤其是 $\text{Eu}^{2+}/\text{Eu}^{3+}$ 、 Sm^{3+} 、 Dy^{3+})通过激发发射特定波长的光谱,也在发光中起到重要作用,特别是在更复杂的晶体化学环境中(Götze, 2000; Fernandez-Cortes *et al.*, 2011; Zhu *et al.*, 2018)。稀土元素的作用往往更为复杂,它们不仅可以独立发光,还能与 Mn^{2+} 等过渡金属发生能量转移,增强整体的发光效果, Sm^{3+} 和 Eu^{3+} 的红色发光在视觉上容易与 Mn^{2+} 发光混淆,但其光谱

一个可以通过特征参数计算的综合参数,并且使用这个综合参数分别与 Fe/Mn、Fe 和 Mn 含量做交会图,发现使用微量和稀土元素降维的综合参数与 Mn 含量绘制的交会图可以很好地将极弱发光组、弱发光组和中发光组分开(式1),说明在白云岩在极弱发光—中发光阶段,其发光程度受微量元素和稀土元素共同影响,同时与 Fe/Mn 比值和 Fe 含量相比,进一步说明其发光程度受 Mn 含量的影响更大些(图8)。

特征却不同。(Mn^{2+} 的发光光谱是宽带发光,主要介于 590~680 nm, Sm^{3+} 的发光光谱是窄带发光,主要在 562 nm、604 nm 和 652 nm 处有明显峰值, Eu^{3+} 的发光光谱也为窄带发光,最显著的发射峰出现在 614 nm (Roeder *et al.*, 1987; Mason and Mariano, 1990; Götze, 2000; Romppanen *et al.*, 2021)。此外,稀土元素在氧化还原条件下的反应(如 $\text{Eu}^{2+}/\text{Eu}^{3+}$ 在氧逸度影响下的发光行为),也为地质条件的分析提供了重要线索。

3.2 成岩阶段对碳酸盐矿物阴极发光的影响

研究区奥陶系大致经历了同生成岩阶段、表生成岩阶段和中晚成岩阶段,分别对应海水环境、淡水环境和埋藏环境(苏中堂, 2011; 刘伟, 2014; 罗清清等, 2020; 孙玉景, 2020; 于洲等, 2023; 刘新社等, 2024)。碳酸盐岩接触海水、大气淡水和埋藏状态的

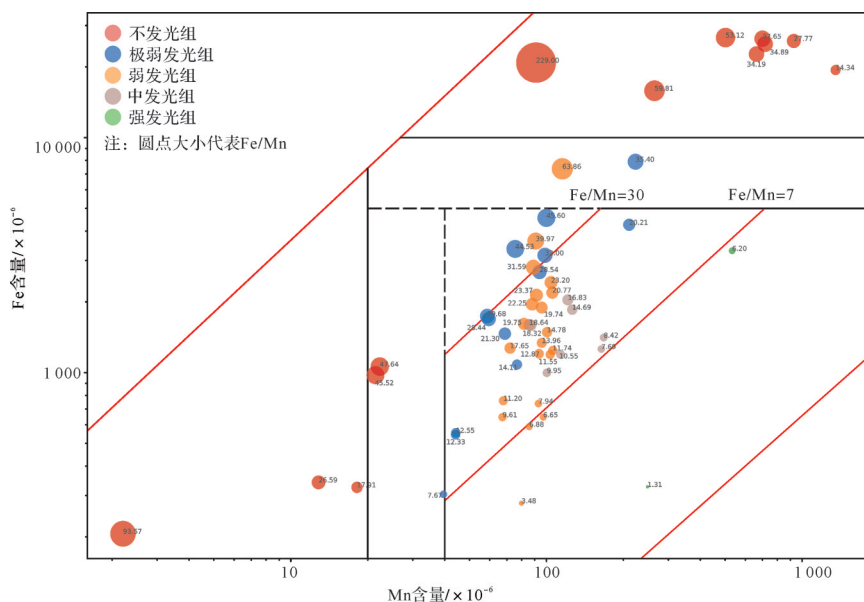


图7 碳酸盐矿物阴极发光与 Fe、Mn 含量之间的关系(底图据黄思静, 1992)

Fig.7 Relationship between cathodoluminescence and Fe, Mn contents in carbonate minerals (base image from Huang, 1992)

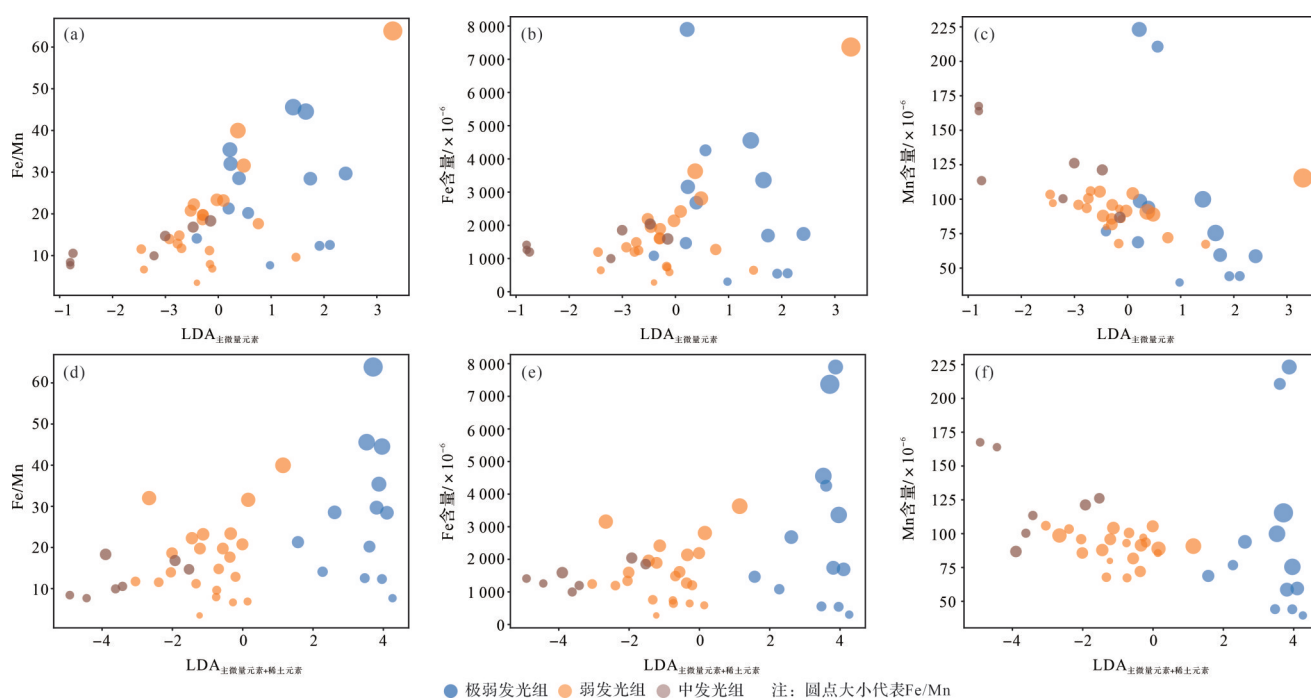


图8 基于线性判别分析的极弱发光组、弱发光组和中发光组的分类图版

Fig.8 Classification of the extremely weak, weak, and moderate luminescence groups based on linear discriminant analysis

孔隙水等成岩流体发生流岩反应进而改变碳酸盐沉积物组成和矿物成分以及主微量、稀土元素含量的变化,进而改变碳酸盐岩矿物的阴极发光程度。随着埋藏深度的增加,成岩流体性质逐渐由氧化向还原转变, Mn^{2+} 、 Fe^{2+} 以及稀土含量增加,碳酸盐矿物配分曲线中LREE亏损和HREE富集特征逐渐消失,且已无Ce异常(Chen *et al.*, 2015; 赵彦彦等, 2019)(图9)。

同生成岩阶段,由于海水中Fe、Mn含量和分配系数均较低,使得原始海相碳酸盐矿物中Fe、Mn含量低,泥晶灰岩与胶结物往往因为其Mn含量小于 40×10^{-6} 在阴极射线下不发光(图2d,f)。在准同生白云石化作用下,形成泥粉晶白云岩及细晶白云岩,白云石为半自形或他形,有序度较低,配分曲线一般表现为平坦型,在阴极射线下发弱—中红色光,此阶段已经开始了 Mn^{2+} 、 Fe^{2+} 含量的富集(图2b,d)。

晚加里东期至海西期,奥陶系整体隆升而暴露地表,并接受长期的大气淡水淋滤和侵蚀,进入表生成岩阶段,近地表的古岩溶作用导致强烈的溶蚀作用发生,岩溶垂向渗流带和水平潜流带中形成大量的淋溶通道,溶孔、溶缝以及溶洞较为发育(岳小娟, 2017; 熊加贝等, 2024)。表生成岩环境的大气淡水通常是氧化性的,会导致孔隙水中的低 Fe^{2+} 和 Mn^{2+} 含

量,从而使得粒状亮晶方解石胶结物表现出不发光或暗发光(Scholle and Ulmer-Scholle, 2003)。值得一提的是,一些晶粒较大的方解石胶结物表现出强烈振荡带状生长的交替强橘黄色光和不发光的现象且稀土元素配分曲线表现出强氧化特征(图2a、图6f),表明此阶段岩层在经历多次暴露地表及大气淡水淋滤,造成岩石溶孔和溶缝中的成岩流体地球化学非均质性,同时受变化的 CaCO_3 饱和程度和结晶速度的影响,呈现复杂的环带阴极发光特征(兰叶芳等, 2015; Xiang *et al.*, 2021)。

从晚石炭纪开始,地层开始新一轮沉积,埋藏深度不断加深,进入中成岩阶段。埋藏基质白云石一般为粗粉晶—粗晶,常见雾心亮边和聚合等构造,在阴极射线下发弱—强红色光(图2g~n, q, r)。此外,胶结物白云石常常具备环带结构,Mn、Fe含量均较高,在阴极射线下发环带发光的现象(图2p),同时会因其Fe含量超过 $10\,000 \times 10^{-6}$ 而导致不发光(图2t),胶结物白云石的稀土元素配分曲线具明显的“帽型结构”(图4b、图6a),其成因可能与弱氧化的孔隙水中LREE被Mn氢氧化物吸附,而HREE被Fe氢氧化物吸附,使其具有富集MREE的特征(Alibo and Nozaki, 1999; Haley *et al.*, 2004; Kim *et al.*, 2012; Prakash *et al.*, 2012; 赵彦彦等, 2019)。

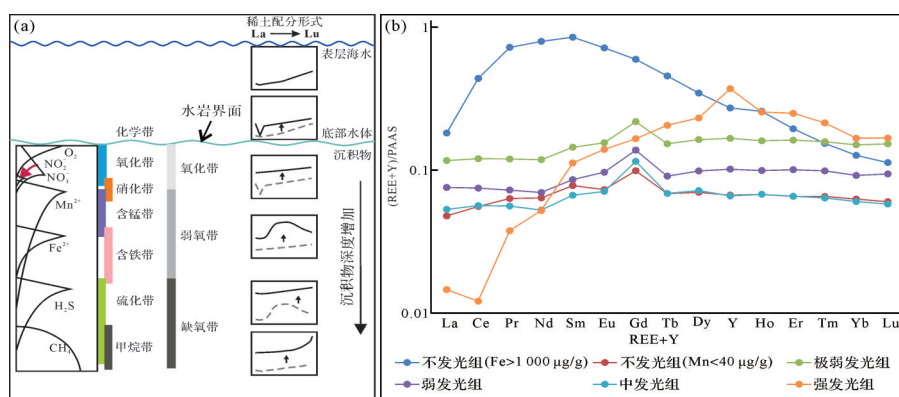


图9 不同发光组稀土配分特征与氧化带至甲烷带的海水和孔隙水的稀土配分特征对比

(a) 氧化带至甲烷带的海水和孔隙水经 PAAS 标准化后的稀土配分特征 (Chen *et al.*, 2015); (b) 不同发光组 REE+Y PAAS 标准化后的配分型式图解 (均值)

Fig.9 Comparison of REE distribution patterns between different luminescence groups and seawater/porewater REE distribution from the oxidation to methane zones

(a) PAAS-normalized REE distribution patterns of seawater and porewater from the oxic zone to the methane zone (Chen *et al.*, 2015); (b) diagram of REE+Y PAAS-normalized distribution patterns for different non-luminescent groups (mean values)

4 结论

(1) 基质白云石主要表现为弱—中红色发光, 配分曲线多为平坦型。粗粉晶和粗晶基质白云石在阴极射线下呈现由中心至边缘依次明亮、暗淡、再明亮的发光特征。胶结物白云石晶粒较大, 配分曲线显示 MREE 富集的“帽型结构”, 环带发光特征明显或不发光。基质方解石通常不发光, 而裂缝中方解石则发橘黄色光或不发光。

(2) 碳酸盐矿物阴极发光程度受 Mn、Fe 及多种稀土元素 (如 La、Ce、Pr、Nd、Sm、Eu、Gd、Tb) 含量和 Fe/Mn 比值的共同影响。不发光组 ($\text{Fe} > 10\,000 \times 10^{-6}$) 具明显 MREE 富集“帽型结构”, 而强发光组则表现出 LREE 左倾, 且 MREE 和 HREE 显著亏损。极弱、弱和中等发光组通过稀土元素与 Mn 含量的交会图可以有效区分, 发光强度与 Mn 含量呈正相关。

(3) 随着埋深增加, 成岩流体由氧化性向还原性转变, 导致 Mn^{2+} 、 Fe^{2+} 及稀土元素含量增加, 碳酸盐矿物的发光程度增强。不同成岩阶段对基质白云石发光影响较小, 各种晶粒大小的白云石均显示弱—中红色发光。弱还原环境下, Mn 和 Fe 含量的增加使胶结物白云石出现环带发光, 进一步增加的 Fe 和 Mn 含量则导致其不发光。

支撑本研究的科学数据已在中国科学院科学数据银行 (Science Data Bank, ScienceDB) 平台公开发布, 访问地址为 <https://doi.org/10.57760/sciencedb.cjxb.00025> 和 <https://cstr.cn/31253.11.sciencedb.cjxb.00025>。

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Factors Influencing Cathodoluminescence in Carbonate Minerals: A case study from the Lower and Middle Ordovician of the southern margin of the Ordos Basin

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Abstract: [Objective] The cathodoluminescence (CL) characteristics of carbonate minerals are closely related to their major/trace and rare earth element (REE) contents. Existing studies primarily focus on the effects of Mn and Fe on CL, often neglecting the role of REEs. This study aims to investigate the influence of major/trace and rare earth elements on the CL characteristics of carbonate minerals, thereby providing geological evidence for inferring mineral genesis, depositional environments, and diagenetic processes. [Methods] CL and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) were used to test carbonate rock samples from the Lower and Middle Ordovician on the southern margin of the Ordos Basin. Statistical methods and classification algorithms were applied to analyze the test data, and common REE indicators were used to evaluate the properties of diagenetic fluids. [Results] The study reveals that matrix dolomite exhibits weak to moderate red luminescence under CL, with both zoned and uniform luminescence. Dolomite cements, with high Mn and Fe contents, are often zoned or non-luminescent. Analysis of variance (ANOVA) and Tukey's Honestly Significant Difference (HSD) post-hoc tests indicate that Fe, Mn, La, Ce, Pr, Nd, Sm, Eu, Gd, and Tb contents, and the Fe/Mn value significantly influence the CL of carbonate minerals. Non-luminescent and strongly luminescent groups are relatively easy to distinguish: non-luminescent minerals have Fe contents greater than $10,000 \times 10^{-6}$ or Mn contents less than 40×10^{-6} . Additionally, the non-luminescent group with Fe contents over $10,000 \times 10^{-6}$ displays REE distribution patterns enriched in Middle Rare Earth Elements (MREE), whereas the strongly luminescent group shows Light Rare Earth Elements (LREE) depletion and low Fe/Mn values. Using comprehensive dimensionality-reduced parameters of major/trace elements and REEs, in conjunction with Mn content, effectively distinguishes the extremely weakly luminescent, weakly luminescent, and moderately luminescent groups. The nature of diagenetic fluids during diagenesis impacts carbonate sediment composition, mineral content, and major/trace element and REE variations, directly influencing carbonate mineral CL. [Conclusions] By combining in situ major/trace element testing with various data processing methods, this study provides a more quantitative understanding of the impact of major/trace element and REE contents on CL intensity. These findings offer valuable insights for scholars studying the factors affecting CL.

Key words: carbonate minerals; cathodoluminescence; LA-ICP-MS; diagenetic stages; Ordovician