

锌绿松石矿物学研究

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[摘要] 锌绿松石是很少见的矿物, 目前已知仅美国内华达州有产出。报道的锌绿松石样品采于湖北郧县云盖寺锌绿松石的杨柿沟矿点。经电子探针分析、X射线粉晶衍射分析和差热分析研究, 样品为含铜锌绿松石。这在我国属首次发现。

[关键词] 矿物学; 锌绿松石; 湖北郧县; X射线衍射; 化学成分; 差热分析

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1 矿物学基本特征

锌绿松石属绿松石—磷铜铁矿族矿物。目前, 锌绿松石少见产出。研究所用标本采于湖北郧县云盖寺绿松石矿杨柿沟矿点。

该区锌绿松石产于寒武系下统水沟口组一套含炭或含泥硅质板岩中^[1, 2] (和绿松石同层产出), 绝大部分为风化淋滤成矿, 多以苹果绿色皮壳状集合体充填于层间氧化带。与绿松石、孔雀石、铁质矿物、石英等共生。锌绿松石硬度为 5, 相对密度 2.602 9, 折射率 1.62, 蜡状光泽强。

2 化学成分

锌绿松石晶体化学式为 $(\text{Zn}, \text{Cu})\text{Al}_6[\text{OH}]_8 \cdot 4\text{PO}_4 \cdot 4\text{H}_2\text{O}$, 三斜晶系。成分理论值为 $w(\text{ZnO})$ 7.99%, $w(\text{CuO})$ 1.95%, $w(\text{Al}_2\text{O}_3)$ 37.53%, $w(\text{P}_2\text{O}_5)$ 34.84%, $w(\text{H}_2\text{O})$ 17.69%; 分析值为 $w(\text{ZnO})$ 5.04%, $w(\text{CuO})$ 0.039%, $w(\text{Al}_2\text{O}_3)$ 34.32%, $w(\text{Fe}_2\text{O}_3)$ 2.39%, $w(\text{P}_2\text{O}_5)$ 34.99%, $w(\text{V}_2\text{O}_5)$ 0.42%, $w(\text{H}_2\text{O}^+)$ 19.42%^[3]。笔者分析数据为 $w(\text{ZnO})$ 4.09%, $w(\text{CuO})$ 2.89%, $w(\text{Al}_2\text{O}_3)$ 37.87%, $w(\text{FeO})$ 1.287%, $w(\text{P}_2\text{O}_5)$ 35.745%, $w(\text{V}_2\text{O}_5)$

0.946%, $w(\text{H}_2\text{O})$ 17.285% (电子探针分析由西安地质矿产研究所刘文峰完成, 仪器型号 JCXA-733, 加速电压 15 kV, 电流 50 μA , 光斑 2 μm)。计算晶体化学式为

$(\text{Zn}_{0.41}\text{Cu}_{0.30}\text{Fe}_{0.15})_{0.86}\text{Al}_{6.03}(\text{OH})_{7.66}(\text{PO}_4)_4.09 \cdot 4\text{H}_2\text{O}$ 。

3 X射线粉晶衍射特征

锌绿松石实测 X 射线粉晶衍射数据及衍射图分别见表 1 和图 1。主要粉晶衍射数据为 0.678 8 (10), 0.616 9 (6), 0.374 9 (10), 0.289 5 (3)。经化学成分和 X 射线粉晶衍射分析, 鉴定为锌绿松石^[3~5]。美国内华达州锌绿松石主要粉晶谱线^[4] 为 0.368 (10), 0.670 (7), 0.614 (7), 0.289 (8), 0.205 (7)。由于湖北郧县和美国内华达州的锌绿松石化学成分略有差别, 因此, X 射线粉晶衍射数据不尽一致, 但总的看, 吻合较好。

美国内华达州锌绿松石以细脉充填或疖状产出于蚀变灰岩中。湖北郧县锌绿松石中含少量孔雀石, 图 1 中以 M 表示。

4 差热分析

锌绿松石中约含 17.285% 的水。水在其中有吸附水、结晶水和结构水 3 种存在方式:^[6]。样品经差热分析鉴定也为锌绿松石^[7], 锌绿松石差热曲线见图 2。

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表 1 锌绿松石实测 X 射线粉晶衍射数据

Table 1 Selected powder eiffraction data measured for faustite

<i>d</i> /nm	<i>I</i> / <i>I</i> ₀	<i>hkl</i>	<i>d</i> /nm	<i>I</i> / <i>I</i> ₀	<i>hkl</i>
0.678 8	10	001	0.214 0	1	300
0.619 6	6	0 $\bar{1}$ 1, $\bar{1}$ 1 $\bar{0}$	0.205 8	2	
0.602 1	1	$\bar{1}$ 01, 11 $\bar{1}$	0.200 7	1	212, 30 $\bar{3}$, 33 $\bar{3}$
0.478 0	3	011, $\bar{1}\bar{1}$ 0	0.189 2	2	311, 0 $\bar{3}$ 3
0.374 9	10	111, $\bar{1}\bar{1}$ 1	0.183 6	1	301, 3 $\bar{2}$ 1
0.342 5	3	$\bar{2}$ 01, $\bar{2}$ 21	0.171 5	1	
0.328 3	3	210, 021	0.160 6	1	213, $\bar{3}$ 31, $\bar{1}$ 3 $\bar{3}$
0.289 5	3		0.157 3	1	322, 3 $\bar{2}$ 1
0.254 2	2	201, 11 $\bar{3}$	0.151 1	1	233, 3 $\bar{1}$ 2
0.235 2	1	0 $\bar{3}$ 2	0.149 3	1	
0.223 5	1	310, $\bar{2}$ 22, 33 $\bar{2}$			

注: ①X 射线粉晶衍射分析由西安地质矿产研究所姚爱民完成; ②X 射线粉晶衍射仪为日本理工 D/MAX- μ A 型, Cu 靶, 电压 45 kV, 电流 80 mA

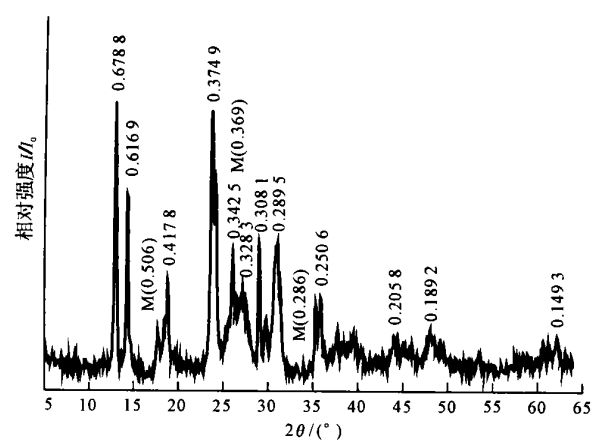
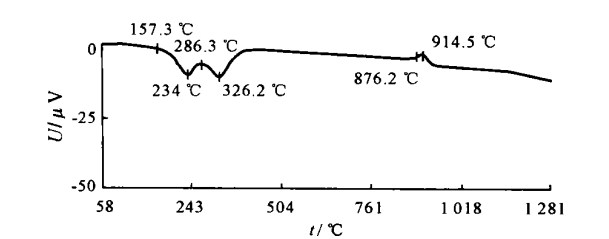


图 1 锌绿松石实测 X 射线粉晶衍射

Fig.1 Selected powder diffraction chart measured for faustite



自测。差热分析仪型号: CRY-2P; 电压: 220 V;
DTA 量程: $\pm 50 \mu V$; 升温速率: $10 \text{ }^{\circ}\text{C}/\text{min}$

图 2 锌绿松石差热曲线

Fig.2 Curve of DTA about faustite

吸附水含量较高的样品, 其颜色较深。当样品经 $300 \text{ }^{\circ}\text{C}$ 灼烧后, 颜色发生明显变化, 由翠绿变为黄绿色。这说明结晶水的存在对其颜色有一定影响。这是因为锌绿松石失去结晶水后, Cu^{2+} 局部对称性发生变化造成的。

5 讨论

(1) 锌绿松石于 1968 年在美国内华达州首次发现, 其 Zn 可被 $w(\text{Cu}) 1.6\%$ 代替, Al 可被 $w(\text{Fe}^{3+}) 1.7\%$ 代替。湖北郧县绿松石化学成分中 $w(\text{Cu}) 2.3\%$, $w(\text{Zn}) 3.28\%$, Zn 含量大于 Cu 含量, 因此为锌绿松石。在我国为首例发现。

(2) 从 X 射线粉晶衍射特征来看, 湖北郧县锌绿松石与文献[3] 数据接近。

(3) 锌绿松石中, Zn 与 Cu 为类质同象代替, 依类质同象代替的程度应有 $\text{ZnAl}_6(\text{OH})_8(\text{PO}_4)_4 \cdot 4\text{H}_2\text{O}$, $\text{CuAl}_6(\text{OH})_8(\text{PO}_4)_4 \cdot 4\text{H}_2\text{O}$ 和 $(\text{Zn}, \text{Cu})\text{Al}_6(\text{OH})_8(\text{PO}_4)_4 \cdot 4\text{H}_2\text{O}$ 三个亚种, 湖北郧县锌绿松石 $(\text{Zn}_{0.41}\text{Cu}_{0.30}\text{Fe}_{0.15})_{0.86}\text{Al}_{6.03}(\text{OH})_{7.66}(\text{PO}_4)_{4.09} \cdot 4\text{H}_2\text{O}$ 中, 若 Zn, Cu, Fe 摩尔数和为 1, 则 Zn 的摩尔数为 0.48, Cu 的摩尔数为 0.35, Fe 的摩尔数为 0.17, 应属中间成分亚种, 可命名为含铜锌绿松石。

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Metallogenic mechanism of gibbsite from accumulated bauxite in western Guangxi province

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Abstract The mineral assemblage, spatial features of minerals distribution, characters of occurrence, generations of minerals forming, chemical compositions, rare earth elements and water contents inside or surrounding ore-body have been securely researched. The results indicate that the gibbsite from accumulated bauxite (Salento-type) in western Guangxi province was formed through hydration of diaspore. The formation of gibbsite was strictly controlled by the concentrations of Al^{3+} , $[SiO_4]^{4-}$ and pH in of underground water. It experienced several periods as precipitation, solidification, devitrification and crystallization of $Al(OH)_3$. In early period kaolinite was formed by means of leaching and secondary quartz was formed in lightly leached position. This kind of bauxite is considered to be not only a new deposit type, and its particular genesis to be shown as a degeneration bauxite deposit as well.

Key words: accumulated bauxite; gibbsite; metallogenic mechanism; hydrolytic dissociation; western Guangxi

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Research on mineralogy of faustite

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Abstract Faustite is one of rare minerals and has been found in Nevada, USA. The samples reported in this paper are collected from Yangshigou pit of Yungaisi turquoise mine in Yunxian county, Hubei province, and recognized as Cu-bearing faustite with electron microprobe analysis, X-ray power diffraction analysis and differential thermal analysis. This is a first discovery of faustite in China.

Key words: mineralogy; faustite; Yunxian county Hubei province; X-ray power diffraction; Chemical component; differential thermal analysis

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