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Fluorite deposits in China: Geological features, metallogenic regularity, and research progress

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\textbf{A B S T R A C T}

Fluorite is one of the important mineral raw materials in the industry. In China, it is mainly distributed in the provinces and regions such as Hunan, Zhejiang, Jiangxi, Inner Mongolia, Fujian, and Henan provinces, boasting huge reserves and large numbers of deposits. However, most of the fluorite deposits are on a small or medium scale. The main fluorite deposits in China were studied in this paper. Their geological features and metallogenic regularity were summarized and compared. Meanwhile, based on their main genetic factors including metallogenic fluid sources and main metallogenic geological processes, they were divided into two groups, namely meso-epithermal deposits and magmatic-hydrothermal deposits. Furthermore, based on the prospecting achievements and research progress obtained in fluorite deposits in recent years, prospecting potential predictions were made for the metallogenic prospect areas and major prospecting areas of fluorite in China. This aims to provide a theoretical basis and direction for future fluorite prospecting in China.

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1. Introduction

As one of the important mineral raw materials in the modern industry, fluorite is mainly applied in the emerging industries (i.e., new energy and new materials) and the traditional fields (i.e., metallurgy, building materials, refrigeration, and optical industry). China is rich in fluorite resources and is importantly positioned in the global fluorite industry since the fluorite deposits in China enjoy high grades and are easy to exploit. Therefore, it is necessary to strengthen the research on metallogenic regularity of fluorite deposits to provide guidance on the deployment of prospecting and exploration, aiming at discovering more fluorite deposits to meet the demand of global industries for fluorite. In this paper, the metallogenic features and regularities of fluorite across China were sorted and summarized by sorting new discoveries about fluorite prospecting made in the last ten years and combining new research achievements obtained recently. It is expected to offer references for the further deployment of fluorite prospecting in China.

2. Overview of fluorite resources in China

Fluorite resources are unevenly distributed in the world. According to the data published by the U.S. Geological Survey, by the end of 2018, the fluorite reserves were $310 \times 10^6$ t in the world and nearly half of the reserves are distributed in Mexico, China, and South Africa. The details are as follows. Mexico boasted fluorite reserves of $68 \times 10^6$ t, accounting for 21.9% of global fluorite reserves. China had the second-largest reserves, which was $42 \times 10^6$ t, and accounted for 13.6% of the global fluorite reserves. The fluorite reserves in South Africa were slightly less than that of China, which was $41 \times 10^6$ t and accounted for 13.2% of global reserves.

China enjoyed continuously increasing identified reserves
of fluorite resources in recent years. According to the statistics in the Summary of Reserves of China’s Mineral Resources in 2018 issued by the Ministry of Natural Resources of the People’s Republic of China, the identified reserves of fluorite resources (minerals, the same hereafter) in China was 257×10^6 t by the end of 2018, including resources of 210.6137×10^6 t, reserve base of 46.5123×10^6 t, and reserves of 16.6502×10^6 t. The identified resources were mainly distributed in Hunan, Zhejiang, Jiangxi, Inner Mongolia, Fujian, Henan, Hebei, and Anhui provinces, accounting for 89.24% of the national resources. Among them, Hunan Province had an identified resources of 98.5578×10^6 t, accounting for 83.33% of the national resources and ranking as the first (Fig. 1). Among the fluorite deposits in China, most of them are lean and only a few of them are rich (CaF_2 content over 65%). According to relevant statistics, the average content of CaF_2 in a single-type fluorite deposit is 54%. There are merely 19.5×10^6 t of rich deposits, accounting for 26.73% of the total fluorite deposit resources. In contrast, the resources of lean deposits account for 73.27% of the total fluorite deposit resources. High-grade rich deposits are unevenly distributed in China and they are mainly located in Zhejiang, Jiangxi, and Inner Mongolia provinces. Furthermore, more than 1400 fluorite deposits (ore occurrences) have been discovered in China, including four super large ones and 40 large ones, whose accumulative identified reserves account for 59.46% of the national accumulative identified resource reserves (Table 1).

3. Main types of fluorite deposits in China

Based on the differences in metallogenic hydrothermal solution and main ore-controlling factors, the fluorite deposits in China can be divided into two groups, namely meso-epithermal deposits and magmatic-hydrothermal deposits. Furthermore, each group has a different second-order metallogenic factor association, thus can be further divided into various types (Table 2).

3.1. Meso-epithermal fluorite deposits

The meso-epithermal fluorite deposits can be divided into the following three types according to their differences in necessary metallogenic factors and provenance of fluorine (the necessary metallogenic factors and provenance of fluorine at the main stage prevail given that some of the deposits underwent multiple metallogenic stages).

(i) Qibaquan type. The fluorite deposits of this type were mainly formed in connection with intrusive rocks, faults, and atmospheric precipitation (geothermal water) as follows. The intrusive rocks served as the provenance of fluorine. The groundwater was turned into thermal brine with the heat provided by magmatic activities. Then the thermal brine...
<table>
<thead>
<tr>
<th>No.</th>
<th>Deposit name</th>
<th>Location</th>
<th>Mineral assemblage</th>
<th>Scale/grade %</th>
</tr>
</thead>
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<tr>
<td>1</td>
<td>Fengxingshan fluorite deposit</td>
<td>Jingde County, Anhui Province</td>
<td>Fluorite, chalcedony, and quartz</td>
<td>Large/85.4</td>
</tr>
<tr>
<td>2</td>
<td>Zhuangcun fluorite deposit</td>
<td>Ningguo City, Anhui Province</td>
<td>Fluorite, quartz, calcite, and chalcedony</td>
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<td>3</td>
<td>Huitan fluorite deposit</td>
<td>Jianyang City, Fujian Province</td>
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<td>Yangjiaowei fluorite deposit</td>
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<td>Nanshanxia fluorite deposit</td>
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<td>Qibaquan fluorite deposit</td>
<td>Gaotai County, Gansu Province</td>
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<td>Tougou-Zhaolugou fluorite deposit</td>
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<td>Daoji fluorite deposit</td>
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<td>9</td>
<td>Dipili fluorite deposit</td>
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<td>Yulin City, Guangxi Province</td>
<td>Fluorite, quartz, and montmorillonite</td>
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<td>Chenlou fluorite deposit</td>
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<td>Fluorite, quartz, and sericite</td>
<td>Large/73.59</td>
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<td>Jianshan fluorite deposit</td>
<td>Xinyang County, Henan Province</td>
<td>Fluorite and quartz</td>
<td>Large/(66.42 for rich deposits, 46.33 for lean deposits)</td>
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<td>14</td>
<td>Huahai fluorite deposit</td>
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<td>15</td>
<td>Shizhuyuan tungsten-stannum-molybdenum-bismuth deposit</td>
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<td>Jiepailing fluorite stannum-lead-zinc deposit</td>
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<td>Yikuangchong polymetallic (fluorite) deposit</td>
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<td>Shuangjiangkou fluorite deposit</td>
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<td>Taolin lead-zinc (fluorite) deposit</td>
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<td>Hongxian fluorite deposit</td>
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<td>Qinglongshan fluorite deposit</td>
<td>Quannan County, Jiangxi Province</td>
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<td>Longping fluorite deposit</td>
<td>Xingguo County, Jiangxi Province</td>
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<td>Nankeng fluorite deposit</td>
<td>Yongfeng County, Jiangxi Province</td>
<td>Fluorite and quartz</td>
<td>Large/50.41</td>
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<td>Sumogagan Obo fluorite deposit</td>
<td>Siziwang Banner, Inner Mongolia</td>
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<td>Super large/63.76</td>
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<tr>
<td>25</td>
<td>Xilimiao fluorite deposit</td>
<td>Siziwang Banner, Inner Mongolia</td>
<td>Fluorite and quartz</td>
<td>Large/52.77</td>
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<td>26</td>
<td>Wulitu fluorite deposit</td>
<td>Akta Right Banner, Inner Mongolia</td>
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<td>27</td>
<td>Bamianshan fluorite deposit</td>
<td>Changshan County, Zhejiang Province</td>
<td>Fluorite, quartz, sericite, and calcite</td>
<td>Large/(31.82–55.17)</td>
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<td>Yinzishan fluorite deposit</td>
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<td>Fluorite, quartz, barite, and adularia</td>
<td>Large/37.56</td>
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<td>Yucun fluorite deposit</td>
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<td>Fluorite, quartz, and barite</td>
<td>Large/69.42</td>
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<td>Ganwukou fluorite deposit</td>
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<td>31</td>
<td>Huangshan fluorite deposit</td>
<td>Kaihua County, Zhejiang Province</td>
<td>Fluorite and quartz</td>
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<td>Xinqiao fluorite deposit</td>
<td>Lin'an City, Zhejiang Province</td>
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<td>Large/54.18</td>
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<td>33</td>
<td>Badu fluorite deposit</td>
<td>Longquan City, Zhejiang Province</td>
<td>Fluorite, quartz, plagioclase, and potassium feldspar</td>
<td>Large/49.76</td>
</tr>
</tbody>
</table>
extracted fluorine elements from intrusive rocks while migrating and fluorite deposits were formed in favorable positions, with faults acting as migration pathways of the thermal brine and metallogenic sites. The magmatic rocks involving in the formation of this type of fluorite deposits included orthopyre primarily and quartz porphyry and siliceous dykes secondarily. The features of this type of fluorite deposits are as follows: Their ore minerals are fluorite; their gangue minerals include quartz primarily and chalcedony secondarily, with cuttings of surrounding rocks being visible occasionally; their ores include fluorite ores primarily and fluorite-barite ores secondarily; their ore-body grades (i.e., the content of CaF$_2$) range from 20% to 95% in general, with an average of about 79%. Typical examples of this type of fluorite deposits include the Huahe fluorite deposit in Hong’an County, Hubei Province, Changkou fluorite deposit in Jiang County, Fujian Province; Chenlou fluorite deposit in Song County, Henan Province.

(ii) Wuyi type. The fluorite deposits of this type were mainly formed in connection with volcanics (or subvolcanic rocks and volcanioclastics), faults, and atmospheric precipitation (or geothermal water) as follows. Early volcanics (or subvolcanic rocks) served as the provenance of fluorine. Atmospheric precipitation (or geothermal water) kept on extracting fluorine from the rock formations during seepage (or circulation). As a result, a fluorine-bearing hydrothermal solution was formed and then was enriched to form deposits in a suitable environment and favorable space while migrating, with faults acting as migration pathways of the thermal solution and enrichment sites of the deposits. The features of this type of fluorite deposits are as follows: The surrounding rocks of their ore bodies mainly include rhyolitic crystallinelastic tuff and ignimbrite; their ore mineral components are relatively simple, which include fluorite mainly and are associated with barite, galena, blende, and chalcopryite in individual areas; their gangue minerals include quartz and chalcedony mostly and calcite, opal, feldspar, chlorite, and pyrophyllite occasionally; their ores mainly include fluorite, quartz-fluorite, fluorite-quartz, and clay-fluorite, with the CaF$_2$ content of more than 80%, 65%–80%, 20%–55% and 80%–90%, respectively in general; they serve as the most important type of fluorite deposits in China, predominating in terms of both number and resources; they are also the main deposits exploited in China. Typical
examples of this type of fluorite deposits include Yangjia fluorite deposit in Wuyi County, Zhejiang Province; Hushan fluorite deposit in Suichang County, Zhejiang Province; Sanbaotun fluorite deposit in Yi County, Liaoning Province. The necessary metallogenic factors of this type of fluorite deposits are volcanics (including subvolcanic rocks and volcanicles) and faults (Fig. 3).

(iii) Bamianshan type. The fluorite deposits of this type were mainly formed in connection with carbonatite (or other sedimentary rocks), faults, and indispensable magmatic activities as follows. Carbonatite (other sedimentary rocks) served as the main source of fluorine. With the heat supplied by magmatic activities, the ore-bearing hydrothermal solution extracted fluorine and calcium elements from source strata, and then precipitated in and filled the contact zones, interlayer fracture zones, and faults. As a result, meso-epithermal fluorite deposits were formed (Figs. 4, 5, 6). The features of this type of fluorite deposits are as follows: Their ore minerals mainly include fluorite, quartz, and sericite, as well as other minerals such as calcite, chlorite, plagioclase, idocrase, graphite, pyrite, and magnetite; their ore association includes fluorite-quartz-sericite, fluorite-quartz, and fluorite-calcite; their ore-body grades range between 20.03% and 87.62%. Typical examples of this type of fluorite deposits include the Bamianshan fluorite deposit in Changshan County, Zhejiang Province, and Yushankucaoping fluorite-barite deposit in Pengshui County, Chongqing City. The necessary metallogenic factors of this type of fluorite deposits are carbonatite (or other sedimentary rocks) and faults.

3.2. Magmatic-hydrothermal fluorite deposits

The metallogenic fluids of magmatic-hydrothermal fluorite deposits are mainly magmatic-hydrothermal solution (mixed with groundwater or atmospheric precipitation in the late metallogenic stage for some fluorite deposits). The magmatic-hydrothermal solution carried fluorine or calcium elements itself or generated fluorine or calcium elements during evolution and differentiation. Fluorine and calcium elements are essential for the formation of fluorite deposits. They were enriched in a suitable metallogenic environment and favorable space by reacting with surrounding rocks. As a result, the magmatic-hydrothermal fluorite deposits were formed. These deposits may be enriched either in faults or rock formations. Some of them may have been formed...
through multiple stages of metallization, but this study only focuses on the mineralization of their main metallogenic stages. The magmatic-hydrothermal fluorite deposits can be divided into the following three types according to their ore-controlling factors (lithologic and structural factors).

(i) Shizhuyuan type. The mineralization of this type of fluorite deposits can be divided into three stages. In the first two stages, the granite emplacement led to the formation of large-area skarnization and greisenization. As a result, tungsten-stannum-molybdenum-bismuth-boron-fluorine deposits were formed. The diagenetic and metallogenic fluids of granite, pegmatite, skarn, and greisen were mostly magmatic-hydrothermal solutions. The skarnization is distributed on the side of the external contact zone of intrusive

![Diagram of mineralization stages](image)

**Fig. 4.** Ore bodies occurring in the contact zone between rock mass and limestone in the Bamianshan deposit in Zhejiang Province (after Geology Institute of China Chemical Geology and Mine Bureau, 2007). 1–mudstone; 2–calcareous mudstone; 3–silty mudstone; 4–fine sandstone; 5–argillaceous limestone; 6–marble; 7–calcareous siliceous hornstone; 8–diopside hornstone; 9–silicified fracture zone; 10–granite; 11–granite porphyry; 12–diorite porphyrite; 13–attitude; 14–borehole and number; 15–Cambrian Xiyangshan Formation; 16–Cambrian Huayansi Formation; 17–Cambrian Yangliugang Formation; 18–Sinian Zhitang Formation.

![Diagram of stratiform ores](image)

**Fig. 5.** Stratiform and lenticular ore bodies occurring in interlayer fracture zones in limestone in the Bamianshan deposit in Zhejiang Province (after Geology Institute of China Chemical Geology and Mine Bureau, 2007). 1–Quaternary; 2–hornfelsized limestone; 3–marbleized limestone; 4–fluoritized limestone; 5–marble; 6–limestone; 7–granite; 8–granite porphyry; 9–fracture zone; 10–fluorite ore body; 11–attitude; 12–borehole and number; 13–Lower Ordovician Yinzhubu Formation; 14–Upper Cambrian Xiyangshan Formation; 15–Upper Cambrian Huayansi Formation; 16–Cambrian Yangliugang Formation.
rock masses near carbonatites. It is formed due to the chemical reactions between metallogenic hydrothermal solution and carbonatite after the metallogenic hydrothermal solution rose from deep parts. The spatial distribution of the skarnization is consistent with the skarn. Meanwhile, four ore zones developed from outside to inside, whose types are marble type (I), skarn type (II), greisen stockwork - skarn type (III), and greisen or greisenized granite type (IV). There is no notable boundary between adjacent ore zones. Instead, these mineral zones are mostly in gradually transitional contact (Fig. 7). The features of this type of deposits are as follows: They have a great variety of minerals; their ore minerals mainly include wolframite, scheelite, molybdenite, bismuthinite, and cassiterite, while their gangue minerals mainly include quartz, topaz, and fluorite; fluorite occurs as associated minerals and is distributed among various ores throughout the deposits, with CaF$_2$ content of usually 10%–20% (17.40% on average). A typical example of this type of fluorite deposits is the Shizhuyuan skarn-type tungsten-stannum-molybdenum-bismuth fluorite deposit in Chen County, Hunan Province. The basic metallogenic factors of this type of fluorite deposits are carbonatite and skarn.

(ii) Sumqagan Obo type. The fluorite deposits of this type were formed mainly under the control of rift basins, strata, folds (faults), and magmatic activity. All of them occur in the crystalline limestone and marble at the bottom of the third member of Lower Permian Dashizai Formation. The fluorite ore bodies occur as laminated or stratiform, with the footwall consisting of foliated rhyolitic porphyry and the roof composed of carbonaceous slate. Yanshanian intrusive porphyritic granite is visible on the periphery of these fluorite deposits. The fluorite deposits of this type were formed mainly under the control of rift basins, strata, folds (faults), and magmatic activity. All of them occur in the crystalline limestone and marble at the bottom of the third member of Lower Permian Dashizai Formation. The fluorite ore bodies occur as laminated or stratiform, with the footwall consisting of foliated rhyolitic porphyry and the roof composed of carbonaceous slate. Yanshanian intrusive porphyritic granite is visible on the periphery of these fluorite deposits.

Fig. 6. Steeply-inclined veined ore body in the tectonic zone in the Bamianshan deposit in Zhejiang Province (after Geology Institute of China Chemical Geology and Mine Bureau, 2007). 1–Quaternary; 2 –hornstonized limestone; 3 –marbleized limestone; 4 –fluoritized limestone; 5 –marble; 6 –limestone; 7 –granite; 8 –granite porphyry; 9 –fracture zone; 10 –fluorite ore body; 11 –attitude; 12 –borehole and number; 13 –Lower Ordovician Yinzhubu Formation; 14 –Upper Cambrian Xiyangshan Formation.

Fig. 7. Profile map of Shizhuyuan tungsten-stannum-molybdenum-bismuth fluorite deposit in Chen County, Hunan Province (after Wang JP et al., 2014). 1–margin-facies, fine granular, porphyritic biotite granite of the first intrusive body in the Early Yanshanian; 2–fine granular biotite granite of the second intrusive body in the early yanshanian; 3–marble; 4–stockwork marble-type ore zone; 5–skarn-type ore zone; 6–greisen stockwork - skarn composite ore zone; 7–greisen-type ore zone.
deposits. The fluorite deposits of this type have simple ore minerals, which mainly include fluorite and a small amount of clay, ferruginous materials, and carbonatite. The ores primarily include quartz-fluorite ores, with CaF$_2$ content of 39%–95% in general. Typical examples of this type of fluorite deposits are the Sumoqagan Obo fluorite deposit in Inner Mongolia and the Obotu fluorite deposit in Siziwang Banner, Inner Mongolia. The necessary metallogenic factors of this type of fluorite deposits are rift basins, limestone, submarine volcanic eruption, folds (faults), and magmatic activity (Fig. 8).

(iii) Qiyishan type. The deposits of this type were mainly formed under the control of carbonatite and faults (tectonic fissures). The carbonatite provided calcium elements needed for the forming of fluorite deposits. The magmatic-hydrothermal solution bearing fluorine reacted with carbonatite when migrating along faults (tectonic fissures) to activate and extract Ca$^{2+}$. Then the fluorine elements and Ca$^{2+}$ were enriched to form fluorite deposits in a suitable metallogenic environment and favorable ore-depositing space. Faults acted as the migration pathways of the metallogenic hydrothermal solution and the metallogenic space of fluorite. The features of this type of fluorite deposits are as follows: Their ore minerals are fluorite and their gangue minerals include chalcedony, quartz, calcite, and limonite; the CaF$_2$ content is usually more than 90% in veined ore bodies and is about 70% in the lenticular and chambered ore bodies. Typical examples of this type of fluorite deposits are the Dongqiyishan fluorite deposit in Ejin Banner, Inner Mongolia, and the Shuangjiangkou fluorite deposit in Hengnan County, Hunan Province. The necessary metallogenic factors of this type of fluorite deposits are carbonatite and faults (tectonic fissures; Fig. 9).

4. Metallogenic regularity of fluorite deposits in China

4.1. Temporal distribution rules of fluorite deposits

The fluorite deposits in China were formed from the Xingkainian (Cambrian) to the Yanshanian according to the statistics of the metallogenic epoch of the deposits in the main metallogenic areas in China. The fluorite deposits of the Yanshanian predominate, followed by those of the Variscan, and those of the Xingkainian, Caledonian, and Indosinian only account for a small percentage. The Yanshanian serves as the main metallogenic epoch of the fluorite deposits in China. Among the identified fluorite deposits in China, 91% were formed in the Yanshanian, about 4% in the Variscan, and 1% in the Himalayan, and less than 1% in the Xingkainian, Caledonian, and Indosinian (Table 3; Fig. 10a).

In China, the most fluorite deposits were formed in the Yanshanian. Large and super-large deposits in China were mostly formed in the Yanshanian and Variscan and only a small number of them were formed in the Himalayan and Indosinian. Meanwhile, only some small deposits or mineralized points were formed in the Xingkainian (Fig. 10b).

Fig. 8. Longitudinal profile of Sumoqagan Obo fluorite deposit in Inner Mongolia (after Nie FJ et al., 2008). 1–carbonaceous argillaceous slate interbedded with crystalline limestone of Dashizhai Formation; 2–rhyolite of Dashizai Formation; 3–marble lens; 4–skarn; 5–fluorite ore body; 6–borehole and number.

Fig. 9. Geologic map of Qiyishan fluorite mining area, Inner Mongolia (after Zhao SM et al., 2002). 1–alluvial and proluvial sand gravel; 2–andesitic tuff and sandy slate; 3–andesite and dacite; 4–marble; 5–Late Yanshanian granite; 6–quartz orthophyre; 7–fluorite-bearing chert vein; 8–chert mineralized vein; 9–fluorite mineralized vein; 10–geological boundary; 11–stratum attitude.
Moreover, the spatial distribution of the metallogenic epochs of fluorite in China is according to certain laws. In detail, the fluorite deposits in Inner Mongolia were formed from the Caledonian to the Yanshanian. In contrast, the fluorite deposits in Zhejiang and Guangdong provinces were mostly formed in the Yanshanian, and a few of the fluorite deposits in Guangdong Province were formed in the Himalayan. Thus it can be seen that the fluorite deposits are gradually younger and younger from north to south. The fluorite deposits in China exhibit the same rule from west to east. In detail, the fluorite deposits in Qinghai and Gansu provinces were mostly formed in the Variscan–Indosinian, while those in Zhejiang Province were all formed in the Yanshanian. This is basically consistent with the distribution rule of the metallogenic epochs of the fluorite deposits in South China achieved by Pei QM (2018).

4.2. Spatial distribution rules of fluorite deposits

Fluorite deposits are widely but unevenly distributed in China. In terms of geographical distribution, they are distributed in all provinces/cities except for Tianjin and

<table>
<thead>
<tr>
<th>Metallogenic epoch</th>
<th>Deposit number</th>
<th>Deposit scale</th>
<th>Main metallogenic areas</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Super large</td>
<td>Large</td>
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<tr>
<td>Himalayan</td>
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<td>1</td>
</tr>
<tr>
<td>Yanshanian</td>
<td>565</td>
<td>1</td>
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</tr>
<tr>
<td>Indosinian</td>
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</tr>
<tr>
<td>Variscan</td>
<td>29</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>Caledonian</td>
<td>8</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Xingkainian</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Total</td>
<td>623</td>
<td>2</td>
<td>41</td>
</tr>
</tbody>
</table>

**Fig. 10.** Distribution of metallogenic epochs of main fluorite deposits (a) and different scales of fluorite deposits (b) in China.
Shanghai cities. However, large and medium fluorite deposits mainly concentrate in coastal areas in east China, central China, and the central and eastern parts of Inner Mongolia.

The magmatic-hydrothermal fluorite deposits are intensively distributed in Inner Mongolia and Hunan areas, with Hunan Province enjoying the highest resources. In terms of geotectonic locations, most of them are distributed in the Tianshan-Xingmeng orogenic system and the Lower Yangtze Block. In terms of deposit types, the magmatic-hydrothermal fluorite deposits mainly include paragenic and associated fluorite deposits. Some of them are paragenic or associated with tungsten, stannum, molybdenum, beryllium, lead, and zinc ores, while some are single-type fluorite deposits that occur in the external contact zone between strata and rock masses. The fluorite ores associated with tungsten, stannum, molybdenum, and beryllium ores tend to form large and super-large associated fluorite deposits, while others are mostly small. The large and super-large magmatic-hydrothermal fluorite deposits were formed in close connection with carbonatite and a typical example is the Shizhuyuan tungsten-stannum-molybdenum-bismuth fluorite associated deposit in Chen County, Hunan Province. It occurs in the internal and external contact zones between the Qianlishan complex and the argillaceous banded limestone in Shetianqiao Formation, with identified resources (CaF$_2$) of 70.66×10$^6$ t and an average grade of 19.00%–21.31%. Another example is the Bamianshan fluorite deposit in Changshan County, Zhejiang Province. It mainly occurs in the external contact zone between early Cretaceous granite and the argillaceous limestone of the upper Cambrian Huayansi Formation, with identified resources (CaF$_2$) of 4.3×10$^6$ t (Wang JP et al., 2014).

The meso-epithermal fluorite deposits are distributed in Zhejiang, Fujian, and Jiangxi provinces in East China primarily and Guangdong, Guangxi, Hebei, and Henan provinces secondarily. In terms of geotectonic locations, they are mainly distributed in the Tianshan-Xingmeng orogenic system, the North China Block, the Qinling-Qilian-Kunlun orogenic system, the Wuyi-Yunkai-Taiwan orogenic system, and the Yangtze Block and are intensively distributed in the Wuyi-Yunkai-Taiwan orogenic system. Furthermore, the meso-epithermal fluorites are hosted in a variety of rocks, including Archean metamorphic rocks, Paleozoic sedimentary rocks, and Mesozoic-Cenozoic volcanic and intrusive rocks. For example, the spatial distribution of Qiushanba-type deposits is associated with intrusive rocks, and magmatic activity provided heat for thermal groundwater to extract fluorine and calcium elements in order to form ore-bearing hot brine. In contrast, the fluorite deposit in Wuyi County, Zhejiang Province was formed in connection with volcanics, which provided essential fluorine elements for the formation of the fluorite deposit. In addition, the meso-epithermal fluorite deposits were mostly formed under the control of large faults and fracture zones, which served as the migration pathways of ore-bearing thermal sources and main ore-hosting space.

### 4.3. Metallogenic evolution of fluorite deposits

The fluorite deposits in China were mainly formed under the influence of factors such as magmatic activity, strata, lithology, and structures. Meanwhile, these factors vary in different geological periods, resulting in different types and intensity of fluorite metallogenesis at different stages.

The fluorite deposits in China were formed in the Xingkainian at the earliest and were intensively formed in the Yanshanian followed by the Variscan. They were mainly formed in two ways: (1) Hydrothermal solution filled in deposits after magmatic activity period; (2) source bed was formed owing to sedimentation, and then the fluorite deposits were formed after extraction, deposition, filling, and superposition induced by hydrothermal solution (China Chemical Geology and Mine Bureau, 2019). Overall, the fluorite deposits were mostly formed due to hydrothermal activity after their wall rocks or source bed were/was formed. Therefore, the metallogenic epochs of fluorine are possibly very new even if ancient metamorphic rocks serve as ore-hosting formations. As shown by relevant statistics, more than 90% of the fluorite deposits in China were formed in connection with the Yanshanian orogeny, and meanwhile, the Yanshanian magmatic activity is the most favorable for the mineralization of fluorite. In contrast, the fluorite deposits formed in other periods mostly occur as the associated minerals of other mineral types and yield small total resources. Generally, the formation of the fluorite deposits tends to be related to late magmatic activities, which is consistent with the metallogenic regularity of fluorite deposits around the world (Wang JP et al., 2014).

As concluded by the Institute of Geochemistry of the Chinese Academy of Sciences based on the systemic testing of fluorine content in the granites in South China, the younger the granite, the higher the fluorine content, and the types and content of fluorine vary in a regular way with the ages of the granites. For example, the fluorine mainly occurs as fluorite and topaz in Yanshanian granites. All these indicate that younger strata and later magmatic activity are more favorable to the enrichment and mineralization of fluorine. Moreover, the chemical properties of the fluorite itself serve as one of the factors causing the late formation of fluorite deposits. The details are as follows. Similar to chlorine, fluorine is relatively chemically active. The fluorite deposits formed in early geological periods may have been disrupted by weathering, eluviation, metamorphism, and hydrothermal activities in the subsequent geological eras. As a result, fluorine was possibly reactivated and migrated and then was re-enriched to form fluorite deposits in new periods (Song SH et al., 1994). Therefore, it is rare to find the fluorite deposits with very high ages, just as very sparse ancient chloride-bearing deposits can be seen in the world.

Structures also play an important role in controlling the formation of fluorite deposits. The formation of fluorite deposits was mainly controlled by faults, followed by folds. All deposits except for those occurring in sedimentary rocks
were controlled by faults and fissures, which served as both pathways for the metallogenic solution and ore-depositing space. The deposits in sedimentary rocks were mostly formed in connection with anticlines. Most of them occur at the anticlines’ cores and both wings near the anticlines’ axis. As indicated by many fluorite deposit examples, in a deposit or an orefield, there always exist the faults that are in the same direction and enjoy the most favorable ore-bearing features among many interconnected, different-attitude faults (if any). These faults are called dominant ore-controlling faults. In the deposits formed in connection with anticlines, the dominant ore-controlling faults tend to be perpendicular to the anticlines’ axis and only a few of them are approximately parallel to the anticlines’ axis. As previously discovered, the main ore-bearing faults of the fluorite deposits in east China have basically the same attitudes and most of the main ore-bearing faults are in NE or NNE trending despite different formation epochs of the fluorite deposits’ wall rocks (China Chemical Geology and Mine Bureau, 2019). In a broad regional scope, such as southeastern coastal areas of north China, central China, south China, and east China where Yanshanian magmatic activity zones are widely distributed, the fluorite deposits show that their dominant ore veins are also mainly in NE trending except a minority in NW trending. Therefore, it can be inferred that the distribution of most fluorite deposits in China are completely controlled by the NE-trending structures in east China. Special attention should be paid to the fact that ore veins of some fluorite deposits are in other directions (Song SH et al., 1994). To determine the tectonic evolutionary process of these fluorite deposits, it is necessary to further study the main mine in mining areas where stand the deposits that occur in marine-facies volcanic sedimentary-rock strata and sedimentary carbonatite.

In the same ore-controlling fault zone, the stress-strain difference varies significantly with location, especially in the locations where the strike, dip, and attitude of the fault zone change distinctly. As a result, the components of metallogenic fluids will diffuse, migrate, and be distributed again (differentiate). The SiO₂ components are relatively enriched in local blocks/segments with compressive - compressive-shear stress-strain, while the CaF₂ components are enriched in local blocks/segments with tensile-tensile-shear stress-strain. Therefore, in the practice of ore prospecting, exploration, and mining, to understand the rules of the differential change in the stress-strain features in different locations of ore-controlling faults will facilitate the prediction and assessment of the concealed ore bodies and industrial ore shoots (Zhang ST and Xu ZZ, 1997).

4.4. Division of metallogenic zones/belts of fluorite deposits

Based on regional metallogenic geological setting and metallogenic regularity as well as 1:2500000-scaled geologic maps and the latest information of the fluorite mines in China, three-order metallogenic zones/belts of fluorite deposits (single mineral type) were proposed in this study according to the requirements and principles of the division and study of metallogenic zones/belts put forward by Wang JP et al. (2014) by referring the division scheme of I-, II-, and III-order metallogenic zones/belts provided in Classification Scheme of Metallogenic Zones (Belts) in China (Xu ZG et al., 2008). In detail, 15 metallogenic zones/belts of three-order fluorite deposits were delineated across China (Table 4; Fig. 11). The I- and II-order metallogenic domains and provinces of fluorite deposits were named and numbered with uniformed titles and numbers in China, while the III-order metallogenic zones/belts of fluorite deposits were mainly named according to their geographical factors. Moreover, to distinguish the III-order metallogenic zones/belts of the fluorite deposits from other metallogenic zones/belts (single mineral type and comprehensive) in China, the symbol “F” was added to the numbers of III-order metallogenic zones/belts of fluorite.

5. Progress in prospecting and research of fluorite deposits in China

5.1. New progress in prospecting of fluorite deposits in China

In the last ten years, multiple large or super-large fluorite deposits have been discovered in east China, and several medium-large fluorite deposits have also been found in Yunnan, Xinjiang, etc. Overall, breakthroughs have been made in prospecting of fluorite deposits in the southern, eastern, northern, and western parts of China, with large resource bases of fluorite deposits being newly discovered in southern Jiangxi Province, Chenzhou City of Hunan Province, and Sonid Right Banner - Xilinhot City of Inner Mongolia. The newly discovered fluorite deposits have three features: (1) Newly added reserves mostly concentrates in traditional advantageous production regions of fluorite deposits, such as Hunan, Zhejiang, Inner Mongolia, and Jiangxi provinces; (2) single-type deposits predominate and serve as the main types of deposits to be explored and utilized despite their low proportion of reserves; (3) a small number associated deposits are included; they yield a high proportion of reserves, but their development and utilization depend on the development of the associated metal mineral types (Li J et al., 2017).

5.2. Main progress in the research of fluorite deposits in China

In recent years, extensive researches have been conducted on fluorite deposits in China, including the fluorite deposits in Siziwang Banner and Chifeng City in Inner Mongolian, North China (Xu DQ, 2009; Zhang ST et al., 2014), Nanling metallogenic belt of fluorite deposits at the junction of Fujian and Jiangxi provinces (Huang GG et al., 2015; Fang GC et al., 2020), the temporal and spatial evolution series of fluorite deposits in Jinhua City, Zhejiang Province (Xu ZZ and Zhang ST, 2013), the associated deposit of fluorite and barite in Wuling Moutain in southwest China (Zou H, 2013; Zou HT et al., 2016), and metallogenic and prospecting prediction models (Wang JP et al., 2018). Meanwhile, research
<table>
<thead>
<tr>
<th>Metallogenic domain No.</th>
<th>Metallogenic domain name</th>
<th>Metallogenic province No.</th>
<th>Metallogenic province name</th>
<th>Metallogenic zone/belt No.</th>
<th>Metallogenic zone/belt name</th>
<th>Typical deposit</th>
<th>I-order tectonic unit</th>
<th>II-order tectonic unit (megafacies)</th>
<th>III-order tectonic unit (facies)</th>
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<td>Dongjiyushan fluorite deposit in Ejin Banner, Inner Mongolia</td>
<td>Tarim Block (No. III)</td>
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<td>IIH2-1</td>
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<td>Qinling-Qilian-Kunlun metallogenic domain</td>
<td>II-5</td>
<td>Alkin-Qilian (orogen) metallogenic province</td>
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<td>Qbaquan fluorite deposit in Gaotai County, Gansu Province</td>
<td>Qinling-Qilian-Kunlun orogenic system (No. IV)</td>
<td>IV-1</td>
<td>IV-1-1</td>
<td>III-20</td>
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<td>Circum-Pacific metallogenic domain</td>
<td>II-12</td>
<td>Da Hinggan Mountains metallogenic province</td>
<td>IIIF-3</td>
<td>Sumoqagan Obo fluorite deposit in Siziwang Banner, Inner Mongolia</td>
<td>Tianshan-Xingmeng orogenic system (No. I)</td>
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<td>I-1-6, I-8-2</td>
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<td>East Inner Mongolia fluorite deposits</td>
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<td>North Hebei - west Liaoning metallogenic belt of fluorite deposits</td>
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<td>Huaibei fluorite deposit in Jingzhou, Hubei Province</td>
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<td>IIIF-6</td>
<td>Huai fluorite deposit in Hanzheng County, Hubei Province</td>
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<td>South Sichuan - north Guizhou metallogenic zone of fluorite deposits</td>
<td>Shaojitan fluorite deposit in Chongqing City</td>
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<td>VI-2</td>
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<td>II-16</td>
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<td>IIIIF-15</td>
<td>Southeast Yunnan - southwest Guizhou metallogenic belt of fluorite deposits</td>
<td>Dachang fluorite deposit in Qinglong County, Guizhou Province</td>
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<td>VI-2</td>
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breakthroughs have been gained for main fluorite ore concentration areas in China. Most especially, Wang JP et al. (2018) determined the rankings by provinces of the predicted fluorite resources in China based on the project of “Nationwide Mineral Resource Potential Assessment” in 2013, and the rankings are basically consistent with the prospecting discoveries made in the last 10 years (except Jiangxi Province only). This not only reveals that the predication theories are accurate but also indicates that there are a substantial number of potential fluorite resources.

5.2.1. North China

Typical fluorite deposits in north China were intensively formed at 154–132 Ma (Pei QM et al., 2017; Cao HW et al., 2013; Xu DQ et al., 2009). The fluorite deposits in Inner Mongolia concentrate in Siziwang Banner and Chifeng City. Their deposit types include sedimentation-transformation type, hydrothermal filling type, and associated type, with the hydrothermal filling type predominating.

As for the Sumoqagan Obo fluorite deposit, the following conclusions can be made based on previous research on rare earth elements and isotope dating (Nie FJ, 2008; Xu DQ, 2009): (1) The spatial distribution of the fluorite ore bodies is closely related to Mesozoic granite; (2) the deposit is the product of multiple stages of magmatic-hydrothermal activity; (3) the metallogenesis of the deposit occurred in Late Hercynian and Middle Yanshanian, with the latter dominating; (4) the deposit is of hydrothermal type, formed in connection with plutonic intrusive rock mass of granites; (5) the province of diagenetic (metallogenic) materials is the mixture of crust- and mantle-derived materials, with the crust-derived components completely dominating.

As for the fluorite deposit of hydrothermal filling type in Chifeng City, the metallogenic fluids were the mixture that mainly originated from atmospheric precipitation (Pei QM et al., 2017; Wang L et al., 2018; Zhang ST et al., 2014; Gao YZ, 2012) and migrated to distant areas. Meanwhile, the metallogenic fluorite elements came from deep terranes with a high content of fluorite, and the metallogenic calcium elements mainly originated from eluviation towards the wall rocks by the metallogenic fluids. Moreover, the water-rock reaction served as the main precipitation mechanism of fluorite deposits (Wang L et al., 2020; Cao HW et al., 2014; Zeng ZF, 2013).

5.2.2. Southeast China

The fluorite deposits in southeast China mainly concentrate in Zhejiang, Fujian, Jiangxi, and Nanling areas. Among them, the fluorite deposits in Zhejiang Province can be divided into three types and two metallogenetic series based on their genesis (Huang GC et al., 2015). The three types are volcanic-subvolcanic hydrothermal filling type, hydrothermal filling type after magmatic activity period, and magmatic-hydrothermal metasomatism type, and the two metallogenetic series are separately associated with the Mesozoic volcanic-subvolcanic hydrothermal solution and Mesozoic magma intrusion. All these provide the prospecting
direction of the fluorite deposits in Zhejiang Province. The metallogenic features and genesis of the fluorite deposits in the Xingguo-Ningdu metallogenic belt in Jiangxi Province were previously studied using new testing techniques and methods, and the comprehensive metallogenic model map of the fluorite deposits in south Jiangxi Province was established (Yang SW, 2019). According to the research on the features of more than 20 deposits in the Nanling area (Fang GC et al., 2020), the fluorite deposits in the Nanling area were mainly formed at 160–135 Ma, and show the trend of getting newer from the middle subzone to western subzone and eastern subzone. The single-type fluorite deposits in south China were formed as follows. The metallogenic hydrothermal solution predominated by atmospheric precipitation circulated and eluviated along the fracture zone, and accordingly, the fluorine elements in granite and the calcium elements in strata were reactivated, enriched, and recrystallized into minerals. As a result, their mineralization was about 10–20 Ma later than their diagenism. As for the associated fluorite deposits in southeast China, they firstly experienced magmatism, hydrothermal process, and metallogenesis, and then minerals were formed from the combination of fluorine elements in granite and calcium elements in strata. Their diagenesis and metallogenesis were nearly synchronous. Furthermore, they experienced a transformation by atmospheric precipitation and recrystallization at a later stage.

5.2.3. Southwest China

The fluorite deposits (mineral occurrences) in southwest China are widely distributed in the west Hunan and Hubei - east Sichuan metallogenic belt on the southeastern margin of Sichuan Basin. They are large associated deposits mostly, with multiple mineral occurrences. They have simple mineral components, with ore minerals being fluorite and barite and gangue minerals mainly including calcite and quartz. Their ore bodies mainly occur in Cambrian-Ordovician strata, showing distinct features of strata-controlled deposits. The fluorite deposits in southwest China were formed under rigorous control of regional NE-trending deep fault zones and NW-trending faults, both of which were active for multiple stages, with the former serving as a regional ore-transmitting structural system and the latter serving as an ore-depositing structural system (Zou H et al., 2013, 2016). The representative deposits in the barite-fluorite metallogenic belt on the southeastern margin of Sichuan Basin (western part of Hunan and Hubei - east Sichuan) yielded the Sm-Nd isotope isochron ages of 104±14 Ma, and thus they were formed in Late Yanshanian (Zou H et al., 2017). They were argued to be strata-controlled deposits featuring meso-epithelial genesis and fault-zone filling and metasomatism according to the study on their geological features, formation conditions, ore-controlling factors, and metallogenic mechanisms (Zou H et al., 2017).

5.2.4. Model for prospecting prediction

Based on the synthesis of many years of researches, Wang JP et al. (2018) built two national prediction models of fluorite deposits (two descriptive prediction and assessment models, for the fluorite deposits of hydrothermal filling type and the fluorite deposits of sedimentation-transformation type each) and nine regional prediction models (for deposit types; Table 2) by applying the “mineral prediction method based on deposit models and integrated geological information” under the guidance of a series of metallogenic theories. The prediction results achieved using the above-mentioned models are as follows: (1) The cumulative identified resources of fluorine minerals (CaF$_2$) is about 190×10$^6$ t and the predicted resources (CaF$_2$) is about 950×10$^6$ t in China by the end of 2012; (2) the predicted resources consists of about 430×10$^6$ t of the resources of single-type fluorite deposits and about 520×10$^6$ t of the resources of associated fluorite deposits; (3) as for the spatial distribution of the predicted resources, the fluorite deposits of sedimentary-transformation type is mainly distributed in Inner Mongolia, Yunnan, and Guizhou provinces and regions, while those of hydrothermal filling type is mainly distributed in Zhejiang, Henan, Fujian, and Hebei provinces. Meanwhile, the top ten provinces (autonomous regions) with the highest predicted resources include Hunan, Zhejiang, Inner Mongolia, Henan, and Fujian.

5.3. Prospect prediction of fluorite deposits in China

Based on the division of metallogenic zones/belts in China, Wang JP et al. (2014) determined three-level metallogenic prediction areas of fluorite deposits across the country according to metallogenic factors and exploration levels (Wang JP et al., 2014; Wu ZQ et al., 1989). In detail, the predicted minimum prospecting target areas were determined in each province/autonomous region, and they are the Level-1 metallogenic prediction areas. Then the Level-1 metallogenic prediction areas were further incorporated into Level-2 metallogenic prediction areas according to prediction factors and regional prediction models. Afterward, the Level-2 metallogenic prediction areas were further incorporated into Level-3 metallogenic prediction areas at the national level based on the provincial metallogenic prospect areas. As a result, 1500 Level-1 metallogenic prediction areas were delineated countrywide, and 530 Level-2 and 198 Level-3 metallogenic prediction areas were determined through the above-mentioned incorporation. The Level-3 metallogenic prediction areas include 22 ones with predicted resources of more than 10×10$^6$ t, 85 ones with predicted resources of 1×10$^6$ –10×10$^6$ t, and 91 ones with predicted resources of less than 1×10$^6$ t.

According to prediction, the future fluorite prospecting areas with the highest available resources include Hunan, Zhejiang, Inner Mongolia, and Henan, which are basically consistent with the regions where prospecting breakthroughs have been made in recent years as mentioned above. This further demonstrates the great prospecting potential of these
areas. Besides the favorable resource endowment, these areas feature advanced mining technologies, improved industrial chains, and a good investment environment owing to long fluorite exploration and development. Therefore, the authors of this paper believe that these areas still serve as the major prospecting areas of fluorite deposits in the future.

6. Conclusions

(i) China is rich in fluorite resources, with identified resources (CaF$_2$) of common fluorite deposits of 2,571.26×10$^6$ t by the end of 2018. It is mainly distributed in the provinces/autonomous regions such as Hunan, Zhejiang, Jiangxi, Inner Mongolia, Fujian, and Henan, whose resources account for 89.24% of the total national resources. The fluorite deposits in China are characterized by small scale and dispersed distribution, with large and medium fluorite deposits being mainly distributed in coastal areas in east China, central China, and the central and eastern parts of Inner Mongolia.

(ii) Based on their differences in metallogenic hydrothermal solution and main ore-controlling factors, the fluorite deposits in China can be divided into two groups, namely meso-epithermal deposits and magmatic-hydrothermal deposits. Among them, the meso-epithermal fluorite deposits can be divided into three types according to their differences in necessary metallogenic factors and provenance of fluorine, namely Qiawanba type, Wuyi type, and Bamianshan type. Meanwhile, the magmatic-hydrothermal fluorite deposits can be divided into three types according to their ore-controlling strata, lithologic features, and structure, namely Shizhuyuan type, Sumoqagan Obo type, and Qiyishan type.

(iii) The fluorite deposits in China were intensively formed in Yanshanian. Meanwhile, their metallogenic intensity gradually increased with their metallogenic epochs getting newer. As a result, large and super-large deposits were mainly formed in the Yanshanian and Variscan. The fluorite deposits are gradually younger both from north to south and from west to east.

The magmatic-hydrothermal fluorite deposits were mainly formed in the Yanshanian. They concentrate in Inner Mongolia and Hunan Province, with the Hunan Province enjoying the highest resources. The meso-epithermal fluorite deposits were also mainly formed in the Yanshanian. They are mainly distributed in Zhejiang, Fujian, and Jiangxi provinces in east China.

(iv) Large resource bases of fluorite deposits have been newly discovered in southern Jiangxi Province, Chenzhou City of Hunan Province, and Sonid Right Banner - Xilinhot City of Inner Mongolia in the last ten years. The newly added reserves mostly concentrate in traditional advantageous production regions of fluorite deposits, such as Hunan Province, Zhejiang Province, Inner Mongolia, and Jiangxi Province. According to prediction, the future fluorite prospecting areas with the highest available resources include Hunan, Zhejiang, Inner Mongolia, and Henan, which are basically consistent with the regions where prospecting breakthroughs have been made in recent years.

CRediT authorship contribution statement

Bei-bei Han and Peng-qiang Shang completed the compilation of fluorite resources, deposit types and metallogenic regularities in China. Yong-zhang Gao completed the research on the new progress of fluorite prospecting in China. Chao-mei Yao and Sen Jao provided theoretical guidance and proofread the research results. All authors discussed the results and contributed to the final manuscript.

Declaration of competing interest

The authors declare no conflict of interest.

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