Discovery of Sr-bearing and LREE daughter minerals in fluid inclusions of Maoniuping REE deposit, Sichuan Province*

XU Jiuhua (徐九华)[1], XIE Yuling (谢玉玲)[1], LI Jianping (李建平)[1] and HOU Zengqian (侯增谦)[2]

1. Department of Geology, University of Science and Technology Beijing, Beijing 100083, China

2. Institute of Mineral Deposits, Chinese Academy of Geological Sciences, Beijing 100037, China

Received December 28, 2000; revised February 5, 2001

Abstract Maoniuping rare earth element (REE) deposit, located in Mianning area of Sichuan Province, is of unique geological characteristics and is large in scale. Some studies have shown that there are large amounts of multiphase fluid inclusions in fluorite, quartz and calcite. Besides the daughter minerals of halite, barite and gypsum, Sr-bearing minerals (celestite, strontianite), apatite and eight light rare earth element (LREE) minerals have been found by scanning electron microscope/energy dispersive spectrometer techniques. The abundant occurrence of these daughter minerals shows that the ore-forming fluid is rich in Sr, Ba and LREE contents, and is related to nordmarkite in genesis.

Keywords: **Mianning REE deposit, fluid inclusion, Sr-bearing daughter mineral, REE daughter mineral, SEM/EDS.**

Maoniuping rare earth element (REE) deposit, located in Mianning County, Sichuan Province, is of unique geological characteristics. It is a large REE deposit only next to the famous Bayan Obo REE deposit. Situated in the north of Panxi Rift Valley zone along the west edge of Yangtze Platform, the deposit was formed in Himalayan period. REE-bearing veins occur in nordmarkite and alkali-feldspar granite. The genesis of the REE veins were categorized as alkali-pegmatite type and carbonatite-vein type by Jiang[1], as acmite-augite-barite pegmatite type and carbonate type by Niu et al.[2,3], and as mesothermal-epithermal hydrothermal type by Yuan et al.[4].

Reports of the studies on daughter minerals in fluid inclusions of REE deposits came into notice in recent years. Xie et al. and Fan et al.[5,6] found REE daughter minerals in fluid inclusions in Bayan Obo REE doposit. Willams-Jones et al.[7] and Samson et al.[8] found barite, celestite and REE daughter minerals in Gallinas Mountains, New Mexico, U.S.A. Buhn et al. found burbankite($[Na,Ca]_3[Sr,REE,Ba]_3[CO_3]_5$)daughter minerals in Kalkfeld carbonatite complex, Namibia[9,10]. Yuan et al. and Niu et al. detected barite, halite and hoevillite daughter minerals[2~4]. Here we report the findings of celestite, strontianite and light rare earth element (LREE) daughter minerals as well as gypsum and apatite daughter minearals in fluid inclusions in Maoniuping REE deposit discovered by scanning electron microscope/energy dispersive spectrometer (SEM/EDS) techniques.

1 Characteristics of fluid inclusions

Five types of ore veins were found in Maoniuping REE deposit, including pegmatitic hamartite-

* Project supported by the National Ascent Program 95-Yu-39 and the National Natural Science Foundation of China (Grant No. 49972031).

acmite-augite-fluorite-barite great veins, fine-coarse granular hamartite-fluorite-barite-calcite great veins and pegmatitic hamartite-fluorite-barite-calcite great veins. Mineralizing types included masstaxitic ores mainly composed of calcite, loose REE ores mainly composed of fluorite and barite, and veinlet ores. According to interpenetration, dissolution and replacement, the three hydrothermal mineralizing stages were recognized as oxide-silicate (stage 1), hamartite-fluorite-barite-calcite (stage 2), and polymetal sulfide (stage 3).

A large amount of fluid inclusions was mainly found in vein minerals of stages 1 and 2, including quartz and fluorite. There are three types of fluid inclusions based on phase features: (i) vapor-liquid fluid inclusions, comprising secondary fluid inclusions along the fractures with 90 ~ 110℃ of homogenization temperatures (t_h), and primary fluid inclusions distributed separately in the growth plane with 215 ~ 370℃ of t_h; (ii) CO_2-rich fluid inclusions, which are primary ones and occur in quartz, fluorite and calcite, with 28.9℃ of CO_2 vapor and CO_2 liquid partial homogenization, and 170 ~ 295℃ of t_h; (iii) multi-phase fluid inclusions containing daughter minerals, which are primary inclusions and mainly occur in fluorite, calcite, and sometimes in quartz (Figure 1).

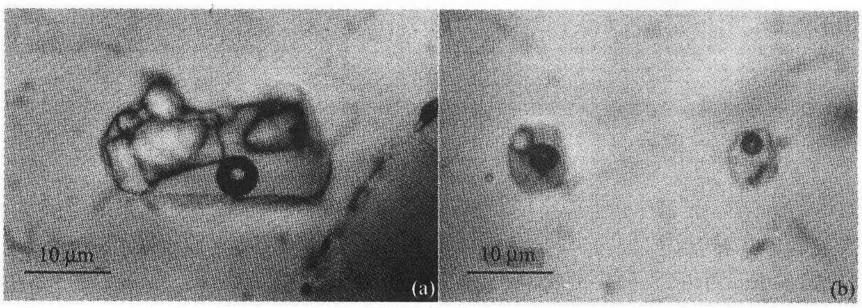

Fig. 1 Fluid inclusions containing daughter minerals in fluorite. (a) Multi-phase fluid inclusions containing daughter minerals; (b) CO_2 fluid inclusions containing daughter minerals.

2 Composition of daughter minerals

SEM/EDS is effective for studying daughter minerals in fluid inclusions[5,6]. Based on petrographic study, specimens containing abundant daughter minerals were selected for preparing SEM/EDS samples. For samples of fluorite and calcite, grains with complete cleavages were selected; and for quartz, grains having smooth fractured surface were selected. The selected samples were put on a glass-slide and covered with carbon. Then the samples were carefully observed under an SEM, so that more tiny fluid inclusions containing daughter minerals could be observed.

2.1 Daughter minerals in fluid inclusions of quartz

Vein quartz was mainly formed in stage 1. Fluid inclusions containing daughter minerals were occasionally seen in quartz, usually smaller than 10 μm in diameter. They were often associated with vapor-aqueous two-phase inclusions, containing one daughter mineral commonly. The melting temperatures (T_m) of daughter minerals were measured at 95 ~ 120℃ in this work, lower than 116 ~ 180℃ as reported by Niu et al.[2,3], so they could be of sodium chloride and sylvine. Some daughter minerals had higher T_m 454 ~ 520℃[2]. SEM/EDS analysis showed that many daughter minerals contained a high Sr and a low S content. They might be strontianite, not celestite. LREE minerals (fluocerine) and calcimangite were also found in fluid inclusions.

2.2 Daughter minerals in fluid inclusions of fluorite

Fluorite formed in stage 2 was widely found in Maoniuping deposit. It occurred as light green or violet masses or veinlets. A lot of fluid inclusions containing daughter minerals could be found in fluorite. The size of fluid inclusions was larger than in quartz, from several micrometers to 60 μm, with irregular or negative crystal shapes. They occurred as isolated bubbles or in threes and fours, showing a primary origin. Daughter minerals in a single inclusion could be up to 5 or 6, 1 to 20 μm in size. CO_2 fluid inclusions containing daughter minerals were also found. Under orthogonal polarized light, these daughter minerals showed anisotropic extinction. Niu et al. have measured the melting temperatures of daughter minerals at 494 ~ 502℃[2,3]. By Laser Raman analysis, those daughter minerals were determined to be barite.

We found the same phenomenon as described by Niu et al.[2] in heating test. Most bubbles of fluid inclusions disappeared at 100 ~ 170℃, but recurred and became larger at 150 ~ 370℃. Unfortunately, these fluid inclusions fractured before daughter minerals dissolved when the temperature was higher than 400℃ ~ 625℃. A few data were in the temperature range of 420 ~ 535℃. The bubbles of two inclusions disappeared at 85℃, while daughter minerals disappeared at 420℃. However, the bubbles appeared again at 455℃ and the inclusions fractured at 490℃. According to the characteristics of SEM/EDS spectra of daughter minerals (Fig. 2), the shapes of daughter minerals-REE-22-5 (Fig. 3) and the chemical composition of host minerals, the daughter minerals were determined and found to be gypsum, apatite and LREE minerals.

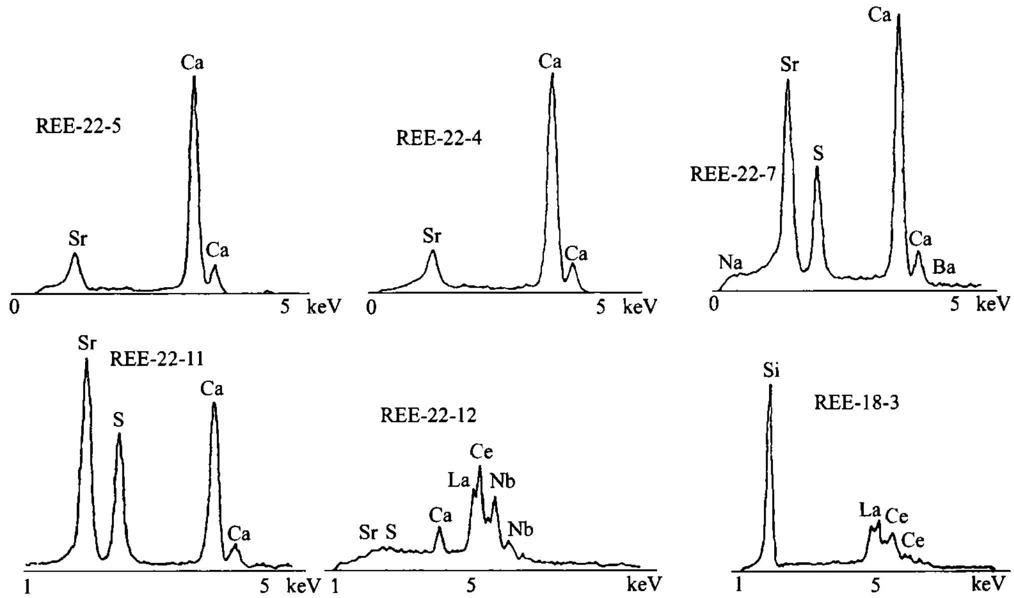

Fig. 2 SEM/EDS spectra of daughter minerals in fluid inclusions of Maoniuping REE deposit. REE-22-4, strontianite in fluid inclusions of calcite (high Sr and low S, with high Ca background); REE-22-7 and REE-22-11, celestite in fluid inclusions of calcite (high Sr and S, with high Ca background); REE-22-12, LREE daughter minerals in fluid inclusions of calcite; REE-18-3, LREE daughter minerals in fluid inclusions of quartz.

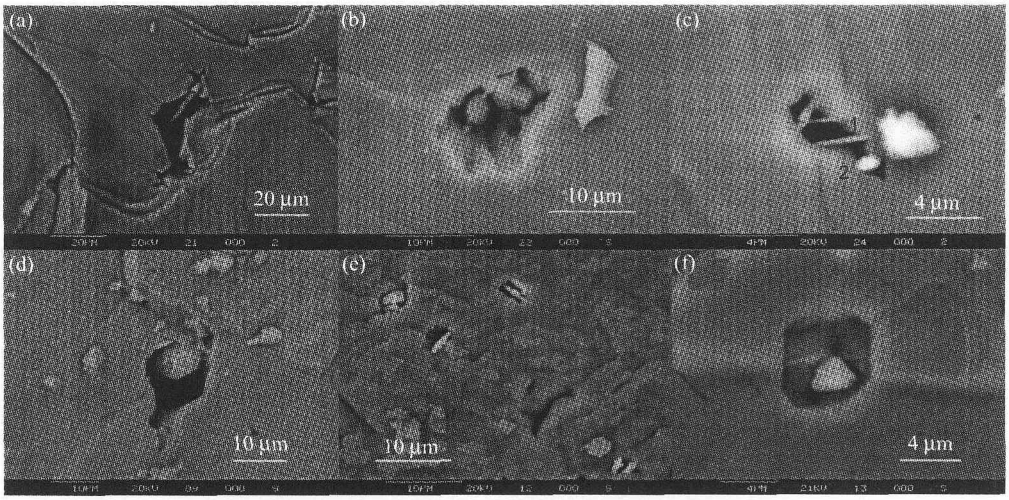

Fig. 3 SEM photographs of daughter minerals in fluid inclusions from Maoniuping REE deposit. (a) Needle-like gypsum in fluid inclusions of fluorite (REE-13-3); (b) apatite in fluid inclusions of fluorite; (c) needle-like strontianite (1: REE-22-4, REE-22-5) and short rod-shaped celestite (2: REE-22-7) in fluid inclusions of calcite; (d) calcimangite in fluid inclusion of quartz (REE-18-4); (e) six slaty La-Ce-Nd REE daughter minerals in four inclusions of calcite; (f) short rod-shaped celestite in fluid inclusion of calcite (REE-22-11). SEM/EDS instrument: S-250MK3, AN10000 energy dispersive spectrometer.

2.3 Daughter minerals in fluid inclusions of calcite

Calcite is also a main gangue mineral in REE ores, formed in stage 2. Fluid inclusions in calcite are abundant, but generally smaller than 5 μm in size. Heating test was done for a few large inclusions. They had similar characteristics to those in fluorite. The bubbles disappeared at 100 ~ 320℃, but recurred at 350℃ and disappeared at 460℃ for one inclusion. Daughter minerals were not dissolved at 615℃. SEM/EDS analysis showed that a great number of fluid inclusions contained daughter minerals. The diameters of daughter minerals were only several micrometers. Two types of Sr-bearing minerals could be found in fluid inclusions in calcite. The first type, which was needle-like and had very low content of S (Fig. 2), might be strontianite. The other type, which was short rod-shaped and contained high S content, must be celestite. Barite and La-Ce-Nd LREE minerals were also found in fluid inclusions.

3 Discussions

There are several different understandings for ore-forming process of Maoniuping REE deposit. Previously it was thought of as the pegmatite type deposit[1], or the hydrothermal deposit related to special magma-salt melt[2,3]. Yuan et al.[4] believed that the ore-forming fluid was not a melt-water mixing fluid, but a typical hydrothermal fluid. He also pointed out that ore-bearing nordmarkite was formed by re-melting, ascending and emplacement of the source crust rocks under the activation of mantle plume and tectonic mobilization in Himalayan period.

Many Sr-bearing minerals (strontianite, celestine) and LREE minerals as daughter minerals in fluid inclusions were found in this study. The heating process of fluid inclusions indicated that ore-forming fluid had super critical-salt melt characteristics. The "daughter minerals" which were not melted above 500℃ were possibly fluid-melt inclusions or mineral grains that were captured by ore-forming fluid during early stages, so they were false daughter minerals. Whether the daughter minerals were real ones or false ones, the ore-forming fluid was rich in Sr, Ba and LREE. Geochemistry study showed that nordmarkite had higher LREE, Sr and Ba contents than other magmatic rocks[4]. The mass numbers of LREE are $(304.7 \sim 3681.0) \times 10^{-6}$, and that of LREE/HREE is 14.3 ~ 56.3, 10 times higher than those of other rocks in the mine area. The mass numbers of Sr are $(728 \sim 4691) \times 10^{-6}$, and those of Ba are $(614 \sim 3942) \times 10^{-6}$, also 10 times higher than those of other rocks. Obviously, ore-forming fluid rich in Sr, Ba and LREE was related to nordmarkite. According to microelemental geochemistry[11], Sr and Ba in hydrothermal fluid mainly originated from wallrocks (nordmarkite for this mine area). Migration of Sr and Ba was related to activity of Potassium. However, the calculated weight of nordmarkite body is about 580 million tons according to geological data and rock density, and the total weight of LREE, Sr and Ba in nordmarkite are 1.2, 1.3 and 1.6 million tons, respectively. Hence, it is hard to form a large REE deposit by hydrothermal metasomatism of nordmarkite body. Based on tectonic characteristics[1] and stable isotope study[4], we believe that there exists source magma rich in LREE, Sr and Ba in the deep mine. The ore-forming fluid rich in LREE and nordmarkite could both originate from the immiscibility of deep magma, so they might be from the same source. The emplacement of LREE mineralization was posterior to the intrusion of nordmarkite, because the LREE veins penetrated into the nordmarkite bodies.

Acknowledgement The authors thank Ms. Qiu Baoqin at Department of Material Engineering of USTB for help in SEM/EDS analysis.

References

1 Jiang, M. Geological and structural features of the Maoniuping REE deposit and its ore-controlling significance. Mineral Deposits (in Chinese), 1992, 11(4): 351.

2 Niu, H. et al. Study on the fluid-melt inclusions in fluorite. Geological Review (in Chinese), 1995, 41(1): 28.

3 Niu, H. et al. A study on inclusions in minerals from Mianning REE deposit in Sichuan Province. Geochimica (in Chinese), 1996, 25(6): 560.

4 Yuan, Z. et al. Maoniuping Rare Earth Ore Deposit, Mianning County, Sichuan Province (in Chinese). Beijing: Seismology Publishing House, 1995.

5 Xie, Y. et al. A discovery of REE minerals in fluid inclusions in the Bayan Obo REE-Fe-Nb deposit. Chinese Science Bulletin, 1996, 41(5): 401.

6 Fan, H. et al. Determining daughter minerals in fluid inclusions under scanning electron microscope. Geological Science and Technology Information, 1998, 17(Sup.): 111.

7 Williams-Jones, A.E. et al. Hydrothermal REE-fluorite mineralization in the Gallinas Mountains, New Mexico, USA. In: Mineral Deposits: Research and Exploration Where do They Meet? (ed., Papunen, H.), Rotterdam: Balkema, 1997, 687.

8 Samson, I. M. et al. Genesis of the Gallinas Mountains REE-fluorite deposits, New Mexico: Evidence from mineral paragenesis and fluid inclusions. In: Proceedings of GAC/MAC Annual Meeting, Ottawa, Canada, 1997.

9 Buhn, B. et al. Composition of nature, volatile-rich Na-Ca-REE-Sr carbonatitic fluids trapped in fluid inclusions. Geochim. Cosmochim. Acta, 1999, 63: 3781.

10 Buhn, B. et al. Burbankite, a (Sr, REE, Na, Ca)-carbonite in fluid inclusions from carbonate-derived fluids: Identification and characterization using Laser Raman spectroscope, SEM-EDS and synchrotron micro-XRF analysis. Am. Mineral., 1999, 84: 1117.

11 Liu, Y. et al. Introduction to Elementary Geochemistry (in Chinese). Beijing: Geological Publishing House, 1987.