Continuous carbonatitic melt–fluid evolution of a REE mineralization system: Evidence from inclusions in the Maoniuping REE Deposit, Western Sichuan, China

Yuling Xie a,⁎, Zengqian Hou b, Shuping Yin b, Simon C. Dominy c,d, Jiuhua Xu a, Shihong Tian e, Wenyi Xu e

a School of Civil and Environmental Engineering, University of Science and Technology Beijing, Beijing 100083, PR China
b Institute of Geology, Chinese Academy of Geological Science, Beijing 100037, PR China
c Snowden Mining Industry Consultants Ltd., Weybridge, Surrey, KT13 0TT, UK
d School of Science & Engineering, University of Ballarat, Ballarat, Victoria 3353, Australia
e Institute of Mineral Resources, Chinese Academy of Geological Science, Beijing 100037, PR China

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A B S T R A C T

The Maoniuping REE deposit is a world-class deposit with 1.2 Mt of REO grading on average 2.89 wt.% REO. It is the largest in the 270-km long Mianning–Dechang REE belt and is associated with Himalayan carbonatite–alkaline complexes in the eastern Indo-Asian collisional zone, Western Sichuan Province, China. The deposit is hosted by nordmarkite stocks and carbonatite sills that display a radiometric age of 40 to 24 Ma and which intruded a Yanshanian granite pluton. The 40.3 to 27.8 Ma REE mineralization occurs as vein systems hosted in nordmarkite and carbonatite with minor altered granite and rhyolite. Four ore types are recognized based on ore texture and mineral assemblage: (1) disseminated; (2) pegmatitic; (3) brecciated; and (4) stockwork (stronger) types. Five mineralizing stages are confirmed according to vein crosscutting relationships, mineral assemblage and microthermometric results, these are: 1) carbonate stage, 2) pegmatite stage, 3) barite–bastnaesite stage, 4) later calcite stage and 5) epigenetic oxidation stage. Varied inclusion assemblages are found in fluorite, quartz, bastnaesite, barite and calcite from stages 1 through to stage 4. The dominant inclusion types include: melt, melt–fluid, CO2-rich fluid and aqueous-rich fluid inclusions. Fluid, melt–fluid and melt inclusion studies indicate that the ore-forming fluid resulted from the unmixing of carbonatite melt and carbonatitic fluid. Initial ore-forming fluids were high-temperature (600 to 850 °C), high-pressure (>350 MPa) and high-density supercritical orhomagmatic fluids, characterized by SO4-rich and multi-component composition (e.g. K, Na, Ca, Ba, Sr and REE). The dominant anion is not Cl, but SO4. The evolution of the ore-forming fluid is from a melt-fluid at high temperature, through a CO2-rich fluid at high to medium temperature to aqueous-rich fluid at low temperature. REE precipitation occurred from a high to medium temperature CO2-rich fluid. The main mechanism for REE precipitation was phase separation of CO2 and aqueous fluids resulting in a decrease of temperature and pressure.

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1. Introduction

Deposits of rare earth elements (REE) usually occur in a continental rift environment, such as observed in the East African Rift (Mitchell and Garson, 1981) or the Proterozoic Langshan–Bayan Obo Rift, North China (Wang and Li, 1992). They generally have a close genetic relationship with mantle-derived carbonatites in rift environments. Such REE deposits have been studied in detail and their genesis is well understood (e.g., Wang and Li, 1992; Buhn and Rankin, 1999; Buhn et al., 2002; Williams-Jones and Palmer, 2002). Recent studies have demonstrated that REE deposits may also occur in continental collisional zones (e.g., Hou et al., 2006a). The Maoniuping REE deposit, a giant deposit in the 270 km-long Himalayan Mianning–Dechang (MD) REE belt in western Sichuan, China, is regarded to be the largest and most typical in a collisional zone (Hou et al., 2009–this issue). It is closely associated with a Cenozoic carbonatite–alkaline complex (Shi, 1993; Yuan et al., 1995), controlled by a Cenozoic strike-slip faulting system, and occurs in the Eastern India-Asian Collision Zone of the eastern margin of the Tibetan Plateau (Hou et al., 2006a; Hou and Cook, 2009–this issue). The deposit is characterized by a large ore tonnage (1.2 Mt REO), young mineralization age (27.8 to 40.3 Ma; Shi, 1993) and a well-developed mineralized vein system. The system provides a unique opportunity to establish the genetic link between REE metallogeny and collisional orogeny, and to further understand the evolution of a REE-bearing ore-forming fluid system in a continental collisional zone.

Many researchers have carried out investigations into the geology, geochemistry and genesis of the Maoniuping REE deposit (Niu and Lin, 1994, 1995a,b; Niu et al., 1996,a,b, 1997, 2003; Yuan et al., 1995; Yang et al., 2000; Xu et al., 2001a,b; 2003a,b, 2004; Wang et al., 2002; Liu et al., 2004). There is still debate on its genesis, especially on the characteristics of ore-forming fluids, the evolution of ore-forming
fluids and REE precipitation mechanisms. Previous studies and new data presented in this contribution indicate that the ore-forming system at Maoniuping is complex, as indicated by numerous types of inclusions trapped in both REE minerals (bastnaesite) and gangue minerals (e.g., calcite, fluorite, quartz, and barite) (Niu et al., 1996a; Yang et al., 2001; Xie et al., 2005, 2007). However, these inclusions, varying from melt- and melt-fluid inclusions to fluid inclusions, probably record a continuous carbonatitic melt-fluid evolution within the REE-mineralization system (Xie et al., 2007). Systematic studies on inclusions enable us to characterize primary ore-forming fluids, establish their affiliation to the collisional magma systems, and assist understanding REE mineralization processes.

This paper reports new observations and data on various inclusions from Maoniuping and provides an alternative interpretation of previous inclusion data presented by the present authors and others. Based on studies of melt/fluid inclusions integrated with geological and geochemical data, we discuss the origin and evolution of ore-forming fluids and REE ore-forming processes. A model for Maoniuping mineralization is accordingly proposed.

2. Geology

The Himalayan Mianning–Dechang (MD) REE belt is located in the western margin of the Yangtze craton, consisting of an Archaean–Proterozoic metamorphic crystalline basement and an overlying sequence of Phanerozoic clastic and carbonate rocks (Cong, 1988; Luo et al., 1998). The western margin of the craton underwent Permian rifting to form a N–S-trending paleorift zone and was involved in the eastern Indo-Asian collisional zone which formed since the Paleocene (Yin and Harrison, 2000; Zhong et al., 2001; Mo et al., 2003). Accompanying Cenozoic collisional orogeny, a series of Cenozoic strike-slip faults and a set of NE-, NNE- and NNW-trending faults....
folds were developed in the eastern Indo-Asian collision zone (Luo et al., 1998; Hou et al., 2006a; 2009-this issue). More than five carbonatite–alkalic complexes occur in the MD belt, all controlled by Cenozoic strike–slip faults. Available data define a relatively short duration for magmatic activity (24 to 40 Ma, peaking at 34 Ma; Zhang and Xie, 1997; Wang et al., 2001; Chung et al., 1998; Hou et al., 2003; Guo et al., 2005).

The geology of the Maoniuping district is described in detail by Hou et al. (2009-this issue). The Maoniuping complex and associated REE mineralization is controlled by a series of NE–NNE trending faults (Fig. 1), and intruded a NS-striking Yanshanian granite pluton with a U–Pb age of 146 Ma (Yuan et al., 1995). The complex comprises a nordmarkite stock with minor carbonatite sills (Fig. 2a; Hou et al., 2009-this issue). The carbonatite bodies are relatively small, but extend continuously downwards. Sometimes nordmarkite breccia clasts can be observed in the carbonatite body (Fig. 2b). The REE orebodies are hosted principally in the nordmarkite stock, carbonatite sills, and to a lesser extent in the undated rhyolite and altered Yanshanian granite; they are overlain by a Triassic coal-bearing sequence.

The carbonatite rocks are generally pink or fawn in colour, due to the presence of purple fluorite and yellow–brown bastnaesite. They have

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**Fig. 2.** Photographs of field outcrops and polished samples from the Maoniuping REE deposit. (a) Fluorite, quartz, aegirine–augite bearing carbonatite (Carb) vein in nordmarkite; (b) nordmarkite breccia in carbonatite; (c) quartz (Q)–barite (Bar)–fluorite (Fl) vein in nordmarkite (Nord); (d) quartz (Q)–barite (Bar)–fluorite (Fl) vein in nordmarkite (Nord); (e) Barite (Bar)–bastnaesite (Bast)–acmite–augite (Acm) vein crosscutting fine-grained quartz (Q) vein; (f) barite (Bar)–bastnaesite (Bast)–acmite–augite (Acm) occurring in the interval of euhedral crystal quartz (Q).
low SiO$_2$ (<10.22 wt.%), FeO (<1.20 wt.%) and MgO (<0.73 wt.%), and a wide range of CaO content (40.7 wt.% to 55.4 wt.%), distinguishing them from magnesiocarbonatites (Yuan et al., 1995). They are extremely enriched in LILE (Sr, Ba) and light REE, but relatively depleted in high-LILE (Hou et al., 2006b). The dominant REE mineral in all four ore types. Bunsite, chevkinite and bastnaesite are enriched in LILE (Sr, Ba) and light REE, but relatively depleted in high-LILE (Yuan et al., 1995). They are extremely enriched in LILE (Sr, Ba) and light REE, but relatively depleted in high-LILE (Hou et al., 2006b).

3. Mineralization

The Maoniuping REE deposit consists of various mineralized veins and stringer/stockwork zones. The deposit consists of approximately 71 orebodies (Pu, 1993), occurring as irregularly shaped veins, lenses and pockets. Individual orebodies range from 10 m to 1,168 m in length, and between 1 m to 30 m in thickness (Yuan et al., 1995). In plan view, they are distributed in an approximately en-echelon pattern (Fig. 2a). The gross strike direction for the en-echelon system is N–S, where individual orebodies strike mainly NNE and dip NW at 65–80° (Fig. 1). The vein system extends NNE, along strike, for 2,650 m and shows a “S” shape in plan, indicating a strike–slip fault control. The ore-bearing veinlets are usually greater than 30 cm thick, and occur as a swarm in the centre of the complex. The mineralized stringers range in thickness between 1 and 30 cm, and commonly comprise parallel vein zones enveloping the central ore zone. The stockwork zone usually occurs at the margins of the veinlets and vein zones.

Four main primary ore types have been recognized: 1) disseminated; 2) pegmatitic; 3) breccia; and 4) stringer (stockwork) ore. Their spatial distribution and major features are summarized in Table 1. Disseminated ore is common in the fenitized wall rock, whereas pegmatitic ore occurs as thick ore veinlets or pockets in the middle of the Maoniuping segment. Breccia ore mainly occurs in the Baozicun (southern) segment of the deposit, and stockwork ore occurs as a NNE-trending halo around the pegmatitic ore. The stockwork ore occurs in the Sanchahe segment, the northern Maoniuping segment, the southern Maoniuping segment, and in the stockwork zone of the middle Maoniuping segment between the pegmatite ore and altered wall rocks.

More than 80 minerals have been identified at Maoniuping (Pu, 1993; Yuan et al., 1995; Xie et al., 2006). Bastnaesite is the dominant REE mineral in all four ore types. Bunsite, chevikinite and cerianite have also been identified. The dominant gangue minerals are calcite, fluorite, barite, aegirine–augite, arfvedsonite, microcline and biotite, with minor galena, pyrite, pyrrhotite, chalcopyrite, hematite, magnetite, rutile and apatite (Hou et al., 2009–this issue).

Based on the mineral assemblages, ore textures and structures, vein cross-cutting relationships, petrography and inclusion data, five mineralization stages are recognized. These comprise:

1) Carbonatite stage: This stage occurs as pink–white carbonatite dyke intruding nordmarkite (Fig. 2a) in the middle segment or as fine pink to light purple fluorite-bearing carbonatite cement of breccia in the southern segment of the deposit. The carbonatite dyke and carbonatite cement of the breccia comprise a calcite–fluorite–acmite–aegirine–arfvedsonite–microcline–pyrite–chalcopyrite–pyrrhotite mineral assemblage. In this stage, minor disseminated REE mineralization occurs in carbonatite.

2) Pegmatite stage: Coarse-pegmatite aegirine–augite–fluorite–barite–bastnaesite, fluorite–barite–calcite–bastnaesite, aegirine–augite–quartz–microcline, and narrow fluorite–quartz–bastnaesite veins formed during this stage. These veins occur in the carbonatite body or crosscutting nordmarkite (Fig. 2c, d). The mineral assemblage varies significantly between the vein types, but no crosscutting relationships have been observed. The mineral assemblage in this stage consists of calcite, fluorite, microcline, phlogopite, biotite, quartz, aegirine–augite, magnesio–arfvedsonite, bastnaesite, chevikinite, pyrite, chalcopyrite and pyrrhotite.

3) Breccia–bastnaesite stage: This stage occurs as a mineral assemblage of barite–bastnaesite in narrow fluorite–quartz–bastnaesite veins or crystal barite and barite–bastnaesite in druses. The bastnaesite–barite veins crosscut the quartz veins (Fig. 2e). Under the microscope, small-scale barite–bastnaesite veins can be found crosscutting quartz and fluorite crystals. The mineral assemblage of this stage is barite, bastnaesite, calcite, celestine, magnetite, hematite, rutile, apatite, galena and unusual Cu-bearing alloys. Two such phases were determined by EPMA and SEM/EDS to be Sn-bearing copper (Cu) and zinc-copperite (Cu2Zn) (Xie et al., 2006). This stage, together with stage 2, formed the main REE body and is the most important REE mineralization stage.

4) Late calcite stage: This stage occurs as white–gray calcite veins, with a mineral assemblage of calcite and strontianite, filling fractures in both wall rock and REE orebodies. The calcite veins crosscut all previous vein generations; no REE mineralization has been observed in them.

5) Epigenic oxidation stage: This stage is dominated by REE-bearing Fe–Mn mineralization, which formed Fe–Mn oxides and an associated cerussite + witherite + wulfenite assemblage (Yuan et al., 1995).

In general, stage 2 is characterized by the appearance of pegmatitic mineralization, whereas stage 3 is characterized by the appearance of porous barite and bastnaesite. Mineralization of stage 2 and stage 3 forms the majority of the economic REE deposit. No crosscutting relationships between the pegmatite and narrow REE veins were observed in the field. Observation of ore textures and micro-vein

<table>
<thead>
<tr>
<th>Ore type</th>
<th>Ore texture</th>
<th>Ore structure</th>
<th>Mineral assemblage</th>
<th>Occurrence</th>
</tr>
</thead>
<tbody>
<tr>
<td>Disseminated ore</td>
<td>REE-minerals occur as euhedral–hypautomorphic crystals in carbonatite, rhyolite and nordmarkite</td>
<td>Disseminations, stringers</td>
<td>Calcite, fluorite, acmite augite, quartz, biotite, Muscovite, microcline, acmite augite</td>
<td>Altered wall rock (granite and rhyolite) and carbonatite</td>
</tr>
<tr>
<td>Pegmatitic ore</td>
<td>Pegmatite, euhedral–hypautomorphic crystals, metasomatic, poikilitic texture</td>
<td>Massive, miarolitic (cluster), dissemination</td>
<td>Calcite, fluorite, quartz, barite, microcline, acmite augite, biotite, arfvedsonite, galena, pyrite, chalcopyrite</td>
<td>Only in the middle of Maoniuping segment</td>
</tr>
<tr>
<td>Breccia ore</td>
<td>Clastic, euhedral–hypautomorphic crystals, interstitial, poikilitic euhedral–hypautomorphic–alloitrocrionic crystals, metasomatic, poikilitic, interstitial, poikilitic</td>
<td>Breccia; Dissemination</td>
<td>Calcite, fluorite, quartz, barite, microcline, mica, biotite, acmite augite, magnetite, hematite, rutile</td>
<td>Baozicun segment</td>
</tr>
<tr>
<td>Stockwork ore</td>
<td>Stringer and stockwork</td>
<td>Stringer and stockwork</td>
<td>Fluorite, quartz, bastnaesite, barite, celestine, calcite, biotite, acmite augite, alloys, magnetite, hematite, rutile</td>
<td>Maily in north and south of Maoniuping segment, Sanchahe segment</td>
</tr>
</tbody>
</table>
crosscutting relationships shows that barite and bastnaesite precipitated later than most quartz and fluorite, and often filled in the interspaces of euhedral quartz and fluorite (Fig. 2f).

4. Sampling and analytical methods

The minerals sampled for the fluid inclusion study include calcite, fluorite, quartz, barite and bastnaesite from mineralization stages 1 to 4. Samples covered all four ore types summarized in Table 1. The sample locations are shown in Fig. 1. Microthermometry (for 23 samples), LRM (Laser Raman Microprobe) (for 43 inclusions in 6 sections) and SEM/EDS (for 5 samples) analysis were performed after careful microscopic observation of 35 sections and 55 doubly-polished sections.

Microthermometry was undertaken using a Linkam THS600 heating-freezing stage, with a measurable temperature range of between −196 and +600 °C (precision of freezing data and homogenization temperature of ±0.1 °C and ±1 °C, respectively) and a Linkam THS1500 heating stage with the measurable temperature range from room temperature to +1500 °C (precision of homogenization temperature of ±1 °C). Microthermometry was undertaken in the Department of Resources Engineering of USTB (University of Science and Technology Beijing) and the Geology and Geophysics Institute of CAS (China Academy of Science). SEM/EDS (Scanning Electron Microscope/Energy Dispersive Spectrometry) analysis were performed at the State Key Laboratory for Advanced Metals and Materials at USTB, using a Cambridge S250 SEM equipped with a Link Systems 860 energy dispersive spectrometer operating at a 20 kV accelerating voltage. The detailed sample preparation method for SEM/EDS used is reported in Xie et al. (2000). The inclusions generally comprise melt–glass and daughter minerals. The melt inclusions melt inhomogeneously at more than 500 °C, in contrast to the trapped minerals that melt homogeneously at their respective melting points. These melt inclusions were trapped during the late magmatic carbonatite stage and survived a later period of hydrothermal alteration. Thus they provide an important method for the study of carbonatites (Aldous, 1980; Andersen, 1986) and carbonatitic fluids.

5. Inclusion results

5.1. Petrography and classification of inclusions

The samples used for the inclusion study were doubly polished sections of fluorite, quartz, calcite, barite and bastnaesite from mineralization stages 1 to 4. A number of inclusion types were identified. These include negative crystals and elongate round, polygonal or irregular shapes with a size range from <1 µm to several tens of µm. Based on their petrographic characteristics at room temperature and phase change characteristics during the heating process, inclusions were grouped into three principal types and eight sub-types. They are as follows:

1. Melt inclusions (M type). These often occur in calcite from carbonatite and gangue fluorite from pegmatite and veinlet (stringer) ore. There are also minor melt inclusions in quartz and arfvedsonite from pegmatitic and veinlet (stringer) ore. The inclusions generally comprise melt–glass and daughter minerals (Fig. 3b); with some containing a minor volatile phase (Fig. 3a). Most of the melt inclusions in calcite and fluorite appear to be trapped minerals at room temperature under the microscope, but have a relatively dark, thick borderline and often contain a daughter mineral or/volatile phase. On heating, the phase change of melt inclusions differs from the trapped minerals. The melt inclusions melt inhomogeneously at more than 500 °C, in contrast to the trapped minerals that melt homogeneously at their respective melting points. These melt inclusions were trapped during the late magmatic carbonatite stage and survived a later period of hydrothermal alteration. Thus they provide an important method for the study of carbonatites (Aldous, 1980; Andersen, 1986) and carbonatitic fluids.

2. Melt–fluid inclusions (ML type). ML type inclusions are abundant in gangue fluorite and relatively rare in quartz. Almost all of them have negative crystal or polygonal shapes. The inclusions show variable size and liquid/vapor/solids ratios. Their petrographic features are similar to the solid-rich L–V–S type of inclusions reported in fluorite–REE deposits in the Gallinas Mountains, New Mexico (Williams-Jones et al., 2000). Most ML inclusions contain several solid phases and have been termed multi-solid inclusions by Niu and Lin (1995b). Based on microthermometric work, the melt phase appears at some point during the heating process and this kind of inclusions is thus termed “melt–fluid type” in this paper. Based on microscopic measurement, it has been determined that the solid phases occupy about 40 to 80 vol.% of the inclusions (Fig. 4). Raman spectroscopy and SEM/EDS results (see below) indicate that the solid phases were dominated by sulfate minerals. ML inclusions with different phase ratios often occur together in clusters, and are sometimes accompanied by melt inclusions or CO2-rich fluid inclusions. Their close spatial association with melt inclusions and CO2-rich fluid inclusions suggests that these inclusions were trapped in the transition stage from melt to fluid. Meanwhile, the melt phase coexisted together with an aqueous phase. The continuous series from low- to high-solid volume percentage melt–fluid inclusion records an immiscible process.
Based on the petrographic character of melt–fluid inclusions at room temperature, two sub-types can be distinguished as follows:

a. ML-1 sub-type: Containing multi-solid phases, net-like sulfate (mirabilite), aqueous and a bubble (Fig. 4a, b). The solid phases occupy ca. 75 vol.% of the inclusion volume. At room temperature, they appear dark brown in color because the net-like sulfate occupies most of the inclusion volume. All ML-1 inclusions include several solid phases. The solid phases show rod-like, globular, and rounded-polyhedron shapes.

b. ML-2 sub-type: Similar to ML-1, but without net-like sulfate in the inclusions (Fig. 4c, d). At room temperature, they look clearer than ML-1 inclusions. They often contain several solid phases with rod-like, globular or rounded-polyhedron shapes. The solid phase accounts for 40 to 80 vol.% of the inclusions. Most solids were confirmed by LRM and EDS as sulfate (see below). Some could not be identified, though LRM results identify them to be a carbonate and sulfate complex (melt glass).

(3) Fluid inclusions (L type). Fluid inclusions are the most abundant type of inclusions in quartz, barite and REE minerals, and include primary and secondary fluid inclusions. In fluorite from stage 2, minor primary fluid inclusions are usually accompanied by melt–fluid inclusions. Most secondary fluid inclusions are distributed as clusters or trails along the healed fissures. In quartz from stage 2, L-type fluid inclusions are the dominant type; some occur as isolated inclusions or clusters with negative crystal shapes, showing the features of pseudo-secondary inclusions. Others are distributed as trails or lines, showing secondary features. All primary and pseudosecondary fluid inclusions contain a liquid CO2 bubble (see below), whereas secondary fluid inclusions contain a vapor phase bubble. Primary CO2-rich fluid inclusions are sometimes accompanied by melt–fluid inclusions in a single cluster. Five sub-types (Table 2) were distinguished on the basis of phase character at room temperature and characteristics during heating.

(a) AC sub-type: Aqueous-liquid CO2 fluid inclusions (Fig. 5a, b, d). These occur in calcite, quartz, barite, bastnaesite and fluorite. They comprise aqueous and liquid CO2, some with vapor CO2 at room temperature. During heating, most of them homogenized to a CO2–H2O critical phase (AC-2); a few homogenizing to an aqueous phase (AC-1). The CO2 bubble represents >20 vol.% of the inclusion volume.

(b) AV sub-type: Aqueous-vapor fluid inclusions (Fig. 6b). This fluid inclusion sub-type generally occurs in fluorite, quartz

Table 2

<table>
<thead>
<tr>
<th>Sub-type</th>
<th>Phase composition</th>
<th>Distribution and occurrence</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC</td>
<td>Aqueous and liquid CO2 or aqueous, liquid and vapor CO2</td>
<td>Very abundant inclusion type in bastnaesite, barite and quartz occurring as isolated inclusions or clusters. Some was found in fluorite or calcite.</td>
</tr>
<tr>
<td>ADC</td>
<td>Aqueous, liquid CO2, one or more daughter minerals</td>
<td>Same as AC sub-type</td>
</tr>
<tr>
<td>C</td>
<td>Liquid CO2 or liquid and vapor CO2</td>
<td>Same as AC sub-type</td>
</tr>
<tr>
<td>AV</td>
<td>Aqueous and vapor</td>
<td>Occurring as isolated inclusions or clusters in calcite from stage 4. Most AV fluid inclusions are found as lines or trails in quartz and fluorite.</td>
</tr>
<tr>
<td>ADV</td>
<td>Aqueous, vapor, one or two daughter minerals</td>
<td>Same as AV sub-type</td>
</tr>
</tbody>
</table>
and calcite as secondary inclusions observed as trails along healed fractures or in calcite from stage 4. This sub-type comprises aqueous and vapor phase. The vapor bubble accounts for a lower percentage (<20 vol.%, mostly 5–10 vol.%) than AC and ADC sub-types. When heated, they homogenize to an aqueous phase at low temperature, mostly below 200 °C.

(c) ADC sub-type: Aqueous daughter minerals–liquid CO₂ fluid inclusions (Fig. 5b). Each comprises one or more daughter minerals, aqueous and liquid CO₂, usually accompanied by AC and C sub-type inclusions. Inclusions of this kind often occur in barite, bastnaesite and quartz as primary fluid inclusions, or in fluorite and igneous calcite as secondary fluid inclusions.

(d) ADV sub-type: Aqueous-daughter minerals–vapor fluid inclusions (Fig. 6a). Inclusions of this kind comprise one or two daughter minerals, aqueous and vapor phase. The solid phase accounts for a much lower vol.% (<15%) than ML inclusions. They are usually accompanied by AV fluid inclusions. These inclusions often occur as secondary fluid inclusions in quartz, fluorite, bastnaesite and barite from stages 2 and 3.

(e) C sub-type: Pure CO₂ fluid inclusion (Fig. 5c). They comprise a liquid CO₂ or liquid and vapor CO₂. Pure CO₂ fluid inclusions often occur in quartz, bastnaesite and barite, and are commonly accompanied by AC and ADC fluid inclusions.

5.2. Inclusion assemblages

Inclusion assemblages vary with host minerals and ore-forming stages in the Maoniuping deposit. From stages 1 to 4, the dominant inclusions vary from melt inclusions (M type), melt–fluid inclusions (ML type), high-medium temperature CO₂-rich fluid inclusions (AC +
ADC+C sub-type) to low-temperature aqueous rich fluid inclusions (AV+ADV sub-type). Four inclusion assemblages were identified in minerals from the different ore-forming stages. They are as follows:

**Melt inclusion assemblage**: Occurring in calcite and fluorite from the carbonatite stage (stage 1), it comprises melt inclusions accompanied by trapped minerals. Because of the birefringence effect, the melt inclusions in calcite are not clear under the microscope. Most melt inclusions have no volatile component at room temperature, but some have an irregular bubble or/and a daughter mineral. They are observed as isolated inclusions or along the growth zone in calcite and fluorite from carbonatite dykes.

**Melt–fluid inclusion assemblage**: This comprises melt inclusions (M type), melt–fluid inclusions (ML type) and minor high-temperature daughter mineral-bearing fluid inclusions (ADC sub-type). They mainly occur in fluorite from stage 2. The melt–fluid inclusion is the dominant type in fluorite from stage 2, and is often accompanied by melt inclusions and daughter mineral-bearing CO₂-rich fluid inclusions. The melt–fluid inclusions have varied solid volume percentages. ML-1 inclusions have a relative stable solid volume percentage and are isolated and with negative crystal shapes. The ML-2 inclusions have a varied solid volume percentage. Under the microscope, this assemblage forms a continuous solid/aqueous/vapor series.

**CO₂-rich fluid inclusion assemblage**: Includes high-medium temperature aqueous-CO₂ fluid inclusions (AC sub-type), aqueous-daughter mineral-bearing fluid inclusions (ADC sub-type) and pure CO₂ inclusions (C sub-type). They are abundant in barite, bastnaesite and hydrothermal calcite from stage 3 or as secondary inclusions in fluorite and quartz from stage 2. Most AC fluid inclusions (AC-2) have a critical homogenization behavior; some (AC-1) homogenize to a liquid phase.

**Aqueous-rich fluid inclusion assemblage**: Includes aqueous–vapor fluid inclusions (AV sub-type) and aqueous-daughter mineral-bearing fluid inclusions (ADV sub-type). They occur in calcite from stage 4 or as secondary inclusions in fluorite, quartz, barite and bastnaesite from stages 2 and 3. Compared to CO₂-rich fluid inclusions, the aqueous-rich fluid inclusion assemblage has a smaller bubble, lower CO₂ content and lower homogenization temperature.

### 5.3. Microthermometric results

#### 5.3.1. Melt inclusions

Microthermometric results are shown in Table 3. At room temperature, the aqueous phase was absent in most of the melt inclusions, but on heating at 500 to 700 °C, the glass phase began to melt inhomogeneously. Firstly there are a few small dark spots or dark cracks appearing in the inclusions and with the increasing temperature, the small bubbles agglomerate into one bubble. Continuing heating, the bubble gets smaller and smaller, and finally homogenizes to a melt phase at 790 to 850 °C. Some of these inclusions deprecitated or leaked prior to homogenization. Some would not homogenize even up to 1100 °C (the host mineral–fluorite–melts at this temperature), which is considered to be due to volume increase and inclusion expansion. Cooling from homogenization to room temperature,

**Table 3**

Microthermometric results of melt and melt–fluid inclusions in fluorite and quartz in the Maoniuping REE deposit.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ore type</th>
<th>Mineral</th>
<th>Type of inclusion</th>
<th>Th (°C)</th>
<th>Range</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>MNP-13</td>
<td>Pegmatite</td>
<td>Quartz</td>
<td>M</td>
<td>790–791(3)</td>
<td>791</td>
<td></td>
</tr>
<tr>
<td>MNP-16</td>
<td>Stringer</td>
<td>Fluorite</td>
<td>M</td>
<td>&gt;737(1)</td>
<td>/</td>
<td></td>
</tr>
<tr>
<td>MNP-125</td>
<td>Pegmatite</td>
<td>Fluorite</td>
<td>M</td>
<td>&gt;778(1)</td>
<td>/</td>
<td></td>
</tr>
<tr>
<td>MNP-17</td>
<td>Stringer</td>
<td>Fluorite</td>
<td>M</td>
<td>705–850(2)</td>
<td>823</td>
<td></td>
</tr>
<tr>
<td>MNP-11</td>
<td>Pegmatite</td>
<td>Fluorite</td>
<td>ML-1</td>
<td>650–850 (2)</td>
<td>705</td>
<td></td>
</tr>
<tr>
<td>MNP-12</td>
<td>Pegmatite</td>
<td>Quartz</td>
<td>ML-1</td>
<td>650–850 (3)</td>
<td>705</td>
<td></td>
</tr>
<tr>
<td>MNP-13</td>
<td>Pegmatite</td>
<td>Fluorite</td>
<td>ML-2</td>
<td>687(1)</td>
<td>687</td>
<td></td>
</tr>
</tbody>
</table>

*a Unsuccessful acquisition of fluid inclusion data. At this temperature, the inclusion comprises a melt phase and a bubble, but the inclusions cannot homogenize because of leakage.

### Fig. 7.

Phase-change in melt–fluid inclusion in fluorite; (a) melt–fluid inclusion at room temperature; (b) the bubble phase disappears; (c) New bubble appears; (d) net-like sulfate disappears; (e) melt phase (sulfate melt) appears; (f) new solid phases occur.
inclusions of this kind cannot return to their original state, but became aqueous-bearing multi-solid inclusions (with multi-solid phase, little aqueous phase and a bubble) with a very high (>80%) solid percentage.

5.3.2. Melt-fluid inclusions

Microthermometric results are listed in Table 3. Most ML inclusions were unable to homogenize because they decrepitate before reaching the homogenization temperature. Some did not homogenize below 1000 °C because of obvious volume-increase and expansion of the inclusion; only a few homogenization temperature data were thus obtained. The homogenizing process of the ML inclusion is complex during heating (Fig. 7). The dominant phase-changes for the ML-1 inclusion are reported as: (1) at 115 to 180 °C the bubble disappeared. This temperature range is similar to the homogenization temperature of AV fluid inclusions; (2) at 240 to 250 °C the net-like sulfate dissolved and the aqueous phase occupied a greater volume percentage (potentially caused by dehydration of mirabilite). The inclusions become clearer after melting of the net-like sulfate; (3) at 350–500 °C, a melt phase appears from a solid phase-melting, and then gets larger with more solid melting; (4) at about 450 to 500 °C some new solid minerals grew along the inclusion wall (the authors believe this may be caused by deformation and volume increase of the inclusion); (5) at 600 to 700 °C much of the solid phase dissolved or melted; and (6) at 600 to 850 °C the inclusion homogenized by critical behavior. The homogenization temperatures of ML inclusions were between 650 and 850 °C in fluorite, and 600 and 750 °C in quartz. Most ML inclusions decrepitated at a lower temperature than their homogenization temperature.

5.3.3. Fluid inclusions

Based on their phase composition at room temperature and homogenizing characteristics during heating, five inclusion sub-types were distinguished (AC, ADC, AV, ADV and C sub-type) in quartz, fluorite, calcite, barite and bastnaesite. Microthermometric results for these different sub-types are shown in Table 4 and Fig. 8.

During heating, the AC-1 sub-type homogenized to an aqueous phase, and the AC-2 sub-type homogenized to the critical phase. All C sub-type homogenized to a liquid CO2 phase. Heating tests for AC and ADC sub-type inclusions were difficult, due to decrepitation; the majority would not homogenize. Microthermometry showed that the AC-1 sub-type had a Th (homogenization temperature) of between 194 and 371 °C, AC-2 has a Th of 227 to 453 °C, and a CO2 density between 0.636 and 0.982 g/cm3 according to the partial homogenization temperature of liquid CO2 and vapor CO2 (Angus et al., 1976; cf. Roedder, 1984 and Lu et al., 1994). For ADC sub-type inclusions, while heating, the daughter minerals melted first at 223–386 °C, then the inclusion homogenized to a liquid phase at 224 to 477 °C. The density of the CO2 in fluid inclusions was estimated as being 0.644 g/cm3 (only one data point was acquired). AV sub-type fluid inclusions have the lowest Th of 101 to 226 °C and a simple homogenizing behavior. The bubbles in most of these inclusions disappear below 200 °C. Cooling measurements on pure CO2 inclusions show that the melting point of CO2 is between −56.5 and −58.5 °C. This is equal to or a little lower than that of the pure CO2 system (Angus et al., 1976; cf. Roedder, 1984 and Lu et al., 1994) and suggests a dominant CO2 system, as well as the possibility of minor other volatile components such as CH4, H2 or N2 present. The C sub-type inclusions have homogenization temperatures of −7.7−14.7 °C. According to the pure CO2 system phase diagram, the density of CO2 was estimated as 0.829–0.972 g/cm3. Results of SEM/EDS and LRM studies (see below) indicate that most daughter minerals in both ADC and ADV sub-type inclusions are sulfates including barite, mirabilite, gypsum, apthitahite and anancite. SO2−4 in aqueous phase was also detected in all fluid inclusions by LRM (see below). Based on LRM and SEM/EDS results, most daughter minerals in ADC and ADV inclusions are sulfate, and SO2−4 exists

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ore type</th>
<th>Mineral</th>
<th>Type of inclusion</th>
<th>Th (°C) Range</th>
<th>Average</th>
<th>Density of CO2 Range</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>MNP-6</td>
<td>Carbonatite</td>
<td>Q</td>
<td>AC</td>
<td>238 (1)</td>
<td>238</td>
<td>0.647–0.868(2)</td>
<td>0.758</td>
</tr>
<tr>
<td>MNP-6</td>
<td>Carbonatite</td>
<td>Q</td>
<td>AV</td>
<td>133–151 (5)</td>
<td>142</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>MNP-12</td>
<td>Pegmatite</td>
<td>Q</td>
<td>AV</td>
<td>124–219 (12)</td>
<td>172</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>MNP-12</td>
<td>Pegmatite</td>
<td>Q</td>
<td>AC</td>
<td>247–371 (7)</td>
<td>296</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>MNP-12</td>
<td>Pegmatite</td>
<td>Q</td>
<td>ADC</td>
<td>237–477 (13)</td>
<td>362</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>MNP-12</td>
<td>Pegmatite</td>
<td>Q</td>
<td>C</td>
<td>/</td>
<td>/</td>
<td>0.923–0.658(4)</td>
<td>0.94</td>
</tr>
<tr>
<td>MNP-12</td>
<td>Pegmatite</td>
<td>Q</td>
<td>AC</td>
<td>/</td>
<td>/</td>
<td>0.636(1)</td>
<td>0.636</td>
</tr>
<tr>
<td>MNP-13</td>
<td>Pegmatite</td>
<td>Q</td>
<td>AC</td>
<td>/</td>
<td>/</td>
<td>0.692–0.807(3)</td>
<td>0.759</td>
</tr>
<tr>
<td>MNP-13</td>
<td>Pegmatite</td>
<td>Q</td>
<td>ADC</td>
<td>328–459 (3)</td>
<td>411</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>MNP-33</td>
<td>Pegmatite</td>
<td>Q</td>
<td>AC</td>
<td>/</td>
<td>/</td>
<td>0.982(1)</td>
<td>0.982</td>
</tr>
<tr>
<td>MNP-33</td>
<td>Pegmatite</td>
<td>Q</td>
<td>AV</td>
<td>166–185 (3)</td>
<td>177</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>MNP-33</td>
<td>Pegmatite</td>
<td>Q</td>
<td>AC</td>
<td>217–357 (5)</td>
<td>278</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>MNP-33</td>
<td>Pegmatite</td>
<td>Q</td>
<td>C</td>
<td>/</td>
<td>/</td>
<td>0.938–0.972(6)</td>
<td>0.957</td>
</tr>
<tr>
<td>MNP-33</td>
<td>Pegmatite</td>
<td>Q</td>
<td>ADC</td>
<td>/</td>
<td>/</td>
<td>0.644(1)</td>
<td>0.644</td>
</tr>
<tr>
<td>MNP-132</td>
<td>Pegmatite</td>
<td>FL</td>
<td>ADC</td>
<td>249–285 (5)</td>
<td>272</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>MNP-132</td>
<td>Pegmatite</td>
<td>FL</td>
<td>AV</td>
<td>181(1)</td>
<td>181</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>MNP-161</td>
<td>Stringer ore</td>
<td>FL</td>
<td>ADC</td>
<td>240–386 (7)</td>
<td>304</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>MNP-161</td>
<td>Stringer ore</td>
<td>FL</td>
<td>AV</td>
<td>224–296 (2)</td>
<td>260</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>MNP-161</td>
<td>Stringer ore</td>
<td>FL</td>
<td>AC</td>
<td>101–153 (16)</td>
<td>122</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>MNP-161</td>
<td>Stringer ore</td>
<td>Q</td>
<td>AV</td>
<td>113–226 (12)</td>
<td>152</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>MNP-153</td>
<td>Stringer ore</td>
<td>Q</td>
<td>AV</td>
<td>108–159 (8)</td>
<td>129</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>MNP-153</td>
<td>Stringer ore</td>
<td>Q</td>
<td>AC</td>
<td>254–324 (2)</td>
<td>289</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>MNP-157</td>
<td>Stringer ore</td>
<td>Cal</td>
<td>AC</td>
<td>218–242 (3)</td>
<td>230</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>MNP-157</td>
<td>Stringer ore</td>
<td>Cal</td>
<td>AV</td>
<td>158–159 (2)</td>
<td>159</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>MNP-157</td>
<td>Stringer ore</td>
<td>Cal</td>
<td>C</td>
<td>/</td>
<td>/</td>
<td>0.829–0.839(2)</td>
<td>0.834</td>
</tr>
<tr>
<td>MNP-28</td>
<td>Stringer ore</td>
<td>Bar</td>
<td>AC</td>
<td>194–253 (4)</td>
<td>219</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>MNP-28</td>
<td>Stringer ore</td>
<td>Bar</td>
<td>AV</td>
<td>186–199 (4)</td>
<td>193</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>MNP-28</td>
<td>Stringer ore</td>
<td>Cal</td>
<td>AV</td>
<td>141–167 (9)</td>
<td>158</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>MNP-28</td>
<td>Stringer ore</td>
<td>FL</td>
<td>AV</td>
<td>137–143 (2)</td>
<td>140</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>MNP-313b</td>
<td>Stringer ore</td>
<td>FL</td>
<td>AC</td>
<td>254–279 (2)</td>
<td>266</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>MNP-313b</td>
<td>Stringer ore</td>
<td>Bast</td>
<td>AC</td>
<td>211–255 (6)</td>
<td>244</td>
<td>/</td>
<td>/</td>
</tr>
</tbody>
</table>

Note: "—" means that no useful data or could not be measured; FL—fluorite; Q—quartz; Bast—bastnaesite; Cal—calcite; Bar—barite.
widely in aqueous phases of all kinds of fluid inclusions. It is concluded that the fluid in all fluid inclusion sub-types is not a typical NaCl (KCl)–H₂O–CO₂ system, so the salinity of the ore-forming fluid cannot be determined by measurements of freezing point or point of CO₂ hydrate decomposition. The CO₂-rich fluid inclusion assemblage (AC, ADC and C fluid inclusions) shows a continuous CO₂/aqueous ratio in the same cluster, implying the immiscible trapping character. Th of AC-2 inclusions (227 to 453 °C) should be the best candidate for the trapping temperature, and the pure CO₂ inclusions were also trapped at almost the same temperature (or a little lower). According to the pure CO₂ phase diagram (cf. Roedder, 1984; Lu et al., 1994), the pressure can be estimated using the isochore method. The capture pressure was estimated as being between 150 and 350 MPa for the CO₂-rich fluid inclusion assemblage. This pressure should reflect the unmixing condition between CO₂ and aqueous fluid. For stage 2, the fluid temperature is higher than that of stage 3, and so stage 2 should be at a higher pressure than stage 3. For stage 4, the fluid temperature is lower than stage 3, and no liquid CO₂, but the vapor can be determined in AV and ADV fluid inclusions. It is concluded that the capture pressure for stage 4 should be much lower than stage 3. According to the Th of AV and ADV fluid inclusions and the lowest CO₂ density of pure CO₂ inclusions, the pressure for stage 4 should be lower than 100 MPa.

5.4. Laser Raman Microprobe (LRM) analysis of inclusions

LRM was performed on the CO₂, aqueous and solid phases in fluid inclusions and melt–fluid inclusions hosted in quartz and fluorite. Selections of spectrograms are shown in Figs. 9 and 10. For ML inclusions, there is strong peak around 3500 cm⁻¹ which indicates an aqueous phase dominated by H₂O. A peak at 981 to 984 cm⁻¹ was also clearly seen, indicating the presence of SO₄²⁻ in the aqueous phase. Interference fluorescence from fluorite masks the peaks which indicates the presence of CO₂ (1386 cm⁻¹) in the bubble phase. The spectrograms of solid-phase in melt–fluid inclusions suggest that the solid phases were dominated by a sulfate assemblage, including mirabilite (Fig. 9a), gypsum, barite, celestine (Fig. 9b), and nahcolite. In some ML inclusions, a solid phase has peaks at 1005, 1069 and 988 cm⁻¹; these may indicate sulfate–carbonate complexes.

In CO₂-rich fluid inclusions (AC, ADC), the aqueous phase was also dominated by H₂O. The peaks at 981 to 984 cm⁻¹ (Fig. 10b, c, f) suggest that SO₄²⁻ was also the dominant anion in the aqueous phase.

Fig. 8. Histogram of homogenization temperature for fluid inclusions in the Maoniuping REE deposit.

Fig. 9. LRM spectrum of melt–fluid inclusions (ML) in fluorite from the Maoniuping REE deposit. (a) Mirabilite daughter mineral in melt–fluid inclusion of fluorite; (b) celestite daughter mineral in melt–fluid inclusion of fluorite.
The peak at 1066 to 1069 cm\(^{-1}\), compared with the spectrum of host quartz, suggests the presence of CO\(_3\)\(^{2-}\) in the aqueous phase. The occurrence of SO\(_4\)\(^{2-}\) and CO\(_3\)\(^{2-}\) is consistent with the presence of sulfate and bicarbonate daughter minerals in the inclusions. The bubbles in AC and ADC sub-type fluid inclusions are dominated by CO\(_2\), according to the strong peaks at 1282 and 1386 cm\(^{-1}\) (Fig. 10a, d). The daughter minerals are also dominated by sulfate minerals. Compared with the host mineral, the spectrogram of the daughter minerals in quartz and fluorite have additional peaks at 1007–1005, 998, 988 and 992 cm\(^{-1}\). These indicate gypsum, celestite, barite and mirabilite.

Fig. 10. LRM spectrum of fluid inclusions in quartz from the Maoniuping REE deposit; (a) CO\(_2\) in fluid inclusion in quartz (AC sub-type); (b) SO\(_4\)\(^{2-}\) in aqueous phase of fluid inclusion in quartz (AC sub-type); (c) H\(_2\)O and SO\(_4\)\(^{2-}\) in aqueous of fluid inclusion (AC sub-type); (d) CO\(_2\) in bubble phase of fluid inclusion (ADC sub-type); (e) NaHCO\(_3\) daughter mineral in fluid inclusion (ADC sub-type); (f) SO\(_4\)\(^{2-}\) in aqueous phase of fluid inclusion (ADC sub-type).
daughter minerals, respectively. Nahcolite was also determined via the strong peak at 1046 cm$^{-1}$ (Fig. 10e). The determination of daughter minerals is based on the inorganic material LRM spectrum database of Renishaw, and reference to Samson et al. (1995) and Rankin (2003).

In aqueous-fluid inclusions (AV, ADV), the aqueous phase is also dominated by H$_2$O. The peaks at 981 to 984 cm$^{-1}$ also suggest that SO$_4^{2-}$ is the dominant anion in the aqueous phase. The bubbles in AV and ADV sub-type fluid inclusions are dominated by H$_2$O, with no peaks at 1282 or 1386 cm$^{-1}$. Sulfate minerals were also confirmed as the dominant daughter phases.

5.5. SEM/EDS analysis of daughter minerals in inclusions

Numerous open inclusions in the prepared samples (fluorite and quartz) were observed under the SEM; most inclusions contained one or more daughter minerals. According to the solid percentage and comparison with the petrographic features of the different inclusion types, the inclusions observed under SEM were defined as ML, ADC and ADV types. EDS analysis showed that most of the daughter minerals in all inclusion types contain S, K and/or Na. Integrating the results of LRM and SEM/EDS analysis, it appears that the daughter phases in melt–fluid and fluid inclusions are dominated by sulfates such as arcanite (K$_2$SO$_4$; Fig. 11b, c), aphthitalite (NaK$_3$[SO$_4$]$_2$; Fig. 11a, c), mirabilite (Na$_2$SO$_4$ 10H$_2$O) and gypsum (CaSO$_4$ 2H$_2$O). Arcanite and aphthitalite are the most common types seen. No typical LRM spectra for arcanite and aphthitalite were available for comparison, so some of the mirabilite determined by LRM could be arcanite or aphthitalite. Carbonate or bicarbonate daughter minerals was also determined by EDS. Barite, strontianite and REE minerals have also been reported as daughter phases in inclusions by Xu et al. (2004).

Fig. 11. Secondary electron images and EDS spectrum of daughter minerals in the Maoniuping REE deposit; (a) aphthitalose (Aph) daughter mineral in quartz; (b) arkanite(Ark) and unidentified (X) daughter mineral in fluorite; (c) aphthitalose (Aph) and arkanite (Ark) daughter mineral in fluorite; Fl—fluorite; Q—quartz.
6. Discussion

Most carbonatites worldwide are believed to be genetically linked to silicate alkaline magmatism. As a result of their enrichment in REE minerals, many carbonatite bodies form economic REE deposits (cf. Rankin, 2003). Significant evidence from phase equilibrium experiments has shown that carbonatites can be generated by primary mantle melting and by the differentiation of carbonated silicate melts, i.e., liquid immiscibility and crystal fractionation (cf. Bell et al., 1999).

The genesis of carbonatite–alkaline complex at Maoniuping has been extensively researched, including aspects of petrology and C, O, Pb, Sr and Nd isotopes (Yuan et al., 1995; Niu et al., 1996b; Wang et al., 2002; Xu et al., 2003a, 2004; Tian et al., 2003;). These results imply an igneous carbonatite and mantle origin. The carbonatite in the Maoniuping area is rich in incompatible elements such as Sr, Ba and REE, with a mantle-source C and O isotope composition, high $^{87}$Sr/$^{86}$Sr and low $\xi$Nd implying a metasomatically enriched mantle source (Xu et al., 2003a). The unmixing of a CO$_2$-rich alkaline silicate magma related to the partial melting of metasomatic mantle is likely to be the source of the carbonatite and nordenkamite.

Carbonatite melt is low density, aqueous-rich (Wyllie, 1966) and much lower viscosity than that of silicate melt (Wolff, 1994). Alkaline-rich fluid in carbonatite melts can decrease the melt density and viscosity. Low-density, low-viscosity carbonatite melts are able to be squeezed into shallow crust (Rankin, 1977; Samson et al., 1995; Buhn and Rankin, 1999) and often result in strong alteration and REE mineralization. Carbonatite fluids play an important role in mineralization and alteration in REE deposits globally. Experimental and field studies have shown that carbonatite magma is rich in volatile components (Roedder, 1973; Palmer and Williams-Jones, 1996; Andersen, 1987; Nesbitt and Kelly 1977; Buhn and Rankin, 1999; Buhn et al., 2002; Williams-Jones and Palmer, 2002; Rankin, 2003). However, how the carbonatite fluid is derived from the carbonatite magma is still open to debate. Besides crystal fractionation, immiscible processes are believed to cause separation between carbonatite melt and carbonatitic fluid (Roedder, 1984; Brooker and Hamilton, 1990; Mitchell, 1997). The genesis and evolution of carbonatite fluids has become a key topic of current geological research (Fan et al., 2001).

6.1. Origin of carbonatite fluid

Microthermometric studies of melt and melt–fluid inclusions provide good evidence for volatile rich melt and an immiscible process between carbonatite magma and carbonatitic fluid. The coexistence of different solid/aqueous ratio melt–fluid inclusions in the same cluster, particularly the occurrence of the melt phase in melt–fluid inclusions while heating up to 350 to 500 °C, indicates inhomogeneity during trapping. The low melting temperatures in melt–fluid inclusions indicate that the residue-melt trapped in melt–fluid inclusions is sulfate melt. Based on microthermometry results, the unmixing occurred between 790 and 850 °C. The melt, melt–fluid and fluid inclusion assemblage also implies a carbonatite magma origin of the ore-forming fluid and continuous evolution from melt to ore-forming fluid.

Carbon, oxygen and hydrogen isotopic results (Tian et al., 2003; Xu et al., 2003b) show that δ$^{13}$C has a range from −52 × 10$^{-3}$ to −86 × 10$^{-3}$, and δ$^{18}$O$_{SMOW}$ has a range from 7.8 × 10$^{-3}$ to 13.3 × 10$^{-3}$, and δ$^{34}$CPD$_{CO_2}$ for CO$_2$ in fluid inclusions has a range from −3 to −5.6 × 10$^{-3}$, which is similar to that of carbonatite. The results imply the characteristic of the carbonatite-related orthomagmatic fluid and their close relationship to a mantle origin. It is concluded that the ore-forming process is closely related to carbonatite–alkaline magmatism, and that the ore-forming fluid results from the unmixing of a volatile-rich carbonatite melt.

6.2. T–P–X properties of carbonatitic fluid

The characteristics of carbonatite fluids in a continental rift environment have been studied by numerous researchers (cf. Morogan, 1994; Samson et al., 1995; Palmer and Williams-Jones, 1996; Smith et al., 2000; Smith and Henderson, 2000; Buhn et al., 2002; Williams-Jones and Palmer, 2002; Rankin, 2003). Although it is not known if these results are applicable to an environment of the type discussed here, their consideration is still helpful in any attempt to understand carbonatitic fluids and their associated mineralization in a continental collision environment.

Rankin (2003) summarized the composition of ore-forming fluids in carbonatite-associated rare metal deposits. Rankin suggests that CO$_2$-rich, L-V (aqueous-vapor), L-V-S (aqueous-vapor-solid) and L-V-MS (aqueous-vapor-multisolid) inclusions are common in carbonatite-related deposits. CO$_2$-rich fluid inclusions are noted in most carbonatite related deposits, however not, for example, in the Oka carbonatite (Samson et al., 1995). The orthomagmatic fluids evolved from carbonatite magmas are Na–K–chloride–carbonate/bicarbonate brines and have variable salt content and rather consistent K/Na ratios. Sulfate and fluoride contents may also be high due to the occurrence of sulphate and fluoride-bearing daughter minerals (Rankin, 2003). CI$^-$ and SO$_4^{2-}$ are the dominant anions present, with minor CO$_3^{2-}$ and HCO$_3^-$, K$^+$, Na$^+$ and Ca$^{2+}$ are the dominant cation with levels of Fe, Sr, Ba, REE, etc. Nahcolite is the most common daughter phase and some other sulfate daughter phases are arcanite, mirabilite, celestine and barite with minor carbonate and fluoride minerals (Rankin, 2003). Similar characteristics are confirmed for the Maoniuping deposit.

Due to the high capture pressure and highly developed cleavage in the host minerals (fluorite, calcite, barite and bastnaesite), microthermometric studies are very difficult to undertake on various inclusion types, particularly for melt–fluid (multi-solid) inclusions in the deposit. This explains why very few microthermometric data have been published for the deposit. For example, Yuan et al. (1995) only give the microthermometric data for low temperature fluid inclusions (AV sub-type) and few for daughter mineral bearing fluid inclusions. Niu and Lin (1995b), Niu et al. (1996a) performed microthermometric work on aqueous-rich fluid inclusions (AV sub-type), CO$_2$-bearing fluid inclusions and melt–fluid inclusions. However, they reported that all melt–fluid inclusions had a vapor phase homogenization behavior. These results were not duplicated in the present study. In our observations, all vapor phase homogenization of melt–fluid inclusions was caused by inclusion destruction (e.g., leakage or explosion). Yang et al. (2001) reported similar microthermometric results from CO$_2$-rich fluid inclusions in quartz and bastnaesite to those reported in the present study. Microthermometric results for melt inclusions, melt–fluid inclusions and pure CO$_2$ inclusions are still unavailable and no clear corresponding relationship was confirmed between different types of inclusions and mineralization stages in the published papers.

According to the petrographic observations and microthermometric results, it is concluded that melt inclusions characterize the carbonatite stage (stage 1); melt–fluid inclusions sponsor the pegmatite stage (stage 2); CO$_2$-rich fluid inclusions dominate the barite–bastnaesite stage (stage 3), but only AC-2 inclusions should be the best candidate for stage 3. The AC-1 and C sub-type inclusions were trapped after phase separation. Aqueous rich fluid inclusions relate to the late calcite stage (stage 4).

A key question to consider is which type of inclusions should be the best samples for earliest orthomagmatic fluids evolved from carbonatite magma? Inclusion petrography shows that there are volatiles in the melt inclusion from both fluorite and calcite of stages 1 and 2. Melt inclusions can transform into the melt and volatile phase during heating, which indicates the volatile–rich characteristic of the carbonatite melt. ML inclusions are dominant in fluorite from the early mineralization stage that follows the carbonatite stage. The ML-2
inclusions have varied solid/aqueous/vapor ratios, implying inhomogenous entrapment. However the ML-1 type inclusions have a stable solid/aqueous/vapor ratio, and show primary inclusion characteristics with negative crystal shape. During heating, most of ML-1 type inclusions explode and only a few homogenized to the critical phase at a high temperature. It is thus likely that the ML-1 inclusions represent the best sample of the earliest orthomagmatic fluid derived from carbonatite magma. High homogenization temperatures, high solid-percentages in inclusions and critical-homogenization behavior imply that the initial ore-forming fluids were high-temperature (~600 to 850 °C), high-pressure (~350 MPa), very high-concentration and supercritical. LRM, SEM/EDS results and daughter mineral assemblages show that K⁺, Na⁺, Ca²⁺, together with Ba²⁺, Sr²⁺ and REE, are the dominant cations. The dominant anions are SO₄²⁻, with minor amounts of HCO₃⁻ and CO₃²⁻. CO₂ in the bubble phase of ML-1 inclusions is usually difficult to confirm by LRM. It is possible that the peaks at 1282 cm⁻¹ and 1386 cm⁻¹ are masked by the fluorescence of fluorite or the absence of CO₂ in inclusions of this kind. No ML-1 inclusions have been observed in quartz, but the LRM spectra for the bubbles in ML-2 inclusions of quartz have peaks at 1282 cm⁻¹ and 1386 cm⁻¹. It is likely that the bubble in ML-1 inclusions from fluorite comprise CO₂.

CO₂-rich fluid inclusion assemblages (AC, ADC and C-type) represent the next step of carbonatitic fluid evolution, since these inclusions are sometimes associated with melt–fluid inclusions and occur principally in barite and bastnaesite from stage 3. The microthermometric and LRM results for CO₂-rich fluid inclusions suggest that the ore-forming fluid in stage 3 has a high CO₂ concentration, moderate to high temperature and high pressure. LRM and SEM/EDS also proved that K⁺, Na⁺ and Ca²⁺ are the dominant cations, together with minor Ba²⁺, Sr²⁺, REE, and the dominant anions are SO₄²⁻. The bubble phase is dominated by liquid CO₂. The similar chemical composition between ML inclusions and CO₂-rich inclusions, and close petrographic relationship, shows their affiliation to the evolution of an ore-forming fluid.

Aqueous-rich fluid inclusions have low temperatures and low captave pressures (<100 MPa), indicating late-stage fluid characteristics. The LRM and SEM/EDS results of AV and ADV inclusions indicate that K⁺, Na⁺, H₂O and SO₄²⁻ dominated the system. The white calcite veins of stage 4 cross-cuts all styles of REE veins and wallrocks, and often occurs as geodes or fracture fillings. That means the calcite of stage 4 precipitated in an extensional environment.

In summary, CO₂, K⁺, Na⁺ and SO₄²⁻ rich carbonatite fluids are likely to be a common characteristic of both the continental rift and collision orogenic environment. But for the temperature of ore-forming fluids, there is a large range reported for different deposits, even for a deposit like Maoniuping. The reason for this is that most microthermometric work on high capture pressure inclusions is unsuccessful. The sulfate daughter minerals rich in K⁺ and Na⁺ might be a characteristic of inclusions related to carbonatite in both continental rift and continental collision orogenic environments.

6.3. Evolution of ore-forming fluid

The evolution of ore-forming fluids is one of the most important subjects of carbonatite research. Ting et al. (1994) suggested an evolutionary path varying from an early CO₂-rich fluid, via medium-high salinity H₂O-rich fluid, to a CH₄-rich fluid using fluid inclusions in apatite from the Sukulu carbonatite (Uganda). Smith and Henderson (2000) propose that fluids varied from high-temperature, high-pressure CO₂-rich, to low-temperature, low-pressure aqueous-rich types, based on studies on fluid inclusions in gangue and REE minerals from the Bayan Obo Fe-REE-Nb deposit. Although, there is still debate on the genesis of the Bayan Obo deposit, results of inclusion studies appear compatible with carbonatitic fluids (Rankin, 2003).

In the Maoniuping REE deposit, different inclusion types, ranging from melt to fluid inclusions, record the evolution of a carbonatitic fluid. According to microthermometric results, the T–P path evolution from carbonatite melt to ore-forming fluid is illustrated in Fig. 12. The evolution of carbonatite fluid is from high-temperature melt–fluids, high-moderate temperature CO₂-rich fluids to low-temperature aqueous rich fluids. Unmixing of melt and fluid occurs at between 790 and 850 °C according to the homogenization temperature of melt inclusions. A large quantity of critical CO₂–H₂O fluid inclusions (AC-2) in bastnaesite and barite indicate that the ore-forming fluid for stage 3 is a kind of H₂O–CO₂ supercritical fluid. Aqueous-CO₂ phase separation occurs at 227 to 453 °C. Secondary fluid inclusions in fluorite and quartz trapped during stage 4 show lower homogenization temperatures and lower CO₂ concentrations. However, the LRM results indicate that the later fluid is also dominated by the K–Na–H₂O–SO₄ system. It can be concluded that from stages 3 to 4, the ore-forming fluid progresses from a high to moderate temperature CO₂-rich fluid to a low temperature aqueous-rich fluid, but K–Na–H₂O–SO₄ still dominated the fluid system.

The mineral assemblage provides some useful information about the evolution of the ore-forming fluid. The mineral assemblage in Maoniuping is similar to that of the Kizilcaoren fluorite-barite-REE deposit, Turkey (Gultekin et al., 2003). However, in contrast to other deposits, Maoniuping also contains some alloys (as determined by SEM/EDS and EPMA). Metallic minerals at Maoniuping are relatively rare and are dominated by Fe-oxides. Sulfide is mainly present as galena and pyrite, with minor chalcocite and pyrrhotite. From stages 1 to 3, the metallic mineral assemblage passes from sulfide-dominated to oxide-dominated. In stages 1 and 2, the dominant minerals are pyrite, chalcocite, pyrrhotite and magnetite. In stage 3, the dominant metallic minerals are magnetite, hematite and rutile, together with native copper, a Cu-Zn alloy and minor galena. The native metal, oxide and lead–sulfide mineral assemblage is special and likely implies unique physico-chemical conditions. From stages 1 to 3, the variation of the metallic mineral assemblages indicates that the ore-forming environment ranged from reductive to oxidative. No metallic minerals were identified in stage 4.

6.4. REE mineralization

REE mineral precipitation mechanism is an important aspect of carbonatitic fluid research. Smith et al. (2000) and Smith and Henderson (2000) proposed that bastnaesite precipitated at a temperature of between 250 and 280 °C from CO₂-rich fluids, and that phase separation provided a mechanism for REE concentration and deposition at the Bayan Obo REE deposit. Palmer and Williams-Jones (1996) and Williams-Jones and Palmer (2002) argue that in the Amba Dongar fluorite deposit, fluorite precipitated by the mixing of
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