REE and Trace Element Geochemistry of Yinachang Fe-Cu-REE Deposit, Yunnan Province, China *

YANG Yaomin (杨耀民)[1,2,3,4], TU Guangzhi (涂光炽)[1], and HU Ruizhong (胡瑞忠)[1]

1) (*Institute of Geochemistry, Chinese Academy of Sciences, Guiyang* 550002, *China*)

2) (*Graduate School, Chinese Academy of Sciences, Beijing* 100039, *China*)

3) (*Key Laboratory of Marine Sedimentary and Environmental Geology of State Oceanic Administration,*
First Institute of Oceanography, State Oceanic Administration, Qingdao 266061, *China*)

4) (*Northwest Geological Exploration Bureau, CNNC, Xi' an* 710054, *China*)

Abstract: REE and other trace elements in ores, wall rocks, alkaline volcanic rocks and dia-
base dikes have been determined in the Yinachang Fe-Cu-REE deposit. Comparative studies of
REE and trace element geochemical characteristics of these geological bodies indicate that the
ores and alkaline volcanic rocks contain abundant REE and Y ($65.9 - 4633$) $\times 10^{-6}$, with
higher abundances of As, Mo, Nb, Co and U than those of the crust. Their chondrite-normal-
ized patterns show a strong enrichment of LREE and a positive Eu anomaly, in contrast to those
of the dolomites which are characterized by slight LREE enrichment and moderate negative Eu a-
nomaly. The REE patterns of ores are similar to those of hydrothermal sediment cores in the East
Pacific Rise, whereas the REE patterns of dolomites are similar to those of PAAS (Post-Archean
Average Shale). In combination with the geological setting of the deposit, the primary ore-form-
ing fluids might have higher REE and volatile elements, and might have been derived from man-
tle degassing, or the alkaline volcanic magmas. The Yinachang Fe-Cu-REE ore deposit is con-
sidered to be of volcanic exhalation-hydrothermal sedimentary origin.

Key wards: rare-earth elements; exhalation-hydrothermal; positive Eu anomaly; LREE
enrichment; Fe-Cu-REE deposit

1 Introduction

The behaviors of the rare-earth elements (REE) during magmatism, metamorphism and meta-
somation are of great geological interest because of their applications in geochronology and geochemi-
cal tracing (e. g. reviews by Faure, 1986; Lipin and Mckay, 1989). Because of their similar geo-
chemical behaviors and low solubilities in water, the REEs have proved themselves to be a powerful
tool for the characterization of provenances when applied to sedimentary rocks (McDaniel et al. ,
1994). Although their behaviors under hydrothermal conditions are poorly understood and documen-
ted as compared with their roles in the evolution of igneous rocks, the REEs are particularly useful
in ore formation modeling as they can provide constraints on the nature, source and composition of
ore-forming hydrothermal fluids, when used in conjunction with fluid inclusion data, isotopic signa-
tures, etc. (Morteani et al. , 1986; Constantopoulos, 1988; Leroy and Turpin, 1988; Vander Au-
wera and Andra, 1991; McDaniel et al. , 1994).

On the western-southern margins of the Yangtze Platform is located one of the most important Cu-Fe polymetallic ore-concentrated zones, where there are a variety of ore types. So it has been attracting ever-increasing attention of many geologists. There have been found some typical REE-enriched deposits associated with Fe and Cu, such as the Yinachang Fe-Cu-REE deposit in Wuding, the Xikuangshan Fe-Cu deposit and the Bijiashan Fe deposit in Dongchuan, and the Yimen Cu deposit (Bai Ge and Yuan Zhongxin, 1985; Gong Lin et al. , 1996; Qi Dexian et al. , 2000). Especially, the REEs have economic signatures in the Yinachang deposit. Several possible mechanisms of ore formation have been proposed for the Yinachang Fe-Cu-REE deposit, including syngenetic sedimentary deposition (Shi Jiaxin, 1981), metamorphism associated with replacement (Zhang Peishan et al. , 1998), possibly carbonatite related-hydrothermal fluids (Bai Ge and Yuan Zhongxin, 1985) and deposition from the exhalative hydrothermal sediments (Zhou Guohua and Liu Jingfen, 1993; Gong Lin et al. , 1996).

The aim of this study is to shed light on the REE signatures of various meta-sedimentary rocks associated with a diversity of sulphide mineralizations in the Yinachang Fe-Cu-REE deposit in Yunnan Province, China, to evaluate the metamorphic and pre-metamorphic influences on the determined REE patterns and to explore the potential of REE studies to provide information about the behaviors of REEs during metamorphism and hydrothermal alteration and to investigate the composition of ore fluids related to ore formation processes.

2 Geological setting

The Kunyang rift lies at the western margin of the Yangtze Platform and to the south of the Kangdian axis. The Yinachang Fe-Cu-REE deposit occurs in the Wuding-Lufeng Basin on the western side of the middle segment of the rift, formed during the Kunyang rift evolution. The depositional setting of the Yinachang deposit has been recognized as a volcanic basin, characterized by volcanism, immature terrigenous and pyroclastic sediments, and the widespread exhalation of metal-bearing brines (Gong Lin et al. , 1996; Huang Yongpin et al. , 1999).

The Yinachang Fe-Cu-REE deposit hosted in the Yinmin Formation of the Kunyang Group which is distributed in an elongated belt confined by the Luzhijiang lithospheric fault and the Xiaojiang-Yimen fault. The ores are stratigraphically restricted to one specified horizon, the main ore-bearing rocks are siliceous dolomites, the foot- and hanging-wall rocks of orebodies are metamorphic garnet-biotite schists whose protoliths are alkaline volcanic rocks (Fig. 1). Diabase dikes and volcanic breccia cut across the ores and strata.

The most prominent feature of orebodies is the ubiquitous fine-scale mineralogical banding. This banding can be regular, wavy, or lensoid, and is defined by alternating mineral bands of siderite, magnetite, chalcopyrite, and fluorite, apatite, pyrite and quartz. Individual bands vary in width from 0.5 mm to 30 cm. Although minerals in most bands are variable in grain size, most bands can reflect the original sedimentary bedding.

There are two types of ore structures: banded ore and massive ore. The ores are dominated by Fe oxides and are of Cu sulphide-rich type; magnetite and chalcopyrite are the dominant metallic minerals, with subordinate pyrite, molybdenite and cobaltite and galenite; the gangue minerals are mainly siderite, albite, dolomite, fluorite, apatite, quartz, and calcite; REE minerals include bastnaesite, monazite, and allanite, and in some cases, apatite, fluorite and siderite contain some rare-earth elements.
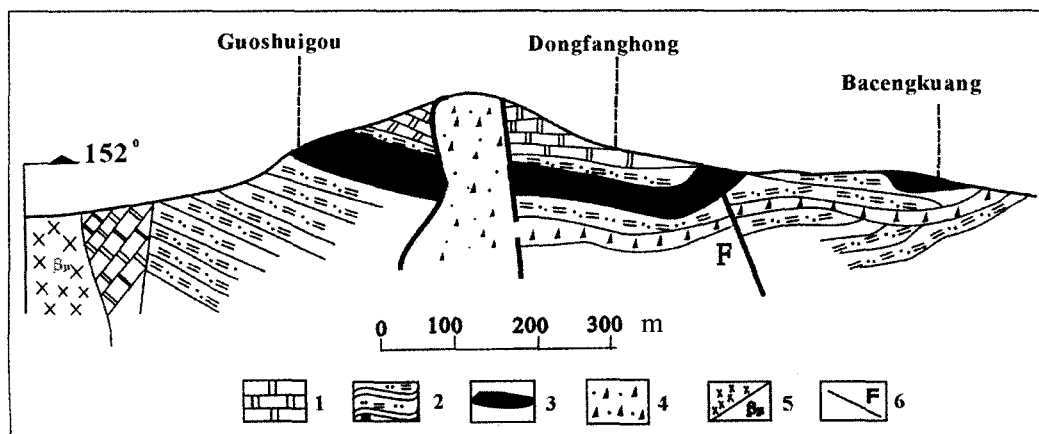
Fig. 1. Cross section of the Yinachang Fe-Cu-REE deposit (modified by Yang Xueming et al. , 1988). 1. Siliceous dolomite; 2. garnet-biotite schist; 3. ore; 4. volcanic breccia; 5. diabase dike; 6. fault.

3 Samples and analytical methods

In this study, 16 fresh samples of various rocks were collected and examined, which can be grouped into six petrogenetic categories: ① siliceous dolomite—main wall rock; ② the foot- and hanging-wall rocks of orebodies—garnet-biotite schist; ③ massive ores; ④ banded ores; ⑤ volcanic breccia; and ⑥ diabase dikes. Detailed petrographic descriptions and geochemical characteristics of a variety of samples were provided by Zhou Guohua and Liu Jingfen (1993) and Yang Yaomin (2004). In laboratory, the samples were washed with water firstly, and dried under room temperature, then 200 grams of each sample were pulverized to 200 mesh. Analyses of the REE and other trace elements in the various rocks were conducted on ICP-MS at the Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences. Relative standard deviation was less than ±5% for each analysis and analytical accuracy was better than 10% for all elements. All REE data have been chondrite-normalized (Boynton, 1984). The Eu anomaly is quantified by δEu, where $\delta Eu = (Eu)_N / [(Sm)_N \times (Gd)_N]^{1/2}$.

4 Results

The REE and trace element contents of all the samples are listed in Table 1, together with the calculated Eu, Ce anomalies and typical element ratios. The primitive chondrite-normalized REE distribution patterns (from Boynton, 1984) are shown in Fig. 2. For interpretative purpose and visual clarity, all samples of the six groups (as described above) with similar petrochemical properties were plotted.

In comparison with the recommended contents of the bulk continental crust (Rudnick and Gao Shan, 2004) , all the siliceous dolomites analyzed are low in abundance for Co, Rb, Sr, Y, Zr, Nb, Mo, Ba, Cs, Hf, Ta, Th, and U. Compositionally, the ores are significantly low in Rb, Sr, Th, Ba, Zr, Cs and high in Co, As, Nb, Mo, U, REE; the garnet-biotite schists are characterized by high abundances of As (10. 8 – 18. 7) $\times 10^{-6}$, Rb (147 – 207) $\times 10^{-6}$, Nb (19. 9 – 20. 0) $\times 10^{-6}$, Mo (22. 7 – 35. 2) $\times 10^{-6}$, Cs (19. 9 – 27. 4) $\times 10^{-6}$, Ba (107 – 1425) $\times 10^{-6}$, Th (9. 23 – 106) $\times 10^{-6}$ and U (1. 5 – 5. 41) $\times 10^{-6}$.

The ores have very high REE and Y abundances with REE + Y enrichments $(726 - 4633) \times 10^{-6}$ and chondrite-normalized REE patterns with a remarkable positive Eu anomaly (Fig. 2B, C), and their δEu values range from 1.77 to 5.16, with no Ce anomaly, and the LREEs are highly enriched as compared to the HREEs. $(La/Yb)_N$ ratios range from 17.3 to 81.1. The massive ores have higher $(La/Yb)_N$ values than the banded ores except for sample DFH-6 whose $(La/Yb)_N$ is equal to 81.8. The REE + Y contents of garnet-biotite schists range from 221×10^{-6} to 281×10^{-6}, and the chondrite-normalized REE patterns are similar to those of ores with positive Eu anomalies (Fig. 2D).

Table 1. Trace element and REE data for various rock types from the Yinachang Fe-Cu-REE deposit and typical carbonatites and the crust ($\times 10^{-6}$)

Sample No.	DB-1	DB-4	YDFH-17	YDFH-18	DB-11	DB-15	YDB-4	YDFH-6	DB-31	DFH-3
Rock type	①		②				③			
Co	1.06	5.49	28.1	23.5	643	15.8	728	411	278	106
As	10.9	20.6	18.7	10.8	774	18.3	1170	488	309	65.2
Rb	2.56	10.2	207	148	0.36	0.62	1.56	0.36	0.173	19.1
Sr	41.5	61.2	15.8	10.9	10.4	43.0	22.6	52.2	49.4	41.6
Y	5.62	5.22	21.6	26.5	39.0	80.5	70.5	92.5	83.2	246
Zr	5.36	8.96	99.9	99.8	3.4	2.61	0.97	0.99	0.31	7.63
Nb	0.29	1.11	19.9	20.0	105	123	106	295	74.3	259
Mo	0.50	0.95	35.2	22.7	284	9.77	1489	688	105	299
Cs	0.07	0.21	27.4	19.9	0.04	0.05	0.19	0.05	0.02	1.79
Ba	20.8	107	1425	997	12.2	28.9	26.0	8.82	17.3	184
Hf	0.14	0.28	2.81	2.75	0.142	0.09	0.13	0.20	0.05	2.19
Ta	0.04	0.07	0.76	0.67	0.247	4.13	0.48	0.89	0.08	5.04
Th	0.33	1.15	9.23	10.6	0.78	4.04	1.27	1.64	1.00	10.4
U	0.81	1.50	5.41	6.27	51.3	5.51	117	150	42.3	77.8
La	2.51	3.24	52.9	69.7	328	237	441	509	436	810
Ce	6.44	7.87	82.6	107	564	456	633	786	798	1336
Pr	0.44	0.71	8.48	10.8	46.8	40.9	68.7	84.5	64.7	135
Nd	bd	bd	28.5	34.9	143	137	228	282	192	470
Sm	0.47	0.84	4.64	5.39	19.5	24.0	31.0	39.7	25.5	73.2
Eu	0.15	0.25	4.99	5.79	18.8	14.1	26.4	21.8	37.2	71.8
Gd	0.55	0.87	5.87	7.28	14.4	19.5	26.1	35.6	19.1	66.2
Tb	0.10	0.13	0.94	1.13	1.86	2.88	3.06	4.65	2.71	8.06
Dy	0.62	0.85	4.61	6.06	10.2	16.5	15.9	24.7	16.3	42.5
Ho	0.14	0.16	0.85	1.07	1.80	3.01	3.22	4.68	3.21	8.53
Er	0.44	0.45	2.20	2.66	4.81	8.11	9.54	13.2	9.05	23.7
Tm	0.07	0.07	0.27	0.35	0.62	1.04	1.21	1.72	1.13	3.04
Yb	0.39	0.42	1.92	1.99	3.17	5.57	6.90	9.19	5.67	16.2
Lu	0.06	0.06	0.25	0.26	0.30	0.53	0.67	0.90	0.50	1.93
$\Sigma REE + Y$	18.0	21.1	221	281	1196	1046	1565	1910	1694	3312
$(La/Yb)_N$	4.32	5.20	18.60	23.63	69.8	28.6	43.1	37.4	51.9	33.7
$(La/Sm)_N$	3.37	2.42	7.17	8.13	10.55	6.21	8.95	8.08	10.77	6.96
$(Gd/Yb)_N$	1.13	1.67	2.47	2.96	3.66	2.82	3.06	3.13	2.72	3.30
δEu	0.91	0.90	2.92	2.82	3.43	2.00	2.83	1.77	5.16	3.15
δCe	1.48	1.25	0.94	0.94	1.10	1.11	0.88	0.91	1.14	0.97
Y/Ho	39.6	31.8	3.2	1.5	21.7	26.7	21.9	19.8	25.9	28.8
Zr/Hf	38.5	31.9	26.1	29.7	24.1	29.3	7.66	4.90	6.31	3.5
Nb/Ta	7.35	16.0	3.8	2.1	425	29.7	219	332	917	51.4
U/Th	2.44	1.30	9.78	11.11	65.6	1.36	92.5	91.3	42.5	7.51

Table 1. (to be continued)

Sample No.	DFH-Ⅲ-1	YDFH-11	GS-1	DFH-6	GS-8	GS-9	GS-12	Typical carbonatite		Crust
Rock type		④			⑤		⑥	a	b	
Co	42.7	49.8	61.0	282	17.9	9.39	31.0	–	–	26.6
As	10.8	17.7	60.9	29.7	12.3	13.7	14.4	18.0	6.0	2.5
Rb	0.15	34.3	1.09	271	151	246	9.30	178	<10	49
Sr	11.8	47.8	67.2	17.5	81.7	32.0	31.1	11979	1608	320
Y	44.8	196	290	190	25.2	22.6	69.5	7	97	19
Zr	0.27	1.21	1.06	4.43	142	131	122	<10	49	132
Nb	62.8	387	514	171	10.7	14.2	20.5	28	584	8
Mo	97.9	797	288	534	1.65	0.68	3.78	125	6.0	0.8
Cs	0.02	3.18	0.12	26.2	4.10	6.74	0.40	6.4	bd	2
Ba	3.54	170	23.7	1571	898	546	38.8	14300	7906	456
Hf	0.05	0.13	0.21	1.44	4.36	4.10	3.56	0.13	<0.3	3.7
Ta	0.29	4.32	5.40	5.62	0.75	1.01	0.93	<0.03	<0.04	0.7
Th	0.71	2.40	0.696	16.6	14.7	18.2	7.08	3.77	61.6	5.6
U	16.9	194	43.0	33.6	4.00	5.00	2.10	10.6	1.1	1.3
La	148	357	574	1412	47.1	21.2	35.0	545	1062	20
Ce	323	474	1276	2092	101	43.0	75.3	645	1974	43
Pr	31.0	49.3	114	151	9.51	3.88	7.04	–	210	4.9
Nd	109	172	497	495	31.9	10.9	23.2	102	750	20
Sm	19.2	29.7	96.2	76.6	6.46	3.22	4.58	7.8	96.8	3.9
Eu	10.7	32.4	48.3	72.1	1.31	0.70	0.88	1.62	24.6	1.1
Gd	14.2	31.1	80.0	58.1	5.10	3.06	3.52	–	–	3.7
Tb	1.92	4.79	12.1	6.94	0.74	0.54	0.46	0.32	7	0.6
Dy	11.1	29.3	70.5	38.8	4.22	3.69	2.61	1.75	33	3.6
Ho	2.02	6.06	12.7	7.01	0.82	0.77	0.48	–	–	0.77
Er	5.61	17.7	32.3	18.2	2.42	2.36	1.52	–	–	2.1
Tm	0.73	2.40	3.85	2.21	0.33	0.35	0.22	–	–	0.28
Yb	4.00	13.9	19.2	11.7	2.18	2.37	1.58	0.46	7.98	1.9
Lu	0.38	1.57	1.78	1.25	0.33	0.35	0.25	0.058	1.06	0.3
ΣREE + Y	726	1416	3129	4633	238	119	226	1311	4263	125
(La/Yb)$_N$	25.0	17.3	20.2	81.1	14.5	6.0	15.0	798.8	89.7	7.1
(La/Sm)$_N$	4.85	7.56	3.75	11.59	4.59	4.14	4.81	43.95	6.90	3.23
(Gd/Yb)$_N$	2.87	1.80	3.37	4.00	1.89	1.04	1.80			1.57
δEu	1.98	3.27	1.68	3.30	0.70	0.68	0.67			0.89
δCe	1.15	0.86	1.20	1.09	1.14	1.14	1.16			1.05
Y/Ho	22.1	32.3	22.8	27.1	30.6	29.6	145			25
Zr/Hf	5.02	9.45	5.03	3.07	32.5	32.0	34.1			35.7
Nb/Ta	219	89.7	95.2	30.5	14.4	14.0	22.1			11.4
U/Th	23.9	80.8	61.8	2.02	0.27	0.27	0.30	2.81	0.02	0.23

Note: Trace elements and REEs analyzed by ICP-MS; " – " no detection; bd. below detection; ① siliceous dolomite; ② garnet-biotite schist; ③ massive ore; ④ banded ore; ⑤ volcanic breccia; ⑥ diabase dike. Typical carbonatite (from Keller and Spettel, 1995): a. natrocarbonatite, O. Lengai 102; b. ferrocarbonatite, Homa Bay. The crust data from Rudnick and Gao Shan, 2004.

The abundance of REEs [(18.0 – 21.1) × 10^{-6}] for the siliceous dolomites is relatively low, with negative Eu anomaly and weak HREE fractionation (Fig. 2A). The REE contents of volcanic breccias and diabase dikes are (119 – 238) × 10^{-6} and 226 × 10^{-6}, respectively, both showing

negative Eu anomalies with $\delta Eu = 0.67$. The chondrite-normalized REE patterns are moderately steep with respect to LREE and flat with respect to HREE (Fig. 2E, F).
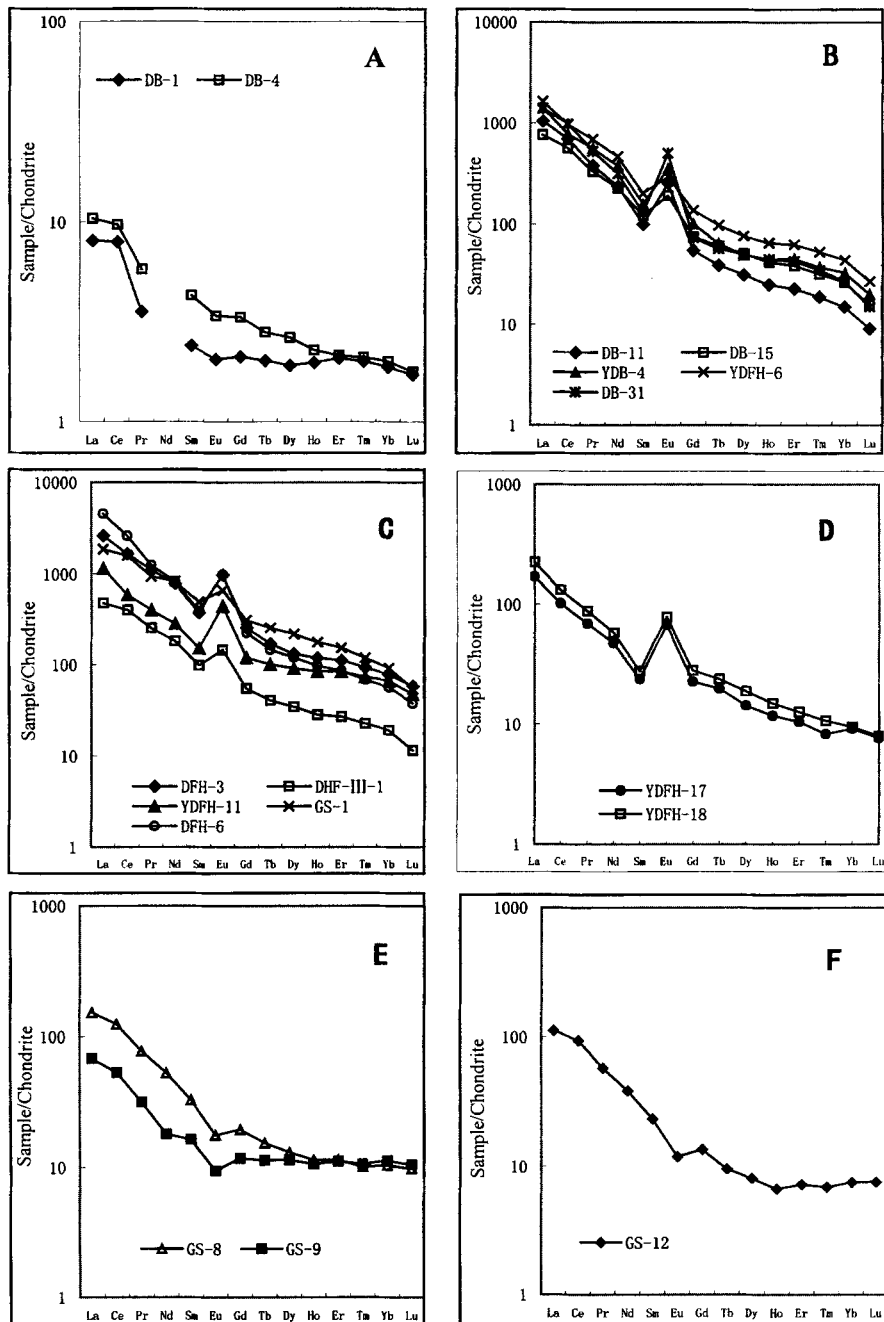

Fig. 2. Chondrite-normalized REE patterns in all samples of the six groups recognized in the Yinachang Fe-Cu-REE deposit. A. Siliceous dolomite; B. massive ore; C. banded ore; D. garnet-biotite schist; E. volcanic breccia; F. diabase dike; all data from Table 1.

5 Discussion

Siliceous dolomites represent the main chemical sedimentation type, and their chondrite-normalized REE patterns are typical of aluminosilicate-free post-Paleoproterozoic marine sedimentary carbonates (Taylor and McLennan, 1985; Bau and Dulski, 1996). The levels of REE in the siliceous dolomites are very low ($< 100 \times 10^{-6}$), in striking contrast to those of ores. Taylor and McLennan (1985) provided the REE data for carbonates and illustrated the similarities between their chondrite-normalized REE patterns and those of shales and sandstones, except that carbonates tend to have much lower concentrations, which would account for the lower REE abundances of the siliceous dolomites. Much difference has been recognized between the ores and the siliceous dolomites, suggesting their different REE sources.

The chondrite-normalized REE patterns of the ores and garnet-quartz schists feature LREE enrichment and remarkable positive Eu anomaly, suggesting that it is very important to study the protoliths of garnet-biotite schists. The biotite K-Ar ages of foot- and hanging-wall rocks of orebodies are 809, 813 and 789 Ma[①], suggesting that garnet and biotite are metamorphic minerals crystallized in the latest stage of the Jinning tectonic movement. The protoliths of garnet-biotite schists are alkaline volcanic rocks (Yang Yaomin, 2004; Bai Ge and Yuan Zhongxin, 1985), whose petrological and geochemical characteristics are consistent with those of the alkaline volcanic rocks in the Dahongshan and Hekou groups, suggesting that a huge volume of alkaline volcanic rocks erupted at the initial stage of Kunyang rifting.

Taylor et al. (1986) demonstrated that the REEs are of immobility during high-grade metamorphism. Except for the loci where partial melting occurred, metamorphism did not affect the primary REE patterns. Parr (1992) reported a lack of association between metamorphic mineral assemblages and REE concentrations in exhalites from the Pinnacles deposit. Exhalites with metamorphic garnets accounting for > 80% exhibited LREE-enriched patterns rather than HREE-enriched ones, as might be expected, if the REE distributions are a function of metamorphic crystallization (garnets are HREE-enriched mineral) (Parr, 1992). This led Parr (1992) to conclude that the data represent the primary REE concentrations of exhalative fluids. Similarly, Lottermoser (1989) suggested the pre-metamorphic REE concentrations in exhalites associated with the Broken Hill deposit can represent the primary REE concentrations of the rocks. The main argument is: apparent lack of mineralogical control on REE distributions and their similarities to the REE patterns found in modern hydrothermal fluids. The REE patterns of garnet-biotite schists also represent those of primary alkaline volcanic rocks, and similarities in REE patterns between the ores and the alkaline volcanic rocks suggest the REEs of ores would be derived from the alkaline volcanic rocks or the hydrothermal fluids which occurred during alkaline volcanic eruption.

If the solution is not enriched in Eu relative to the other REEs, in the process of sedimentation the occurrence of fractionation between Eu and the other REEs will make Eu preferentially enter into the sedimentary phase, giving rise to positive anomalies. This can occur if a phase is precipitating, which has a special affinity for Eu, or if the properties of Eu in the solution differ from those of the other REEs so as to promote the partitioning of Eu as a trace element into all solid phases. Both mechanisms require the properties of Eu^{3+} in solutions or solids do not differ significantly from those of the other trivalent REE (Graf, 1977). It appears, however, that the remarkable anomaly observed in the Yinachang ore samples did not result from Eu fractionation during precipitation. If Eu

---

① 1/50000 Geological Map of Wuding Region (Bureau of Geology and Mineral Resources of Yunnan Province).

is preferentially incorporated into one of the precipitating phases, the magnitude of Eu anomaly should be related to the mineralogy of the samples, but the major minerals such as magnetite and chalcopyrite in the ore and gangue minerals such as siderite and fluorite all display pronounced positive Eu anomalies (Yang Yaomin, 2004). In addition, the Al_2O_3 contents of ores are very low (about 0.3%, Yang Yaomin, 2004), the positive Eu anomalies of ores were not caused by detrital feldspar. The most logical conclusion is that the ore-forming fluid was already enriched in Eu and the positive Eu anomalies of ores are attributed to hydrothermal solutions (Michard et al., 1983).

Geochemical compositions and REE patterns of ores are unlike those of normal sediments and volcanic breccias and diabase dikes. The consistent REE patterns for various types of ores indicate that there has not occurred REE fractionation during ore precipitation, so the nearly parallel REE patterns of ores are considered as a reflection of those of primary ore-forming fluids from which the ores were precipitated. In addition, more research suggested that the ore-forming fluids that exhibit LREE enrichments and pronounced positive Eu anomalies could not be derived from seawater, formation water and meteoric water (Wang Jinbing and Li Chaoyang, 1991; Bi Xianwu and Hu Ruizhong, 1998). In conjunction with the deposit and its geological setting in the initial stage of Kunyang rifting and the Sm-Nd isotope constraints, it is shown that the REE of ores are derived from the mantle and the ore-forming ages are consistent with those of the ore-hosted strata (Yang Yaomin, 2004), and the primary ore-forming fluids may have originated from volatile-rich fluids as a result of either differentiation of a alkaline magma or mantle degassing. Positive Eu anomalies found in the primitive ore fluids suggested that the REEs were derived from relatively hot and reducing fluids (Sverjersky, 1984).

Exhalites formed in modern hydrothermally active areas, e. g. the Red Sea, are enriched in both LREE and Eu. Hydrothermal solutions (Michard et al., 1983) and hydrothermal precipitates (Bau et al., 1996; German, 1999) from the East Pacific Rise also have steep, LREE-enriched REE patterns with remarkable positive Eu anomalies. This is in direct contrast to the REE patterns of metalliferous Fe-Mn sediments precipitated on the sea floor, which exhibit flat patterns and negative Ce and Eu anomalies very similar to those of seawater (Alt, 1988). Therefore, ancient exhalites formed in the submarine hydrothermal center are expected to have LREE-enriched patterns with positive Eu anomalies. The REE patterns in Yinachang ores are similar to those of modern seafloor hydrothermal sediments (Fig. 3), indicating an ancient hydrothermal sedimentary origin of the Yinachang deposit. The primary ore-forming fluids might be REE- and volatile element-high fluids derived from mantle degassing or alkaline volcanic magmas. The Yinachang Fe-Cu-REE ore deposit is thought to be of volcanic exhalation-hydrothermal sedimentary origin.

As compared with the carbonatite rocks, although the ores have similar chondrite-normalized REE patterns, there are significant differences in the composition of trace elements, such as Sr (1608 – 11979) $\times 10^{-6}$ and Ba (7906 – 14300) $\times 10^{-6}$, their contents being much higher than those of Yinachang ores (Mills et al., 1995). At the same time, the occurrence of carbonatite rocks is associated with alkaline minerals and strong alkaline metasomatism (e. g. fenite, nepheline and osannite; Woolly et al., 1989; Yang Xueming et al., 1998). The carbonatites usually do not show positive Eu anomalies but negative Eu anomalies or no Eu anomaly. Those characteristics of carbonatites have not been observed in the Yinachang deposit. Thus, the Yinachang deposit seems not to be genetically related with carbonatites.

6 Conclusions

Analyses of various rock types from the Yinachang Fe-Cu-REE deposit demonstrated that in the

whole process of multi-phase metamorphism, the primary REE distribution patterns remained essentially unchanged; the REEs can be considered immobile in the analyzed rocks. A number of conclusions can be drawn from the identification of primary REE patterns in mineralized and unmineralized metavolcano-sediments from the Yinachang deposit:

(1) The ores are strikingly enriched in Co, As, Mo, U, Fe, and Cu, similar to the modern seafloor hydrothermal sediments, but different from siliceous dolomites which are normal chemical sedimentary rocks.

(2) The chondrite-normalized REE patterns of ores closely resemble those of the primary ore fluids, exhibiting LREE enrichments and pronounced positive Eu anomalies. These patterns can be compared most closely with those of fresh hydrothermal sediments on seafloor in the EPR. In addition, similarities in REE patterns between the ores and the hanging- and foot-wall rocks of ores suggested that ore deposition occurred during volcanic eruption, and the REEs of ores were derived from the mantle.
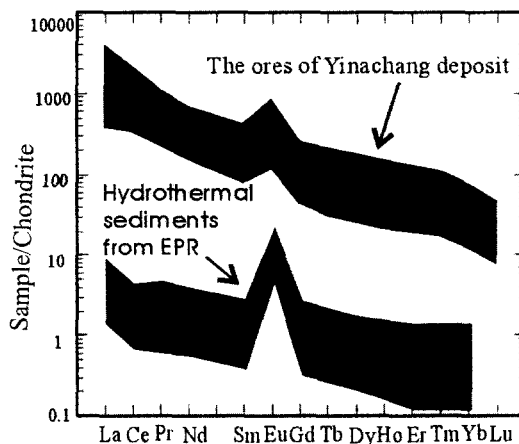

Fig. 3. The variation trend of REE in hydrothermal sediments from the EPR (East Pacific Rise) (data from German et al. , 1999) and ores from the Yinachang deposit.

(3) The Yinachang Fe-Cu-REE ore deposit is considered to be of volcanic exhalation-hydrothermal sedimentary origin.

References

Alt, J. C. , 1988, Hydrothermal oxide and nontronite deposits on the Eastern Pacific [J] : Marine Geology, v. 81 , p. 227 – 239.

Bai Ge and Yuan Zhongxin, 1985, Geology and mineral resources of carbonatites, Bulletin of Institute of Mineral Deposits (vol. 1) , Chinese Academy of Geological Sciences [M] : Beijing, Geological Publishing House, p. 99 – 140 (in Chinese).

Bau, M. and P. Dulski, 1996, Distribution of yttrium and rare-earth elements in the Penge and Kuruman Fe-formations, Transvaal Supergroup, South Africa [J] : Precambrian Res. ,v. 79, p. 37 – 55.

Bi Xianwu and Hu Ruizhong, 1998, REE geochemistry of primitive ore fluids in the Ailaoshan gold belt, southern China [J] : Chinese Journal of Geochemistry, v. 17, p. 91 – 96.

Boynton, W. V. , 1984, Cosmochemistry of the rare-earth elements: meteorite studies, in P. Henderson, ed. , Rare-earth element geochemistry, developments in geochemistry II [C] : Amsterdam, Elsevier, p. 63 – 114.

Constantopoulos, J. , 1988, Fluid inclusions and rare-earth element geochemistry of fluorite from south-central Idaho [J] : Econ. Geol. , v. 83 , p. 626 – 636.

Faure, G. , 1986, Principle of isotope geology [M] : New York, John Wiley, p. 1 – 247.

German, C. R. , M. Palmer, and J. M. Edmond, 1999, Geochemistry of a hydrothermal sediment core OBS Vent-field, 21°N East Pacific Rise [J] : Chem. Geol. , v. 155 , p. 65 – 75.

Gong Lin, He Yite, Chen Tianyou et al. , 1996, Proterozoic rift copper deposits in Dongchuan, Yunnan Province [M] : Beijing, Metallurgical Industry Press, p. 1 – 251 (in Chinese).

Graf, J. L. , 1977, Rare-earth elements as hydrothermal traces during the formation of massive sulfide deposits in volcanic rocks [J] : Econ. Geol. , v. 72 , p. 527 – 911.

Huang Yongping, Wu Jianmin, and Wang Ziping, 1999 , Geology and geochemistry of thermal-water sedimentary rocks of the Yinmin Formation in the Dongchuan copper ore field [J] : Geology and Prospecting, v. 35 , p. 15 – 18 (in Chinese with English abstract).

Keller, J. and B. Spettel, 1995, The trace element composition and petrogenesis of natrocarbonatites, in K. Bell and J. Keller, eds. , Carbonatite Volcanism [C] : Heidelberg, Spring-Verlag Berlin, p. 70 – 86.

Leroy, J. L. and L. Turpin, 1988, REE, Th and U behavior during hydrothermal and supergene processes in a granitic environment [J]: Chem. Geol. , v. 68, p. 239 – 251.

Li Zhiqun, 1996, Study on metallogenic geochemistry of iron and copper deposits in the Yinmin Formation of the Kunyang Group in the Middle Proterozoic suberathem [J]: Mineral Resources and Geology, v. 10, p. 100 – 107 (in Chinese with English abstract).

Lipin, B. R. and G. A. Mckay, 1989, Review in Mineralogy 21: Geochemistry and mineralogy of rare-earth elements [M]: Mineralogical Society of America, p. 1 – 331.

Lottermoser, B. G. , 1989, Rare-earth element study of exhalites within the Willyama Supergroup, Broken Hill Block, Australia [J]: Mineralium Deposita, v. 24, p. 92 – 99.

Lottermoser, B. G. , 1992, Rare-earth elements and hydrothermal ore formation processes [J]: Ore Geology Reviews, v. 7, p. 25 – 41.

McDaniel, D. K. , S. R. Hemming, S. M. McLennan, and G. N. Hanson, 1994, Resetting of neodymium isotopes and redistribution of REEs during sedimentary processes: The Early Proterozoic Chelmsford Formation, Sudbury Basin, Ontario, Canada [J]: Geochim. Cosmochim. Acta, v. 58, p. 931 – 941.

Michard, A. , F. Albarede, G. Michare et al. , 1983, Rare-earth elements and uranium in high-temperature solutions from East Pacific Rise hydrothermal vent field (13°N) [J]: Nature, v. 303, p. 775 – 777.

Mills, R. A. and H. Elderield, 1995, Rare-earth element geochemistry of hydrothermal deposits from the active TAG Mound, 26°N Mid-Atlantic Ridge [J]: Geochim. Cosmochim. Acta, v. 59, p. 3511 – 3524.

Morteani, G. , P. Moeller, and J. Hoefs, 1986, Rare-earth element and oxygen isotope studies of altered Variscan granites, western Ham (Germany) and southern Sardinia (Italy) [J]: Chem. Geol. , v. 54, p. 53 – 68.

Parr, J. M. , 1992, Rare-earth element distribution in exhalites associated with Broken Hill-type mineralization at the Pinnacles deposit, New South Wales, Australia [J]: Chem. Geol. , v. 100, p. 73 – 91.

Qi Dexian, Tian Yulong, Yan Yongfeng et al. , 2000, Geochemistry of the Shizishan copper deposits, Yunnan [J]: Acta Geologica Sinica, v. 74, p. 74 – 84 (in Chinese with English abstract).

Rudnick, R. L. and Gao Shan, 2004, Composition of the continental crust, in H. D. Holland and K. K. Turekian, eds. , Treatise on Geochemistry [C]: London, Elsevier Pergamon, p. 1 – 64.

Shi Jiaxin, 1981, The deposit characteristics and the genesis discussion on Yinachang Nb-bearing Fe-Cu-REE deposit in Wuding [J]: Geologic Science and Technology Information of Yunnan, n. 1, p. 1 – 11 (in Chinese with English abstract).

Sverjersky, D. A. , 1984, Europium equilibrium in aqueous solution [J]: Earth Planet. Science Letters, v. 67, p. 70 – 78.

Taylor, S. R. and S. McLennan, 1985, The continental crust: Composition and evolution [M]: London, Blackwell Sci. Publ. , 312p.

Taylor, S. R. , R. L. Rudnick, S. M. McLennan et al. , 1986, Rare-earth element pattern in Archean high-grade metasediments and their tectonic significance [J]: Geochim. Cosmochim. Acta, v. 50, p. 2264 – 2279.

Vander Anwera, J. and L. Andra, 1991, Trace elements (REE) and isotopes (O, C, Sr) to characterize the metasomatic fluid sources: Evidence from the skarn deposit (Fe, W, Cu) of Traversella (Ivrea, Italy) [J]: Contrib. Mineral. Petrol. , v. 106, p. 325 – 339.

Wang Jingbin and Li Chaoyang, 1991, REE geochemistry, Jingding ultra-large Pb-Zn deposit [J]: Geochimica, v. 20, p. 359 – 361 (in Chinese with English abstract).

Woolly, A. R. and K. R. C. Kempe, 1989, Carbonatites: Nomenclature, average chemical compositions, and element distribution, in K. Bell, ed. , Carbonatites: Genesis and Evolution [A]: London, Unwin Hyman, p. 1 – 14.

Yang Xueming, Yang Xiaoyong, and M. J. Le Bas, 1998, Carbonatites: A probe rock for the tectonic settings of continental lithosphere and mantle metasomatism [J]: Acta Geophysica Sinica, v. 41, (suppl.), p. 228 – 235 (in Chinese with English abstract).

Yang Yaomin, 2004, Study on the geochemistry of Fe-Cu-REE deposit in the Kunyang Group in Mid-Proterozoic—Exemplified by the Yinachang Fe-Cu-REE deposit [D]: Guiyang, Institute of Geochemistry, Doctoral Dissertation, p. 1 – 99 (in Chinese).

Zhang Peishan, Tao Kejie, Yang Zhuming et al. , 1998, Rare-earth element mineralogy in China [M]: Beijing, Science Press, p. 1 – 234 (in Chinese).

Zhou Guohua and Liu Jingfen, 1993, Preliminary discussion on exhalative sedimentation in Yinachang iron and copper deposit in Yunnan [J]: Mineral Geology of NW in China, v. 2, p. 4 – 7 (in Chinese with English abstract).