



Abstract

Sr and Nd isotope geochemistry of fluorites from the Maoniuping REE deposit, Sichuan Province, China: implications for the source of ore-forming fluids

Z.L. Huang^{a,b,*}, C. Xu^{a,c}, C.Q. Liu^a, D.R. Xu^{a,c}, W.B. Li^{a,c}, T. Guan^a

^a Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, China

^b The School of Earth Sciences, University of Leeds, Leeds LS2 9JT, UK

^c Graduate School, Chinese Academy of Sciences, Beijing 100039, China

Abstract

Fluorites are one of the main vein minerals in the Maoniuping REE deposit, Sichuan Province, China. This paper analyzes the Sr and Nd isotopic compositions of fluorites in the orefield. Their ($^{87}\text{Sr}/^{86}\text{Sr}$)₀ and ($^{143}\text{Nd}/^{144}\text{Nd}$)₀ (0.706031–0.706237 and 0.512370–0.512412, respectively) are similar to those of carbonatites (0.706074–0.706149 and 0.512383–0.512406, respectively) and syenites (0.705972–0.706302 and 0.512378–0.512405, respectively) in the orefield and all lie in the narrow range between EM I and EM II in the diagram of ($^{87}\text{Sr}/^{86}\text{Sr}$)_i vs. ($^{143}\text{Nd}/^{144}\text{Nd}$)_i. In combination with other geological and geochemical data, we suggested that the ore-forming fluids of the Maoniuping REE deposit mainly came from syenite–carbonatite magmas.

© 2003 Elsevier Science B.V. All rights reserved.

Keywords: Maoniuping REE deposit; Fluorites; Sr and Nd isotope; Ore-forming fluids

1. Introduction

Fluorites are common vein minerals in many deposits. Studies have shown that the Sr and Nd isotope geochemistry of fluorites play an important role in constraining the source and evolution of ore-forming fluids (Halliday et al., 1990; Galindo et al., 1994, 1997; Simonetti and Bell, 1995; Menuge et al., 1997). The Maoniuping REE deposits, Sichuan Province, China, is a large-scale primary REE deposit. In China,

this REE deposit is only smaller in scale (primary REE deposit) than the Bayan Obo REE deposit, Inner Mongolia. Fluorites not only are one of the main vein minerals in the Maoniuping REE deposit, but also themselves are potentially recovered as by-products. Although some scholars studied the fluorites in the orefield from inclusions (Niu et al., 1997; Xu et al., 2001; Yang et al., 2001) and REE geochemistry (Yuan et al., 1995; Niu et al., 1996; Xu et al., 2002), few Sr and Nd isotopic compositions of fluorites were reported. Thus, the geochemistry of fluorites in the orefield was not used to discuss the source and evolution of ore-forming fluids. This paper analyzes the Sr and Nd isotopic compositions of fluorites in the Maoniuping REE deposits, summarizes the Sr and Nd

* Corresponding author. Institute of Geochemistry, Chinese Academy of Sciences, Guanshui Road 73, Guiyang 550002, China. Fax: +86-851-5895574.

E-mail address: hzligcas@sohu.com (Z.L. Huang).

Table 1
The Sr and Nd isotopic compositions of fluorites in the Maoniuping REE deposits

Sample REE-type ^b	Ore-6-1		MNP-135		MNP-127		Ore-5-1		MNP-69		MNP-151		Carbonatite ^a	Syenite ^a	Granite ^a
	LRE-rich purple	LRE-rich purple	LRE-rich colorless	LRE-rich colorless	LRE-flat green	LRE-flat green	LRE-flat purple	LRE-flat purple	LRE-depleted green	LRE-depleted green	LRE-depleted colorless	LRE-depleted colorless			
Rb (ppm)	0.037	0.056			0.331	0.084			0.038	0.026			0.178-0.438	145-169	141-177
Sr (ppm)	3.329	3.980	3.980	3.025	3,025	3,119	3,119	3,119	6,173	2,374	2,374	2,374	9,527-27,815	276-467	48.1-82.1
⁸⁷ Rb/ ⁸⁶ Sr	3.25e-05	6.35e-05			3.13e-05	7.96e-05	7.96e-05	7.96e-05	1.83e-05	2.62e-05	2.62e-05	2.62e-05	0.706719-0.706863	0.897-1.77	4.97-10.6
⁸⁷ Sr/ ⁸⁶ Sr	0.706031	0.706213	0.706213	0.706213	0.706027	0.706027	0.706027	0.706208	0.706237	0.706084	0.706084	0.706084	0.706074-0.706149	0.706719-0.706863	0.733631-0.7444731
(⁸⁷ Sr/ ⁸⁶ Sr) _i	0.706031	0.706213	0.706213	0.706213	0.706027	0.706027	0.706027	0.706208	0.706237	0.706084	0.706084	0.706084	0.706074-0.706149	0.705972-0.706302	0.725747-0.736017
ε _{Sr}	22.2	24.8	24.8	22.2	22.2	24.7	24.7	25.2	25.2	23.0	23.0	23.0	22.9-23.9	21.4-26.1	304-449
Sm (ppm)	26.0	33.8	33.8	18.0	18.0	32.6	32.6	33.0	33.0	26.1	26.1	26.1	55.0-93.7	15.1-99.5	3.78-18.3
Nd (ppm)	129	98.0	98.0	85.2	85.2	99.8	99.8	102	102	81.2	81.2	81.2	332-601	157-1,022	19.7-179
¹⁴⁷ Sm/ ¹⁴⁴ Nd	0.09511	0.1544	0.1544	0.1287	0.1287	0.2199	0.2199	0.2377	0.2377	0.1586	0.1586	0.1586	0.0888-0.1001	0.0568-0.0780	0.0619-0.1161
¹⁴³ Nd/ ¹⁴⁴ Nd	0.512431	0.512409	0.512409	0.512422	0.512422	0.512413	0.512413	0.512437	0.512437	0.512412	0.512412	0.512412	0.512405-0.512427	0.512391-0.512427	0.512419-0.512494
(¹⁴³ Nd/ ¹⁴⁴ Nd) _i	0.512412	0.512379	0.512379	0.512397	0.512397	0.512370	0.512370	0.512390	0.512390	0.512381	0.512381	0.512381	0.512383-0.512394	0.512378-0.512405	0.512370-0.512403
ε _{Nd}	-3.7	-4.3	-4.3	-4.0	-4.0	-4.0	-4.0	-4.1	-4.1	-4.3	-4.3	-4.3	-3.7 to -4.2	-3.7 to -4.2	-1.6 to -2.2

Isotope results normalized to ¹⁴⁶Nd/¹⁴⁴Nd = 0.7219 and ⁸⁶Sr/⁸⁶Sr = 0.1194; uncertainties are given at the 2σ level; (⁸⁷Sr/⁸⁶Sr)_i, (¹⁴³Nd/¹⁴⁴Nd)_i, ε_{Sr}, and ε_{Nd} values have been calculated for *t* = 30 Ma.

^a After Xu et al. (2003).

^b After Xu et al. (2002).

isotopic features of fluorites, and in combination with the REE geochemistry of fluorites and the REE geochemistry and isotope data of rocks and other vein minerals in the orefield, discusses the source of ore-forming fluids.

Wang et al. (2001) and Xu et al. (2003) described the geological setting of the Maoniuping REE deposit. Devonian–Permian (D-P) argillaceous clastic rocks and carbonates and Tertiary (T) diluvium talus outcrop in the orefield. The magmatic rocks in the orefield include Yanshanian granites (Mianxi granites), Himalayan syenites and carbonatites, and a few age-unknown basalts and rhyolites. The Himalayan syenites and carbonatites are closely associated with REE mineralization in time and space. The ore types are mainly barite–pegmatite-type and calcite–pegmatite-type and subordinate thin-network-type. The major ore mineral is bastnaesite and the vein minerals are mainly fluorite, barite, calcite, feldspar, quartz, mica and aegirine–augite.

Fluorites diverse in color and different in grain size occur in every ore type. On the basis of the REE

distribution patterns, Xu et al. (2002) divided the fluorites in the orefield into three types, i. e., LRE-rich, LRE-flat and LRE-depleted and suggested that the three types of fluorites may be the products of the same source but at different stages of evolution.

Presented in this paper are the Sr and Nd isotopic compositions of fluorites of every REE-type and different color from every ore-type in the Maoniuping REE deposit. The Sr, Nd isotopic compositions of fluorites were analyzed at the Institute of Geology and Geophysics, Chinese Academy of Sciences. The analytical procedures are described by Xu et al. (2003). The analytical result of standard sample NBS987 is $^{87}\text{Sr}/^{86}\text{Sr} = 0.710234 \pm 7$ and La Jolla is $^{143}\text{Nd}/^{144}\text{Nd} = 0.511838 \pm 8$.

2. Results

Listed in Table 1 are the Sr and Nd isotopic compositions of fluorites in the Maoniuping REE deposits. Five fluorites with different REE-type and

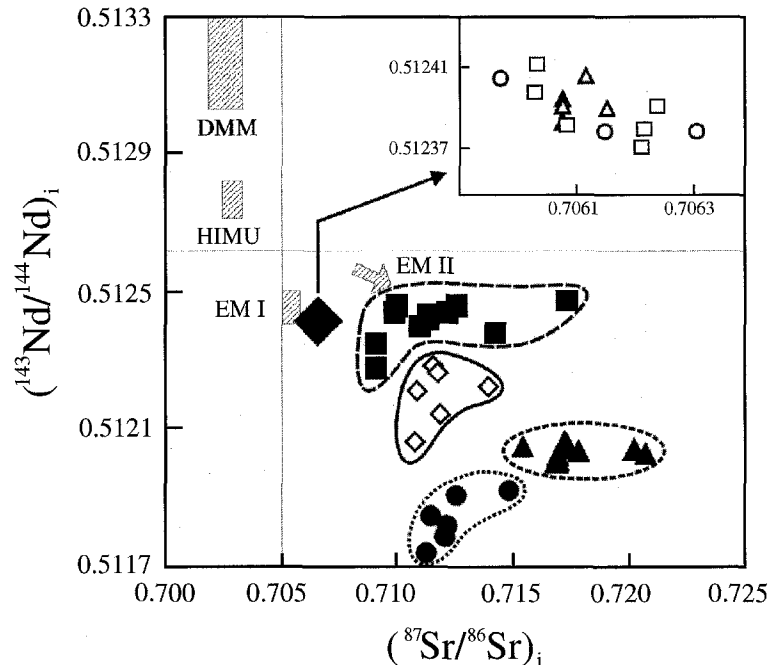


Fig. 1. $(^{87}\text{Sr}/^{86}\text{Sr})_i$ vs. $(^{143}\text{Nd}/^{144}\text{Nd})_i$ diagram of fluorites in the Maoniuping REE deposit. \diamond , fluorites in Galway, Ireland (Menuge et al., 1997); \blacktriangle , Sierra del Guadarrama, Spain (Galindo et al., 1994); \bullet , Sierras Pampeanas, Argentina (Galindo et al., 1994); \blacksquare , fluorites in Amba Dongar, India, which are host-carbonatites (Simonetti and Bell, 1995); \blacklozenge , fluorites, carbonatites and syenites in Maoniuping REE deposits (\triangle , fluorites; \square , carbonatites; \circ , syenites); DMM, HIMU, EM I and EM II after Zindler and Hart (1986).

different color from every ore-type are generally consistent with each other in Sr and Nd isotopic compositions. Their $(^{87}\text{Sr}/^{86}\text{Sr})_i$ range from 0.706031 to 0.706237, $(^{143}\text{Nd}/^{144}\text{Nd})_i$ from 0.512370 to 0.512412, ε_{Sr} from 22.22 to 25.2 and ε_{Nd} from -4.3 to -3.7 . The Sr and Nd isotopic compositions of one fluorite far away from the orebody (sample MNP-151) are similar to those of fluorites from the ores (Table 1). These characteristics show that all fluorites in the orefield come from the same source. The result is consistent with Xu et al. (2002).

As can be seen from Fig. 1, the Sr and Nd isotopic compositions of fluorites in the Maoniuping REE deposit are different from those of fluorites in Galway, Ireland (Menuge et al., 1997), Sierra del Guadarrama, Spain (Galindo et al., 1994), and Sierras Pampeanas, Argentina (Galindo et al., 1994), which are granite-hosted and those of fluorites in Amba Dongar, India, which are carbonatite-hosted (Simonetti and Bell, 1995). From Table 1, it can be seen that the Sr and Nd isotopic compositions of fluorites are similar to those of carbonatites and syenites, but are different from those of granites in the orefield. In Fig. 1, the values of fluorites, carbonatites and syenites in the orefield lie in the narrow range between EM I and EM II, relatively close to EM I mantle end-member. This feature shows that the ore-forming fluids of the Maoniuping REE deposit are related to the magmatism of syenite-carbonatite.

3. Discussion and conclusions

Fluorites are one of the main vein minerals in the Maoniuping REE deposit and their growth occurred throughout the paragenetic sequence. The Sr and Nd isotope geochemistry of fluorites in the orefield have recorded some important information about the source of the ore-forming fluids. Because the $(^{87}\text{Sr}/^{86}\text{Sr})_i$ of fluorites in many deposits lie in between those of two (or more than two) geological bodies, lots of previous investigations have shown that the fluorites (or relevant ores) are the origin of fluid mixing (Deans and Powell, 1968; Ruiz and Richardson, 1988; Ruiz et al., 1985; Barbieri et al., 1987; Halliday et al., 1990; Canals and Cardellach, 1993; Galindo et al., 1994, 1997; Simonetti and Bell, 1995; Menuge et al., 1997). For example, the $(^{87}\text{Sr}/^{86}\text{Sr})_i$ of fluorites in Amba

Dongar, India (0.70910–0.71729), lie in between those of the carbonatites (0.70549–0.70628) and the host Bagh sandstones (0.75359–0.78274), and Simonetti and Bell (1995) suggested that the fluorites in Amba Dongar, India, were the products of mixing between carbonatite-derived, F-rich fluids and crustal-derived fluids. The $(^{87}\text{Sr}/^{86}\text{Sr})_i$ of fluorites in the Maoniuping REE deposit are similar to those of carbonatites and syenites but are different from those of granites in the orefield (Table 1; Fig. 1), showing that the fluids of fluorites in the orefield are relatively simple fluids which were derived mainly from the magmas of syenite-carbonatite. This conclusion can be supported by the following evidence.

(1) Syenites and carbonatites in the Maoniuping REE deposit are closely related to REE mineralization in time and space. In space, the syenites and carbonatites are the main host rocks and the distribution of two types rocks and ore bodies are controlled by the NE Haha fault zone (Wang et al., 2001; Xu et al., 2003). In time, the two types of rocks and REE mineralization are Himalayan in age. Yuan et al. (1995) reported that the K–Ar ages of syenites and carbonatites in the orefield were 28–48 Ma and 31.7 ± 0.7 Ma, respectively, and the isotopic age of the vein minerals arfvedsonite and biotite in the ores were 23 and 27 Ma– 40 ± 0.7 Ma, respectively.

(2) It is confirmed by many investigations that carbonatite magmas can differentiate F-rich fluids (Deans and Powell, 1968; Gittins et al., 1990; Jago and Gittins, 1991; Simonetti and Bell, 1995). The Nd isotope can be used to trace the source of F in fluorites (Ronchi and Touray, 1993; Simonetti and Bell, 1995). In Fig. 1, although the $(^{87}\text{Sr}/^{86}\text{Sr})_i$ of fluorites in the Maoniuping REE deposit are different from those of fluorites in Amba Dongar, India, the $(^{143}\text{Nd}/^{144}\text{Nd})_i$ values are similar to the latter. The $(^{143}\text{Nd}/^{144}\text{Nd})_i$ of fluorites (0.51240–0.51247) are similar to those of fluorites (0.51248–0.51253) in Amba Dongar, India, and Simonetti and Bell (1995) suggested that the F in fluorites from this orefield is mainly derived from carbonatites. So, we consider that the F in fluorites from the Maoniuping REE deposit is mainly derived from magmas of syenite-carbonatite.

(3) Xu et al. (2003) reported that the REE contents of syenites (ΣREE : 369–3,354 ppm; six samples) and carbonatites (ΣREE : 2,207–3,808 ppm; eight samples) in the orefield are obviously higher than those of

basalts (Σ REE: 131–216 ppm; three samples), rhyolites (Σ REE: 112–200 ppm; three samples) and granites (Σ REE: 132–432 ppm; 17 samples). It is shown that syenites and carbonatites in the orefield have the potential of providing ore-forming materials. Studies have indicated that the LRE-rich fluids could be separated from the silicate–carbonatite magmatic system in the processes of evolution (Wendlandt and Harrison, 1979; Ngwenya, 1994; Bulakh et al., 2000; Nasraoui et al., 2000; Groves and Vielreicher, 2001; Zaitsev et al., 2002).

(4) The $\delta^{13}\text{C}_{\text{PDB}}$ and $\delta^{18}\text{O}_{\text{SMOW}}$ values of the vein mineral calcites in the Maoniuping REE deposit are -6.6‰ to -7.0‰ and 6.4‰ – 7.4‰ respectively (eight samples; Xu et al., 2003). These values are within the range of $\delta^{13}\text{C}_{\text{PDB}}$ and $\delta^{18}\text{O}_{\text{SMOW}}$ for primary carbonatites (-4‰ to -8‰ and 6‰ – 10‰ , respectively). Moreover, the $\delta\text{D}_{\text{H}_2\text{O}}$ and $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values of the vein mineral quartz in the orefield are -52‰ to -77‰ and 7.8‰ – 9.4‰ , respectively (three samples; unpubl.). These values also are within the range of $\delta\text{D}_{\text{H}_2\text{O}}$ and $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ for magmatic waters (-50‰ to -90‰ and 6‰ – 10‰ , respectively). These stable isotopic compositions showed that the ore-forming fluids of the Maoniuping REE deposit are characterized as being of mantle source. This conclusion is also supported by the results of inclusion studies by Niu et al. (1997) and Yuan et al. (1995).

Acknowledgements

This research project was financially supported jointly by the Major State Basic Research Program of the People's Republic of China (No. G1999043203) and the Pre-selected Projects under the State Climbing Program (No. 95-Pre-39). We thank Dr. Andrew McCaig in the School of Earth Science, Leeds University, UK, for reviewing and improving this manuscript.

References

Barbieri, M., Bellanca, A., Neri, R., Tolomeo, L., 1987. Use of strontium isotopes to determine the sources of hydrothermal fluorite and barite from Northwestern Sicily (Italy). *Chem. Geol.* 66, 273–278.

- Bulakh, A.G., Nesterov, A.R., Zaitsev, A.N., Pilipiuk, A.N., Wall, F., Kirillov, A.S., 2000. Sulfur-containing monazite-(Ce) from late-stage mineral assemblages at the Kandaguba and Vuoriyarvi carbonatite complexes, Kola peninsula, Russia. *Neues. Jahrb. Mineral. Monatsh.* 5, 217–233.
- Canals, A., Cardellach, E., 1993. Strontium and sulphur isotope geochemistry of low-temperature barite–fluorite veins of the Catalan Coastal Ranges (NE Spain): a fluid mixing model and age constrains. *Chem. Geol.* 104, 269–280.
- Deans, T., Powell, J.L., 1968. Trace elements and strontium isotopes in carbonatites, fluorites and limestones from India and Pakistan. *Nature* 218, 750–752.
- Galindo, C., Tornos, T., Darbyshire, D.P.F., Csquet, C., 1994. The age and origin of the barite–fluorite (Pb–Zn) veins of the Sierra del Guadarrama (Spanish Central System, Spain): a radiogenic (Nd, Sr) and stable isotope study. *Chem. Geol.* 112, 351–364.
- Galindo, C., Pankhurst, R.J., Casquet, C., Conigold, J., Baldo, E., Rapela, C.W., Saavedra, J., 1997. Age, Sr- and Nd isotope systematics, and origin of two fluorite lodes, Sierras Pampeanas, Argentina. *Int. Geol. Rev.* 39, 948–954.
- Gittins, J., Beckett, M.F., Jago, B.C., 1990. Composition of the fluid phase accompanying carbonatite magma: a critical examination. *Am. Mineral.* 75, 1106–1109.
- Groves, D.I., Vielreicher, N.M., 2001. The Phalabowra (Palabora) carbonatite-hosted magnetite–copper sulfide deposit, South Africa: an end-member of the iron-oxide copper–gold–rare earth element deposit group? *Miner. Depos.* 36, 189–194.
- Halliday, A.N., Shepherd, T.J., Dickin, A.P., Chesley, J.T., 1990. Sm–Nd evidence for the age and origin of a Mississippi Valley type ore deposit. *Nature* 344, 54–56.
- Jago, B.C., Gittins, J., 1991. The role of fluorine in carbonatite magma evolutions. *Nature* 349, 56–58.
- Menuge, J.F., Feely, M., O'Reilly, C., 1997. Origin and granite alteration effects of hydrothermal fluid: isotopic evidence from fluorite veins, Co. Galway, Ireland. *Miner. Deposita* 32, 34–43.
- Nasraoui, M., Toulkeridis, T., Clauer, N., Bilal, E., 2000. Differentiated hydrothermal and meteoric alterations of the Lueshe carbonatite complex (Democratic Republic of Congo) identified by a REE study combined with a sequential acid-leaching experiment. *Chem. Geol.* 165, 109–132.
- Ngwenya, B.T., 1994. Hydrothermal rare earth mineralization in carbonatites of the Tundulu complex, Malawi: processes at the fluid/rock interface. *Geochim. Cosmochim. Acta.* 58, 2061–2072.
- Niu, H.C., Shan, Q., Lin, M.Q., 1996. REE geochemistry of magmatogenic barite and fluorites (in Chinese with English abstract). *Acta Mineral. Sin.* 16, 382–388.
- Niu, H.C., Shan, Q., Lin, M.Q., 1997. Fluid-melt and fluid inclusions in Mianning REE deposits, Sichuan, Southwest China. *Chin. J. Geochem.* 16, 256–262.
- Ronchi, L.H., Touray, J.C., 1993. The Ribeira fluorite district, South Brazil. *Miner. Depos.* 28, 240–252.
- Ruiz, J., Richardson, C.K., 1988. Strontium isotope geochemistry of fluorite, calcite and barite of the cave-in-rock fluorite district, Illinois. *Econ. Geol.* 88, 203–210.
- Ruiz, J., Kesler, S.E., Jones, L.M., 1985. Strontium isotope geochemistry of fluorite mineralization associated with fluorine-rich

- igneous rocks from the Sierra Madre occidental, Mexico: possible exploration significance. *Econ. Geol.* 80, 33–42.
- Simonetti, A., Bell, K., 1995. Nd, Pd, and Sr isotope systematics of fluorite at the Amba Dongar carbonatite complex, India: evidence for hydrothermal and crustal fluid mixing. *Econ. Geol.* 90, 2018–2027.
- Wang, D.H., Yang, J.M., Yan, S.H., 2001. A special orogenic type REE deposit in Maoniuping Sichuan, China: geology and geochemistry. *Res. Geol.* 51 (3), 177–188.
- Wendlandt, R.F., Harrison, W.J., 1979. Rare earth partitioning between immiscible carbonate and silicate liquids and CO₂ vapor: result and implications for the formation of light rare earth-enriched rocks. *Contrib. Mineral. Petrol.* 69, 409–419.
- Xu, J.H., Xie, Y.L., Li, J.P., Hou, Z.Q., 2001. The Sr- and LREE-bearing daughter minerals in fluid inclusions from the Maoniuping REE deposits, Sichuan Province, China (in Chinese). *Proc. Nat. Sci.* 11, 543–547.
- Xu, C., Huang, Z.L., Qi, L., Xiao, H.Y., Li, W.B., Liu, C.Q., 2002. REE geochemistry of fluorites in the Maoniuping rare-earth deposit. *Geochimica* 31, 180–189 (in Chinese with English abstract).
- Xu, C., Huang, Z.L., Liu, C.Q., Qi, L., Xiao, H.Y., Li, W.B., 2003. The geochemistry of carbonatites in the Maoniuping REE deposit, Sichuan Province, China. *Sci. China (D)* 44 (in press).
- Yang, Z.X., Williams-Jones, A.F., Pu, G.P., 2001. A fluid inclusion study of Maoniuping REE deposits, Sichuan Province. *J. Mineral. Petrol.* 21 (2), 26–33 (in Chinese with English abstract).
- Yuan, Z.X., Shi, Z.M., Bai, G., Wu, C.Y., Chi, R., Li, X.Y., 1995. The Maoniuping Rare Earth Ore Deposit, Mianning County, Sichuan Province. Geological Publishing House, Beijing. In Chinese with English abstract, 155 pp.
- Zaitsev, A.N., Demény, A., Sinder, S., Wall, F., 2002. Burbankite group minerals and their alteration in rare earth carbonatites source of elements and fluids (evidence from C–O and Sr–Nd isotopic data). *Lithos* 62, 15–33.
- Zindler, A., Hart, S., 1986. Chemical geodynamic. *Ann. Rev. Earth Sci.* 14, 493–571.