



## Review

# A synthesis and new perspective on the petrogenesis of kamafugites from West Qinling, China, in a global context



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## ABSTRACT

We discuss the overall characteristics of a recently recognized kamafugite province in West Qinling, China, using field observations and geochemical data. We discuss the petrogenesis of the kamafugites using new bulk-rock major and trace element data and Sr–Nd isotope compositions of representative samples together with the literature data (in Chinese) and comparing them with type kamafugite suites from Italy, Brazil and Uganda. All these four kamafugite suites show OIB-like rare earth element (REE) patterns, but are much more enriched than OIB in the progressively more incompatible elements. The West Qinling kamafugite samples resemble closely the Ugandan and Brazilian suites in having a negative anomaly of K, P and Ti and a positive Nb–Ta anomaly, yet the Italian suite shows conspicuously a negative Nb–Ta anomaly. The four kamafugite suites have different  $\epsilon_{\text{Nd}}(t)$  values and  $^{87}\text{Sr}/^{86}\text{Sr}_i$  ratios, implying their distinct sources and source histories. We consider that the ideal sources for kamafugite magmas are most likely metasomatized sub-continental lithosphere with components of ancient seafloor subducted calcareous terrigenous sediments. The close association of kamafugite with carbonatite worldwide, including the West Qinling suite, is consistent with both being derived from a single  $\text{CO}_2$ -rich silicate parental magma segregated during ascent as a result of decompression-induced immiscibility. In terms of both sources (or source histories) and processes, our simple interpretation can effectively explain the petrogenesis of all the apparently different kamafugite suites suggests that the petrogenesis of kamafugites may actually be simple. Further effort should aim to test whether our interpretation is indeed valid globally.

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## Contents

1. Introduction	87
2. Geology and samples	87
3. Analytical methods and procedure	89
4. Geochemistry of West Qinling kamafugites	89
4.1. Major and trace element data	89
4.2. Sr–Nd isotope data	90
5. Comparison with type kamafugites from Italy, Uganda and Brazil	90
6. Discussions	93
6.1. Magma evolution	93
6.2. Immiscibility between kamafugitic magma and carbonatic magma	93
6.3. The nature of the sources	94
7. Conclusions	94
Acknowledgements	95
Appendix A. Supplementary material	95
References	95

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## 1. Introduction

Kamafugite is a term describing several alkaline volcanic rocks including katungite, mafurite and ugandite following the study of alkaline volcanic rocks in the Toro-Ankole volcanic field (Sahama, 1974). These rocks are characterized by the presence of modal kalsilite, melilite and perovskite as a result of their extreme silica under-saturation, low Al, K-enrichment and extremely high Ca (Tappe et al., 2003). IUGS recommendations (Le Maitre, 2002) for the kalsilite-bearing rocks eliminate the local names but retain the term kamafugite as a rock series name. Kamafugitic rocks have low  $\text{Al}_2\text{O}_3$  but high CaO (usually > 12%), and represent primitive ultrapotassic rocks which are rare yet found on all continents (Tappe et al., 2003). Foley et al. (1987) consider kamafugite as a potential end-member among peralkaline magmas. Tappe et al. (2005) suggested that kamafugites may be genetically related to some ultramafic lamprophyres, and some of these may even contain diamonds (Digonnet et al., 2000; Tappe et al., 2004). It is thus important to understand the petrogenesis of kamafugitic rocks and their derivatives.

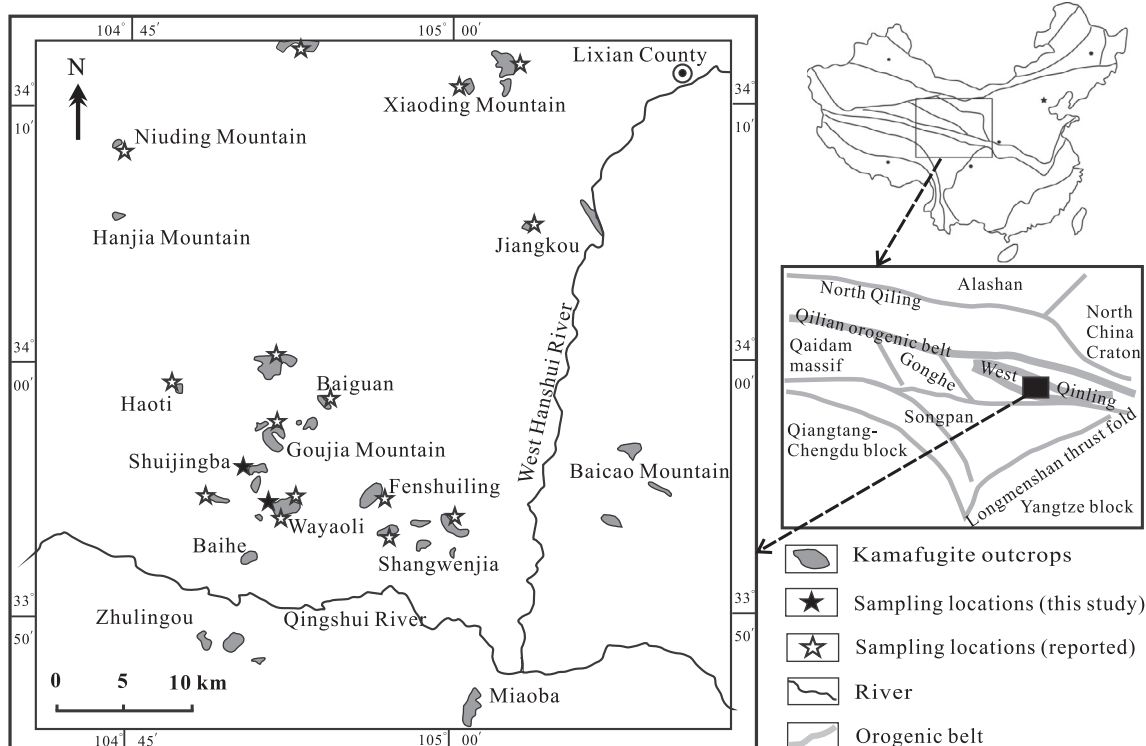
Since Holmes and Harwood (1932) first described the upper Pleistocene (<50 ka, Boven et al., 1998) kalsilite-bearing lavas that were named later by Sahama (1974) as kamafugite series in South-west Uganda, kamafugites have been reported in a number of locations worldwide (e.g., Yu et al., 2001a, 2001b, 2003a, 2003b, 2004, 2005, 2009; Wang and Li, 2003; Dong et al., 2008; Carlson and Nowell, 2001; Prelevic et al., 2005), in particular the well-studied type examples such as the middle Pleistocene kamafugites in Italy (Gallo et al., 1984; Stoppa and Cundari, 1998; Peccerillo, 1999; Stoppa et al., 2002; Di Battistini et al., 2001; Federico and Peccerillo, 2002), the late Cretaceous suite in Brazil (Gibson et al., 1995; Sgarbi and Gaspar, 2002). However, the origin of kamafugites remains not well understood (Foley, 1992; Gittins and Harmer, 2003). An important observation is that most kamafugites worldwide coexist with carbonatites, including all the cases mentioned above. A genetic link between kamafugite and carbonatite melts may indeed exist

as proposed for Uganda (Bailey and Collier, 2000; Stoppa et al., 2000; Tappe et al., 2003; Rosenthal et al., 2009), Italy (Stoppa and Lavecchia, 1992; Stoppa and Cundari, 1995; Stoppa and Woolley, 1997) and Brazil (Brod et al., 2001, 2008; Junqueira-Brod et al., 2005; Barbosa et al., 2012) kamafugites. However, a genuine petrogenetic relationship between kamafugite and carbonatite melts have not been convincingly established. In this context, Gittins and Harmer (2003) summarized three scenarios: (1) a silicate parental magma capable of crystallizing carbonate minerals to form carbonatite; (2) carbonatite and kamafugite have different parent magmas; (3) a carbonate-rich silicate magma splits into two immiscible liquids, one carbonatite magma and the other silicate magma.

Although much effort has been expended on the petrogenesis of the West Qinling Miocene kamafugite–carbonatite association since its recognition (Yu et al., 2001a, 2001b, 2003a, 2003b, 2004, 2005, 2009; Wang and Li, 2003; Dong et al., 2008), little is known to the international community about this kamafugite province except for a descriptive report in English in a rarely accessible journal (see Yu et al., 2003b). The purpose of this paper is to introduce this important kamafugite province to the international community and to offer our new petrogenetic perspectives using new data on representative kamafugite samples together with the data in the Chinese literature (see references by Yu and the co-workers). In discussion, we compare the West Qinling kamafugite suite with those of type kamafugite suites from Uganda, Brazil and Italy with the aim of better understanding the petrogenesis of the West Qinling kamafugite in a global context by exploring the possibility of kamafugite and carbonatite magmas being the two products of immiscibility from a single primitive carbonate-rich silicate melt.

## 2. Geology and samples

The West Qinling kamafugites are distributed in Lixian County, Gansu Province, China (in the area of 104°40'–105°15'E, 33°44'–34°15'N), geologically in the complex Caledonian–Hercynian West

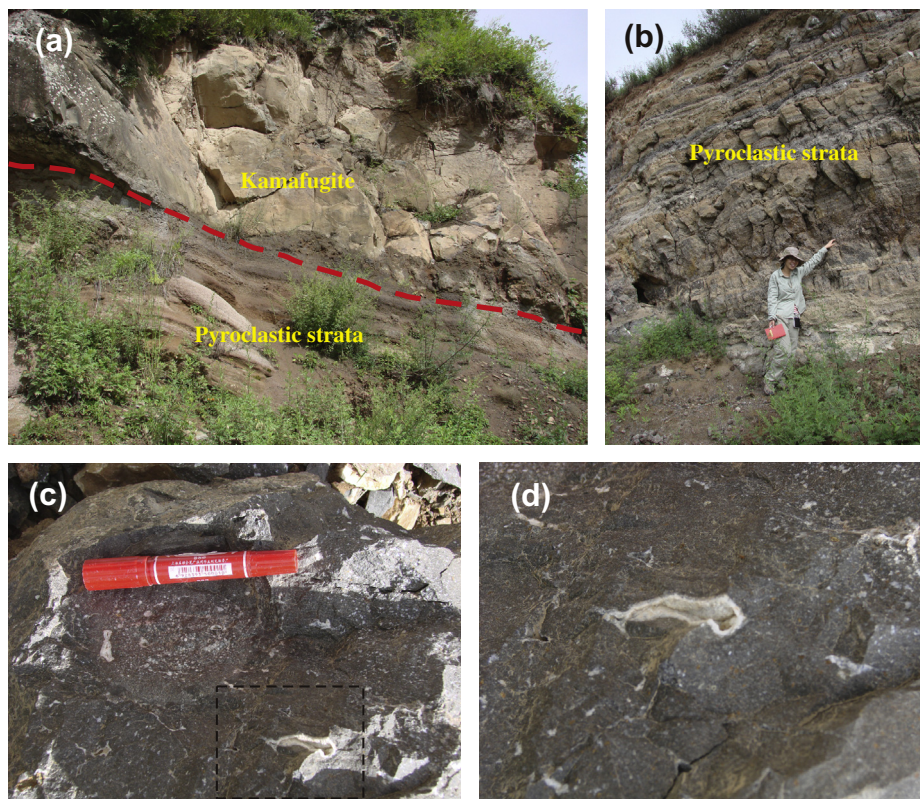


**Fig. 1.** Sketch map of the West Qinling kamafugite distribution (after Yu et al., 2005). Locations of samples for our new data are indicated with closed stars. Open stars indicate sample locations of the literature data. The two simplified maps on the right show the geographic/geological context of the West Qinling kamafugite field.

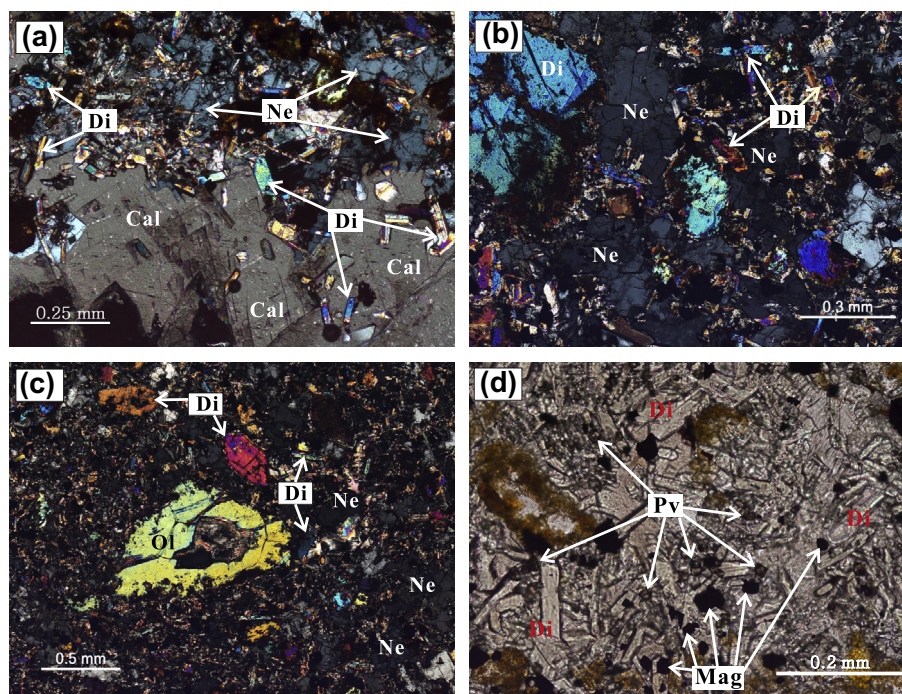


Qinling Orogenic Belt near the triple junction of the Yangtze Craton, North China Craton and Tibetan Plateau (Fig. 1). The North China–Yangtze collision in the early Mesozoic and the Tibetan Plateau

uplift since the Cenozoic (Gao et al., 1996; Zhang et al., 2001; Xu et al., 2002) further complicated the geology of the region. The West Qinling kamafugites have a Cenozoic eruption age of



**Fig. 2.** (a) Outcrops of West Qinling kamafugites, coexisting with pyroclastic strata. (b) Stratified pyroclastics, composed of carbonatite and kamafugitic clasts. (c) Hand specimen of kamafugite and carbonatite “inclusions” with varying shape and size widespread in kamafugite. (d) Close-up of portion of (c) as indicated, showing the carbonate Ocelli with voids.



**Fig. 3.** Photomicrographs of the West Qinling kamafugites. (a) Sample LN10-002 (XPL), silicate minerals (nepheline and diopside) spread around a carbonate globule; (b) Sample LN10-004-1 (XPL), diopside and nepheline phenocrysts in the diopside matrix; (c) Sample LN10-004-2 (XPL), olivine, nepheline and diopside phenocrysts; (d) Sample LN10-024 (PPL), diopside phenocrysts and quenched microlites spread randomly. Perovskite and magnetite are throughout the matrix.

~23 Ma (Yu et al., 2005) with >30 outcrops scattered in a ~3000 km<sup>2</sup> area (Yu et al., 2003a, 2003b, 2004). They mainly occur as pipes/diatreme-tuff rings and subvolcanic intrusions with a single outcrop diameter normally <1 km<sup>2</sup>. There are also lava flows that cover areas of a few square kilometers (Yu et al., 2003b). The West Qinling kamafugites on all outcrops showing coexistence with carbonatite lava flows and pyroclastic strata (Fig. 2a and b), provides a prime opportunity to study the petrogenesis of this rare rock association.

An interesting observation is the amygdale-like carbonatite inclusions with varying shape and size abundant in the kamafugites (Fig. 2c and d). These called 'Ocelli' (Wang et al., 2007) are half-hollowed on outcrop and hand specimen scales with abundant fine euhedral diopside crystals at the rims under microscope (Fig. 3a).

The West Qinling kamafugites are porphyritic with 5–10 vol.% phenocrysts dominated by anhedral olivine (1–2 mm in size), and to a lesser extent by subhedral–anhedral clinopyroxene and nepheline (0.5–1 mm in size). The groundmass consists of euhedral clinopyroxene and interstitial nepheline. Euhedral Ti-magnetite and perovskite, both as microphenocrysts and microlites, are important accessory phases in most samples (Fig. 3a–d). See Yu et al. (2003b) for petrographic details.

### 3. Analytical methods and procedure

A total of 13 kamafugite samples were collected from West Qinling, from which we chose four freshest ones for detailed geochemical analysis. Weathered surfaces, pen marks and saw marks were ground off and thoroughly cleaned. The samples were then crushed into chips of 40 mesh size to remove painstakingly phenocrysts under a binocular with the aim of obtaining kamafugite melt compositions best represented by the fresh matrix. The matrix material was then ultrasonically-cleaned with Milli-Q water and dried before powdered using an agate mortar to less than 200 mesh for whole rock analysis.

Bulk-rock major elements were determined using X-ray fluorescence (XRF) method on fused glass beads, and a wide range of trace elements were analyzed by solution inductively coupled plasma mass spectrometry (ICP-MS) after acid digestion of samples in Teflon bombs at the State Key Laboratory of Continental Dynamics of Northwest University, Xi'an, China. Analytical details and analysis of reference materials are reported in Rudnick et al. (2004). Bulk-rock Sr–Nd isotopes were analyzed using Thermo Neptune Multi-collector inductively coupled plasma Mass Spectrometer (MC ICP-MS) at Durham University, UK (Dowall et al., 2003). Major element compositions of the carbonate globules were obtained using electron probe micro-analyzer JXA8100 at Chang'an University, China. The operating conditions were a 15 kV accelerating potential with a probe current of 10 nA and the electron beam diameter was 5 µm.

### 4. Geochemistry of West Qinling kamafugites

The new bulk-rock major and trace element data for West Qinling kamafugites are given in Table 1, and the new Sr–Nd isotope data are given in Table 2. We also give the literature data in Appendix 1.

#### 4.1. Major and trace element data

The West Qinling kamafugite samples have low SiO<sub>2</sub> (35.9–43.2 wt.%; average [N = 71] = 39.7 wt.%), moderate K<sub>2</sub>O (0.16–4.21 wt.%; average [N = 71] = 2.03 wt.%), varying total alkalis (0.65–7.03 wt.%), low Al<sub>2</sub>O<sub>3</sub> (6.03–11.0 wt.%; average [N = 71] = 8.83 wt.%) and high CaO (10.7–18.1 wt.%; average [N = 71] = 13.5 wt.%). They have high P<sub>2</sub>O<sub>5</sub> (up to 1.70 wt.%) and MgO (up to 17.5 wt.%) with varying Mg<sup>#</sup> (0.56–0.76). In the TAS diagram (Fig. 4), most of the West Qinling samples plot in the foidite field. Importantly, the West Qinling kamafugite samples have high Ni (78–612 ppm; average [N = 49] = 297 ppm,) and Cr (150–825 ppm; average [N = 49] = 362 ppm), which correlate positively with Mg<sup>#</sup> (Fig. 5a and b).

**Table 1**  
Bulk rock major (wt.%) and trace element (ppm) analysis for West Qinling kamafugites.

	LN10-001	LN10-002	LN10-015	LN10-029		LN10-001	LN10-002	LN10-015	LN10-029
SiO <sub>2</sub>	38.8	39.9	39.7	39.9	Sr	1367	1299	1526	1582
TiO <sub>2</sub>	3.27	3.32	3.31	4.26	Y	32.8	33.2	34.6	38.2
Al <sub>2</sub> O <sub>3</sub>	7.71	7.94	7.96	9.64	Zr	398	395	410	425
<sup>1</sup> Fe <sub>2</sub> O <sub>3</sub>	11.0	11.2	11.3	12.5	Nb	136	137	141	148
MnO	0.15	0.14	0.17	0.15	Cs	0.38	0.51	0.36	0.64
MgO	16.8	15.1	15.1	8.91	Ba	729	1626	1590	910
CaO	12.8	13.0	13.1	13.3	La	122	126	129	111
Na <sub>2</sub> O	1.79	2.43	2.03	3.44	Ce	237	239	244	215
K <sub>2</sub> O	1.05	1.48	1.28	3.31	Pr	26.8	27.3	28.0	25.2
P <sub>2</sub> O <sub>5</sub>	1.46	1.20	1.45	1.12	Nd	102	103	107	96.9
LOI	4.87	3.99	4.42	3.11	Sm	18.0	18.2	18.7	17.9
Total	99.63	99.68	99.68	99.56	Eu	5.17	5.34	5.49	5.36
Mg <sup>#a</sup>	0.75	0.73	0.73	0.59	Gd	13.4	13.6	13.9	14.1
K <sub>2</sub> O + Na <sub>2</sub> O	2.84	3.91	3.31	6.75	Tb	1.74	1.76	1.8	1.87
					Dy	8.05	8.18	8.45	9.00
Li	12.9	14.2	12.7	14.6	Ho	1.22	1.23	1.28	1.41
Be	2.29	2.08	2.27	2.29	Er	2.82	2.83	2.91	3.31
Sc	18.7	18.7	19.6	21.6	Tm	0.32	0.32	0.33	0.38
V	161	153	174	235	Yb	1.74	1.75	1.78	2.12
Cr	661	614	650	505	Lu	0.22	0.22	0.23	0.28
Co	55.9	57.8	59.3	53.0	Hf	8.09	8.17	8.27	9.10
Ni	424	450	449	292	Ta	6.19	6.28	6.42	7.77
Cu	84.4	85.5	97.7	58.1	Pb	5.98	4.76	5.69	2.85
Zn	117	117	123	128	Th	16.0	16.1	16.2	13.7
Ga	15.9	16.4	16.6	19.1	U	3.41	3.43	3.45	3.64
Ge	1.33	1.39	1.37	1.43	δEu	0.97	0.99	1.00	0.99
Rb	30.5	37.4	34.4	69.3	[La/Yb] <sub>N</sub>	50.6	51.5	51.9	37.7

<sup>a</sup> Mg<sup>#</sup> = molar Mg/(Mg + Fe<sup>2+</sup>); FeO (wt.%) = 0.8998 × Fe<sub>2</sub>O<sub>3</sub> (wt.%).



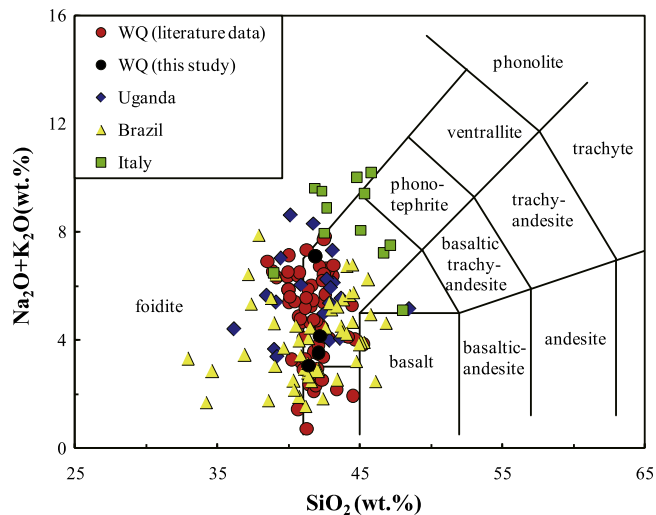
**Table 2**  
Bulk rock Sr–Nd isotope analysis for West Qinling kamafugites.

	$^{87}\text{Rb}/^{86}\text{Sr}$	$^{87}\text{Sr}/^{86}\text{Sr}$	$2\sigma$	$^{87}\text{Sr}/^{86}\text{Sr}_i$	$^{147}\text{Sm}/^{144}\text{Nd}$	$^{143}\text{Nd}/^{144}\text{Nd}$	$2\sigma$	$^{143}\text{Nd}/^{144}\text{Nd}_i$	$\varepsilon_{\text{Nd}}(t)$
LN10-001	0.0642	0.704336	0.000015	0.704315	0.1094	0.512838	0.000008	0.512822	3.6
LN10-002	0.0827	0.704281	0.000010	0.704254	0.1101	0.512853	0.000011	0.512837	3.9
LN10-015	0.0649	0.704779	0.000010	0.704758	0.1088	0.512829	0.000009	0.512813	3.4
LN10-029	0.1259	0.703996	0.000010	0.703955	0.1150	0.512856	0.000007	0.512839	3.9

(a)  $^{87}\text{Rb}/^{86}\text{Sr}$  and  $^{147}\text{Sm}/^{144}\text{Nd}$  are calculated using whole-rock Rb, Sr, Sm and Nd contents in Table 1.

(b)  $^{87}\text{Sr}/^{86}\text{Sr}_i = ^{87}\text{Sr}/^{86}\text{Sr} - ^{87}\text{Rb}/^{86}\text{Sr} \times (e^{\lambda t} - 1)$ ;  $^{143}\text{Nd}/^{144}\text{Nd}_i = ^{143}\text{Nd}/^{144}\text{Nd} - ^{147}\text{Sm}/^{144}\text{Nd} \times (e^{\lambda t} - 1)$ . In the calculation,  $t = 23$  Ma.

(c)  $\varepsilon_{\text{Nd}}(t) = [(^{143}\text{Nd}/^{144}\text{Nd}_i)/(^{143}\text{Nd}/^{144}\text{Nd}_{\text{CHUR}}) - 1] \times 10,000$ ;  $^{143}\text{Nd}/^{144}\text{Nd}_{\text{CHUR}} = 0.512638$ .



**Fig. 4.** The TAS ( $\text{Na}_2\text{O} + \text{K}_2\text{O}$  vs.  $\text{SiO}_2$ ) diagram to show West Qinling (WQ) kamafugite compositions. For comparison, the type examples such as the Italy (Conticelli and Peccerillo, 1992; Di Battistini et al., 2001; Castorina et al., 2000; Peccerillo, 2004; Lavecchia et al., 2006), Uganda (Tappe et al., 2003; Stoppa et al., 2000), and Brazil (Carlson et al., 1996; Araujo et al., 2001; Sgarbi and Gaspar, 2002; Junqueira-Brod et al., 2005; Carlson et al., 2007; Melluso et al., 2008) kamafugites are also plotted together with the West Qinling kamafugite data in the literature (Yu et al., 2003b, 2004, 2009; Wang and Li, 2003; Dong et al., 2008). And all the data had been volatile corrected (Le Maitre, 1989).

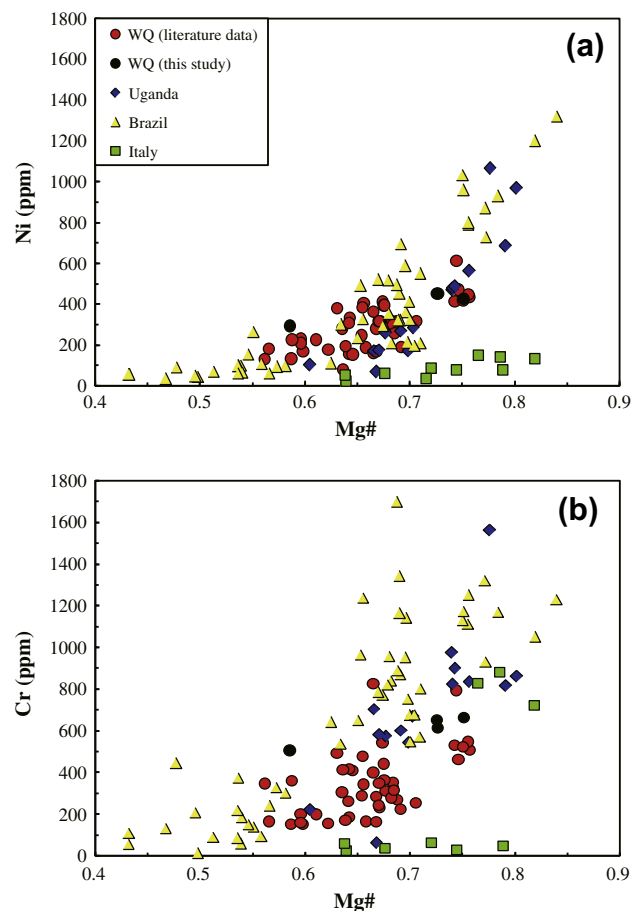
The West Qinling kamafugite samples are highly enriched in light rare earth elements (LREE) and other incompatible trace elements. They have OIB-like (but more enriched) REE patterns (Fig. 6a) with  $[\text{La}/\text{Yb}]_N = 37.7\text{--}51.9$ . In the primitive mantle normalized spider diagram (Fig. 6b), they display negative anomalies for Rb, K, Pb, P and Ti, and no anomalies for HFSEs (e.g., Nb, Ta, Zr and Hf).

#### 4.2. Sr–Nd isotope data

The four new  $^{87}\text{Sr}/^{86}\text{Sr}_i$  ratios are all in the range of reported  $^{87}\text{Sr}/^{86}\text{Sr}_i = 0.703810\text{--}0.705390$  (Yu et al., 2001a, 2004, 2009; Dong et al., 2008), with an average value of 0.704385 ( $N = 42$ ). The  $^{143}\text{Nd}/^{144}\text{Nd}_i$  ratios give  $\varepsilon_{\text{Nd}}(t)$  values in a narrow range (1.31–5.74). Fig. 7 shows the new Sr and Nd isotopic data and the literature data (Yu et al., 2001a, 2004, 2009; Dong et al., 2008). The mantle array, DM, HIMU, EMI, EMII mantle isotope end-members are also indicated for comparison. Most of the West Qinling kamafugite samples plot within the mantle array with several samples off to the higher  $^{87}\text{Sr}/^{86}\text{Sr}_i$  values in the vicinity of the bulk silicate earth (BSE).

### 5. Comparison with type kamafugites from Italy, Uganda and Brazil

In order to better understand the petrogenesis of the West Qinling kamafugites, we compare them with the well-known and bet-

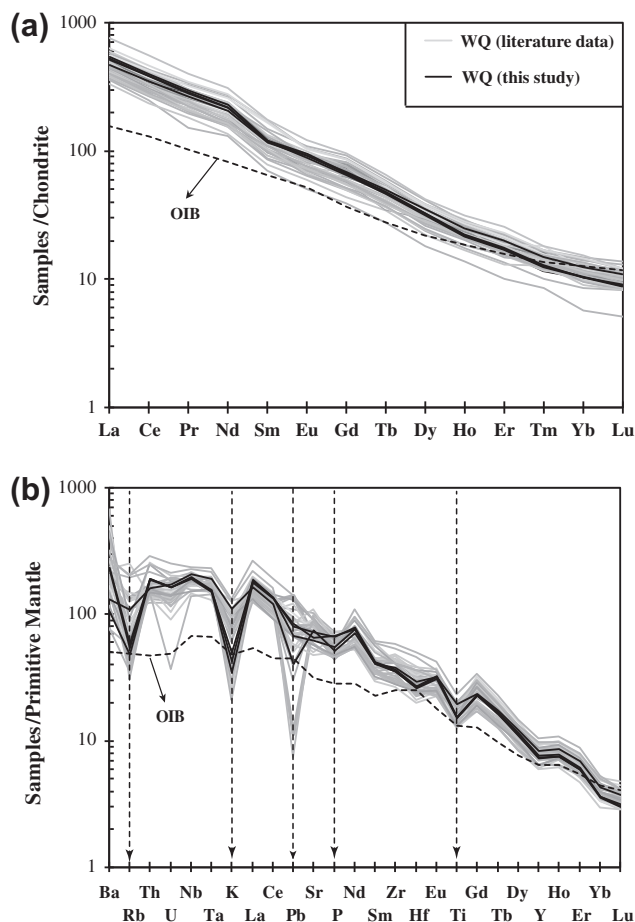


**Fig. 5.** (a) Ni vs.  $\text{Mg}^\#$  and (b) Cr vs.  $\text{Mg}^\#$  diagrams to compare kamafugites from West Qinling with several type worldwide. The data sources are: Conticelli and Peccerillo (1992), Carlson et al. (1996), Castorina et al. (2000), Di Battistini et al. (2001), Araujo et al. (2001), Sgarbi and Gaspar (2002), Tappe et al. (2003), Wang and Li (2003), Lavecchia et al. (2006), Carlson et al. (2007), Melluso et al. (2008), Dong et al. (2008), Yu et al. (2004, 2009).

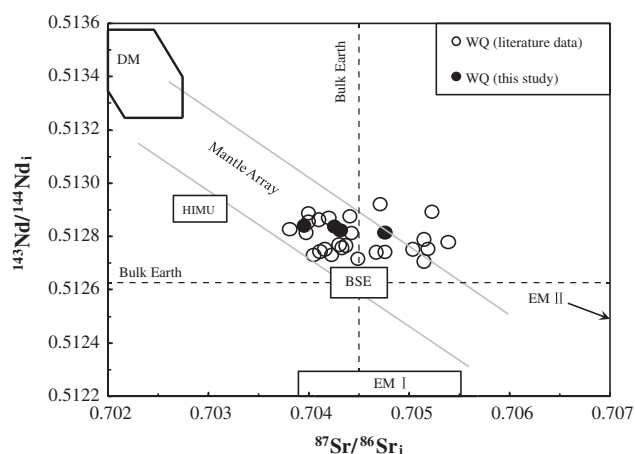
ter-studied kamafugite suites worldwide, in particular those type suites from Italy (Gallo et al., 1984; Stoppa and Cundari, 1998; Peccerillo, 1999; Stoppa et al., 2002; Di Battistini et al., 2001; Federico and Peccerillo, 2002), Uganda (Bailey and Collier, 2000; Stoppa et al., 2000) and Brazil (Gibson et al., 1995; Sgarbi and Gaspar, 2002).

All the four kamafugite suites share the same characteristics of low  $\text{SiO}_2$  ( $<46$  wt.%, Figs. 4 and 8), low  $\text{Al}_2\text{O}_3$  (average  $[N = 158] \approx 8.4$  wt.%), high CaO (average  $[N = 158] \approx 13.1$  wt.%) and high MgO (average  $[N = 158] \approx 13.1$  wt.%). The Brazil suite shows the largest range of  $\text{SiO}_2$  (30.0–45.7 wt.%, Figs. 4 and 8) and  $\text{Mg}^\#$  (0.42–0.84, Figs. 5a and b and 9). The Italian suite exhibits highest  $\text{K}_2\text{O}$  contents (4.6–9.6 wt.%, Fig. 8) and total alkalis (up to 9.9 wt.%, Fig. 4).

Fig. 5a and b illustrates that the West Qinling kamafugite samples lie on a trend defined by the Ugandan and Brazilian suites,

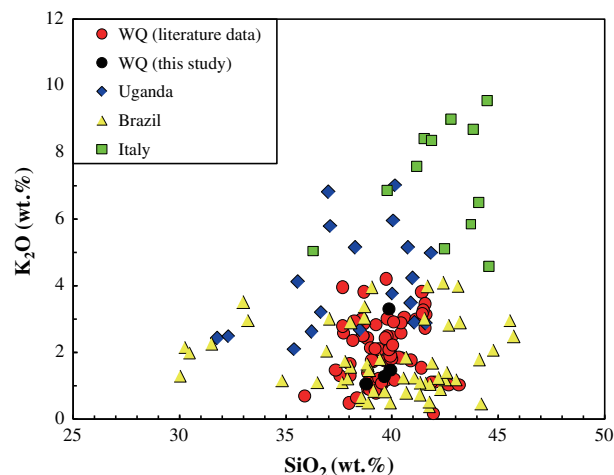


**Fig. 6.** (a) Chondrite normalized REE patterns, and (b) primitive mantle normalized incompatible element patterns of the West Qinling kamafugites. For comparison, West Qinling kamafugite data in the literature (Yu et al., 2001a, 2009; Wang and Li, 2003; Dong et al., 2008) and average OIB (Sun and McDonough, 1989) are also plotted. Chondrite and primitive mantle values are from Sun and McDonough (1989).

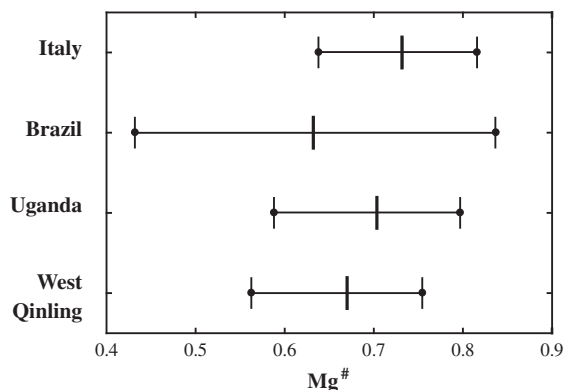


**Fig. 7.** Nd and Sr isotopic compositions of the West Qinling kamafugites. Solid circles are our new data and open circles are the literature data (Yu et al., 2001a, 2004, 2009; Dong et al., 2008). The mantle array is defined by MORB and ocean island basalts (DePaolo, 1981; O'Nions et al., 1977). The hypothetical mantle isotope end members DM, HIMU, EM I, EM II are after Zindler and Hart (1986).

which are broadly consistent with varying extents of fractional crystallization of olivine and spinel (also clinopyroxene) with decreasing  $\text{Mg}^\#$ . However, the Italian sample suite shows the



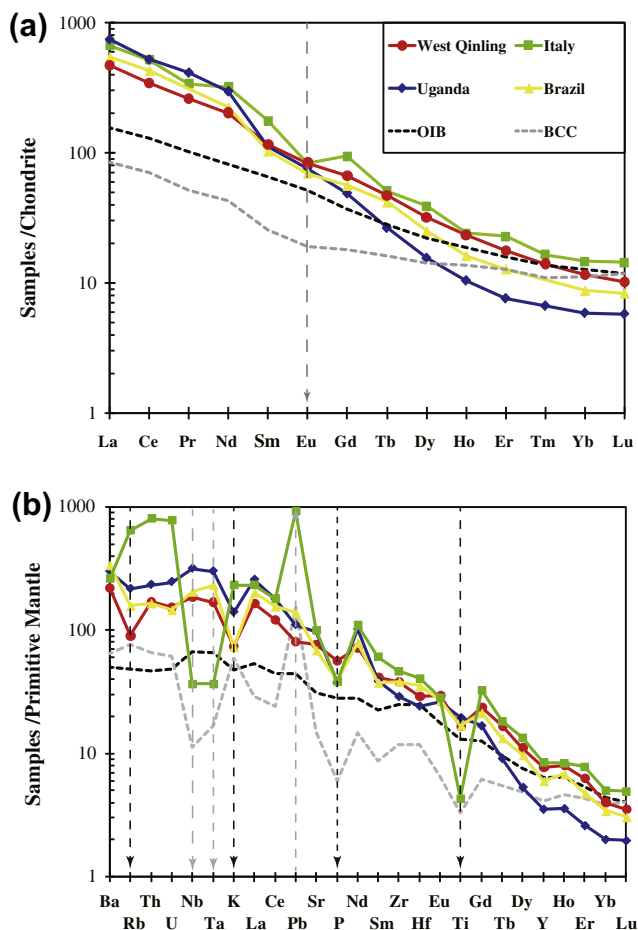
**Fig. 8.**  $\text{K}_2\text{O}$  vs.  $\text{SiO}_2$  for kamafugite suites from West Qinling (Yu et al., 2001a, 2004, 2009; Wang and Li, 2003; Dong et al., 2008), Italy (Conticelli and Peccerillo, 1992; Castorina et al., 2000; Di Battistini et al., 2001; Lavecchia et al., 2006), Brazil (Carlson et al., 1996; Araujo et al., 2001; Sgarbi and Gaspar, 2002; Carlson et al., 2007; Melluso et al., 2008) and Uganda (Tappe et al., 2003; Stoppa et al., 2000). The Italy suite has the highest  $\text{K}_2\text{O}$  while the Brazil suite has the largest range of  $\text{SiO}_2$ .



**Fig. 9.** Comparison of  $\text{Mg}^\#$  for kamafugite suites from West Qinling, Uganda, Brazil and Italy. The Brazil suite has the largest range of  $\text{Mg}^\#$ , from 0.42 to 0.84. The average  $\text{Mg}^\#$  for the four suites is 0.67 ( $N = 71$ ), 0.70 ( $N = 19$ ), 0.63 ( $N = 55$ ) and 0.73 ( $N = 12$ ), respectively. The worldwide kamafugite data are from Conticelli and Peccerillo (1992), Carlson et al. (1996), Castorina et al. (2000), Stoppa et al. (2000), Di Battistini et al. (2001), Araujo et al. (2001), Sgarbi and Gaspar (2002), Tappe et al. (2003), Wang and Li (2003), Peccerillo (2004), Junqueira-Brod et al. (2005), Lavecchia et al. (2006), Carlson et al. (2007), Melluso et al. (2008), Dong et al. (2008), Yu et al. (2001a, 2003b, 2004, 2009).

lowest Ni and lower Cr concentration at a given  $\text{Mg}^\#$  relative to the Uganda and Brazil suites, suggesting somewhat different magma sources or source histories.

Kamafugites from West Qinling, Uganda and Brazil show extreme enrichment in incompatible elements (Fig. 10a and b) with high LREEs, low HREEs and elevated LREEs/HREEs ratios, suggesting the presence of garnet as a residual phase in the melting region. The  $[\text{La}/\text{Yb}]_N$  ratios of West Qinling, Uganda and Brazil suites are 31.1–63.3, 93.7–153.1 and 23.1–197.4, respectively. This suggests the possibility that all these three kamafugite suites share similarly enriched sources. The Italian suite displays a similar REEs patterns with  $[\text{La}/\text{Yb}]_N = 23.0$ –104.4, but an obvious negative Eu anomaly ( $\text{Eu}/\text{Eu}^* = 0.54$ –0.80). Because the Italian suite is similarly primitive in terms of  $\text{Mg}^\#$  (Fig. 9), the negative Eu anomaly is most likely a source inheritance (see Niu and O'Hara, 2009), rather than the effect of plagioclase crystallization as plagioclase is not a liquidus phase in kamafugitic rocks, which is consistent with plagioclase



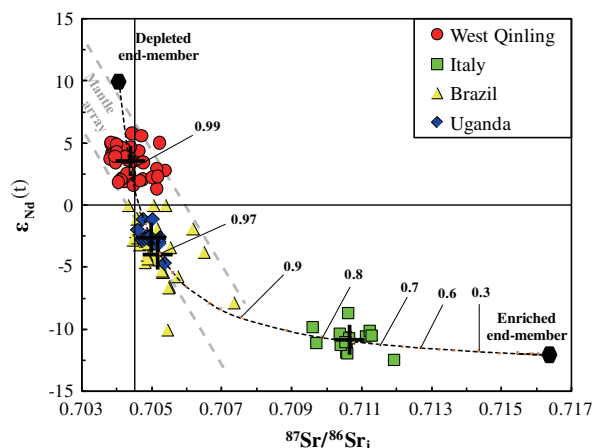
**Fig. 10.** (a) Chondrite normalized REE patterns, and (b) Primitive mantle normalized incompatible elements patterns of average West Qinling kamafugites and world type suites from Uganda, Brazil and Italy. For comparison, average ocean island basalts (OIB; Sun and McDonough, 1989) and model bulk continental crust (BCC; Rudnick and Gao, 2003) are also plotted for comparison. Normalization values are from Sun and McDonough (1989). The trace element data for kamafugites worldwide are from Conticelli and Peccerillo (1992), Carlson et al. (1996), Castorina et al. (2000), Di Battistini et al. (2001), Araujo et al. (2001), Sgarbi and Gaspar (2002), Tappe et al. (2003), Wang and Li (2003), Peccerillo (2004), Lavecchia et al. (2006), Carlson et al. (2007), Melluso et al. (2008), Dong et al. (2008), Yu et al. (2001a, 2009).

absence and phenocrysts or microcrysts in the rocks. The slightly varying REE patterns (e.g., LREEs/HREEs variation) among these world kamafugites may result from (1) source variation, (2) varying extent of melting, and (3) different magma evolution histories, recognizing that (3) is largely determined by (1) and (2).

Significant differences among the four sample suites are conspicuous on the primitive mantle normalized spidergram. Kamafugites from West Qinling, Uganda and Brazil have negative Rb, K, P and Ti anomalies (Fig. 10b), while they all have elevated abundances of large ion lithophile elements (LILEs, e.g., Ba, Rb, Th, U, etc.), similar to, but much more enriched than, average OIB. The depletion of Rb, K, P and Ti may be caused by feldspathoid/nepheline, apatite and perovskite fractionations. The Italian kamafugite suite samples are distinctively different; they are depleted in Nb, Ta, P and Ti and rich in Rb, Ba, Th, U, K, especially Pb, a typical signature of “island arc rocks” or continental crustal materials (i.e., the familiar “arc signature” or “crustal signature”). Lavecchia et al. (2006) suggested this distribution requires a high  $\text{CO}_2$  fugacity in the source region to allow HFSE fractionation which could also produce the Eu anomaly. While this interpretation may be possible, it is more likely a source inheritance, that is, the Italian

suite most likely has a continental crustal material contribution in the course of their petrogenesis (see below).

Broadly, the West Qinling, Uganda and Brazil suites have similar trace element systematics, whereas the Italy suite differs (Fig. 10a and b). In Sr–Nd isotope space, all the sample suites together define a curvilinear trend from the West Qinling suite with the most depleted mantle signature ( $^{87}\text{Sr}/^{86}\text{Sr}_i = 0.70381\text{--}0.70539$ ,  $\varepsilon_{\text{Nd}}(t) = 1.3\text{--}5.7$ ), to the Uganda suite ( $^{87}\text{Sr}/^{86}\text{Sr}_i = 0.704594\text{--}0.705374$ ,  $\varepsilon_{\text{Nd}}(t) = -4.7$  to  $-1.2$ ), to the Brazilian suite ( $^{87}\text{Sr}/^{86}\text{Sr}_i = 0.704311\text{--}0.707339$  and  $\varepsilon_{\text{Nd}}(t) = -10.0$  to  $-1.0$ ), and to the most enriched end given by the Italian suite ( $^{87}\text{Sr}/^{86}\text{Sr}_i = 0.709604\text{--}0.711930$ ,  $\varepsilon_{\text{Nd}}(t) = -12.5$  to  $-8.7$ ) (Fig. 11). While the former 3 suites define a trend almost parallel to the mantle array, extending into the enriched field with high  $^{87}\text{Sr}/^{86}\text{Sr}_i$  and low  $\varepsilon_{\text{Nd}}(t)$ , the Italian kamafugite samples plot in a distinct region with even lower  $\varepsilon_{\text{Nd}}(t)$  and higher  $^{87}\text{Sr}/^{86}\text{Sr}_i$  away from the mantle array. With all the four suites considered, the data define an overall mixing relationship between a depleted end-member (more depleted than the West Qinling suite) and an enriched end-member (more enriched than the Italy suite), probably involving mature continental crustal material as suggested by the “crustal signature” (Fig. 10b). Crustal contamination (Conticelli and Peccerillo, 1992; Serri et al., 1993; Peccerillo, 2003; Tappe et al., 2003; Conticelli et al., 2004) could be invoked, yet the Italian kamafugite samples are very primitive with  $\text{Mg}^\# = 0.64\text{--}0.82$ , which rules out crustal assimilation as the cause of the enriched isotopes and “crustal signature” in terms of incompatible elements (Fig. 10a and b). However, terrigenous sediment contribution to the magma source region is a more likely possibility (see Fig. 11). Mantle lithosphere metasomatism is possible (Castorina et al., 2000; Tainton and McKenzie, 1994), but this would require the metasomatic agent to have a continental crustal signature in the first place (Niu et al., in preparation).



**Fig. 11.** Plot of  $\varepsilon_{\text{Nd}}(t)$  vs.  $^{87}\text{Sr}/^{86}\text{Sr}_i$  for West Qinling, Uganda, Brazil and Italy kamafugites. The dashed curve represents the hypothetical curve for a simple binary mixing between a depleted end-member and an enriched end-member (varying amounts of terrigenous sediments involved, see text in detail). In the mixing calculation, we assume the depleted end-member with  $\text{Sr} = 36$  ppm,  $\text{Nd} = 0.2$  ppm,  $^{87}\text{Sr}/^{86}\text{Sr} = 0.704000$ ,  $^{143}\text{Nd}/^{144}\text{Nd} = 0.513150$  and the enriched end-member with  $\text{Sr} = 327$  ppm,  $\text{Nd} = 27$  ppm,  $^{87}\text{Sr}/^{86}\text{Sr} = 0.716200$ ,  $^{143}\text{Nd}/^{144}\text{Nd} = 0.512000$ . The mixing curve is marked in fractions of the depleted end-member in the mixture. The mantle array is defined by MORB and ocean island basalts (DePaolo, 1981; O’Nions et al., 1977) and the black crosses represent suite averages. The worldwide kamafugites isotopes data are from Conticelli and Peccerillo (1992), Carlson et al. (1996), Castorina et al. (2000), Di Battistini et al. (2001), Araujo et al. (2001), Tappe et al. (2003), Peccerillo (2004), Carlson et al. (2007), Dong et al. (2008), Yu et al. (2001a, 2004, 2009).



## 6. Discussions

### 6.1. Magma evolution

All the data and above discussion argue explicitly that kamafugites are of mantle origin (very high  $Mg^\#$ ) through partial melting of highly enriched (or pre-metasomatized) sources in the garnet peridotite stability field. The varying incompatible elements abundances and radiogenic isotopes ratios of the kamafugites reflect their source differences inherited from previous histories.

As mantle-derived melts with  $Mg^\# > 0.72$  are in equilibrium with mantle olivine, melts with  $Mg^\# > 0.72$  can all be considered as close to primary melts, and the melts with varying  $Mg^\#$  values higher than 0.72 could be interpreted as primary melts resulting from varying extent and pressure of melting (see Niu and O'Hara, 2008). However, with the exception of the Italian suite, the positively correlated variation of  $Mg^\#$  with Ni and (also Cr) may suggest that primary kamafugite melts could all have very high  $Mg^\#$ , perhaps  $\geq 0.84$  (Fig. 9). In this case, most of the West Qinling, Uganda, Brazil and Italian samples would represent products of fractional crystallization (of olivine, spinel, clinopyroxene) from their respective primary magmas (Fig. 5a and b). However, it should be noted that our new data on the 4 West Qinling kamafugites are carefully selected groundmass materials that represent the melt with varying  $Mg^\#$  from 0.59 to up to 0.75, yet the literature data represent bulk-rock compositions that represent the mix between the melt (groundmass) and cumulate phenocrysts (e.g., olivine, spinel, etc.). Hence, the  $Mg^\#$  vs. Cr and  $Mg^\#$  vs. Ni trends defined by bulk-rock composition of all the sample suites (Fig. 5a and b) are likely the effect of both fractional crystallization and crystal accumulation. It follows that the unusually low Cr and Ni of the Italian samples (Fig. 5a and b) must have inherited from source rocks with low Ni and Cr (see below).

The average  $Mg^\#$  value of 0.71 ( $N = 110$  kamafugite samples) plus the high contents of incompatible elements of all these type kamafugites manifests the overall primitive nature of these magmas with no or rather limited crustal contamination.

### 6.2. Immiscibility between kamafugitic magma and carbonatic magma

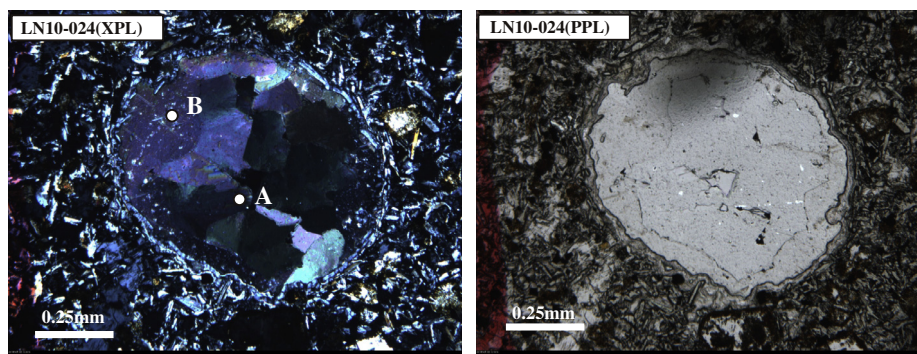
An important observation is that of the 450 carbonatite occurrences, 377 of them are clearly associated with highly alkaline magmatic rocks (Woolley, 2003). Specifically, many kamafugite suites are known to be associated with carbonatite, including, for example, those from Italy (Lavecchia and Stoppa, 1996; Stoppa and Woolley, 1997; Stoppa et al., 2002), the west branch of the East African rift (Vinogradov et al., 1980; Stoppa et al., 2000; Rosenthal et al., 2009; Eby et al., 2009), Brazil (Brod et al., 2001, 2008; Barbosa

et al., 2012) and West Qinling (Yu et al., 2001a). With all these considered, we hypothesize that kamafugite and carbonatite have formed/solidified from two immiscible liquids derived from a common  $CO_2$ -rich silicate parental magma with the immiscibility taking place probably during ascent/decompression. This is probably true for the West Qinling kamafugite-carbonatite association in particular.

The West Qinling kamafugite suite is characterized by the sequence of, from bottom to top, carbonatite flows/tuffs/debris, kamafugite volcanic breccias, vesicular and massive kamafugite flows (see Fig. 2; also see Yu et al., 2003b), a similar volcanic sequence being observed in San Venzano and Cupaello, Italy (Stoppa and Cundari, 1995). In addition, Yu et al. (2003b) found that carbonatite ejecta and massive blocks are mixed with kamafugite breccias and lapilli. This texture is very similar to carbonatitic-kamafugitic tuffs from Uganda and Italy (Stoppa et al., 2003). All these observations substantiate our hypothesis that both kamafugite and carbonatite share a common parental magma. Furthermore, on both outcrop and hand-specimen scales, the kamafugite samples contain abundant “vesicles” of varying shape and size partially filled with carbonate minerals with voids (or “Ocelli”; Fig. 2c), which are not carbonate amygdalae, but are most consistent with being parcels of trapped carbonatite melt at the time of kamafugite host magma eruption (thus being quenched/solidified). Because of the lower liquidus and solidus temperatures of carbonatite melts, they crystallized/solidified as the host kamafugite had already cooled under sub-solidus conditions. This later and lower-temperature crystallization of carbonate minerals together with associated degassing explains the volume shrink and thus the voids. This further corroborates our hypothesis that both kamafugite and carbonatite melts share a common parental magma.

In addition, there are abundant carbonatite globules with characteristic textures in the kamafugite host (see Fig. 12). Electron probe analysis shows a large compositional variation between the rim and core of a carbonatite globule. For example,  $MgO$  decreases from  $\sim 19.9$  wt.% at the rim (dominated by dolomite) to  $\sim 0.3$  wt.% in the core (dominated by calcite), while  $CaO$  increases from 36.9 wt.% to 62.1 wt.% accordingly. The high  $MgO$  and low  $CaO$  rim reflects the tendency towards equilibrium with (driven by the compositional gradient) the host kamafugitic matrix. As it is physically difficult to develop such large compositional gradient in the solid state, we interpret the compositional gradient to have developed in the molten state, which is again consistent with our hypothesis that the carbonatite globules were once part of, and exsolved from, the  $CO_2$ -rich silicate parental magma (see below).

Our single parental magma hypothesis on the petrogenesis of the West Qinling kamafugite-carbonatite association has been suggested in the literature (Freestone and Hamilton, 1980; Kjarsgaard and Peterson, 1991; Hamilton and Kjarsgaard, 1993; Petibon



**Fig. 12.** Photomicrographs (PPL and XPL) of a carbonate globule hosted in West Qinling kamafugite. The globule changes in composition from dolomite dominated rim to calcite dominated core (see text in detail).



et al., 1998; Eby et al., 2009) that the process of “immiscibility” can effectively explain the relationship between kamafugite and carbonatite association, a concept which has been discussed since the discovery of natrocarbonatitic lavas in the crater of the Oldoinyo Lengai volcano in Tanzania (Dawson, 1962). That is, a  $\text{CO}_2$  highly enriched primary silicate magma formed at depth with high mutual solubility may segregate into two coexisting, but mutually immiscible separate melts, a carbonate melt parental to the carbonatite and a silicate melt parental to the kamafugite melt.

The stratigraphic inter-layering of the two magmatic lithologies in West Qinling (see Fig. 2a and b) is the most convincing evidence for the carbonate–kamafugite cogenetic association. The carbonatite “Ocelli” and “globules” are further evidence for incomplete separation of the two immiscible liquids on smaller scales. After the kamafugitic melt has quenched and solidified during eruption, the immiscible carbonate melt droplets remain in the liquid state. The subsequent cooling resulted in the progressive solidification of the silica-rich carbonate melt, crystallizing silicate minerals at the outer edges and carbonate minerals within the globules, which are consistent with the observation that subhedral–euhedral diopside crystals spread around the carbonate globules in thin sections (see Figs. 3a and 12). The breakdown of carbonate contributes Ca to the melt for diopside crystallization at the outer rims and the exsolved  $\text{CO}_2$  explains the voids or the “Ocelli”, and hence also the ascent and explosive nature of the volcanism (e.g., pyroclastic).

In conclusion, we suggest that the West Qinling carbonatite and kamafugite must have shared a common parental magma, a  $\text{CO}_2$ -rich silicate magma characterized by high CaO, low  $\text{SiO}_2$ , and highly enriched incompatible elements. The process of immiscibility occurred during magma ascent from depth as a result of decrease solubility of  $\text{CO}_2$  in the host melt, thus an originally one single compositionally uniform melt segregated into two different melts, kamafugite melt and carbonate melt. Our observations and interpretation for the West Qinling carbonate–kamafugite association may have general significance for worldwide kamafugite petrogenesis (see below), but further effort is needed to verify this hypothesis.

### 6.3. The nature of the sources

Kamafugite is one of the most enriched (in incompatible elements) rock types in nature. The highly elevated abundances of incompatible elements and strongly fractionated LREE/HREE patterns of all these kamafugite samples worldwide (Fig. 10a and b) are consistent with being their derivation from highly enriched sources that may have had been previously enriched or refertilized by low-degree melt metasomatism (O'Reilly et al., 1991; Niu and O'Hara, 2003; Pilet et al., 2008). Furthermore, the elevated  $[\text{La}/\text{Yb}]_N$  ratios and especially the high  $[\text{Sm}/\text{Yb}]_N$  are consistent with the presence of garnet as a residual phase in the melting region. The latter is supported by the garnet lherzolite xenoliths (there are also xenoliths of pyroxenite, dunite, harzburgite, etc.) from the West Qinling kamafugite suite (Yu et al., 2001b; Su et al., 2009, 2010, 2011).

The West Qinling kamafugites display the low  $^{87}\text{Sr}/^{86}\text{Sr}$  and high  $^{143}\text{Nd}/^{144}\text{Nd}$  (Figs. 7 and 11), which is consistent with (1) their being mantle origin and (2) the more recent metasomatism (recent enough for highly elevated abundances of incompatible elements without enough time for isotopic ingrowths). Yu et al. (2001b, 2004) suggested that the lithosphere thickness in West Qinling is 80–120 km, and the depth of magma produced is  $\sim 92$  km. It is possible that the West Qinling kamafugitic magmas or their parental magmas (prior to carbonatite melt segregation) may have originated at the base of the lithosphere or lithosphere–asthenosphere boundary zone (LAB). This LAB may be associated with a layer of melt enriched in volatiles ( $\text{CO}_2 + \text{H}_2\text{O}$ ), alkalis and incompatible elements (Niu, 2008; Niu and O'Hara, 2009; Humphreys and Niu,

2009). This inference is also supported by experimental (Pilet et al., 2008) and modeling (Pilet et al., 2011) studies that melting of metasomatic veins at the base or deep part of the metasomatized lithosphere will produce melts with elemental compositions matching those of extreme alkaline lavas.

Note that the Italy kamafugite suite is characterized by the “crustal signature” (or “arc signature”), i.e. relative depletion in high field strength elements (HFSEs: Nb, Ta, Ti), a negative Eu anomaly (Fig. 10a and b) and high Sr and low Nd isotopic ratios (Fig. 11). However, the very high  $\text{Mg}^\#$  ( $\sim 0.73$ ,  $N = 12$ ) and low  $\text{SiO}_2$  ( $< 45$  wt.%) and highly enriched incompatible elements are neither consistent with island arc petrogenesis nor with continental crust assimilation. With all the conceivable possibilities considered, we propose that (1) the Italian kamafugite suite, as all other suites, results from melting of metasomatized mantle lithosphere as we argue above; (2) the metasomatic agent may be low-degree melts genetically associated with ancient subducted seafloor carbonate with terrigenous sediments incorporated in the lithosphere; (3) the amount of the terrigenous sediments involved determines the composition of the metasomatic agent, hence the metasomatized lithosphere source for the kamafugite. These will effectively explain all the kamafugite characteristics as summarized below (Fig. 11).

We consider that all the kamafugite suites may have been formed the same way through low-degree melting of metasomatized mantle lithosphere. However, the prior metasomatism and metasomatic agent may differ. With all the elemental characteristics and Sr–Nd isotopes considered, we propose that the metasomatic agent must have been carbonatitic in nature, and may have ultimately originated from subducted seafloor carbonate as part of the terrigenous sediment package with the continental crustal signature. The varying contribution of the terrigenous sediments as the ultimate origin of the metasomatic agent in the continental mantle lithosphere is best illustrated by the mixing curve in Fig. 11. Of the four kamafugite suites, the Italian suite, for example, must have the highest amount of subducted terrigenous sediments in the source (or the metasomatic agent derived from them) as characterized by the “crustal signature” (i.e., Nb, Ta and Ti depletion) with high Sr and low Nd isotopes, while the West Qinling suite has involved least amount of the terrigenous sediments.

Our new perspective may be over simplistic, but at least it works for the whole four suites together in combination of the trace element characteristics (Fig. 10a and b) and isotopes (Fig. 11). While the West Qinling and the world type suites of carbonatitic–kamafugitic association are all different to some extent, the fact that our simple hypothesis can effectively explain all these different suites means that this is a good hypothesis that can be further tested and quantified.

## 7. Conclusions

- (1) The West Qinling kamafugite shares similar geochemical properties with type kamafugite suites worldwide (e.g., those from Uganda, Brazil and Italy) in having low  $\text{SiO}_2$ , high CaO and elevated abundances of incompatible elements.
- (2) The association of all these kamafugite suites with carbonatite points to a genetic link between these two lithologies. This link is particularly convincing for the case of the West Qinling kamafugite suite in terms of stratigraphic associations, outcrop/hand-specimen characteristics and petrography.
- (3) The kamafugite and carbonatite are two “immiscible” melts segregated from a common  $\text{CO}_2$ -rich silicate parental magma by means of immiscibility during ascent.
- (4) The ultimate sources of the primary magmas are likely metasomatized mantle lithosphere with the metasomatic agent being carbonatitic melt. The metasomatic agents

may have derived from subducted seafloor carbonate rocks along with terrigenous sediments. The West Qinling suite, for example, has involved least amount of the terrigenous sediments while the Italian suite must have involved the largest amount of terrigenous sediments in their respective histories of the lithospheric mantle development.

- (5) Our hypothesis on the petrogenesis of kamafugite is simple, but effective to explain all those suites from different continents. Further effort should aim to test and quantify the hypothesis.

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## Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jseas.2013.09.012>.

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