

Supplementary Information Appendix for

Differentiation between carbonate and silicate metasomatism based on lithium isotopic compositions of alkali basalts

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ANALYTICAL METHODS

Li concentration and Li isotopic values were analyzed for a suite of 44 West Qinling samples including 18 MABs and 26 CABs. Li isotopic analyses were completed at the CAS Key Laboratory of Crust-Mantle Materials and Environments, University of Science and Technology of China, and School of Resources and Environmental Engineering, Hefei University of Technology. The procedures of dissolving, column, and isotopic analysis have been detailed reported on [Sun et al. \(2018\)](#). Briefly, ~50 mg whole-rock sample powders were dissolved in screw-top beakers by mixing of optima-grade concentrated HF-HNO₃-HCl. After a series of steps of dissolving and drying, clear solutions were obtained and used for column geochemical separation. Separation efficiency was checked by ICP-MS, aiming to guarantee the Na/Li ratios <3 and recovery >99.9%. Finally, Li isotopic compositions were determined by the standard-sample bracketing method using a Nu Plasma multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS). The reference materials BHVO-2G and BCR-2G were processed through whole processes with samples for accuracy check, and yield δ⁷Li values of +4.4 ± 0.3‰ for BHVO-2G and -0.8 ± 0.3‰ for BCR-2G, consistent with reported values ([Magna et al., 2006](#)).

TABLE DR1-4

Table. 1. The Li isotopic compositions of Cenozoic alkali basalts and Mesozoic alkali basalts from West Qinling orogen

Locations	Sample NO.	Li (($\mu\text{g/g}$)	$\delta^7\text{Li } (\text{\textperthousand})$	Locations	Sample NO.	Li (($\mu\text{g/g}$)	$\delta^7\text{Li } (\text{\textperthousand})$
Haoti	14HT01	12.3	7.1	Madang	12LZ02	22.6	-3.3
	14HT02	13.9	5.7		12LZ04	23.4	-2.4
	14HT03	14.3	6.0		12LZ05	24.5	-2.9
	14HT04	8.88	4.2		12LZ06	19.4	-1.9
	14HT05	9.47	5.9		12LZ08	27.0	2.2
	14HT07	11.3	4.1		12LZ12	30.0	1.4
	14HT08	20.4	7.5		12LZ13	43.3	3.4
	14HT10	10.9	5.6	Ganjia	12LZ14	18.6	4.7
	14LX01	19.1	7.6		12LZ17	24.5	-0.5
	14LX03	14.3	8.8		12LZ18	26.5	-0.1
Caihua	14LX04	22.5	5.2		12LZ19	32.7	-0.7
	14LX05	10.0	4.3		12LZ24	101	0.1
Fenshui	14FS01	21.0	11.2		12LZ25	69.7	2.0
	14FS02	13.0	8.1		12LZ26	92.0	2.4
	14FS03	18.8	4.4	Duomaohé	12LZ28	82.2	1.0
	14FS04	12.8	9.2		12LZ23	66.0	-1.7
	14FS05	20.5	6.1		12LZ29	64.3	-0.2
	14FS06	16.6	8.4		12LZ30	67.4	-1.0
	14LX06	13.9	8.2				
	14LX11	27.7	3.2	Standards	BHVO-2G	3.69	4.3
	14LX17	12.5	9.6		GSP-2	42.5	-0.9
	14LX18.	12.2	8.9				
	14LX22	10.3	7.4				
	14LX23	9.54	7.4				
	14LX24	9.15	7.7				
	14LX25	16.5	5.6				

	272	231	195	303	129	235	171	180	262	258	250	232	234	238	237	236	246	237
Ni	272	231	195	303	129	235	171	180	262	258	250	232	234	238	237	236	246	237
Sc	21.8	23.1	23.1	26.8	21.8	19.1	22.5	18.2	16.5	19.7	21.2	14.5	13.9	18	16	17.6	14.9	17.3
V	210	226	220	214	198	219	218	218	216	218	222	263	248	251	247	253	254	257
Cu	55.8	50.7	38.2	36.7	73.8	54.1	52.4	56.2	51.2	50.9	54.1	45.1	46.8	53	53.8	51.6	58.2	53.2
Pb	1.77	2.5	2.47	2.35	3.48	3.47	2.03	2	3.29	3.44	3.64	5.47	4.49	3.79	4.88	4.39	3.44	3.75
Zn	66.5	72.3	72.7	76.5	87.9	80.2	68.5	68.1	78.5	79.9	80.1	107	104	107	105	106	107	108
Li	22	22.6	22.8	20.1	25.2	26.2	42.9	17	25.5	26.4	29.6	99.8	69.4	94.8	73.8	60.5	65.9	58.7
Co	51.3	52	51.8	58	42.5	49.7	43.5	45.1	52.1	51.5	51	54.6	54.3	54.3	54.1	54.9	56.5	56.2
Ga	16.9	18.6	18.4	17.5	19.6	19.7	17.5	18.1	19.1	18.9	19.3	21.8	21.6	21.6	21.5	21.7	22	22.1
La	21.5	25.3	25.5	22.7	20.6	26.3	21	21	24.6	25	25.7	39.8	38.2	38.5	37.7	39	39.6	39.6
Ce	45.2	52.8	53.5	48.3	44.5	54.5	45.2	45	51.5	52.5	54	81.8	79.5	80.2	77.9	81	81.8	81.9
Pr	5.57	6.33	6.38	5.75	5.51	6.56	5.56	5.51	6.21	6.31	6.47	9.7	9.5	9.5	9.26	9.69	9.87	9.76
Nd	23	26.4	26.4	23.9	23	26.8	23.8	23.3	25.7	26.2	26.8	40.3	38.8	38.8	38.1	39.7	39.7	40.1
Sm	5.24	5.91	5.91	5.17	5.45	5.99	5.21	5.38	5.78	5.87	6.01	8.46	7.99	8.25	8.04	8.2	8.22	8.46
Eu	1.77	2.02	1.94	1.83	1.77	1.87	1.9	1.87	1.84	1.86	1.93	2.52	2.46	2.53	2.38	2.48	2.57	2.56
Gd	5.17	5.74	5.56	5.28	5.55	5.61	5.56	5.52	5.41	5.42	5.64	7.05	6.94	7.05	6.85	6.99	7.14	7.24
Tb	0.8	0.87	0.85	0.82	0.86	0.86	0.88	0.88	0.81	0.83	0.85	1.01	0.96	0.98	0.95	0.99	0.98	1.01
Dy	4.55	4.96	4.74	4.52	4.86	4.73	5.04	4.96	4.51	4.59	4.82	5.2	5.06	5.2	5.08	5.01	5.34	5.31
Ho	0.88	0.95	0.93	0.89	0.96	0.87	1	0.96	0.85	0.85	0.87	0.89	0.9	0.91	0.9	0.9	0.9	0.93
Er	2.34	2.38	2.46	2.42	2.55	2.26	2.54	2.65	2.15	2.25	2.33	2.23	2.21	2.26	2.28	2.23	2.31	2.2
Tm	0.33	0.35	0.34	0.33	0.37	0.31	0.38	0.37	0.29	0.3	0.32	0.29	0.28	0.29	0.3	0.28	0.3	0.29
Yb	1.99	2.07	2.14	2.08	2.2	1.85	2.38	2.19	1.81	1.93	1.97	1.66	1.58	1.72	1.69	1.62	1.66	1.71
Lu	0.29	0.3	0.29	0.3	0.33	0.27	0.33	0.34	0.27	0.27	0.29	0.21	0.21	0.24	0.22	0.23	0.24	0.23
Y	23	25.2	24.5	24.2	25.5	22.9	26.1	26.2	22.4	22.9	23.7	23.5	22.9	23.9	23.6	23.6	23.8	24

Note □ Major and trace element concentrations are from Dai et al., (2014, 2017; 2018)

12LZ28	3.68	826	0.0129	0.704319	0.7043	8.04	38.1	0.127667	0.512849	5	534	0.22	5.55	0.00572	0.282969	8.8	459	-0.22
12LZ23	3.71	844	0.0127	0.704123	0.704105	8.2	39.7	0.125003	0.512856	5.2	506	0.23	5.79	0.00569	0.282977	9.1	446	-0.33
12LZ29	4.08	828	0.0143	0.704133	0.704113	8.22	39.7	0.125253	0.512858	5.2	504	0.24	5.9	0.00589	0.282978	9.1	447	
12LZ30	3.79	867	0.0126	0.704264	0.704246	8.46	40.1	0.127666	0.512854	5.1	526	0.23	5.81	0.00575	0.282975	9	451	-0.35

Note □ Sr-Nd-Hf-Mg isotope data are from Dai et al., ([2014](#), [2017](#); [2018](#))

Table. 4. The element concentrations and isotopic ratios of all endmembers used for the modeling are in Fig. 3A.

	Li ($\mu\text{g/g}$)	$\delta^7\text{Li} (\text{\textperthousand})$	Sr ($\mu\text{g/g}$)	$^{87}\text{Sr}/^{86}\text{Sr}$
Mantle	1.5	3.5	21.1	0.7026
Altered oceanic crust	8	13	110	0.7052
Carbonates	1.5	25	220	0.709
Silicate sediments	74	-4.5	120	0.708

Notes□ the values of Li and Sr contents and their isotopic composition for the mantle are from Marschall et al. (2017); Salters and Stracke, (2004), for the carbonates are from Penniston-Dorland et al. (2017); Wang et al. (2018); for the altered oceanic crust are from Chan et al. (1992, 2002); Zhou et al. (2014); Wang et al. (2018)□ for the silicate sediments are from Tang et al. (2014); Tian et al. (2020).

FIGURES DR1-6

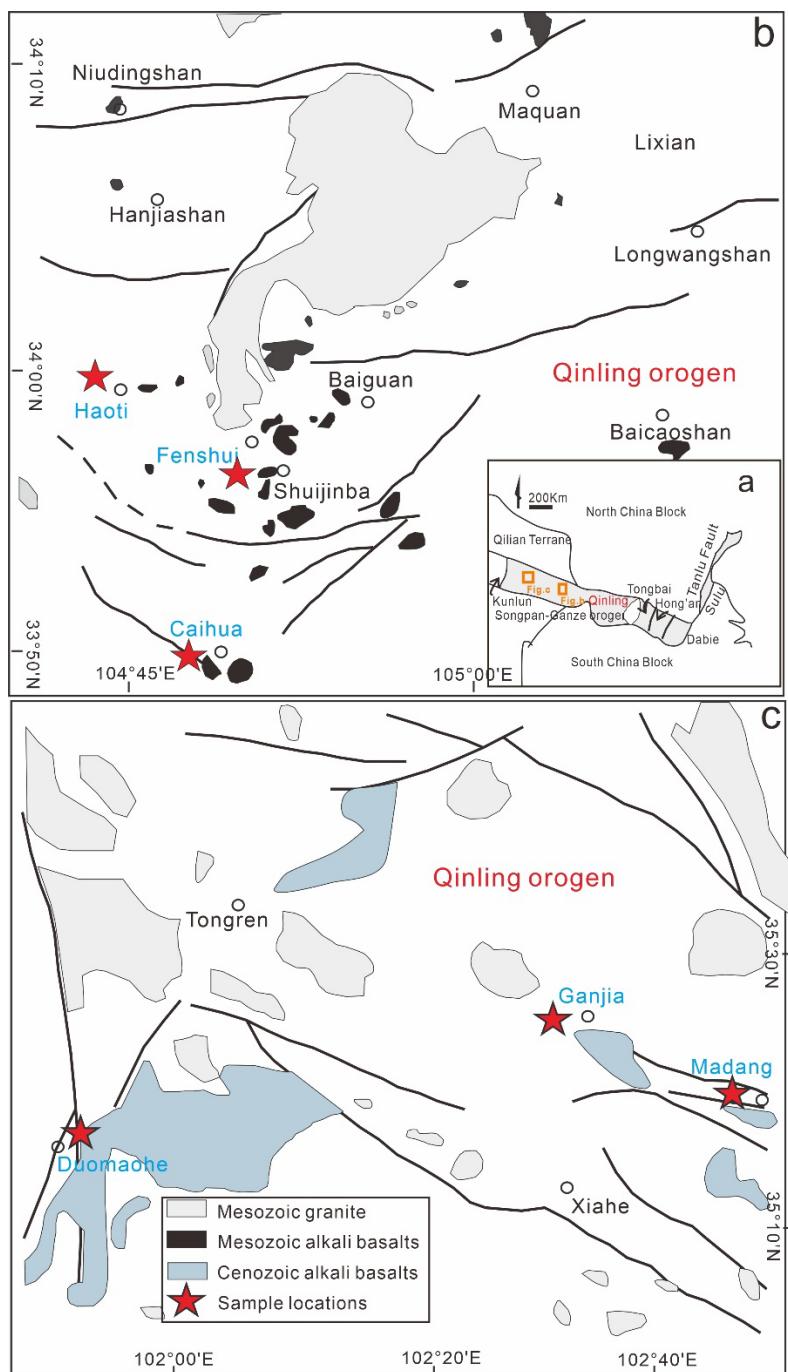


Figure 1. The geological information of the Cenozoic alkali basalts and Mesozoic alkali basalts and from the West Qinling orogen, modified after Dai et al., (2017). The Qinling orogen, located in central China, is a product of a series of tectonic processes from oceanic subduction and arc-continental subduction in the Paleozoic to continental-continental collision in the Early Mesozoic (Wu and Zheng, 2013; Dong and Santosh, 2016). This orogen is

commonly subdivided into the East Qinling orogen and the West Qinling orogen by the Baoji-Chengdu railway. The main rock types contain sedimentary cover, voluminous granitoid, and a certain amount of volcanic rocks, and the latter is dominated composed of alkali basalts, andesite, and rhyolite (Dai et al., 2014). In particular, these alkali basalts provide a good opportunity to probe into the nature of the mantle source under the Qinling orogen and uncover the metasomatic types occurring in the Paleotethyan oceanic subduction channel.

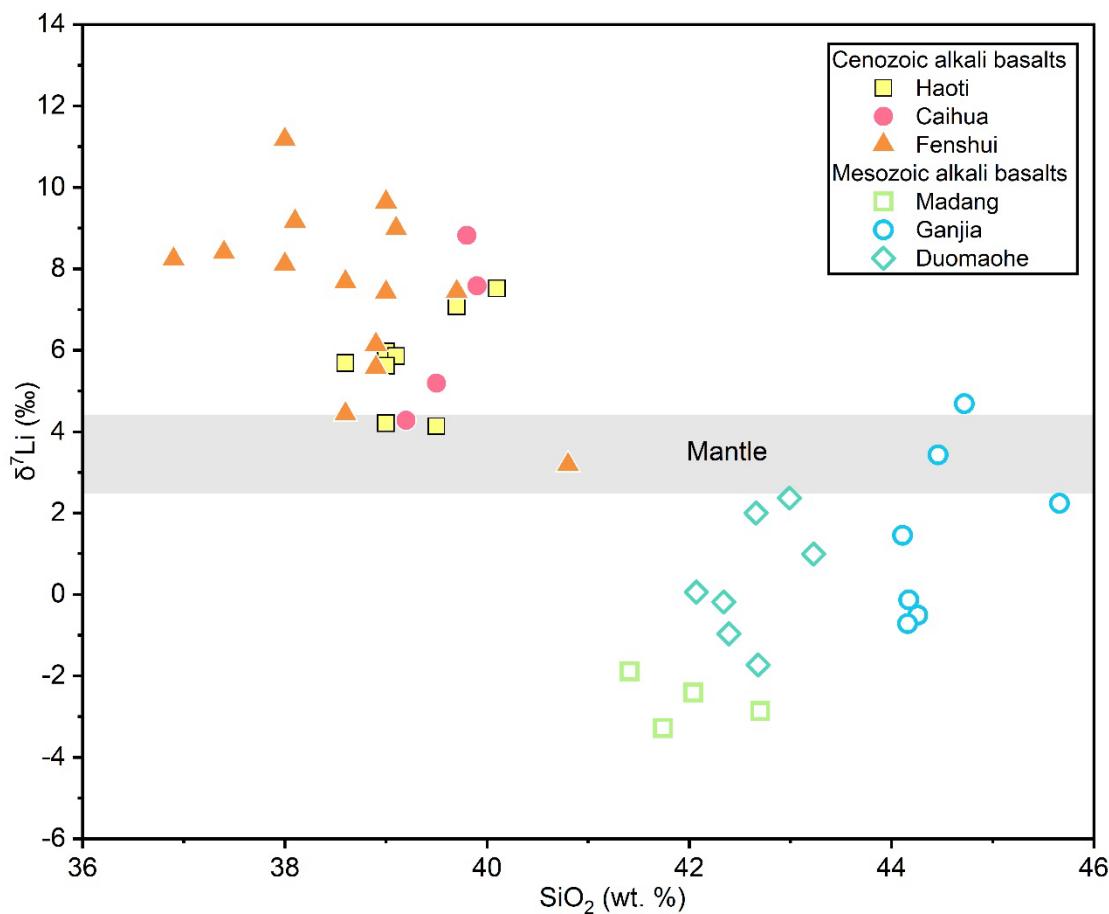


Figure 2. The plot of $\delta^7\text{Li}$ vs. SiO_2 . There is no correlation between $\delta^7\text{Li}$ value and SiO_2 content indicating that the Li isotopic compositions of the investigated alkali basalts samples were not modified by crustal contamination.

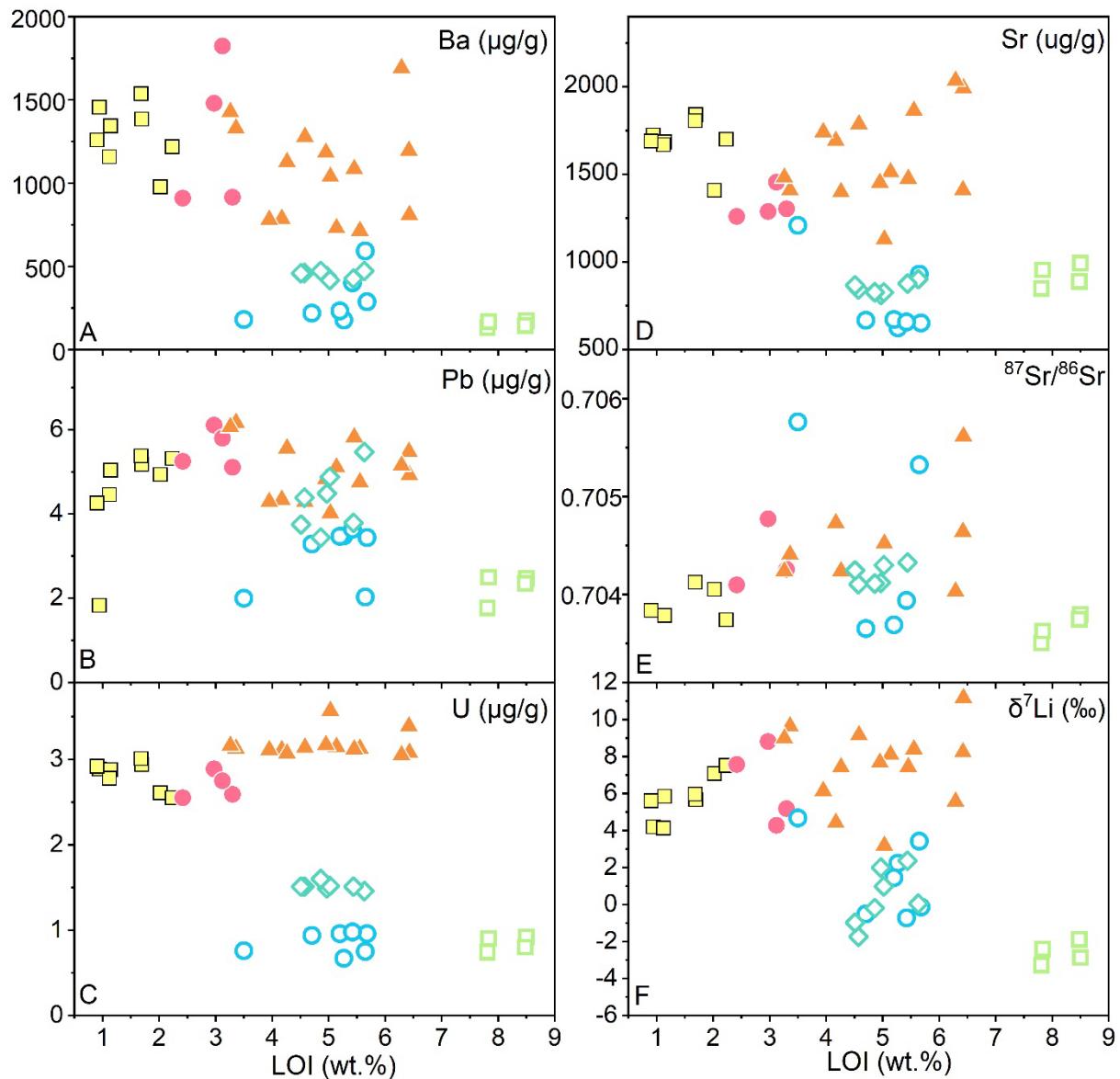


Figure 3. Plots of LOI values versus Ba, Pb, U, and Sr contents and Sr-Li isotopic ratios for two series of basalts from West Qinling orogen. There are no correlations between LOI values and Ba, Pb, U, and Sr contents as well as Sr-Li isotopic ratios, indicating the weathering process has a limited influence on the element and isotope compositions of the studied basalts.

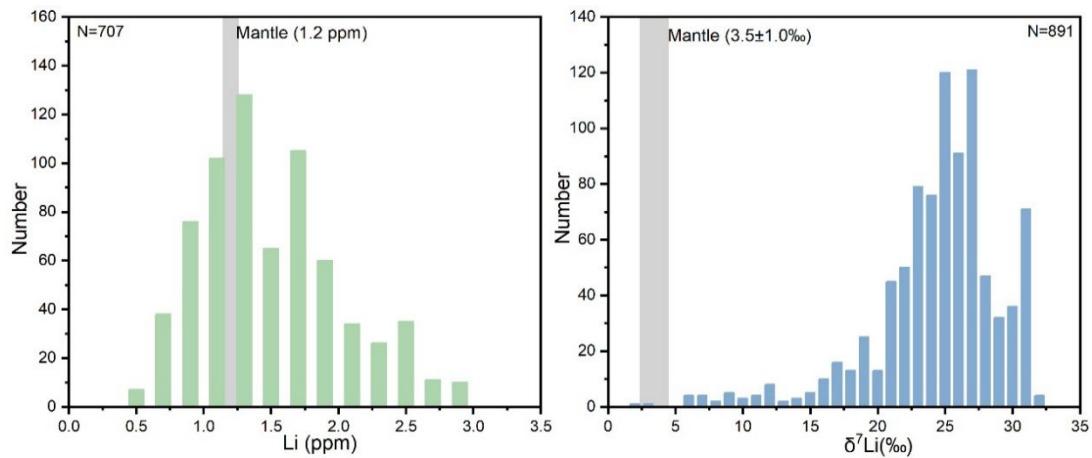


Figure 4. A comparison of Li contents and $\delta^7\text{Li}$ values for the marine carbonates (You and Chan, 1996; Marriott et al., 2004; Misra et al., 2012; Pogge et al., 2013, 2019; Lechler et al., 2015; Sun et al., 2018; Dellinger et al., 2020) and mantle (Marschall et al., 2017).

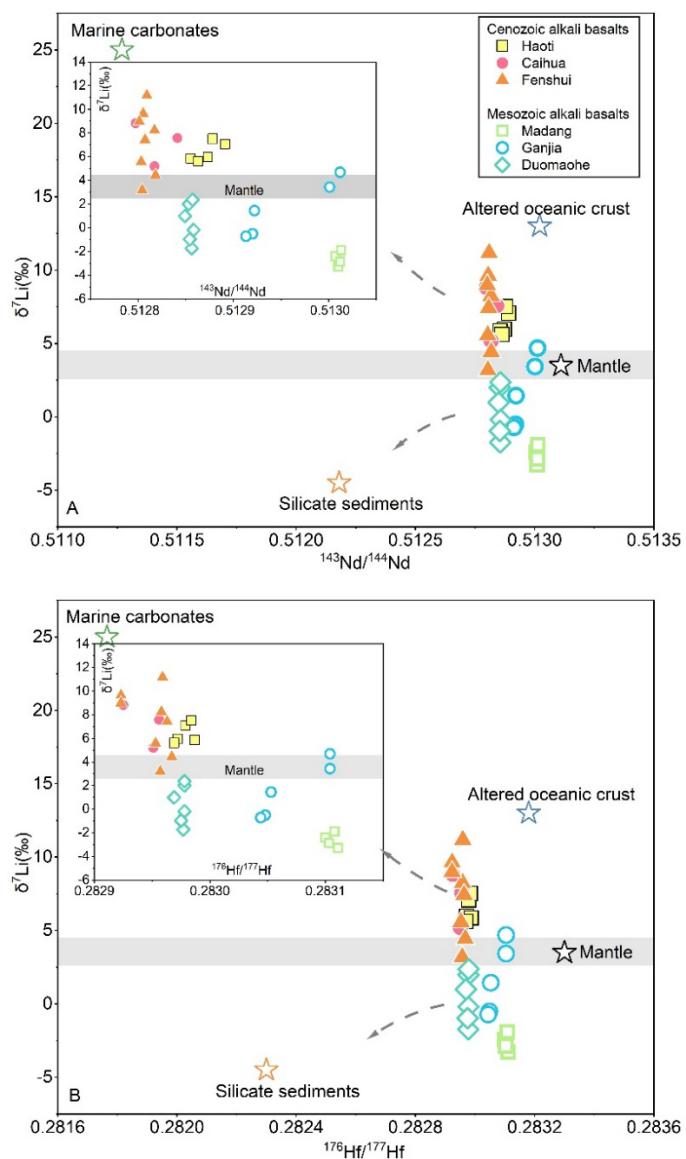


Figure 5. The plots of $\delta^7\text{Li}$ values vs. $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{166}\text{Hf}/^{177}\text{Hf}$ values. The $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{166}\text{Hf}/^{177}\text{Hf}$ values of Cenozoic and Mesozoic basalts fall closer to the carbonate and silicate sediments, respectively, than to the oceanic crust.

Notes: the $\delta^7\text{Li}$, $^{143}\text{Nd}/^{144}\text{Nd}$, and $^{166}\text{Hf}/^{177}\text{Hf}$ values for the mantle are from Marschall et al. (2017); Salters and Stracke, (2004), for the silicate sediments are from Plank et al., (2014); Tang et al. (2014), for the carbonates are from Penniston-Dorland et al. (2017); Wang et al. (2018); for the altered oceanic crust are from Chan et al. (1992, 2002); Zhou et al. (2014).

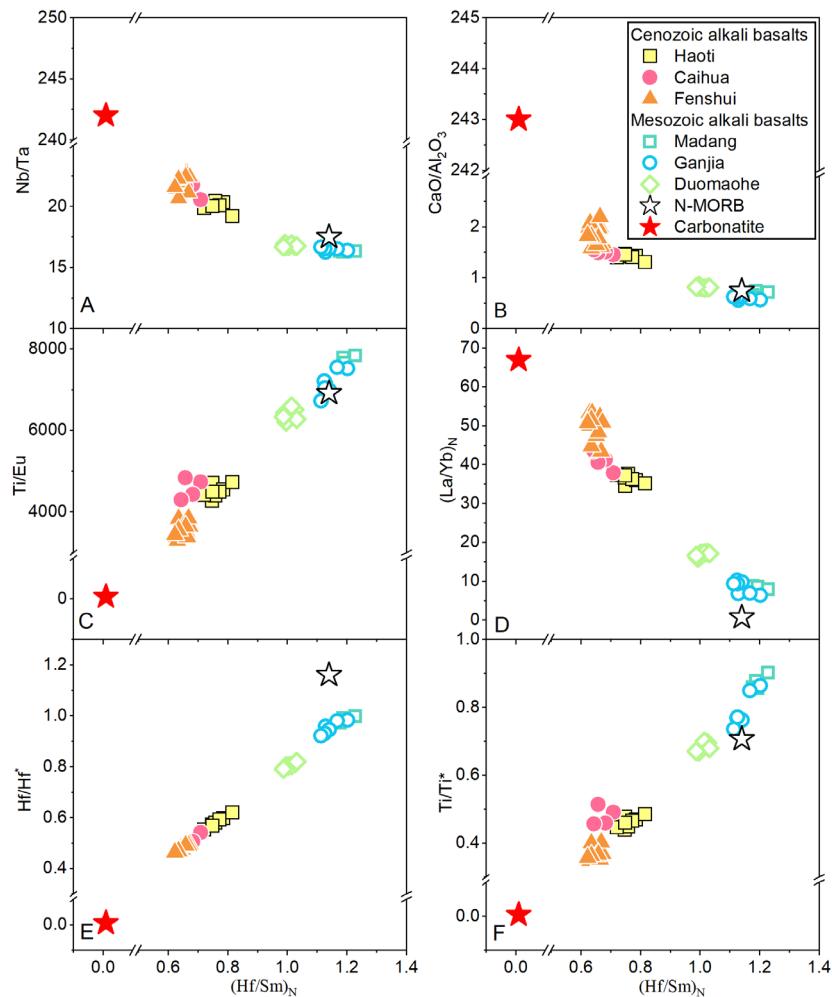


Figure 6. Variation of $(\text{Hf/Sm})_N$ vs. Nb/Ta (A), CaO/Al₂O₃ (B), Ti/Eu (C), (La/Yb)_N (D), Hf/Hf* (E), Ti/Ti* (F) for the Cenozoic alkali basalts and Mesozoic alkali basalts from West Qingling orogen, showing systemic differences in major-trace elemental features. Also shown

are the compositions of the MORB ([Hofmann, 1988](#)) and average oceanic carbonatite ([Hoernle et al., 2002](#)). The major and trace element compositions of the Cenozoic alkali basalts plot toward average carbonatite, whereas those of the Mesozoic alkali basalts are close to the MORB.

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