

Recycled crust controls contrasting source compositions of Mesozoic and Cenozoic basalts in the North China Craton Yongsheng Liu^{1,2} Shan Gao² Peter B. Kelemen³ & Wenliang Xu⁴

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Abstract

Mesozoic and Cenozoic basalts of varying ages are widespread in the North China Craton. Mesozoic basalts with ages > 110 Ma are characterized by superchondritic Nb/ Ta ratios (20.1 ± 0.3 (2 σ)) and low Nb and Ta contents. Low Nb/Ta ratios (15.4 ± 0.3 (2 σ)) and high Nb and Ta contents characterize the < 110 Ma basalts. Both the > 110 Ma and < 110 Ma basalts have Fe/Mn ratios higher than basaltic melt formed by partial melting of peridotite with the same MgO and CaO contents. The > 110 Ma basalts have island-arc-type trace-element patterns (i.e., depletion in Nb and Ta), whereas OIB-type trace-element patterns (e.g., no depletion in Nb and Ta) are characteristic of the < 110 Ma basalts. Based on Δ Fe/Mn values for olivine, clinopyroxene, orthopyroxene and garnet, high Fe/Mn ratios and negative correlations of Fe/Mn with Yb (Y) of the < 110 Ma basalts suggest clinopyroxene/garnet-rich mantle sources. The lower Fe/Mn ratios and positive correlations of Fe/Mn with Y and Yb in the > 110 Ma basalts suggest orthopyroxene/ garnet-rich mantle sources.

Combining these data with Sr-Nd isotopes, we present a conceptual model to explain the contrasting geochemical features of the > 110 Ma and < 110 Ma basalts in a relatively consistent geodynamic framework. Preferential melting of recycled ancient lower continental crust during Mesozoic lithospheric thinning resulted in:

- 1. peridotite-melt/fluid reaction that formed the orthopyroxene/garnet-rich mantle sources for the > 110 Ma basalts, and
- 2. peridotite + rutile-bearing eclogite mixing that formed the clinopyroxene/garnetrich mantle sources for the < 110 Ma basalts.

Introduction

Mafic crustal materials, such as oceanic crust or lower arc and continental crust, can be recycled back into the convecting mantle, the former by subduction and the latter by foundering or delamination (*Gao et al.*, 2004; *Kay & Kay*, 1991; *Kelemen et al.*, 2003; *Lee et al.*, 2006; *Lustrino*, 2005; *Rudnick*, 1995; *Sobolev et al.*, 2007; *Yuan et al.*, 2000). Then, because of their lower melting points (at a given pressure) compared to peridotite (*Hirschmann & Stolper*, 1996; *Keshav et al.*, 2004; *Pertermann & Hirschmann*, 2003b; *Yaxley*, 2000), they can melt preferentially to produce a high-Si liquid (*Rapp et al.*, 1999; *Yaxley & Green*, 1998). As this melt infiltrates peridotite, it converts olivine to pyroxene to form garnet- and pyroxene-rich lenses/veins in the peridotite reaction and foundering of eclogite during subduction and/or delamination would produce garnet pyroxenite reservoirs in the mantle and influence the geochemistry of subsequent magmatism.

Case study of the North China Craton

Coupled with late Mesozoic and Cenozoic tectonothermal reactivation, the ancient, cratonic mantle lithosphere of the North China Craton (NCC) is believed to have been removed from the base of the eastern block (*Gao et al.*, 2002; *Griffin et al.*, 1998; *Menzies et al.*, 1993; *Wu et al.*, 2003; *Xu*, 2001). Mesozoic high-Mg# adakitic lavas suggest that mafic lower continental crust had been recycled into the convecting mantle during the lithospheric thinning (*Gao et al.*, 2004; *Xu et al.*, 2002).

Preferential partial melting of recycled mafic crustal rocks in the mantle could lead to three types of mixing/reaction:

- 1. silicic melt-peridotite reaction by equilibrium infiltration,
- 2. mechanical mixing of peridotite and silicic melt by injection and freezing of melts in cold lithospheric mantle, and
- 3. solid-state mechanical mixing of peridotite and the eclogitic residues after silicic melt extraction.

Mesozoic and Cenozoic basalts of varying ages were studied here to investigate these processes. The > 110 Ma and < 110 Ma basalts show contrasting trace element patterns (Figure 1). The former were characterized by island-arc-type trace element patterns, while the later have ocean-island-basalt (OIB)-type trace-element patterns.



Figure 1 CI-normalized REE patterns and PM-normalized trace-element patterns. Each line represents a basalt locality. Chondrite (CI) values from Taylor & McLennan (1985), Primitive Mantle (PM) values from McDonough & Sun (1995). Click <u>here</u> or on Figure for enlargment.

Contrasting Nb/Ta ratios of the > 110 Ma and < 110 Ma basalts

The > 110 Ma basalts are characterized by superchondritic Nb/Ta ratios (20.1 ± 0.3 (2σ , n = 25)), and low Nb (Ta) contents, while the < 110 Ma basalts have lower Nb/Ta ratio (15.4 \pm 0.3 (2σ , n = 45)) and high Nb (Ta) contents (Figure 2). Rutile strongly partitions Nb and Ta from melt ($\Delta_{(Nb,Ta)}^{rutile/melt} >> 1$), and effectively fractionates Nb from Ta ($\Delta_{Nb/\Delta Ta}^{rutile/melt} = 0.21 - 1.0$; *Foley et al.*, 2000; *Green & Pearson*, 1987; *Klemme et al.*, 2005; *Schmidt et al.*, 2004; *Stalder et al.*, 1998; *Xiong et al.*, 2005). The contrasting Nb/Ta ratios of the > 110 Ma and < 110 Ma basalts could be attributed to processes involving rutile.

The negative correlations between MgO and Nb and Ta, expected for partial melting of an ol + cpx + opx assemblage, indicate that both Nb and Ta are highly incompatible during mantle melting for the > 110 Ma basalts (Figure 2a). Therefore, their low Nb and Ta contents and high Nb/Ta ratios suggest low-Nb and Ta mantle sources with high Nb/ Ta ratios. The positive correlations between MgO and Nb and Ta for the < 110 Ma basalts indicate that Nb and Ta are compatible during mantle melting (Figure 2a). Their constant Nb/Ta ratios, regardless of MgO contents, suggest that Nb/Ta ratios of the melts were buffered by Nb (Ta)-rich Ti-Fe oxides (*e.g.*, rutile and ilmenite; Figure 2b).



Figure 2 Plots of MgO-Nb (Ta) and -Nb/Ta ratio and Mg#-Ni and -Cr. Mid-Ocean-Ridge Basalts (MORB; <u>PetDB</u>) and Hawaiian OIB (Gaffney et al., 2004; Mukhopadhyay et al., 2003; Norman and Garcia, 1999) are also shown for comparison.

Peridotitic mantle metasomatized by small-degree melts of rutile-bearing eclogite would be characterized by high Nb/Ta ratios, low Nb and Ta concentrations, and low HREE abundances. In contrast, mechanical mixing of the complementary rutile-bearing eclogitic residues with deeper mantle peridotite would develop mantle garnet- and clinopyroxene-rich reservoirs with high Nb and Ta contents but low Nb/Ta ratios. In both cases, mixing or reaction with the peridotite would result in dilution of TiO₂ contents such that rutile would no longer be a primary phase during partial melting of resulting hybrid sources. Subsequent re-melting of the metasomatized peridotite could have given rise to the high Nb/Ta and low Nb and Ta contents of the > 110 Ma basalts while re-melting of the peridotite-eclogite residue mixtures could have given rise to the low Nb/Ta and high Nb and Ta contents of the < 110 Ma basalts.

High Fe/Mn ratios caused by garnet-pyroxenite sources

A statistical review of previous experiments indicates that, for less than 50% melting, high Fe/Mn ratios (> 60) in "primitive" basalts point to an eclogite/pyroxenite source, while lower values suggest a peridotite source (Figure 3a). Unlike Hawaiian basalts, most of the high Fe/Mn Chinese basalts do not have high Ni, Cr and SiO₂ contents (Figures 2c, d), and thus were not derived from ol-free pyroxenitic sources formed by high-Si melt-peridotite reaction (*Sobolev et al.*, 2005). This can be resolved if the pyroxenitic sources

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were formed by mechanical mixing of rutile-bearing eclogite and peridotite. Such mantle sources can explain well the high Fe/Mn ratios, negative Fe/Mn-Yb (Y) correlations of the < 110 Ma basalts (Figure 3b). The good positive correlation between Sc and Yb for the < 110 Ma basalts (except for those from Caiyuan) is consistent with garnet-rich sources (Figure 3d).



Figure 3 (a) Plots of Fe/Mn ratios versus MnO contents of basaltic melts formed by partial melting of pyroxenites (Keshav et al., 2004; Kogiso & Hirschmann, 2001; Kogiso et al., 2004; Pertermann & Hirschmann, 2003a) and dry peridotites (Baker & Stolper, 1994; Falloon & Danyushevsky, 2000; Hirose & Kushiro, 1993; Laporte et al., 2004; Pickering-Witter & Johnston, 2000; Schwab & Johnston, 2001; Walter, 1998; Wasylenki et al., 2003). Products of melt-peridotite reaction and melts of high Fe/Mn peridotitic material were not compiled in (a). Hawaiian basalts (Huang et al., 2007; Humayun et al., 2004) and Iceland basalts (Qin & Humayun, 2008; Thomas Find et al., 2006) were shown for comparison. (b) Plots of Nb/Ta ratio vs. Fe/Mn ratio. (c, d) Plots of Yb vs. Sc and Fe/Mn ratio. MPRI, BMI and MMPE in (b, c) are partial melts of mixtures of peridotite + secondary pyroxenite formed by peridotite-melt reaction by infiltration (MPRI) and injection (BMI), and mechanical mixture of peridotite + eclogite (MMPE). Melting degrees are 1%, 10% and 10% for MPRI, BMI and MMPE, respectively. Each plus on the lines represents a 10% increment of pyroxenite. MMP80E are partial melts of 20% peridotite + 80% eclogite. Each circle on the line represents an increment of 10% partial melting. Fe/Mn ratio from Humayun et al. (2004) and Nb/Ta ratio from Pfänder et al. (2007) for Hawaiian OIB.

Fe/Mn ratios of the > 110 Ma basalts are still higher than MORB values (Figure 3b) and values predicted for melting of dry peridotite (Figure 3a). These observations also suggest pyroxene/garnet-rich mantle sources. Although REE patterns and low HREE contents of these > 110 Ma basalts demonstrate garnet signature (Figure 1), the negative correlation between Sc and Yb suggests that their mantle sources are pyroxene-dominated (Figure 3d). Their positive correlations between Fe/Mn ratio and HREE are inconsistent with abundant garnet in the source either (Figure 3c). These observations suggest that mantle sources for the > 110 Ma basalts could be gar-bearing opx-rich pyroxenite or veined peridotite composed of Iherzolite and gar-bearing opx-rich pyroxenite.

Towards a unified model for the Mesozoic and Cenozoic basalts

Those composite xenoliths found in the Cenozoic basalts (*Liu et al.*, 2005) and Mesozoic high-Mg diorite (*Chen & Zhou*, 2005) in the NCC could have sampled the Mesozoic pyroxenite-veined peridotite formed by melt-peridotite reactions. Although opx-rich pyroxenite formed by the melt-rock reaction would not be significantly enriched in highly incompatible elements, low degree melting (~ 1%) of pyroxenite + peridotite mixture could produce high Nb/Ta ratios and trace element patterns of > 110 Ma basalts (Figures 3d and 4a). As an alternative, we modeled melting of mixtures of "crystallized eclogite melt" and peridotite. Injection of silicic melts into cold peridotite, in the form of a dike or grain boundary melt as well as melt-peridotite reaction, can be approximated as simple melt-solid mixing in a closed system. Because the eclogite-derived melt is enriched in highly incompatible elements compared to the peridotite wallrock, addition of a few percent melt can substantially change the incompatible element and Sr-Nd isotopic compositions of the mixture. Partial melts of such mixtures at a relatively high melting degree (10%) show not only the island arc-type trace element compositions (Figure 4b) and high Nb/Ta ratios (Figure 3b), but also Sr-Nd isotopic compositions of the > 110 Ma basalts (Figure 4d).



Figure 4 (a) Partial melts of mixture formed by melt-peridotite reaction by infiltration (MPRI). Silicic melt was assumed to be produced by 10% partial melting of recycled lower continental crust. (b) Partial melts of mixture formed by peridotite-melt reaction by injection (BMI). (c) Partial melts of mechanical mixtures of peridotite and residual eclogite (MMPE). Peridotite was assumed to be composed of 65% ol + 15% cpx + 15% opx + 5% sp, and converted to pyroxenite (40% cpx + 30% opx + 30% gar) after addition of eclogite melt. Partial melts were simply calculated according to batch melting mode. Each thin line represents a 10% increment of secondary pyroxenite for MPRI and BMI, and eclogite for MMPE. The thick lines are maximum and minimum values of the > 110 Ma basalts in (a, b) and < 110 Ma basalts in (c). (c-f) Sr-Nd isotopic compositions of partial melts of MPRI, BMI and MMPE. Model calculations were conducted using the Xuhuai eclogite/garnet clinopyroxenite xenoliths (Wang et al., 2005) for the composition of recycled lower continental crust. Nd and Sr isotopic compositions of the > 110 Ma mantle peridotites were represented by harzburgite xenoliths with the most radiogenic Nd from the 133 Ma Laiwu pyroxene-diorite (143 Nd/144 Nd=0.51263; Xu et al., 2003) and the average ⁸⁷Sr/⁸⁶Sr of continental lithospheric mantle (Pearson & Nowell, 2002). Nd and Sr isotopic compositions of the < 110 Ma mantle peridotites were represented by Iherzolite xenoliths from the 22.8 Ma Hannuoba basalt (¹⁴³Nd/¹⁴⁴Nd = 0.51318, ⁸⁷Sr/⁸⁶Sr = 0.70316; Song & Frey, 1989). Sr and Nd isotopic compositions of the basalts were collected from literatures. Each plus on the lines represents a 10% increment of secondary pyroxenite for MPRI and BMI, and eclogite for MMPE.

Cpx phenocrysts with reverse zoning (i.e., high FeO, MnO, Na,O, and Al,O, contents in the core) in the Cenozoic basalts suggest presence of crustal pyroxenite in their mantle sources (Wang et al., 2007). Melting of mechanical mixtures of rutile-bearing eclogitic residues with mantle peridotite to the point of rutile exhaustion would yield melts with features of the < 110 Ma basalts (e.g., low Nb/Ta ratios, high Fe/Mn ratios and OIB-type trace element patterns; Figures 3b and 4c). Our calculations suggest that 30-100% eclogite/garnet clinopyroxenite is required to produce the OIB-type trace element compositions of the < 110 Ma basalts for 10% partial melting (Figure 4c). Such a high eclogite/garnet clinopyroxenite proportion could be attributed to lower solidi for pyroxenite compared to peridotite. At a given pressure, eclogite-garnet clinopyroxenite will be preferentially sampled during partial melting, particularly at low melt fraction. Therefore, the net proportion of pyroxenite in the melted part of the mixture could be significantly higher than that in the whole mixture. The highly variable Sr-Nd isotopic compositions of the < 110 Ma basalts can be produced by partial melting of such a mixture using the Xuhuai eclogite/garnet clinopyroxenite xenoliths as the recycled continental crust (Figure 4f).

To summarize, we suggest that the differentiated Nb/Ta and high Fe/Mn ratios of the basalts are fingerprints of the Mesozoic delamination and foundering of deep lithosphere. The sources of the > 110 Ma basalts were garnet-bearing opx-rich pyroxenite or pyroxenite-veined peridotite formed by reaction and/or mixing between peridotite and eclogite-derived felsic melts, while the sources of the < 110 Ma basalts were mechanical mixtures of peridotite and eclogitic residues formed by the earlier stage of felsic melt extraction.

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