Carboniferous appinitic intrusions from the northern North China craton: geochemistry, petrogenesis and tectonic implications

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Abstract: Laser ablation inductively coupled plasma mass spectrometry zircon U–Pb dating and geochemical study document Carboniferous (c. 320–317 Ma) appinitic intrusions from the northern North China craton. The rock suite mainly consists of hornblende diorites and monzodiorites, with an SiO₂ range from 46.8 to 55.4%. These rocks exhibit high alkali contents, strong enrichment in large ion lithophile elements and light rare earth elements, and depletion in high field strength elements, with radiogenic ^87Sr/86Sr ratios of 0.7058–0.7093, unradiogenic ε Nd(t) of −9.3 to −13.9 and zircon ε Hf(t) from −8.5 to −18.4. These geochemical features suggest that their generation may involve a distinctive two-stage process: (1) a precursory metasomatism stage of mantle peridotites by melts from subduction-related sediments; (2) a delayed partial melting stage probably initiated by post-subduction transcurrent movements along pre-existing lithospheric shear zones. These mafic to intermediate intrusions, plus other coeval mafic–ultramafic complexes and high Ba–Sr granites from neighbouring regions, not only witness a heterogeneously enriched subcontinental lithospheric mantle along the northern North China craton, but also attest to a reworking-dominated metacratic process within a post-subduction transtensional regime.

Supplementary material: Data on mineral composition, zircon dating and Hf isotopic composition are at http://www.geolsoc.org.uk/SUP18513.

Of all the mafic–ultramafic rocks associated with granites, the appinitic suite represents the most puzzling but may be the most edifying. After its introduction from the Appin district of Scotland (Bailey & Maufe 1916), the appinitic suite has been widely documented from various calc-alkaline granitoid batholiths worldwide (Ayrton 1991; Bowes & Košler 1993; Fowler & Henney 1996; Fowler et al. 2001, 2008; Atherton & Ghani 2002; Castro et al. 2003; Ye et al. 2008). It includes a wide variety of mafic rocks characterized by hydrous mineral assemblages of hornblende and biotite and by an overall andesitic to basaltic composition of calc-alkaline to shoshonitic affinity (Bowes & Košler 1993; Fowler & Henney 1996; Pitcher 1997; Fowler et al. 2001, 2008; Atherton & Ghani 2002; Castro et al. 2003). Of particular note is that it can be likened to the low-silica components from various sanukitoid suites worldwide (Stern et al. 1989; Kovalenko et al. 2005; Lobach-Zhuchenko et al. 2005; Heilimo et al. 2010; Qian & Hermann 2010). The appinitic suite is revealing in that (1) it commonly forms the mafic precursors of granitoid batholiths and thus testifies to mantle involvement in granite genesis (Fowler & Henney 1996; Pitcher 1997; Bea et al. 1999; Fowler et al. 2001, 2008; Atherton & Ghani 2002; Castro et al. 2003), and (2) it is generally characteristic of the final stage of orogeny and even indicative of critical post-subduction events such as slab break-off or delamination (Atherton & Ghani 2002; Kovalenko et al. 2005; Ye et al. 2008; Heilimo et al. 2010). Therefore, constraining the origin and tectonic affiliation of appinitic suites can be of much help not only in providing important clues to sources of orogenic magmas, but also in understanding the tectonic evolution of ancient convergent plate margins.

The northern North China craton has been a convergent plate margin during Palaeozoic times, mainly in response to multiple orogenic cycles associated with the closing of the Palaeo-Asian Ocean in the Central Asian Orogenic Belt. This resulted in several episodes of Palaeozoic magmatism in the region (Zhang & Zhai 2010, and references therein). It is clear that resolving this protracted convergent history requires our understanding of the tectonic affiliation of these magmatic events with corresponding orogenic processes in the Central Asian Orogenic Belt.

In this contribution, we present new laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) zircon U–Pb age, whole-rock geochemistry and Sr–Nd isotopes, and in situ zircon Hf isotopic compositions for the Carboniferous mafic to intermediate intrusive rocks from southern Inner Mongolia along the northern North China craton to: (1) document the geochemical characteristics of these rocks; (2) trace their magma sources and constrain their petrogenesis; (3) probe the tectonic environment in which they evolved.

Geological background

With the Central Asian Orogenic Belt on the north and the Qinling–Dabie–Sulu Orogenic Belt on the south, the North China craton comprises two Archaean continental blocks (Eastern and Western) separated by a Proterozoic Trans-North China Orogenic Belt (Zhao et al. 2001) (Fig. 1a). The Eastern and Western blocks developed independently from late Archaean to early Palaeoproterozoic time and collided to form a coherent craton at c. 1.85 Ga (Zhao et al. 2001). The craton features a basement of dominantly Archaean to Palaeoproterozoic tonalitic–trondhjemitic–granodioritic (TTG) gneisses and metavolcanic and metasedimentary rocks. Subsequent covers include
the Mesoproterozoic clastic sedimentary succession of the Changcheng System, Cambrian to middle Ordovician marine sedimentary rocks, Carboniferous–Permian continental clastic rocks and Mesozoic basin deposits (Zhao et al. 2001; Kusky et al. 2007).

With a roughly east–west trend, the Central Asian Orogenic Belt consists of island arcs, ophiolites, oceanic islands, accretionary wedges, oceanic plateaux and micro-continents (Xiao et al. 2003; Windley et al. 2007). The northern China–Mongolia tract covers a vast area from southern Mongolia to northern China along the

Fig. 1. (a) Major tectonic divisions of China. Also shown are the subdivisions of the North China craton (Zhao et al. 2001). EB, Eastern block; TNCO, Trans-North China orogen; WB, Western block. Rectangle marks area of (b). (b) Tectonic framework of Central and South Inner Mongolia (modified from Jian et al. 2008). Rectangle marks area of (c). (c) Sketch geological map of south Inner Mongolia (modified from Ma 2002). (d) Sketch geological map of the Siziwangqi appinitic intrusions (modified from IMBGMR 1972, 1975), with the sample locations shown.
middle-eastern segment of this orogenic belt, with the Solonker suture zone being its most prominent tectonic feature. This zone separates two opposite-facing continental blocks and is generally regarded to mark the final closure of the Palaeo-Asian Ocean (Fig. 1b) (Jian et al. 2008, 2010). The northern block includes the Hutag Uul terrane of South Mongolia (Badarch et al. 2002) and the northern orogen (early to mid-Palaeozoic) in northern China (Jian et al. 2008). The southern block comprises the southern orogen (early to mid-Palaeozoic) and the northern margin of the North China craton (Jian et al. 2010), with the Chifeng–Bayan Obo fault as the boundary between two units.

To the north of the fault lie the Bainainiao arc chain and the Ondor Sum subduction–accretion complex, both forming an extricate, nearly east–west-trending belt (Wang et al. 1991; Xiao et al. 2003). The former mainly contains calc-alkaline tholeiitic basalts to minor felsic lavas, alkaline basalts, agglomerates, volcanic breccias and tuffs, as well as gabbros, granodiorites and granites (Jian et al. 2010). The latter is dominated by undeformed pillow basalts, calc-alkaline volcanic rocks and mylonitic metacherts from south to north at its type locality in the Ulan valley (Xiao et al. 2003; de Jong et al. 2006).

During late Palaeozoic to early Mesozoic time, the northern North China craton experienced several magmatic events (Zhang & Zhai 2010, and references therein), resulting in a Middle Devonian mafic–ultramafic complex (Zhang et al. 2009a) and alkaline intrusions (Zhang et al. 2010a). Carboniferous foliated calc-alkaline plutons (Zhang et al. 2007, 2009b), Early Permian high-K calc-alkaline I-type and A-type granitoids (Zhang & Zhai 2010; Zhang et al. 2011a), and latest Permian to Early Triassic high-K calc-alkaline to alkaline intrusive rocks (Zhang et al. 2009b, 2010b).

The Siziwangqi region of southern Inner Mongolia is situated along the western segment of the northern North China craton (Fig. 1c). It features a Precambrian basement and Phanerozoic tectonic–magmatic events typical of the North China craton. The basement contains the lower amphibolite- to granulite-facies Archaean grey tonalitic gneisses and greenstones of the Jining group and the late Palaeoproterozoic low-grade metamorphic to unmetamorphosed rock sequences of the Zhaitai and Bayan Obo groups. The latter have a deposition time of c. 1750 Ma and are commonly interpreted to result from late Palaeoproterozoic rift after cratonization of the North China craton at c. 1.85 Ga (Li et al. 2007). Late Carboniferous to early Permian volcano-sedimentary sequences sporadically crop out in the northern part of the region and extend into the neighbouring orogenic belt. Jurassic to Cretaceous continental sedimentary rocks are present primarily in basins developed unconformably on the Precambrian basements.

Multiple phases of Phanerozoic igneous rocks intrude the Archaean and Palaeoproterozoic metamorphic rocks in the region. However, they are not well constrained up to now owing to few precise geochronological data. Based on field intrusive relations and petrography (IMBGMR 1972, 1975), they appear to occur in three episodes: the Caledonian (Early Palaeozoic), Hercynian (Late Palaeozoic) and Indosinian (Triassic) to Yanshannian (Jurassic and Cretaceous). The Caledonian suite is represented by a few strongly deformed dioritic stocks and enclaves with nearly east–west-trending foliation. The Hercynian suite consists of earlier minor phases of alkaline complexes with an age of c. 410 Ma (Zhang et al. 2010a) and mafic to intermediate intrusions, and later major phases of granodiorite–granite batholith formation. The Indosinian to Yanshannian suite comprises a few granitoid batholiths and numerous granite porphyritic dykes. These Phanerozoic igneous rocks were then covered by Cenozoic flood basalts and sediments.

**Analytical methods**

Major element compositions of minerals were measured on a JEOL JXA-8100 electron microprobe at the Institute of Geology and Geophysics, Chinese Academy of Sciences (IGGCAS). The operating conditions were 15 kV accelerating voltage, 10 nA beam current and 3 µm spot diameter. Well-defined natural mineral standards were applied for calibration. The analytical errors are generally less than 2%.

Zircons were separated from representative rock samples using standard density and magnetic separation techniques and purified by handpicking under a binocular microscope. Cathodoluminescence (CL) images were obtained for zircons prior to analyses, using a JXA-8100 microprobe at IGGCAS to reveal their internal structures.

Zircons were dated by ICP-MS using an Agilent 7500a system equipped with a 193 nm laser, housed at the State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences in Wuhan, China. Harvard zircon 91500 was used as a standard and the standard silicate glass NIST as the reference material. The spot diameter was 30 µm. The detailed analytical technique is similar to that described by Liu et al. (2010). The common-Pb corrections were made using the method of Anderson (2002) and the data were processed using the GLITTER (Griffin et al. 2008) and ISOPLOT (Ludwig 2001) programs.

Fresh rock samples were ground in an agate mill to c. 200 µm mesh powder for geochemical analyses. For major element determination, mixtures of whole-rock powder (0.5 g) and Li2B4O7 + LiBO2 (5 g) were heated and fused into glass discs and analysed by X-ray fluorescence spectroscopy (XRF) with a Shimadzu XRF 1500 sequential spectrometer at the IGGCAS. The analytical uncertainties are better than 5% as revealed by long-term measurements of Chinese national standards GSR-1 (granite) and GSR-3 (basalt). Loss on ignition was measured as the weight loss of the samples after 1 h heating under a constant temperature at 1000°C.

Trace element abundances were obtained by ICP-MS on a VG-PQII system also at the IGGCAS. Samples were dissolved in distilled HF + HNO3 in 15 ml high-pressure Teflon bombs at 120°C for 6 days, dried and then diluted with 1% HNO3 to 50 ml for analysis. A blank solution was prepared and the total procedural blank was <50 ng for all trace elements. Indium was used as an internal standard to correct for matrix effects and instrument drift. Precision for all trace elements is estimated to be 5% and accuracy is better than 5% for most elements, monitored by analyses of Chinese national standard samples GSR-1 and GSR-3.

Whole-rock Sr and Nd isotopic compositions were measured on a Finnigan Mat 262 thermal ionization mass spectrometer at the IGGCAS, following the procedure described by Zhang et al. (2008). Procedural blanks were <100 pg for Sm and Nd and <500 pg for Rb and Sr. 143Nd/144Nd was corrected for mass fractionation by normalization to 146Nd/144Nd = 0.7219. 87Sr/86Sr ratios were normalized to 88Sr/86Sr = 0.1194. The measured values for the BCR-2 Nd standard and BCR-2 Sr standard were 143Nd/144Nd = 0.512641 ± 0.000010 (2σ, n = 4) and 87Sr/86Sr = 0.705018 ± 0.000011 (2σ, n = 4) during the period of data acquisition.

*In situ* zircon Hf isotopic analyses were conducted by multicollector (MC)-ICP-M using the Neptune X system, equipped with a 193 nm laser at the IGGCAS. Spot size of 32 µm was used for analysis, with a laser repetition rate of 10 Hz at 100 mJ. The detailed analytical procedure and correction for interferences follow those described by Wu et al. (2006). The 176Hf/177Hf and 176Lu/177Hf ratios of the standard zircon (91,500) during analysis were 0.282270 ± 0.000023 (2σ, n = 15) and 0.00028, similar to the
commonly accepted $^{176}$Hf/$^{177}$Hf ratio of 0.282284 ± 0.000003 (1σ) measured using the solution method (Woodhead et al. 2004).

Field relations and petrography

The Hercynian mafic to intermediate complexes are located c. 30–80 km to the SE of Siziwangqi town (Fig. 1d). They occur either as small stocks intruding the Archaean gneisses or as xenoliths hosted in the Hercynian granodioritic to granitic rocks (IMBGMR 1972, 1975). However, contacts between the complexes and the Archaean basement are not exposed because of cover by Cenozoic sediments (Fig. 1d). The complexes have been intruded by slightly younger granites and feldspathic veinlets.

The rocks commonly have modal mineralogies of hornblende diorite, diorite and monzodiorite, with fine- to medium-grained intergranular textures. Hornblende diorites, with more than 75% amphibole, commonly occur as small blocks surrounded by massive diorite and monzodiorite. The most common medium-grained diorites typically comprise euhedral to subhedral amphibole (45–50%), and plagioclase (40–50%), and subhedral to anhedral biotite (3–10%). Accessory phases (<2%) include euhedral to subhedral apatite, subhedral zircon, euhedral titanite and magnetite. Amphiboles show a wide range of $X_{\text{Mg}} (=\text{Mg}/(\text{Mg} + \text{Fe}^*))$; 0.44–0.67 and are classified as Mg-hornblende and actinolite (Leake et al. 1997). They are locally altered to chlorite and epidote. Plagioclases generally have an anesite to albite composition ($\text{An}_{26,36,49}\text{Ab}_{50,70,80}\text{Or}_{56,97}$) and show mild to moderate sericitization. Flaky biotites are characterized by moderate Al contents and variable $X_{\text{Mg}}$ of 0.44–0.56, with moderate chloritization.

With the amount of alkaline feldspar increasing, diorites can grade into monzodiorites. Typical samples contain 45–60% plagioclase, 15–25% amphibole, 8–20% biotite, 5–12% alkalai feldspar and 2–5% quartz, and accessory apatite, zircon and titanite. The textures and compositions of major constituents are similar to those of the diorite: green Mg-hornblende with $X_{\text{Mg}}$ of 0.55–0.71, subhedral plagioclase ($\text{An}_{25,60,26}\text{Ab}_{70,80}$), anhedral alkali feldspar ($\text{Or}_{56,97}\text{Ab}_{35,55}$), subhedral flaky biotite with $X_{\text{Mg}}$ of 0.56–0.61.

Results

Zircon U–Pb data

Zircons from sample SZ07-15 are mostly subhedral, stubby to elongate prisms. They are about 80–220 µm long with length-to-width ratios between 2.1 and 5:1. In CL images, they commonly show low, homogeneous luminescence, with occasional oscillatory zoning (Fig. 2a). Twenty analyses on 20 grains yield U concentrations from 50 to 794 ppm, Th from 31 to 2031 ppm and Th/U ratios from 0.45 to 2.56. All spots define a weighted mean $^{206}$Pb/$^{238}$U age of 320 ± 2 Ma with an MSWD of 2.9 (Fig. 2b).

Zircons from sample SZ07-26 are typically subhedral elongated crystals with 50–130 µm in size. Most grains display internal oscillatory zoning (Fig. 2c). Measured U concentrations from 16 analyses on 16 grains vary from 59 to 300 ppm and Th from 42 to 526 ppm. All analyses have Th/U ratios of 0.58–2.24 and yield a weighted mean $^{206}$Pb/$^{238}$U age of 317 ± 3 Ma with an MSWD of 1.6 (Fig. 2d).

Zircons from sample JN07-37 are clear, euhedral to subhedral, stubby to elongate prisms, with a length from 60 to 180 µm and well-developed oscillatory zoning (Fig. 2e). Twenty-two measured grains yield U concentrations from 105 to 752 ppm and Th from 51 to 1906 ppm. All analyses have Th/U ratios from 0.6 to 2.54 and result in a weighted mean $^{206}$Pb/$^{238}$U age of 319 ± 2 Ma with an MSWD of 1.7 (Fig. 2f).

Major oxides and trace elements

Major and trace element analyses are presented in Table 1. The rocks are basic to intermediate in composition ($\text{SiO}_2$ 46.8–55.5%), with high contents of total Fe$_2$O$_3$ (6.76–11.47 %), K$_2$O (1.11–3.94%), CaO (4.81–9.39%) and TiO$_2$ (0.6%–1.70%), low P$_2$O$_5$ (0.14–0.79%), and varying abundances of MgO (3.63–11.38%), Al$_2$O$_3$ (10.59–19.74 %), Cr (4–323 ppm) and Ni (25–167 ppm). Their Mg-numbers range from 43 to 69. In the total alkali v. silica plot (Le Maitre 2002) (Fig. 3a), the samples scatter in the fields of gabbro, gabroic diorite, monzogabbro and monzodiorite. They exhibit a transitional character between medium- to high-K calc-alkaline and shoshonitic (Fig. 3b), with aluminum saturation index (ASI = molar $\text{Al}_2\text{O}_3/(\text{CaO} + \text{K}_2\text{O} + \text{Na}_2\text{O}$)) of 0.50–0.90.

In Figure 4, most samples roughly define a continuous evolution trend: $\text{SiO}_2$, CaO and Fe$_2$O$_3$* (total Fe as ferric iron) are positively correlated with MgO, whereas Al$_2$O$_3$, K$_2$O, Na$_2$O, TiO$_2$ and P$_2$O$_5$ are negatively correlated. Likewise, compatible elements such as Sc, Cr, Ni and V increase with increasing MgO, whereas Sr, Ba, Pb, Nb and Y decrease with increasing MgO. Th and Zr vary irregularly with increasing MgO. In addition, Cr is positively correlated with Ni (Fig. 4).

With respect to other trace elements, the rocks are characterized by moderate light rare earth element (LREE) enrichment ($\text{La}_n/\text{Yb}_n = 7.33–38.5$) and small negative Eu anomalies (Eu/ Eu* = 0.86–1.0; Fig. 5a). In the primitive mantle (PM)-normalized trace element diagrams (Fig. 5b), they show enrichment in large ion lithophile elements (LILE, such as Sr, Ba, Rb) and LREE, but strong depletion in high field strength elements (HFSE) with pronounced Nb, Ta, P and Ti troughs.

Whole rock Sr–Nd and zircon Hf isotopic compositions

Whole-rock Sr–Nd isotope data, together with the calculated initial Sr–Nd isotopic compositions, are presented in Table 2. As shown in a plot of $\varepsilon_{\text{Nd}}(t)$ v. $\text{Sr}/\text{Sr}_\text{SMOW}$ (Fig. 6), the rocks have initial $\text{Sr}/\text{Sr}_\text{SMOW}$ ratios from 0.7058 to 0.7093 and moderately negative $\varepsilon_{\text{Nd}}(t)$ values from −9.92 to −13.40.

As presented in Figure 7, zircons from sample SZ07-15 show a range of initial $^{176}$Hf/$^{177}$Hf ratios from 0.28205 to 0.28216 and $\varepsilon_{\text{Hf}}(t)$ values from −14.2 to −18.4, with crustal model ages of 2.24–2.49 Ga. Zircons from sample SZ07-26 exhibit a range of initial $^{176}$Hf/$^{177}$Hf ratios from 0.28209 to 0.28238, $\varepsilon_{\text{Hf}}(t)$ from −8.5 to −11.7 and crustal model ages between 2.24 and 2.41 Ga. Zircons from sample JN07-37 display a range of initial $^{176}$Hf/$^{177}$Hf ratios from 0.28218 to 0.28225, $\varepsilon_{\text{Hf}}(t)$ from −11.4 to −13.8 and model ages from 2.05 to 2.21 Ga.

Discussion

Petrogenesis

The well-defined zircon U–Pb ages presented in this study, plus a recently reported zircon U–Pb age of c. 330 Ma for a nearby dioritic stock (Zhou et al. 2009), firmly established an emplacement time of Carboniferous for the Hercynian mafic to intermediate complexes in the Siziwangqi region.

With their satellitic occurrence as small plutons or enclaves and hornblende-dominated mafic mineral character, the Siziwangqi rocks bear a remarkable resemblance to the appinite suite from the Hercynian basement rocks of Carboniferous for the Hercynian mafic to intermediate complexes in Europe (Ayton 1991; Bowes & Köslér 1993; Fowler & Henney 1996; Fowler et al. 2001, 2008; Atherton & Ghani 2002; Castro...
As in the case of these counterparts, the high-MgO content in many high-silica samples from the present rocks bestow a high-Mg andesitic affinity on them (Fig. 8). Furthermore, with their elevated alkali, Ba–Sr abundances and high LILE/HFSE and LREE/HFSE ratios, the Siziwangqi rocks are reminiscent of the low-silica counterparts from numerous sanukitoid suites worldwide (Kamei et al., 2004; Kovalenko et al., 2005; Tatsumi 2006; Heilimo et al., 2010; Qian & Hermann 2010).

Fig. 2. (a, c, e) Cathodoluminescence (CL) images of the dated zircons and (b, d, f) zircon U–Pb concordia diagrams for samples SZ07-15, SZ07-26 and JN07-37 from the appinitic intrusions from southern Inner Mongolia.
| Sample: | SZ07-11 | SZ07-15 | SZ07-16 | SZ07-14 | SZ07-22 | SZ07-23 | SZ07-25 | SZ07-26 |
|--------|---------|---------|---------|---------|---------|---------|---------|---------|
| Rock type: | M.D | D | D | D | D | D | D | M.D |
| Longitude (E): | 111°56.230' | 111°56.230' | 111°56.230' | 111°56.230' | 111°56.230' | 111°56.230' | 111°56.230' | 111°56.230' |
| Latitude (N): | 41°25.387' | 41°25.387' | 41°25.387' | 41°25.387' | 41°25.387' | 41°25.387' | 41°25.387' | 41°25.387' |
| SiO₂ | 55.45 | 49.91 | 49.29 | 55.42 | 55.31 | 54.43 | 54.37 | 54.98 |
| TiO₂ | 1.31 | 1.58 | 1.56 | 1.04 | 0.79 | 0.85 | 0.89 | 0.81 |
| Al₂O₃ | 15.78 | 19.49 | 19.74 | 16.86 | 11.94 | 13.46 | 13.57 | 12.27 |
| Fe₂O₆* | 7.35 | 9.75 | 9.40 | 6.76 | 8.51 | 4.82 | 4.82 | 8.51 |
| MnO | 0.09 | 0.10 | 0.11 | 0.10 | 0.14 | 0.13 | 0.13 | 0.13 |
| MgO | 5.32 | 3.63 | 4.05 | 4.80 | 9.03 | 8.20 | 8.16 | 9.07 |
| CaO | 4.81 | 6.97 | 6.97 | 5.23 | 7.70 | 7.79 | 7.83 | 7.82 |
| Na₂O | 3.50 | 4.46 | 4.05 | 4.59 | 2.63 | 2.77 | 2.71 | 2.40 |
| K₂O | 3.94 | 2.17 | 2.33 | 2.95 | 1.75 | 1.73 | 1.83 | 1.78 |
| P₂O₅ | 0.77 | 0.63 | 0.45 | 0.61 | 0.24 | 0.23 | 0.27 | 0.23 |
| LOI | 1.22 | 0.75 | 1.52 | 1.60 | 1.36 | 1.45 | 1.42 | 1.55 |
| Total | 99.54 | 99.44 | 99.47 | 99.97 | 99.40 | 99.47 | 99.59 | 99.55 |
| Mg-no. | 58.9 | 42.4 | 46.0 | 58.4 | 67.8 | 65.9 | 65.8 | 67.9 |
| Sc | 11.2 | 13.1 | 18.0 | 14.2 | 30.9 | 28.8 | 29.4 | 30.0 |
| V | 129.5 | 188 | 164 | 118 | 149 | 153 | 156 | 150 |
| Cr | 113 | 4.30 | 4.73 | 124 | 292 | 202 | 207 | 268 |
| Co | 24.5 | 24.5 | 25.8 | 20.6 | 36.0 | 36.0 | 35.5 | 36.7 |
| Ni | 66.4 | 27.8 | 15.0 | 71.9 | 167 | 152 | 157 | 190 |
| Ga | 20.5 | 25.1 | 23.0 | 18.8 | 14.1 | 16.0 | 16.8 | 15.1 |
| Rb | 106 | 47.8 | 76.4 | 73.8 | 41.2 | 74.5 | 66.3 | 50.6 |
| Sr | 1070 | 1343 | 1303 | 1172 | 512 | 709 | 689 | 598 |
| Y | 16.2 | 21.6 | 21.9 | 14.68 | 17.5 | 18.1 | 19.2 | 17.2 |
| Zr | 280 | 215 | 198 | 158 | 140 | 147 | 160 | 126 |
| Nb | 13.3 | 12.0 | 10.0 | 9.41 | 7.46 | 8.09 | 9.31 | 6.60 |
| Cs | 13.7 | 1.63 | 7.75 | 4.71 | 2.12 | 3.99 | 4.99 | 2.80 |
| Ba | 1722 | 117 | 1092 | 1617 | 592 | 737 | 796 | 720 |
| Hf | 7.28 | 5.26 | 4.69 | 4.01 | 3.75 | 3.88 | 4.21 | 3.47 |
| Ta | 0.62 | 0.34 | 0.45 | 0.57 | 0.40 | 0.52 | 0.67 | 0.35 |
| Pb | 15.4 | 12.2 | 10.3 | 14.5 | 9.24 | 12.9 | 11.9 | 10.0 |
| Th | 9.16 | 8.28 | 1.66 | 11.2 | 5.15 | 4.79 | 5.94 | 4.05 |
| U | 2.22 | 0.93 | 0.62 | 2.03 | 2.80 | 1.78 | 2.29 | 2.69 |
| La | 63.9 | 55.8 | 20.4 | 58.7 | 29.4 | 27.4 | 29.6 | 25.6 |
| Ce | 131 | 109 | 48.8 | 114 | 56.1 | 57.3 | 65.2 | 53.8 |
| Pr | 16.3 | 13.6 | 6.93 | 14.3 | 6.74 | 7.18 | 7.87 | 6.54 |
| Nd | 62.0 | 51.4 | 29.4 | 52.7 | 25.3 | 28.8 | 30.0 | 26.3 |
| Sm | 11.1 | 9.55 | 6.75 | 9.05 | 5.07 | 5.69 | 5.84 | 5.05 |
| Eu | 2.58 | 2.50 | 1.88 | 2.08 | 1.44 | 1.57 | 1.70 | 1.45 |
| Gd | 7.69 | 7.58 | 5.71 | 5.60 | 4.18 | 4.73 | 5.07 | 4.45 |
| Tb | 0.89 | 1.02 | 0.84 | 0.67 | 0.61 | 0.68 | 0.71 | 0.63 |
| Dy | 3.94 | 5.43 | 4.71 | 3.08 | 3.53 | 3.77 | 3.90 | 3.44 |
| Ho | 0.66 | 1.02 | 0.90 | 0.55 | 0.69 | 0.74 | 0.77 | 0.67 |
| Er | 1.56 | 2.59 | 2.34 | 1.40 | 1.81 | 1.93 | 1.98 | 1.75 |
| Tm | 0.20 | 0.35 | 0.32 | 0.19 | 0.26 | 0.28 | 0.28 | 0.26 |
| Yb | 1.22 | 2.18 | 2.00 | 1.09 | 1.72 | 1.77 | 1.81 | 1.50 |
| Lu | 0.17 | 0.31 | 0.29 | 0.16 | 0.25 | 0.25 | 0.26 | 0.23 |
| Laᵦ/Ybᵦ | 37.70 | 18.39 | 7.33 | 38.46 | 12.25 | 11.08 | 11.75 | 12.23 |
| Eu/Eu* | 0.86 | 0.90 | 0.93 | 0.89 | 0.95 | 0.92 | 0.96 | 0.94 |

**Table 1. Major and trace element data for the appinitic intrusions from southern Inner Mongolia**
### APPINITIC ROCKS FROM NORTH CHINA CRATON

| Sample | SZ07-27 | SZ07-28 | SZ07-30 | SZ07-31 | JN07-37 | JN07-39 | JN07-40 | JN07-42 |
|---|---|---|---|---|---|---|---|---|
| Rock type: | D | H.D | D | D | D | D | D | D |
| MnO | 0.11 | 0.13 | 0.10 | 0.14 | 0.12 | 0.10 | 0.11 | 0.15 |
| MgO | 4.55 | 11.37 | 7.49 | 11.38 | 6.29 | 5.88 | 5.65 | 9.04 |
| CaO | 7.56 | 9.39 | 8.82 | 9.09 | 7.91 | 8.09 | 7.75 | 9.29 |
| Na₂O | 3.60 | 2.26 | 2.81 | 1.99 | 3.62 | 3.33 | 3.36 | 3.16 |
| K₂O | 2.03 | 1.11 | 1.85 | 1.37 | 2.02 | 1.89 | 2.07 | 1.35 |
| P₂O₅ | 0.79 | 0.15 | 0.28 | 0.14 | 0.29 | 0.18 | 0.14 | 0.14 |
| LOI | 2.30 | 1.98 | 1.92 | 1.45 | 1.81 | 1.92 | 1.97 | 1.16 |
| Total | 99.44 | 99.48 | 99.46 | 99.45 | 99.46 | 99.53 | 99.58 | 99.86 |
| Mg-no. | 44.0 | 69.0 | 61.4 | 69.1 | 62.1 | 58.6 | 57.4 | 67.6 |
| Sc | 12.1 | 48.0 | 29.9 | 49.5 | 23.2 | 28.9 | 236 | 166 |
| V | 198 | 236 | 215 | 242 | 156 | 235 | 236 | 166 |
| Cr | 2.49 | 137 | 63.9 | 138 | 122 | 119 | 88.2 | 323 |
| Co | 26.8 | 46.8 | 40.4 | 49.5 | 29.9 | 29.4 | 29.9 | 40.4 |
| Ni | 25.5 | 86.4 | 68.0 | 96.4 | 66.1 | 47.8 | 47.0 | 106 |
| Ga | 34.6 | 30.7 | 46.5 | 37.9 | 64.9 | 62.1 | 62.7 | 32.6 |
| Rb | 20.5 | 18.22 | 17.2 | 18.5 | 18.8 | 19.6 | 19.6 | 15.7 |
| Sr | 1215 | 558 | 1036 | 436 | 846 | 837 | 736 | 541 |
| Y | 85.1 | 158 | 124 | 134 | 150 | 112 | 547 | 416 |
| Zr | 8.34 | 5.86 | 3.84 | 6.36 | 7.98 | 6.93 | 7.95 | 5.17 |
| Nb | 1.11 | 0.42 | 1.33 | 0.70 | 1.35 | 1.47 | 1.61 | 0.50 |
| Cs | 2.40 | 4.14 | 3.39 | 3.72 | 3.93 | 3.30 | 2.97 | 3.49 |
| Ta | 0.42 | 0.31 | 0.24 | 0.40 | 0.54 | 0.37 | 0.61 | 0.32 |
| Pb | 7.60 | 7.27 | 6.57 | 5.91 | 12.7 | 13.1 | 14.01 | 10.9 |
| Th | 2.84 | 3.96 | 1.86 | 3.95 | 6.70 | 6.70 | 12.24 | 5.42 |
| U | 0.64 | 0.62 | 0.46 | 0.81 | 1.82 | 1.65 | 2.80 | 2.44 |
| La | 28.9 | 20.9 | 18.4 | 22.9 | 23.1 | 27.9 | 28.5 | 18.6 |
| Ce | 66.0 | 41.5 | 41.8 | 45.3 | 49.6 | 54.0 | 53.3 | 34.5 |
| Pr | 9.44 | 5.02 | 5.59 | 5.48 | 6.78 | 6.64 | 6.17 | 4.68 |
| Nd | 37.7 | 20.5 | 22.9 | 21.5 | 25.9 | 26.6 | 24.0 | 17.6 |
| Sm | 8.20 | 4.70 | 5.22 | 4.63 | 5.67 | 5.76 | 5.23 | 3.70 |
| Eu | 2.45 | 1.30 | 1.54 | 1.34 | 1.53 | 1.60 | 1.51 | 1.04 |
| Gd | 6.84 | 4.38 | 4.53 | 4.45 | 4.61 | 4.52 | 4.61 | 3.33 |
| Tb | 0.96 | 0.67 | 0.67 | 0.67 | 0.71 | 0.81 | 0.72 | 0.52 |
| Dy | 4.95 | 3.70 | 3.64 | 3.76 | 3.93 | 4.70 | 4.09 | 3.02 |
| Ho | 0.89 | 0.73 | 0.73 | 0.72 | 0.80 | 0.94 | 0.84 | 0.61 |
| Er | 2.18 | 1.89 | 1.87 | 1.96 | 2.08 | 2.39 | 2.19 | 1.68 |
| Tm | 0.29 | 0.27 | 0.26 | 0.28 | 0.31 | 0.35 | 0.32 | 0.26 |
| Yb | 1.71 | 1.70 | 1.53 | 1.66 | 2.00 | 2.16 | 2.05 | 1.65 |
| Lu | 1.00 | 0.87 | 0.97 | 0.91 | 0.92 | 0.88 | 0.94 | 0.90 |

*Mg-number = 100 × molar Mg/(Mg + Fe); (FeOt = 0.9 × Fe₂O₃*). H.D, hornblende diorite; D, diorite; M.D, monzodiorite.

Such petrological and mafic geochemical characters (low silica contents, high MgO, Cr and Ni) are distinct from those of any crustal materials (Rudnick & Gao 2003) or crustally derived melts (e.g. Patiño Douce & Beard 1995; Patiño Douce & McCarthy 1997), thus arguing strongly for a mantle derivation. This is consistent with enriched mantle parentage generally envisaged for typical appinitic rocks (Bowes & Kosler 1993; Fowler & Henney 1996; Fowler et al. 2001, 2008; Ye et al. 2008) and various sanukitoid suites (Kovalenko et al. 2005; Heilimo et al. 2010). However, the moderate Mg-numbers and low transitional metal abundances in some samples indicate that they may have experienced some crystal fractionation, most probably of plagioclase, amphibole, biotite, titanite and apatite, as reflected by systematic variations of major oxides and compatible trace elements with MgO and the Cr–Ni fractionation vectors (Fig. 4).

In general, the geochemical signatures of appinitic and sanukitic affinity in the Siziwangqi rocks can be attributed to: (1) hydrous melting of mantle peridotites as a result of the addition of aqueous fluids from slab dehydration (e.g. Hirose 1997); (2) partial melting of subducting lithosphere and interaction of the resultant silicic melts with overlying mantle peridotites (Kelemen 1995); (3) melting of subducting sediments and subsequent melt–mantle interaction (Shimoda et al. 1998; Tatsumi 2006); (4) crustal influence during magma ascent (Castro et al. 2003; Qian & Hermann 2010; Rapp et al. 2010).

Given their cratonic occurrence, the Siziwangqi rocks could have been produced by the assimilation models that applied to
other cratonic sanukitoids. However, they lack any petrographic characters indicative of magma mixing at crustal levels as in the case of the Hanxin high-Mg diorites from the North China craton (Qian & Hermann 2010). In terms of trace elements, the present rocks have much higher Sr abundance (436–1343 ppm) than that of continental crust in general (Rudnick & Gao 2003) and local upper crust country rocks (25–140 ppm) as represented by the khondalites of Zhaertai and Bayan Obo groups (Li et al. 2007; Peng et al. 2010). Furthermore, they show Sr and Nd isotopic compositions distinct from those of the Archaean TTG gneiss-like lower crust component of the North China craton (εNd(t) = −25 to −43) (Jahn et al. 1987, 1999). This argues against such potential basement or country rock assimilants as the source of enrichments observed in the Siziwangqi rocks. However, the Archaean mafic lower crustal component of the craton may have played a role, considering that it directly hosts the Siziwangqi rocks and the data for the rocks also point toward the field for it (Fig. 6). Such contamination would result in negatively correlated εNd(t) and Mg-number, or positively correlated Nd(t) and Mg-number.

Three petrogenetic scenarios can be more quantitatively tested by a simple mixing model (Lugmair & Marti 1978) and an assimilation–fractional crystallization (AFC) model (DePaolo 1981) based on the Sr and Nd isotopes of potential end-members, given that conceivable lithospheric mantle end-member can be represented by the Ordovician kimberlites (Yang et al. 2009) and some Devonian primitive mafic–ultramafic rocks (Zhang et al. 2009a). On one hand, simple mixing calculations show that the assimilation of >50% lower crust component into mantle-derived magma is required to match the observed Sr and Nd isotopic compositions of the present rocks (Fig. 6). Such a proportional crustal contribution cannot be reconciled with the mafic composition of the Siziwangqi rocks. On the other hand, an AFC process would result in intermediate to felsic alkaline magmas like the middle Devonian Sandaoqou alkaline complex from the same region (Fig. 6; Zhang et al. 2010a).

Given the arguments above, the Siziwangqi rocks seem to maintain a relatively primary affinity from a subduction-related enriched mantle parentage. Specifically, those samples with high Mg-number (>65) and Cr (150–242 ppm) abundances are most likely to have a composition closest to parental basaltic melts in terms of elemental and isotopic compositions. Accordingly, variable Nd isotopic compositions in these samples attest to a highly heterogeneous enriched mantle source, which may have been formed through some subduction-related metasomatic events.

As is implied in various petrogenetic models for appinitic and sanukitie magmas, the metasomatic agents of subduction affinity can be slab-derived fluids (e.g. Hirose 1997), melts from basaltic oceanic crust (Kelemen 1995) or sediment-derived silicic melts (Fowler et al. 2001, 2008; Tatsumi 2006), with each yielding distinctive trace element and isotopic imprint in the metasomatized mantle. Hence their nature can be fingerprinted by ratios between particular elements. For instance, the plot of Ba/La v. Th/Ta is good at discriminating hydrous fluids and melts (McCulloch & Gamble 1991), whereas Ba/Th v. La/Sr can distinguish sediment-related melts from oceanic crust-derived ones. In our case, both plots highlight a dominant contribution from sediment-derived melts (Fig. 10). Low ratios of Rb/Cs (8–73), Ce/Pb (3.2–9.0) and U/Pb (0.06–0.30) in the present rocks are also similar to those of modern oceanic sediments (e.g. Plank & Langmuir 1998). Equally revealing is the elevated εNd values of 0.7058–0.7093 in the rocks, a well-documented hallmark for subducted sediments (Plank & Langmuir 1998; Patino et al. 2000). This closely resembles the sanukitoids of the Setouchi volcanic belt (Japanese arc), whose mantle source was fertilized by subducted sediment-derived melts (Shimoda et al. 1998; Tatsumi 2006).

Further complexity arises from the fact that the subducted sediments could include components as diverse as terrigenous sediments, pelagic clays and chemical precipitates (Fe–Mn crusts) (e.g. Plank & Langmuir 1998; Marini et al. 2005). These components tend to exhibit distinct REE and HFSE signatures corresponding to their different behaviour during sedimentary processes (Altherr et al. 2004; Marini et al. 2005). Terrigenous sediments thus have higher ratios of Hf/Sm and Hf/Nd and lower Lu/Hf ratio than pelagic clays and chemical precipitates. The concomitant isotopic variation is a nonradiogenic signature for the former and more radiogenic one for the latter. In our case, the relatively high Hf/Sm (0.44–0.94) and low Nd/Hf (5–16) ratios in the Siziwangqi rocks point to the involvement of a terrigenous component with detrital zircon. On the other hand, the high Ba/Th and Ba/La in...
some samples could be due to certain amounts of such Ba-enriched sedimentary component as pelagic clays, whereas the high Sr/Nd ratios (17–45) suggest a significant contribution of carbonate components in the subducted sediment. Therefore, the observed elemental variation, coupled with variable but consistent unradiogenic Nd and Hf isotopic signature, can be explained by the addition of somewhat heterogeneous terrigenous–hemipelagic components to the mantle sources of the Siziwangqi appinitic magmas.

Timing of metasomatism and geodynamic setting

For the protracted evolution of the northern North China craton as a convergent plate margin during Palaeozoic time, various palaeotectonic reconstructions suggest that the Early Palaeozoic orogenic cycle developed through interaction of the oceanic lithosphere that contained the North China block (and South China and other micro-continents) with active margins rimming East...
et al. (2010) southward subduction in the Solonker suture zone (Zhang et al. 2008, 2011), the Andean-style continental arc developed there as a result of the initiation until c. 294–280 Ma (Jian et al. 2000; Zhang et al. 2007, 2009), with which we previously concurred (Zhang & Zhai 2010).

These seemingly discrete Phanerzoic subduction events, together with the recently documented Palaeoproterozoic ridge-subduction event (Peng et al. 2010), imply that multiple subduction-related metasomatic events may have occurred in the region. It is not easy to discriminate these events. However, it is likely that the metasomatism is related to the subduction process that finally led to the Devonian amalgamation between the North China craton and the Bainaimiao arc terrane (Zhang et al. 2010a), given the comparable unradiogenic isotopic values in the Siziwangqi rocks and modern oceanic sediments (Plank & Langmuir 1998; Marini et al. 2005), and the following argument against an active continental arc model for the northern North China craton during late Palaeozoic time.

Admittedly, the Andean-style active continental arc model is an expedient choice for explaining the magmatic activities along ancient convergent plate margins. However, its application to the Carboniferous situation in the northern North China craton presents serious challenges. First, it seems to contradict the recent proposition that the southward subduction in the Solonker zone did not initiate until c. 294–280 Ma (Jian et al. 2010). Second, the sparsely
scattered Carboniferous plutons along the northern North China craton contrast sharply with the large-scale active continental arc magmatism that generally constitutes a significant fraction of an active continental margin, as typified by the Mesozoic Cordilleran batholiths (Ducea 2001; Wenner & Coleman 2004) and the Mesozoic to Cenozoic magmatic rocks from the Central Andes (e.g. Lucassen et al. 2006; Mamani et al. 2010). Third, although several Andean examples illustrate some contribution of ancient crust materials to active continental arc magmatism, significant enrichment is observed only in more restricted geological time and coincident with crustal thickening (Ducea & Barton 2007; Mamani et al. 2010; Collins et al. 2011). The contribution from subarc...
depleted mantle sources and resultant significant crustal growth remain a central theme during the long history of the Andean continental arc evolution. This is not the case in the late Palaeozoic northern North China craton. This study and previous investigations on the Early Devonian to Early Permian magmatic rocks from this region consistently document predominant magma sources of subcontinental lithospheric mantle and lower crust (Zhang et al. 2007, 2009a, b, 2010a, 2011a; Chen et al. 2009). This implies that only slight amounts of juvenile materials, if any, have been added during this period.

Not coincidently, such a reworking-dominated crustal evolutionary scenario is compatible with the two contrasting Phanerozoic orogenic systems recorded by zircon hafnium isotope data from orogens worldwide since 550 Ma ago (Collins et al. 2011). Represented by the North American case, the symmetrical, external (circum-Pacific) system features a contracting Hf isotopic array towards more radiogenic signature, reflecting semi-continuous subduction of oceanic lithosphere beneath continental lithosphere and concomitant protracted addition of juvenile crust to the orogenic segments (Bahlburg 2011; Collins et al. 2011). By contrast, the asymmetrical, internal orogenic system, with the Central Asian Orogenic Belt as one essential component, displays a fanning Hf isotopic array, testifying to the long-term subduction that led to fragmentation and collision of ancient continents or continental fragments (Collins et al. 2011). Superimposed on this predominantly north-directed subduction scenario is short-term, localized south-dipping subduction possibly triggered by intermittent slab flipping during closure of back-arc basins or subduction ribbons (Collins et al. 2011), as is exemplified by the specific case of flipping from north to south in the Solonker suture zone during Early Permian time (Zhang et al. 2011b).

Noting its dual cratonic and reactivated characters, we suggest that the late Palaeozoic situation in the northern North China craton can be likened to a metacratonic evolution (Zhang et al. 2011a). As exemplified by the Saharan metacraton, a metacraton evolves from a region between a rigid, unaffected craton and a mobile belt completely affected by an orogeny (Abdelsalam et al. 2002; Liégeois et al. 2003). It has been remobilized during an orogenic event but is still recognizable through its rheological, petrological, geochronological and isotopic characteristics (Liégeois et al. 2003; De Waele et al. 2006). In general, a metacratonic evolution can be driven by a succession of events including collisional process, linear lithospheric delamination along mega-shear zones, regional extension and post-collisional dismembering (Abdelsalam et al. 2002; Liégeois et al. 2003). These processes are conducive to episodic magmatism with long-term memory of cratonic geochemical signature, recurrent transcurrent movements along pre-existing lithospheric shear zones, coexisting low- and high-grade metamorphism, and favourable fluid circulation (Abdelsalam et al. 2002; Liégeois et al. 2003; De Waele et al. 2006; Ennih & Liégeois 2008).

More specifically, numerous case studies have documented a viable regime of post-subduction slab breakoff for triggering mantle melting to form appinitic and sanukitic magmas (Atherton & Ghani 2002; Kovalenko et al. 2005; Lobach-Zhuchenko et al. 2005; Ye et al. 2007; Heilimo et al. 2010). In our case, the present rocks, plus other previously documented coeval hornblende-rich mafic complexes and adakitic granites from neighbouring regions (Zhang et al. 2007, 2009a, b), are reminiscent of the high Ba–Sr appinite–granite suite from the British Caledonides (Fowler & Henney 1996; Fowler et al. 2001, 2008; Atherton & Ghani 2002) and the Tibet Plateau (Ye et al. 2008). Such a characteristic magmatic association has been invariably attributed to post-orogenic slab breakoff (Atherton & Ghani 2002) or slab delamination (Ye et al. 2008). Equally remarkable is the occurrence of late Palaeozoic eclogites in the region studied (Ni et al. 2006). With their protolith age of c. 438 Ma and high-pressure metamorphic age of c. 325 Ma (Ni et al. 2006), these eclogites may represent the metamorphic products of previously subducted Palaeo-Asian

Fig. 8. Plot of SiO₂ v. FeO*/MgO. The field for high-Mg andesites is from Kamei et al. (2004).

Fig. 9. Plots of (a) ⁸⁷Sr/⁸⁶Sr v. Mg-no and (b) ε²⁰Nd(t) v. Mg-no.
APPINITIC ROCKS FROM NORTH CHINA CRATON 349

Fig. 10. (a) Ba/La v. Th/Yb and (b) Ba/Th v. La$_y$/Sm$_y$ plots for the appinitic intrusions from southern Inner Mongolia. In (a), continuous-line vector, slab-derived fluids; dashed-line vector, sediment input in the source as represented and discussed by Woodhead et al. (2001). Global subducting sediment (GLOSS) compositions are from Plank & Langmuir (1998). In (b), subscript ‘N’ denotes chondrite-normalized values; the fields for arc and Setouchi high-Mg andesites (HMA) are from Tacumi (2006).

Conclusions

LA-ICP-MS zircon U–Pb dating constrains a Carboniferous emplacement age of c. 320–317 Ma for a series of mafic to intermediate intrusions from southern Inner Mongolia along the northern margin of the North China craton. These rocks exhibit a hornblende-dominated appinitic petrographic character and a sanukitic geochemical affinity. Geochemical and isotopic tracing demonstrates that a distinctive two-stage process contributed to their generation: a precursory metasomatism stage of mantle peridotites by melts from subduction-related sediments, and a lagged partial melting stage probably owing to post-subduction slab breakoff or delamination event. These appinitic intrusions, plus other coeval mafic–ultramafic complex and high Ba–Sr granites from neighbouring regions, only witness a heterogeneously enriched subcontinental lithospheric mantle along the northern North China craton, but also attest to a metacratic process within a post-subduction transastensional regime possibly featuring multiple slab breakoff events.

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