

# American Journal of Science

MARCH 2008

## SHRIMP U-Pb AND CAMECA 1280 OXYGEN ISOTOPE RESULTS FROM ANCIENT DETRITAL ZIRCONS IN THE CAOZHUANG QUARTZITE, EASTERN HEBEI, NORTH CHINA CRATON: EVIDENCE FOR CRUSTAL REWORKING 3.8 Ga AGO

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**ABSTRACT.** The Caozhuang quartzite, located in Eastern Hebei Province in the eastern part of the North China Craton, has long been known to contain the oldest detrital zircon population in China. A suite of 30 zircons with preliminary ages >3.7 Ga were selected for detailed SHRIMP U-Pb and CAMECA 1280 oxygen isotope analyses. SHRIMP U-Pb dating reveals that ages range from 3860 to 3135 Ma, the former being the oldest <sup>207</sup>Pb/<sup>206</sup>Pb zircon age so far obtained from the North China Craton. Values of δ<sup>18</sup>O range from 5.4 to 7.5 permil, similar to Archean igneous zircons worldwide, but the average value for the 30 zircons is 6.6 permil, which is ~0.3 permil higher than suite averages for detrital zircons from the Jack Hills and Beartooth Mountains and nearly 1 permil higher than magmatic zircons from igneous rocks of the Superior Province and Barberton. These elevated values of δ<sup>18</sup>O suggest reworking of a significant amount of juvenile crust, older than 3.8 Ga, that underwent a low temperature supracrustal history and was distributed throughout the source region in north-east China.

### INTRODUCTION

The North China Craton (NCC) is the largest crustal block in China and is commonly subdivided into three components (fig. 1, inset); the Eastern and Western Blocks, separated by the Trans-North China Orogen (Zhao and others, 2001). Archean rocks dominate in the two major blocks, whereas the Trans-North China Orogen is a Late Paleoproterozoic continent-continent collisional belt along which the discrete Eastern and Western Blocks amalgamated to form the North China Craton at ~1.85 Ga (Zhao and others, 2005).

Within the Eastern Block near Anshan (fig. 1, inset), the oldest rocks in the NCC (Liu and others, 1992; Song and others, 1996; Wan and others, 2005; Liu and others, 2007), with weighted mean <sup>207</sup>Pb/<sup>206</sup>Pb zircon ages up to 3811 ± 4 (Song and others, 1996), crop out over an area of ~20 km<sup>2</sup>, and are some of the most ancient rocks known on Earth. They consist of various tonalite-trondhjemite-granodiorite (TTG) components, in association with younger granitic rocks with zircon ages ranging from 3.3 to 2.5 Ga (Liu and others, 2008). The only other region in the NCC where such ancient zircons have been obtained is from the Huangbaiyu area, where detrital

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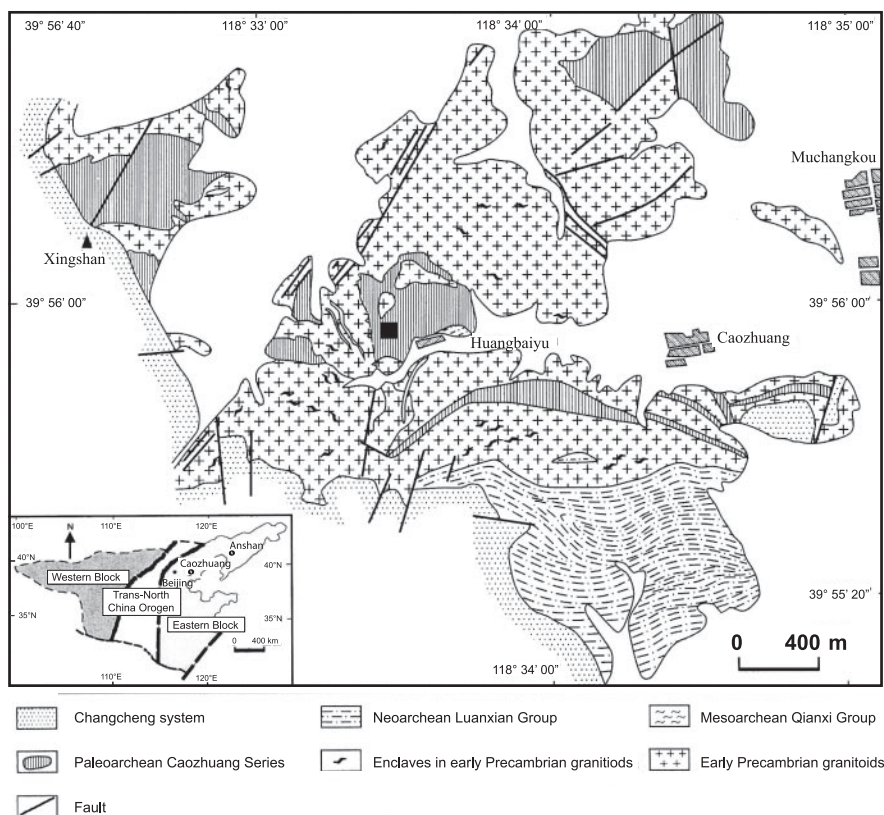


Fig. 1. Map of the Caozhuang area, with the sample site marked by a dark square. Inset shows the location within the North China Craton (based on Zhao and others, 1998). The dark square marks the sample site.

zircons in the Caozhuang quartzite record  $^{207}\text{Pb}/^{206}\text{Pb}$  ages  $>3.8$  Ga (Liu and others, 1992; Wu and others, 2005); these are the subject of the present study.

Jahn and others (1987) first recognized that ancient rocks might be present in the Huangbaiyu area of eastern Hebei Province (fig. 1), when they published a Sm-Nd whole-rock isochron age of  $\sim 3.5$  Ga from amphibolites of the Qianxi complex. Even though this has now been questioned (Liu and others, 2007), because amphibolites of different type and potentially different ages were incorporated on the same isochron, further study in the area (Liu and others, 1992) identified ancient zircons in the Caozhuang 'series' at Huangbaiyu, also considered to be a part of the Qianxi complex. This is a sequence of sporadically outcropping supracrustal rocks that consist of banded iron formation (BIF), fuchsite-bearing quartzite, impure marble, biotite-plagioclase gneiss, biotite schist and amphibolite. A total of 81 analyses of 61 zircons by SHRIMP ion microprobe from a sample of fuchsite quartzite yielded a range of  $^{207}\text{Pb}/^{206}\text{Pb}$  ages from 3.55 to 3.85 Ga (Liu and others, 1992). Most zircons showed oscillatory zoning and were considered to be detrital igneous grains, although one 3.55 Ga grain had a Th/U ratio of 0.02, which Liu and others (2007) consider might be of metamorphic origin.

More recently, Wu and others (2005) investigated zircons from another sample of fuchsite quartzite from a nearby outcrop at Huangbaiyu, using LA-ICP-MS and

LA-MC-ICP-MS techniques, respectively, to determine U-Pb ages and Lu-Hf systematics. A similar spread of ages was obtained, although many analyses showed strong lead loss and the oldest grain reported was  $3800 \pm 15$  Ma. Most  $^{176}\text{Hf}/^{177}\text{Hf}$  values ranged from 0.28034 to 0.28065, with model ages of 3.63 to 3.96 Ga (Wu and others, 2005). On an  $\epsilon_{\text{Hf}(t)}$  versus  $^{207}\text{Pb}/^{206}\text{Pb}$  age plot, the data define a linear trend. Four zircons have  $\sim 3.8$  Ga model ages and  $\epsilon_{\text{Hf}(t)}$  values of  $1.8 \pm 3.7$ , which are close to chondritic. The results were considered to indicate that the granitoid source rocks of the zircon were derived by partial melting of juvenile crust that was itself derived from a mantle that showed a lack of crust-mantle differentiation. They concluded that no large-scale crustal growth occurred in the source area prior to  $\sim 3.8$  Ga.

The other area in the North China Craton where ancient zircons have been identified is the Anshan area in NE China (fig. 1) (Liu and others, 1992; Song and others, 1996; Wan and others, 2005; Liu and others, 2007, 2008). Here, three different rock sequences contain 3.8 Ga rocks: the Baijiafen, Dongshan and Shengoushi complexes (Liu and others, 2008). These are intimately associated with somewhat younger Archean rocks, including the 3.3 Ga Chentaigou granite, 3.3 Ga Chentaigou supracrustal rocks, and 3.1 Ga Lishan trondhjemite, as well as rocks with emplacement ages as young as 2.5 Ga (Liu and others, 1992; Song and others, 1996; Wu and others, 1998; Wan and others, 1998, 1999, 2001, 2002, 2005).

Since a detrital igneous grain from the Caozhuang quartzite had an age of  $3851 \pm 4$  Ma (Liu and others, 1992), making it the oldest known zircon from the North China Craton, we chose this area to determine the oxygen isotope composition of a suite of ancient zircon grains in search of evidence for a reworked crustal component and to investigate if there was any systematic variation in oxygen isotope ratio with age.

#### ANALYTICAL TECHNIQUES

##### *U-Pb Geochronology*

For this study, a mount was prepared of  $\sim 200$  grains selected from the original sample CF89-26 of Liu and others (1992). The zircons were mounted along with fragments of standard zircons Temora (Black and others, 2003) and 91500 (Wiedenbeck and others, 1995, 2004) and then cast in epoxy resin in a 2.5 cm diameter mount and ground to expose the center of the grains. The grains were imaged optically using transmitted and reflected light and, following carbon coating, by scanning electron microscopy (SEM) using back-scattered electrons (BSE) and cathodoluminescence (CL); the latter images being used to select the initial analytical sites. The mount was then cleaned and gold coated.

A preliminary investigation of the U-Pb ages was undertaken using the Beijing SHRIMP II ion microprobe. Single analyses were made on each of 53 grains utilizing single-cycle runs through the mass stations and the resulting  $^{207}\text{Pb}/^{206}\text{Pb}$  ratios were calculated. Most grains ranged in age from 3.9 to 3.5 Ga, with two younger ages ( $\sim 2.4$  and  $\sim 2.7$  Ga) attributed to the analyses being positioned on grains showing an extensive network of cracks. Zircons with ages greater than 3.7 Ga were recorded on the photographic image for future study.

Following oxygen isotope analysis, the grain mount was re-photographed in reflected light in order to keep a precise record of the location of the analytical sites, and then re-polished and gold coated. Because of the fragility of certain grains (some plucking and loss of material occurred) it was decided not to embed the CZ3 standard directly in the mount: instead a pristine mount containing CZ3 was prepared and gold coated at the same time as the CF89-26 mount so as not to introduce possible complications due to variations in the gold composition or thickness.

Final U-Pb analyses reported in this study were made after oxygen isotope analysis, using the SHRIMP II at Curtin University following procedures outlined in Nelson

(1997) and Williams (1998). Spot size ranged between 20 to 30  $\mu\text{m}$  and each analysis site was rastered over 120  $\mu\text{m}$  for two minutes to remove any common Pb on the surface or contamination from the gold coating. Seven-cycle runs were made through the mass stations and the detrital zircons were run along with 11 analyses of the CZ3 zircon standard that records an age of 564 Ma. The mount containing CZ3 was loaded into the second sample holder in the source chamber and repeatedly analyzed after every four analyses of zircons from the CF89-26 mount. The mass resolution used to measure Pb/Pb and Pb/U isotopic ratios was 5935 (1%) and the Pb/U ratios were normalized to those measured on the standard zircon [CZ3 - ( $^{206}\text{Pb}/^{238}\text{U} = 0.0914$ )]. The uncertainty associated with the measurement of Pb/U isotopic ratios on the standard, at 1 standard deviation, was 0.72 percent during the analytical run. The measured  $^{204}\text{Pb}$  values in the unknowns were similar to those recorded for the standard zircon and so common lead corrections were applied assuming an isotopic composition of Broken Hill lead, since the common lead is considered to be mainly associated with surface contamination in the gold coat (Nelson, 1997). All ages have been calculated using the U and Th decay constants recommended by Steiger and Jäger (1977). Data reduction was performed using both the Krill 007 (P. D. Kinny, Curtin University) and Squid/Isoplot (Ludwig, 2001) programs, applying the  $^{204}\text{Pb}$  correction: the Krill data were used for production of table 1. Uncertainties on individual analyses are based mainly on counting statistics and are at the 1 $\sigma$  level. Errors on pooled analyses are quoted at 2 $\sigma$  or 95 percent confidence.

#### *Oxygen Isotope Ratio*

Following initial identification of grains >3.7 Ga and prior to oxygen isotope analysis, a piece of KIM-5 zircon standard (Valley, 2003) was inserted into the mount, which was then carefully re-ground.

Oxygen isotope analyses were performed on a CAMECA IMS-1280 high-resolution, multi-collector ion microprobe at the University of Wisconsin – Madison. A  $^{133}\text{Cs}^+$  primary ion beam was focused to a diameter of 10  $\mu\text{m}$  with sample current of  $\sim 3$  nA. Secondary O $^-$  ions were accelerated by  $-10$  kV with a normal-incidence electron gun for charge compensation. The secondary optics were similar to those described in Kita and others (2007). Instrument parameters include: transfer lens magnification of 200, contrast aperture (CA) 400  $\mu\text{m}$  diameter, field aperture (FA) 4000 x 4000  $\mu\text{m}$  square, entrance slit 122  $\mu\text{m}$  width, energy slit 40 eV width, and exit slit width 500  $\mu\text{m}$ . The intensity of  $^{16}\text{O}$  was  $\sim 3 \times 10^9$  cps depending on the primary intensity (ca.  $10^9$  cps/nA). Mass resolving power was ca. 2500, sufficient to separate hydride interferences on  $^{18}\text{O}$ . Two multi-collector Faraday Cups (FC) were used to measure  $^{16}\text{O}$  and  $^{18}\text{O}$  simultaneously, equipped with different amplifiers ( $10^{10}$  and  $10^{11}$   $\Omega$  resistors, respectively). The base line of the FC amplifiers was measured only once, because the drift during the day was insignificant compared to the noise level of the detectors ( $\leq 1000$  cps for FC with  $10^{11}$   $\Omega$  resistor). Magnet control was by NMR probe with stability better than 10 ppm/10 hours. At each analysis position, any small misalignment of the secondary optics due to changing stage position was automatically corrected before each analysis. Data were corrected for instrumental mass fractionation (IMF) using fragments of the zircon standard KIM-5 mounted in the sample block (Valley, 2003). Standards were measured four times every 10 to 20 sample analyses and the average value of IMF for the total of 8 standard analyses that bracket the sample analyses was used as the IMF correction. The external error of all 21 standard analyses was 0.13 permil (1SD, 1SE = 0.03‰). The averages for each group of 8 or 9 bracketing standard analyses vary from 0.10 to 0.15 permil and represent the spot-to-spot precision of sample analyses. Oxygen isotope ratios are reported in standard permil notation relative to Standard Mean Ocean Water (VSMOW).



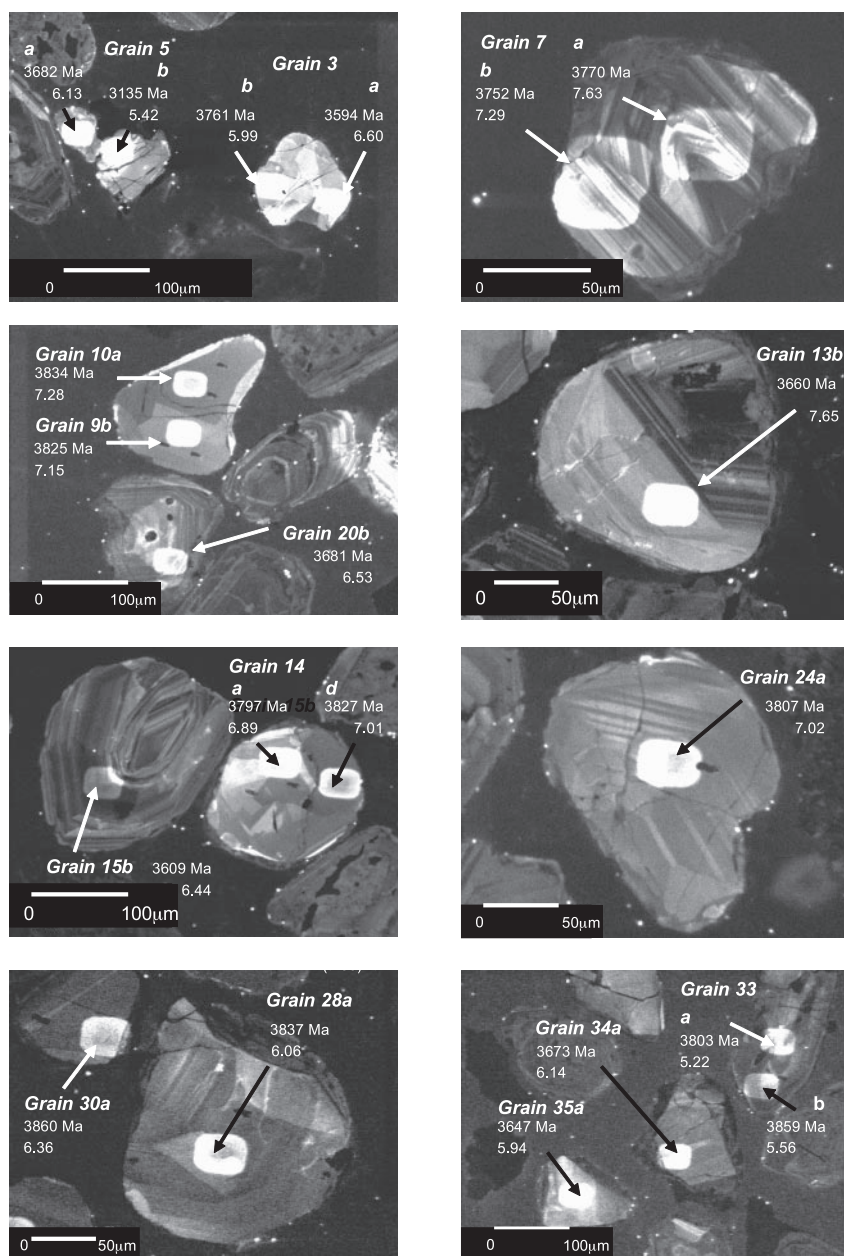


Fig. 2. Cathodoluminescence (CL) images showing the majority of zircons analyzed in this study. The grain number and analytical site are identified, together with the  $^{207}\text{Pb}/^{206}\text{Pb}$  age and  $\delta^{18}\text{O}$  value for that site, matching the data presented in table 1. The light elliptical areas on the zircon surfaces mark the site of SHRIMP U-Pb analyses.

## RESULTS

### *U-Pb Data*

The least altered zircons were selected for analysis and these were colorless to lilac, although all showed variable amounts of internal cracking and some contained

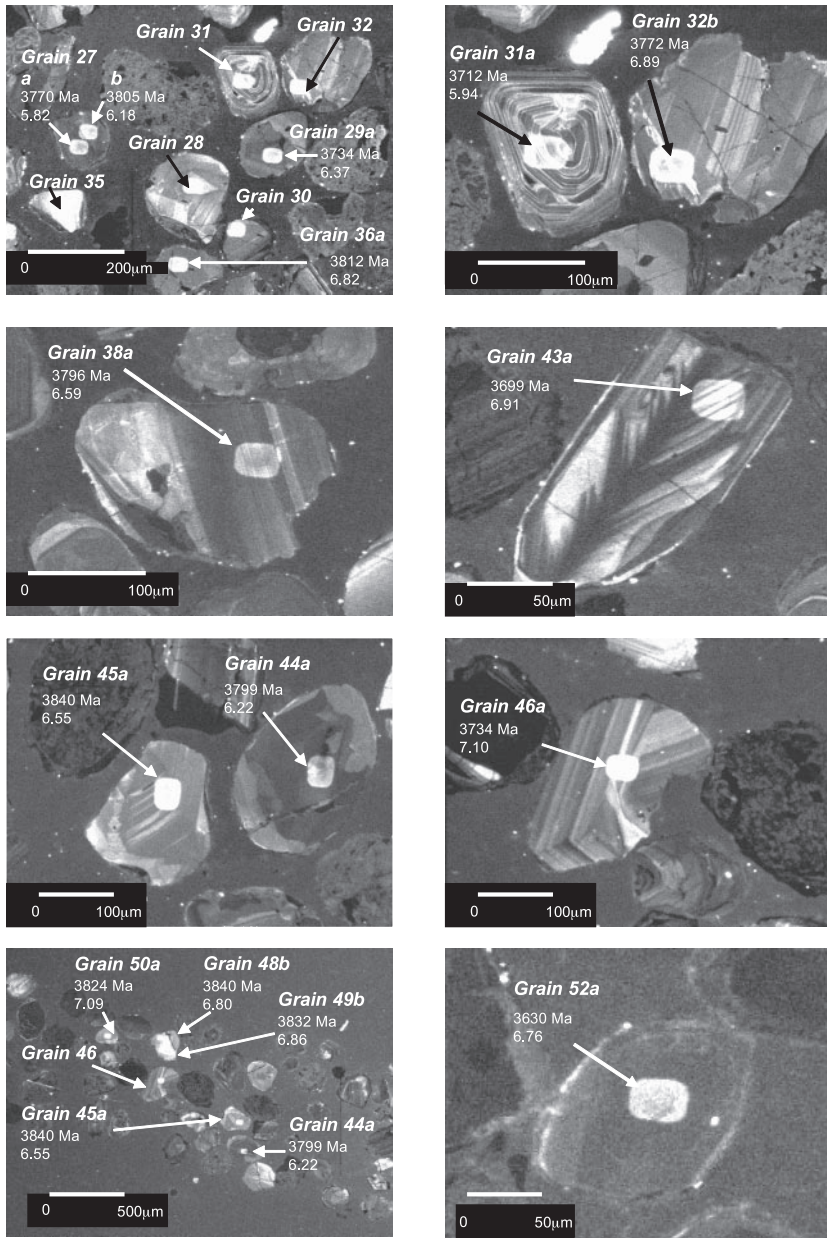


Fig. 2. (continued)

inclusions of apatite. A few dark brown metamict grains were also present in the mount, but these were not investigated further. Cathodoluminescence (CL) images of most zircons analyzed in this study are presented in figure 2.

The zircons ranged from ovoid to subhedral in shape and were up to ~300 μm in length. As in the original study (Liu and others, 1992) we attribute the rounding to abrasion during transport. Of the total of 53 grains initially analyzed using one-cycle

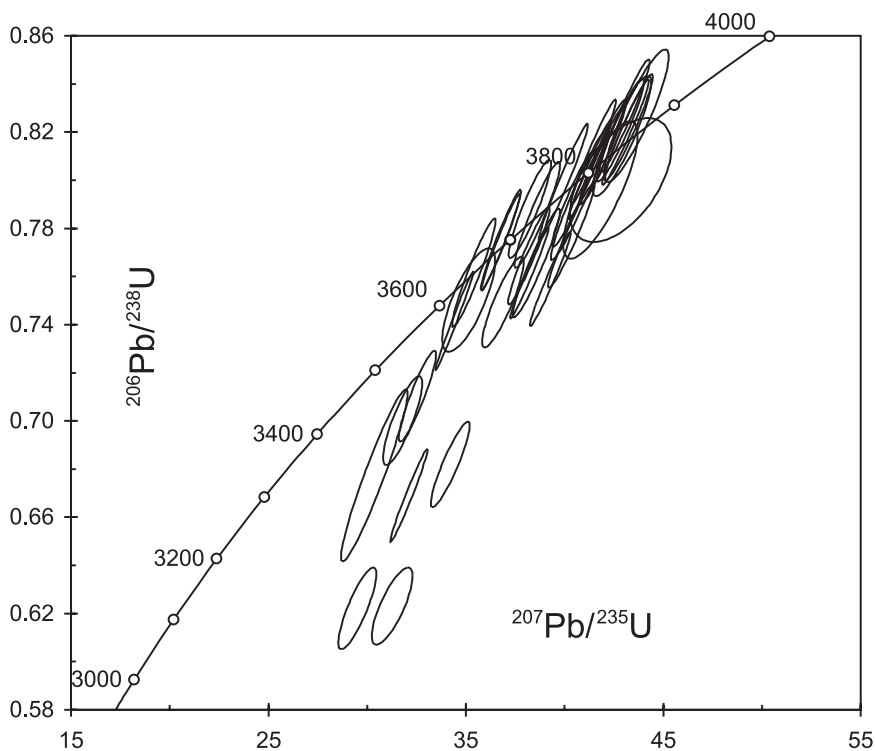


Fig. 3. Concordia plot of U-Pb SHRIMP data for zircons analyzed from the Caozhuang quartzite. Note that the three most discordant sites in table 1 are omitted in order that the detailed relationship of the older analyses might be clearly shown.

runs on the Beijing SHRIMP, 32 recorded ages in excess of 3.7 Ga. In the following discussion, we retain the original numbers used in the Beijing single-cycle runs and these are listed in table 1. Note that analyses 9 and 10 were collected on a single grain, as were analyses 48 and 49; all other grains have a unique number.

During re-polishing following insertion of the KIM-5 standard as a prelude to oxygen isotope analysis, zircons 8 and 17 were lost. Grain 8 had recorded a one-cycle  $^{207}\text{Pb}/^{206}\text{Pb}$  age of 3.86 Ga and grain 17 a  $^{207}\text{Pb}/^{206}\text{Pb}$  age of 3.72 Ga. During oxygen isotope studies, it was decided to obtain data at several sites within the remaining 30 grains (see below). Where possible, subsequent seven-cycle SHRIMP analyses were placed directly over these oxygen sites; where grain-size or closer spacing of oxygen sites demanded, the U-Pb data were collected at sites that had recorded the highest  $\delta^{18}\text{O}$  value.

The results of 38 SHRIMP Th-U-Pb analyses are presented in table 1 and are shown on a concordia diagram in figure 3. The data show some degree of discordance, but, as a population, are less discordant than either the original data set of Liu and others (1992) or that obtained by Wu and others (2005) from the same area and rock type using ICP-MS techniques.

The  $^{207}\text{Pb}/^{206}\text{Pb}$  ages range from  $3860 \pm 3$  Ma to  $3135 \pm 16$  Ma, with 13 sites recording ages of 3700 to 3800 Ma and 14 sites ages  $>3800$  Ma (table 1). With respect to the total population, the U and Th contents and the Th/U ratios show a range from 40 to 505 ppm, 6 to 414 ppm and 0.11 to 1.30, respectively; with average values of 161 ppm U and 85 ppm Th and an average Th/U ratio of 0.60. For zircon sites recording

ages between 3700 to 3800 Ma, the average values are 173 ppm U, 83 ppm Th, with an average Th/U ratio of 0.48. Finally, for the zircon sites with ages >3800 Ma, the average values are 154 ppm U, 106 ppm Th, with an average Th/U ratio of 0.80. The higher average Th/U ratio for the oldest zircon population is a striking feature.

With respect to age, the two oldest sites (grains 33B and 30A) record  $^{207}\text{Pb}/^{206}\text{Pb}$  ages of  $3859 \pm 3$  Ma (37% discordant) and  $3860 \pm 3$  Ma (2% discordant). The previous oldest zircon age obtained from this sample was  $3851 \pm 4$  Ma (8% discordant) recorded by Liu and others (1992). Excluding the two oldest grains, the seven next oldest concordant zircon sites define a concordia age of  $3832 \pm 4$  Ma with an MSWD of 1.2, which appears to identify a single population that is the oldest known from the North China Craton. However, the oldest rock currently identified from China is a  $3811 \pm 4$  Ma gneiss (sample Ch28) from Dongshan Scenic Park, Anshan (Song and others, 1996), so the source of the  $\sim 3832$  Ma population cannot be matched to known outcrops in the craton.

#### Oxygen Isotope Data

A total of 67 analyses were made on 30 zircons for oxygen isotope ratio. These data are bracketed by five groups of the KIM-5 zircon data totalling 21 spot analyses on the standard (table 2). Most zircons were analyzed twice, matching the original U-Pb analytical sites in the one-cycle runs on the Beijing SHRIMP, although three larger crystals were analyzed at a maximum of four sites.

The values of  $\delta^{18}\text{O}$  are quite homogeneous within each zircon. Only 2 crystals show variability greater than the 2SD precision on KIM-5, and all are within  $\pm 3\text{SD}$ . The two grains with variability of 2 to 3SD (#3 and #5) also show zonation in age of >150Ma. Thus, with the possible exception of these two grains, there is no evidence for zoning or heterogeneity in the oxygen isotope ratios of these zircons, supporting the conclusion that carefully chosen zircons preserve primary values of  $\delta^{18}\text{O}$  acquired upon crystallization (Valley and others, 1994; Peck and others, 2003; Cavosie and others, 2006; Page and others, 2007). Furthermore, if these zircons had exchanged oxygen isotopes during subsequent metamorphism, then analyses acquired near zircon rims would be expected to approach equilibrium with the surrounding high  $\delta^{18}\text{O}$  quartzite, but this is not seen.

Values of  $\delta^{18}\text{O}$  are plotted against age in figure 4 using the average  $\delta^{18}\text{O}$  for each zircon and the age of its oldest spot. Detrital zircons older than 3.7 Ga from the Beartooth Mountains, Montana (Valley and others, 2005) and older than 3.9 Ga from the Jack Hills, Western Australia (Cavosie and others, 2005) are shown for comparison. The average  $\delta^{18}\text{O}$  of the detrital zircons from the Chinese sample is 6.54 permil and the full range in values is 5.4 to 7.5 permil.

#### DISCUSSION

The  $\delta^{18}\text{O}$  values for zircons in this study fall within the range that is reported for igneous zircons of Archean age worldwide: 5 to 7.5 permil. These values include the range of zircons that have equilibrated with melts of primitive mantle composition, 4.7 to 5.9 permil, or they are mildly elevated above those values (Valley and others, 2005). While the range of  $\delta^{18}\text{O}$  values is similar, the Caozhuang quartzite detrital zircons have the highest average  $\delta^{18}\text{O}$  of any group of Archean zircons reported to date. The average value for zircons from this locality in eastern Hebei is 6.54 permil, which is  $\sim 0.3$  permil higher than that for other early Archean detrital zircons [fig. 4, Jack Hills  $6.28 \pm 0.09\text{‰}$  (1SE, 1SD=0.6)  $n = 41$ ; Beartooth Mountains  $6.2 \pm 0.15\text{‰}$  (1SE, 1SD=0.5)  $n = 10$ ]. Furthermore, the detrital zircons from the Caozhuang quartzite are on average nearly 1 permil higher in  $\delta^{18}\text{O}$  than magmatic zircons separated from Archean igneous rocks from the Superior Province of Canada ( $5.71 \pm 0.06\text{‰}$  [1SE, 1SD=0.6], 3.0 to 2.7 Ga,  $n = 104$  (King and others, 1998, 2000; Valley and others,

TABLE 2

*Ion microprobe analysis of oxygen isotope ratio from 10 micron spots on detrital zircons from sample CF89-26 of the Caozhuang quartzite in eastern Hebei, NE China*

Analysis #	Sample, spot		$\delta^{18}\text{O}$		IMF	$\delta^{18}\text{O}$		Grain Ave.	Age Ma $^{207}\text{Pb}/^{206}\text{Pb}$
			Raw	Error 2SD		VSMOW	Error 2SD		
133	CF89-26	KIM-5	7.23	0.19					
134	CF89-26	KIM-5	7.04	0.18					
135	CF89-26	KIM-5	6.95	0.12					
136	CF89-26	KIM-5	6.88	0.16					
137	CF89-26	KIM-5	6.82	0.19					
		<b>Average standard (2SD)</b>	<b>6.98</b>	<b>0.30</b>	<b>1.89</b>				
		<b>133-137, 152-155 (N=9)</b>							
138	CF89-26	9a	8.92	0.21		7.03	0.30	7.09	
139	CF89-26	9b	9.04	0.20		7.15	0.30		3825
140	CF89-26	10a	9.17	0.20		7.28	0.30	7.12	3834
141	CF89-26	10b	8.84	0.18		6.95	0.30		
142	CF89-26	14a	8.78	0.21		6.89	0.30	6.93	3797
143	CF89-26	14b	8.90	0.17		7.01	0.30		
144	CF89-26	14c	8.71	0.23		6.82	0.30		
145	CF89-26	14d	8.90	0.22		7.01	0.30		3827
146	CF89-26	18a	8.77	0.16		6.88	0.30	6.86	3793
147	CF89-26	18b	8.74	0.27		6.85	0.30		
148	CF89-26	32a	8.71	0.22		6.82	0.30	6.86	
149	CF89-26	32b	8.78	0.21		6.89	0.30		3772
150	CF89-26	28a	7.94	0.21		6.05	0.30	6.00	3837
151	CF89-26	28b	7.82	0.20		5.94	0.30		
152	CF89-26	KIM-5	7.15	0.22					
153	CF89-26	KIM-5	6.90	0.17					
154	CF89-26	KIM-5	6.80	0.18					
155	CF89-26	KIM-5	7.04	0.23					
		<b>Average standard (2SD)</b>	<b>6.99</b>	<b>0.27</b>	<b>1.90</b>				
		<b>152-155, 181-184 (N=8)</b>							
156	CF89-26	31a	7.84	0.20		5.95		5.94	3712
157	CF89-26	31b	7.82	0.22		5.93			
158	CF89-26	29a	8.27	0.20		6.37		6.40	3734
159	CF89-26	29b	8.32	0.14		6.43			
160	CF89-26	30a	8.26	0.25		6.36		6.31	3860
161	CF89-26	30b	8.16	0.15		6.26			
162	CF89-26	36a	8.72	0.18		6.82		6.81	3812
163	CF89-26	36b	8.70	0.20		6.80			
164	CF89-26	38a	8.49	0.20		6.59		6.53	3796
165	CF89-26	38b	8.37	0.17		6.47			
166	CF89-26	27a	7.72	0.18		5.82		6.00	3770
167	CF89-26	27b	8.08	0.26		6.18			3805
168	CF89-26	35a	7.84	0.26		5.94		5.94	3647
169	CF89-26	34a	8.04	0.12		6.14		6.03	3673
170	CF89-26	34b	7.83	0.21		5.93			
171	CF89-26	33a	7.12	0.20		5.22		5.39	3803
172	CF89-26	33b	7.46	0.22		5.56			3859
173	CF89-26	52a	8.66	0.17		6.76		6.60	3630
174	CF89-26	52b	8.35	0.17		6.45			
175	CF89-26	45a	8.45	0.16		6.55		6.47	3840
176	CF89-26	45b	8.28	0.22		6.38			
177	CF89-26	44a	8.12	0.25		6.22		6.16	3799
178	CF89-26	44b	7.99	0.20		6.09			
179	CF89-26	48a	8.61	0.22		6.71		6.76	
180	CF89-26	48b	8.70	0.21		6.80			3840
181	CF89-26	KIM-5	7.07	0.22					
182	CF89-26	KIM-5	7.01	0.25					
183	CF89-26	KIM-5	7.10	0.22					
184	CF89-26	KIM-5	6.82	0.42					

TABLE 2  
(continued)

Analysis #	Sample, spot	$\delta^{18}\text{O}$	Error	IMF	$\delta^{18}\text{O}$	Error	Grain Ave.	Age Ma $^{207}\text{Pb}/^{206}\text{Pb}$
		Raw	2SD		VSMOW	2SD		
	<b>Average standard (2SD)</b>	<b>6.92</b>	<b>0.26</b>	<b>1.83</b>				
	<b>181-184, 201-204 (N=8)</b>							
185	CF89-26 49a	8.59	0.19		6.76		6.81	
186	CF89-26 49b	8.69	0.23		6.86			3826
187	CF89-26 50a	8.92	0.19		7.09		7.09	3824
188	CF89-26 50b	8.90	0.26		7.07			
189	CF89-26 50c	8.94	0.19		7.11			
190	CF89-26 46a	8.93	0.19		7.10		7.09	3734
191	CF89-26 46b	8.92	0.19		7.09			
192	CF89-26 43a	8.74	0.19		6.91		6.94	3699
193	CF89-26 43b	8.79	0.20		6.96			
194	CF89-26 41a	7.67	0.17		5.84		5.96	
195	CF89-26 41b	7.92	0.26		6.09			3647
196	CF89-26 24a	8.85	0.18		7.02		6.96	3807
197	CF89-26 24b	8.72	0.19		6.89			
198	CF89-26 13a	9.40	0.17		7.57		7.52	
199	CF89-26 13b	9.48	0.26		7.65			3660
200	CF89-26 13c	9.17	0.21		7.34			
201	CF89-26 KIM-5	6.83	0.24					
202	CF89-26 KIM-5 mass calibration	6.78	0.17					
203	CF89-26 KIM-5	6.81	0.18					
204	CF89-26 KIM-5	6.92	0.15					
	<b>Average standard (2SD)</b>	<b>6.86</b>	<b>0.19</b>	<b>1.77</b>				
	<b>201-204, 217-220 (N=8)</b>							
205	CF89-26 20a	8.23	0.24		6.46		6.49	
206	CF89-26 20b	8.30	0.18		6.53			3681
207	CF89-26 7a	9.40	0.21		7.63		7.46	3770
208	CF89-26 7b	9.06	0.20		7.29			3752
209	CF89-26 5a	7.90	0.12		6.13		5.78	3682
210	CF89-26 5b	7.19	0.15		5.42			3135
211	CF89-26 3a	8.37	0.28		6.60		6.29	3594
212	CF89-26 3b	7.76	0.18		5.99			3761
213	CF89-26 19a	7.98	0.21		6.21		6.01	3773
214	CF89-26 19b	7.59	0.21		5.82			
215	CF89-26 15a	8.47	0.18		6.70		6.57	
216	CF89-26 15b	8.21	0.21		6.44			3609
217	CF89-26 KIM-5	7.03	0.24					
218	CF89-26 KIM-5	6.92	0.17					
219	CF89-26 KIM-5	6.86	0.18					
220	CF89-26 KIM-5	6.75	0.15					
					Sample Average		6.54	
					Standard Deviation		0.52	

2005), Barberton in southern Africa ( $5.53 \pm 0.21\%$  [1SE, 1SD=0.7], 3.5 to 2.7 Ga,  $n = 11$ , King, ms, 2001) or the central zone of the North China Craton ( $5.52 \pm 0.2\%$ ,  $n=3$ ; Valley and Liu, unpublished data). Most of the zircons have an average  $\delta^{18}\text{O}$  that is above 5.9 permil, outside the mantle range and, even if a conservative uncertainty of  $\pm 0.4$  permil is attached to each analytical value, over 60 percent of the zircons are still too high in  $\delta^{18}\text{O}$  to represent primitive melt compositions.

The elevation of average  $\delta^{18}\text{O}$  in Archean detrital zircon populations in general, and the Caozhuang sample in particular, could have one of several causes relating to the analytical technique, sedimentary processes, or the genesis of their host rock.

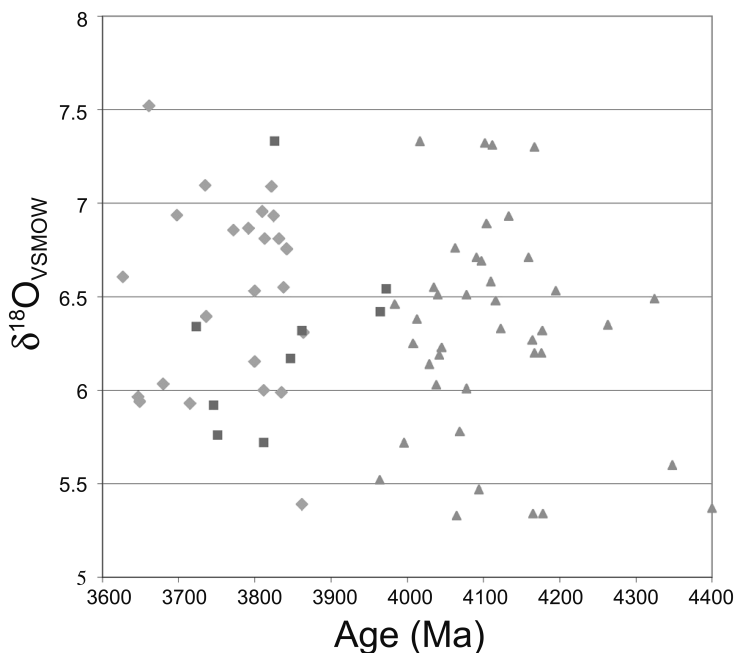


Fig. 4. Oxygen isotope ratio vs. U-Pb age for  $>3.6$  Ga detrital zircons of igneous origin. The range in values of  $\delta^{18}\text{O}$  from 5 to 7.5‰ is similar to that seen for zircons separated from other Archean igneous rocks, however a majority of samples are mildly elevated relative to values in high temperature equilibrium with mantle magmas, 4.7 to 5.9‰. [Data from this study, North China Craton (diamonds); Cavosie and others, 2005, Jack Hills (triangles); and Valley and others, 2005, Beartooth Mountains (squares)].

While the differences of 0.3 to 1.0 permil are shown to be significant based on the calculated standard errors ( $\text{SE} = \text{SD}/\text{N}^{0.5}$ ) or a t-test, these are measures of precision of the ion microprobe technique and do not address possible systematic errors that could influence accuracy. It is known that polishing relief, X-Y position in the mount, and the location of the standard can cause significant systematic error, but that with care these effects can be minimized to less than 0.3 permil (Valley and Kita, 2005). For this reason, we have mounted and polished the KIM-5 standard in the same mount as the sample zircons and all analyzed spots are within 5mm of the center of the mount.

It is likely that detrital zircons are sorted by size and shape, and that metamict grains are preferentially destroyed, but to create a systematic change in  $\delta^{18}\text{O}$  by sedimentary sorting would require a fortuitous and unknown process. It is more likely that the high values of this study result from the source rock. One possibility would be if a small percentage of the zircons are metamorphic in origin or have metamorphic overgrowths, since metamorphic zircons are typically higher in  $\delta^{18}\text{O}$  due to formation at lower temperatures and incorporation of oxygen from a supracrustal reservoir. However, all of the zircons in this study are homogeneous in  $\delta^{18}\text{O}$ , within 3SD as predicted by Poisson distribution, showing that there are no high  $\delta^{18}\text{O}$  overgrowths. Furthermore, CL images of the majority of grains (fig. 2) show oscillatory zoning, consistent with a magmatic origin; a view supported by the average Th/U ratio for all grains of 0.60.

The final alternative is that the original igneous parent rocks were higher in  $\delta^{18}\text{O}$  and more evolved than those from the other terranes that have been sampled. If correct, this explanation would have important implications for the geological evolu-

tion of the North China Craton. Such elevated values indicate that portions of high  $\delta^{18}\text{O}$  crust, a consequence of re-melting of rocks previously altered at the Earth's surface, were incorporated into the Early Archean magmas now represented by the detrital zircons analyzed in this study. The presence of mildly enriched magmas supports the evidence that continental crust had evolved in the North China Craton prior to 3.8 Ga (Liu and others, 2008) and that it underwent early reworking.

At first evaluation, this might suggest that the parent magmas to these zircons incorporated material with a crustal history that may significantly predate 3.8 Ga and that these ancient evolved rocks were distributed across the source area of the detrital zircons. Furthermore, the eastern Hebei detrital zircons show evidence of abrasion and long distance transport, suggesting that the area of evolved crust may have been extensive. Such a scenario has previously been proposed for the Jack Hills detrital suite with elevated  $\delta^{18}\text{O}$  as early as 4.3 Ga (Cavosie and others, 2005). However, on the contrary, the Hf data obtained from a suite of zircons from the same locality at Huangbaiyu in eastern Hebei Province by Wu and others (2005) indicated that the values were close to chondritic, leading the authors to suggest derivation of the host granitoid magma by remelting of juvenile crust that originated from a mantle that had not undergone significant differentiation.

This disparity can best be explained by invoking the rapid reworking of altered juvenile crust. It is well established that reworking can take place within a few million years, or less in magmatic complexes with repeated intrusion and contamination of the magma by altered wallrock, as for example in the granites of Skye (Monani and Valley, 2001) and the rhyolites of Yellowstone Plateau (Bindeman and Valley, 2001). On a larger scale, multiple orogenic events are recorded in the Grenville Province over a period of  $\sim 200$  Ma, resulting in extensive and rapid reworking on a geological time-scale (Peck and others, 2000). It would thus appear that such a process was operative in the source area of the most ancient zircons obtained so far from the North China Craton, indicating that crust formed at  $\sim 3.9$  to 3.8 Ga underwent rapid reworking between 3.86 to 3.60 Ga.

#### CONCLUSIONS

New SHRIMP U-Pb and CAMECA 1280 oxygen isotope data acquired on zircons collected from a fuchsite quartzite of the Caozhuang 'series' in the Qianxi complex at Huangbaiyu, eastern Hebei Province, China, reveal the following key features:

- (1) The oldest zircon  $^{207}\text{Pb}/^{206}\text{Pb}$  ages so far recorded from China -  $3859 \pm 3$  Ma (37% discordant) and  $3860 \pm 3$  Ma (2% discordant) - are present in Caozhuang quartzite sample CF89-26.
- (2) Seven zircon grains record a Squid concordia  $^{207}\text{Pb}/^{206}\text{Pb}$  age of  $3832 \pm 4$  Ma, probably reflecting a single population and from a source older than the oldest known rock in the North China Craton.
- (3) The average  $\delta^{18}\text{O}$  value for the 30 zircons analyzed for oxygen isotope ratio is 6.5 permil. This is  $\sim 0.3$  permil higher than suite averages for detrital zircons from the Jack Hills and Beartooth Mountains and nearly 1 permil higher than magmatic zircons from igneous rocks of the Superior Province and Barberton. The total range of  $\delta^{18}\text{O}$  (zircon) values from 5.4 to 7.5 permil is consistent with the range of mildly elevated values reported previously for Archean zircons (Peck and others, 2000; Cavosie and others, 2005; Valley and others, 2005).
- (4) These results suggest that strong reworking of altered continental crust only slightly older than 3.8 Ga occurred in the North China Craton, at least in the zircon source region. Since the available Hf isotopic data appear to preclude significantly older crust in the area, these results attest to rapid reworking of altered juvenile crust.

## ACKNOWLEDGMENTS

We thank Adam Frew for assistance with the SHRIMP analyses. We also thank Yong-Fei Zheng and an anonymous reviewer for their helpful suggestions. This research was supported by the US National Science Foundation (EAR020734) and Department of Energy (93ER14389). This is the Institute for Geoscience Research (TIGeR) publication number 74.

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