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°DISTRIBUTION AND SIGNIFICANCE OF PRE-NEOPROTEROZOIC ZIRCONS IN JUVENILE NEOPROTEROZOIC IGNEOUS ROCKS OF THE ARABIAN-NUBIAN SHIELD

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ABSTRACT. Igneous rocks of the Arabian-Nubian Shield (ANS) have lithologic associations (ophiolites, calc-alkaline igneous rocks, immature sediments) and radiogenic isotopic compositions consistent with formation as juvenile continental crust as a result of accreting intraoceanic arc systems during 880 to 630 Ma, with crustal differentiation continuing until ~570 Ma. ANS igneous rocks locally contain zircons with ages that are much older than this, leading some researchers to infer the presence of pre-Neoproterozoic crust at depth in spite of Nd isotopic evidence that ANS crust is overwhelmingly juvenile. The ANS is flanked by pre-Neoproterozoic crust but geochronology and isotopic compositions readily identify such tracts. We have compiled U-Pb zircon ages for 302 samples of ANS igneous rocks that have been analyzed for the age of individual zircons (2372 ages) and find that a significant proportion (~5%) of these have ages older than 880 Ma (zircon xenocrysts). Zircon xenocrysts are more common in volcanic than plutonic rocks and mafic relative to felsic igneous rocks. Four explanations are considered: 1) contamination during sample processing; 2) involvement of pre-Neoproterozoic crust; 3) incorporation of detrital zircons from sediments; and 4) inheritance from a mantle source. Possibilities 1 and 2 are discounted, and we conclude that the presence of pre-880 Ma zircon xenocrysts in ANS igneous rocks with mantle-like isotopic compositions indicates either incorporation of sediments or inheritance from the mantle source region, or both.

Key words: Zircon, Arabian-Nubian Shield, Geochronology, Neoproterozoic, Continental crust.

INTRODUCTION

Studies of how Earth's crust formed have advanced greatly because of two isotopic techniques. Radiometric age determinations—telling us when the igneous rocks in question formed—especially by analyzing U and Pb in zircons (Harley and Kelly, 2007; King, 2008); now are remarkably precise and routine. Determinations of the isotopic composition of ancient rocks, particularly of Sr, Nd, Hf, and Pb, corrected for post-crystallization radiogenic growth yield complementary information in the form of "initial" isotopic compositions of the newly formed igneous bodies. Initial isotopic compositions can be used to infer the nature of the melt source (Faure, 2001; Dickin, 2005) and are especially useful for distinguishing rocks that formed directly by mantle melting (±crystal fractionation) versus those that formed by remelting of crust that existed for a significant period of time (100's of m.y.) prior to melt generation. Continental crust dominated by igneous rocks with initial isotopic compositions that approximate the expected isotopic composition of the mantle when the melt solidified are referred to as "juvenile crust"; this includes juvenile crust remelted soon (a few m.y.) after formation. In contrast, crust dominated by igneous rocks with isotopic compositions different from those expected for the mantle of the age of the igneous

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rocks may be the result of the remelting of pre-existing continental crust, in which case the crust is referred to as "reworked," "rejuvenated" or "remelted."

Juvenile versus reworked crust can also be distinguished by whether isotopic compositions are relatively homogeneous and mantle-like (in the first case) or variable (in the second case). This is because the isotopic composition of the convecting asthenospheric mantle varies little geographically, such that the isotopic composition of juvenile crust is monotonous, whereas continental crust has a range of isotopic compositions reflecting lateral and vertical variations in Rb/Sr, Sm/Nd, Lu/Hf, U/Pb, *et cetera.* As a result, melts of older continental crust have great variations in initial isotopic composition that reflect radionuclide parent-daughter ratios that are distinct from asthenospheric values. Furthermore, juvenile crust generally is associated with abundant mantle-derived "oceanic" igneous rocks—such as peridotite, basalt, and andesite—whereas reworked crust has fewer or no oceanic lithologies. Radiogenic isotopes are sufficiently sensitive that the presence of melts of reworked ancient crust can generally be detected even where relatively small proportions of such melts are mixed with melts of more depleted and well-mixed asthenosphere.

This simple story becomes more complicated when subcontinental lithosphere rather than asthenosphere is the mantle source (Carlson and others, 2005). Continental lithospheric mantle comprise stable "keels" that do not homogenize with time. This lithosphere tends to preserve the various geochemical fractionation events that affected it, such as depletions due to melt extraction and enrichments due to subduction-related metasomatism. Ancient subcontinental lithospheric mantle often has distinct isotopic compositions indicating isolation from the asthenosphere for a long time. Nevertheless, distinct isotopic compositions are readily inferred to identify old lithospheric material, which could be the continental crust, lithospheric mantle, or both.

Zircon ages can also help distinguish juvenile versus reworked crust. This is because zircons are among the most refractory of minerals, quite difficult to destroy by dissolution or melting. Consequently, igneous rocks from reworked crust invariably contain zircons that are mixtures of crystals formed with the melt and others inherited from the protolith, significantly older than the igneous rock itself. In the past it was very difficult to determine the ages of single zircons but now it is routine and by several methods: thermal ionization mass spectrometry (TIMS), evaporation techniques, secondary ion mass spectrometry (SIMS), and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) techniques (see Davis and others, 2003 for a superb review of zircon geochronology). In most instances, the presence of zircons with radiometric ages that are significantly greater than the crystallization age of their host rock implies the participation of older crust, especially where the host rock has initial isotopic compositions that also indicate crustal reworking.

But there are also instances where igneous rocks have isotopic compositions indicating that they are juvenile contributions from the mantle but contain zircons with ages that are significantly older than the crust itself. This paradox exists for the Arabian-Nubian Shield (ANS) and may be present for other tracts of Neoproterozoic juvenile crust, such as the Central Asian Orogenic Belt (Kröner and others, 2007). This apparent contradiction can be resolved by closer examination of the information. The Sr and Nd isotopic compositions relate to the considered magma and its source. If enough lithologies of a crustal tract are analyzed for Sr and Nd isotopic compositions, the latter can be considered as representative of the studied crust. This is not the case for inherited zircons: zircon is a very resilient mineral, difficult to dissolve or to destroy and, except in alkaline-peralkaline magmas, it keeps the memory of the different stages of crystallization that it experienced (for example, Bendaoud and others, 2008). Additionally, because of the analytic techniques now available, zircons provide robust ages but these are the ages of the mineral, not necessarily the rock; in some cases the zircon ages may be quite ancient relative to the age of the rock. Instances occur, for example, of oceanic basalts and gabbros—known to be only a few million years old—that contain ancient zircons (Pilot and others, 1998; Belyatsky and others, 2008; Bortnikov and others, 2008). In situations like this, a fundamental question concerns the source of the zircons: the ancient zircons cannot come from ancient crust—there is none.

New approaches are needed if we are to understand the significance of ancient zircons in otherwise juvenile igneous rocks. In this contribution, we present a new perspective on this problem, by summarizing the distribution of ancient zircons in Neoproterozoic crust of the Arabian-Nubian Shield ANS (fig. 1). We define zircon xenocrysts for the purposes of our study as zircons that are significantly older than the

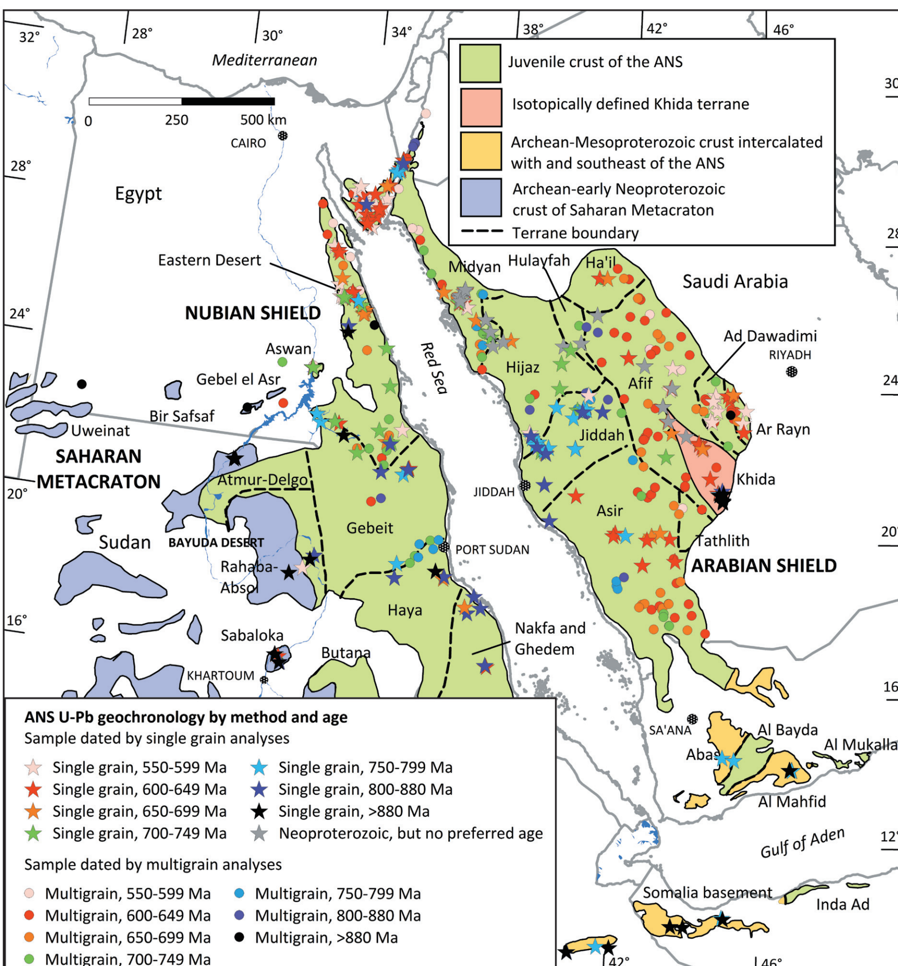

Fig. 1. Distribution of igneous rocks with ages determined by U-Pb or Pb-Pb analyses of zircon (Locations given in Appendix A Table A1, http://earth.geology.yale.edu/~ajs/SupplementaryData/2010/07SternTableA1.doc). Locations are plotted on a simplified map of the Arabian-Nubian Shield, from Johnson and Woldehaimanot (2003). Terrane boundaries are generally marked by ophiolite-decorated sutures (Stern and others, 2004). Samples are distinguished showing those with conventional multigrain ages and those with single grain analyses, including Pb-Pb evaporation and SIMS determinations.

igneous rock that contains them. We consider the implications of these data for understanding the related problems of ANS crust formation and the significance of more ancient zircons in otherwise juvenile-appearing continental crust.

THE ARABIAN-NUBIAN SHIELD

The Arabian-Nubian Shield (fig. 1) is mostly juvenile continental crust created in Neoproterozoic time, as demonstrated by oceanic lithologies such as ophiolites (Stern and others, 2004) and by mantle-like isotopic compositions of especially Sr and Nd (Stern, 2002a; Stoeser and Frost, 2006). The ANS comprises several arc terranes that formed beginning about 880 Ma and that coalesced thereafter; collision between fragments of East and West Gondwana beginning ~630 Ma terminated arc accretion but magmatism and deformation continued until ~570 Ma. The ANS became a stable continental region by the beginning of Cambrian time at ~540 Ma. Massive volumes of granitic magma were emplaced at various stages in the evolution of the ANS (Johnson and Woldehaimanot, 2003).

ANS igneous rocks are the focus of our study. We do not have an estimate of the proportion of plutonic versus metavolcanic and volcanic rocks for the whole ANS but it should be similar to proportions for the Arabian Shield, where plutonic rocks cover 25 percent more area than layered basement rocks (metavolcanics and metasediments).

Lower crustal xenoliths brought up through ANS crust by Cenozoic volcanic eruptions are gabbroic, with isotopic compositions indicating formation in Neoproterozoic time (McGuire and Stern, 1993), as do upper mantle xenoliths (Nasir and Rollinson, 2009). Older crust that was reworked during the Neoproterozoic bounds the ANS to the west (Saharan metacraton; Abdelsalam and others 2002; Küster and others, 2008) and south (Windley and others, 1996; Whitehouse and others, 2001). A region of reworked older crust is inferred to be present in the Khida terrane in the eastern part of the ANS, and evidence for late Mesoproterozoic crust in the north has recently been presented (Be'eri-Shlevin and others, 2009c). There is, however, no evidence to date for pre-Neoproterozoic crust beneath the Arabian Platform to the east of the ANS (fig. 1). Within the bulk of the ANS, other than in these regions of documented older crust, there is scant evidence of crustal reworking, either in the form of S-type granites or isotopic compositions indicating the presence of more ancient, reworked crust. All researchers agree that, with the exception of the aforementioned older crust fragments and an uncertain boundary with the Saharan Metacraton to the west, the ANS is a remarkable example of juvenile crust formation by Neoproterozoic plate tectonics (Patchett and Chase, 2002).

COMPILATION OF DATA

We compiled available U-Pb and Pb-Pb zircon ages from the ANS (Appendix A table A1, http://earth.geology.yale.edu/~ajs/SupplementaryData/2010/07SternTableA1.doc). Locations of 559 samples with zircon age determinations on igneous rocks only are shown in figure 1 and listed in Appendix A, table A1, http://earth.geology.yale.edu/~ajs/SupplementaryData/2010/07SternTableA1.doc. This figure distinguishes between zircon ages where many zircons were analyzed (conventional multigrain, 252 ages, circles) and those where individual zircons were analyzed (307 rock ages, stars), using either whole-grain techniques TIMS (14 rock ages) or evaporation techniques (108 rock ages) or point analyses using SIMS (182 rock ages) or LA-ICP-MS (3 rock ages).

Conventional multigrain analyses give useful crystallization ages where zircon xenocrysts are not significant, and such age determinations in tandem with Rb-Sr whole-rock dating efforts over the past 30 years have revealed the most important times of Neoproterozoic igneous activity as well as the presence of older crust to the west (Sultan and others, 1994) and to the south (Lenoir and others, 1994; Whitehouse and others, 2001) of the ANS (fig. 1). But such analyses cannot easily identify the presence of ancient xenocrystic zircons. Multigrain fractions that define discordia between Neoproterozoic and older ages indicate that such xenocrysts exist but large uncertainties on upper intercept ages may suggest that xenocrysts of more than one age are present. In contrast, samples dated using single zircon techniques generally obtain individual ages for several (~5-10) grains from each sample and use acceptable results (defined by the researcher, generally on the basis of concordant ages, low common Pb, moderate U contents, Th/U, etc.) to infer the age of the rock. Zircon xenocrysts, if present, are readily identified.

Single zircon age determinations are powerful tools for identifying magmatic zircon and distinguishing these from older xenocrysts, if present. Pb-Pb evaporation of single zircon only provides ^{207}Pb/^{206}Pb ages and cannot reveal whether a zircon has lost Pb (Kober, 1986). This technique is nevertheless suitable for identifying zircon xenocrysts, although Pb-loss can result in erroneous ages. SIMS ages have blossomed since the first high precision ages with this technique were reported (Compston and others, 1982). SIMS ages typically have uncertainties that are significantly greater than those done by the best TIMS labs (Bowring and Schmitz, 2003) but make up for this by allowing more zircons in more rocks to be dated. SIMS U-Pb zircon ages of the ANS have become increasingly important since the first such study by Kröner and others (1987). LA-ICP-MS ages are similar to SIMS ages, except that spots are larger (~30-65 μm vs. ~15-30 μm) and generally deeper (thus sampling a much larger zircon volume) and analyses are faster. This technique can rapidly provide a large number of ages and for this reason is increasingly utilized to date detrital zircons (for example, Dickinson and Gehrels, 2008). There are currently few LA-ICP-MS zircon ages for ANS igneous rocks but more are likely to be reported in the future.

Single zircon studies of ANS igneous rocks reveal that >880 Ma zircons—which are older than ANS juvenile crust and so must be xenocrystic—are locally found (fig. 2). As shown in figure 2, 29 igneous rock samples from the juvenile ANS crust (igneous rocks with ages <880 Ma), or about 9 percent of the igneous zircons dated by single-zircon methods, are xenocrystic. [For this discussion, a zircon is identified as xenocrystic if it is 200-million years or more older than the host rock. This is an arbitrary but conservative limit, useful for the purposes of this study.] In terms of the entire zircon population from ANS rocks dated by single-zircon methods, about 5 percent of the zircons give ages greater than 880 Ma (table 1). There is nothing spatially systematic about the occurrences of igneous rocks with >880 Ma zircon xenocrysts; they are found on both sides of the Red Sea and are not concentrated near regions of older crust that are known to exist to the west or south (fig. 2). The occurrence of >880 Ma xenocrysts does seem to be sensitive to lithology however; they are almost four times as abundant in volcanic rocks (~11% of 660 zircons) than in plutonic rocks (~3% of 1733 zircons).

Table 1 summarizes salient statistics about the single zircon ages in our database (Appendix A, table A2, http://earth.geology.yale.edu/~ajs/SupplementaryData/2010/08SternTableA2.doc). A total of 2393 zircon ages were compiled, of which ~72 percent are from plutonic rocks (mostly granitic) and ~28 percent are from volcanic rocks. About 64 percent of these we consider to be sufficiently concordant (<10% discordant) to provide useful age information (62% of plutonic zircon ages, 69% of volcanic zircon ages); the slightly more discordant nature of plutonic zircons probably reflects their higher U contents and consequently more damaged lattices. There are a small number of alkali granites and ring complexes of Paleozoic and Mesozoic age in the ANS (for example, Abdel-Rahman and Martin, 1990), but these are of no interest to our study. Igneous rocks in our database yielding <550 Ma ages are actually all Neoproterozoic (N=166, 6.5%). There is a profound unconformity between Cam-

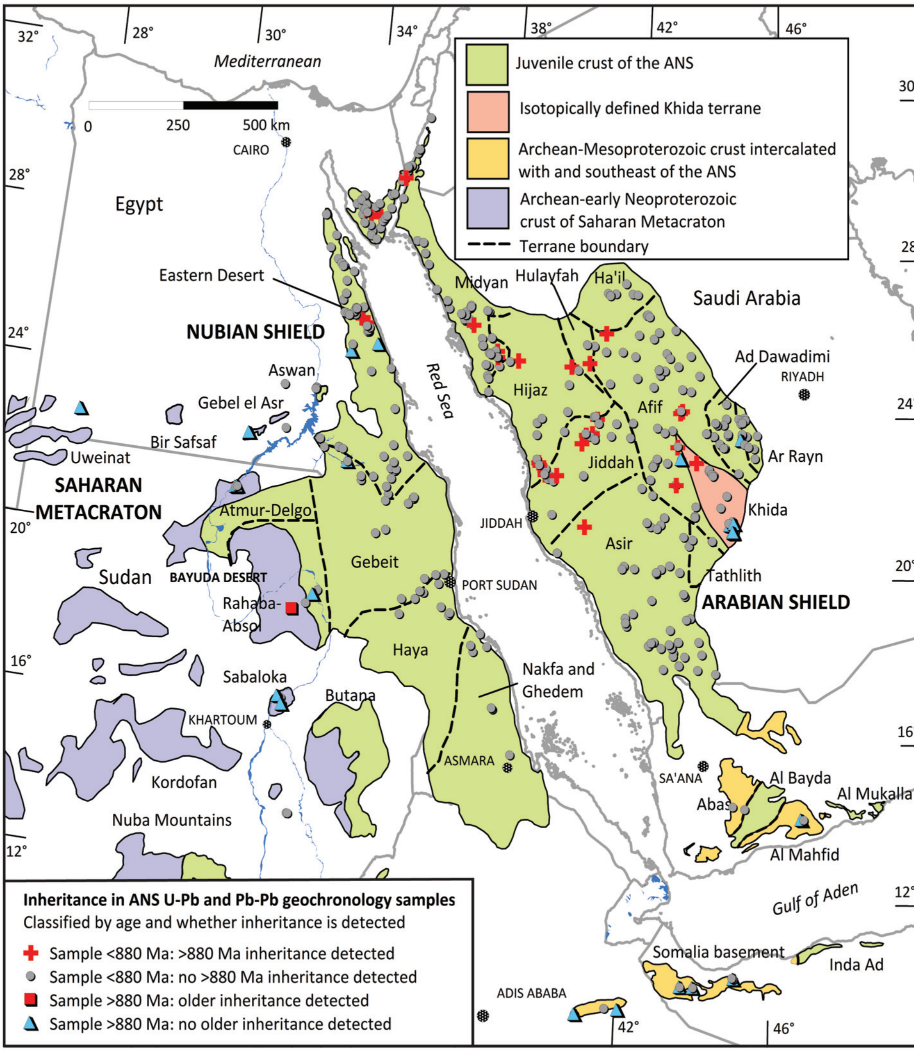

Fig. 2. Summary of zircon geochronologic results indicating the presence or absence of pre-880 Ma xenocrystic zircons. See text for discussion.

brian sandstones and underlying basement that is well preserved in Arabia (Avigad and others, 2005). Because this unconformity formed at ~550 Ma and no igneous rocks intrude it, we infer that zircon ages for basement igneous rocks of less than ~550 Ma are geologically unreasonable, whether or not they are concordant. These ages are excluded from further consideration here.

The age distribution of zircons from igneous rocks that are <10 percent discordant and older than 550 Ma is summarized in figures 3A–C. Figure 3A shows all data, which are dominated by Neoproterozoic ages. Figure 3C summarizes the distribution of 1430 zircon ages that are Neoproterozoic (93.5% of "concordant" ages); these are dominated by 600 to 625 Ma ages, largely from granitic plutons (the database contains almost 3× as many ANS plutonic zircon ages than metavolcanic zircon ages). This age

Table 1

Variations in single zircon ages with lithology

	Total	Plutonic	Volcanic	Felsic Pluton.	Mafic Pluton.	Felsic Volc.	Mafic Volc.
Total	2393	1733	660	1325	408	476	184
%T	100	72.4	27.6	55.0	17.2	20.1	7.8
%L <10% disc. >550 Ma	64.0	62.2	68.8	61.1	65.4	67.0	73.4
N <10% disc. >880 Ma	101	43	58	22	21	31	27
%T <10% disc. >880Ma	100	40.8	59.2	19.4	21.4	31.6	27.6
N >880 Ma	126	51	75	23	28	44	31
%L <10% disc. >880 Ma	4.2	2.3	8.8	1.4	5.1	6.5	14.7
%L >880 Ma	5.3	2.9	11.3	1.7	6.9	9.2	16.8

N = number of grains; %T = percentage of all grains; %L = percentage of grains from that lithology; disc. = discordant; Pluton. = Plutonic; Volc. = Volcanic.

distribution is not representative of ANS crust, which largely formed at 700 to 800 Ma, but is contemporary with terminal collision between fragments of E. and W. Gondwana at c. 630 Ma. There are 100 pre-880 Ma single zircon ages that are <10 percent discordant, ~4 percent of all single zircon ages and ~6.5 percent of all "concordant" zircon ages (fig. 3B).

There may be some compositional control on preservation of zircon xenocrysts. ANS granitic rocks that are >610 Ma are largely wet and thus cool (<800 °C), subduction-related "I-type" plutons (Chappell and White, 2001), formed under conditions that favor preservation of zircon xenocrysts (Watson and Harrison, 1983). In contrast, ANS granitic rocks <610 Ma include a large proportion of dry, hot (>900 °C), post-orogenic "A-type" plutons (King and others, 2001), formed under conditions that favor dissolution of zircon xenocrysts (Watson and Harrison, 1983). We do not have sufficient geochemical data on dated samples to more clearly distinguish ANS I-type from A-type granitic rocks, but there is little difference observed between the two age groups in terms of pre-Neoproterozoic zircon xenocrysts. There are 50 plutons with ages between 550 and 610 Ma; these have 658 zircon ages >550 Ma of which 1.7 percent are >880 Ma. There are 73 plutons with ages >610 Ma containing 826 zircon ages >550 Ma, of which 2.4 percent are >880 Ma.

ANS metamorphosed volcanic rocks have proportionately more xenocrystic zircons than do plutonic rocks. Table 1 shows that volcanic rocks surveyed here contain 50 percent more xenocrystic zircons than do plutonic rocks, even though there are about 3× as many plutonic as volcanic rocks analyzed. This means that xenocrystic zircons are proportionately ~5× more common in volcanic rocks relative to plutonic rocks. Even though Arabian Shield plutonic rocks cover 25 percent more area than layered basement rocks (metavolcanics and metasediments), this implies that the vast majority of ANS xenocrystic zircons are found in the metavolcanics.

Another significant observation is that mafic igneous rocks have a higher proportion of zircon xenocrysts than do felsic igneous rocks, both for plutonic rocks (2.3 vs. 8.8%) as well as volcanic rocks (6.5 vs. 14.7%). Zircons in mafic volcanic rocks thus contain proportionately ~10× more zircon xenocrysts than do felsic plutonic rocks (1.7 vs. 16.8%).

The pre-880 Ma zircons in ANS igneous rocks show four main pulses (fig. 3B): Neo-Mesoproterozoic (0.9-1.15 Ga), late Paleoproterozoic (1.7-2.1 Ga), Paleoproterozoic-Neoarchean (2.4-2.8 Ga) and Paleoarchean (>3.2 Ga). Crust with these ages is documented from Yemen, southern Arabian Shield, Sudan, SW Egypt, and perhaps—

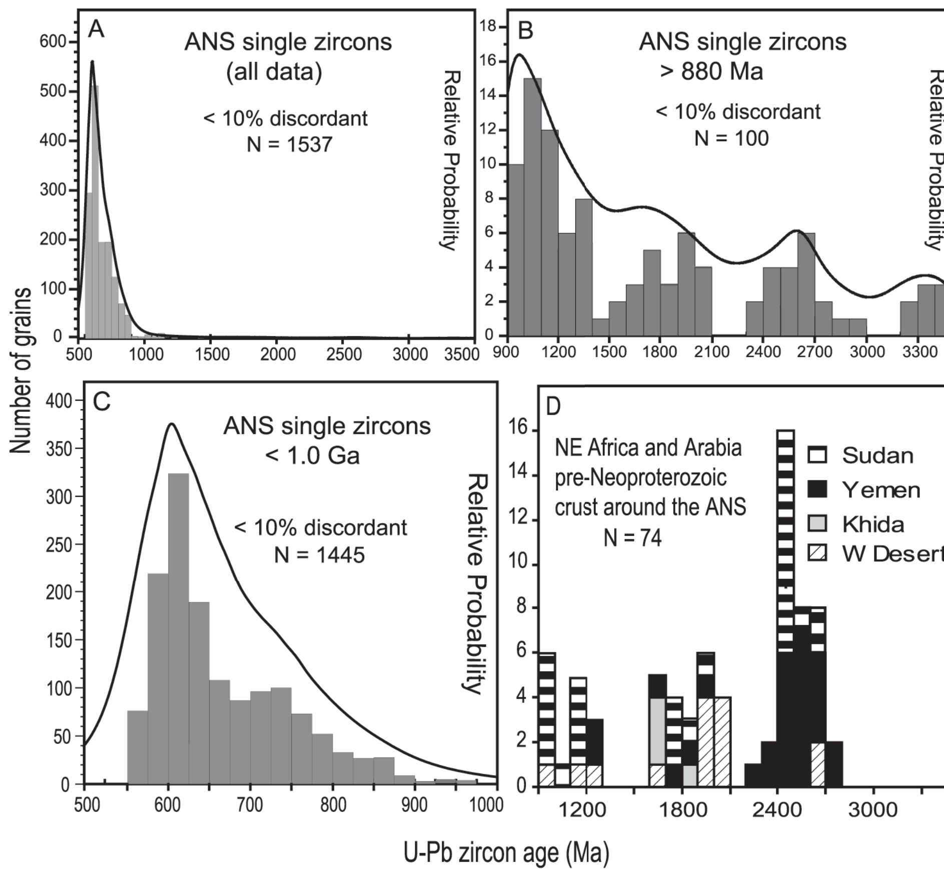

Fig. 3. Distribution of single zircon ages from the ANS (A-C) and pre-Neoproterozoic crust in the region (D). A–C: Histograms (gray bars) show actual ages, curves show density probability distribution, from Isoplot (Ludwig, 2003). Discordant ages are inferred from $^{207}Pb/^{206}Pb$ for >1.0 Ga, $^{206}Pb/^{238}U$ for <1.0 Ga. (A) All ANS zircon ages that are <10% discordant. Bin size = 50 m.y. (B) All zircon ages >900 Ma that are also <10% discordant. Bin size = 100 m.y. (C) Zircon ages <1.0 Ga that are <10% discordant. The peak of ages 600 to 625 reflects disproportionate sampling of granitic rocks, not reflective of abundance of rocks of different ages in the shield. Bin size = 25 m.y. (D) Ages of pre-Neoproterozoic crust around the ANS, from Ali and others (2010) modified to show additional ages for Bayuda Desert (Sudan) igneous rocks (Küster and others, 2008). Bin size = 100 m.y.

because they are found in metasediments—N. Sinai. The distribution of pre-880 Ma crust identified by magmatic zircon ages in (Khida terrane) and around (Yemen; Saharan metacraton) the ANS is shown in figure 3D. This shows three clusters of ages that are quite similar to the youngest 3 clusters of pre-ANS xenocrystic zircons: 900 Ma to 1.25 Ga, 1.55 to 2.1 Ga, and 2.3 to 2.7 Ga. ~900 Ma zircons are known from igneous rocks in the Bayuda Desert, Sudan (Küster and others, 2008) and the recent discovery of sediments in Sinai containing only ~1.0 Ga zircons (Be'eri-Shlevin and others, 2009c) strongly suggests the presence of Grenville/Kibaran crust here as well. These occurrences help explain the presence of a strong secondary peak of this age in detrital zircons from Cambro-Ordovician sandstones of Jordan and Israel (Avigad and others, 2005). The second and third pulses are known to exist around the ANS, but pre-3.2 Ga crust is not known from anywhere in the region. These peaks are also similar to global age clusters, inferred from igneous rock ages (Condie and others, 2009).

Neodymium Isotopic Systematics

Sm-Nd isotopic data for all available whole-rock samples (some of which also have single-zircon ages) are tabulated in Appendix A, table A3, http://earth.geology.yale.edu/~ajs/SupplementaryData/2010/09SternTableA3.doc along with Nd model ages calculated using both the DePaolo (1981) and Goldstein and others (1984) models. These data are graphically presented in figures 4 and 5. Figure 4 shows ε_{Nd} (t) versus age for these samples, distinguishing samples of ANS juvenile crust (both with and without pre-880 Ma xenocrysts) as well as data for pre-880 Ma crust from the ANS periphery. ANS juvenile crust samples all have positive $\varepsilon_{Nd}(t)$. In contrast, samples of Neoproterozoic age and older from the Khida terrane and Saharan metacraton have $\varepsilon_{Nd}(t)$ that are zero or negative. Igneous rocks with significant contributions from older crust will plot between the mantle composition and that of the older crust, depending on the relative contributions of each. If the ANS samples with zircon xenocrysts experienced a significant contribution from older crust, they should have intermediate $\varepsilon_{Nd}(t)$. There is no obvious difference on this diagram between those samples with and without xenocrystic zircons. This does not mean that there is no contribution from older crust but, if any, it should be very low considering the sensitivity of Nd isotopes to such inputs.

Figure 5 shows the Nd isotopic data differently, as calculated Nd model ages for samples with single zircon ages that also have $^{147}Sm/^{144}Nd = 0.165$ or less; that is, for samples that are likely to yield meaningful Nd model ages (Stern, 2002a). We believe that the DePaolo model gives more realistic Nd model ages, for reasons explained by Stern (2002a) and Liégeois and Stern (2010) but others prefer the Goldstein and others (1984) model so this is also shown. It should be noted that model ages calculated using the Goldstein and others (1984) model are typically ~200 m.y. older than those calculated with the DePaolo (1981) model. Caution is thus required when interpreting Goldstein and others (1984) Nd model ages that are a few hundred millions of years older than the crystallization ages as indicating the involvement of older crust. This effect is evident from comparing the histograms in figure 5. Figure 5A [Goldstein and others' (1984) model] has a mean Nd model age for ANS juvenile crust (no xenocrysts) of 0.99±0.2 Ga whereas a Nd model age of 0.79±0.20 Ga is calculated using the DePaolo (1981) model. Igneous rocks from older crust in the region have much older mean Nd model ages of 2.15±0.40 Ga (Goldstein and others, 1984) and 1.98±0.39 Ga (DePaolo, 1981). There are relatively few samples (13) of ANS juvenile crust with zircon xenocrysts and Sm-Nd isotopic data, but these define a mean that is slightly higher than samples of ANS juvenile crust with no detectable zircon xenocrysts (0.92±0.17 Ga (DePaolo, 1981) and 1.15±0.13 Ga (Goldstein and others, 1984). This could be taken as evidence for some participation of older crust but the large standard deviations indicate complete overlap with the juvenile ANS (no xenocryst) data, so nothing conclusive can be said in this regard. Samples of <880 Ma igneous rocks of the Khida terrane that contain ancient zircon xenocrysts provide a good example of older crust involvement. These give Nd model ages that reflect that of the Paleoproterozoic basement (1.91±0.42 Goldstein model age; 1.72±0.45 Ga DePaolo model age).

What Is the Source of Pre-Neoproterozoic Xenocrystic Zircons in Juvenile Crust of the Arabian-Nubian Shield?

One explanation for the source of zircon xenocrysts in otherwise juvenile ANS igneous rocks is that these were introduced during sample processing. This is unlikely since 3 different facilities independently processed samples showing pre-Neoproterozoic zircon xenocrysts (University of Texas at Dallas, University of Oslo, and Curtin University). We conclude that the pre-880 Ma zircons come from the rocks themselves. A second explanation is that these have been picked up from older crust beneath the region. This is the explanation for ~20 Ma Himalayan leucogranites, which contain

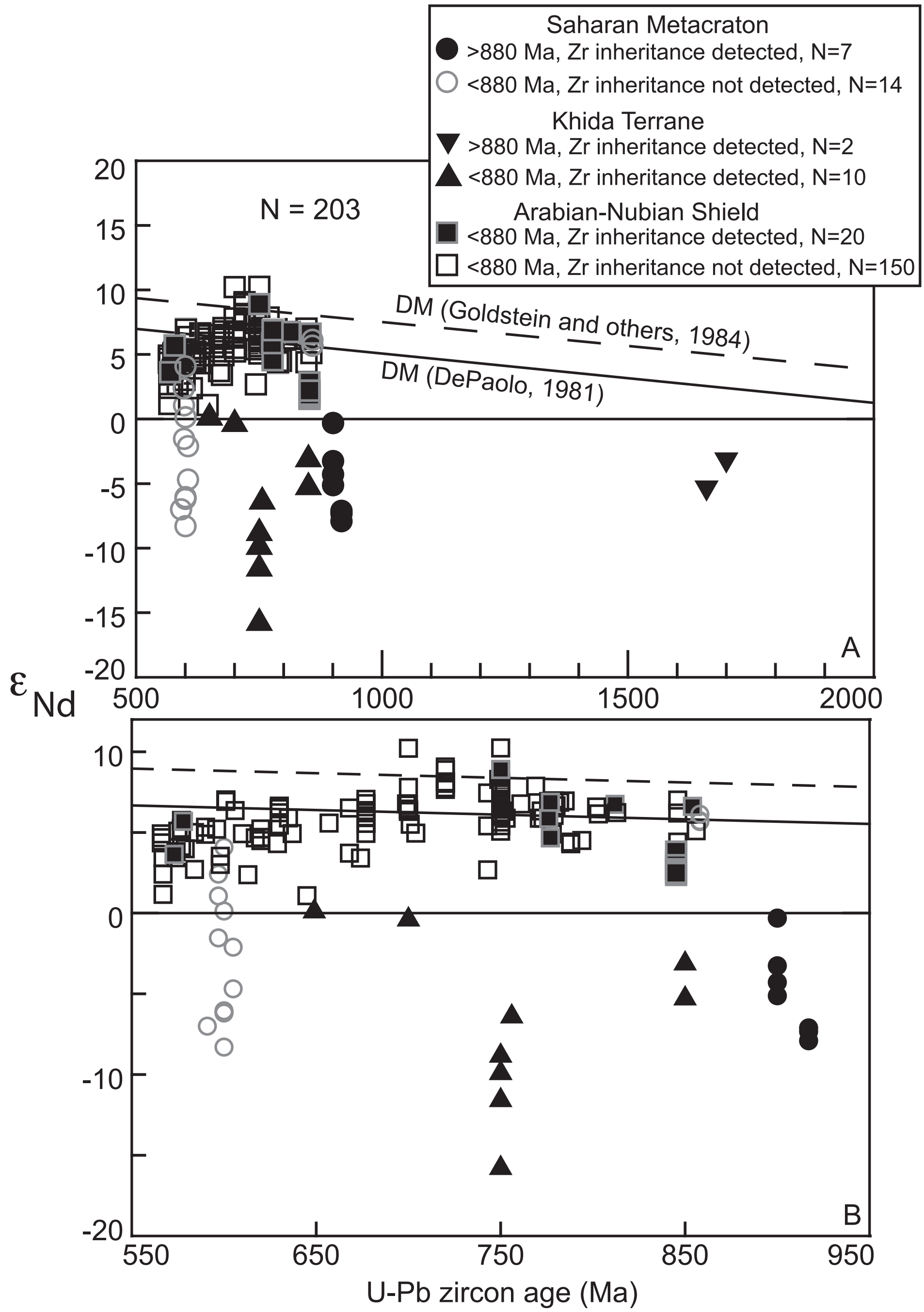

Fig. 4. Initial ε_{Nd} versus crystallization age for: (A) all Neoproterozoic igneous rocks of the Arabian-Nubian Shield and pre-Neoproterozic rocks from Khida Terrane (Saudi Arabia) and Saharan Metacraton rocks and (B) detail for Neoproterozoic rocks. Samples with pre-Neoproterozoic zircon xenocrysts are distinguished. Also shown are reference lines for the chondritic uniform reservoir (CHUR) and the depleted mantle (DM) evolution curves of DePaolo (1981) and Goldstein and others (1984). Data sources: Küster and others, 2008; Moussa and others, 2008; Hargrove and others, 2006a, 2006b; Zimmer and others, 1995; B. H. Ali and others, 2009; Woldmichael and others, 2010; Stacey and Hedge, 1984; Agar and others, 1992; Whitehouse and others, 2001; Claesson and others, 1984; Stoeser and Frost 2006; Duyverman and others, 1982; Bokhari and Kramers 1981; Liégeois and Stern (2010).

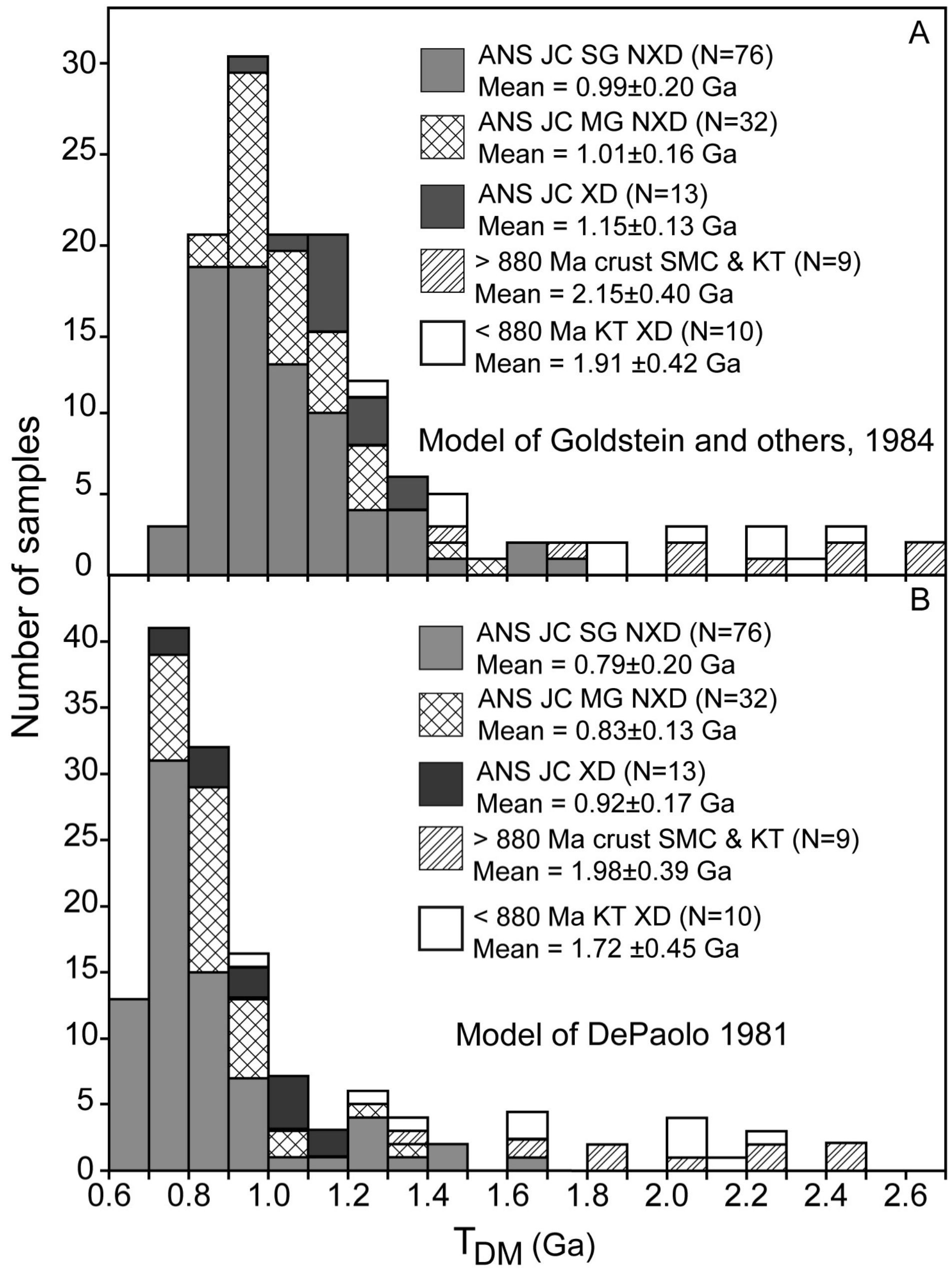

Fig. 5. Nd model ages for ANS igneous rocks with and without >880 Ma zircon xenocrysts and surrounding pre-880 Ma crust, calculated using the algorithms of Goldstein and others (1984) (A) and DePaolo (1981) (B). JC = juvenile crust; SMC = Saharan metacraton; KT = Khida terrane; SG = single grain zircon age; MD = multigrain zircon age; NXD = no ancient zircon xenocrysts detected; XD = ancient zircon xenocrysts present. Uncertainties are ±1 standard deviation. See text for further discussion.

abundant xenocrystic zircons (Zhang and others, 2004), mostly as cores around which younger zircon has grown (Lee and Whitehouse, 2007). In this case, the immediate presence of older crust is documented and granites have Nd isotopic compositions that reflect the wholesale participation of older continental crust ($\varepsilon_{Nd}(t) = -11$ to -18; Ayres and Harris, 1997). S-type Lachlan fold belt (Australia) peraluminous granites (formed by melting pelitic sediments at relatively low T; Clemens and Wall, 1981) have zircons that reflect ages of zircons in their metasedimentary source (Keay and others, 1999). Lachlan I-type metaluminous granites also have abundant xenocrysts of older zircon, which may derive from metasediments as well (Kemp and others, 2005). In all these cases, radiogenic isotopic compositions provide strong evidence that older materials were involved in generating these melts; Lachlan granites show Sr- and Nd-isotopic characteristics indicating mixing between mantle melt, crust, and sediments (McCulloch and Chappell, 1982; Keay and others, 1999).

Himalayan leucogranites and Lachlan I- and S-type granites are good examples of how radiogenic isotopes and xenocrystic zircons together indicate that older continental crust or sediment were significantly involved in magma genesis. But such clear evidence is not seen for the ANS, where there is no indication from rocks that older crust was involved, other than in the Khida terrane (Stoeser and Frost, 2006) (fig. 4). The Khida terrane contains, at its extreme eastern margin, Paleoproterozoic granite, anorthosite, schist and gneiss exposed in outcrops over a small area. The terrane elsewhere consists of Neoproterozoic rock (greenschist- and amphibolite-facies volcanosedimentary assemblages and a large granite batholith), which yields Pb and Sr isotope signatures suggesting that much of the region is underlain by older continental crust (Stacey and Stoeser, 1983; Stacey and Hedge, 1984; Stoeser and Frost, 2006). Tracts of older crust elsewhere are restricted to the periphery of the ANS, not within its core area, and are confined to terranes limited by shear zones (Abas, Al Mahfid, and Rahaba-Absol Terranes; fig. 2).

For most of the ANS upper crust, isotopic studies demonstrate that it is juvenile (Stern, 2002a; Stoeser and Frost, 2006; Be'eri-Shlevin and others 2009a). Nor is there any evidence of pre-Neoproterozoic material at depth. Exposures of amphibolitic and gneissic middle crust in Egypt (Meatiq and Hafafit domes) are geochronologically and isotopically juvenile Neoproterozoic crust (Andresen and others, 2009; Liégeois and Stern, 2010). Lower crustal xenoliths brought up by Cenozoic volcanic eruptions are gabbroic, with isotopic compositions indicating formation in the Neoproterozoic (McGuire and Stern, 1993). A similar conclusion is drawn for mantle xenoliths (Henjes-Kunst and others, 1990; Blusztajn and others, 1995; Nasir and Rollinson, 2009). Lu-Hf isotopic studies suggest that mantle lithosphere of Mesoproterozoic age lies beneath Jordan (Shaw and others, 2007), but this xenolith locality lies well north of ANS exposures. These observations reinforce the conclusion that there are no significant undetected tracts of pre-Neoproterozoic lithosphere at depth in the ANS core region that could provide the xenocrystic zircons, apart from the Khida terrane.

Another possibility is that far-travelled clastic sediments carried old zircons into a broad marine basin now occupied by the ANS and that subsequent melts rising through this incorporated some old detrital zircons by assimilation (Hargrove and others, 2006a). Such sediments are known from the Central Eastern Desert of Egypt and N. Arabia, where the Atud/Nuwaybah Diamictite is thought to represent poorly sorted clastic material that was transported by icebergs from the Saharan metacraton (Ali and others, 2010). Atud/Nuwaybah Diamictite contains clasts and matrix with zircons that are mostly ~750 Ma but a significant proportion of the zircons are more ancient, with age distributions similar to those in figure 3B. However, a problem with invoking the Atud/Nuwaybah diamictite as a source of pre-Neoproterozoic zircon xenocrysts is that xenocryst-rich metavolcanic sequences occur below the diamictite, at least at Wadi Kareim, the one site where stratigraphic relationships are clear (K. A. Ali and others, 2009). Nevertheless, it may be that old detrital zircons also occur in fine-grained clastic metasediments in the ANS away from the area of Atud/Nuwaybah

Diamictite outcrops and at different stratigraphic levels. Such metasedimentary sequences cover large areas of the ANS and detrital zircons in these generally have not been studied. Old zircons from metamorphosed wackes in the SE Desert of Egypt are known: Wüst and others (1987) reported Pb-Pb zircon evaporation ages of 2.4 Ga for Wadi Miyah metasediments and ~1.5 and 2.45 Ga for metasediments along Wadi Allaqi. There is also an older (~800 Ma) diamictite just south of the Thurwah-Bir Umq suture (Mahd adh Dhahab diamictite; Stern and others, 2006) that may reflect an older glaciation; this could be the source of xenocrystic zircons reported by Hargrove and others (2006b). The c. 900 to 920 continental tract identified in Bayuda Desert, Sudan (Rahaba-Absol Terrane; Küster and others, 2008) contains abundant inherited zircons. Erosion of this segment before ANS rocks were thrust over it could also provide the needed zircons in sediments.

However, there is no convincing evidence that ancient detrital zircons were incorporated in ANS juvenile magmas as a result of magmas digesting sediments. We know of no occurrences where metasedimentary xenoliths can be directly linked to an igneous rock with ancient xenocrystic zircons (although such has not yet been sought), especially for mafic lavas, which have the highest proportion of zircon xenocrysts. Furthermore, isotopic systems should reflect the participation of pre-Neoproterozoic material, similar to that expected for the involvement of older crust. This has not been observed; Nd T_{DM} model ages for ANS juvenile crust are only slightly older than the magmatic ages (Stern, 2002a) and ε_{Nd} is always strongly positive (fig. 4) other than for the Khida terrane.

Hargrove and others (2006b) were perplexed by the presence of xenocrystic zircons in the Tharwah ophiolite in the western part of the Arabian Shield. The presence of pre-Neoproterozoic (~1250 Ma) zircons in this ophiolite was first inferred from multigrain U-Pb zircon studies of Pallister and others (1988) and confirmed using SIMS zircon dating by Hargrove and others (2006b). Ophiolites form by decompression melting of asthenosphere during seafloor spreading (generally in forearc or backarc basin tectonic settings), and the incorporation of older zircons from older crust or sediments is especially difficult to explain.

A final possibility is that the ancient zircons were present in the mantle region where ANS juvenile melts were generated, and these were directly entrained with juvenile ANS melts rising to the surface. For this to happen, four conditions must be satisfied: 1) zircons must be carried into the mantle; 2) zircons must be preserved in mantle conditions; 3) zircons must be entrained in mantle melts to be carried to the surface; and 4) zircons and the age information they carry must survive steps 1 to 3. It is not difficult to envision how zircons—which are generated by crystallization of mostly felsic melts in the crust—might be injected into the mantle. Subduction of sediments and continental crust carry zircons of various ages into the mantle today. It is more difficult to imagine how water-rich fluids evolved from dehydration of the subducted slab—which should have low density and viscosity—could entrain dense zircons ($\rho = 4.85$ g/cc) and carry these upwards through channels, cracks or whatever porosity exists in and above subduction zones at 3 to 4 GPa (corresponding to typical depths for subducted slabs beneath arc volcanoes; Syracuse and Abers, 2006). Such fluids are also likely to be very corrosive (Manning, 2004) so the survival of entrained zircons is questionable. Diapiric ascent of low density material from the slab (Hall and Kincaid, 2001) is more likely to entrain subducted zircons; this is nevertheless only one of several ways that slab-derived fluids and melts might migrate upwards towards the region of melt generation in the mantle wedge (Stern, 2002b). Processing through subduction zones seems presently to be the most popular way to explain the occurrence of zircon xenocrysts in mafic and ultramafic rocks (Bea and others, 2001; Liati and others, 2004; Yamamoto and others, 2004), but we know of no examples where subducted zircons are documented to have been recycled through a subduction zone and been erupted at a modern arc volcano or emplaced as plutons in arc crust. Such an inventory of zircons would have to be made at an intra-oceanic arc, where contamination by older continental crust can be precluded. 5000 analyses of zircons from the intraoceanic Izu-Bonin-Mariana and Fiji arcs has yielded no zircons with ages older than when subduction began there (K. Tani, personal communication 2009).

Alternatively, the subduction of zircons and mixing into the mantle may occur long before mantle melting and entrainment of xenocrysts. This could happen in the shallow mantle "wedge" above the subducted slab, where zircon xenocrysts might be stored for millions of years before this mantle was partially melted. Or subducted crust and sediments (and their zircons) could sink into the lower mantle. It is hypothesized that subducted slabs sink to the bottom of the mantle to form "slab graveyards" (Lay and others, 2004) which then are heated to form mantle plumes; entrainment of zircons in such melts could be responsible for recycling ancient zircons. To our knowledge, no one has sought zircon xenocrysts in oceanic hotspot mafic igneous rocks as a test of this possibility.

Another way that ancient zircons might be introduced into the mantle would be if and when dense lower crust "delaminates" or founders into the mantle (Kay and Kay, 1993; Bédard, 2006). This way of introducing ancient zircons into the mantle is similar to that proposed by Pilot and others (1998), who suggested that during Atlantic opening, delaminated continental lithosphere sank into the shallow mantle and was convectively transported to the ridge axis. Lower crust that founders into the mantle is already warm and easily melted (Anderson, 2005). Delamination of Gondwana lower crust is widely considered to explain the unusual isotopic composition of Indian Ocean MORB (for example, Escrig and others, 2004), and a pre-Neoproterozoic episode of lower crust foundering may have introduced ancient zircons into the mantle beneath what later became the Arabian-Nubian Shield. A final possibility is that zircons were "gardened" into the upper mantle by impacts of large meteorites. This might have been important early in Earth history, but became much less important after Archean time (Koeberl, 2006).

Once incorporated into the mantle, it appears that zircon could survive storage there. Zircon can survive at least up to 1500 °C and 20 GPa, equivalent to >600 km deep in the Earth (Tange and Takahashi, 2004). Detrital zircons carried by deep subduction into the diamond zone also persist, as demonstrated by zircons from ultra-high pressure metamorphic terranes (Claoué-Long and others, 1991; Hermann and others, 2001; Usui and others 2003). Ancient xenocrystic zircons are known to exist in mantle peridotite (Bea and others, 2001; Liati and Gebauer, 2002; Liati and others, 2004; Yamamoto and others, 2004; Zheng and others, 2006). Liati and Gebauer (2002) documented 1.6 to 1.8 Ga, 208 Ma, 74 Ma, and 35 to 26 Ma zircons from spinel peridotites and pyroxenite xenoliths brought up in 80 Ka basanites at Kilbourne Hole, SE New Mexico, USA. Liati and others (2004) also report that Late Cretaceous kimberlites from Namibia contain garnet peridotites (with calculated T = 900 °-1000 °C and P = 3.3-3.5 GPa) that contain zircons with U-Pb ages of ~1000 Ma, 750 Ma, and 630 Ma, ages that correspond to major crust-producing events in the Damaran orogen. Yamamoto and others (2004) document a significant proportion of Mesoproterozoic and Paleoproterozoic zircons in chromitites of the Cretaceous Luobusa ophiolite of southern Tibet. Zheng and others (2006) found that altered spinel peridotite mantle xenoliths in Jurassic diatremes from N. China had zircons clustering ~3.2 Ga, 2.3 to 2.4 Ga and mostly 210 to 240 Ma. Bea and others (2001) report zircons in dunite from the subduction-related Ktylym Alaska-type ultramafic body in the Ural Mountains of Russia. Most analyzed Ktylym zircons gave ages reflecting diapir formation at 350 to 370 Ma but some preserve older, probably original magmatic ages of 410 Ma to 2.8 Ga.

It also appears that mantle zircons can survive melting and entrainment in mafic melts because ancient zircons are now commonly reported from Mid-Atlantic Ridge gabbros (Pilot and others, 1998; Belyatsky and others, 2008; Bortnikov and others, 2008) Xenocryst-bearing gabbros were first reported in ODP Leg 153 drill cores from the Kane Fracture Zone area (~23°30′N) near the Mid-Atlantic Ridge by Pilot and others (1998). These gabbros formed ~1 Ma and contained a significant number of zircons with Paleozoic and Proterozoic $^{207}Pb/^{206}Pb$ evaporation ages. Ancient zircon xenocrysts have also been reported from the Markov Deep (6°N) along the Mid-Atlantic Ridge, where Bortnikov and others (2008) dated 150 grains from deformed gabbronorite by the U-Pb SHRIMP technique, identifying two groups of zircons (". . . practically indistinguishable under the microscope . . . ," p. 864) with ages <2.3 Ma and 87 Ma to 3.12 Ga. The younger group was interpreted to date the gabbro crystallization whereas the older group was interpreted as xenocrysts. Sharkov and others (2009) found that all ancient xenocrysts were rimmed by a thin selvedge of newly-formed zircon, which was too thin to date. Finally, Belyatsky and others (2008) recognized two groups of zircons in gabbros from near the Mid-Atlantic Ridge ~13°N. Weakly colored, prismatic zircons with well-developed zoning and faceting yielded ages <1 Ma (corresponding to the time of gabbro crystallization) whereas poorly faceted, yellowish-brown zircons yielded mostly 2700±20 Ma and 1750±12 Ma ages.

Regardless of how zircons formed in the crust are introduced into the mantle, they are resilient enough to often survive extensive melting and be carried back to the surface in magmas. This is the simplest explanation for the presence of ancient zircons in mid-Atlantic ridge MORB-type gabbros (Pilot and others, 1998; Belyatsky and others, 2008; Bortnikov and others, 2008). This is probably the origin of inherited zircons found in some ophiolites (for example, Whattam and others, 2006), including the Neoproterozoic Thurwah ophiolite of Saudi Arabia (Pallister and others, 1988; Hargrove and others, 2006a). Such an explanation for the origin of ANS xenocrystic zircons is difficult to prove but the possibility should be entertained for the presence of ancient zircons in juvenile ANS crust, especially in mafic igneous rocks.

The possibility that ancient zircon xenocrysts are common in Neoproterozoic igneous rocks of the ANS, especially mafic igneous rocks, encourages new thinking about geochronologic efforts and results in the region. We need to figure out how to distinguish magmatic zircons from xenocrysts in ANS igneous rocks. We need to consider the presence of ancient zircons in juvenile igneous rocks as telling us something important about the evolution of the mantle source, and figure out what this might have been. We need to recognize the likelihood that pre-Neoproterozoic zircons found in immature wackes may come from volcanic sources and not necessarily from ancient continental crust. Above all, ancient zircons in juvenile ANS igneous rocks should be considered to be "signal," not "noise" for understanding the crustal evolution of this region.

CONCLUSIONS

Our overview of zircons in ANS juvenile crust leads to several useful conclusions:

1) A substantial fraction of ANS igneous rocks contain xenocrystic zircons that are much older than the igneous rocks that host them.
2) Whole rock isotopic compositions—in this case, Nd isotopic compositions (including T_{DM} model ages)—best characterize the pedigree of the entire igneous rock and the melt source, whereas zircon xenocrysts yield ages that pertain to that crystal only. From this perspective it follows that the juvenile character of the ANS shown by Sr and Nd isotopes cannot be challenged by the presence of old zircon xenocrysts, although very small tracts of heretofore undetected older crust could contribute small amounts of material.

3) Pre-Neoproterozoic zircon xenocryst abundances in ANS igneous rocks show strong compositional dependence. Such xenocrysts are more common in volcanic than plutonic rocks, and much more common in mafic relative to felsic rocks, with the result that they are ~10× more likely to be found in mafic volcanic than felsic plutonic rocks.
4) The occurrence of most ANS old xenocrystic zircons in mafic (mantle-derived) igneous rocks compared to felsic (crust-derived) igneous rocks suggests that remobilization of ancient crust is not the principal process responsible for emplacing the zircons. Rather, the distribution of the xenocrystic zircons favors the interpretation that zircon xenocrysts resided in the mantle and were entrained when this mantle was melted to form juvenile ANS crust.
5) The pre-Neoproterozoic zircon xenocrysts present in some ANS igneous rocks originated either in a crustal tract outside the ANS and were transported into the ANS and introduced in the crust or were stored in the mantle source and were entrained with mantle melts. Experimental studies to determine if mantle zircon is likely to persist through episodes of partial melting would help differentiate between these two possibilities.
6) The resilient character of zircons is an advantage for dating igneous rocks but much caution is needed for understanding the significance of xenocrystic zircons, especially when present in mafic igneous rocks, the composition of which inhibits zircon crystallization.
7) Global inventories of old xenocrystic zircons in juvenile and oceanic igneous rocks—including active tectonic environments— could provide additional constraints.

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Appendix A

Appendix A table A1, Appendix A table A2, and Appendix A table A3 are provided as supplementary data tables. The URLs are:

http://earth.geology.yale.edu/~ajs/SupplementaryData/2010/07SternTableA1.doc
http://earth.geology.yale.edu/~ajs/SupplementaryData/2010/08SternTableA2.doc
http://earth.geology.yale.edu/~ajs/SupplementaryData/2010/09SternTableA3.doc

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