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Notes

Geochemical Fingerprinting of the Earth's Oldest Rocks

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In this issue of *Geology*, Turner et al. (2014, p. 139) take a new look at the geochemistry of amphibolite-facies lavas from Nuvvuagittuq (O'Neil et al., 2011), possibly the Earth's oldest volcanic rocks (O'Neil et al., 2012). Geochemical fingerprinting had already been used to identify a possible subduction signature in some of these lavas (O'Neil et al. 2011), but Turner et al. additionally emphasize the similarity between the Nuvvuagittuq geochemical stratigraphy and that of the Izu-Bonin-Mariana (IBM) forearc (Ishizuka et al. 2011), the type area for intra-oceanic subduction initiation (Stern and Bloomer, 1992). The sinking of the slab following subduction initiation in the IBM forearc led to influx of mantle asthenosphere beneath an extending lithosphere, resulting in the eruption of forearc basalts (FAB) (Reagan et al., 2010), essentially mid-oceanic-ridge basalt (MORB) with a small but variable subduction component. In the IBM forearc, these are overlain by boninite-like rocks, marking the transition from a slab sinking vertically to a one subducting with a horizontal component, and then by island arc tholeiites or calc-alkaline rocks, marking the start of normal subduction (Ishizuka et al., 2011). Turner et al. interpret the lower (high-Ti) unit from Nuvvuagittuq as FAB, the middle (low-Ti depleted) unit as boninite and the upper (low-Ti enriched) unit as island arc, calc-alkaline lavas, They thus potentially strengthen the hypothesis for a subduction origin of the Nuvvuagittuq lava sequence by interpreting the sequence as a whole.

If a subduction initiation model, or indeed any subduction-based model, is true, there are implications for the tectonic evolution of the Earth, and also for the origin of life, because submarine hydrothermal systems in arc terranes contain high concentrations of many elements needed for life. But is it true? A key question is: can geochemical fingerprinting based on Recent lavas be applied to an early Archean world, different, for example, in mantle temperatures and crustal rheologies? Opinion is divided between three types of approach, debated in some detail at the 2006 Penrose Conference "When did Plate tectonics Start?"(Condie and Pease, 2008).

The first is uniformitarian as in Turner et al. and in most publications on Archean volcanic rocks, where plate tectonic processes are assumed to resemble those of today, allowing direct comparison between Archean and present-day lavas. The second is selective uniformitarian, in which Archean plate tectonic scenarios are assumed to resemble the small subset of present scenarios most applicable to a hotter world. For subduction, the focus has been on plume-subduction interactions, subduction of ridges and young lithosphere, and flat-slab subduction (e.g., Polat and Kerrich, 2006; Smithies et al., 2003). The third is non-uniformitarian, in which the Earth is seen as having evolved from a magma ocean to a stagnant lid convective mode before plate tectonics developed (cf. Sleep, 2000). In this case, subduction-like geochemical signatures must be explained in other ways, e.g., by delamination and recycling of over-thickened, plume-generated crust (Bédard, 2006).

To evaluate whether uniformitarian geochemical fingerprinting methods are valid for Nuvvuagittuq, one can start by looking at the basis of fingerprinting recent volcanic arc lavas. Subduction of oceanic lithosphere into hot mantle leads to release of aqueous fluids into the mantle wedge above, the prime trigger for melting. These fluids carry elements extracted from the subducting plate, with the precise suite depending on such factors as the temperature of the mantle-slab interface, and the composition of subducted materials. Volcanic arc lavas thus show enhanced concentrations of the most subduction-mobile elements, such as the large ion lithophile elements (LILEs), including the alkali and alkali earth metals (e.g., K, Rb, Ba, and Sr), the light rare earth elements (LREEs, especially La, Ce, and Nd), and the transuranium elements (Th and U). The concentration of the subduction-mobile elements (Th, La, and K) relative to the more subduction-immobile elements (Nb and Ta) gives the negative Nb anomaly diagnostic of arc volcanism in geochemical patterns (e.g., Turner et al.'s figure 2). The projection of Th/Yb versus Nb/Yb makes it possible to plot data on multiple samples, and quantify and interpret the Nb anomaly (Pearce, 2008). The oldest Nuvvuagittuq lavas plot at least partly in the MORB-OIB (ocean island basalt) array of this diagram (i.e., no Nb anomaly), whereas the younger lavas plot in the volcanic arc field (O'Neil et al., 2011; Turner et al., 2014), which forms part of the basis for the hypothesis that the lava sequence formed following subduction initiation.

One should, however, be cautious, because the Nb anomaly can form in other ways, for instance through contamination by continental crust. Average continental crust resembles volcanic arc andesites in also having Nb anomalies, so that magma from a continental, anorogenic terrane can attain arc-like geochemical characteristics by extensive assimilation (e.g., Thompson et al., 1982). Another way is through of melting, or interaction with, sub-continental lithospheric mantle (SCLM). Tertiary lavas from the Basin and Range volcanic province in the western United States, for example, geochemically resemble present-day Japanese arc lavas, probably because they inherited that signature from an underlying Palaeoproterozoic terrane with a subduction history (e.g., Hawkesworth et al., 1995). In addition, high-temperature metamorphism is a potential problem: if the lava itself or surrounding sediments is raised to near-solidus temperatures, the spiked pattern of arc lavas may be reproduced.

Thus the question is whether the Nb anomalies could have resulted from a process other than subduction, particularly in lavas such as the Nuvuatittuq, which erupted in the earliest Archean when mantle and crustal temperatures probably were much higher than today. Archean komatiitic magmas, for instance, were hot enough to melt even basic, igneous crust (Sparks, 1986), so that contamination could have been ubiquitous. One can usually distinguish true subduction anomalies from false ones created by contamination in the Th/Yb-Nb/Yb diagram: diagonal trends with variable Th addition could best be explained by contamination, but MORB-parallel trends by subduction (Pearce, 2008). Only one of the Nuvvuagittuq Units meets this criterion: the upper low-Ti (enriched) pattern (O'Neil et al., 2011, their figure 10b).

Inherited anomalies do not matter for Nuvvuagittuq: if anomalies were inherited from an earlier subduction terrane, the time at which subduction started on Earth is simply pushed back further. More critical is element mobility in the upper amphibolite metamorphic facies. Three closely spaced samples in the high Ti-unit with similar Nb and Ta have Th values of 0.81, 0.18, and 0.36 (O'Neil et al., 2011), indicating that Th is indeed mobile as such short length-scale variations are typical of alteration. Thus at least one potential subduction signal was almost certainly due to alteration, and the same is possibly true for the low-Ti (depleted) unit. The low-Ti (enriched) unit, however, may have been enriched in Th before metamorphism, so that similar metasomatic effects were less important.

Confirmatory evidence for a subduction origin of the Nuvvuatittuq lavas might include direct and indirect evidence for high water contents (e.g, vesicular lavas, explosive volcanic activity, porphyry copper-style

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mineralization, calc-alkaline iron-enrichment trends, and order of crystallization), but the exposure is not sufficient for absence of features to be considered significant. As Turner et al. emphasized, one can also look at the whole stratigraphy, because volcanic arcs do not all have a single composition, but follow a life cycle (cf. Shervais, 2001), starting at their birth, followed by growth, including mid-life crises such as ridge subduction or flat subduction events, and ending with their death, usually by collision, with final resurrection of arc-like volcanism by extraction of a stored subduction signal in the subcontinental mantle lithosphere. Preservation of a significant part of this life cycle (birth in this case) adds weight to any conclusion.

So, how should these data be interpreted? First, I think that it is not impossible that the lower two units are subduction-related, but the evidence is flimsy. Th-Nb systematics are prejudiced by Th mobility and, following Smithies et al. (2004), the low-Ti (depleted) lavas seem much more like Whitney type "boninites" (derived from a depleted plume) than Whundo-type boninites (subduction-related), as proposed by O'Neil et al. (2011). My interpretation is that it is the upper unit (low-Ti, enriched) which most resembles boninites from the IBM forearc and could be subduction-related. Not only does the Th-addition appear to be real, but the silica (admittedly mobile) is higher at mafic compositions. In addition, Zr and Hf are enriched not only relative to Ti, as both O'Neil et al. (2011) and Turner et al. recognized, but also relative to REE if the least metasomatised samples are chosen. This may be due to a shallow, slab melt component and results in positive anomalies on an extended REE plot. Such anomalies are a ubiquitous feature of subduction initiation boninites in the IBM system, disappearing in the later, normal arc volcanics (Hickey-Vargas, 1989; Pearce et al., 1999). Thus there is a good case for an infant arc origin for at least the upper unit, based on a uniformitarian approach to fingerprinting.

Two key issues remain: (1) could hot, and probably thick, oceanic-type crust have had sufficient negative buoyancy to sink in the Hadean in the same way as it did in the IBM system to initiate subduction, and (2) is subduction initiation the only explanation? For example, negative Nb-Ta anomalies and positive Zr-Hf anomalies might also be expected in the subduction-free world of Bédard (2006) and others, if the mantle was chemically modified by a component produced by high-temperature melting of delaminated, metabasaltic crust. Nonetheless, O'Neil et al. (2011) and Turner et al. have highlighted one of the best locations to test the hypothesis of subduction on early Earth, and compare it to a non-subduction alternative, although they may not yet have definitively fingerprinted the Earth's oldest rocks.

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