Mineral Environments on the Earliest Earth

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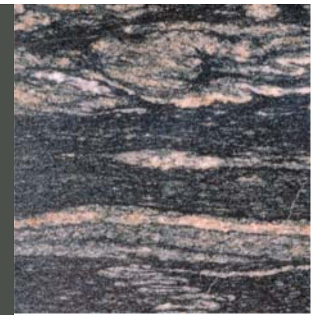

The 4.03 Ga Acasta Gneiss from the Slave Craton of northwestern Canada is Earth's oldest-known rock unit. In this polished section (about 10 cm wide), the gneiss contains strongly deformed granite veins 3.6 billion years old. Courtesy of W. Bleeker

The oldest vestiges of crust and marine environments occur only in a few remote areas on Earth today. These rocks are Hadean–Eoarchean in age (~4.5 to 3.6 billion years old) and represent the only available archive of the mineral environments in which life originated. A mineral inventory of the oldest rocks would thus help to constrain the likeliest minerals involved in the origin of life. Such a survey is important from the perspective of mineral evolution, as the emergence of life and subsequent global changes caused by organisms were responsible for more than half the 4400 known minerals on the modern Earth.

Keywords: Hadean, Archean, tonalite–trondhjemite–granodiorite, supracrustal rocks, banded iron formation, origin of life, mineral evolution

THE DAWN OF GEOLOGY

The first 700 million years of Earth history, called the Hadean Eon (from ~4.5 to ~3.85 billion years ago, or Ga for giga-annum), is poorly documented because of the lack of a significant rock record. Nevertheless, a mineral inventory of crustal rocks from this eon and from the subsequent Eoarchean Era (3.85 to 3.60 Ga) may yield information for constraining the nature of the aqueous environments in which life emerged. The availability of specific minerals in the earliest surface environments, where prebiotic chemical reactions took place, was likely a key factor for the emergence of life and was strongly influenced by Hadean–Eoarchean rock types. Determining the mineral inventory of Hadean and Eoarchean metamorphic rocks is challenging, however, due to extensive metamorphic recrystallization and metasomatism resulting from high-temperature crustal fluids. These processes likely changed and homogenized the chemical and mineral compositions of Hadean–Eoarchean protoliths (the precursor lithologies of the metamorphic rocks). These alterations likely reduced the diversity of rock-forming minerals in ancient metamorphic rocks. Protoliths of metamorphic rocks can generally be inferred from a variety of mineralogical, geological, and geochemical criteria. Here I document the mineral diversity of the first billion years of Earth history in the context of mineral evolution at the time of life's emergence.

Following planetary accretion and differentiation, mineral diversity rapidly increased from the approximately 60 different mineral phases found in unaltered meteorites—the starting point of planetary mineral evolution (Hazen et al. 2008). The initial mineral diversity of Earth's crust depended on a sequence of geochemical and petrological processes that included volcanism and degassing on the surface, fractional crystallization and assimilation reactions in the mantle, crystal settling in magma chambers, and regional and contact metamorphism in the crust. Processes in the original mafic crust at plate boundaries initiated large-scale fluid–rock interactions and ultimately produced granitoids, metamorphic belts, and zones of surface weathering.

Oceans have influenced Earth's surface since about 4.4 Ga. Interactions between the crust and the anoxic ocean–atmosphere system during the Hadean–Eoarchean should have led to a progressive increase in ocean-water ion content and to the deposition of silt, carbonate, chert, iron-rich sediment, and evaporite. Although the oldest rocks are highly metamorphosed, their mineral diversity contains clues about the nature of the earliest habitable environments. The rise of life in oceans during the Hadean or Archean (the latter from 3.85 to 2.5 Ga) slowly began to change Earth's mineralogical landscape. By the time biological processes began to affect Earth's surface mineralogy, large-scale surface mineral deposits were being precipitated under the combined influences of early Hadean crustal recycling and an anoxic atmosphere and ocean. Combined with the formation of later pegmatites and hydrothermal ore deposits, these processes resulted in an estimated 1500 different mineral species by the end of the Archean (Hazen et al. 2008; Hazen and Ferry 2010 this issue).

INITIATION OF IGNEOUS ROCK EVOLUTION

Early Crust and Mantle Differentiation

The first granitoid rocks resulted from partial melting in the mantle, after the initial formation of basaltic crust. Hadean and Eoarchean orthogneisses (i.e. formed from igneous rocks) are generally inferred to have granitoid protoliths of the tonalite–trondhjemite–granodiorite (TTG) series. These plutonic rocks are thought to have formed from the melting of older, hydrated, mafic crust (Nutman et al. 2007; Nutman and Friend 2009) and are composed mostly of quartz, plagioclase, biotite, and K-feldspar (Table 1). A wide variety of minor mineral species are also found in Eoarchean TTG-type rocks. The tectonic context during the formation of TTG suites is still debated, owing to uncertainties regarding the existence of plate tectonics and the styles of subduction at that time.

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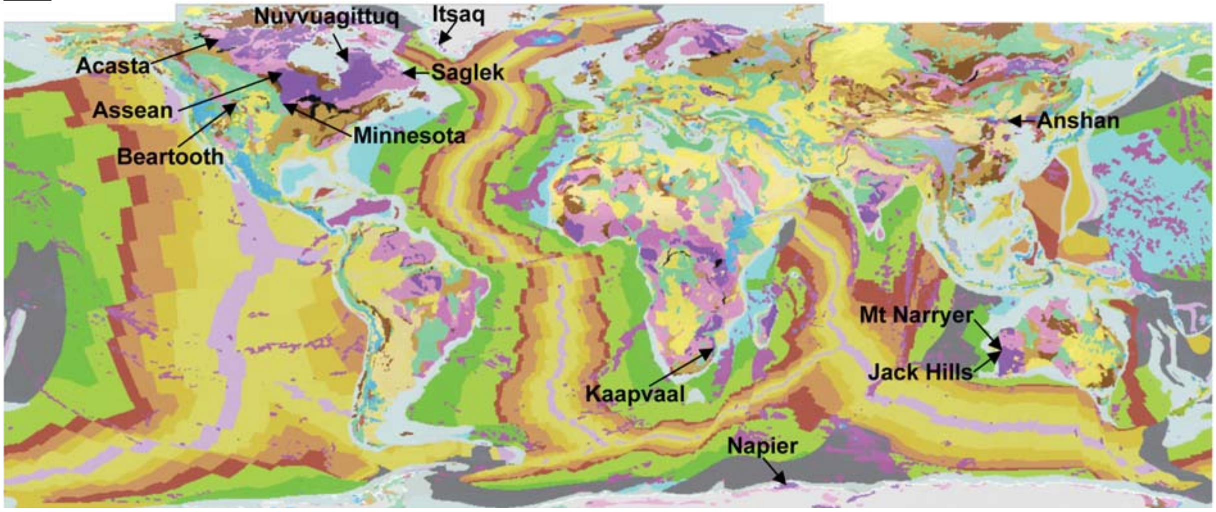

FIGURE 1 World geological map showing the localities described in the text. The darkest pink color (e.g. in northern Ontario and Québec, Canada) represents Archean cratons, while other colors relate to younger rocks. SOURCE: HTTP://PORTAL.ONEGEOLOGY.ORG/

Hadean Time Capsules

Earth's oldest minerals are tiny detrital zircon grains from the Mesoarchean (3.2 to 2.8 Ga) Jack Hills conglomerate in the Yilgarn Craton, Western Australia (FIG. 1). These grains have yielded a range of Hadean–Archean ages up to 4.4 Ga (Wilde et al. 2001; Mojzsis et al. 2001). Their trace element compositions have been interpreted to indicate that granitic continental crust was produced within 200 million years of Earth's accretion. Oxygen isotopes of Hadean zircon are often heavier than in the mantle; this fact suggests that early Hadean oceans were involved in the recycling of continental crust during subduction (Cavosie et al. 2005). While views diverge on the degree of hydration of early Hadean crust and the styles of tectonic processes, there is consensus on the existence of granitoid crust and probably of supracrustal assemblages within 200 million years of Earth's formation. These developments are significant, because the recycling of continental crust is a process central to the global carbon cycle and to mineral diversification.

Numerous mineral inclusions have been reported from Hadean zircon grains, including quartz, muscovite, biotite, K-feldspar, plagioclase (albite), chlorite, hornblende, and many less common mineral species (FIG. 2, TABLE 1; Trail et al. 2004; Nemchin et al. 2008; Hopkins et al. 2008). This remarkable suite of mineral inclusions is the only terrestrial archive currently known for the oldest mineralogical diversity on Earth. Collectively, these mineral inclusions in pre–4.0 Ga zircon grains are characteristic of silica-saturated, peraluminous crust, such as TTG-type granitoids and their subducted-hydrated equivalents, and possibly supracrustal assemblages. However, because of their limited distribution, these postulated early Hadean granitoid masses were likely recycled into the mantle prior to the end of the Hadean and thus are not preserved, and outcrops of them are not currently known.

THE HADEAN–EOARCHEAN ROCK RECORD

The Oldest Rocks on Earth

The Acasta orthogneisses in the Slave Craton are generally accepted as the oldest rocks on Earth (FIG. 1, which shows all localities mentioned in this section). These highly deformed rocks have been dated to be as old as 4.06 Ga and inferred to have various protoliths, including TTGs, amphibolite, gabbro, granite, and diorite (Bowring and Williams 1999). Their mineral assemblages are typical of TTGs and are dominated by plagioclase, quartz, hornblende, feldspar, and biotite, along with various minor phases (TABLE 1; Iizuka et al. 2007). Interestingly, a zircon xenocryst dated at 4.20 Ga from a sample of Acasta Gneiss, and presumed to be inherited from an older rock and incorporated in the tonalitic melt, was found to have an inclusion of apatite. The weathering of the oldest Hadean TTGs may thus have been a source of phosphorus for the early ocean and have contributed to its nutrient budget (see below).

TABLE 1 MINERALS COMMONLY REPORTED FROM HADEAN ZIRCON GRAINS AND HADEAN–EOARCHEAN ORTHOGNEISSES

	Major minerals	Minor minerals#
Minerals in Hadean–Eoarchean TTG gneisses*	quartz, plagioclase (albite, anorthite), K-feldspar (microcline, orthoclase, perthite), biotite, muscovite, amphibole, epidote	zircon, titanite, apatite, garnet, chlorite, phengite, clinopyroxene, orthopyroxene, tourmaline, sulfides
Mineral inclusions in pre–4.0 Ga zircon grains	quartz, muscovite, plagioclase (albite), K-feldspar, biotite, chlorite, hornblende	titanite, apatite, monazite†, xenotime†, Ni-rich pyrite, thorite, rutile, iron oxyhydroxides†, diamond, graphite

* Minerals reported in tonalite–trondhjemite–granodiorite (TTG) gneisses of the Acasta, Mt. Narryer, Napier, Anshan, Nuvvuagittuq, Itsaq, and Saglek complexes.

These minerals are not always found in the listed rock types.

† These minerals may be secondary alteration phases as they often occur within cracks in zircon.

Table 2 MINERALS AND MINERAL GROUPS COMMONLY REPORTED FROM EOARCHEAN SUPRACRUSTAL VOLCANOSEDIMENTARY ROCKS

Rock type	Possible protoliths	Major minerals	Minor minerals*
Metavolcanic rocks	greenstone, komatiite, amphibolite, ultramafic rock	olivine, clinopyroxene, garnet, orthopyroxene, biotite, chlorite, amphibole (hornblende)	serpentine, antigorite, magnetite, talc, magnesite, epidote, phlogopite, kyanite, chromite, rutile, ilmenite, sulfides, dolomite, calcite, K-feldspar, plagioclase, cordierite, apatite
Banded iron formation	BIF, ferruginous chert	quartz, magnetite, amphibole	clinopyroxene, orthopyroxene, olivine, garnet, chlorite, tremolite, calcite, magnesite, hematite, gœthite, apatite, sulfides, zircon, graphite
Schist (metapelite)	ferruginous shale, mudstone, siltstone, argillite	quartz, biotite, amphibole, garnet, chlorite	muscovite, sillimanite, kyanite, staurolite, andalusite, cordierite, plagioclase, epidote, microcline, clinozoisite, tourmaline, magnetite, ilmenite, rutile, graphite, sulfides, zircon
Quartzite	chert, sandstone?	quartz, amphibole	magnetite, clinopyroxene, orthopyroxene, biotite, chlorite, epidote, plagioclase, zircon, fuchsite, hematite, sulfides, carbonate
Calc-silicate and metacarbonate rocks	limestone?, chert? metasomatic contact? hydrothermal edifice?	quartz, siderite, dolomite, calcite, ankerite, magnesite, magnetite	clinopyroxene, orthopyroxene, olivine, amphibole, garnet, phlogopite, biotite, feldspar, muscovite, chlorite, epidote, fuchsite, apatite, hematite, sulfides, graphite

* These minerals are not always found in the listed rock types.

The oldest rocks in Antarctica are part of the Napier Gneiss Complex, located in Enderby Land. Highly metamorphosed gneissic granites and tonalites at Mount Sones contain zircon grains with ages up to 3.93 Ga (Black et al. 1986), which gave these rocks the status of the oldest rocks on Earth until the discovery of the pre–4.0 Ga Acasta Gneiss. It is unclear, however, if the parent melt inherited these >3.9 Ga zircon grains, and a reevaluation of the original datasets suggests that the main zircon population in the orthogneiss precursors, presumably recording the magmatic protolith age, is instead 3.85 Ga (Harley and Kelly 2007). Eoarchean orthogneisses and paragneisses at Mount Sones, many with uncertain protoliths, include pyroxene granulites, garnet quartzites, garnet–sillimanite metapelites, and rare sapphirine-bearing gneisses.

The recent discovery of Hadean–Eoarchean volcanosedimentary supracrustal rocks in the Nuvvuagittuq Supracrustal Belt in northern Québec (David et al. 2002) has reignited excitement about the possibility of finding other Hadean crustal remains. Unusual amphibolites from this belt have been dated directly at 4.28 Ga with a $^{146}Sm/^{142}Nd$ model age (O'Neil et al. 2008). Zircon grains from felsic gneisses interpreted to crosscut a banded iron formation (BIF) unit have ages of ~3.75 Ga, which represents the minimum age of the belt (Cates and Mojzsis 2007). Thus far, no zircon grains of Hadean age have been found in the Nuvvuagittuq Supracrustal Belt, and therefore a Hadean age for the belt has yet to be confirmed. Metasedimentary rocks in the Nuvvuagittuq Supracrustal Belt include BIFs with varied mineralogy (magnetite + amphibole ± quartz ± hematite ± carbonate; Fig. 3). Other possible metasedimentary rocks in the belt include schists (quartz + biotite + garnet ± hornblende), polymictic conglomerates, and metacarbonate rocks (quartz + carbonate + magnetite ± hematite) (Table 2; O'Neil et al. 2007).

Eoarchean Supracrustal Assemblages

Besides occurrences in the Nuvvuagittuq Supracrustal Belt, there are very few exposures of Eoarchean metasedimentary rocks worldwide. Examples include the Itsaq Gneiss Complex in southwestern Greenland, the Saglek Complex of the Nain Craton in northern Labrador (Canada), and possibly the Narryer Gneiss Complex of Western Australia and the Anshan area of the North China Craton. Other localities that may preserve Eoarchean supracrustal rocks, but that are currently known to contain only orthogneisses or their weathered components, include the Kaapvaal Craton in southern Africa, with TTGs as old as ~3.7 Ga (Kröner et al. 1996); the Minnesota River valley and northern Michigan, with components up to ~3.8 Ga in age (Goldich and Hedge 1974); and the Assean Lake area of northern Manitoba, which contains Archean metasedimentary rocks hosting detrital zircon grains with ages up to 3.8 Ga (Böhm et al. 2003).

The Itsaq Gneiss Complex of southwestern Greenland is dominated by tonalitic and granitic orthogneisses, with subordinate quartz diorite and ferruginous gabbro, which intruded older supracrustal rocks between 3.87 and 3.62

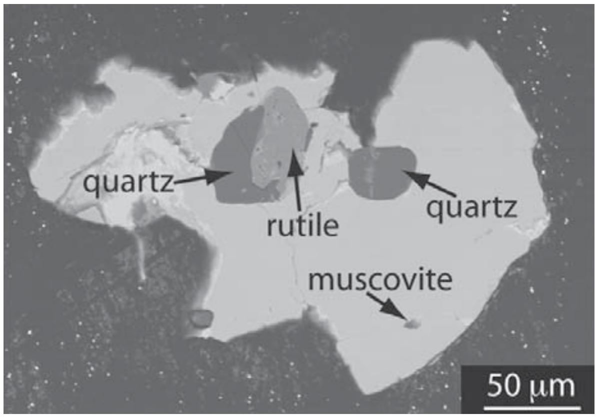

Figure 2 Secondary electron image of a Jack Hills zircon dated at 4.061 ± 0.014 Ga using an ion microprobe and the U–Pb method. This zircon contains a large polyphase inclusion of quartz and rutile and smaller inclusions of quartz and muscovite. Image from Hopkins et al. (2008)

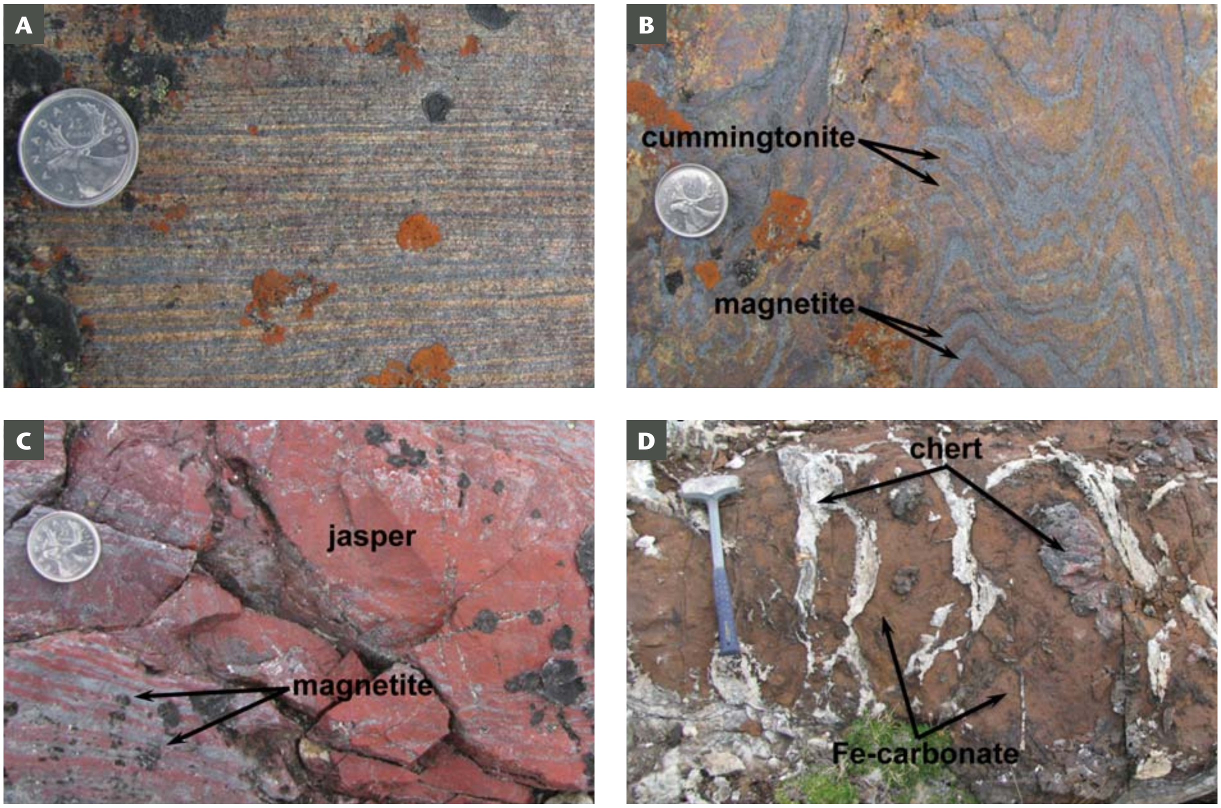

Figure 3 Diversity of banded iron formations and other rock types from the >3.75 Ga Nuvvuagittuq Supracrustal Belt. Outcrop photos: (**A**) Finely laminated quartz–magnetite–cummingtonite BIF, (**B**) cummingtonite–magnetite ± quartz BIF with convoluted beds, (**C**) quartz–hematite–magnetite–amphibole BIF, and (**D**) chert and siderite metacarbonate rock closely associated with the jasper BIF. The coin in A, B, and C is 2.3 cm wide, and the hammer in D is 40 cm long.

billion years ago (Nutman et al. 2007). The oldest supracrustal rocks in the Itsaq Gneiss Complex are those of the Isua Supracrustal Belt and the Akilia Association, which collectively include amphibolite, felsic volcanic rocks, and gabbro–anorthosite, as well as metasedimentary units of BIF, metapelite, ferruginous quartzite, and possible metaconglomerate (Nutman and Friend 2009). The Isua Supracrustal Belt is the most extensive single geological unit in which Eoarchean supracrustal rocks are found. It contains possible metasedimentary rocks, including schists with uncertain protolith, typically composed of the assemblage quartz + biotite + garnet + plagioclase. Banded iron formations deposited in marine environments are common and dominated by quartz, magnetite, and amphibole (Table 2). Calc-silicate rocks in the Isua sequence are composed of quartz + carbonate + diopside + tremolite + garnet assemblages and are commonly in close association with chert, BIF, and ultramafic and ferruginous schists (anthophyllite + talc + magnesite + chlorite, and quartz + garnet + biotite). Based on their close association with ultramafic schists and metasomatic veins, these complex calc-silicate rocks have been interpreted to be metasomatic in origin (Rose et al. 1996), although others have proposed a possible volcanosedimentary origin.

The Saglek Complex of Labrador is composed of the Eoarchean Nulliak supracrustal assemblage and TTG gneisses. Igneous zircon cores from orthogneisses in the area have Eoarchean ages up to 3.8 Ga (Schiøtte et al. 1989). Rocks of the Saglek Complex have been correlated with the Itsaq Gneiss Complex in southwestern Greenland on the basis of similarities in their age, metamorphic history, and modern geotectonic setting on the west side of the Labrador Sea. The Nulliak supracrustal assemblage is dominated by amphibolite and other metavolcanic rocks derived from komatiite and tholeiite (Nutman et al. 1989). Supracrustal rocks of sedimentary origin, including BIF dominated by quartz + magnetite + amphibole ± pyroxene assemblages and possible metapelitic schists composed of the assemblage quartz + sillimanite + garnet + biotite, are also present. In some areas, BIF is associated with calc-silicate rocks composed of quartz, carbonate, diopside, amphibole, and other minor phases.

The Narryer Gneiss Complex of Western Australia is dominantly composed of Paleoarchean to Neoarchean TTG orthogneisses, but also contains some Eoarchean crust. The Mesoarchean Jack Hills rocks (which host Hadean zircon grains) are located near the southern margin of the Narryer terrain and represent one of the few supracrustal belts in the complex. The oldest rocks in the Narryer terrain are known as the Manfred Complex and include meta-anorthosite and other orthogneisses with ages up to 3.73 Ga (Kinny et al. 1988). Supracrustal enclaves located in the vicinity of Mount Narryer that may have Eoarchean ages include mafic and ultramafic rocks, BIF, metaconglomerate, quartzite, and calc-silicate rocks.

Last, Eoarchean crust is also present in the Anshan area of eastern China. Granitoid gneisses from this area contain zircon grains with ages up to 3.8 Ga (Liu et al. 1992). These TTG-type orthogneisses typically consist of variable mixtures of quartz, phengite, plagioclase, K-feldspar, and hornblende (Liu et al. 2008). Minor bands of quartz and biotite within these TTGs may represent Eoarchean metasedimentary enclaves. Younger Paleoarchean supracrustal rocks also occur in the Anshan area and include units of amphibolite, BIF, quartz–biotite schist, and quartzite.

HADEAN–EOARCHEAN SURFACE ENVIRONMENTS

The Oldest Preserved Marine Environments

A simplistic view of surface environments in the Hadean and Archean posits a mostly mafic crust with sporadic volcanism, a weakly reducing atmosphere with N_2 and CO_2 as the dominant gases, and anoxic oceans with some prebiotic macromolecules and other organic compounds. Low- and high-temperature reactions between organic molecules and minerals in oceanic environments ultimately gave birth to life on Earth (Cody 2005). The original mineral diversity of Hadean–Eoarchean marine environments in which life originated is now represented by metamorphic and metasomatic minerals in the limited archive of the oldest geological record.

Eoarchean sedimentary rocks deposited in marine environments either incorporated detrital components from nearby weathered rocks or formed under the influence of hydrothermal activity on the seafloor. Protoliths of metapelitic schists include mudstone and siltstone, whereas protoliths of quartzite may include both chert and sandstone (Table 2). Eoarchean BIF and ferruginous chert have chemical sedimentary precursors that precipitated on the seafloor from siliceous and ferruginous gels, probably under hydrothermal conditions. Precursor minerals for biotite and garnet in these rocks may have included ferruginous aluminosilicates, phyllosilicates, and other hydrated silicates that form during the weathering of feldspars and mica. Chlorite, biotite, amphibole, and garnet crystallize from mineral reactions between quartz and intermediate phases of ferruginous silicates and/or from reactions involving carbonate and quartz (Klein 2005). Pyroxene can form from reactions between Fe-rich carbonate and quartz, but also from the dehydration of amphibole during prograde metamorphism. Notably, graphite is common in most of these Eoarchean rock types, but its origin, and that of its carbon, is ambiguous. Possible sources of reduced carbon in graphite from Eoarchean metasedimentary rocks include abiotic synthesis from the catalyzed reduction of carbon monoxide with hydrogen (e.g. Fischer–Tropsch-type reactions), decarbonation of carbonates during metamorphism, mantle fluids containing methane and carbon dioxide, extraterrestrial delivery by meteorites, prebiotic organic compounds, and remains of microorganisms from the depositional environment.

Possible Mineralogical Evidence of Early Life

Six elements—carbon, hydrogen, oxygen, nitrogen, sulfur, and phosphorus—dominate every living organism. These elements are found in a variety of igneous rock-forming minerals, but can also be incorporated in various sedimentary minerals formed during the decomposition of biological organic matter or from metabolic by-products. Evidence for early life in Eoarchean metasedimentary rocks is a highly contentious subject, and no mineral associations in these rocks provide unambiguous evidence for early life (Schopf 2006). Apart from the petrological and mineralogical context, stable isotopes and trace element compositions of specific minerals may provide independent lines of evidence consistent with a biological influence on their geochemistry.

Graphite is known to occur in Eoarchean BIFs, schists, and calc-silicate rocks, but to assess the possible sources of this carbon, stable isotope and elemental compositions need to be determined. Biological metabolisms involved in carbon fixation impart carbon isotope fractionation, but these signatures are blurred by high-temperature metamorphism, which also strongly fractionates carbon isotopes. For instance, some Eoarchean schists and metaturbidites of marine origin from the Isua Supracrustal Belt contain bands of graphite globules with ^{13}C-depleted carbon, which has been interpreted as evidence of Eoarchean life (Rosing 1999). Another example of possible mineralogical remains of early life is the occurrence of apatite–graphite associations in an Eoarchean quartz–pyroxene rock from the island of Akilia, which also contains ^{13}C-depleted carbon (Mojzsis et al. 1996). Apatite–graphite associations also occur in a quartz–magnetite–amphibole BIF from the Nuvvuagittuq Supracrustal Belt (Fig. 4). Apatite–graphite associations can form as a result of postdepositional diagenetic maturation and oxidation of organic matter, a process that releases phosphate into pore solutions.

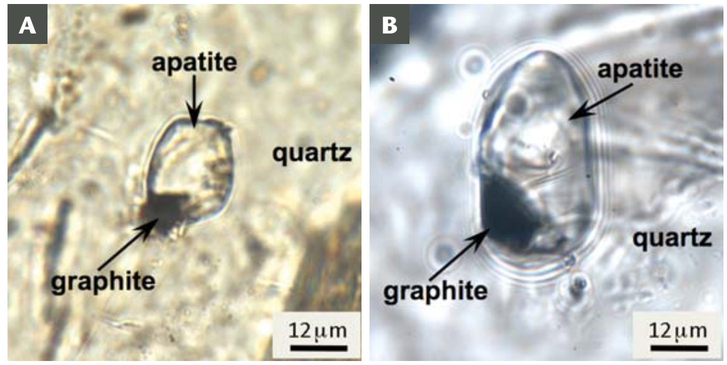

Figure 4 Apatite grains associated with graphite from (**A**) an Eoarchean cummingtonite–magnetite–quartz BIF from the Nuvvuagittuq Supracrustal Belt and (**B**) an Eoarchean quartz–pyroxene rock from the island of Akilia

Other possible geochemical evidence for Eoarchean life may exist in phyllosilicates, sulfides, and Fe oxides. During the decomposition of marine sedimentary organic matter, ammonium and hydrogen sulfide can be released into sediment pore solutions and subsequently be incorporated structurally in phyllosilicates and sulfides, respectively. Quartz–garnet–mica schists from the Isua Supracrustal Belt contain biotite with high concentrations of structural ammonium that is occasionally ^{15}N-depleted; signatures that are possibly consistent with a biological source for nitrogen (Papineau et al. 2005). However, while the sulfur isotope composition of sulfides in Eoarchean metasedimentary rocks may preserve evidence of biological fractionation, no unambiguous signature has been found so far (Papineau and Mojzsis 2006). Nevertheless, there are hints from the Akilia quartz–pyroxene rock that such signatures may exist (Mojzsis et al. 2003). Finally, Eoarchean BIFs from localities in Greenland and elsewhere contain ^{56}Fe-enriched minerals that may be consistent with biological Fe-metabolisms (Dauphas et al. 2004). These results and interpretations are contentious, however, and future work should aim to discover similar evidence in metasedimentary rocks from other Eoarchean supracrustal belts.

SUMMARY AND OUTLOOK

The mineral diversity of Hadean–Eoarchean surface environments has been blurred by repeated metamorphic and metasomatic events and decreased by geochemical homogenization. However, insights into the earliest mineral environments can still be gained from the mineralogy of Hadean zircon inclusions and from Eoarchean metaigneous and metasedimentary rocks. On the basis of the various Hadean–Eoarchean rock types found today, it can be concluded that ancient mineral diversity was less than today's, with perhaps no more than about 1500 different mineral species (Hazen et al. 2008). While trace levels of oxygen could have been present in local Archean oases, it was not until the Paleoproterozoic (2.5 to 1.6 Ga) that both a significant accumulation of atmospheric oxygen and a significant leap in mineral evolution occurred. Such global oxygenation events and associated biogeochemical processes were responsible for the irreversible and significant increase in Earth's mineral inventory.

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