Not So Hot “Hot Spots” in the Oceanic Mantle

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Excess volcanism and crustal swelling associated with hot spots are generally attributed to thermal plumes upwelling from the mantle. This concept has been tested in the portion of the Mid-Atlantic Ridge between 34° and 45° (Azores hot spot). Peridotite and basalt data indicate that the upper mantle in the hot spot has undergone a high degree of melting relative to the mantle elsewhere in the North Atlantic. However, application of various geothermometers suggests that the temperature of equilibration of peridotites in the mantle was lower, or at least not higher, in the hot spot than elsewhere. The presence of H2O-rich metasomatized mantle domains, inferred from peridotite and basalt data, would lower the melting temperature of the hot spot mantle and thereby reconcile its high degree of melting with the lack of a mantle temperature anomaly. Thus, some so-called hot spots might be melting anomalies unrelated to abnormally high mantle temperature or thermal plumes.

The concept of hot spots has played an important role in the theory of plate tectonics (1–3). Oceanic hot spots are areas of thicker than normal crust and excess volcanism and are commonly marked by islands. They are generally attributed to anomalously high temperatures of upwelling mantle plumes, which result in overabundant production of melt and in crustal swelling (1–4). In this report I discuss data from one such inferred hot spot, the Azores hot spot complex (AHS), located between 34° and 45°N in the Mid-Atlantic Ridge (MAR). These data imply that this so-called hot spot may not be caused by anomalously high upper-mantle temperatures, but rather by a mantle with a composition different from that underlying normal segments of the Mid-Atlantic Ridge.

The geochemical nature of the oceanic upper mantle has been inferred from studies of the melts extracted from it (oceanic basalts) or of the solid residue left behind in the mantle after melt extraction (oceanic peridotites). The reconstructed primary mineralogy of oceanic peridotites [olivine + orthopyroxene (opx) + clinopyroxene (cpx) + spinel] suggests that they equilibrated in the spinel peridotite facies [pressure >8 to 9 kbar at 1000° to 1300°C (5)]. I compare the chemistry of these mantle-equilibrated relics in samples of peridotite bodies emplaced in young (<35 million years old) North Atlantic crust (Fig. 1) and representing the uppermost sub-Atlantic mantle [see (6–8) for methods and raw data].

Regional, long-wavelength (~1000 km) variations of peridotite modal and mineral composition (Fig. 2), detected along the MAR (6, 9), must reflect fundamental regional differences in upper mantle composition, thermal structure, or both (10). The chemistry of the primary minerals, namely their content of Mg, Cr, and other refractory elements versus that of Al, Fe, and other incompatible elements (10–12), suggest that greater amounts of melt [up to >20% melting relative to a pyrolite-like source (6)] have been extracted from the mantle rocks in the AHS region than elsewhere in the MAR, where the degree of melting can be as low as 8% (6). These regional variations along the MAR are associated with variations of geophysical parameters (Fig. 2) such as zero-age sea-floor depth (13) and geoid residual anomaly (14), and basal properties such as Na2O content (15) and La/Sm ratio (16). Basalt Na2O content has been related to the degree of partial melting undergone by the source material in the mantle (15). It is inversely correlated with the 100Cr/(Cr + Al) ratio of spinels in peridotite. Along with other mineral chemistry relations (6), it provides independent support for high degree of melting of the AHS mantle.

This high degree of melting could reflect higher upper-mantle temperatures in the AHS than elsewhere along the MAR, consistent with the notion that the anomalously region is a hot spot (15, 16). If temperature differences in the upper mantle were the sole cause of the different degrees of melting, estimated differences in mantle temperature between mid-ocean ridge segments with the highest and lowest extent of melting should be ~250° to ~300°C at equivalent depths in the melting region (15). If we consider only the North Atlantic part of the ridge, these differences are reduced somewhat. The temperature differences would be smaller at shallower depth in the mantle where final subsolidus equilibration of the peridotite occurs, but should still exceed 100°C.

In order to test the assumption that mantle temperature is the cause of differences in the degree of melting along the MAR, I have calculated peridotite equilibration temperatures using the Wells’ (17) and Lindsley’s (18, 19) geothermometers. Both are based on the temperature dependence of reactions between coexisting opx and cpx (20, 21). Among the various proposed peridotite geothermometers, these appear to be the most reliable, particularly for peridotites equilibrated in the spinel lherzolite stability field (22). However, because of the limitations of these and other peridotite geothermometers, I regard the estimated temperatures (Fig. 2) as expressing relative trends rather than absolute values (23). The calculated temperatures are generally consistent within each geotectonic area (24–26).
The geothermometry estimates for the peridotites from the AHS, although limited in number by the absence of primary cpx in many of the highly refractory samples, include samples from three areas: Oceanographer fracture zone, 43°N fracture zone, and DSDP Site 556. Average estimated temperatures of equilibration of peridotites from the AHS appear to be lower, or at least not higher, than those of peridotites from elsewhere along the MAR (Fig. 2). The calculated temperatures may actually reflect cooling rates of the upwelling mantle bodies (27).

Experimental work has shown that Al2O3 isopleths in opx and the partitioning of Al between opx and spinel in spinel peridotite are controlled primarily by bulk composition and temperature; the partitioning is relatively independent of pressure (22, 28, 29). Thus, peridotites that equilibrated at high temperature should have high Al2O3 opx/spinel ratios. However, relatively low values were observed in samples from the AHS region (Fig. 2). These data complement the geothermometry calculations and suggest again that the AHS rocks did not equilibrate at higher temperature than other MAR peridotites. Although the estimated temperatures probably do not represent mantle temperatures during melting but subsolidus re-equilibration temperatures, we would expect them to be higher in a hot spot than in a non–hot spot region. An upper-mantle column above a stable hot spot should be hotter than a column away from a hot spot at equivalent depths. Mantle upwelling and thus cooling rate should be faster in a hot spot than elsewhere and should result in a higher equilibration temperature. These results imply that the high degree of melting of the AHS mantle may not be caused by a higher mantle temperature than elsewhere along the MAR (27).

The absence of a temperature anomaly could be reconciled with a high degree of melting if the mantle of the AHS was enriched in H2O and CO2. The presence of H2O and CO2 (either as free phases or in minerals such as amphiboles, phlogopite, and carbonates) lowers the solidus temperature of peridotite (30–35). This effect is not trivial: even traces of CO2 or H2O, or both, can lower the melting temperatures by hundreds of degrees (32). Partial melting would thus be enhanced even in a normal mid-ocean ridge thermal regime.

The notion that the upper mantle in the AHS is enriched in H2O and other volatiles is supported independently by basalt and peridotite data. Mid-ocean ridge basalts (MORB) from the AHS region contain two to three times as much H2O as normal MORB; are enriched in volatiles such as Cl, Br, and F; and tend to have lower SiO2 content, which is consistent with melting from an H2O-enriched source (36). This evidence has led Schilling et al. (36) to suggest that the AHS behaves also as a "wet spot" and is the locus of metasomatism.

The high La/Sm ratio and general enrichment in light rare-earth elements (LREE) of the AHS basalts (Fig. 2) cannot be explained by increased degrees of melting but requires the addition of an incompatible element-enriched component in the source (16, 37). The abundance of incompatible large-ion lithophile elements (LILE) K, Rb, Cs, Sr, and REE have been estimated in the mantle parental material of normal MAR basalts and in that of AHS basalts for a range of mantle primary modal compositions and of degrees of partial melting (37). This calculation shows that the AHS mantle is strongly enriched in LILE relative to normal MAR mantle (Fig. 3) and that the enrichment is greatest for elements with largest ionic radii (37). These results can be interpreted by considering data obtained from the Zabargad peridotite complex in the Red Sea, a mantle body from a pre-oceanic rift and consisting of undepleted spinel lherzolite veined by metasomatic LILE-enriched
amphibole peridotite (38). The LILE distribution of the Zabargad spinel lherzolite plots close to the estimated sub-Atlantic normal parental mantle (Fig. 3A). This result agrees with mineral chemistry and Nd-Sr isotopic data suggesting that the Zabargad spinel lherzolites could be a potential source of MORB (38, 39). The LILE pattern for the Zabargad metasomatic amphibole peridotite plots instead close to the estimated parental mantle for the AHS area (Fig. 3B). That the equivalent of normal oceanic mantle and of hot spot mantle can be found side-by-side as meter-scale heterogeneities in the Zabargad peridotite body supports the notion that a variably veined mantle can also occur beneath the Atlantic, such that the so-called hot spot mantle contains a high proportion of metasomatic component, and the normal ridge mantle a low proportion.

Thus, a variety of data supports the hypothesis that the upper mantle in the AHS area is enriched in H2O. Wet mantle that upwells adiabatically would cross the wet solidus at a higher pressure than a similar but dry mantle body (Fig. 4). Partial melting during further ascent would lead to cooling because of expenditure of latent heat of fusion (41–44). Because a dry peridotite starts melting at lower pressure, its pressure-temperature (P-T) trajectory during upwelling is displaced toward higher temperature relative to that of the wet peridotite, and should reach final equilibration at a higher temperature. The relatively low equilibration temperatures estimated for the AHS area could thus reflect a subsolidus trajectory at lower temperature because of the H2O- and CO2-enrichment relative to the normal MAR mantle.

When and where was this metasomatized mantle created? Basalt 3He/4He ratios are lower in the AHS region than in normal MORB (44). This contrasts with most other hot spots such as Hawaii and Iceland, which show 3He/4He ratios higher than those in MORB (44–46). The low 3He/4He ratio of the AHS area implies that the mantle has either lost 3He (relative to normal MORB mantle) by degassing, or has had an addition of U and Th (44). One possibility is the incorporation in the mantle of old, subducted, partially degassed oceanic crust (44, 47). However, He degassing could result from a metasomatic event (44, 46), which is consistent with the observed enrichment of LILE in the AHS mantle (Fig. 3).

Preferred sites of degassing of the Earth and of mantle metasomatism are continental rifts (48–51) such as the East African–Red Sea rifts where thinning and breaking of the continental lithosphere allows release of mantle volatiles that elsewhere are trapped beneath a thick lithospheric lid. The metasomatized mantle domains inferred for the AHS area might be remnants of proto-Atlantic rift mantle that were left behind during the opening of the North Atlantic. The possibility of having relics of subcontinental mantle beneath the axial region of the Atlantic has been suggested before (52) and has been proposed recently in order to account for Sr-Nd-Pb isotope systematics of some hot spot oceanic islands (53) and of basalts from the Oceanographer fracture zone (54), well within the AHS area. Basalts from some Atlantic hot spot islands show Sr-Nd-Pb isotope systematics similar to those of East African rift volcanic rocks, for which a metasomatized, H2O and CO2-enriched mantle source has been advocated (51).

Direct samples of the inferred metasomatized H2O-rich mantle domains of the AHS were not obtained, probably because the peridotites from the AHS are highly refractory and the metasomatic components, including mantle-equilibrated amphibole and phlogopite, were extracted during partial melting. However, an example of strongly metasomatized mantle similar to the inferred source of the AHS anomaly has been preserved in the Atlantic islets of St. Peter-Paul (SPP), located near the equator.

The mantle exposed at SPP is a mylonitic spinel peridotite containing variable amounts of amphibole and is associated with hornblende (55, 56). In terms of mineral, trace element, and isotopic chemistry, their undepleted composition, and low estimated temperatures of equilibration (Fig. 2), the SPP peridotites are different from MAR peridotites but similar to those at Zabargad (57). Thus, the SPP mantle body may have been spared going through fast upwelling in a hot thermal regime, which would have resulted in higher temperatures of equilibration and in significant partial melting, as is generally seen in MAR peridotites. The LILE distribution of the SPP peridotites (56), just as that of the Zabargad metasomatized amphibole peridotites (38), falls within the range of the estimated mantle source of the AHS basalt (Fig. 3). Moreover, the 3He/4He ratio of SPP rocks is lower than that of normal MORB (58) and similar to that of rocks from the AHS area (Fig. 2). In terms of Sr-Nd-Pb isotope systematics, the mantle rocks

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**Fig. 3.** Estimated chondrite-normalized LILE element content in parental mantle for normal MAR basalts and for AHS basalt, from (37), compared with LIL content of Zabargad spinel lherzolites (A) and of Zabargad metasomatized amphibole (amph.) peridotites (B), from (38, 39). The LILE element distribution of average St. Peter-Paul Island amphibole peridotite, from (56), is also shown.

**Fig. 4.** Qualitative and schematic diagram illustrating partial melting and P-T paths of upwelling “dry” and “wet” peridotitic upper mantle bodies.
at SPP are compatible with the inferred source of ocean island (hot spot) basalt (56) and of East African rift basalt (51). Thus, on the one hand SPP fits the requisites of the mantle source for the AHS basalt. On the other hand, its similarity with the inferred mantle at Zagbard and in the East African rift suggests that SPP might be a fragment of pre-oceanic rift mantle left behind from the opening of the proto-Atlantic rift (57). The probable age of the metamorphic event that affected SPP [155 million years ago (56)] lies within the age of the continental rifting that preceded the opening of the equatorial Atlantic.

The AHS region has positive zero age crustal depth and residual geoid anomalies (Fig. 2). If we assume that there are no temperature differences between the AHS mantle and normal MAR mantle, the AHS axial topographic high must be due to the increased thickness of the crust and of the residual mantle column, in that refractory harzburgite is less dense than fertile lherzolite (59). An additional factor is introduced in these estimates, however, if metasomatized peridotite is abundant in the AHS mantle, because low-density phases would then be abundant. If the metasomatized mantle domains of the AHS region are similar to Zagbard amphibole peridotite with about 20% modal amphibole (38), and with, in addition, plagiopogene and carbonates, their density could be lowered close to ~3.2 g/cm³ relative to that of unmetasomatized (3.3 g/cm³) spinel lherzolite. The thickness of the metasomatized mantle column would determine the extent of the positive topographic anomaly. The geoid high could then be largely due to topography.

In summary, I suggest that the presence of metasomatized, H₂O- and CO₂-rich domains in the 34° to 45°N mantle, rather than anomalously high mantle temperatures, can account for the main features of the AHS area, such as (i) the high melting anomaly; (ii) the enriched nature of the basalt; and (iii) the positive zero age depth, crustal thickness, and geoid anomalies. Thus, the suggestion of an Azores hot and wet spot (34) is modified into the idea of a wet but not particularly hot spot. One implication is that estimates of mantle temperature beneath mid-ocean ridges based on degree of melting and volume of released melt must take into account the areal heterogeneity of upper-mantle composition (particularly in terms of H₂O and other volatiles) and, consequently, of melting temperature. Other implications are that not all hot spots are necessarily loci of unusually high mantle temperature, and that mantle metasomatism related to recent or ancient degassing events may play the major role in the enhanced melting and crustal swelling associated with some of them.

REFERENCES AND NOTES

9. The mineral chemistry of mantle-equilibrated phases olivine, opx, cpx, and spinel changes as a result of increasing degrees of partial melting of the upwelling mantle. The changes reflect the incompatible behavior during melting of some elements such as Al, Ca, Fe, and Mg, which partition with the melt, and the refractory behavior of other elements such as Mg and Cr, which stay with the residue. As a result, the spinel 100 Ca(Cr + Al) ratio increased in peridotites with increasing degree of melting, whereas the Al content of pyroxene decreases. If care is not taken, the changes due to subsolidus re-equilibration and to low-temperature alteration, and if reasonable assumptions are made concerning initial mantle peridotite composition, degrees of melting can be estimated by calibration of the mineral chemistry data with experimental results (6, 9, 11, 12). The spinel 100 Cr(Cr + Al) ratio found in peridotites from the AHS area is matched closely with the Fo content of olivine and 100 Mg(Mg + Fe) ratio of opx, and inversely with Al content of opx (6–8). These relationships support the concept of a high degree of melting in the AHS area.
14. E. M. Klein and T. E. Langmuir, ibid. 92, 8089 (1987). These authors normalized the Na₂O content of basalt to 8% MgO in order to eliminate effects due to low-pressure fractionation.
22. Temperature estimates from Wells' equations reproduce experimental data within 70°C (17); those from Lindsay's equations are within about 50°C (18, 19). Exsolution of cpx from opx and vice versa tends to lower the estimated temperatures. Low (<5%) by volume degrees of exsolution are generally evident in pyroxenes from North Atlantic peridotites. No attempt was made to reconstruct pre-exsolution compositions. This effect results in a more or less systematic lowering of the estimated temperatures, which should not significantly affect the trend of relative temperature variations along the MAR upper mantle. The calculated temperature values for Wells and Lindsay are related, although the Lindsay geothermometer tends to give higher values (Fig. 2) and a higher scatter in each area.
23. Average calculated temperatures for each area (that is, for each fracture zone or DDP site) fall between 940° and 1120°C. The temperatures with the lowest average estimated temperatures are the fracture zone at 43°N and DDP site 556, both within the AHS region. Temperatures of from about 750°C have been obtained from only some samples from the Gibbs, Atlantis, and Vema fracture zones that contain low-Ca cpx [with ≤48 mole percent wollastonite component (woll)] in contrast with the high-Ca (40–45%) cpx commonly found in oceanic peridotites. These low-Ca cpx appear to be enriched in Fe and Ti relative to common cpx of oceanic peridotites (25). Similar low Ca, high Fe cpx found in peridotite nodules have been attributed to exchange of the peridotite with hot magma intrusions at mantle depth (26).
26. Both Wells' (17) and Lindsay's (18, 19) geothermometers estimate the closure temperature of reactions between cpx and cpx in peridotite. The estimated temperatures may be affected by the cooling rate of the upwelling mantle bodies. Cooling rate is affected by upwelling rate (see for instance A. Lane, in Am. Soc. Earth. Sci. Bull. 1966). M. Sleep, J. Geophys. Res. 86, 5121 (1981).
Hematite Nanospheres of Possible Colloidal Origin from a Precambrian Banded Iron Formation

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Exceptionally small spheres (nanospheres) of hematite (diameters between 120 and 200 nanometers) occur in the Marra Mamba Iron Formation of the Hamersley Basin, Australia. The nanospheres are clustered into small aggregates and may have formed by structural ordering and dehydration of colloidal iron hydroxide particles. Individual spheres consist of numerous thin, curved hematite platelets surrounding a central void that is approximately half the diameter of the sphere; this texture suggests that they formed by a volume reduction of the original colloidal particles by ~12.5%. The occurrence of hematite nanospheres supports the hypothesis that some of the iron was deposited colloiddally during the development of banded iron formations, approximately 2.5 billion years ago.

THE ORIGIN OF PRECAMBRIAN IRON formations, the world’s oldest and largest iron deposits, has been a source of continuing interest and occasional controversy for many decades (1–6). They occur as layered rocks on all continents and provide the bulk of mined iron. Potentially, they indicate the character and history of the early Earth’s oceans, atmosphere, and biosphere (5–9); they have been used to infer the evolution of Earth’s atmosphere in Precambrian time. The methods of concentrating, transporting, and then depositing the vast quantities of iron in these extensive sedimentary units provide serious geological and geochemical problems.

Colloidal transport and deposition has been proposed as one means of moving the extraordinary amounts of iron to the basins where the iron ultimately was deposited (10, 11). But direct observational evidence has been both sparse and equivocal. Spherical structures 5 to 40 μm in diameter are common in iron formations, but there is dispute over whether they indicate purely chemical colloidal processes (12–15), organic activity (16), or recrystallization (17). In this paper we describe tiny hematite spheres that have diameters only 1/40 to 1/200 of known spherical features in iron formations. We propose these spheres as strong indicators of colloidal processes during deposition of the iron formations.

We studied two samples that were selected to be representative of regions of drill core separated vertically by ~2 m. The core (D.D.H. No. 270, located 38 km west of Wittenoom, Australia) is from the Marra Mamba Iron Formation, which is of the Lake Superior type (17a). This formation was deposited about 2.5 billion years ago, at the approximate boundary between the Archean and Proterozoic ages and is the lowermost member of the Hamersley Group of Western Australia (18). In addition to the hematite, the samples contain quartz, magnetite, stilpnomelane, ankerite, minnesotaite or t alc, and fibrous riebeckite (crocodilite). Specimens were examined at 400 and 120 kV with JEOL JEM-4000EX and Philips 400T transmission electron microscopes (19).

In all the grains that we observed, the hematite occurs in tiny clusters between quartz grains. Most hematite aggregates are smaller than 2 μm in diameter, and they have relatively sharp boundaries with the quartz (Fig. 1). Electron-diffraction patterns show rings as a result of the polycrystalline character of the aggregates (Fig. 2 and Table 1). These aggregates consist of spheres that have diameters between 120 and 200 nm (Fig. 3); we call them “nanospheres.” The hematite nanosphere clusters are widespread in the specimens we studied. Only circular shapes were observed in our transmission electron microscopy (TEM) images, indicating that the hematite has a spherical rather than cylindrical form.

The TEM images of the nanospheres show marked contrast between the outer shells and central areas (Fig. 3). These cores show light contrast and produce neither electron-diffraction patterns nor lattice fringes in TEM observations; only the outer shells consist of hematite. These shells consist of thin, subparallel, platy crystals, each approximately 3 to 5 nm thick (Fig. 4). Completely circular single crystals were not observed; instead, many curved crystals are joined to form spherical structures.

The appearance of the hematite nanospheres is similar to that of Fe-Si-Al-oxihydroxides that crystallized from gel spheres (20). The presence of central voids suggests that the nanospheres also formed by void nucleation (21) from colloidal gels rather than by nucleation crystallization or spinodal decomposition. The central voids apparently formed during shrinkage caused by both ordering and dehydration.

Fine-grained hematite in weakly meta-

Fig. 1. Low-magnification TEM image showing a hematite cluster (Hmt) in quartz (Qtz).

Fig. 2. Electron-diffraction pattern of hematite showing ring features. The ten innermost reflection rings are numbered; their interplanar spacings and indices are given in Table 1.