calcite growth is an important first step toward establishing a physical model for the thermodynamic and kinetic consequences of Mg<sup>2+</sup> incorporation during biomineral formation.

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# African Hot Spot Volcanism: Small-Scale Convection in the Upper Mantle Beneath Cratons

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Numerical models demonstrate that small-scale convection develops in the upper mantle beneath the transition of thick cratonic lithosphere and thin oceanic lithosphere. These models explain the location and geochemical characteristics of intraplate volcanos on the African and South American plates. They also explain the presence of relatively high seismic shear wave velocities (cold downwellings) in the mantle transition zone beneath the western margin of African cratons and the eastern margin of South American cratons. Small-scale, edge-driven convection is an alternative to plumes for explaining intraplate African and South American hot spot volcanism, and small-scale convection is consistent with mantle downwellings beneath the African and South American lithosphere.

Cratons are regions of continents that have not been affected by tectonic processes for more than one billion years. Relatively low surface heat flow (1), diamond inclusions in kimberlites (2), and a relatively cold and thick keel (3) with high seismic velocities to about 250 km depth (4) distinguish cratons from other continental lithosphere. Although cratons are commonly envisioned as stable regions of Earth's lithosphere, the change in lithospheric thickness and, hence, the relatively strong lateral temperature and viscosity contrasts at the edges of cratons induce a small-scale form of convective flow in the mantle beneath the craton margin. Numerical (5) and laboratory (6) investigations indicate that such convective flow, commonly termed edge-driven convection, consists of down-



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- 30. We examined layer growth on the {1014} face of calcite, while macroscopic measurements of solubility were determined from a composite of different surfaces. Nonequilibrium facets are generated by collisional fracture in mass crystallizers or are caused by the presence of Mg<sup>2+</sup> and other impurities in the growth solution (2, 3, 31). Because the present study pertains to only one crystallographic facet, a direct solubility comparison is not valid.
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wellings extending as deep as the mantle transition zone (about 660 km) beneath the margins of cratons and upwellings at about 500 to 1000 km distance from the margins of cratons. Previous workers have suggested that edge-driven convection may be responsible for the formation of the Bermuda Rise (7), the North Atlantic Tertiary Volcanics (8), and flood basalt magmatism at the peripheries of cratonic provinces (9). Here, we suggest that intraplate volcanos (hot spots) on the African and South American plates (Fig. 1) are linked to edge-driven convection on the basis of numerical simulations of mantle flow and images of seismic velocity anomalies in the African upper mantle.

Our model of edge-driven convection is based on the temperature and velocity fields, computed using a compressible convection formulation for a two-dimensional Cartesian geometry (Fig. 2) (10). The initial thermal structure of an ocean basin is calculated using the solution for a moving plate, whereas the thermal structure of the cratonic lithosphere is calculated using the half-space solution and assuming that the

Fig. 1. Location of hot spots (triangles), cratons (gray shading), and plate boundaries (gray line). The boundaries of cratons are defined seismically: they circumscribe regions of S20RTS at 100 km depth where the shear wave velocity perturbation from the PREM model is 4% or larger. The hotpots are taken from the list compiled by Sleep (20). The intraplate "African hot spots" are denoted by white triangles (afr1, Ahaggar; afr2, Tibesti; afr3, Jebel Mara; afr4, Cape Verde; afr5, Canary; afr6, Mt Cameroon; afr7, Vema; afr8, Victoria; and afr9, Comores), as are the "South American" hotspots (sa1, Fernando; sa2, Arnold; and sa3, Trindad). "Plate Boundary" hot spots are denoted with black triangles (pb1, Ascension;

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Fig. 2. The temperature anomalies (adiabatic temperature profile removed) and velocity fields from calculations with a step change in lithospheric thickness. The width of the ocean basin (thin lithosphere) is 600 (A) and 1800 km (B). In each calculation, the width of the ocean basin is fixed throughout time. Both panels are taken 50 My after the initial condition. The temporal evolution of the calculation in panel (B) is shown in (C) and (D) at 20 My and 100 My after the initial condition, respectively. The parameters used in these calculations are described in the text and notes. Because of the symmetry of the boundary conditions, only the left half of the ocean basin is shown; the solution can be reflected about the left edge of the model. Because the flow is confined to the upper mantle, only a subregion of the the calculation is shown; the width and depth of the calculation extend to 2890 km.





Distance (deg)

Fig. 3. (A) Horizontal cross sections through S20RTS at at depths of 100, 350, and 600 km. Relative high- and low-velocity regions are indicated by blue and red, respectively, with an intensity that is proportional to the amplitude of the velocity perturbation from the PREM. Green lines represent plate boundaries. White lines circumvent regions in the mantle where the

seismic velocity at a depth of 100 km is larger than in the PREM by 4% or more. These regions roughly outline the location of Precambrian cratons. (B) A 140°-wide cross section through S20RTS across South America and southern Africa. The green circles indicate locations of earthquakes in the Harvard Centroid Moment Tensor catalog.

low Vs

craton is uniformly 500 million years (My) old (11). The model also contains solidsolid phase transformations at 410 and 660 km depth (12), which confine edge-driven convection to the upper mantle (13). The viscosity of the fluid depends on pressure and temperature, following the creep properties of olivine (14). The location of the craton with respect to the edges of the computational domain is fixed in each calculation. The distance between the edge of the craton and the ocean ridge is varied from 400 to 1600 km in a series of calculations to study the pattern of the smallscale flow as the width of the ocean basin is increased.

When the ocean basin is narrow (Fig. 2A), an upwelling forms along the edge of the computational domain, which represents the central spreading axis of the ocean basin. A downwelling forms beneath the craton, slightly on the craton side of the craton-ocean margin. As the width of the ocean basin increases with time (Fig. 2B), the upwelling moves off the spreading axis while the downwelling remains fixed with respect to the craton-ocean boundary. The resulting edge-driven convection cell is, at most, 800 to 1000 km wide regardless of the location of the craton. Edge-driven convection reaches a peak velocity of about 30 mm/year at an elapsed time of about 80 to 100 My. After 100 My, the vigor of the flow slowly decreases. The cratonic root in our model is cold and hence more viscous than the surrounding mantle. This is sufficient to stablize a cratonic root for up to a billion years (15). We infer that the intraplate African and South American hotspots (denoted by white triangles in Fig. 1), which are located 600 to 1000 km from the margins of the African and South American cratons, are the surface manifestation of the upwelling flow seen in the edge-driven convection model (Fig. 2), and not deep mantle plumes. Because Africa is thought to have remained nearly stationary with respect to the deep mantle (16), edge-driven convection may be easier to detect under African than at moving cratons, where the plate-scale flow could significantly alter the pattern of edge-driven flow.

Although previous studies of edge-driven convection have focused on the hot, upwelling flow, downwelling flow directly beneath the margin of the cratonic lithosphere is also a characteristic component of edge-driven convection (5-8). These downwellings form beneath the margins of the thick cratonic lithosphere and have a similar magnitude thermal anomaly (although of opposite sign) to the upwellings. Evidence for downwelling flow associated with edge-driven convection is now available through the recently derived seismic tomographic model, S20RTS (Fig. 3) (17). At 350 km depth, model S20RTS yields an elongated, 1 to 2% high-velocity anomaly beneath the Atlantic coast of Africa and, albeit with a lower amplitude, a high-velocity anomaly in the transition zone, located beneath eastern Brazil and the central Atlantic Ocean. These anomalies are nearly equally as strong as high-velocity anomalies seen in S20RTS beneath subduction zone regions (e.g., South America and the western Pacific). High shear velocity anomalies are located at the eastern and western flanks of the South American and African cratons, respectively, and they extend to about 600 km depth (Fig. 3). Resolution tests indicate that the depth extent of shear velocity anomalies in the transition zone is poorly resolved. However, we can rule out the possibility that, due to incomplete data coverage, high-velocity structures in the uppermost 200 km of the mantle beneath cratons have been projected into the transition zone [Web fig. 1 (18)]. Because subduction beneath Africa has not occurred since the Triassic, we infer that the high-velocity structure reflects mantle downwellings beneath the western margin of the West African, Congo, and Kaapvaal cratons associated with edge-driven convection. The magnitude of the high shear velocity anomalies are consistent with the magnitude of the cold thermal anomalies in the numerical models (about 200°C) (19).

It is intriguing that in the North Atlantic, the youngest and narrowest part of the Atlantic basin, hot spots occur on the ridge axis (Iceland and Azores), while in the Central and Southern Atlantic there are a significant number of off-ridge hot spots (Bermuda, Madeira, Canary Islands, Cape Verde, Fernando, Arnold Seamount, Trindad, Mount Cameroon, and Vema). This is also consistent with the predictions of edge-driven convection. S20RTS (17) also indicates the presence of a high-velocity anomaly in the 300 km depth range beneath the eastern United States, which may be related to the Bermuda hot spot. Although this anomaly is significantly weaker than the African anomaly, it suggests that edge-driven convection may be responsible for other hot spots as well.

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- 11. The solution for the thermal evolution of a cooling half-space has the form,

$$\theta(t) = \theta_{o} \operatorname{erf}\left[\frac{-z}{2\sqrt{\kappa t}}\right]$$

where  $\theta$  is temperature, t is time,  $\kappa$  is thermal diffusivity, z is the depth, and  $\theta_0$  encompasses the initial conditions. In the plate solution, time is related to the distance from the spreading axis, x, by the relation  $x = v_{\text{plate}} \times t$ , where  $v_{\text{plate}}$  is the plate velocity. [A. R. Leeds, L. Knopoff, E. G. Kausel, *Science* **186**, 141 (1974)].

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 In a uniform composition mantle, in the absence of melting we can write,

 $\delta T \, \approx \, \frac{\left(\delta V_{s} / V_{s}\right)}{\left(\partial ln V_{s} / \partial ln T\right)_{p}}$ 

where T is temperature and  $V_s$  is the seismic shear velocity. Ignoring anelastic contributions to the velocity, which are probably small for cold anomalies in the upper mantle,

$$\delta T \approx \frac{-(\partial \ln \rho / \partial \ln V_s)_p}{\alpha} (\delta V_s / V_s)$$

where  $\rho$  is density and  $\alpha$  is the coefficient of thermal expansion. Choosing reasonable upper mantle values

# Direct Condensation of Carboxylic Acids with Alcohols Catalyzed by Hafnium(IV) Salts

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In order to promote atom efficiency in synthesis and to avoid the generation of environmental waste, the use of stoichiometric amounts of condensing reagents or excess substrates should be avoided. In esterification, excesses of either carboxylic acids or alcohols are normally needed. We show that the direct condensation of equimolar amounts of carboxylic acids and alcohols can be achieved with the use of hafnium(IV) salts, such as commercially available hafnium(IV) chloride and hafnium(IV) *tert*-butoxide. The present method can be applied to direct polyesterification and may be suitable for large-scale operations.

The replacement of current chemical processing with more environmentally benign alternatives is an increasingly attractive subject (1). Esterification is one of the most fundamental and important reactions in organic synthesis [(2), and references cited therein].Although several methods have been explored and developed [(2), and references cited therein], the use of large amounts of condensing reagents and activators should be avoided in order to promote green chemistry and atom efficiency. The direct condensation of carboxylic acids with alcohols using small amounts of catalysts is the most ideal method, but in most cases, large excess amounts of either carboxylic acids or alcohols are used in this condensation to give esters in high yield (3-18). We describe highly efficient and direct ester condensation with equimolar amounts of carboxylic acids and alcohols catalyzed by hafnium(IV) chloride and alkoxides (19-21).

We first investigated the catalytic activities of various metal salts [10 mole percent (mol%)], which promote the model reaction of 4-phenylbutyric acid (1 equivalent) with benzyl alcohol (1 equivalent) in toluene at reflux with removal of water (calcium hydride in a Soxhlet thimble) for 1.5 hours (condition A in Table 1). Both HfCl<sub>4</sub> and ZrCl<sub>4</sub> (15, 16) were highly effective catalysts for the present reaction. Hafnium(IV) tert-butoxide was also effective, whereas  $Zr(OEt)_4$  was inert. Although Ti(IV) (10, 11) and Sn(IV) (12-14) salts are well known to be good esterification catalysts, their catalytic activities were lower than those of Hf(IV) and Zr(IV) salts. Various other metal salts and organometallics such as 3,4,5-F<sub>3</sub>C<sub>6</sub>H<sub>2</sub>B(OH)<sub>2</sub> (22, 23), BCl<sub>3</sub> (6, 7), AlCl<sub>3</sub> (8), SiCl<sub>4</sub> (9), ScCl<sub>3</sub>, Sc(OTf)<sub>3</sub> (Tf, OSO<sub>2</sub>CF<sub>3</sub>) (24-26), FeCl<sub>3</sub>, CoCl<sub>2</sub>, NiCl<sub>2</sub>, ZnCl<sub>2</sub>, GaCl<sub>3</sub>, GeCl<sub>4</sub>, SbCl<sub>5</sub>, LaCl<sub>3</sub>, and PbCl<sub>2</sub> were either less active or inert.

Next, to identify esterification catalysts with a high turnover frequency, we reexamined several metal salts, which were suggested by the above screening, for the same reaction as above, but under different conditions [reflux for 12 hours in the presence of 1 mol% of catalysts (condition B in Table 1)]. As expected,  $HfCl_4$  and  $Hf(Ot-Bu)_4$  gave the corresponding esters quantitatively, but Zr(IV) and Sn(IV) gave the corresponding esters in low yield. Interestingly, Ti(IV) gave better results than other metal halides and metal alkoxides except Hf(IV). Thus, Hf(IV)was shown to be the most effective metal catalyst for direct esterification.

The commercially available  $HfCl_4 \cdot (THF)_2$ (THF, tetrahydrofuran) is hydrolytically more stable than  $HfCl_4$  and is lower in price than the corresponding alkoxides. To optimize the reacfor  $\alpha$  and  $(\partial lnp/\partial lnV_s)_p,~\delta T\approx -1.0~\times~10^4~dV_s/V_s,$  which for a 2% velocity anomaly corresponds to 200 degrees.

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tion conditions regarding the removal of water and solvents for the esterification of phenylbutyric acid with cyclohexanol in the presence of 0.2 mol% of HfCl<sub>4</sub>·(THF)<sub>2</sub>, we evaluated, using <sup>1</sup>H nuclear magnetic resonance (NMR) analysis, the percentage of cyclohexanol condensed with 4-phenylbutyric acid over time (Fig. 1). We found that heating the reaction mixture in toluene under azeotropic reflux conditions to remove water through a Soxhlet thimble with 4 Å molecular sieves gave the best result. However, heating the reaction mixture without solvents at the same temperature as above was less effective, and the reaction rate was reduced after  $\sim 2$  hours had passed. A similar tendency was observed in control experiments in the absence of any catalysts. These experimental results indicate that not only catalytic activity but also the efficiency of water removal are very important for the present esterification system.

To explore the generality and scope of the above Hf(IV)-catalyzed esterification, we examined the reaction with various structurally diverse carboxylic acids and alcohols. (Table 2). Less than 0.2 mol% of  $HfCl_4$ ·(THF)<sub>2</sub> was

**Table 1.** Direct esterification of 4-phenylbutyric acid and benzyl alcohol for different conditions. The esterification of 4-phenylbutyric acid (1 mmol) and benzyl alcohol (1 mmol) in toluene (5 ml) was carried out in a flask fitted with a pressure-equalized addition funnel (containing a cotton plug and ~1 g of calcium hydride and acting as a Soxhlet extractor) surmounted by a reflux condenser under argon. *i*-Pr, isopropyl. For condition A, the reaction mixture was heated under reflux conditions in the presence of 10 mol% of catalyst for 1.5 hours. For condition B, the reaction mixture was heated under reflux conditions in the presence of 1 mol% of catalyst for 12 hours.

Catalyst	Yield (%)	
	A	В
SnCl	34	48
TiCl	28	73
Ti(Oi-Pr),	34	82
ZrCl	77	-
ZrCl <sub>4</sub> ·(THF) <sub>2</sub>	84	38
Zr(OEt)₄	0	-
HfCl₄	83	_
HfCl (THF),	82	>99
Hf(Ot-Bu)	82	>99
HfO <sub>2</sub>	<5	-

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