equivalent to organonickel^{II} precursors leads to oxidatively induced C–C reductive elimination.

By combining an organonickel^{II} precursor supported by a ligand that coordinates the nickel with three heteroatom donors with a CF_3^+ oxidant, isolable organonickel^{IV} complexes were obtained. These complexes were partners for formation of C–X bonds (where X denotes oxygen-, sulfur-, and nitrogen-based reagents) in excellent yields and under mild reaction conditions. Preliminary kinetic experiments support a mechanistic pathway in which an organonickel^{IV} bond is attacked by the heteroatom nucleophile. The high oxidation state of the metal serves to ensure the bound carbon atom is highly electrophilic and susceptible to facile C–X bond formation.

Although further mechanistic details remain to be unraveled, the involvement of a thoroughly characterized organonickel^{IV} in carbon-heteroatom bond formation opens vistas for constructing new types of molecules and materials under mild conditions. Key aspects of these transformations include the ability to use an economically more attractive metal as the catalyst; exploitation of the lability of the nickel-ligand bonds to promote selective reactions under mild conditions; and the formation of new C–X bonds in which the carbon atom is sp^3-hybridized, which constitutes the most challenging reaction of this class. Future opportunities will entail exploring and developing a fundamental understanding of the range of ligands and oxidants that can successfully partner to facilitate nickel^{IV} cross-coupling reactions. The utility of this work will be greatly enhanced if the efficacy of other oxidants, ideally O_2 (*13*), could be demonstrated. ■

REFERENCES AND NOTES

1. N. M. Camasso, M. S. Sanford, *Science* **347**, 1218 (2015).
2. H.-F. Klein, A. Bickelhaupt, T. Jung, G. Cordier, *Organometallics* **13**, 2557 (1994).
3. R. F. Service, *Science* **330**, 308 (2010).
4. J. Bowers *et al*., *Nat. Methods* **6**, 593 (2009).
5. C. E. Garrett, K. Prasad, *Adv. Synth. Catal.* **346**, 889 (2004).
6. P.-L. T. Boudreault *et al*., *J. Am. Chem. Soc.* **129**, 9125 (2007).
7. The market value of Pd per troy ounce is more than 1500 times that of nickel, as of February 2015.
8. G. Bender, E. Pierce, J. A. Hill, J. E. Darty, S. W. Ragsdale, *Metallomics* **3**, 797 (2011).
9. Y. Z. Zhou, D. A. Sliwa, S. W. Ragsdale, in *Handbook of Porphyrin Science with Applications to Chemistry, Physics, Materials Science, Engineering, Biology and Medicine, Vol. 19: Biochemistry of Tetrapyrroles*, K. M. Kadish, K. M. Smith, R. Guilard, Eds. (World Scientific, Singapore, 2012), pp. 1–44.
10. P. A. Lindahl, *J. Biol. Inorg. Chem.* **9**, 516 (2004).
11. V. B. Phapale, D. J. Cárdenas, *Chem. Soc. Rev.* **38**, 1598 (2009).
12. P. Sehnal *et al*., *Chem. Rev.* **110**, 824 (2010).
13. M. T. Kieber-Emmons, C. G. Riordan, *Acc. Chem. Res.* **40**, 618 (2007).

10.1126/science.aaa7553

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How climate influences sea-floor topography

Sea-floor hills show the same periodicity as glacial cycles

By **Clinton P. Conrad**

Earth's sea floor is created along great volcanic ridges that spread at rates of a few centimeters per year beneath every ocean basin. The volcanic and tectonic processes at these mid-ocean ridges ultimately determine the characteristics of the sea floor and the oceanic crust beneath it. These processes occur beneath several kilometers of rock and seawater, seemingly far removed from climatic variations above sea level. Thus, it is surprising that both Crowley *et al.* (*1*), on page 1237 in this issue, and Tolstoy (*2*) found ice age periodicity in hilly topography on the flanks of ridges submerged beneath the Southern and Pacific Oceans.

After its creation at the mid-ocean ridges, Earth's sea floor forms the abyssal hills (see the figure). If we could view this terrain without its cover of water, it would appear as gentle rolling hills hundreds of meters high and spaced kilometers apart. The abyssal hills are oriented roughly parallel to the ridges where they are formed and are carried across the ocean basins by sea-floor spreading.

Over the course of tens of millions of years, the abyssal hills become buried by sediments, but they are nevertheless observable in bathymetric surveys across vast expanses of sea floor (*3*). This coverage makes the abyssal hills the most extensive geological feature on Earth, but their remoteness means that they remain largely unexplored and poorly understood. Detailed bathymetric surveys, obtained using sonar that images a swath of sea floor beneath a ship, have only been obtained for a small portion of the sea floor. Close examination of these images informs our understanding of how the abyssal hills are created. In particular, extensional faults associated with mid-ocean ridge rifting are thought to be important (*4*). Such faults are observable in bathymetric surveys of newly created abyssal hills near ridge crests and are prevalent in computer models of rifting (*5*).

Comprehensive bathymetry of the Australian-Antarctic ridge south of Tasmania, observed from a South Korean icebreaker, allowed Crowley *et al.* to examine an unusually long record of abyssal hill fabric. They found that the abyssal hills exhibit characteristic spacing of about 23,000, 41,000, and 100,000 years. Working separately but concurrently, Tolstoy also detected 100,000-year periodicity in the abyssal hill fabric of the East Pacific Rise, a ridge west of South America (*2*).

> ***"...the diversity of abyssal hill fabrics observed on the sea floor may result from a range of interactions between climate-induced melting variations and tectonic deformation processes."***

These periods are familiar to paleoclimatologists: They are the primary Milankovitch cycles of cooling and warming of Earth's surface climate. Caused by periodic fluctuations in Earth's rotation, obliquity, and orbit, respectively, the Milankovitch cycles result from changes in the amount and location of radiation reaching Earth's surface and can produce large climate swings between ice ages and warm interglacial periods. For example, Earth has warmed since the last Ice Age, which peaked between 20,000 and 30,000 years ago. The ice sheets that once covered much of North America and Eurasia have melted, causing sea level to rise by about 120 m.

How do Milankovitch cycles induce topographic variations on the sea floor? Oceanic crust is formed from magma produced as hot rocks rise toward the ridge crest, where decreased pressure causes them to melt. The eruption and refreezing of this magma produces the oceanic crust,

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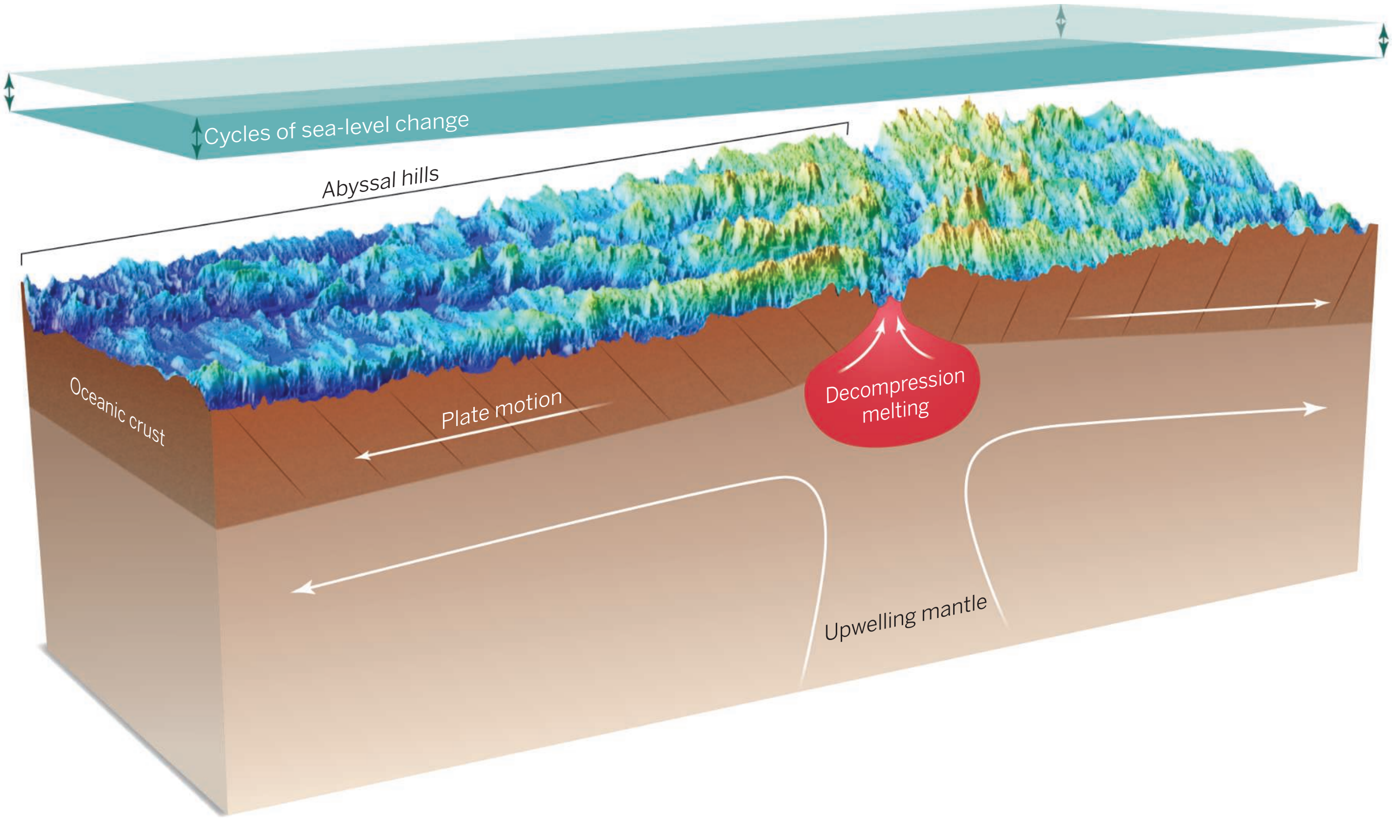

How the sea floor gets its hills. High-resolution bathymetry (*10*) of the North Atlantic's mid-ocean ridge (near 26°N, 46°W), showing the abyssal hills that form near the ridge axis and are carried across the ocean basin by sea-floor spreading. Crowley *et al.*'s observations suggest that Ice Age cycles of sea-level rise and fall cause sea-floor pressure changes that induce periodic variations in rates of decompression melting beneath the ridge. These variations change rates of ridge-axis volcanism and contribute to the abyssal hill fabric.

ILLUSTRATION: ADAPTED BY P. HUEY/*SCIENCE*

but the temperatures involved are much larger than those associated with climate change; seawater temperature variations should thus not affect submarine volcanism. Instead, climate change can affect volcanism by changing belowground pressures, which affect the melting behavior of rocks (*6*, *7*). Indeed, periods of increased volcanic activity in Iceland have been associated with deglaciation and the resulting decompression melting of rocks (*8*).

Both Crowley *et al.* and Tolstoy (*2*) attribute their observations of Milankovitch cycles in the abyssal hills to a similar mechanism. As the climate cools and ice sheets form, the associated sea-level drop causes pressure to decrease at the mid-ocean ridges. This accelerates melting there, which causes more magma to erupt at the ridge. The result is a region of thicker oceanic crust, which is observed as an abyssal hill. Conversely, periods of warming climate lead to the valleys between the abyssal hills.

Crowley *et al.* show that the 100-m variations in sea level associated with Milankovitch cycles can produce hundreds of meters of bathymetric relief, sufficient to explain the observed height of the abyssal hills. Such large variations are possible because changes in the rate of melt production depend on rates of sea-level change, which were indeed rapid in the past: The last major deglaciation produced 100 m of sea-level rise over 10,000 years, an average rate of 1 cm/year. For comparison, sea level is currently rising 3 mm/year and accelerated to this rate only during the past century (*9*). Such rates would need to be sustained for thousands of years to perceptibly affect the abyssal hills currently forming along Earth's mid-ocean ridges.

Because sea-level changes are global in nature, climatic variations are likely to influence abyssal hill fabrics along every ridge. Of course, Crowley *et al.* studied a location where the climatic signal is likely to be strongest. The Australian-Antarctic ridge exhibits little complicating topography, such as volcanic seamounts or transform faults, and has a spreading rate of 3 cm/year—fast enough to separate crustal thickness variations, but slow enough to avoid wide lava flows that might smear them. Detection of Milankovitch cycles in the abyssal hills of other sea floor will be challenging and may be complicated by other processes, such as extensional faulting. Indeed, the diversity of abyssal hill fabrics observed on the sea floor may result from a range of interactions between climate-induced melting variations and tectonic deformation processes. Furthermore, the Milankovitch climate fluctuations may themselves be affected by variations in CO_2 emissions associated with volcanic pulsations at the mid-ocean ridges (*2*). Understanding these interactions will require new high-resolution observations of the abyssal hills, examined in the light of past climate change. ■

REFERENCES

1. J. W. Crowley, R. F. Katz, P. Huybers, C. H. Langmuir, S.-H. Park, *Science* **347**, 1237 (2015).
2. M. Tolstoy, *Geophys. Res. Lett.* 10.1002/2014GL063015 (2015).
3. J. A. Goff, W. H. F. Smith, K. M. Marks, *Oceanography* **17**, 24 (2004).
4. K. C. Macdonald, P. J. Fox, R. T. Alexander, R. Pockalny, P. Gente, *Nature* **380**, 125 (1996).
5. W. R. Buck, A. N. B. Poliakov, *Nature* **392**, 272 (1998).
6. P. Huybers, C. Langmuir, *Earth Planet. Sci. Lett.* **286**, 479 (2009).
7. D. C. Lund, P. D. Asimow, *Geochem. Geophys. Geosyst.* **12**, Q12009 (2011).
8. J. Maclennan, M. Jull, D. McKenzie, L. Slater, K. Grönvold, *Geochem. Geophys. Geosyst.* **3**, 1 (2002).
9. C. C. Hay, E. Morrow, R. E. Kopp, J. X. Mitrovica, *Nature* **517**, 481 (2015).
10. W. B. F. Ryan *et al.*, *Geochem. Geophys. Geosyst.* **10**, Q03014 (2009).

ACKNOWLEDGMENTS

I thank P. Wessel for helpful comments. Supported by NSF grant EAR-1151241.

10.1126/science.aaa6813

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