

also not amenable to regenerative self-repair processes. The reactive sites of heterogeneous catalysts are located within chemically robust inorganic lattices, often allowing better retention of activity (5, 6), which may include regeneration by simple dissolution-deposition recycling (7). However, these materials are generally less adaptable to device fabrication and mechanistic analyses.

The chemically inert, inorganic polyoxometalate (POM) ligand anions have been used previously to provide a framework for assembly of catalytically active Ru_4O_4 clusters (8, 9). These compounds span the interface between molecular catalysts in solution and solid-phase particulate catalysts, combining the best features of both. Moreover, their relatively high catalytic activity toward water oxidation remains undiminished after many cycles of O_2 formation. However, one serious disadvantage common to many other water oxidation catalysts is the use of ruthenium (or iridium) in the catalytic center. These elements are among the least abundant metals in Earth's crust, more so even than platinum, which calls into question their availability for large-scale application to photoproduction of H_2 or organic fuels.

Seeking alternatives, Yin *et al.* surveyed a group of previously synthesized POM complexes that contain Co, an Earth-abundant

metal, for water-oxidizing capabilities (see the figure, panel B). Of the eight compounds investigated, one displayed performance characteristics that were comparable to those of the Ru_4O_4 POM complex ion. This discovery vindicates the strategy implicit in the use of POM ligands to construct superior soluble catalysts. The synthetic versatility of this class of compounds should allow structure-function relations to be explored, which is the key to informed development of more active catalysts. A second highly desirable aspect of these compounds is their capacity for self-assembly, which might be exploited for periodic catalyst rejuvenation similar to that recently demonstrated for cobalt phosphate precipitates (7).

Much of the early research on metal ion-catalyzed water oxidation took a biomimetic approach. Attempts were made at duplicating the structural features of the inorganic core of the biological oxygen-evolving complex, now known to be an asymmetrical $\text{Mn}_4\text{O}_4\text{Ca}$ cluster, in simpler multicentered coordination complexes, without much success. Recent discoveries, primarily with Ru complexes, have provided examples of catalysis by mono- (10, 11), di- (12, 13), and tetranuclear complexes (8, 9), some of which have been shown or are predicted to react by very different pathways (3, 10–14). A striking example of this variability in structural morphology is found in

the POM-ligated catalysts, where the tetra-ruthenate core adopts an adamantane (cuboidal) arrangement (8, 9), but the four cobalts are aligned in a near-linear array between the two POM ligands (1). What is clear from this recent body of work is that there are numerous ways to form O_2 from two water molecules, and that the options for catalyst development available to inorganic chemists are far greater than previously recognized.

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10.1126/science.1187721

CLIMATE CHANGE

Tracking Earth's Energy

Kevin E. Trenberth and John T. Fasullo

By measuring the net radiative incoming and outgoing energy at the top of Earth's atmosphere, it is possible to determine how much energy remains in the Earth system. But where exactly does the energy go? The main energy reservoir is the ocean, which sequesters energy as heat. Because energy is exchanged between the atmosphere and the ocean, this heat can resurface at a later time to affect weather and climate on a global scale. A change in the overall energy balance will thus sooner or later have consequences for the climate. Existing observing systems can measure all the required quantities, but it nevertheless remains a challenge to obtain closure of the energy budget. This inability to properly track energy—due to either inadequate mea-

surement accuracy or inadequate data processing—has implications for understanding and predicting future climate.

To understand how energy is taken up and later released by the climate system, consider the natural variability from El Niño Southern Oscillation. The cold sea surface temperatures in the equatorial Pacific present in normal or La Niña conditions create conditions favorable for fewer clouds and more sunshine and a build-up of heat in the ocean as a precursor of El Niño (1). The spread of warm waters across the Pacific, together with changing winds, in turn promotes evaporative cooling of the ocean, moistening the atmosphere and fueling tropical storms and convection over and around the anomalously warm waters. The changed atmospheric heating alters the jet streams and storm tracks and controls weather patterns for the duration of the El

Where has the energy from global warming gone?

Niño event (2). The loss of heat can in turn lead to La Niña.

A strong La Niña event in 2007–2008 spilled over to the 2008–2009 northern winter, causing cooler than normal weather across North America and elsewhere (3). By June 2009, the situation had reversed as the next, comparatively moderate El Niño emerged. Multiple storms barreled into Southern California in January 2010, consistent with expectations from the El Niño.

The human influence on climate, mostly by changing the composition of the atmosphere, must influence energy flows in the climate system (4). Increasing concentrations of carbon dioxide (CO_2) (see the figure) and other greenhouse gases have led to a post-2000 imbalance at the top of the atmosphere of $0.9 \pm 0.5 \text{ W m}^{-2}$ (5); it is this imbalance that produces “global warming.” It is possible to track how much extra

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energy has gone back to space as the planet warms (6) and where the rest of the energy has accumulated (7) (see the figure). Over the past 50 years, the oceans have absorbed ~90% of the energy added to the climate system; the rest has gone into melting sea and land ice and heating the land surface and atmosphere (4). CO₂ concentrations have further increased since 2003, and even more heat should have accumulated at a faster rate since then. Where has this energy gone (see the figure)?

The difference between the incoming and outgoing energy—the planetary energy imbalance—at the top of the atmosphere is too small to be measured directly from satellites. Nevertheless, the satellite measurements are sufficiently stable from one year to the next, so that by measuring incoming solar radiation and outgoing infrared radiation, it is possible to track changes in the net radiation (8, 9). This includes tracking the slight decrease in solar insolation since 2000 with the ebbing 11-year sunspot cycle; this decrease is enough to offset 10 to 15% of the estimated net human-induced warming (7).

In 2008, for the tropical Pacific during La Niña conditions, extra energy absorption at the top of the atmosphere was observed as expected (9). Since 2004, ~3000 Argo floats have provided regular temperature soundings of the upper 2000 m of the ocean, giving new confidence in the ocean heat content assessment—yet, ocean temperature measurements from 2004 to 2008 suggest a substantial slowing of the increase in global ocean heat content (see the figure, panel A) (10). If the extra energy has not gone into the ocean, where has it gone?

Another perspective on where energy from global warming has gone comes from rising sea level. Since 1992, sea level observations from satellite altimeters at millimeter accuracy have revealed an essentially linear global increase of ~3.2 mm per year, with an enhanced rate of rise during the 1997–1998 El Niño and a brief slowdown in the 2007–2008 La Niña. Since 2003, gravity measurements from the Gravity Recovery and Climate Experiment (GRACE) of the change in glacial land ice and water have shown an increase in ocean mass. This eustatic compo-

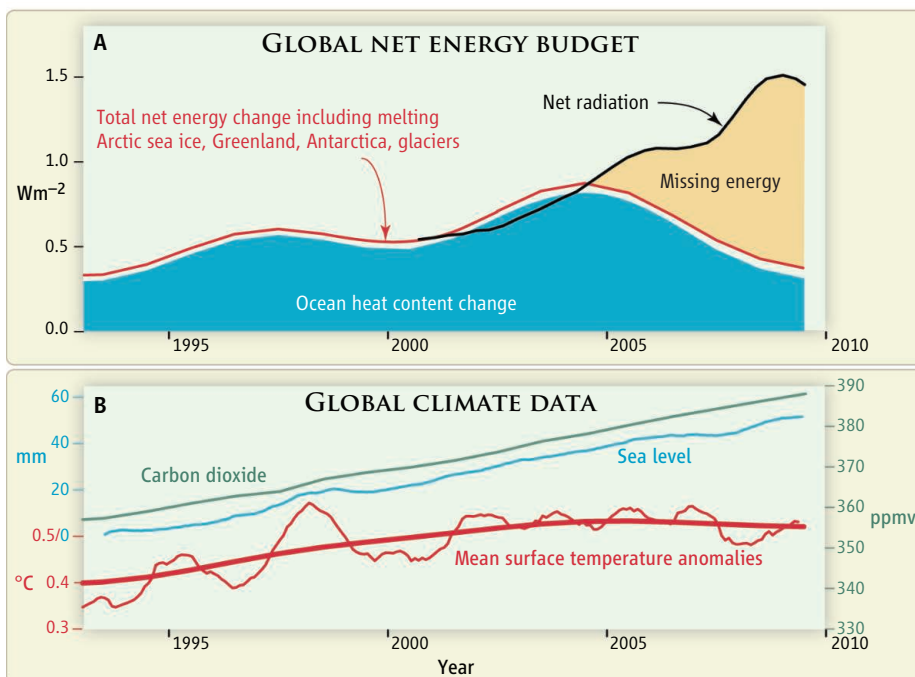
nent of sea level rise may have compensated for the decrease in the thermosteric (heat-related expansion) component (11, 12). However, for a given amount of heat, sea level rise can be achieved much more efficiently—by a factor of 40 to 70 typically—by melting land ice rather than expanding the ocean (7). So, although some heat has gone into the record-breaking loss of Arctic sea ice, and some has undoubtedly contributed to the unprecedented melting of Greenland (13) and Antarctica (14), it does not add up to anywhere near enough to account for the measured energy difference at the top of the atmosphere.

Closure of the energy budget over the past 5 years is thus elusive (7). State-of-the-art observations are unable to fully account for recent energy variability. Is the warming associated with the latest El Niño a manifestation of the missing energy reappearing?

Proposals for addressing global warming now include geoengineering, whereby tiny particles are injected into the stratosphere to emulate the cooling effects of stratospheric aerosol of a volcanic eruption (15). Implicitly, such proposals assume understanding and control of the energy flow, which requires detailed tracking of energy within the climate system. How can we understand whether the strong cold outbreaks of December 2009 are simply a natural weather phenomenon, as they seem to be, or are part of some change in clouds or pollution, if we do not have adequate measurements?

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Where does the energy go? (A) Estimated rates of change of global energy. The curves are heavily smoothed and somewhat simplified. From 1992 to 2003, the decadal ocean heat content changes (10) (blue), along with the contributions from melting glaciers, ice sheets, and sea ice and small contributions from land and atmosphere warming (7), suggest a total warming (red) for the planet of $0.6 \pm 0.2 \text{ Wm}^{-2}$ (95% error bars). After 2000, observations from the top of the atmosphere (9) (black, referenced to the 2000 values) increasingly diverge from the observed total warming (red). (B) The observed steady increases in carbon dioxide and sea level contrast with the variability in global surface air temperature. Shown are the 12-month running means of global mean surface temperature anomalies relative to 1901 to 2000 from NOAA [red (thin) and decadal (thick)] in degrees Celsius (scale lower left), carbon dioxide concentrations (green) in parts per million by volume (ppmv) from NOAA (scale right), and global sea level adjusted for isostatic rebound from AVISO (Archiving, Validation and Interpretation of Satellite Oceanographic Data) (blue, relative to 1993, scale at left in millimeters). Decadal filter from (4).

10.1126/science.1187272