It is clear from Veselago's and more recent work that a negative refractive index leads to some very strange optics. For example, Pendry (*9*) has shown theoretically that a negative material could out-perform a conventional lens because it acts not only on the propagating rays that are controlled by conventional optics but also on the evanescent waves, which decay rapidly with distance and cannot be accessed by conventional imaging optics. All the information about the source could thereby be brought to the focus: We would have the perfect lens. For the first time, Shelby *et al.*'s material, when fully optimized to reduce loss, provides the opportunity to validate this extraordinary concept.

These ideas are not confined to microwave frequencies. We have shown (*10*) that microstructured "Swiss Roll" materials can have enhanced positive or negative permeability at radio frequencies (~20 MHz). Shelby *et al.* suggest that it may be possible to make metamaterials for the infrared but consider it unlikely that viable materials in the visible will be achieved. The materials may nevertheless find a wide variety of applications, but it is perhaps too early to say where we shall first see them used.

But what about the speed of light? Does a negative refractive index mean that light travels backward? Not in any conventional sense. The metamaterial is highly dispersive; that is, its refractive index varies rapidly with frequency. This results in a difference between the group velocity of light, which measures the speed at which information or energy is transported, and the phase velocity, which measures the speed of the individual light wavefronts. The wavefronts do indeed move backward, consistent with the negative *n*, but energy is still transported forward. Hence, the materials do obey the laws of physics while opening up new possibilities for manipulating radiation.

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PERSPECTIVES: ATMOSPHERIC SCIENCE

Solving the PSC Mystery

Margaret A. Tolbert and Owen B. Toon

Lurking in the depths of the polar night poised to activate chlorine for ozone destruction, most polar stratospheric clouds (PSCs) are never seen from Earth, although they can have a vertical extent and breadth comparable to that of the United States. Long considered a curiosity, they became infamous after the ozone hole was discovered. Recent field campaigns are beginning to shed light on the composition of these clouds and the mechanisms by which they affect stratospheric composition and chemistry.

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Nacreous clouds resembling giant abalone shells floating in the sky are a form of PSCs formed by wind flow over mountains. These opalescent clouds have been reported sporadically for over a hundred years from Scandinavia, and Edward Wilson noted them on Robert Falcon Scott's 1901 Antarctic expedition (see the first figure) (*1*). In the mid-20th century, scientists measured their altitudes over Scandinavia near 25 km and showed that water vapor condenses in stratospheric mountain waves at temperatures near –80°C to form micrometer-sized ice particles (*2*, *3*). The beautiful pink and green coloration of the clouds in the twilight sky was shown to result from forward diffraction of sunlight by the particles, whose size distribution is locally nearly monodisperse but whose mean size varies along the profile of the wave.

A colorful curiosity? This drawing by Edward Wilson, "Opalescent alto stratus and snow drift," shows the sky and clouds at McMurdo Sound, Antarctica, 17 August 1903. His diary notes "If a dozen vivid rainbows were broken up by a heavy wind and scattered in wavy ribbands and flecks of curl and fleecy cloudlike forms ... we would have something like the beautiful appearance of this cloud colouring" (*1*).

CREDIT: THE SCOTT POLAR RESEARCH INSTITUTE

With the advent of satellites came the recognition that PSCs were common in the polar winter, particularly above Antarctica (*4*). Still, PSCs were considered essentially irrelevant for atmospheric chemistry and climate until Farman *et al.* discovered the Antarctic ozone hole in the mid-1980s (*5*).

Like a murder mystery, the discovery of severe ozone loss above Antarctica was accompanied by distinct clues, some of which were red herrings. Solomon and co-workers were the first to identify the essential clues (*6*, *7*). The ozone loss occurred in the only place on Earth cold enough for clouds to form in the stratosphere (where most ozone is located), in spring when sunshine was available, and during an epoch when chlorine levels in the stratosphere were reaching record levels. They postulated that chlorine was converted from the inert "reservoir" species $ClONO_2$ and HCl to active species by heterogeneous reactions on PSCs. The active chlorine species could then react catalytically with ozone as long as sunlight was present (see blue arrows in the second figure). Laboratory studies quickly provided the rates of key heterogeneous reactions on PSCs. The overall mechanism was confirmed in a series of field campaigns, which showed conversion of chlorine from reservoir to reactive species near PSCs and unprecedented concentrations of reactive chlorine in conjunction with severe ozone loss.

Other clues in the ozone loss mystery suggested that condensed HNO_3 was an important component of PSCs (*8*, *9*), and nitrate was soon detected in them (*10*, *11*). Laboratory work (*12*) showed that nitric acid trihydrate (NAT) was the thermodynamically stable form of HNO_3/ice in the polar stratosphere. The Antarctic stratosphere is "denitrified" when HNO_3 is permanently removed through sedimentation of large PSC particles. Denitrification removes gaseous nitric acid that could otherwise interrupt the catalytic ozone loss cycle by reforming the reservoir species $ClONO_2$ (see the red arrows in the second figure) (*8*). But denitrification is not the only way to keep chlorine in its active forms. Portmann *et al.* (*13*) have argued that because low temperatures are maintained in the Antarctic vortex until well past the spring equinox, reactivation of $ClONO_2$ on PSCs or dilute liquid sulfate aerosols yields ozone loss

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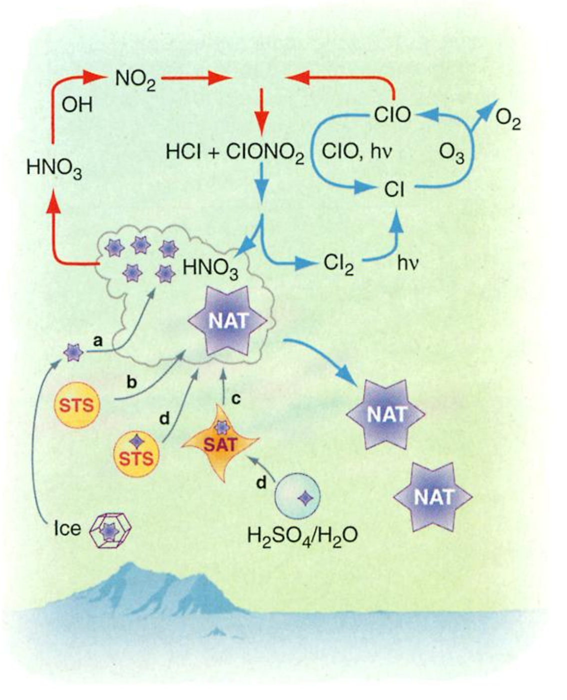
comparable to or greater than that due to denitrification alone.

In contrast, the Arctic stratosphere is normally not denitrified during winter, and neither cold temperatures nor PSCs linger to the equinox in a typical year. Consequently ozone losses have not been as severe in the Arctic. Several studies, including (*14*, *15*), have suggested that in the future, lower stratospheric temperatures could promote longer lasting PSCs and Arctic denitrification, leading to increased ozone loss. Unfortunately, both denitrification and ozone loss predictions are uncertain because the composition and formation mechanism of the particles responsible for denitrification and chlorine activation have still not been established. It is clear, however, that denitrification requires large HNO$_3$-containing particles with a substantial fall velocity.

Some PSCs are known to be liquid particles composed of supercooled ternary solutions (STS) of sulfuric acid, nitric acid, and water. Because STS particles are liquid, they do not require nucleation for their formation. They therefore all grow at about the same rate, and thus do not reach sizes large enough for sedimentation and denitrification. The solids in PSCs may be NAT, metastable nitric acid dihydrate, more water-rich hydrates, or amorphous solids. As the most stable form, NAT is the most likely candidate for efficient removal of nitric acid from the vapor phase. Laboratory studies indicate that there is a substantial nucleation barrier to NAT formation (*16–18*). Selective nucleation of a small number of NAT particles thus has the potential to result in large HNO$_3$-containing particles that can denitrify the atmosphere. NAT therefore seems the obvious culprit for denitrification, but until recently there was no laboratory or field evidence for the occurrence of NAT in the atmosphere.

Intensive PSC studies during the 1999–2000 SAGE III Ozone Loss and Validation Experiment/The European Stratospheric Experiment on Ozone (SOLVE/THESEO) in the Arctic provided new evidence about PSC properties. The winter of 1999–2000 was exceptionally cold with abundant PSCs, substantial denitrification, and major springtime stratospheric ozone loss. The first detection of NAT in the atmosphere was made during SOLVE/THESEO by Voigt *et al.*, who found NAT particles less than 2 μm in diameter in a nacreous cloud (*19*). Solid particles, presumably NAT, can be present far downwind of the ice clouds formed over mountains (*20*). These NAT particles probably initially form on small ice crystals. When the ice evaporates, small NAT particles may remain (path a in the second figure), but they are too small to denitrify the stratosphere by falling. Wave clouds are widespread and undoubtedly important for activating chlorine but they are probably not important for denitrification, and the mechanisms of NAT formation in them may not be relevant to the clouds that do denitrify.



Possible mechanisms. The gas phase ozone destruction cycle is shown in blue and the conversion of chlorine from active to reservoir species by nitric acid in red. Reservoir species are also converted to active species on the surfaces of PSC particles. The possible paths to the formation of NAT particles (a to d) are explained in the text. Paths b to d may produce NAT particles large enough for denitrification to occur, but the mechanism has not yet been established.

Recent satellite observations have shown that the Antarctic denitrifies before it dehydrates (*15*). Theoretical studies (*21*, *22*) also suggest that falling NAT particles can denitrify the stratosphere without involvement of ice. During the SOLVE/THESEO mission, Fahey *et al.* (*23*) observed that PSCs deep in the polar night contained nitric acid particles large enough (10 to 20 μm in diameter) to fall a substantial distance before they evaporated. No ice clouds were observed or predicted. Fahey *et al.*'s data thus solve the long-standing puzzle of how the stratosphere is denitrified: by falling nitric acid particles, likely NAT.

Some of the PSC puzzles have thus been solved, but several questions remain to be resolved through future studies. Are the large particles really made of NAT? How did they form? How much difference does it make to ozone loss if they do in fact denitrify the stratosphere?

Large NAT particles can only form if a small fraction of the STS particles freeze. The frozen particles can then grow by picking up nitric acid vapor because the vapor pressure of NAT is less than that of STS. Indeed, Fahey *et al.* show that only about 1 in 10^5 particles becomes large enough to fall at an appreciable rate. Such selective nucleation has also been observed for cirrus ice clouds in the troposphere.

Selective nucleation in the stratosphere may occur in several ways (see the second figure). First, recent laboratory experiments (*24*) suggest that NAT may nucleate homogenously out of the largest STS particles if the temperature remains near 190 K for more than 1 day (path b). However, the data were obtained at temperatures well below those of the stratosphere and in solutions that did not contain sulfuric acid. A substantial extrapolation is thus required. Recent work (*25*) shows that such a nucleation process may create a "polar freezing belt" where dentrification occurs. Second, a small fraction of the ambient sulfate particles may freeze forming sulfuric acid tetrahydrate (SAT). Theoretical and laboratory studies have shown that NAT can form on SAT under stratospheric conditions (path c) (*26*, *27*). However, laboratory studies of sulfuric acid show that it supercools rather than freezes in the stratosphere. Finally, very rare heterogeneous nuclei in the stratosphere may cause sulfuric acid to form SAT or may cause STS to freeze directly to NAT (path d). Candidates for freezing nuclei in the stratosphere would be micrometeorites, spacecraft debris, volcanic ash, or particles from the troposphere.

Theories and laboratory experiments may help us limit the choices of nucleation mechanisms, but capture and examination of large NAT particles will be needed to see if they do form on special nuclei. It also remains to be shown whether denitrification matters to ozone loss. A colder stratosphere is likely to display more ozone depletion regardless of dentrification. But theoretical predictions (*15*) suggest that denitrification could increase expected ozone losses in a future, colder Arctic by up to 30%. As greenhouse gases continue to cool the stratosphere over the next few decades, we may find out how important extended PSC lifetimes and denitrification are to stratospheric ozone loss.

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PERSPECTIVES: ECOLOGY

Keystone Species—Hunting the Snark?

William Bond

Ecologists widely acknowledge that physical and chemical resources, such as soil and climate, set the potential limits to the characteristics of an ecosystem, but whether they also set the actual limits is the subject of vigorous debate (*1*). Do plant and animal species, as they interact with one another, shift the ecosystem far from the conditions that one would predict from the resources available? We know that invasive species, introduced accidentally or intentionally, often have major, and sometimes entirely unexpected, repercussions on the invaded environment (*2*). Less is known about whether native species have similarly powerful impacts on their ecosystems. One of the difficulties with assessing the impact of native or invading species is that ecosystems often respond slowly to the addition or removal of species. This slow response is epitomized by the marathon 23-year study of a desert ecosystem reported by Ernest and Brown on page 101 of this issue (*3*).

In 1977, Brown and his colleagues set up experiments in the Chihuahuan desert of southeastern Arizona in the United States that were designed to exclude a guild of seed-eating rodent, the kangaroo rat (*Dipodomys*), from a desert ecosystem. By cutting calibrated holes in the fencing around their study plots, the investigators were able to selectively exclude kangaroo rats, the largest of the seed-eating desert rodents, but not smaller rodent species. Fast forward 10 years, and, as one might predict, smaller seed-eating rodents and seed-eating ants that normally would have had to compete with kangaroo rats for seeds were more abundant in the study plots than in the control plots. The plant community in the study plots had also changed because seed predators were now selecting different seeds. The repercussions extended to birds whose numbers declined because of changes in plant cover and even to a fungal pathogen, which increased because of the denser population of its host plant (*4*).

Pocket monsters. The kangaroo rat (*Dipodomys*) (**inset**) and the pocket mouse (*Chaetodipus baileyi*).

CREDIT: KANGAROO RAT, TOM MCHUGH/PHOTO RESEARCHERS, INC; POCKET MOUSE, JOHN & GLORIA TVETEN/KAC PRODUCTIONS

The experiments continued long after the initial results were reported, and now, in their new work, Ernest and Brown provide an update 20 years on. They report that in 1996 there was a sudden change in the ecosystem of the fenced study plots with the arrival of the seed-eating pocket mouse (*Chaetodipus baileyi*). This species, just small enough to get through the holes in the fencing, quickly colonized the study plots and is now consuming nearly as many seeds as the kangaroo rats once did. So will the ecosystem revert to its original condition now that the pocket mouse can apparently compensate for the loss of the kangaroo rats, or will the compensation be only partial because of the unique properties of the new colonizer?

The Ernest and Brown study indicates that single species, or small guilds of species, can have marked influences on ecosystem properties through a complex chain of direct and indirect effects. Species with a large biomass (mass per unit area) or productivity (rate of biomass production) might be expected to have impressive impacts on large ecosystems. What many ecologists find intriguing is that some species, such as the kangaroo rat, seem to have effects on ecosystems out of all proportion to their relative abundance. Robert Paine first labeled such species "keystone" species (*5*). Challenging the then-current notion that diversity in an ecosystem brings stability, he pointed out that a single rare predator species feeding on a dominant herbivore could effectively control the ecosystem by indirectly opening up living space for less competitive herbivores.

The keystone concept has great popular appeal. Stories of complex chains of events triggered by small beginnings hold wide fascination. Because other kinds of interactions could also have impacts on many species, the keystone concept has expanded to encompass species as diverse as pathogens and pollinators. Keystone species are so influential that one might predict that they would be a major focus of conservation policies. Protected areas without a keystone species, for example, would be subject to cascading losses of species as the effects worked their way through the system. For legislation and policy to take special account of keystone status, we would need to know which species are keystones, how common they are, in which ecosystems they occur, and the magnitude and nature of their effects on ecosystems (*6*, *7*). But is the keystone concept of practical use for flagging species for legal or policy purposes? Critics have given an emphatic "no" and argued for abandoning the seductive metaphor altogether (*7*, *8*).

A principal problem is that evidence for the existence of most purported keystones is anecdotal. Experimental work of the kind conducted by Ernest, Brown, and their colleagues is the exception. Another difficulty relates to the idea that a keystone species is much more important than others relative to its proportional abundance. That begs the question of how important any species is in an ecosystem. In theory, we could experimentally delete species one by one, measure the ecosystem impacts, and generate a frequency distribution of im-

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