along a bound coordinate at or near the transition state geometry. It is remarkable that only a single such progression is seen in Wenthold's spectrum; this is the result of the high symmetry of the anion and neutral species. Overall, the paper represents an important expansion of transition state spectroscopy from the type of model chemical reactions usually studied by chemical physicists to much more complex species of interest to the wider chemistry community.

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## To See a World in 80 Kilograms of Rock

### Allan Treiman

Of the more than 7500 known meteorites. only 12 are certain to have come from Mars. As the only available samples of Mars, they have become the basis for much of what is known (or hypothesized) about Mars (1). In one sense, the martian meteorites are returned planetary samples no less scientifically important than the Apollo and Luna samples. The martian meteorites are all basalts and related rocks, with a total mass of only 80 kg, and have been subjected to every conceivable analysis; paraphrasing Churchill, "never has so much been learned by so many from so little." The most exciting studies in the last year (including reports at the 27th Lunar and Planetary Science Conference held in Houston in March) emphasize three areas: water, the earliest history of Mars, and how the meteorites got to Earth. In addition, preliminary data on the newest martian meteorite (the twelfth) have just arrived.

Water once flowed on and near the surface of Mars. Valley networks suggest rivers or abundant ground water more than 4 billion years ago, and huge outflow channels bespeak catastrophic floods in the more recent past of this planet. Martian water is recorded in the meteorites by alteration minerals, deposited from the water or formed by chemical reactions with the water. The martian origin of the alteration minerals is certain; they predate the meteorites' scorching passages through Earth's atmosphere.

Nearly all of the martian meteorites contain alteration minerals, meaning that liquid water was widespread (although not abundant) in Mars (2). The youngest martian meteorites crystallized from magma ~170 million years ago, so their water-deposited grains must be younger still. The most abundant of the alterations are veinlets of clays, hydrous iron oxides, and salt minerals in the Lafayette meteorite. These veinlets formed from reaction between the rock and warm water (<70°C), as suggested by their mineralogy and by oxygen isotope ratios in the clays and host rock ( $\delta^{18}$ O ~ +14 and +4.5, respectively); their age is ~300 million



A small slice of Mars. Thin section of the Lafayette martian meteorite, real colors; field of view is 2.3 mm across. The clear (white) cracked grains are pyroxene and olivine. The orangebrown patches are clays and iron oxides formed when the rock was altered on Mars. [Photo from the author]

years (3). The oldest martian meteorite, ALH84001, is devoid of water-bearing alteration minerals but does contain late-stage Mg and Fe carbonate minerals. The temperature at which these carbonates formed is quite uncertain (estimates range from  $0^{\circ}$  to 700°C) (4). Still, the absence of water-bearing alteration minerals in ALH84001 seems inconsistent with the abundant evidence

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for liquid water on ancient Mars.

The earliest history of Mars, before 4.0 billion years ago, is important in itself and as a proxy for Earth's earliest history; little is known of this epoch on Earth because no rocks from that time are preserved. So, it was exciting when Rb-Sr and Sm-Nd radio-isotope studies showed that the ALH84001 martian meteorite formed 4.5 billion years ago, and therefore must be from Mars's most ancient terrane, the southern highlands. The K-Ar radio-isotope system yields a younger age of 4.0 billion years, which probably represents impact metamorphism (5). These ages are comparable to the oldest crystallization ages and the most common impact ages found in lunar highlands rocks, further suggesting a common history of planet formation and impact cratering. It seems likely that early Earth shared these experiences, but it is not clear that ALH84001, a pyroxenite, sheds any light on the nature of Earth's early crust.

Four of the martian meteorites, the Chassigny and the nakhlites, provide a strong constraint on Mars's very early history. These meteorites contain excesses of the isotope <sup>142</sup>Nd, which arose from a decay of <sup>146</sup>Sm (half-life, 103 million years). The solar system contained a little <sup>146</sup>Sm at its inception 4.566 billion years ago, but it had effectively decayed away within a few half-lives. Therefore, the excess <sup>142</sup>Nd must derive from

material that had excess <sup>146</sup>Sm very early in the solar system, 4.54 billion years ago in this case, only 30 million years after the solar system formed. Mars must have been a full-fledged planet by this time. Further, the material with excess <sup>142</sup>Nd must have been preserved intact, inside Mars, from 4.54 billion years until 1.33 billion years ago, when the Chassigny and the nakhlites formed (6). How could this isotopically anomalous material have been preserved in an actively convecting planet for more than 3 billion years?

The passage of rocks from Mars to Earth always seemed improbable: the martian meteorites were accepted as such only after gas identical to

Mars's atmosphere was found in them. Even so, their transport to Earth seemed to require singular events: ejection from Mars by a large asteroid impact followed by a unique fragmentation history in space. Recent work, however, shows that  $\sim 3\%$  of rocks ejected from Mars will come to Earth, without fragmentation, on relatively short time scales (<20 million years) (7). In addition, the me-

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teorites' petrology and cosmic ray exposure ages suggest at least three sites of origin, and possibly six (8). Production of martian meteorites now seems embarrassingly easy. So why don't we have more, especially more highland rocks?

The newest martian meteorite is QUE94201, a fragment of basalt similar to the other martian basalts (9). It is uniquely depleted in "incompatible" elements, those that do not easily fit into common silicate minerals. This meteorite is twice or more as depleted as the other martian meteorites, and five times as depleted as comparable terrestrial basalts. The how and why of this geochemical anomaly are not yet known.

Even after years of intense study, the martian meteorites will likely continue as crucial resources. In effect, the meteorites are sample

return missions, albeit from unknown parts of Mars. With the present interest in life on Mars, it seems likely that the martian meteorites will be studied intensely for traces of extraterrestrial organic compounds. More practically, the compositions of martian water (required for life) will be studied in the meteorites' alteration minerals. The meteorites will continue to provide geochemical and isotopic clues about the earliest events in the solar system: accretion, planet formation, core formation, and mantle differentiation. NASA is now studying a Mars sample return mission for 2005; given Mars's complexity, it seems unlikely that any returned sample would duplicate a martian meteorite. Rather, a returned sample would increase the value of the martian meteorites by providing a firm geological context by which to judge them.

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# The "Bio" in Biochemistry: Protein Folding Inside and Outside the Cell

### R. John Ellis

 ${f T}$ o understand how organisms work, biochemists first convert an organism into a soup. They then study these soups and the molecules purified from them to unravel the chemical mechanisms inside the living cell. The more chemically defined such in vitro systems become, the more sophisticated are the analytical techniques that can be applied to them. But as these systems become more defined, they differ more and more from whole cells. So, biochemists continually question the relevance of such in vitro systems to the living cell. As David Green pointed out many years ago, a clever engineer can make a vacuum cleaner from the wreck of an automobile, but this does not show that cars contain vacuum cleaners. The report by Frydman and Hartl in this issue (1)

addresses this problem with respect to the role of molecular chaperones in assisting protein folding.

Molecular chaperones are a class of unrelated proteins that assist in the correct folding, association, and breakdown of certain other proteins but which then dissociate from these proteins before they perform their



Will the real chaperone process please stand up. The two types of in vitro system used to study chaperonepolypeptide chain interactions yield different folding patterns. (A) Chemically

ess f in nedifally Small chaperone (*M*<sub>r</sub> less than 100,000) Large chaperone (*M*<sub>r</sub> more than 800,000)

defined system containing full-length polypeptide chains. (**B**) Crude protein-synthesizing extract, where several ribosomes move along each messenger RNA molecule, adding amino acids progressively to the growing polypeptide chain.

normal biological roles (2). Some, but not all, molecular chaperones are also stress proteins, because their help in assembling proteins is particularly required when organisms are subjected to environmental stresses that cause proteins to unfold. Classic experiments by Anfinsen (3), and subsequently many others, showed that pure proteins that have been unfolded by chemical denaturing agents will often refold spontaneously to their correct functional conformations on dilution or removal of the denaturing agent.

or reverses incorrect interactions, but does not have an actual positive effect—hence the aptness of the analogy to the human chaperone. Because it is not yet possible to study directly the binding of molecular chaperones to polypeptide chains in living cells, two types of in vitro system are being used.

In the first system, a pure protein is denatured by high concentrations of chemicals such as guanidinium chloride and then diluted into a buffer containing pure molecular chaperones. In the second system, a crude

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Because no molecules other than the solvent were present, these experiments led to the important conclusion that all the steric information for polypeptide chains to refold correctly is contained within their primary structures. However, success in such refolding experiments is favored by protein concentrations much lower than those found in-

side cells. At concentrations similar to those of the cell, proteins often aggregate because partially folded chains can interact with one another incorrectly through transiently exposed hydrophobic areas (4). Misfolded chains can also arise when partially folded intermediate states become trapped and are unable to proceed toward functional conformations at suitable rates. How do cells tackle these problems?

Over the past decade, it has become clear that molecular chaperones combat both problems by binding transiently to interactive surfaces exposed during the folding process. These proteins are called chaperones because their binding prevents

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