mate in a neighboring community, she could not, so far as we know, select a specific male as father. The phenotypic benefit thought to account best for multiple mating in chimpanzees is infanticide prevention, on the theory that males forgo aggression toward infants of mothers with whom they remember mating (*5*). In the Taï case, mating with the neighbors could provide an insurance against future encounters with them when she is accompanied by her offspring.

But why should the female ever encounter the neighboring males in the future? Males have been dying at a high rate in the Taï study community. Could the cuckolding copulations be a preemptive safeguard against a take-over by neighbors? This might explain the curious observation that no neighboring females have been seen mating with the males of the study community. If so, the Gagneux *et al.* result may prove to be a rare phenomenon even among chimpanzees, specific to an unusual historical moment. Or is she insuring herself against a bad fruit-season in her own range, when she might need to eat in a neighboring range? That would suggest extra-group matings will be found commonly in other populations. Genetic data are being compiled quickly in other chimpanzee sites and should soon show whether high rates of extra-group paternity are common.

Until this year, no one suspected that female chimpanzees were so active in pursuit of their reproductive interests, yet they are probably doing still more than we appreciate. Chimpanzee and human social systems differ importantly in the characteristics of the female relationships, so there are certainly no direct analogies for human sociobiology. But these studies remind us that even where females interact rarely or subtly, female initiative can be a major force in the evolution of social systems. Selective impact doesn't necessarily correspond with social power.

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ISOTOPE FRACTIONATION

Vibrations Under Pressure

Simon M. F. Sheppard

Pressure is one of the key variables in Earth science, ranging from an extremely small fraction of 1 atm in the upper atmosphere ($\sim$1 Pa or $\sim 10^{-5}$ atm) to probably more than 3.5×10^{11} Pa at Earth's center. However, unlike temperature, pressure has rarely played a role in the interpretations of the variations in the stable isotope ratios of elements such as hydrogen (D/H) and oxygen (^{18}O/^{16}O) that are observed in natural solids and fluids. Dreisner (*1*), on page 791 of this issue, and a number of recent studies (*2*–*4*) suggest that the pressure dependence of some isotope equilibrium fractionation factors may not be negligible. The results are important from both a theoretical and experimental point of view and for the applied geochemistry community.

Why has the effect of pressure on how isotopes partition themselves among coexisting phases been assumed to be negligible? A pressure effect implies that molar volume changes with isotopic substitution. The zero-point vibrational energy of a molecule plays a critical role in the calculation of isotopic effects based on spectroscopic data and statistical mechanics. Because the zero-point energy decreases to a small extent with increase in the heavier isotope content of the molecule, bond lengths of molecules decrease slightly with an increase in heavy isotope content. These effects are more extreme for hydrogen (as D substitutes for ^{1}H) than for all other elements, leading to estimated changes of molar volume of up to 0.3% between the pure ^{1}H and D isotopic end members (*5*). In natural systems, changes of molar volume for isotope exchange reactions are much smaller because typical isotopic fractionations between phases are only a few percent for hydrogen and a few tenths of a percent for oxygen. Without excluding pressure effects at pressures that reign in Earth's mantle (>1 GPa), the theoretical and experimental study of Clayton *et al.* (*5*) found no measurable evidence for a pressure effect between 0.05 and 2 GPa for oxygen isotopes in the calcium carbonate–water system.

Dreisner's contribution (*1*) shows that for isotopic exchange reactions involving a fluid such as water, changes of pressure can measurably influence the fractionation factor. The vibrational frequencies of gases, liquids and solids change with pressure and temperature (*P*-*T*). Unlike a solid, the density of a fluid varies more rapidly under certain *P*-*T* conditions than others. The region of strongest density variations is around the critical point of the fluid. This region is also where the vibrational frequencies of water change more rapidly. Thus, at constant temperature, a mineral-water fractionation factor changes with the density of the fluid. The effect for hydrogen isotopes can be large, whereas the maximum effect for oxygen is only slightly larger than the typical measurable precision.

In contrast to Dreisner, who studied a region of relatively low pressure, Polyakov and Kharlashina (*2*) and Gillet *et al.* (*4*) explore the pressure effect on the reduced partition coefficient to high pressures and temperatures (<3 GPa, <1200 K). Their calculations showed that the effect is significant for oxygen isotope fractionations, increasing with decreasing temperature for Polyakov and Kharlashina but increasing temperature for Gillet *et al.* These contradictions are probably related to differences in the assumptions.

Importantly, both Dreisner and Gillet *et al.* exploit a much broader experimental data base than has previously been the case, including high-pressure, high-temperature spectroscopic data. To calculate fractionation factors, suitable spectroscopic data have to be incorporated into a model. Since the landmark paper by Urey in 1947 (*6*) on the calculation of the thermodynamic properties of isotopic substances, the spectral data have been essentially restricted to both ambient *P*-*T* conditions and molecules with natural isotopic compositions. Except for gases, harmonic or quasi-harmonic assumptions are the rule. Usually little to no data on the shifts of the modes with variations of pressure, temperature, and isotopic composition are available. This information is essential for precise anharmonic calculations, which are needed to evaluate correctly the pressure effect. There may also be a lack of mode assignments.

Natural isotopic compositions for D/H and ^{18}O/^{16}O isotope ratios are about 1/7000 and 1/500, respectively. The heavy isotope is very much in the minority. The effect of isotopic substitution of the heavier isotope on the vibration frequencies is usually calculated from some model with its inherent un-

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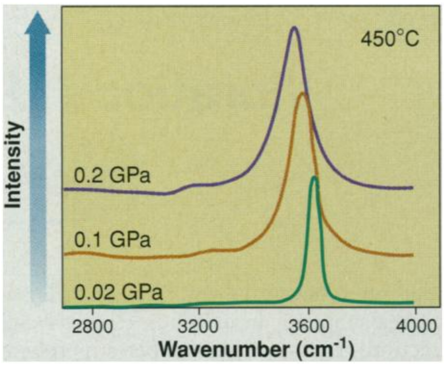
certainties. In rare cases, spectra are recorded on the mineral completely or heavily enriched in the rarer heavy isotope. For example, Gillet *et al.* (*4*) did this for calcite and were able to carry out a detailed mode assignment. With spectral data over a large pressure and temperature range, they demonstrate convincingly the importance of carrying out anharmonic calculations in order to derive thermodynamic parameters (specific heat, coefficient of thermal expansion, and so on) that agree with the measured values over geologically interesting *P-T* ranges.

Spectral data on geological materials over an important range of both pressure and temperature conditions are still quite limited. The situation is changing fast since the construction of a number of high-temperature, high-pressure cells with windows: diamond anvil and optical cells. High-quality spectroscopic data (see figure) are measured in situ under the working conditions, typically <35 GPa and <2000 K (*7–9*).



Variation of the Raman spectra of water with pressure varying from 0.02 to 0.2 GPa at 450°C in an optical cell (*8*). At constant pressure, the frequency of the maximum intensity increases along with temperature. Such *P-T* frequency changes are input data to the model calculations.

The interpretation of the small variations in the isotopic composition of natural materials depends on the application of high-precision fractionation factors derived from spectroscopic data and calculations, empirically or experimentally, and how they vary with thermodynamic parameters. Pressure is a variable that now must be taken into account, at least for hydrogen isotopes, in fluid-bearing systems at low to moderate pressures, such as those that occur in the oceanic crust and the middle to upper continental crust. Further studies will define more precisely the limits of these pressure effects. The significance of pressure variations on interphase isotopic fractionations under mantle conditions (>1 GPa) is another direction that merits further exploration.

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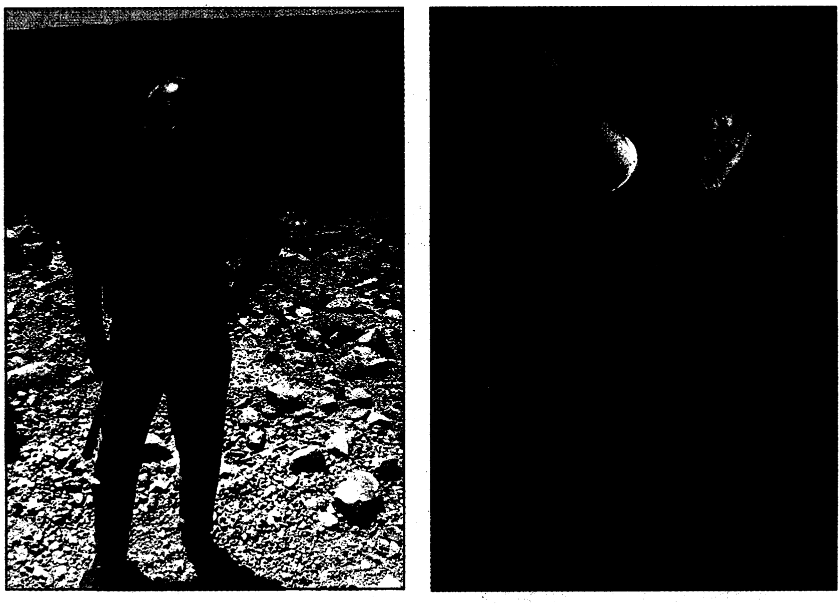
RETROSPECTIVE

Eugene M. Shoemaker (1928–1997)

Susan W. Kieffer

The life of a renowned leader in the science community was lost on 18 July 1997, when Eugene M. Shoemaker was fatally injured in an auto accident in Australia. Gene was doing field work on the impact craters that he so much enjoyed exploring. His field partner, astronomy colleague, and wife, Carolyn, survived the accident.

Gene leaves many legacies that will benefit scientists and humankind for generations to come. He, with Carolyn, formulated and conducted a sky survey of nearly two decades duration in which they discovered and cataloged earth-crossing asteroids and comets. This survey culminated in the codiscovery, with David Levy, of Comet Shoemaker-Levy, which provided a spectacular display of impacts into the jovian atmosphere in 1994. The whole world—scientists and nonscientists alike—gained new insights into the dynamics of comets, the phenomenon of impact, and the planetary science of Jupiter.


PHOTOS: G. MARULLO

At Meteor Crater, Arizona, and with Carolyn Shoemaker at Palomar Observatory.

Gene led the creation of planetary science as a discipline distinct from astronomy by bringing fundamental geologic principles to the mapping of the planets. Starting in the 1960s, he used geologically well-known principles of stratigraphy to interpret the ancient and modern histories of the planets of the solar system. He helped create an alliance between NASA and the U.S. Geological Survey (USGS) with the formation of the Branch of Astrogeology in the USGS and guided a major program of mapping the planets using geologic techniques to interpret remote sensing data. Early involvement in the unmanned Ranger and Surveyor programs evolved into scientific leadership in the manned Apollo program. He helped train astronauts in geologic principles for their visits to the moon and was involved in interpretation of the lunar rocks

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