pressin increase permeability to water but do not change sodium transport (*9*). If the secondary messenger concept is correct, the dissociation with vasopressin analogs of effects on short-circuit current and water permeability implies independent and different secondary messengers. Calcium ions, on the other hand, appear to diminish the increase in water permeability induced by vasopressin but not the increase in short-circuit current (*10*). The different sensitivity of the toad bladder to cyclic AMP and cyclic GMP as manifested by the water flow experiments raises the possibility that vasopressin may give rise to its separate effects by generating these two cyclic nucleotides.

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References and Notes

1. G. A. Robison, R. W. Butcher, E. W. Sutherland, *Ann. Rev. Biochem.* **37**, 1492 (1968).
2. J. Orloff and J. S. Handler, *J. Clin. Invest.* **41**, 702 (1962).
3. W. I. Baba, A. J. Smith, M. M. Townshend, *Quart. J. Exp. Physiol.* **52**, 416 (1967).
4. J. J. Grantham and M. Burg, *Amer. J. Physiol.* **211**, 255, (1966).
5. R. W. Butcher and E. W. Sutherland, *J. Biol. Chem.* **237**, 1244 (1962); D. F. Ashman, R. Lipton, M. M. Melicow, T. D. Price, *Biochem. Biophys. Res. Commun.* **11**, 330 (1963); J. G. Hardman, J. W. Davis, E. W. Sutherland, *J. Biol. Chem.* **241**, 4812 (1966); L. R. Chase and G. D. Aurbach, *Proc. Nat. Acad. Sci. U.S.* **58**, 518 (1967).
6. H. H. Ussing and K. Zerahn, *Acta Physiol. Scand.* **23**, 110 (1951).
7. P. J. Bentley, *J. Endocrinol.* **17**, 201 (1958).
8. Cyclic AMP and cyclic CMP were purchased as free acids and cyclic TMP and 5′-GMP as sodium salts from Sigma Chemical Company, St. Louis, Missouri. Cyclic GMP was obtained as a potassium salt from Calbiochem, Los Angeles, California.
9. R. Walter, J. Rudinger, I. L. Schwartz, *Amer. J. Med.* **42**, 653 (1967).
10. M. J. Petersen and I. S. Edelman, *J. Clin. Invest.* **43**, 583 (1964).
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Silicon Oxynitride Stability

Abstract. *Silicon oxynitride occurs as a mineral (sinoite) in meteorites. Equilibrium measurements are reported which provide information on the approximate ratios of pressures of oxygen to nitrogen required for existence of this phase under equilibrium conditions at elevated temperatures. This ratio is approximately 10^{-15} at 1400° to 1500°C.*

Silicon oxynitride was first reported about 10 years ago by Forgeng and Decker (*1*) who obtained this phase when air was admitted to the reaction chamber during a study of the formation of silicon nitride. Subsequently, silicon oxynitride has been studied as a possible refractory material at elevated temperatures (*2*) and as a film on silicon substrates (*3*). The main impetus for the interest in silicon oxynitride in recent years, however, has come from the discovery of this compound as a mineral (sinoite) in the Jah deh Kot Lalu meteorite (*4*) and subsequently in four additional meteorites of the enstatite chondrite type (*5*). The appearance of this mineral in these meteorites, which are reported to bear textural characteristics suggesting equilibrium assemblages (*5*), provides a possible clue to the conditions of the environment in which these materials were formed. We report here data which serve to establish the order of magnitude of such equilibrium relations.

The approximate stability of silicon oxynitride, Si_2N_2O, was determined by two methods. The first method involved the reaction of SiO_2 with a gas phase of known oxygen and nitrogen pressures in an open system according to the reaction

$$2SiO_{2(s)} + N_{2(g)} = Si_2N_2O_{(s)} + 3/2\ O_{2(g)} \quad (1)$$

For this reaction, the change in standard free energy ($\Delta G°$) is expressed as

$$\Delta G°_{(Eq.\ 1)} = \Delta G°_{Si_2N_2O} - 2\Delta G°_{SiO_2} = -2.303\ RT \log_{10} \frac{P_{O_2}{}^{3/2}{}_{equil}}{P_{N_2\,equil}} \quad (1a)$$

This equilibrium was studied experimentally by passing gas mixtures of H_2O, H_2, and N_2 over silica at 1400° and 1500°C and determining, by x-ray diffraction, the presence or absence of Si_2N_2O in the reaction product. The partial pressure of nitrogen in the gas mixture was kept constant at approximately 0.5 atm, and the desired partial pressures of water were obtained by passing hydrogen gas through a saturator filled with a saturated sodium chloride solution held at selected temperatures in the range of −15° to −7°C. The oxygen pressure of the gas phase can then be calculated from the known equilibrium constant for the reaction

$$2H_2O_{(g)} = 2H_{2(g)} + O_{2(g)} \quad (2)$$

As the temperature of the sodium chloride solution was reduced, thereby decreasing the H_2O pressure and hence the O_2 pressure, a point was reached where Si_2N_2O appears as a phase. The temperature of the solution was then increased by a few degrees to increase slightly the H_2O, and thereby the O_2, pressure. This causes the Si_2N_2O phase to disappear, and establishes the reversibility of the reaction. Initial attempts to study the reaction between the H_2O–H_2–N_2 gas mixture and crystalline SiO_2 at 1400° and 1500°C were unsuccessful, because of the sluggishness of the reaction. In later, successful experiments, a more reactive SiO_2 of unit activity was obtained by using a silica-saturated CaO–SiO_2 liquid for the equilibration experiments at 1500°C, and a silica-saturated CaO–MgO–SiO_2 liquid for the equilibration experiments at 1400°C. The silicate liquids were contained in silica crucibles in a vertical Pt-wound furnace. Temperatures were measured with a Pt versus 90 percent Pt 10 percent Rh thermocouple, and are judged to be accurate to ± 5°C (Table 1).

In an open system, only relatively small amounts of Si_2N_2O were formed. It is suspected that this may be related to loss of silicon monoxide (SiO) at the relatively high temperatures and low oxygen pressures of the experiments. To minimize or circumvent these difficulties, and to check the data obtained in the open system, a second experimental method was developed which involved the study of an alloy-oxide plus oxynitride-gas equilibrium in a closed system. This method provided silicon, oxygen, and nitrogen in highly reactive forms in a gas phase without appreciable loss of materials by volatilization, and still provided means of controlling both the nitrogen and oxygen pressures of the system. Briefly, the method was as follows. Within a silica

Table 1. Data for the equilibrium of Eq. 1.

Parameter	Values	
	1400°C	1500°C
P_{N_2}(atm)	0.5	0.5
P_{O_2}(calculated, atm)	$10^{-15.8}$	$10^{-14.8}$
$\frac{P_{O_2}}{P_{N_2}}$	$10^{-15.5}$	$10^{-14.5}$
$\Delta G°_{(Eq.\ 1)}$(kcal)	179.5	177.6
$\Delta G°_{Si_2N_2O}$(kcal)	−107.5	−102.4

Table 2. Data for the equilibrium of Eq. 5.

Parameter	Value	
	1400°C	1500°C
P_{N_2}(atm)	0.05	0.05
Alloy composition (X_{Si})	0.38	0.36
$\Delta G^\circ_{(Eq.\ 5)}$(kcal)	−32.6	−30.3
$\Delta G^\circ_{Si_2N_2O}$(kcal)	−104.4	−100.3

glass tube, sealed under vacuum, were two silica boats, one containing a chromium nitride (Cr_2N)-metallic chromium buffer, the other containing a mixture of silica and a silicon-nickel alloy of known composition, with a large excess of the alloy phase. The Cr_2N-Cr buffer maintains within the silica tube a constant nitrogen pressure determined by the equilibrium

$$2Cr_2N_{(s)} = 4Cr_{(s)} + N_{2(g)} \quad (3)$$

at any selected temperature. The silica-silicon–nickel mixture defines the oxygen pressure inside the silica tube, at any selected temperatures, according to the equilibrium

$$SiO_{2(s)} = (Si)_{alloy} + O_{2(g)} \quad (4)$$

The alloy composition is varied until a composition is found at which just a trace of Si_2N_2O is formed. When this condition exists, the free-energy change for the reaction

$$1/2\ SiO_{2(s)} + 3/2\ (Si)_{alloy} + N_{2(g)} = Si_2N_2O_{(s)} \quad (5)$$

is calculated as

$$\Delta G^\circ_{(Eq.\ 5)} = \Delta G^\circ_{Si_2N_2O} - 1/2\ \Delta G^\circ_{SiO_2} = -2.303\ RT \log_{10} \frac{1}{P_{N_2\,equil} \cdot a_{Si\,equil}^{3/2}} \quad (5a)$$

The Cr_2N-Cr equilibrium is known from the work of Seybolt and Oriani (*6*), and a_{Si} values of Si–Ni alloys are known from the work of Schwerdtfeger and Engell (*7*). Although the latter data were obtained at slightly higher temperatures than those in our work, the data can be applied with good accuracy to the present problem because the temperature coefficient of the activity coefficients is known, and is small.

In some of the initial experiments, difficulties were encountered as a result of diffusion of nitrogen and oxygen from the air through the wall of the silica glass tubes. This difficulty was eliminated in succeeding runs, either by using another silica tube outside the reaction tube, with a Cr getter between the two tubes, or by using thicker-walled silica glass tubes.

Runs were made at 1400° and 1500°C. In the former the equilibration time was about 72 hours, and, in the latter, about 12 hours (Table 2).

The free-energy values obtained by the two experimental methods are in reasonable agreement. The ratios of oxygen to nitrogen pressures of the gas phase in equilibrium with SiO_2 and Si_2N_2O at a total pressure of 1 atm calculated from the closed-tube runs are $10^{-16.0}$ and $10^{-15.2}$ at 1400° and 1500°C, respectively, as compared to the values of $10^{-15.5}$ and $10^{-14.5}$ obtained in the runs in the open system. These values provide a basis for speculations concerning the environmental conditions under which the enstatite chondrites were formed, or to which they have been exposed at some time during their existence.

Combination of the free-energy data for Si_2N_2O obtained in our work and the previously available free-energy data for SiO_2 and Si_3N_4 gives the free-energy change for the reaction

$$SiO_{2(s)} + Si_3N_{4(s)} = 2Si_2N_2O_{(s)} \quad (6)$$

as $\Delta G^\circ_{(Eq.\ 6)} \cong -10$ kcal at 1400° and 1500°C. This value should be considered to be only approximate, because of the possibility of some mutual solid solubility among the three phases involved. Attempts to react SiO_2 and Si_3N_4 by solid-state reaction in a closed silica tube in the temperature range of 1300° to 1650°C for periods up to 72 hours failed to produce any silicon oxynitride, presumably because of extreme sluggishness of the reaction. However, mixtures of SiO_2, Si_3N_4, and Si_2N_2O reacted slowly at 1500°C and higher temperatures to increase the proportion of Si_2N_2O, thus confirming the negative value of $\Delta G^\circ_{(Eq.\ 6)}$.

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References and Notes

1. W. D. Forgeng and B. F. Decker, *Trans. AIME* **212**, 343 (1958).
2. M. E. Washburn and R. W. Love, *Amer. Ceram. Soc. Bull.* **41**, 447 (1962); M. E. Washburn, *Refractories J.* **39**, 412 (1963).
3. D. M. Brown, P. V. Gray, F. K. Heumann, H. R. Philipp, E. A. Taft, *J. Electrochem. Soc.* **115**, 311 (1968); C. M. Drum, *J. Appl. Phys.* **39**, 4458 (1968).
4. C. A. Anderson, K. Keil, B. Mason, *Science* **146**, 256 (1964).
5. B. Mason, *Geochim. Cosmochim. Acta* **30**, 23 (1966).
6. A. U. Seybolt and R. A. Oriani, *Trans. AIME* **206**, 556 (1956).
7. K. Schwerdtfeger and H.-J. Engell, *ibid.* **233**, 1327 (1965).
8. Contribution No. 68-55 from College of Earth and Mineral Sciences, Pennsylvania State University, University Park. Supported by the U.S. Atomic Energy Commission under contract No. AT(30-1)-2781, AEC publication No. (NYO-2781-37).

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Extraparticulate Chain Interaction between Different Electron Transport Particles

Abstract. *Interaction or cross-linking between the respiratory chains of the electron transport particles of bacterial origin occurs with a mixture of active and inactive particles. Interaction between bacterial particles and liver submitochondrial particles also occurs. Irradiation of the bacterial particles at 360 nanometers resulted in the destruction of quinone and consequent loss of ability of reduced nicotinamide adenine dinucleotides to reduce cytochromes b, c_1, c, and a plus a_3. A mixture of both irradiated and untreated particles in the presence of the reduced dinucleotide resulted in the reduction of cytochromes c and a plus a_3 in an amount equivalent to the total concentration of these cytochromes in both types of particles. In contrast, the amount of cytochrome b reduced was equivalent to half the particle concentration or to that observed with the active particles alone. The rate of reduction of cytochromes c and a plus a_3 with the mixture of particles was similar to that with the active particles alone. The interaction or cross-linking between the particulate respiratory chains of bacteria or of bacterial and mammalian systems occurs after cytochrome b and before or at cytochrome c.*

The possibility of intra- and extra-chain interaction of the respiratory assemblies as well as the possibility of cross-linking of respiratory components within the respiratory chain has been suggested from kinetic studies (*1*) by the use of selective respiratory inhibitors or dyes (*2*, *3*) and from studies