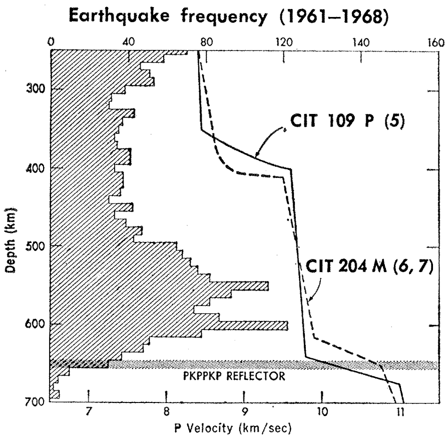

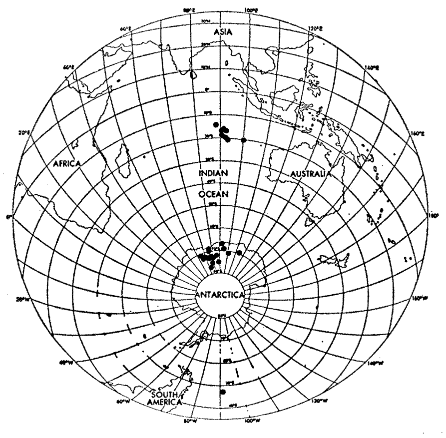

Fig. 3 (left). Earthquake frequency and *P* velocity as a function of depth below the earth's surface. The *PKPPKP* reflector is centered at 650 km. Fig. 4 (right). Reflection points for observations of *PKPPKP* waves reflected within the upper mantle.

travel time can be adjusted to bring the two structures into good agreement.

The data on the reflected *PKPPKP* that are presented here appear related to either the top or the bottom of the lower transition region, and hence may be considered as further evidence for the existence of such a transition region. The two-way travel time through the transition region is about 8 seconds for both structure models. The total absence on all records of another reflected *PKPPKP* phase both preceding and following by 8 seconds the single observed phase suggests that the top and bottom of the lower transition zone do not consist of the same order of discontinuity.

The fact that reflections from the upper transition region were not observed suggests that the transition zone may be defined by third-order rather than second-order discontinuities. The alternative explanation, that this zone may not be global in extent, can be rejected on the ground that one would hardly expect to find the transition from the spinel to the postspinel phase without the transition from olivine to spinel.

Reflection points for *PKPPKP* from the deep transition zone are plotted in Fig. 4. They form two groups: one in the Indian Ocean for Peru-Brazil data and the other at the edge of the Antarctic continent for observations from Novaya Zemlya. At least for these regions, it appears that the deep transition zone is independent of major differences in the earth's surface features.

The partition of energy on reflection from the proposed transition zones of the upper mantle is difficult to assess, since details concerning changes in density and precise thicknesses have not been completely resolved. For a simple model of steeply incident waves on a plane boundary, which has a 7.5 percent increase in density and 9.5 percent increase in compressional velocity, the reflection coefficient is approximately 0.15. If the major portion of the density jump in the upper mantle were evenly distributed between the two transition zones, as Anderson (*8*) suggests, one would expect to observe reflections from the shallow transition zone. The observed data suggest that the physical parameters of the deeper region are more sharply defined.

It is evident from the foregoing presentation that these new data have important consequences for future studies of the upper mantle. A thorough search of seismograms from high-magnification stations for well-recorded *PKPPKP* phases is now being made to assist in accurately describing zones of reflection in the upper mantle and their global extent (*9*).

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9. Since this paper was submitted for publication we have learned of a paper (R. D. Adams, *Bull. Seismol Soc. Amer.*, in press). Adams studied precursors arriving 10 to 70 seconds before normal *PKPPKP* waves, and interpreted them as reflections from discontinuities or inhomogeneities in the upper mantle. One of the events used by Adams was the deep-focus earthquake we analyze in the present paper. We find that an alternative explanation of Adams' data is the unreported phase *SKKKP*. This phase is conspicuous on the records we studied, but we did not comment on it because it is apparent from the $dT/d\Delta$ of 4.4 sec/deg that this phase is not a reflection of *PKPPKP* from a discontinuity within the upper mantle (E. R. Engdahl and E. A. Flinn, *Bull. Seismol. Soc. Amer.*, in press.
10. We thank R. D. Adams for making a copy of his paper available to us in advance of publication. We also thank D. L. Anderson and Miss I. Lehmann for discussions. Supported in part by the Advanced Research Projects Agency, Nuclear Test Detection Office, under project VELA UNIFORM, and accomplished under the technical direction of the Air Force Technical Applications Center under contract F-33657-68-C-0945.

30 August 1968

Potassium-Sodium Ratios in Aqueous Solutions and Coexisting Silicate Melts

Abstract. *Silicate melts were equilibrated with aqueous chloride solutions at temperatures between 770° and 880°C and a total pressure of 1.4 to 2.4 kilobars. The ratio of potassium to sodium in the aqueous phase was (0.74 ± 0.06) times the corresponding ratio in the coexisting melt over the entire range of temperature and pressure for all chloride concentrations between 0.2 and 4.2 moles per kilogram.*

During the course of a series of experiments designed to clarify the distribution of cations between silicate melts and aqueous solutions, we have determined the concentration of sodium and potassium in granitic melts and in coexisting chloride solutions at temperatures between 770° and 880°C and pressures between 1.4 and 2.4 kb. A starting glass was prepared by mixing 37 percent (by weight) clear vein quartz with 30 percent (by weight) albite from Amelia Court House, 6 percent (by weight) anorthite from Naxos, Greece, and 27 percent (by weight) adularia (63 percent orthoclase and 37 percent

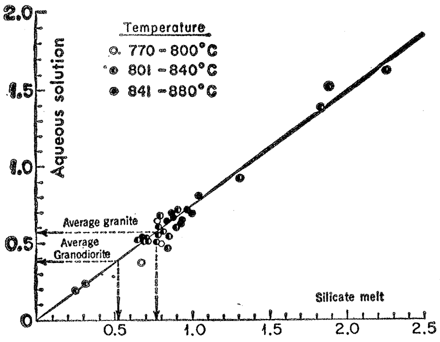

Fig. 1. The potassium-sodium ratio ($m_{\mathrm{K}}/m_{\mathrm{Na}}$) in coexisting aqueous solutions and granitic melts between 770° and 880°C.

albite) from an Alpine vein. This mixture was then melted; the melting and regrinding procedure was repeated five times to ensure homogeneity. The composition of the glass, as determined by x-ray fluorescence and atomic absorption techniques, was in good agreement with the composition calculated on the basis of the mineralogical composition of the mixture.

Carefully weighed samples (0.1 to 0.2 g) of starting glass and of aqueous chloride solution were sealed in gold capsules. These were placed in Stellite cold-seal bombs and were brought up to temperature at the desired total external (water) pressure. At the end of the run the bombs were rapidly quenched with air and then with an air-water mixture. The capsules were removed from the bombs, dried, and weighed. A portion of solution was removed from the capsules by means of a hypodermic syringe, weighed, and analyzed for cations and chloride (*1*) by atomic absorption spectroscopy. The capsules were then opened completely, and the glass bead was dried, weighed, examined petrographically, and analyzed chemically. Small amounts of quartz were the only crystalline products observed in the glass beads, and fluid inclusions were found only in glass from runs which were quenched abnormally slowly.

Our data for the distribution of sodium and potassium between the aqueous and silicate phases are summarized in Figs. 1 and 2. The material balance for sodium and potassium was checked for all runs; only those values were used for which the difference between the weight of these elements before sealing and after quenching the capsules was less than 10 percent. The ratio of the concentration of potassium to sodium in the aqueous phase (in moles per kilogram) is related to the same ratio in silicate melts at temperatures between 770° and 880°C by the expression

$$(m_{\mathrm{K,aq}}/m_{\mathrm{Na,aq}}) = (0.74 \pm 0.06) \times (m_{\mathrm{K,sil}}/m_{\mathrm{Na,sil}}) \qquad (1)$$

where m represents moles per kilogram of solution or of melt. The distribution coefficient $k'_{\mathrm{K,Na}}$ of potassium and sodium between the aqueous and silicate phase, defined by the expression

$$k'_{\mathrm{K,Na}} = \frac{(m_{\mathrm{K,aq}}/m_{\mathrm{Na,aq}})}{(m_{\mathrm{K,sil}}/m_{\mathrm{Na,sil}})} \qquad (2)$$

therefore has the value (0.74 ± 0.06). In Fig. 2 the value of $k'_{\mathrm{K,Na}}$ for individual runs has been plotted as a function of the chloride concentration of the aqueous phase. The lack of dependence of $k'_{\mathrm{K,Na}}$ on $m_{\mathrm{Cl,aq}}$ is striking. In our experiments equilibrium was approached from several directions. The data of Fig. 2 show that values of $k'_{\mathrm{K,Na}}$ are independent of the duration of runs in excess of 24 hours, and that equilibrium was apparently reached in all the reported runs.

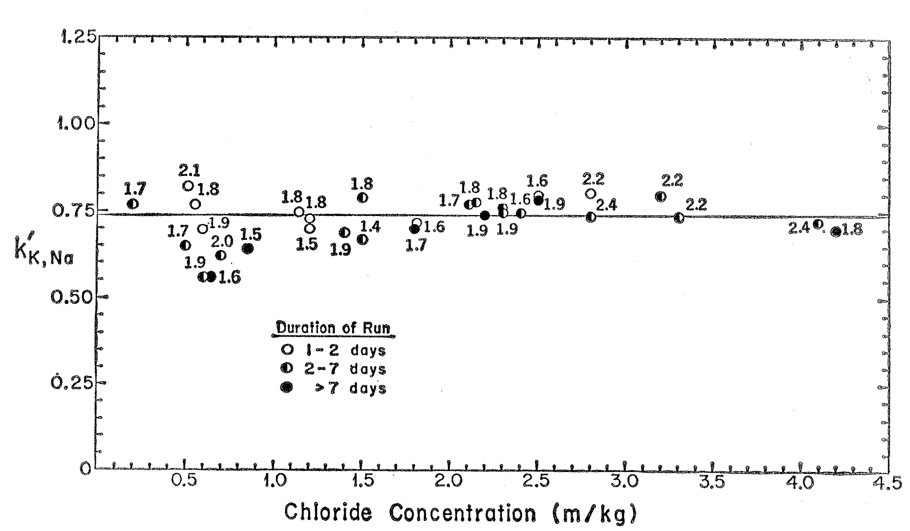

Fig. 2. The distribution coefficient $k'_{\mathrm{K,Na}}$ as a function of the chloride concentration of aqueous solutions in equilibrium with granitic melts; the numbers near data points refer to the total pressure in kilobars.

These data represent an extension of published results. Orville (*2*) has shown that the ratio ($m_{\mathrm{K,aq}}/m_{\mathrm{Na,aq}}$) in chloride solutions in equilibrium with two alkali feldspars increases with temperature from (0.259 ± 0.006) at 500°C to (0.351 ± 0.007) at 670°C, and that this ratio is independent of the chloride content of the aqueous phase between 0.2*M* and 2.0*M*. Our value of the ratio ($m_{\mathrm{K,aq}}/m_{\mathrm{Na,aq}}$) in an aqueous phase in equilibrium with an average granite melt (*3*) between 770° and 880°C is 0.57 (Fig. 1); the ratio is similarly independent of the chloride content of the aqueous phase. In experiments with Spruce Pine pegmatite, Burnham (*4*) has found that the ratio (K/K + Na) is slightly lower in an aqueous phase than in the coexisting condensed phases at temperatures between 500° and 900°C.

The salts in the aqueous phase in our runs were probably largely undissociated. Franck (*5*) has found that the dissociation of KCl at 750°C and a vapor density of 0.4 g/cm^3 (pressure approximately 1.6 kb) is 1.2×10^{-4}. In a 1-molar KCl solution at this temperature and pressure only about 1 percent of the salt would be dissociated. At higher pressures the dissociation constant increases rapidly, but even at the highest pressures in our experiments the fraction of dissociated salt was almost certainly less than 10 percent of the amount present. The distribution coefficient $k'_{\mathrm{K,Na}}$ was therefore determined largely by the equilibrium constant $k_{\mathrm{K,Na}}$ for the reaction

$$\mathrm{KCl_{aq}} + \mathrm{Na^+_{sil}} \rightleftharpoons \mathrm{K^+_{sil}} + \mathrm{NaCl_{aq}} \qquad (3)$$

$$k_{\mathrm{K,Na}} = \frac{a_{\mathrm{K^+,sil}} \times a_{\mathrm{NaCl,aq}}}{a_{\mathrm{Na^+,sil}} \times a_{\mathrm{KCl,aq}}} = \frac{\gamma_{\mathrm{K^+,sil}}\ \gamma_{\mathrm{NaCl,aq}}}{\gamma_{\mathrm{Na^+sil}}\ \gamma_{\mathrm{KCl,aq}}} \times k'_{\mathrm{K,Na}} \qquad (4)$$

where γ_{iA} is the activity coefficient of species i in phase A. The activity coefficient product ($\gamma_{\mathrm{K^+,sil}}\ \gamma_{\mathrm{NaCl,aq}}$)/($\gamma_{\mathrm{Na^+,sil}}\ \gamma_{\mathrm{KCl,aq}}$) is independent not only of the ratio of potassium to sodium in the two phases, but also of the concentration of salt in the aqueous phase and of the total pressure between 1.4 and 2.4 kb.

The data in Fig. 3 indicate that hy-

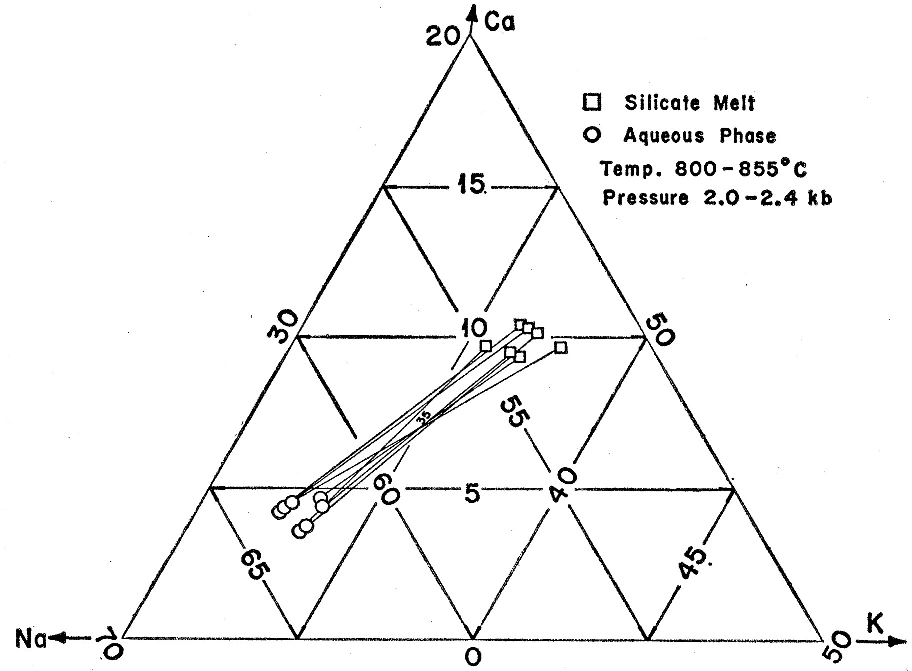

Fig. 3. The mole percent of potassium, sodium, and calcium in coexisting chloride solutions and granitic melts; the chloride concentration in the aqueous phase was between 2 and 4 mole/kg.

drothermal solutions tend to be depleted in calcium relative to the silicate melts with which they are in equilibrium. This is true to an even greater extent for magnesium. On the other hand, the concentration of chloride in the aqueous phase is between 10 and 100 times greater than that in the associated silicate melts. After the runs at 800° to 855°C and pressures of 2.0 to 2.4 kb were quenched, the pH of the 2- to 4-molar chloride solutions (initial pH 4.2) changed to between 1.5 and 2.0.

Our data define the initial ratio of potassium to sodium in hydrothermal solutions derived from siliceous magmas in a geologically interesting range of temperatures and pressures. During the reaction of such solutions with silicate wall rocks on cooling, the ratio of potassium to sodium tends to decrease and ultimately to approach 0.02, the value of $m_{\mathrm{K}}/m_{\mathrm{Na}}$ in ocean water. Sawkins (*6*) and Rye (*7*) have shown that the hydrothermal solutions responsible for the deposits of lead-zinc ore at Providencia, Zacatecas, Mexico, were probably derived from the deeper levels of the granodiorite stock at Providencia-Concepción del Oro. The range of ($m_{\mathrm{K}}/m_{\mathrm{Na}}$) represented in two samples of fresh granodiorite analyzed by us and in three samples analyzed by Dittrich (*8*) was 0.56 to 0.86. Hydrothermal solutions derived from melts of such composition would have ratios of potassium to sodium between 0.41 and 0.64. Rye and Haffty (*9*) have found ratios of potassium to sodium between 0.09 and 0.43 in inclusion fluids from minerals of the Providencia ore bodies. The higher values are characteristic of the most concentrated ($2.5M$ to $6M$) chloride solutions. These findings are consistent with the hypothesis that the solutions were derived from the granodiorite magma, and that the more concentrated solutions have suffered only a small reduction in the ratio of potassium to sodium by reaction with the enclosing wall rocks.

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Sexual Pheromone in Some Fishes of the Genus Hypsoblennius Gill

Abstract. *A pheromone found in the males of some species of* Hypsoblennius *apparently facilitates male courtship by releasing sexual appetitive behavior and by increasing sexual receptivity.*

Nonvisual communication is common in sexual behavior (*1*). Pheromones in fishes have been reported to serve for species and individual recognition (*2–4*), and as stimuli involved in courtship behavior (*3, 5, 6*). Both chemical (*6, 7*) and auditory (*8*) signals have been implicated in the courtship behavior of blenniid fishes. This report describes a pheromone response that involves social facilitation of sexual behavior between males of some *Hypsoblennius* species. Most of the previously reported sexual pheromone responses in fishes involve recognition or intersexual communication (*3, 5, 6, 7*). In the three-spined stickleback, courtship of the male is enhanced by the odor of his own nest (*9*). This response is similar to the enhancement of sexual receptivity noted in *Hypsoblennius*, but no mention is made of the effects of this pheromone on other males in regard to sexual receptivity or sexual appetitive behavior.

The three species studied are territorial bottom fish found in shallow-water, much-broken habitats. *Hypsoblennius jenkinsi* (Jordan and Evermann), from California, is morphologically similar to its apparent counterpart in Peru, *H. robustus* (Hildebrand); *H. gentilis* (Girard), from California, is less similar and seemingly is a more primitive member of the species group (*10*). The sexual behavior of these three species is similar in most respects (*10*). When a female approaches a ripe male, he responds by displaying in a head-up posture from his refuge or dwelling place, and on further approach by the female, by quivering his body. The female enters the male's refuge, deposits her eggs, and leaves them to the care of the male. Sexually ripe males are frequently attracted to courting males, often from beyond the visual field.

Isolated 12-gallon (45-liter) aquariums were used. Both ends of each tank were constantly supplied with seawater through tubes that emptied just above the surface of the water. Glass lines for introduction of the stimulus emptied in either end with the tank's water supply in order to avoid collateral