

condition could be fulfilled only if the separation between the boron atom and the sodium ion were not smaller than the sum of the radii of both (on the assumption of 2.40 Å separations of sodium ion from three oxygens of one cage).

If the calculations would not invalidate the above condition, the argument for the hexaborate cage structure might have added support. Consequently, the differences between alternatively calculated distances, indicated as *A* and *B* in Table 4, for sodium ions from the respective cage centers were calculated. The derived distances denoted by *B* are self-evident. The data used for deriving the distances denoted by *A* were (i) the sodium ion–oxygen atom separation equal to 2.40 Å; (ii) the oxygen distance from cage center (Table 1); and (iii) the angle between the lines from the cage center to the adjoining peripheral boron and oxygen atoms (that is,  $\theta_2$ , Table 1). From the data in Table 4, for disodium octaborate, the difference +0.12 Å attests that the sodium ions would not be sterically hindered in their allocation opposite boron atoms of the cage. For disodium hexaborate, the difference –0.01 Å is so small that it can be ignored, and thereby the necessary condition for some sodium ions allocated in front of boron atoms may be validated. Finally, for disodium tetraborate the large negative difference –0.30 Å rules out the above possibility.

The suggested structures of polyborate ions, and the possible allocations of cations around them, may afford a basis for the interpretation of the unresolved ionic networks in the polyborate salts. For example, for disodium tetraborate the most compact structural unit in the ionic network may be the dodecahedral one (Fig. 4). In the model shown, each tetrahedron represents the  $B_4O_6^{--}$  cage ion with a shared sodium ion at each corner.

The formation of polyborate salts is associated with considerable volume reduction with respect to the original volumes of boron oxide and metal oxide (13, p. 213). This effect is absent in polysilicate formation (13, p. 201). Eversteijn, Stevels, and Waterman (14) hold that the above difference may be due to different structural transformations in boron oxide and silicon dioxide networks, caused by the cation of the metal oxide. They admit, however, that more experimental and theoretical work would be required to confirm (or reject) their conjecture.

Formation of the suggested cage-type polyborate ions may readily account for this phenomenon (15).

The tendency of boron oxide to form cage structures might also account for different solubilities of boron oxide in molten sodium halides. In molten sodium fluoride (mp 992°C), boron oxide is completely soluble (16). In other sodium halides, its solubility diminishes with the increase in atomic number of the halide (17). Moreover, Harrison (18) shows that molten sodium chloride dissolves boron oxide as the  $B_4O_6$  species, which may be cage-structured (19). The chloride ion, with an ionic radius of 1.81 Å (9), would be too large to fit inside the  $B_4O_6$  cage even if its radius could be reduced by  $4 \times 0.20$  Å, thus becoming 1.00 Å (upon donation of four pairs of its electrons to the four boron atoms of the cage). However, up to four chloride ions could be coordinated external to boron atoms (Fig. 5). This coordination could make possible some dissolution of covalent boron oxide in the ionic medium of molten sodium chloride. The tendency of halide ions to form complexes with the  $B_4O_6$  cages should diminish with the decrease in negative-charge density of the halide ion. Accordingly, the solubility of boron oxide is smaller in molten sodium bromide than in sodium chloride, and is the lowest in sodium iodide (17). Also, with the increase in the vibrational energy of the complexes of boron oxide-halide ion, fewer halide ions should tend to coordinate with the  $B_4O_6$  cages. Hence, the solubility of boron oxide in molten sodium halides (other than fluoride) diminishes with a rise in temperature (17).

The complete solubility of boron oxide in molten sodium fluoride, on the other hand, may be attributed to the small ionic radius, 1.36 Å (9), of the fluoride ion. Hence it should be feasible for this ion, by donating four electron pairs to four boron atoms, to become occluded by the  $B_4O_6$  cage. The heretofore stoichiometrically inexplicable formation of  $B_4O_6F^-$  ions might thereby be clarified.

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18 April 1966

## Mars: New Absorption Bands in the Spectrum

Abstract. *New absorption bands have been found in the near-infrared spectrum of Mars by Fourier spectroscopy. They are tentatively identified in part as due to reduced gases in the Martian atmosphere.*

During the 1965 opposition of Mars, spectra were obtained at the Observatoire de Haute-Provence, France, by means of Fourier-transform spectroscopy. The Michelson interferometer used is described and samples of typical spectra of Mars and Venus, together with solar spectra for comparison, are given in (1); the complete spectra are being prepared for publication.

The Mars spectra were obtained from 5700 to 6950  $\text{cm}^{-1}$  (1.44 to 1.75  $\mu$ ) with a resolution of about 1  $\text{cm}^{-1}$ , and from 4050 to 4550  $\text{cm}^{-1}$  (2.20 to 2.47  $\mu$ ) with a resolution of about 4  $\text{cm}^{-1}$ . They are reproducible and include the expected telluric and solar lines.

The Mars spectra were obtained mainly in order to measure absorption by lines in the 1.6- $\mu$   $\text{CO}_2$  bands to enable more precise estimation of the surface pressure. The  $\text{CO}_2$  bands did indeed appear in the spectra, with the lines in the low-frequency branches resolved, but they were severely overlapped by unexpected absorption fea-

tures that extend through most of the spectrum, that cannot be attributed to solar or telluric lines, and that are therefore inferred to be caused by gaseous components of the Martian atmosphere. The features were not discovered in previous spectra, obtained by conventional techniques (see 2), because of insufficient spectral resolution.

The characteristics and extent of the additional spectra indicate that reduced gases, including substituted methanes, are probably at least partially responsible for them; absorption amplitudes suggest individual mole fractions of the order of  $10^{-3}$ .

Quantitative identification of the gases responsible for the newly discovered spectra is now being attempted, and the preliminary results are promising. The purpose of this report is to call attention to the success of inter-

ferometry in obtaining spectra of planets with sufficient resolution in the PbS region to resolve rotational fine-structure, and to note the presence of constituents in the Martian atmosphere that may have important implications for the possibility and nature of life on Mars.

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27 April 1966

## Potassium:Rubidium Ratio in Ultramafic Rocks: Differentiation History of the Upper Mantle

**Abstract.** *The increase in K:Rb ratio with decrease in potassium content found in basaltic rocks does not seem to apply to ultramafic rocks. The ratios in a series of alpine ultramafic rocks and ultramafic inclusions in basalts and kimberlite pipes are about 200 to 500—significantly lower than those in oceanic tholeiites. This characteristic of ultramafic rocks appears to be consistent with a simplified model in which early differentiation of the primitive mantle led to formation of an upper mantle region enriched in alkali elements and having a low K:Rb ratio. Alpine ultramafic rocks may be residuals from such an upper mantle region.*

The importance of the K:Rb ratios in igneous rocks with regard to understanding of their differentiation trends and of the nature of the source materials has been emphasized (1, 2). In general it has been demonstrated that the K:Rb ratio decreases with increase in differentiation (increase in K content)—as is to be expected from simple geochemical consideration of the difference in ionic radii of these elements. Gast (2) has shown in particular that the K:Rb ratios in some oceanic tholeiites are as high as 1800 and vary systematically with the K content; on the basis of the similarity of these ratios in oceanic tholeiites and in achondritic meteorites and of other evidence (3), he suggests that the compositions of the upper mantle and of achondritic meteorites may be similar.

In that the K:Rb ratios indicate the source materials and differentiation his-

tory of the upper mantle, measurement of the ratio in ultramafic rocks, presumably derived from the upper mantle, is of great interest. We have determined the ratios by the isotope-dilution method in a series of alpine peridotites and ultramafic inclusions in basalts and kimberlite pipes (Table 1 and 2; Fig. 1); in Fig. 1 the ratio is plotted against the K content of these rocks, with data on volcanic rocks and achondrites (2), chondrites (4), and carbonaceous chondrites (5) for comparison.

The ratios in these ultramafic rocks range from about 200 to 500; similar ratios in a dunite, a pyroxenite, and an eclogite from Japan, and in a number of eclogites, have been reported (6, 7). From detailed study of mylonitized peridotites from St. Paul's Rocks, Hart (6) described ratios as high as 1000, with a linear relation between ratio and K content; he sug-

gested that the relation reflected either mechanical mixing of two end-member rock types or differentiation processes.

The K:Rb ratios of ultramafic rocks show two notable features. Firstly, they do not attain the high values found in oceanic tholeiites, although the K contents of the rocks are much lower; in general they somewhat resemble those of the alkali basalts and crustal material. Secondly, whereas the basaltic data show an apparent relation between K:Rb ratio and K content, the ultramafic rocks seem to show none. The continuity in the relation between K:Rb ratio and K content seems not to exist for ultramafic rocks that are extremely poor in alkali. We now propose to explore the view that the uniformly low K:Rb ratios in these ultramafic rocks are a natural consequence of the differentiation history of the materials from which they are formed.

The Rb-Sr isotopic relations in alpine-type ultramafic rocks have been interpreted (8) as consistent with a mantle differentiation history: Shortly after Earth's accretion, fractional melting of the primitive mantle material led to a concentration of lithophilic and radioactive elements in the upper mantle (9) in a first-stage differentiation process. Continental sialic crust subsequently developed by further fractionation of lithophilic and radioactive elements from this upper mantle, whose geochemical characteristics were set by the first-stage differentiation process. The alpine ultramafic rocks are residual systems produced by the differentiation processes that led to formation of the continental crust; as a consequence, the subcontinental upper mantle is depleted in radioactive elements relative to the suboceanic upper mantle. The ultramafic inclusions in basalts are interpreted as fragments of refrac-

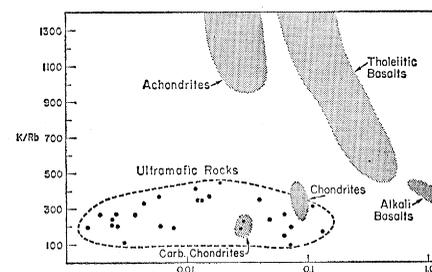


Fig. 1. Potassium:rubidium ratios in some ultramafic rocks, volcanic rocks, and meteorites. Data for achondrites, tholeiitic basalts, and alkali basalts are from (2); for chondrites, from (4); and for carbonaceous chondrites, from (5).