

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.

JANINE CONNES

PIERRE CONNES

Observatoire de Meudon and Centre National de la Recherche Scientifique, Bellevue, Seine-et-Oise, France

LEWIS D. KAPLAN

Jet Propulsion Laboratory, Pasadena, California

References

1. J. Connes and P. Connes, *J. Opt. Soc. Amer.* **56**, 896 (1966).
2. V. I. Moroz, *Mém. Soc. Roy. Sci. Liège* **9**, ser. 5, 406 (1964).
3. G. P. Kuiper, *Commun. Lunar Planetary Lab.* **2**, 79 (1964).

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-

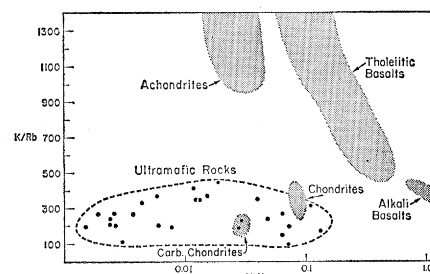


Fig. 1. Potassium:rubidium ratios in some ultramafic rocks, volcanic rocks, and meteorites. Data for achondrites, tholeiitic basalts, and alkali basalts are from (2); for chondrites, from (4); and for carbonaceous chondrites, from (5).

Table 1. Concentrations of K and Rb and K:Rb ratios in some alpine peridotites. NZ, New Zealand; G, Greenland; N, Norway; A, Australia; NF, Newfoundland; V, Venezuela.

Source	K (ppm)	Rb (ppm)	K:Rb
<i>Dunite</i>			
Dun Mtn., NZ	23.9	0.111	215
Papua	61.2	.302	203
Shikoku, Japan	24.2	.099	244
Tulameen, B.C.	26.5	.130	204
Cantwell, Alaska	19.3	.072	268
Siorarssuit, G	643	2.42	266
Konya, Turkey	36.9	0.140	263
Almklovdalen, N	44.2	.131	337
<i>Serpentine</i>			
Kalgoorlie, A	119	.284	419
Bett's Cove, NF	236	1.036	228
<i>Peridotite</i>			
Mt. Albert, Quebec	59.3	0.158	375
Tinaquillo, V	25.8	.093	277

tory basaltic residue from the upper mantle, formed subsequent to the early differentiation.

In this context, the main characteristic of such a differentiation history is the close coupling between the crust and an already differentiated upper mantle whose geochemical characteristics would have been established by the composition of the primitive mantle material and the nature of the first-stage differentiation process. As we have noted, the first-stage differentiation process was such that it caused enrichment of lithophilic and radioactive elements in the upper mantle. If one assumes that the K:Rb ratio of the primitive mantle material was of the order of 1500 or greater (2), the first-stage differentiation process mentioned resulted in lower K:Rb ratios in the upper mantle. In that the ratio is re-

Table 2. Concentrations of K and Rb and K:Rb ratios in some ultramafic inclusions in basalts and kimberlites. A, Austria; M, Mexico; T, Tanganyika; SA, South Africa; NZ, New Zealand; Ant, Antarctica.

	K (ppm)	Rb (ppm)	K:Rb
<i>Peridotite inclusions</i>			
Kerguelen Is.	190	0.420	452
Galapagos Is.	123	.352	349
Kapfenstein, A	31.1	.271	115
Chihuahua, M	152	.413	368
Ludlow, Calif.	77.9	.398	196
Monduli, T	727	3.67	198
Wesselton Pipe, SA	641	4.45	143
Bultfontein Pipe, SA	483	2.03	238
<i>Garnet peridotite inclusion</i>			
Kankanui, NZ	938	1.73	542
<i>Eclogite inclusion</i>			
Visser Pipe, T	716	7.52	95
<i>Dunite inclusion</i>			
Ross Is., Ant	216	1.15	188

lated to the extent of differentiation, one may have in fact variation in ratio values in the mantle, both vertically and laterally.

The alpine-type ultramafic rocks are residual in nature and their alkali elemental concentrations are so low that, for approximation, we can consider that both K and Rb were totally removed from them into the crust. Therefore a general idea of the ratio in the upper mantle regions after the early-stage differentiation is given by the K:Rb ratio of the average continental crust. The ratios in these ultramafic rocks are low primarily because the rocks formed from material of the upper mantle—wherein the ratio had been lowered by the aforementioned first-stage differentiation process. The primitive basalts with high K:Rb ratios are, according to this view, derived from source materials that were less (or not at all) differentiated in this first stage.

If this somewhat oversimplified interpretation were correct, we would expect the alpine ultramafic rocks and the ultramafic inclusions to show more radiogenic Pb and Sr isotopes, as well as relatively more fractionated light rare-earth elements, than the primitive basalts with high K:Rb ratios. Isotopic analyses of lead from these ultramafic rocks are not yet available, but the $\text{Sr}^{87}:\text{Sr}^{86}$ ratios are definitely more radiogenic than those of oceanic tholeiites (8, 10). Similarly, the abundances of rare-earth elements in some of these ultramafic rocks show greater enrichments of the light rare-earth elements than do those of the oceanic tholeiites (11, 12).

The close relation between continental crustal material and the lithophilic element-enriched upper mantle has been mentioned; we suggest that the scatter of the K:Rb ratio, in common igneous rocks, around a value of 300 (13) may result from crustal material forming from an upper-mantle material having approximately the same K:Rb ratios.

Finally we suggest that the K:Rb ratios in ultramafic rocks are consistent with the idea of an early-stage differentiation of the primitive mantle material, during which lithophilic and radioactive elements were concentrated in the regions of the upper mantle (8, 9, 11).

ALAN M. STUEBER
V. RAMA MURTHY*

Department of Earth Sciences,
University of California, San Diego

References and Notes

1. P. Lessing, R. W. Decker, R. C. Reynolds, *J. Geophys. Res.* **68**, 5851 (1963); W. H. Taubeneck, *ibid.* **70**, 475 (1965); B. Gunn, *ibid.*, p. 6241.
2. P. W. Gast, *Science* **147**, 858 (1965).
3. ———, *J. Geophys. Res.* **65**, 1287 (1960); G. J. Wasserburg, G. J. F. MacDonald, F. Hoyle, W. A. Fowler, *Science* **141**, 465 (1964); A. E. J. Engel and C. G. Engel, *Science* **144**, 1330 (1964); *ibid.* **146**, 477 (1964).
4. A. A. Smales, T. C. Hughes, B. Mapper, C. McInnes, R. K. Webster, *Geochim. Cosmochim. Acta* **28**, 209 (1964).
5. V. R. Murthy and W. Compston, *J. Geophys. Res.* **70**, 5297 (1965).
6. S. R. Hart, *Geol. Soc. Amer. 77th Annual Meeting Program* (1964), p. 19; S. R. Hart, L. T. Aldrich, G. R. Tilton, G. L. Davis, T. E. Krogh, M. Yamaguchi, in *Carnegie Inst. Washington Year Book* **64** (1965), p. 287.
7. K. S. Heier and W. Compston, in preparation.
8. A. M. Stueber and V. R. Murthy, *Geochim. Cosmochim. Acta*, in press.
9. F. Birch, *Geol. Soc. Amer. Bull.* **76**, 133 (1965); A. E. Ringwood, *Geochim. Cosmochim. Acta* (1965).
10. M. Tatsumoto, C. E. Hedge, A. E. J. Engel, *Science* **150**, 886 (1965); M. Tatsumoto, *Trans. Amer. Geophys. Union* **46**, 165 (1965).
11. R. A. Schmitt, R. H. Smith, J. E. Lasch, A. W. Mosen, D. A. Olehy, J. Vasilevskis, *Geochim. Cosmochim. Acta* **27**, 577 (1963).
12. F. A. Frey and L. A. Haskin, *J. Geophys. Res.* **69**, 775 (1964); L. A. Haskin and F. A. Frey, *Science* **152**, 299 (1966).
13. K. Heier and S. R. Taylor, in *Physics and Chemistry of the Earth*, V. F. Press, L. H. Ahrens, S. K. Runcorn, Eds. (Macmillan, New York, 1964).
14. Work supported by NSF grant gp-3448.

* Present addresses: Department of Terrestrial Magnetism, Washington, D.C.; Department of Geology and Geophysics, University of Minnesota, Minneapolis.

16 May 1966

Mechanism for Intercalation of Kaolinite by Alkali Acetates

Abstract. *The relative strengths of the hydrogen bonds in kaolinite-alkali salt-water systems control kaolinite-salt interactions. A new technique for intercalation results in formation of a kaolinite-salt complex free of excess salt.*

We have achieved intercalation by drying a paste obtained by treating kaolinite with aqueous potassium acetate solutions. This method produces an expanded lattice free from detectable excess salt which is easily and reversibly interconverted to a partially collapsed dehydrated form. Intercalation occurs over a specific range of salt-to-water molecular ratios; this range may be approached from either low or high ratios with samples in equilibrium with controlled relative humidity atmospheres. A mechanism for the interactions between kaolinite, salt, and water is proposed.

Preferential penetration of kaolinite by potassium acetate was first achieved