

Titanoclinohumite: A Possible Mineralogical Site for Water in the Upper Mantle¹

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Titanium-rich clinohumite and layered structure minerals are observed in kimberlite and as inclusions in pyropic garnets from the Moses Rock dike, a kimberlite-bearing breccia dike in San Juan County, Utah. Associated clinopyroxenes observed as inclusions within similar pyropes and also in kimberlite are estimated to have equilibrated at depths ranging from about 50 to 150 km at modest temperatures, generally less than 1000°C. The presence of titanoclinohumite, a high-density hydrous phase, is of considerable interest as a possible site for volatiles in the earth's upper mantle. The dehydration of hydrous phases such as titanoclinohumite within the upper mantle (1) may provide water as a free phase, (2) could be important in the genesis of kimberlite and alkali-basalt magma, and (3) may be one means of producing a low-velocity zone in the upper mantle.

INTRODUCTION

Titanoclinohumite has been observed in thin sections and in heavy mineral concentrates from kimberlite collected at the Moses Rock dike in San Juan County, Utah. This dike is one of a cluster of breccia-filled kimberlite-bearing diatremes located in northeast Arizona and southeast Utah, which are known to contain rock and mineral fragments believed to be derived from a wide vertical column ranging from the surface extending into the upper mantle [Shoemaker, 1956, 1962; Watson, 1967; McGetchin, 1968a; McGetchin and Silver, 1968, 1969]. Kimberlite dikes and pipes characteristically contain abundant hydrous phases, such as serpentine, talc, mica, chlorite, amphibole, in addition to olivine, pyroxene, garnet, spinel, and other less abundant minerals. Kimberlite generally is believed to be emplaced as volatile-rich multiphase (probably fluidized) systems [Davidson, 1964; Shoemaker, 1962; Watson, 1967; McGetchin, 1968a, b], directly from the upper mantle at depths of 100 to 200 km [O'Hara, 1967; McGetchin and Silver, 1968].

This implies significant local concentration of volatiles in the upper mantle and raises the question of where H₂O might reside at depth. If bound in hydrous minerals, amphibole [Oxbrough, 1964], biotite and phlogopite [Kushiro *et al.*, 1967] are prime candidates because these phases are commonly observed in kimberlite and peridotite.

It is our suggestion that humite group minerals, specifically, titanoclinohumites, may be an important mineralogical site for bound water in the upper mantle and may be more abundant than commonly recognized because of their similarity to olivine in optical, physical, and chemical properties. It is implied that decomposition of titanoclinohumite to olivine, rutile, or other titanium-rich phases such as ilmenite or geikielite and free volatiles may have played an important role in the genesis of kimberlite at the Moses Rock dike and may be an important upper mantle process.

OCCURRENCE OF TITANOCLINOHUMITE AT MOSES ROCK DIKE

Titanoclinohumite is observed in several textural modes at Moses Rock dike, as grains in kimberlite commonly associated with olivine and as mineral inclusions within pyropic garnets.

Kimberlite at Moses Rock dike is a highly serpentinized, mica-bearing, peridotite microbreccia consisting of millimeter-sized angular mineral fragments, mostly olivine and pyroxene,

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more rarely, garnet, spinel, and mica, with subordinate small rock fragments, all set in a fine-grained groundmass of serpentine, chlorite, and talc. Serpentine, talc, and chlorite constitute about 80% of the rock by volume. As a discrete mappable rock unit, kimberlite is rare, occupying only about 1% of the area within the dike.

Clinohumite grains in the kimberlite occur as individual angular fragments averaging 1 mm in size, and less commonly as intergrowths (epitaxial?) with olivine in a single grain. Olivine clasts in kimberlite generally are partly serpentinized; titanoclinohumite is similarly altered but to a somewhat lesser degree than the olivine. This is clearly demonstrated when olivine and clinohumite occur together in the same grain.

Chrome-rich pyrope garnets, up to about 5 mm in diameter occurring in kimberlite at Moses Rock, are concentrated at the surface of the ground in aprons of ejecta surrounding ant hills. Mineral inclusions within these garnets include olivine, clinopyroxene, orthopyroxene, rutile, geikielite, ilmenite, mica, and titanoclinohumite. One particularly interesting pyrope specimen contains olivine, mica (?), clinohumite, and geikielite within the same grain. Mineral chemistry of the garnets and a large suite of associated inclusions is described elsewhere [McGetchin, 1968a; McGetchin and Silver, 1968, 1969].

IDENTIFICATION AND COMPOSITION

Titanoclinohumite was identified optically in thin sections of kimberlite. It is distinguished from olivine in ordinary light because of its brownish-yellow color.

Four grains from heavy mineral concentrates were picked, mounted, and analyzed for major elements (Si, Ti, Cr, Fe, Mg, Mn) with the Caltech microprobe (Table 1, analyses 1, 2, 3, 4). Data were reduced by the method of *Bence and Albee* [1968]. Grains from these separates were powdered and positively identified as clinohumite by X-ray diffraction.

The density of several titanoclinohumite grains was determined by buoyancy tests in calibrated heavy liquids to be 3.27 ± 0.02 , identical within error limits to the density of the associated olivine.

The most distinctive feature of these analyses is their high TiO₂ contents.

The Mg/(Mg + Fe) range is similar to that observed in olivine grains from Moses Rock kimberlite (89 to 94, in olivine); where olivine and clinohumite were observed to coexist in the same grain, both had approximately the same Mg/(Mg + Fe) ratio. This is shown in the analyses of coexisting olivine and titanoclinohumite (see Table 1, analyses 5, 6 and 10, 11). It is also true of coexisting titanoclinohumite and olivine inclusions in pyrope (see Table 1, analyses 8 and 9).

Total water contents can only be estimated by difference of the oxide summation from 100%, but suggested values are all between 1 and 2 wt %, in agreement with available wet chemical data (Table 1, analysis 14). The fluorine content is assumed to be characteristically low, in accordance with other workers' observation on titanoclinohumite.

OCCURRENCES AND STRUCTURE OF CLINOHUMITE

Balk [1954] observed clinohumite at the Buell Park diatreme near Fort Defiance, Arizona, about 95 miles southeast of the Moses Rock dike. Chemical analyses of a Buell Park sample (Table 1, analysis 14) show that major chemical constituents fall within the ranges defined by the Moses Rock specimens analyzed so far. The principal anion in the Buell Park titanoclinohumite is hydroxyl ion, not fluorine.

Titanium-rich clinohumites containing 2.92% TiO₂ have been reported from Bhandara District, India, in phlogopite and tremolite-bearing marble [*Muthuswami*, 1958]. In the southern Urals clinohumite containing 5.40% TiO₂ was described in association with low-titanium, forsterite-rich olivine by *Borneman-Starynkevich and Myasnikov* [1950].

The crystal structures of the humite group minerals are currently under investigation. *Gibbs and Ribbe* [1969] and *Jones et al.*, [1969] have shown that humite group minerals consist of units of Mg(F, OH)O alternating with Mg₂SiO₆(F, OH).

Machatschki [1930] suggested that Ti replaces Si in the humite series, but *Deer et al.* [1962, pp. 52, 53] argue that no apparent silica deficiency accompanies high titanium contents. Moses Rock titanoclinohumites are possibly slightly silica-deficient, but only by about 1 to 2%, a value essentially at the error limits. *Jones et al.* [1969] suggest that titanium sub-

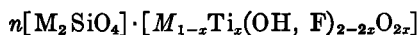
TABLE 1. Microprobe Analyses of Mineral Grains from Moses Rock Kimberlite

	Analysis													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
SiO ₂	36.0	36.3	36.1	35.8	37.0	41.8	43.1	36.5	41.8	37.1	52.1	37.54	35.90	35.34
TiO ₂	4.7	5.6	5.0	5.0	5.0	0.01	0.18	6.8	0.03	5.1	n.d.	0.22	5.59	5.11
Al ₂ O ₃	0.00	0.00	0.00	0.00	n.d.	n.d.	23.4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	.00
Cr ₂ O ₃	0.11	0.04	0.05	0.04	0.08	0.01	1.73	0.03	0.03	0.09	n.d.	n.d.	n.d.	0.10
*FeO	6.9	7.5	9.3	10.8	10.3	10.3	8.9	6.4	6.4	7.4	7.4	5.58	11.21	{ 1.23 = Fe ₂ O ₃ 10.23 = FeO
MgO	50.0	49.3	48.1	47.1	47.8	50.3	20.5	49.1	53.3	49.8	52.1	53.03	44.16	46.45
MnO	0.11	0.12	0.13	0.18	0.17	0.17	0.39	0.04	0.04	0.10	0.11	0.62	0.50	0.23
CaO	n.d.	n.d.	n.d.	n.d.	0.02	n.d.	4.7	0.02	0.03	0.02	0.03	0.01	0.01	0.07
Na ₂ O	n.d.	n.d.	n.d.	n.d.	0.08	0.14	0.06	0.01	0.01	0.08	0.13	n.d.	n.d.	n.d.
F	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	3.08	0.00	0.06
H ₂ O	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	2.46	2.64	1.14
P ₂ O ₅	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.12
Total	97.82	98.86	98.68	98.92	100.45	102.73	102.96	98.90	101.64	99.6	101.3	100.08	98.77	99.95
(Mg/Mg + Fe) _{atom}	0.928	0.921	0.903	0.886	0.892	0.897	0.805	0.932	0.936	0.923	0.926			

Key to Analyses:

- 1, 2, 3, 4, titanoclinohumite grains from Moses Rock kimberlite.
 - 5, 6, coexisting titanoclinohumite and olivine grains from Moses Rock kimberlite. Analysis 5 is titanoclinohumite; 6 is olivine.
 - 7, 8, 9, pyrope garnet (PG-2) containing mineral inclusions of titanoclinohumite, olivine, geikielite, and an unidentified dark colored layered mineral (phlogopite?). Analysis 7 is pyrope; 8 is titanoclinohumite; 9 is olivine.
 - 10, 11, coexisting titanoclinohumite (analysis 10) and olivine (analysis 11) from Moses Rock kimberlite.
 - 12, 13, Titanoclinohumites [Jones et al., 1969, Table 1].
 - 14, titanoclinohumite from Buell Park [Balk, 1954], (analyst, H. B. Wiik, Helsinki).
- * Fe as FeO

stitutes for Mg with a general humite formula of the form



where $x < 1$, M includes octahedral coordinated cations (Mg, Fe, Mn, Ca, Zn, etc.), and $n = 4$ for clinohumite. This formula suggests that the ratios Mg:Ti:Si in clinohumites should vary systematically between 9:0:4 (for $x = 0$) and 8:1:4 (for $x = 1$).

Analysis of titanoclinohumites from Moses Rock kimberlite and other previously published analyses (Table 1) fall on the compositional join between $Mg(OH, F)_2 \cdot 4Mg_2SiO_4$ and $TiO_2 : 4MgSiO_4$, in agreement with the suggested formula of Jones *et al.* [1969], and exclude the possibility of Ti for Si substitution.

DISCUSSION AND CONCLUSIONS

The textural relationships almost preclude the genesis of titanoclinohumite in the Moses Rock kimberlite as a late stage alteration product of olivine and indicate that titanoclinohumite coexisted with chrome-pyropes and olivine prior to serpentinization. Titanoclinohumite coexists with olivine of both higher and lower Mg/(Mg + Fe) ratios. Olivine grains separated from Moses Rock kimberlite have Mg/(Mg + Fe) ratios between 88 and 94. Samples with low Mg/(Mg + Fe) ratios are believed to be derived from a spinel-bearing peridotite (lherzolite) assemblage with aluminum-rich pyroxenes; those with high Mg/(Mg + Fe) ratios, from garnet-bearing peridotite (lherzolite) assemblage with aluminum-poor pyroxenes. Pressure and temperature estimates on mineral phases intimately associated with clinohumite in pyropes and in the kimberlite suggest that these minerals probably were derived directly from the mantle [McGetchin and Silver, 1968]. Minerals in kimberlite from the Moses Rock dike probably represent mechanically disintegrated lherzolite from the mantle, and to a much lesser extent from the vent walls, *not* crystals associated with a silicate melt [McGetchin, 1968a, 1969a]. It is inferred that titanoclinohumite was present with both garnet-bearing and spinel-bearing assemblages in the mantle under the Moses Rock dike before transport to the surface during the emplacement of kimberlite.

The decomposition of hydrous minerals, such as titanoclinohumite, could supply part of the

necessary volatiles responsible for the eruption and associated emplacement of kimberlite at Moses Rock dike. Rutile, chrome-bearing ilmenite, and geikielite are titanium-rich phases common among the dense minerals concentrated from Moses Rock kimberlite and could result from decomposition reactions involving titanoclinohumite, in part.

Liberation of free volatiles in the upper mantle by the decomposition of hydrous minerals including titanoclinohumite may be a geologically important phenomenon and could be involved in the genesis of volatile-rich eruptive systems, such as kimberlite, carbonatites, and alkali-basalts, and may be a means of producing the low-velocity layer in regions of low surface heat flow where calculated upper mantle temperatures appear to be too low to permit partial melting.

Titanoclinohumite may be added to the list of possible volatile-bearing mineral phases within the mantle, along with phlogopite, amphibole, and hydrous pyroxenes.

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