

Chevkinite from the Little Chief Granite porphyry stock, California

S. DOUGLAS McDOWELL

*Department of Geology and Geological Engineering
Michigan Technological University
Houghton, Michigan 49931*

Abstract

Electron microprobe analyses of chevkinite(?) from a Miocene granite porphyry stock are consistent with the general structural formula proposed by Gottardi (1960) and yield a mineral formula of:



where $A = Ce_{1.3}Ca_{1.1}La_{0.8}Nd_{0.4}Pr_{0.1}M_{0.3}$; $B = Fe^{2+}$; $C = Ti_{0.7}Al_{0.7}Fe_{0.2}^{+3}Mg_{0.3}M_{0.1}$; $D = Ti$.

Crystallization of the chevkinite, both as microphenocrysts and groundmass grains, took place at approximately 700–750°C, 1.5 kbar, near H₂O-saturation, and oxygen fugacities of approximately 10⁻¹⁵ atm. Compositional changes from microphenocrysts to groundmass grains reflect differentiation of the granitic magma, and include enrichment in Mn, Nb, La, and possibly Fe³⁺, and depletion in Ca, Al, Ti, Mg, Pr, Sm, Nd, and possibly Y and Gd. Substitution within the chevkinite follows the general equality



Within the two A sites, a higher-coordinated A₂^{IX} site and a slightly lower-coordinated A₁^{VIII-IX} site, the approximate substitution 0.95Ca + 0.05Pr = 0.5La + 0.5Ce occurs, with most of the exchange occurring in the A₂ site. Under extreme differentiation and La enrichment, substitution does occur in both A sites, with the general form La ≈ 0.10 Sm + 0.45 Ce + 0.45 Nd.

Introduction

The rare earth (REE)-titanium-silicate mineral chevkinite (perrierite?) has been found in trace quantities in the Little Chief Granite, a Miocene porphyry stock located in the Panamint Range west of Death Valley, California. Six grains from four specimens of the stock have been analyzed with the electron microprobe (Tables 1 and 2).

The chevkinite occurs as small (<0.4mm) slightly elongate (length/width = 2.5) prismatic crystals which are rectangular in longitudinal section. The form of the grains is identical to that illustrated by Izett and Wilcox (1968). The mineral is strongly pleochroic, ranging from dark red-brown to black in most grains, although a range in pleochroic colors from light yellow-brown to black was observed in a single grain which was cut perpendicular to the prism axis. The extreme pleochroism and strong absorption prevented any reliable optic data from being obtained. It was not possible to unambiguously distin-

guish whether this mineral is chevkinite or perrierite, an analogue of chevkinite which has a slightly different structure and composition [Bonatti (1959); Bonatti and Gottardi (1966); Ito (1967); Ito and Arem (1971); Calvo and Faggiani (1974)]. A comparison of the chemistry of the analyzed mineral with other chevkinite and perrierite analyses [Vlasov (1964); Segalstad and Larsen (1978)], as well as the extreme optical absorption of the grains (Izett and Wilcox, 1968), suggests that the mineral is probably chevkinite.

The chevkinite is closely associated with ilmenite, magnetite, and apatite, and often forms aggregates with those minerals. It occurs as inclusions in the outer portions of hornblende and feldspar phenocrysts, and itself contains inclusions of apatite and zircon.

Phenocryst crystallization in the Little Chief Granite (McDowell, 1978) took place in the temperature range 700–750°C, at load pressures near 1.5 kbar, and oxygen fugacities near 10⁻¹⁵ atm. Groundmass

Table 1. Microprobe analyses (weight percent) of chevkinite from the Little Chief Granite

	Groundmass		Avg.	Microphenocrysts				Avg.
	63-1	63-2	Gnd.	77	146-1	146-2	263	Microph.
SiO ₂	19.67	19.81	19.74	20.50	20.26	20.33	19.90	20.25
Al ₂ O ₃	2.10	2.00	2.05	2.92	2.85	2.79	2.83	2.85
TiO ₂	17.55	16.78	17.16	18.80	18.06	18.76	18.03	18.41
ThO ₂	0.92	1.02	0.97	0.49	1.44	0.79	1.59	1.08
UO ₂	0.08	0.19	0.14	0.00	0.02	0.13	0.01	0.04
ZrO ₂	0.56	0.26	0.41	1.02	0.29	1.17	0.66	0.79
FeO*	8.93	9.75	9.34	7.09	7.23	7.27	7.19	7.20
MgO	0.51	0.53	0.52	0.92	1.01	0.85	1.00	0.95
NiO	-	-	-	0.04	0.04	-	-	0.04
MnO	0.81	1.06	0.93	0.25	0.20	0.11	0.08	0.16
CaO	4.49	4.04	4.27	5.78	5.08	5.67	5.11	5.41
SrO	0.04	0.01	0.03	0.04	0.05	0.06	0.06	0.05
BaO	0.32	0.07	0.19	0.14	nd	0.17	nd	0.08
PbO	0.04	0.15	0.10	0.00	nd	nd	0.08	0.02
ZnO	0.02	-	0.02	-	nd	-	-	-
Na ₂ O	nd	nd	nd	nd	nd	nd	nd	nd
K ₂ O	0.02	nd	0.01	nd	nd	nd	nd	nd
V ₂ O ₃	nd	nd	nd	nd	nd	nd	nd	nd
Cr ₂ O ₃	nd	0.02	0.01	0.03	nd	0.07	0.03	0.03
Y ₂ O ₃	0.16	0.05	0.11	0.05	0.23	0.24	0.16	0.17
La ₂ O ₃	12.36	17.89	15.12	10.74	10.96	11.44	10.79	10.98
Ce ₂ O ₃	19.16	17.32	18.24	17.30	18.06	17.85	18.01	17.81
Pr ₂ O ₃	0.97	0.78	0.88	1.56	1.28	2.03	1.34	1.55
Nd ₂ O ₃	5.72	2.91	4.32	5.87	5.65	5.49	5.64	5.66
Sm ₂ O ₃	0.84	0.36	0.60	0.93	0.77	0.88	0.94	0.88
Gd ₂ O ₃	0.36	nd	0.18	0.75	0.20	0.24	0.53	0.43
Dy ₂ O ₃	0.13	0.31	0.22	0.20	0.09	0.00	0.23	0.13
Yb ₂ O ₃	nd	nd	nd	0.08	nd	nd	0.18	0.07
P ₂ O ₅	0.03	0.01	0.02	0.06	0.08	0.05	0.07	0.07
Nb ₂ O ₅	0.14	0.32	0.23	0.07	0.13	0.02	0.12	0.09
Ta ₂ O ₅	0.11	nd	0.06	0.05	0.09	0.06	0.03	0.06
F	0.28	0.19	0.24	0.22	0.20	0.21	0.26	0.22
Cl	-	-	-	0.03	0.04	0.01	-	0.03
S	-	-	-	nd	nd	-	-	-
Σ	96.36	95.84	96.10	95.94	94.32	96.68	94.86	95.45

*Total iron nd = not detected - = not analyzed for

crystallization took place under similar temperatures but at load pressures near 0.5 kbar under water-saturated conditions. Four of the analyzed chevkinite grains (77, 146-1, 146-2, 263) are distinctly larger than the surrounding groundmass minerals, and grain 146-2 is included in phenocrystic hornblende. This suggests that chevkinite started to crystallize late in the period of phenocryst crystallization when the magma was less than 50 percent crystalline. The crystallization range of chevkinite is similar to that of apatite. Grains 63-1 and 63-2 are significantly smaller than the surrounding groundmass minerals and may represent crystals which nucleated during groundmass crystallization.

Analytical procedures

The chemical analyses listed in Table 1 were made by the writer, using a M.A.C. electron microprobe at California Institute of Technology during September, 1975. All corrections were made using a rare-earth-element (REE) analysis program developed by M. Johnson, A. A. Chodos and A. L. Albee during 1975 for microprobes with a 38.5 degree takeoff angle. The procedure follows that of Bence and Albee (1968) and Albee and Ray (1970), and is essentially the same as that used by Amli and Griffin (1975), using a variety of minerals and glasses, both synthetic and natural, as standards. As a guide to the detection limits of these analyses, weight percent oxide values below 0.05 percent are unreliable, while values between 0.05 and 0.10 percent are questionable but indicate that the element is definitely pres-

Table 2. Structural formulas (atomic proportions) for chevkinite from the Little Chief Granite, calculated to Σ cations = 13

	Groundmass		Avg.	Microphenocrysts				Avg.
	63-1	63-2	Gnd.	77	146-1	146-2	263	Microph.
(A)								
Ca	0.970	0.878	0.924	1.215	1.094	1.192	1.104	1.151
Sr	0.005	0.001	0.003	0.004	0.006	0.007	0.007	0.006
Ba	0.025	0.005	0.015	0.010	nd	0.013	nd	0.006
Pb	0.002	0.008	0.005	nd	nd	nd	0.004	0.001
Th	0.041	0.046	0.043	0.021	0.064	0.034	0.071	0.048
U	0.004	0.009	0.007	nd	0.001	0.006	0.001	0.002
(B)								
La	0.920	1.338	1.129	0.777	0.813	0.829	0.802	0.805
Ce	1.416	1.286	1.351	1.243	1.330	1.284	1.329	1.297
Pr	0.071	0.058	0.065	0.112	0.094	0.145	0.098	0.112
Nd	0.413	0.211	0.312	0.411	0.406	0.385	0.406	0.402
Sm	0.059	0.025	0.042	0.062	0.054	0.059	0.065	0.060
Gd	0.024	nd	0.012	0.048	0.013	0.016	0.036	0.028
Dy	0.009	0.020	0.015	0.012	0.006	nd	0.015	0.008
Yb	nd	nd	nd	0.002	nd	nd	0.006	0.002
Y	0.017	0.006	0.012	0.006	0.025	0.025	0.018	0.018
(C)								
ΣA	3.976	3.891	3.868	3.923	3.906	3.995	3.962	3.946
(D)								
Fe+2	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
(E)								
Ti	0.665	0.560	0.612	0.776	0.733	0.771	0.734	0.754
Al	0.500	0.477	0.489	0.675	0.677	0.646	0.674	0.668
Zr	0.055	0.026	0.040	0.097	0.028	0.112	0.065	0.076
Nb	0.013	0.029	0.021	0.006	0.011	0.002	0.011	0.007
Ta	0.006	nd	0.003	0.003	0.005	0.003	0.001	0.003
P	0.005	0.022	0.009	0.010	0.013	0.009	0.012	0.011
(F)								
Fe+3	0.508	0.654	0.581	0.165	0.216	0.193	0.212	0.196
Ni	-	-	-	0.006	0.006	-	-	0.006
Zn	0.003	-	0.003	-	-	-	-	-
Mn	0.139	0.182	0.161	0.041	0.035	0.018	0.014	0.027
Cr	nd	nd	-	nd	nd	0.011	0.004	0.004
Mg	0.155	0.161	0.158	0.269	0.302	0.249	0.300	0.280
(G)								
ΣC	2.049	2.111	2.080	2.048	2.026	2.014	2.027	2.029
(H)								
Ti	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000
Si	3.971	4.015	3.993	4.023	4.074	3.991	4.011	4.025
F	0.179	0.122	0.150	0.137	0.127	0.130	0.166	0.140
Cl	-	-	-	0.010	0.014	0.003	-	0.009

nd = not detected - = not analysed for

ent, with the added stipulation that the heavier the element, the lower the detection limit.

Composition and structural chemistry

The oxide totals of the analyzed chevkinites are in the range 94.3 to 96.7 weight percent. An oxide-by-oxide comparison of the microprobe analyses with chevkinite wet-chemical analyses tabulated by Vlasov (1964) and microprobe analyses by Segalstad and Larsen (1978) indicates excellent agreement for all oxides, allowing for some substitution of Ca for Ce in the Ca-rich Little Chief chevkinites. However, most chevkinites contain approximately 1.5 weight percent of the heavier REE (Dy–Lu and Y), while very few of these elements (only Dy, Yb, and Y) were analyzed for in the present investigation. M. Johnson (unpublished microprobe data) has found approximately 1.2 weight percent $Tb_2O_3 + Ho_2O_3 + Lu_2O_3 + Er_2O_3$ in chevkinite from Pikes Peak batholith. Semi-quantitative examination of the Little Chief chevkinite with an energy-dispersive system option on the microprobe suggests that minor quantities of hafnium might be present. Thus approximately 1.5 percent of various minor elements might be missing from the analyses in Table 1. There is also uncertainty as to the valence states of some of the elements. Iron, calculated as FeO in Table 1, is most certainly present in part in the trivalent state, while Ce may be partly in the tetravalent state.

The structural chemistry of perrierite was originally investigated by Bonatti (1959) and Gottardi (1960), and further refined by Bonatti and Gottardi (1966) and by Calvo and Faggiani (1974). An idealized structural formula is:



where $A = REE^{3+}, Ca^{2+}, Th$; $B = Fe^{2+}, Mg^{2+}, Mn^{2+}$; $C = Ti^{4+}, Fe^{3+}, Mg^{2+}, Al^{3+}, Fe^{3+}$; $D = Ti^{4+}$, and rare Mg^{2+}, Fe^{2+} ; $Z = Al^{3+}, Si^{4+}$.

The structure may be briefly described as consisting of two distinct layers parallel to (001). One layer is made up of two types of octahedral chains (C,D) lying side by side and elongate parallel to b , while the other layer is made up of octahedral chains (B), also elongate parallel to b , which are cross-linked by Si_2O_7 units to form a ladder-like array. The layers are joined by sharing one tetrahedron edge of each Si_2O_7 unit with an octahedron edge in the D chain. In the "interlayer" cavities that remain, two distinct A sites (A_1 and A_2) of irregular coordination occur.

Structural formulas for the chevkinite from the

Little Chief Granite are listed in Table 2. Following Gottardi (1960), all formulas have been calculated on the basis of 13 cations.

It is clear from the table that the tetrahedral (Z) site is filled with Si, and Al^{IV} substitution is negligible. Again following Gottardi, 2,000 cations of Ti have been assigned to the D site, with the remainder placed in the C site. The structural analysis of Calvo and Faggiani (1974) suggests that the D site, which is strongly distorted and approaching five-fold coordination, is approximately 80–90 percent Ti.

The electron microprobe yields a total Fe analysis only, and this has been reported in Table 1 as FeO. In two analyses reported by Gottardi, essentially all the Fe^{2+} is accommodated in the B site, a straight chain of regular octahedra. The metal–oxygen distances obtained by Gottardi (1960) and by Calvo and Faggiani (1974) for this site are consistent with its being occupied by Fe^{2+}, Mg^{2+} or Mn^{2+} , but not Ca^{2+} as was originally suggested by Bonatti and Gottardi (1954). It is not necessary to assign Ca^{2+} to the B site in most analyses reported in the literature, although in the recent analyses of Segalstad and Larsen (1978) significant amounts of Ca^{2+} were assigned to the B site, due to the low Al content of the analyzed grains. In Table 2, the B site has been filled with iron as Fe^{2+} , and the remaining iron has been assigned to the C site as Fe^{3+} . The $Fe^{3+}/(Fe^{2+}+Fe^{3+})$ ratios thus obtained (0.14–0.40) are reasonably consistent with those reported in the literature, which usually range from 0.1 to 0.5 (see Vlasov, 1964; Jaffe *et al.*, 1956; and Kauffman and Jaffe, 1946, for compilations of chevkinite/perrierite analyses by wet-chemical methods). The total positive charge of the average chevkinite in Table 2 is approximately +43.4, which is sufficiently close to the ideal negative charge of –44 to give confidence in the calculated ferrous and ferric iron contents.

Gottardi (1960) originally suggested that the two A sites had ten-fold coordination. His actual measured metal–oxygen distances for the A_1 site in natural perrierite indicate, however, that this site is strongly collapsed and has seven metal–oxygen distances in the range 2.36–2.48 Å and three at greater than 2.9 Å. The more detailed structural analysis by Calvo and Faggiani (1974), on synthetic and compositionally simple perrierite and chevkinite, suggests that the A_1 site has eight- to nine-fold coordination and the A_2 site has nine-fold coordination. Thus, in natural chevkinites there may be two REE sites with slightly differing coordination.

Table 3. Summary of rare-earth oxide distribution in chevkinite and perrierite analyses; rare-earth oxide sum = 100 percent by weight

	La	Ce	Pr	Nd	Sm	Gd	Tb	Dy	Ho	Er	Yb	Lu
Little Chief Granite; microprobe analysis, S. D. McDowell (This paper)												
63-1	31.0	49.0	2.5	14.5	2.1	0.9		0.3			nd	
63-2	45.2	43.8	2.0	7.4	0.9	nd		0.8			nd	
77	28.8	46.3	4.2	15.7	2.5	2.0		0.5			0.2	
146-1	29.6	48.8	3.5	15.3	2.1	0.5		0.2			nd	
146-2	30.2	47.1	5.4	14.5	2.3	0.6		nd			nd	
263	28.7	47.8	3.6	15.0	2.5	1.4		0.6			0.5	
Pikes Peak Quartz Syenite; microprobe analysis, M. Johnson (unpublished data) (Barker and others, 1975)												
P551	28.7	47.8	3.3	15.9	1.0	nd	0.6	nd	0.4	0.1	0.4	1.7
Oslo Region, Norway, syenite pegmatite; microprobe analyses (Segalstad and Larsen, 1978)												
A	49.7	41.1	4.9	3.2	nd	nd	0.4	0.3	0.1	nd	0.1	nd
B	40.4	46.3	5.0	6.5	nd	nd	0.4	nd	0.2	nd	0.3	nd
C	47.4	41.2	4.9	5.1	nd	nd	0.3	nd	tr	nd	0.2	nd
D	49.4	39.9	5.1	4.8	nd	nd	0.3	nd	tr	nd	0.1	nd
Other chevkinite/perrierite analyses tabulated by Vlasov (1964, p. 31), wet chemical analyses												
Q Syen.	28	50	3.9	14	1.7	1.2						
Ab-Ne Syen.	39	47	3.3	10	0.5							
Alk. Syen.	27	55		18								
Alk. Q. Syen.	29	49	4.9	15	1.8							
Granite Peg.	27	52		18	1.8	1.1		1.2				
Granite Peg.	21	44	6	23	6.9							
Alk. Syen. Peg.	34	51	3.8	11	0.2							
Alk. Grn. Peg.	20	43	5.5	21	4.9	3.2		2.3				

nd = not detected tr = trace

REE distribution

The distribution of REE in chevkinite has been summarized in Table 3 and plotted in Figure 1. The agreement between the older wet-chemical data tab-

ulated by Vlasov (1964) and the microprobe analyses reported in this paper is excellent. A strong preference for the even-numbered light (Ce-group) REE is indicated, although the recent analyses by Segalstad

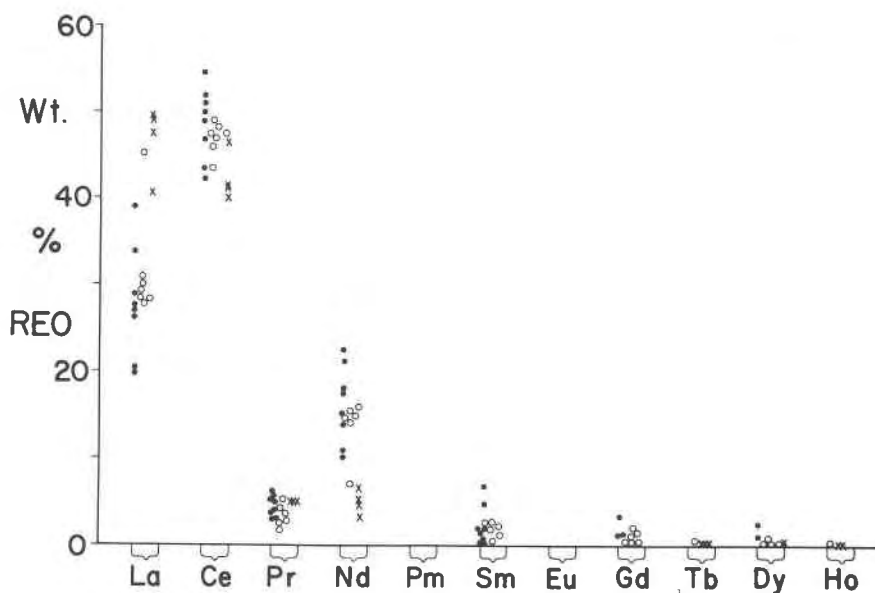


Fig. 1. Distribution of REE in chevkinite/perrierite. Large open circles: microprobe analyses of grains from the Little Chief Granite and Pikes Peak quartz syenite (latter by M. Johnson, unpublished data). Small dots: wet-chemical analyses tabulated in Vlasov, 1964; crosses: microprobe analyses of grains from syenite pegmatite (Segalstad and Larsen, 1978). Weight percent rare-earth oxides = 100 percent.

and Larsen (1978) and the small groundmass grain (63-2) from the Little Chief Granite show relative enrichment of La, depletion of heavier REE, and a lesser preference for the even-numbered REE.

In Tables 1 and 2, the chevkinite analyses have been divided into ground-mass (average 1) and microphenocryst (average 2) grains. Relative to the earlier microphenocryst chevkinite, the later groundmass chevkinite is depleted in Ca, Al, Ti, and Mg and enriched in Mn and possibly Fe^{3+} . All these trends are consistent with those observed during the differentiation of granitic magma. With reference to the minor elements, the groundmass chevkinite is enriched in La and Nb, and depleted in Pr. Groundmass grain 63-2, the smallest grain analyzed, is strongly enriched in La and Nb, but depleted in Pr, Sm, Nd, and possibly Y and Gd. No changes in Fe^{2+} could be discerned, due to the artificial filling of the B site with iron as Fe^{2+} and assignment of the remaining iron to the C site as Fe^{3+} .

In comparison with chevkinite from other magmatic environments (Fig. 2, after Fleischer, 1965), the chevkinite from the Little Chief Granite is most similar to that from alkali quartz syenite. The general trend for chevkinite is similar to that of commonly occurring REE-bearing minerals such as monazite, allanite, epidote, and apatite (Fleischer, 1965). As with these other minerals, in chevkinite there is a gross enrichment in the light REE from granite pegmatite through syenite or quartz syenite to feldspathoidal syenite or syenite pegmatite. Note again the extreme enrichment of the smallest groundmass chevkinite grain in the light REE. The magma chamber of the Little Chief Granite (McDowell, 1978) is almost identical to that proposed by Lipman (1971) as a source magma chamber for the voluminous, compositionally-zoned ash flow tuffs of the Great Basin area. Thus the chevkinite from the Little Chief Granite may be compositionally similar to much of the chevkinite examined by Izett and Wilcox (1968) from volcanic ash deposits.

REE substitutions

The substitution of REE for Ca in high-coordination sites has been well documented in many minerals, and is also verified for the A sites in the chevkinite of the Little Chief Granite (Fig. 3A). However, if the elemental variations within the A sites are examined in more detail, several patterns emerge. With the exception of the La-enriched groundmass grain (solid triangle in Fig. 3A-G), Ca varies inversely

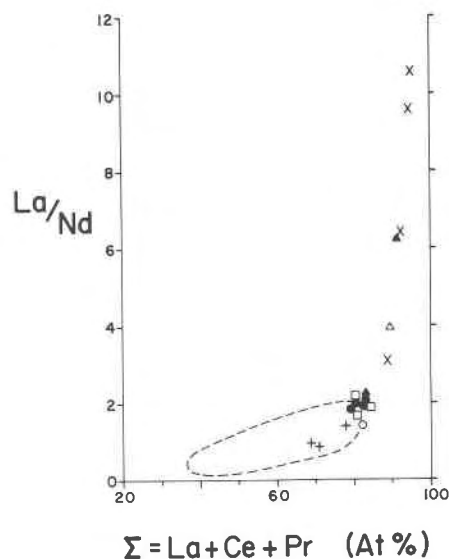


Fig. 2. Compositional variations of REE in chevkinites from various igneous occurrences. Solid circles (microphenocrysts) and solid triangle (groundmass) from Little Chief Granite. Other data from Vlasov (1964) and Segalstad and Larsen (1978). + = pegmatite in alkali granite; X: pegmatite in alkali syenite; open square: alkali quartz syenite; open triangle: albite-nepheline syenite; open circle: alkali syenite. Dashed line encloses field of granitic bulk compositions (after Fleischer, 1965).

with La (Fig. 3B) and Ce (Fig. 3C), directly with Pr (Fig. 3D), and not at all with the heavier REE Nd (Fig. 3E) and Sm (Fig. 3F). The La/Ce ratio remains approximately constant (Fig. 3H). The slopes of the curves suggest that the actual substitution within the A sites is approximately

$$0.95\text{Ca} + 0.05\text{Pr} = 0.5\text{La} + 0.5\text{Ce}$$

The efficacy of REE-for-Ca substitution decreases markedly with increasing atomic number, or decreasing effective ionic radius through the lanthanide contraction. The eight-fold crystal radii for the trivalent lanthanides (Shannon and Prewitt, 1969) in angstroms are La (1.32), Ce (1.28), Pr (1.28), Nd (1.26) and Sm (1.23). Divalent Ca has 1.26 Å radius in eight-fold coordination. Whatever the actual coordination and effective radius of the REE or Ca in chevkinite, it is clear that Ca here substitutes only for the lighter and larger La and Ce. The distribution of Ca in the two A sites is not known. If there are two A sites with slightly different coordination, the larger REE would prefer the higher-coordinated site (A_2). The substitutionally-inert heavier and smaller REE presumably occupy the lower-coordinated site (A_1), and in apparently constant amounts. Calcium, since it proxies for the larger REE, presumably substitutes

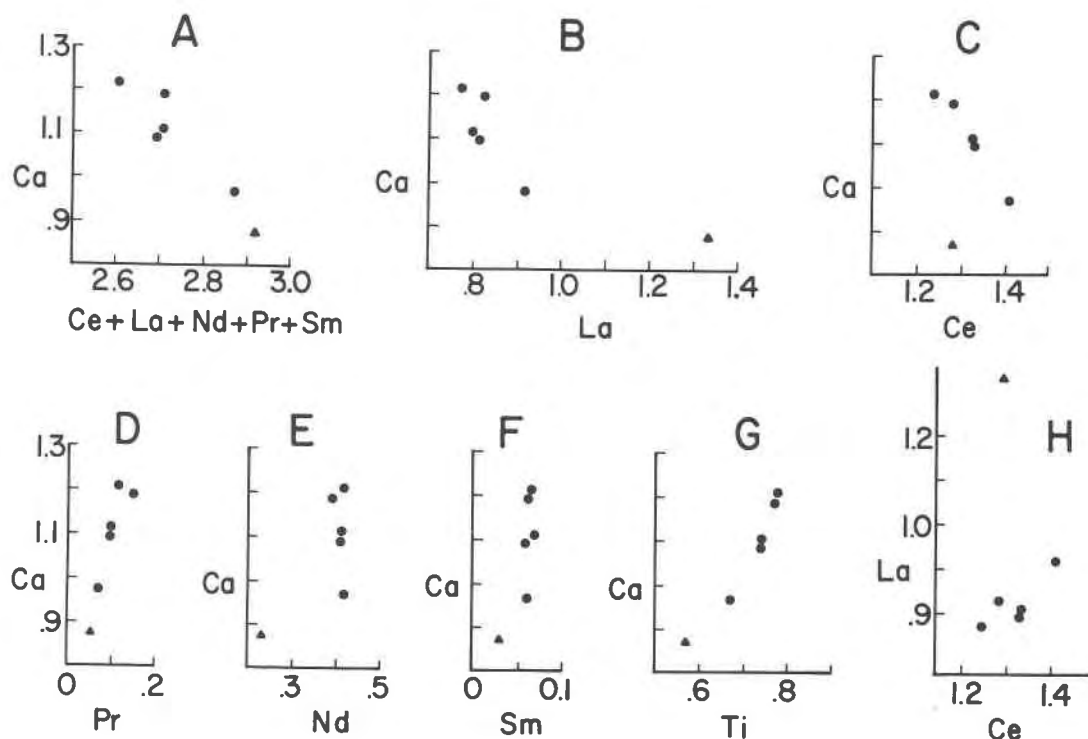


Fig. 3. Elemental substitutions in chevkinite from the Little Chief Granite, in molecular proportions. See text for detailed explanation.

into the A_2 site. Thus it is suggested that the Ca (+Pr?) for La and Ce substitution occurs predominantly in the A_2 site, with the excess cations residing in constant amounts in the A_1 site. The sum $Ca+Pr+La$ is near 2.0 for most of the chevkinite structural formulas, suggesting that these three cations dominate the A_2 site. Thus only the small amounts of Ce necessary for substitution with Ca occur in the A_2 site, while the bulk of the Ce is found in the A_1 site.

The similar crystal radii for Pr and Ce would suggest that they should behave in an almost identical manner, yet they clearly do not. Note that these two elements do not preserve their relative differences in radii with increase in coordination number from six to eight (Shannon and Prewitt, 1969, Fig. 2C), and are exceptional in that respect. The difference in their behavior in chevkinite, assuming that they both are in the trivalent state, strongly indicates that their effective ionic radii are distinctly different, and throws doubt on the eight-fold radii of Ce or Pr as determined by Shannon and Prewitt (1969) using radii vs. cell volume data.

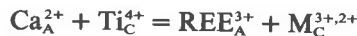
The substitution scheme in the La-enriched groundmass grain (63-2, solid triangle, Fig. 3) is dis-

tinctly different from that of any of the other chevkinite grains. While the overall REE for Ca + Pr substitution is continuing to operate in this grain (Fig. 3A), an additional substitution of approximately

$$La \approx 0.10 Sm + 0.45 Ce + 0.45 Nd$$

has operated in the A sites. The high concentration of La in this grain requires substitution to take place in both A sites, forcing Nd and Sm in A_1 to be involved in the exchange.

In order to maintain charge balance in the structure, the generalized substitution



occurs in many Ca-REE minerals. That this substitution also occurs in the chevkinite of the Little Chief Granite is indicated in Figure 3G by the direct relationship between Ca and Ti. Plotting of the chevkinite compositions of Table 2 indicates many regular compositional variations within the C site [Ti varies inversely with Mn and (?) Fe^{3+} , directly with Al^{3+} and Mg^{2+}]. However, because of the uncertainties in the valence states of many of the cations and of the actual distribution of Fe, Mn, and Mg be-

tween the B and C sites, no more exact correlations are warranted at this time.

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