Transition metal rutiles and titanates from the Deadhorse Creek diatreme complex, northwestern Ontario, Canada

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Abstract

The main mineralized zone of the West subcomplex of the Deadhorse Creek diatreme complex, northwestern Ontario possesses an exotic mineralogy. Mineralization involves the first-order transition metals (principally Sc, Ti, V, Cr, Mn, and Fe), the second-order transition metals (principally Zr and Nb), the lanthanides, the actinides (principally Th and U), Be, Ba and Sr. Minerals include phenacite, zircon, uraninite, thorite, monazite-(Ce), xenotime-(Y), barylite, thortveitiite, hollandite, tyuyamunite, a number of unknown and as yet undescribed species, and those minerals more specifically described in this paper. These are Cr-V-Nb rutile, V-rich members of the crichtonite series, and a titanate of general composition $(Cr,V^{3+},Fe^{3+})_2(Ti,V^{4+},Nb)O_5$.

Similar to rutiles reported from alkaline rocks in general, the Deadhorse Creek rutiles are enriched in Cr and Nb, with the latter element attaining some of the highest recorded values. V contents are also unusually high and this element is thought to exist in both the tri- and tetravalent states.

The V-rich crichtonites are essentially vanadium analogues of crichtonite and lindsleyite. *M*-site Nb and V are the highest yet recorded. *A*-site cations are dominated by Ba and Sr with an inverse relationship together with lesser but significant amounts of Ca and Pb. Although not of upper mantle origin, they plot in the upper mantle LIMA quadrant of TiO_2 *vs.* $FeO + Fe_2O_3 + MgO$ (Haggerty, 1991).

$(Cr,V^{3+},Fe^{3+})_2(Ti,V^{4+},Nb)O_5$ is thought to be a member of an homologous series of type $(Cr,V^{3+},Fe^{3+})_{2p}(Ti,V^{4+},Nb)_{2p+q}O_{5p+4q}$ with $p = 1$ and $q = 0$ and a V_3O_5-type structure. Whether this structure is ultimately derived from that of rutile or from α-PbO_2 by crystallographic shear is not known.

The rutiles and titanates discussed here are thought to have formed from hydrous alkaline solutions which have scavenged the necessary elements from a mafic/ultramafic source. The origin of the solutions is not specifically known although the magmatic activity associated with the spatially related Coldwell alkaline complex and/or the Prairie Lake complex are both potential sources. Both complexes contain the necessary mafic/ultramafic rocks.

KEYWORDS: rutile, titanates, diatreme, Ontario, Canada.

Introduction

THE Deadhorse Creek diatreme complex occurs approximately 25 km west of Marathon, northwestern Ontario, 20 km south of the Prairie Lake carbonatite complex and slightly to the west of the Coldwell alkaline complex. First described by Mitchell and Platt (1977), the diatreme complex is one of a number in the general region outlined by Sage (1982). The complex consists of an elongated zone of brecciated rock, approximately 1600 by 400 m in area, which transects the Neoarchaean Schreiber – White River greenstone belt of the Wawa subprovince. Sage (1982) considers the diatreme complex to be fault-controlled, and to represent the altered and brecciated top of an unexposed carbonatite intrusion intruded during the Neohelikian Keweenawan magmatic event. This latter assumption has not been substantiated.

A wide size-range of angular to sub-rounded clasts, predominantly of local greenstone lithologies, are embedded in a finely ground matrix in which secondary amphibole and carbonate are developed. Reddening and bleaching of the clasts indicate syn-

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and post-depositional alteration processes and late-stage scapolite (metasomatic?) is occasionally observed. Sage (1982) also notes the proximity of diabase, biotite syenite and carbonate-rich lamprophyre dykes.

The rutiles and titanates described here come from the West subcomplex (Sage, 1982), and more particularly from a west–northwest trending mineralized zone which extends some 140 by 30 m (Smyk *et al.*, 1989, 1993). This zone transects the heterolithic diatreme breccia of the subcomplex as well as an associated carbonatite dyke. Smyk *et al.* (1989, 1993) have briefly noted the occurrence of phenacite, an unknown calcium zirconium silicate, zircon, uraninite, thorite, monazite-(Ce), and xenotime-(Y) in the main mineralized zone.

We are in general agreement with these observations. However, our SEM-based studies indicate a more complex mineralization involving first-order transition elements (principally Sc, Ti, V, Cr, Mn and Fe), second-order transition elements (principally Zr and Nb), lanthanides, and actinides (principally Th and U). In addition to the minerals mentioned above, we have also identified barylite ($BaBe_2Si_2O_7$), thortveitite ($Sc_2Si_2O_7$), hollandite, tyuyamunite ($Ca(UO_2)V_2O_8{\cdot}5{-}8H_2O$), an unknown Th vanado-silicate of probable formula $Th(V^{5+},Si)O_4OH$. With the exception of the Th vanado-silicate, these minerals are comparatively rare when compared with those described by Smyk *et al.* (1993).

The transition metal rutiles and titanates are believed to have formed from metasomatizing solutions which have used either contemporary hydraulic fractures or pre-existing regional fracture patterns. The exact nature of these fluids, particularly with respect to their CO_2-H_2O activities, oxygen fugacity and pH, is as yet unknown. However, similarities to Ti-rich phases found in alkali metasomatized mantle materials (Haggerty, 1991), and the close proximity of contemporary alkaline intrusions, strongly infers an alkaline character to these fluids.

Analytical methods

The phases discussed below were principally analysed by standard energy-dispersive methods using a Hitachi 570 SEM and a Link Isis analytical system attached with a Super ATW thin window detector of resolution 133 eV. Analyses were obtained with an accelerating voltage of 20 kV at a working distance of 28 mm using metal, oxide and mineral standards. Spectral reduction was performed using the Link Isis SEM QUANT software with full ZAF correction.

The authors were aware of possible analytical errors due to energy overlaps amongst the transition metals themselves and Ba. Consequently, standard transition metal oxides and metals were analysed as unknowns to determine the severity of the problem. Observation of spurious elements occurred but these were insignificant (generally < 0.3 wt.%) compared with the observed values in the minerals under discussion. Where possible, the energy dispersive analyses were confirmed using wavelength electron microprobes at the University of Manitoba, Purdue University, and The Natural History Museum, London.

The small size of many of the analysed minerals gave concern to possible elemental contamination from adjacent grains. Care was taken to appraise this by determining the nature of the surrounding phases. If the authors felt that such contamination was significant (i.e. >2%), analyses were rejected. For the remaining analyses, the contaminating elements, if present, are not reported, and for comparative purposes, the analyses have been normalized to 100%.

Ti-rich phases

Table 1 indicates the compositional ranges of three Ti-rich phases which occur as widely-scattered small (generally less than 50 μm) anhedral-to-subhedral prismatic-to-equant grains. No textural evidence exists for the presence of precursor phases. Figures 1*a* to 1*d* delineate the compositional fields of these phases which we have tentatively identified as Cr-V-Nb rutile, V-rich crichtonite ($AM_{21}O_{38}$), and an unnamed phase approaching the compositional formula $(Cr,V^{3+},Fe^{3+})_2(Ti,V^{4+},Nb)O_5$.

Cr-V-Nb rutile

Of the three Ti-rich phases, rutile is the most abundant although this phase is still comparatively rare. Generally subhedral, it occurs as very small scattered grains with high average atomic number in back-scattered images. In these respects, it is similar to the other Ti-rich phases discussed here. The compositional range is shown in Table 1, with representative analyses given in Table 2. Variations of V, Cr, Fe, and Nb with reference to TiO_2 are shown in Fig. 1*a*–*d*.

The Deadhorse Creek rutiles are enriched in Cr and Nb and in this respect, they are similar to rutiles reported from alkaline rocks in general (Fig. 2). The Nb contents may be considerable and attain some of the highest reported concentrations (Tables 1 and 2). Distinct negative correlations exist between Ti and Cr, and Ti and Nb (Fig. 1*b* and *d*). The Deadhorse Creek rutiles are unusual in their enrichment of V with concentrations reaching 14.1 wt.% V_2O_3 (Tables 1 and 2). This V-enrichment is in keeping

TABLE 1. Compositional ranges of Ti-rich minerals

	Rutile	Crichtonite	M_3O_5 (CS)
TiO_2	42.64–81.98	51.61–58.14	26.29–33.88
SiO_2	na	0.03–0.41*	na
ZrO_2	na	0.03–0.35*	na
Nb_2O_5	6.85–32.13	1.43–6.99	3.67–10.21
Cr_2O_3	1.65–9.59	0.96–4.34	19.88–25.43
V_2O_3	4.76–14.11	12.05–16.43	23.17–29.80
Sc_2O_3]	0.26–0.61*	0.26–1.93	0.64–1.02
Al_2O_3	na	na	0.21–0.59
FeO_T	0.36–3.10*	12.52–13.99	10.96–12.30
MnO	na	0.52–1.73	na
BaO	na	1.63–4.35	na
SrO	0.19–1.37*	1.66–3.64	0.33–1.04
PbO	0.49–1.01*	0.97–2.75	0.29–1.01*
CaO	0.23–2.79*	0.22–0.55	0.20–0.23

* Incomplete data in range; na = not analysed. CS: Crystallographic shear-based structures. FeO_T Total Fe calculated as FeO.

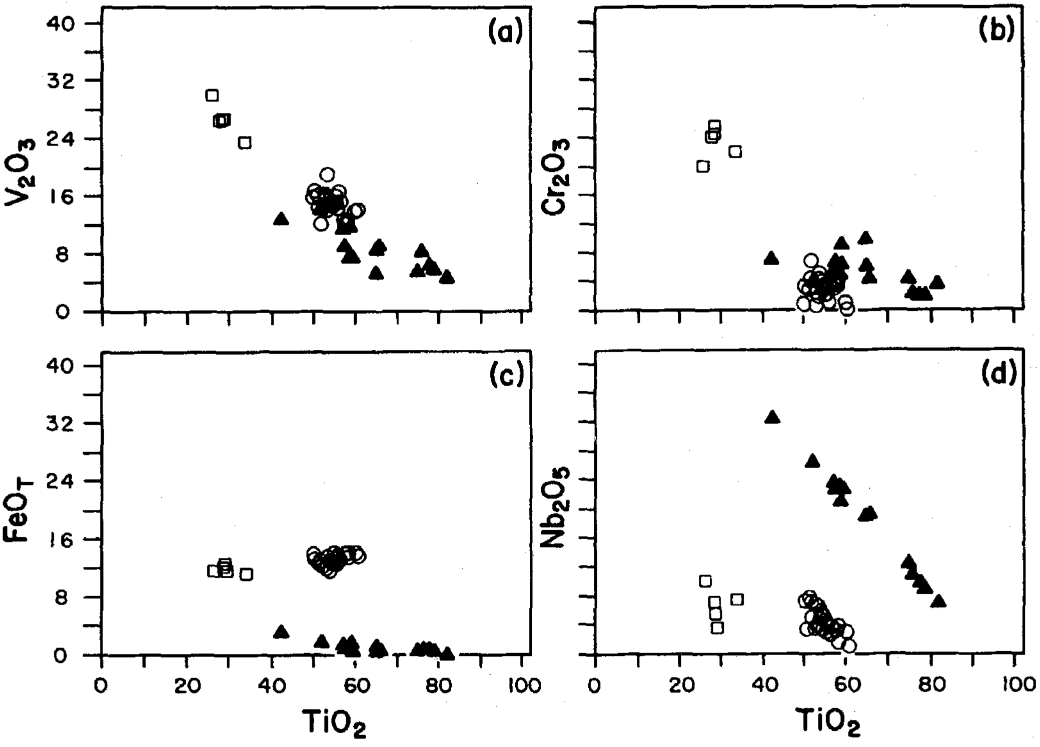

FIG. 1*a*–*d*. Variations of wt.% V_2O_3 (*a*) Cr_2O_3 (*b*) FeO_T (*c*) Nb_2O_5 (*d*) with respect to wt.% TiO_2 for Cr-V-N rutile (closed triangles), V-rich crichtonite (open circles), and $(Cr,V^{3+},Fe^{3+})_2(Ti,V^{4+},Nb)O_5$ (open squares).

TABLE 2. Representative analyses of Cr-V-Nb rutiles

Analysis Sample	1 C3025	2 C3025	3 C3025	4 C3024	5 C3024	6 C3026
TiO_2	52.17	57.05	58.60	59.26	65.05	75.84
Nb_2O_5	26.30	23.41	22.86	22.55	18.90	12.40
Cr_2O_3	3.43	4.78	4.50	8.76	9.59	4.25
V_2O_3	14.09	11.39	11.68	7.47	5.15	5.52
PbO	na	na	na	1.01	0.48	0.98
Sc_2O_3	0.33	0.56	0.24	0.45	0.34	0.38
Fe_2O_3*	1.92	1.38	1.40	0.50	0.49	0.40
CaO	0.41	0.42	0.11	nd	nd	0.23
SrO	1.35	1.01	0.61	na	na	na
Total**	100.0	100.0	100.0	100.0	100.0	100.0
Structural formulae calculated on the basis of 2 oxygens						
Ti	0.590	0.636	0.649	0.658	0.710	0.808
Nb	0.179	0.157	0.152	0.151	0.124	0.079
Cr	0.041	0.056	0.052	0.102	0.110	0.048
V	0.170	0.135	0.138	0.083	0.060	0.063
Pb	–	–	–	0.004	0.002	0.004
Sc	0.004	0.007	0.003	0.006	0.004	0.005
Fe^{3+}	0.022	0.015	0.016	0.006	0.005	0.004
Ca	0.007	0.007	0.002	0.000	0.000	0.004
Sr	0.012	0.009	0.005	–	–	–
Cations	1.025	1.022	1.017	1.015	1.015	1.015

* Total Fe calculated as Fe_2O_3.
** Analyses recalculated to 100%.
nd = not detected, na = not analysed.

with the enhanced V contents observed in the other Ti-rich phases discussed here. As with Cr and Nb, V shows an inverse relationship to Ti (Fig. 1*a*). Small amounts of Pb, Sc, Fe and Ca are also detectable (Table 1). Based on a rutile structural formula of TiO_2, total replacement of Ti varies between 18 and 53 at.% of which V+Cr+Nb generally accounts for a minimum of 80%.

The fundamental chemical unknown of these unusual rutiles is the valency states of the transition metals. Traditionally, Cr and Nb are considered to exist in the tri- and pentavalent states respectively. V is more of an enigma although in the charge-coupled substitution $M^{3+} + M^{5+} = 2Ti^{4+}$, V is commonly considered as a pentavalent cation (Waychunas, 1991). For descriptive purposes, V is reported as V^{3+} in Tables 1 and 2. However, we present arguments suggesting that at least some V is in the tetravalent state.

Compositional and charge difficulties arise when considering the standard charge-coupled substitutions generally ascribed to Ti replacement in rutile. For the coupled substitution $M^{3+} + M^{5+} = 2Ti^{4+}$ (with M^{5+} =

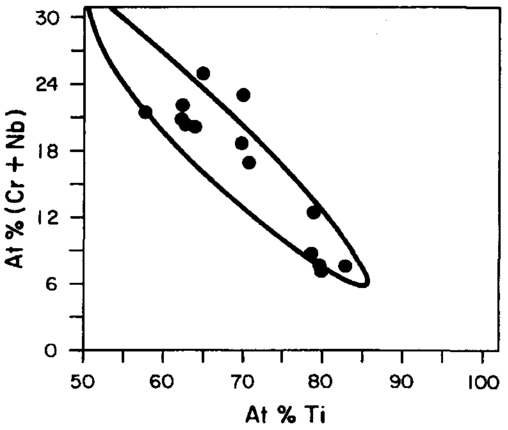

FIG. 2. At.% (Cr+Nb) *vs.* at.% Ti for Cr-V-Nb rutiles. Enclosed area represents the general field of alkaline rock rutiles (Haggerty, 1991).

Nb^{5+} + V^{5+}), the considerable excess of V and Nb cations over the remaining potential trivalent cations (i.e. Fe, Cr and Sc) in the Deadhorse Creek rutiles (Table 2) generates a large positive charge imbalance on the rutile lattice. The relatively small proportions of divalent cations would not counteract this effect by the coupled substitution $2M^{5+} + M^{2+} = 3Ti^{4+}$.

Alternatively, considering V as a trivalent cation produces a general excess of trivalent cations compared with pentavalent cations (Table 2) and a net negative charge imbalance on the rutile lattice. Treating V as a multivalent cation alleviates the situation but there seems no logic to suggest that these valency states are tri- and pentavalent particularly as V^{4+} has a similar ionic radius to Ti^{4+} (58pm *vs.* 60.5pm), and possesses a rutile-like structure as the oxide VO_2 which occurs naturally as paramontroseite. Consequently, we suggest that V in the Deadhorse Creek rutiles exists in both the tri- and tetravalent states.

Additional support for this argument is seen in Fig. 3 which projects the rutile compositions onto the Nb-Cr-V (at.%) compositional triangle. All but four of the observed compositions are constrained by the compositional field $CrNb(O_4)$-$VNb(O_4)$-$CrVNb(O_6)$. The four errant compositions lie adjacent to the $VNb(O_4)$-$CrVNb(O_6)$ sideline. Of these compounds, $CrNbO_4$ and $CrVNbO_6$) have been synthesized with a rutile-like structure, tetragonal symmetry, and a *P*4$_2$*mnm* space group (JCPDS-ICDD Diffraction Files 36-788 and 34-366, 1993, respectively). Unit cell dimensions are also similar to those of rutile (a = 4.5937, c = 2.9587 Å); i.e. $CrNbO_4$: a = 4.6443 and c = 3.0125 Å; $CrVNbO_6$: a = 4.606 and c = 2.989 Å.

$CrVNbO_6$ was synthesized by heating Cr_2O_3 and $V_2Nb_2O_9$ in an evacuated silica tube for 3 days at 1000°C indicating a formula $Cr^{3+}V^{4+}Nb^{5+}O_6$ (JCPDS-ICDD Diffraction File 36-788). $CrNbO_4$ is reportedly obtained by heating Cr_2O_3 and Nb_2O_5 at 1000°C for 24 hours (JCPDS-ICDD Diffraction File 34-366) suggesting the formula $Cr^{3+}Nb^{5+}O_4$. No information is available on $VNbO_4$ but the similarity in ionic radii of V^{3+} and Cr^{3+} suggests it will also posses a rutile-like structure with V in the trivalent state.

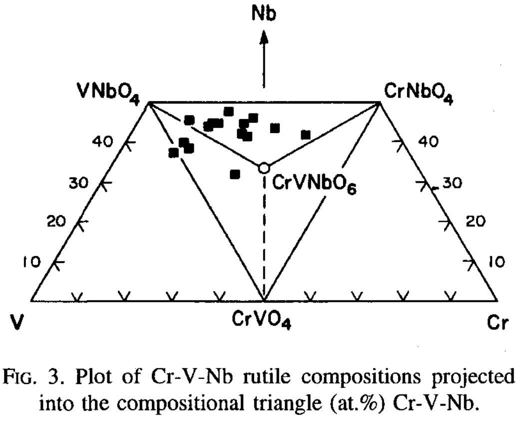

FIG. 3. Plot of Cr-V-Nb rutile compositions projected into the compositional triangle (at.%) Cr-V-Nb.

The traditional wisdom in rutile chemistry, and mineral chemistry in general, is to treat Cr cations as trivalent, and Nb and V as pentavalent cations. We have no crystallographic evidence to contradict this. However, we would suggest that V in these rutiles may well exist in both the tri- and tetravalent states and not in the pentavalent state as generally accepted (Waychunas, 1991). If so, in addition to the charge-coupled substitutions mentioned above, the simple substitution $V^{4+} = Ti^{4+}$ must also be considered. Finally, it may be observed that the octahedral coordination of Ti atoms and the trigonal planar coordination of O atoms in the rutile-structure is also one favoured by ionic dioxides where the radius ratio of metal to oxygen favours six-fold coordination (i.e. V).

V-rich crichtonite ($AM_{21}O_{38}$)

Representative analyses of this subhedral to anhedral phase are given in Table 3, compositional ranges are given in Table 1, and the comparative compositional fields for V, Cr, Fe and Nb with respect to Ti are shown in Fig. 1*a–d*. From the formula $AM_{21}O_{38}$, the smaller *M*-site cations are dominated by Ti (56–62%), in general agreement with members of the crichtonite family (Haggerty, 1991). Other important *M*-site cations are V (14–19%), Fe (15–17%), Cr (1–5%), and Nb (1–5%). Minor amounts of Sc, Mn, Zr, Si are also present. This phase may be essentially classified as a Fe-Cr-Nb vanadian titanate, and as such it is compositionally distinct from other members of the crichtonite mineral series (Haggerty *et al.*, 1983).

Conventionally, members of this series have been defined on the dominant large *A* cation: i.e. Ba (lindsleyite), K (mathiasite), Sr (crichtonite), Pb (senaite), Ca (loveringite), Na (landauite), U + *REE* (davidite) (see Haggerty, 1991 for references). The crichtonites from Deadhorse Creek are dominated by *A*-site Ba and Sr with lesser but significant amounts of Ca and Pb (Tables 1 and 3). K, Na, *REE* and U are essentially absent. Ba and Sr have a pronounced inverse relationship (Fig. 4*a*) suggesting that these crichtonites are members of Ba-Sr series. With increasing Ba, there is a concomitant increase in Ca and Pb (Fig. 4*b*); the increase in Pb being more pronounced. By conventional nomenclature therefore, these crichtonites would be classified as either crichtonite or lindsleyite. However, they differ from previously reported analyses of these minerals in the *M*-site cation enrichment of V (Tables 1 and 3). As such, they should be considered as vanadium analogues of both crichtonite and lindsleyite.

TABLE 3. Representative analyses of V-rich crichtonites

Analysis	1	2	3	4	5	6
Sample	C3000	C3000	C3024	C3024	C3025	C3025
TiO_2	55.26	54.45	58.14	51.61	57.64	56.13
SiO_2	0.32	0.15	na	0.17	0.06	0.07
ZrO_2	na	0.31	0.35	0.20	0.27	na
Nb_2O_5	2.83	3.27	1.43	6.99	2.94	2.68
Cr_2O_3	2.12	2.96	3.99	4.34	3.80	0.96
V_2O_3	15.83	14.65	12.36	14.32	12.21	16.43
Sc_2O_3	1.65	1.93	0.26	0.26	0.36	0.75
Fe_2O_3*	4.61	5.44	5.43	3.73	4.99	5.11
FeO*	8.37	8.29	8.49	9.52	9.06	8.34
MnO	0.52	0.67	1.46	1.35	1.70	0.78
BaO	3.63	2.88	3.58	2.67	2.13	4.35
SrO	1.66	2.19	1.85	2.21	3.64	1.81
PbO	2.75	2.59	2.43	2.30	0.97	2.26
CaO	0.45	0.22	0.23	0.33	0.23	0.33
Total**	100.0	100.0	100.0	100.0	100.0	100.0
Structural formulae with stoichiometry of 22 cations and 32 oxygens:						
M Cations						
Ti	12.442	12.270	13.062	12.852	11.762	12.672
Si	0.095	0.044	na	0.018	0.051	0.019
Zr	na	0.045	0.051	0.039	0.029	na
Nb	0.384	0.443	0.194	0.394	0.958	0.363
Cr	0.502	0.700	0.943	0.890	1.039	0.228
V	3.801	3.521	2.962	2.903	3.480	3.956
Sc	0.429	0.504	0.067	0.094	0.070	0.197
Fe^{3+}	1.040	1.226	1.220	1.112	0.851	1.154
Fe^{2+}	2.097	2.077	2.122	2.247	2.412	2.095
Mn	0.132	0.170	0.371	0.428	0.346	0.199
Total	20.922	21.000	20.992	20.977	20.998	20.883
A Cations						
Ba	0.426	0.339	0.419	0.247	0.317	0.512
Sr	0.287	0.381	0.320	0.626	0.389	0.315
Pb	0.222	0.209	0.196	0.077	0.187	0.182
Ca	0.143	0.071	0.073	0.073	0.109	0.108
Total	1.078	1.000	1.008	1.023	1.002	1.117

* FeO and Fe_2O_3 calculated on a stoichiometry of 22 cations and 32 oxygens.
** Analyses recalculated to 100%.
na = not analysed.

Lindsleyite and mathiasite (LIMA) are restricted to metasomatized upper mantle rocks and apart from their obvious chemical differences to other members of the crichtonite family, they are also distinguished by the presence of Nb (Haggerty, 1991). The Deadhorse Creek crichtonites are similar to the LIMA phases in this latter respect although they are richer in Nb (Table 3) and have the highest recorded Nb content of any member of the crichtonite series. Interestingly, they also plot in the upper mantle LIMA quadrant of the TiO_2 *vs.* $FeO+Fe_2O_3+MgO$ diagram (Fig. 5 and Haggerty,1991) and as such, they are the only non-LIMA crichtonites so to do. Perhaps this quadrant would be more fittingly termed the alkali metasomatic quadrant.

The geologic setting of the Deadhorse Creek diatreme obviously predicates against an upper mantle ultramafic environment. However, we

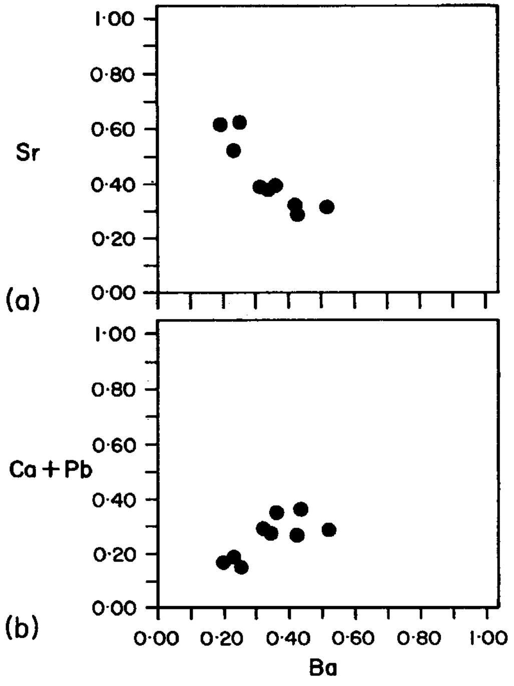

FIG. 4*a* and *b*. Variations of at.% Sr (*a*) and at.% (Ca+Pb) (*b*) with respect to at.% Ba for the V-rich crichtonites.

believe that alkali metasomatizing fluids are responsible for the formation of the crichtonite phases in both parageneses. The alkali fluids in the low-pressure environment of Deadhorse Creek have been able to scavenge a source of V (absent in the upper mantle), Cr, Nb, Ba and Sr. The source of these is discussed below.

Phase $(Cr,V^{3+},Fe^{3+})_2(Ti,V^{4+},Nb)O_5$

Table 4 is our complete data set of this extremely rare phase. Variations of selected elements with reference to TiO_2 are shown in Fig. 1*a–d*. In the absence of specific knowledge of the transition metal valency states, conventional valencies were assigned. Structural formulae so calculated show a strong correlation to the general formula M_3O_5 with the cation sites dominated by Cr, V, Fe^{3+}, Ti and to a lesser extent Nb (Table 4). This provides a reasonable basis on which to discuss the possible nature of this rare phase, the exact nature of which must await future crystallographic analysis.

Initially, this Ti-rich phase, with the general formula M_3O_5 may be considered part of the family of minerals with a pseudobrookite structure, particularly as such minerals can contain significant amounts of Cr and V (Bowles, 1988). With the exception of analysis 4 (Table 4), the ratio of M^{3+}:(Ti+Nb) slightly exceeds 2:1 suggesting a formula of M_2^{3+}(Ti,Nb)O_5. This could indicate a solid-solution variant of pseudobrookite. Analysis 4 shows an excess of Ti (+Nb) over this general consideration.

However, serious problems arise with the retention of the pseudobrookite structure when considerable amounts of Cr replace Fe^{3+}. Although Kwestroo and Roos (1960) have shown that the pseudobrookite structure of Fe_2TiO_5 can be retained with up to 15 at.% Cr, Grey and Reid (1972) observed that increasing contents of Cr produced more complex structures with the eventual loss of the pseudobrookite structure. Between 15 and 50 at.% Cr, a two phase region of pseudobrookite and V_3O_5 structural types exists, and for the composition $FeCrTiO_5$, a single phase of structural type V_3O_5 is stable. This latter structure is stable with up to 85 at.% Cr. We are not aware of the effects of V substitution but suggest that the pseudobrookite structure would suffer the same fate with significant V replacement. Consequently, with less than 25 at.% Fe^{3+} (Table 4), it seems most unlikely that the phase under discussion would retain either a pseudobrookite structure or could be categorized as a solid-solution variant of pseudobrookite.

Low-pressure studies of the system $Cr_2O_3 - TiO_2$ (Grey and Reid, 1972; Grey and Mumme, 1972) have revealed discrete phases with the general formula $Cr_2Ti_{n-2}O_{2n-1}$ with $n = 3–9$. Compounds of $n = 6$, 7, 8, and 9 are isomorphous with members of the homologous series Ti_nO_{2n-1} and V_nO_{2n-1} which have structures related to rutile by crystallographic shear. The lower homologue Cr_2TiO_5 ($n = 3$), when stabilized by Fe_2TiO_5 or Al_2TiO_5 is isomorphous with V_3O_5 (Asbrink *et al.*, 1959). From studies of the system $Cr_2O_3 - Fe_2O_3 - TiO_2$, Grey and Reid (1972) have also identified the homologous series $(Cr,Fe)_2Ti_{n-2}O_{2n-1}$ with $n = 3,4,5$. Compounds of the type $(Cr_xFe_{1-x})_2TiO_5$ ($n = 3$ and $0.85 \geqslant x \geqslant 0.50$) are isomorphous with V_3O_5, the structure of which may be derived from that of rutile by crystallographic shear parallel to $(12\bar{1})$ rutile. Grey and Reid (1972) also suggest that the V_3O_5 structure can be derived from the application of crystallographic shear to the α-PbO_2 structure by the application of step shear parallel to $[110]_{\alpha\text{-}PbO_2}$. This stabilizes the high pressure α-PbO_2 structure at atmospheric pressure by partial collapse of the structure to rutile-like blocks.

Within the system $Cr_2O_3 - Fe_2O_3 - TiO_2 - ZrO_2$, Grey *et al.* (1973) have identified a single series of homologues and polysomatic intergrowths having the

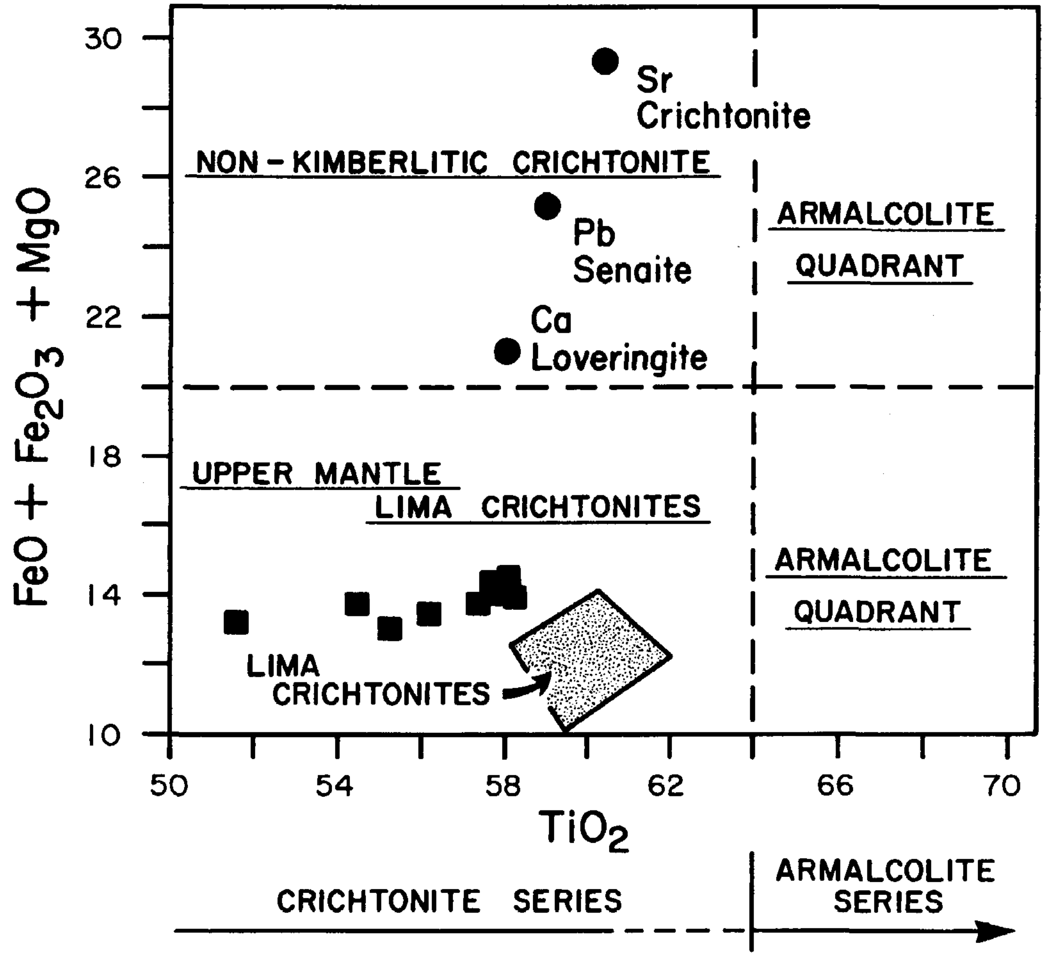

FIG. 5. Plot of ($FeO+Fe_2O_3+MgO$) *vs.* TiO_2 for the V-rich crichtonites (solid squares). Solid circles represent compositional points for Crichtonite(Sr), Senaite(Pb), and Loveringite(Ca). Both the stippled area of LIMA crichtonites and the four quadrant division of the diagram are after Haggerty (1991).

general formula $pM_3O_5 \cdot qM_2O_4$ or $(Cr,Fe)_{2p}(Ti,Zr)_{p+2q}O_{5p+4q}$, where p and q are integers. For $p = 1$ and $q = 0$ (i.e. $(Cr,Fe)_2(Ti,Zr)O_5$), the structure is again of the V_3O_5 type.

The compounds discussed above have broad similarities with the mineral phase reported here, although the former are much simpler in composition. The major discrepancies are the presence of considerable V in the natural compounds, the presence of Nb (not Zr), and the presence of small amounts of Sc, Al, Sr, Pb and Ca. However, by analogy with the above compounds, we suggest that the structure of this phase may well be isomorphous with V_3O_5 leading to the assumption that V exists in both the V^{3+} and V^{4+} states. Consequently, we express the general formula of the natural phase as $(Cr,V^{3+},Fe^{3+})_{2p}(Ti,V^{4+},Nb)_{2p+q}O_{5p+4q}$ with $p = 1$ and $q = 0$; i.e. $(Cr,V^{3+},Fe^{3+})_2(Ti,V^{4+},Nb)O_5$. Replacement of Ti by small but significant amounts of Nb^{5+} (not Zr) must produce either omission solid solutions or coupled replacements involving divalent cations. Certainly the analyses suggest the latter might occur. Whether the V_3O_5-type structure is ultimately derived from that of rutile or from that of α-PbO_2 by crystallographic shear is beyond the scope of this paper.

TABLE 4. Crystallographic shear-based oxides (M_3O_5)

Analysis Sample	1 C3024	2 C3024	3 C3006	4 C3025	5 C3025
TiO_2	28.53	28.15	28.80	33.55	25.95
V_2O_3	26.24	26.06	26.22	22.95	29.42
Cr_2O_3	24.02	23.68	25.10	21.58	19.63
Sc_2O_3	0.69	0.82	1.01	0.96	0.63
Al_2O_3	0.27	0.20	0.58	0.35	0.41
Fe_2O_3*	13.55	13.14	12.68	12.06	12.77
SrO	1.03	0.70	0.79	0.33	0.61
PbO	na	na	1.00	0.53	0.29
CaO	0.22	0.21	0.20	0.20	0.21
Nb_2O_5	5.45	7.04	3.62	7.49	10.08
Total**	100.0	100.0	100.0	100.0	100.0
Structural formulae calculated on the basis of 5 oxygens:					
Ti	0.847	0.836	0.857	0.984	0.776
V	0.831	0.825	0.832	0.718	0.938
Cr	0.750	0.739	0.786	0.666	0.617
Sc	0.024	0.028	0.035	0.033	0.022
Al	0.012	0.010	0.027	0.016	0.019
Fe^{3+}	0.403	0.390	0.378	0.354	0.382
Sr	0.024	0.016	0.018	0.007	0.014
Pb	–	–	0.011	0.006	0.003
Ca	0.010	0.009	0.008	0.009	0.009
Nb	0.097	0.126	0.065	0.132	0.181
Cations	2.998	2.979	3.017	2.925	2.961

*Fe calculated as Fe_2O_3; na = not analysed.
** Analyses recalculated to 100%

Discussion

The complex mineralization of the West subcomplex mineralized zone requires fluids variously enriched in Be, Zr, Ba, Sr, Th, U, *REE*, Nb, Sc, Fe, Ti, Cr, V, Mn, and Pb. The exact nature of these fluids is unknown, and we are not certain of their source or sources. Serious consideration must be given to fluids associated with both the alkaline magmatism of the Coldwell complex, and the carbonatitic and alkaline magmatism associated with the Prairie Lake Complex. Migrating regional fluids cannot be totally discounted. It seems unlikely, however, that any fluid at source would possess the elemental complexity necessary to explain the observed mineralization. Either subsequent elemental scavenging has occurred or alternatively, the mineralization may represent the product of diverse fluids periodically invading the same fracture system.

Smyk *et al.* (1993) equate the mineralization to the emplacement of the adjacent Coldwell complex, citing as evidence the enrichment of Be, Zr, and *HREE* commonly associated with rare-metal occurrences hosted by agpaitic syenites and peralkaline granites. One concern with this hypothesis is the essential absence of the required Coldwell magmas. Apart from minor peralkaline residual differentiates of the Center 1 ferroaugite syenites (Mitchell and Platt, 1978), no peralkaline syenites or granites are observed. Indeed the Centre 2 nepheline syenites are miaskitic (Mitchell and Platt, 1982) and the Centre 3 syenites are essentially metaluminous (Mitchell *et al.*, 1993).

Although casting some doubts on the specific arguments of Smyk *et al.* (1993), we would agree that the Coldwell complex is potentially a source of at least some of the mineralizing fluids associated with the Deadhorse Creek occurrence. Hydrous fluids emanating from the Coldwell syenites are alkaline, and evidence for the formation of accessory zircon, chevkinite, monazite, pyrochlore, columbite, allanite, fersmite, fergusonite and *REE*-fluorcarbonates in the Centre 3 syenites (McLaughlin, 1990; McLaughlin and Mitchell, 1989) suggests that such fluids may be enriched in certain essential elements (e.g. Zr, *REE*, Nb etc.) required for minerals of Deadhorse Creek. There is no evidence for any source of the Be and this remains enigmatic.

Moreover, Smyk *et al.* (1993) give no compelling reason to discount the coeval carbonatite magmatic systems in the region (e.g. Prairie Lake) as another potential source of the mineral forming fluids. Certainly such fluids could well be charged with many of the required elements, again with exception of Be.

With respect to the minerals described in this paper, neither fluids from the Coldwell syenites nor from the local carbonatites would inherently account for the enrichment in Cr,V,Sc,Fe,and Ti. Scavenging of these elements from a mafic/ultramafic source seems the most likely scenario. Some support for this argument is given by Pan and Fleet (1992) who have described a large number of V-bearing minerals from the Hemlo gold deposit located some 60 km east of the present location. They ascribe the complex formation of these minerals in part to metasomatic introduction of V, along with Cr, from local mafic and ultramafic sources.

No evidence for mafic and ultramafic sources exists in the Archaean country rocks adjacent to the Deadhorse Creek complex. Again, however, the Coldwell and Prairie Lake complexes present themselves as possible sources. Gravity profile modelling by Mitchell *et al.* (1983) has inferred that the infrastructure of the Coldwell complex consists of 3–5 km thickness of felsic rocks which overlie a gabbroic zone some 3–5 km in thickness, and a lower zone of ultramafic rocks approximately 3 km in thickness. At the present level of exposure, gabbroic rocks are found associated with Center 1 and Center 2 magmatism. Ijolites are also a common component of the Prairie Lake complex.

We would suggest, therefore, that the phases discussed here were ultimately precipitated in fracture zones from hydrous fluids, probably alkaline in character, which have scavenged elements from a mafic/ultramafic source.

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