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The Marathon Dikes. I: Zirconium-rich titanian garnets and manganoan magnesian ulvöspinel–magnetite spinels

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Abstract

The Marathon Dikes are a large group of predominantly Proterozoic Keweenawan dikes, of highly variable character, near Marathon, N.W. Ontario. Rare zirconium-rich titanian garnets and unusual manganoan magnesian ulvöspinel–magnetite series spinels have been identified in a composite ultramafic carbonate-rich lamprophyre from McKellar Harbour, N.W. Ontario. They are associated with olivine, phlogopite, calcite, apatite, melilite (?), and perovskite.

The zirconium-rich titanian garnets show variable amounts of ZrO_2, ranging from 3.56–19.53 weight percent. Individual crystals are zoned. An unusual set of end-member molecules, involving in the main Mg-melanite, Fe^{2+}-melanite, 'schorlomite,' Al-kimzeyite, Fe^{3+}-kimzeyite, and andradite, is necessary to describe the garnets. The spinels are characterized by high Mg, variable but generally high Mn, and relatively high Ti.

Zirconium-rich titanian garnets and Mn-rich spinels seem to form in low-silica activity magmatic rocks such as carbonatites and carbonated ultramafic alkaline rocks.

Introduction

The name Marathon Dikes is proposed for a set of Proterozoic, predominantly Keweenawan dikes near Marathon, N.W. Ontario (48°43′N; 86°22′W). These dikes form a complex group of lamprophyric, diabasic, and felsic intrusions, the latter ranging in composition from nepheline syenite to granite. They intrude both the Schreiber–White River greenstone belt of the Archaean Superior Province and the large Coldwell Alkaline Complex of Keweenawan age. Undoubtedly some of the dikes, particularly the more felsic varieties, are related genetically to this complex. However, we make no distinction in this paper on the basis of any such relationship. The term Marathon Dikes is strictly geographical.

The highly variable character of the dikes coupled with their abundance (in excess of 200) make it advisable to report important mineralogical and petrological data in a series of communications. The first paper describes rare zirconium-rich titanian garnets and unusual manganoan magnesian ulvöspinel–magnetite series spinels from an ultramafic carbonate-rich lamprophyre.

Lamprophyre

The meter-wide parent dike cross cuts the Schreiber–White River greenstone belt in the vicinity of McKellar Harbour, N.W. Ontario (48°48′N; 86°44′W). Internal structures (*e.g.* mineral flow alignments) and variations in mineral proportions and compositions strongly suggest a composite dike made up of a number of thin individuals. A representative analysis is given in Table 1.

Mineralogically, the dike consists of olivine, phlogopite, lath-shaped minerals (?melilite) pseudomorphed by andraditic garnet, calcite, perovskite, apatite, zirconium-rich titanian garnet, and spinels. Representative analyses of some of these phases are given in Table 2. All the mineral analyses were made on a Cambridge Instruments' Microscan V microprobe, using either energy-dispersive or wavelength-dispersive techniques as indicated on the respective tables.

Zirconium-rich titanian garnets

Small (<0.2 mm) deep reddish-orange to pale reddish-orange subhedral garnets are found in the more

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Table 1. Dike analysis

SiO_2	26.70	Rb	52	or	0.47
Al_2O_3	4.52	Sr	1180	an	7.24
Fe_2O_3	10.69	Y	50	lc	7.42
FeO	4.02	Zr	421	ne	0.14
MgO	16.75	Nb	280	di	15.99
CaO	17.21	Ba	1100	ol	24.03
Na_2O	0.03			he	7.04
K_2O	1.68	K/Rb	268	mt	5.29
MnO	0.35			il	5.77
TiO_2	3.04			ap	5.33
P_2O_5	2.44			cc	15.56
CO_2	6.84				
H_2O_T	5.38	Differentiation Index			8.03
Total	99.65				

carbonate-rich areas of the parent dike. Representative analyses of these zirconium-rich titanian garnets and their structural formulas are given in Table 3. Fe_2O_3 and FeO were calculated from total iron assuming stoichiometry on the basis of 8 cations and 12 oxygens. We have no way of evaluating the Ti^{4+}:Ti^{3+} ratio, although it is evident that titanium-rich garnets invariably contain a small proportion of Ti^{3+} (Huggins *et al.*, 1977b). In common with 'normal' schorlomites and melanites these zirconium-rich titanian garnets have an excess of divalent cations and tetravalent cations, coupled with a deficiency of $Si^{4+}$and trivalent cations, when compared to the ideal garnet formula of $M_3^{2+}M_2^{3+}Si_3O_{12}$.

The considerable variation in ZrO_2 is a function of random spot analyses on zoned crystals. Analyses 4 and 9, and 5 and 11 (Table 3) are core/rim analyses of two crystals. These indicate an outward increase of ZrO_2 accompanied by a decrease in SiO_2, Fe_2O_3, and total iron. No zoning is apparent optically.

As an indication of the solid solutions and the possible structural locations of the various cations, we have calculated, from the structural formulas, the end-member molecules shown in Table 4. Significant differences exist between the molecules calculated here and those calculated in other schemes for more common garnets (*e.g.* Rickwood, 1968). (1) All Cr^{3+} is calculated as uvarovite. (2) The 8-fold coordination sites are occupied predominantly by Ca. Mn first and then Mg, in the form of spessartine and pyrope respectively, are considered to satisfy any deficiencies in these sites. This is somewhat arbitrary as Fe^{2+} (almandine) is a valid substitute as are small amounts of Zr^{4+}. Ito and Frondel (1967) have, for example, successfully synthesized $Ca_{2.5}Zr_{0.5}Zr_2Fe_3^{3+}O_{12}$. (3) As the size of Zr^{4+} effectively precludes it from all tetrahedrally coordinated sites, we have assigned it entirely to the octahedral sites. The presence of Zr^{4+} is best explained by the coupled substitution:

$$Zr^{4+}_{(VI)} \rightleftarrows (Al,Fe^{3+})_{(VI)};\ (Al,Fe^{3+})_{(IV)} \rightleftarrows Si^{4+}_{(IV)}$$

This gives rise to the molecules Al-kimzeyite ($Ca_3Zr_2Al_2SiO_{12}$) and Fe^{3+}-kimzeyite ($Ca_3Zr_2Fe_2^{3+}SiO_{12}$). As Al has a greater tetrahedral site preference than Fe^{3+} (Huggins *et al.*, 1977a), we form Al-kimzeyite before Fe^{3+}-kimzeyite. Both these molecules and limited solid solutions between them have been synthesized by Ito and Frondel (1967). (4) Zr^{4+} and its associated coupled substitution cannot account for the total Si^{4+} deficiency in the analyzed garnets. The additional coupled substitution:

$$Ti^{4+}_{(VI)} \rightleftarrows Fe^{3+}_{(VI)};\ Fe^{3+}_{(IV)} + Ti_{(IV)} \rightleftarrows Si^{4+}_{(IV)}$$

may therefore be considered. This generated the molecule $Ca_3Ti_2Fe_2^{3+}TiO_{12}$ termed schorlomite by Rickwood (1968). Ito and Frondel (1967) failed to synthesize this molecule, although solid solutions between it and andradite have been successfully synthesized for compositions more Si-rich than $Ca_3Fe_2^{3+}Ti_{1.5}Si_{1.5}O_{12}$ (Huckenholz, 1969). Andradite is formed after $Ca_3Ti_2Fe_2^{3+}TiO_{12}$ in an amount proportional to the available Fe^{3+} remaining after all previous calculations. (5) Any and all remaining cations at this

Table 2. Representative mineral analyses

	Olivine**		Phlogopite***		Perovskite****	
SiO_2	40.33	39.38	36.01	37.61	0.20	0.25
Al_2O_3	nd	nd	16.96	15.07	nd	0.41
TiO_2	nd	nd	2.63	1.87	54.06	55.10
FeO*	12.61	18.05	5.85	7.22	2.24	1.64
MnO	0.20	0.55	nd	0.23	nd	nd
MgO	47.11	42.12	21.93	22.32	nd	nd
CaO	0.32	0.29	nd	0.29	39.51	38.80
K_2O	nd	nd	9.93	9.94	nd	nd
NiO	0.25	nd	nd	nd	nd	nd
Total	100.82	100.39	93.31	94.55	96.01	96.20
Structural Formula						
Si	0.996	1.001	5.289	5.489		
Al^{iv}	-	-	2.711	2.511		
Al^{vi}	-	-	0.221	0.078		
Ti	-	-	0.290	0.205		
Fe^{2+*}	0.261	0.384	0.717	0.880		
Mn	0.005	0.012	-	0.028		
Mg	1.733	1.596	4.798	4.852		
Ca	0.009	0.008	-	0.045		
K	-	-	1.857	1.847		
Ni	0.006	0.000	-	-		

nd element not detected; * Fe calculated as FeO
** structural formula based on 4 oxygens; *** structural formula based on 22 oxygens; **** Nb and rare earth elements detectable by energy dispersion. All analyses by energy dispersion.

Table 3. Garnet analyses

Analyses Number	1	2**	3	4	5**	6**	7	8**	9	10	11**	12	13**	14**	15**	16**
SiO_2	28.82	26.34	28.22	27.58	27.09	26.95	24.64	23.80	24.59	24.80	23.50	22.21	21.53	21.66	21.86	20.97
TiO_2	11.74	13.26	11.47	9.08	8.85	10.34	12.90	10.60	9.87	10.51	10.19	10.01	10.33	10.12	10.12	9.83
ZrO_2	3.56	5.85	5.94	8.06	8.61	9.78	11.35	11.92	13.00	13.68	13.77	17.84	18.43	18.63	18.69	19.53
Al_2O_3	0.80	0.71	0.49	2.44	2.56	1.04	2.68	2.46	3.71	1.64	3.14	3.09	3.00	3.05	3.04	3.32
Y_2O_3	ND	0.07	ND	ND	0.07	0.07	ND	0.10	ND	ND	0.11	ND	0.04	0.03	0.04	0.06
Cr_2O_3	0.00	0.01	0.14	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.20	0.00	0.03	0.03	0.00	0.00
Fe_2O_3*	18.65	16.69	17.31	17.97	16.79	14.82	11.83	16.99	14.02	12.51	15.18	10.70	11.08	10.42	10.00	11.48
FeO*	1.82	2.05	1.63	0.21	1.08	2.14	2.80	0.41	0.82	2.78	1.25	2.51	2.63	2.75	3.11	1.83
MnO	0.24	0.09	0.31	0.00	0.07	0.16	0.26	0.12	0.00	0.00	0.11	0.19	0.05	0.13	0.08	0.10
MgO	1.94	2.05	2.50	2.12	1.87	2.51	2.84	2.07	3.11	2.67	2.23	2.63	2.41	2.56	2.57	2.52
CaO	32.45	31.93	32.10	32.67	31.81	31.37	30.88	31.64	30.83	30.87	31.03	30.11	30.23	29.95	29.89	30.26
Nb_2O_5	ND	0.00	ND	ND	0.00	0.08	ND	0.00	ND	ND	0.00	ND	0.00	0.00	0.00	0.00
Total	100.02	99.05	100.11	100.13	98.80	99.26	100.18	100.12	99.95	99.46	100.61	99.29	99.76	99.33	99.40	99.90
Structural Formula based on 8 cations: 12 oxygens																
Si	2.459	2.299	2.422	2.370	2.369	2.363	2.147	2.098	2.147	2.202	2.068	2.006	1.948	1.966	1.982	1.901
Ti	0.753	0.870	0.740	0.587	0.582	0.682	0.845	0.073	0.648	0.702	0.674	0.680	0.703	0.691	0.690	0.670
Zr	0.148	0.249	0.249	0.338	0.367	0.418	0.483	0.513	0.554	0.593	0.591	0.786	0.813	0.825	0.827	0.864
Al	0.080	0.073	0.050	0.247	0.264	0.108	0.275	0.256	0.382	0.172	0.326	0.329	0.320	0.326	0.325	0.355
Y	ND	0.003	ND	ND	0.003	0.003	ND	0.005	ND	ND	0.005	ND	0.002	0.001	0.002	0.003
Cr	0.000	0.001	0.010	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.014	0.000	0.002	0.002	0.000	0.000
Fe^{3+}*	1.198	1.096	1.118	1.162	1.105	0.978	0.776	1.127	0.921	0.836	1.005	0.727	0.754	0.712	0.682	0.783
Fe^{2+}*	0.130	0.149	0.117	0.015	0.079	0.157	0.204	0.030	0.060	0.207	0.092	0.190	0.199	0.208	0.236	0.139
Mn	0.017	0.007	0.023	0.000	0.005	0.012	0.019	0.009	0.000	0.000	0.008	0.015	0.004	0.010	0.006	0.008
Mg	0.247	0.267	0.320	0.272	0.244	0.328	0.369	0.272	0.405	0.353	0.292	0.354	0.325	0.346	0.347	0.340
Ca	2.967	2.986	2.952	3.009	2.981	2.948	2.883	2.988	2.884	2.937	2.925	2.914	2.930	2.912	2.903	2.939
Nb	ND	0.000	ND	ND	0.000	0.003	ND	0.000	ND	ND	0.000	ND	0.000	0.000	0.000	0.000

ND Not Determined. * $Fe^{3+}:Fe^{2+}$ ratio to satisfy 8 cation: 12 oxygen requirements.
** Wavelength dispersive analyses. All other analyses by energy dispersion.

stage are considered to be in octahedral coordination. Ti^{4+}, Mg, and Fe^{2+} remain and are presumed to form garnet molecules involving the substitution:

$$Ti^{4+}_{(VI)} + (Mg,Fe^{2+})_{(VI)} \rightleftarrows 2R^{3+}_{(VI)}$$

Fe-melanite ($Ca_3Fe^{2+}TiSi_3O_{12}$) and Mg-melanite ($Ca_3MgTiSi_3O_{12}$) are therefore calculated in amounts proportional to the remaining available cations. (6) In these calculations we have ignored the trace amounts of Y^{3+} and Nb^{5+}.

The manganoan magnesian ulvöspinel–magnetite spinels

The spinels are unusual in that high TiO_2 is coupled with high MgO together with variable MnO. End-member spinel molecules given in Table 5 are calculated on an ulvöspinel–magnetite basis rather than on a jacobsite–magnetite basis because of the high TiO_2 contents. The spinels are thus considered to be members of the manganoan magnesian ulvöspinel–magnetite series.

Spinels containing high proportions of Mn_2TiO_4 together with high Mg_2TiO_4 have not been previously described, as far as we are aware.

Discussion

Melanites and schorlomites with minor amounts of ZrO_2 have been reported from a variety of undersaturated alkaline rocks (*e.g.* Dowty, 1971), whereas zirconium-rich titanian garnets have been reported from only a handful of localities, namely: Oka, Quebec [1 analysis: 3.7 weight percent ZrO_2, Nickel (1957)]; Iron Hill, Colorado [1 analysis: 4 weight percent ZrO_2; Dowty (1971)]; the Vuoro–Yarvi massif, Kola peninsula [1 analysis: 13.11 weight percent ZrO_2; Borodin and Bykova (1961)]; the Gulinski massif, N. Siberia [1 analysis: 10.73 weight percent ZrO_2; Borodin and Bykova (1961)]; and Magnet Cove, Arkansas, the type locality for kimzeyite [4 analyses: 20.25 weight percent ZrO_2; Milton and Blade (1958); 3.5–4.0 weight percent and 29.9 weight percent ZrO_2; Milton *et al.* (1961); 16.74 weight percent ZrO_2; J. J. Fahey, personal communication from E. Dowty].

Table 4. Garnet end-member molecules mole percent

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Spessartine	0.57	0.23	0.77	0.00	0.17	0.40	0.63	0.30	0.00	0.00	0.27	0.50	0.13	0.33	0.20	0.27
Pyrope	0.53	0.23	0.83	0.00	0.47	1.33	3.27	0.10	3.87	2.10	2.23	2.37	2.20	2.60	3.03	1.77
Uvarovite	0.00	0.05	0.50	0.00	0.00	0.00	0.00	0.05	0.00	0.00	0.70	0.00	0.10	0.10	0.00	0.00
Al-Kimzeyite[1]	4.40	2.60	1.10	12.35	12.60	3.65	9.85	12.40	16.20	6.50	13.80	13.60	13.65	13.35	13.00	15.75
Fe^{3+}-Kimzeyite[2]	5.20	9.85	11.35	4.55	5.75	17.25	14.30	13.25	11.50	23.15	15.75	25.70	27.00	27.90	28.35	27.45
Schorlomite[3]	13.10	15.07	10.97	9.73	8.80	7.30	12.33	12.97	9.96	6.83	11.37	6.93	7.97	6.97	5.75	7.83
Andradite	41.60	29.90	33.60	43.80	40.70	24.35	12.15	30.15	24.60	11.80	23.15	3.70	2.75	0.75	0.00	3.85
Fe^{2+}-Melanite[4]	13.00	14.90	11.70	1.50	7.90	15.70	20.40	3.00	6.00	20.70	9.20	19.00	19.90	20.80	23.60	13.90
Mg-Melanite[5]	20.47	26.00	29.17	27.20	23.00	28.80	27.00	26.90	27.87	28.87	23.53	28.20	25.90	26.80	25.60	28.70
Residual	1.13	1.17	0.01	0.87	0.61	1.22	0.07	0.07	0.00	0.05	0.00	0.00	0.40	0.40	0.47	0.48

1. $Ca_3Zr_2Al_2SiO_{12}$; 2. $Ca_3Zr_2Fe^{3+}_2SiO_{12}$; 3. $Ca_3Ti_2Fe^{3+}_2TiO_{12}$; 4. $Ca_3Fe^{2+}TiSi_3O_{12}$; 5. $Ca_3Mg^{2+}TiSi_3O_{12}$

The parageneses of these zirconium-rich titanian garnets and those from McKellar Harbour are closely related to carbonatites and/or carbonated ultramafic alkaline rocks. Haggerty (1976) also considers the presence of Mn-bearing spinels as indicative of carbonatitic magmas, although, unlike those described here, many of these are best described as members of the magnesioferrite–jacobsite–magnetite series. Spinels containing 0.5–13.5 weight percent MnO have been described from the Oka carbonatites and alnöites by McMahon and Haggerty (1977), but these spinels are poor in TiO_2 (8 percent) relative to the spinels from McKellar Harbour. The formation of spinels depends primarily however on particular physicochemical conditions rather than specific magma types. These Mn-spinels might therefore be expected to form in any magma with low silica activity and high CO_2, CaO, and MgO, *i.e.* alnöites, mica peridotites, monchiquites, *etc.*

Table 5. Spinel analyses

	1	2	3	4	5	6	7	8
TiO_2	15.23	17.27	13.90	16.68	17.29	16.17	18.99	15.88
Al_2O_3	7.97	6.86	6.42	7.88	8.22	8.32	7.83	1.49
Cr_2O_3	4.01	1.26	1.23	2.26	2.38	4.54	0.0	0.24
FeO*	52.13	55.87	61.84	58.72	57.72	56.45	59.28	71.18
MnO	9.69	8.43	7.48	3.76	2.61	1.9	0.75	0.81
MgO	7.10	7.19	4.75	7.57	8.57	9.8	10.33	5.91
	96.13	96.88	95.62	96.87	96.79	97.18	97.18	95.51
Recalculated analyses**								
Fe_2O_3	29.41	30.18	35.40	29.19	27.87	28.71	28.73	39.17
FeO	25.67	28.72	29.99	32.45	32.64	30.62	33.43	35.97
	99.08	99.9	99.17	99.79	99.58	100.06	100.06	99.43
Mol.% end member molecules								
$MgAl_2O_4$	13.6	11.4	11.4	13.2	13.5	13.7	12.5	2.6
$MgCr_2O_4$	4.6	1.4	1.5	2.5	2.6	5.0	-	0.3
$FeCr_2O_4$	-	-	-	-	-	-	-	-
Mg_2TiO_4	9.3	13.1	6.3	12.2	14.6	16.6	21.9	17.5
Mn_2TiO_4	17.8	15.1	14.3	6.8	4.6	3.4	1.3	1.5
Fe_2TiO_4	22.6	26.8	26.5	34.3	35.2	31.1	34.9	34.2
Fe_3O_4	32.1	32.1	40.0	31.1	29.3	30.2	29.3	43.8

*Total Fe calculated as FeO; ** and FeO and Fe_2O_3 calculated from total Fe by Carmichael's (1967) method.

The paragenesis of the garnets and spinels from McKellar Harbour is remarkably similar to that described by Borodin and Bykova (1961) from Vuori–Yarvi. Here the 'zirconium schorlomites' are found in veinlike bodies of carbonatite associated with forsterite, apatite, phlogopite, perovskite (rich in Nb and rare earths), and "magnetite" (composition unknown).

No evidence for carbonatite magmatism has previously been reported for the immediate region of McKellar Harbour, although Keweenawan carbonatitic activity is known from Prairie Lake (49°02′N; 86°44′W) some 20 miles to the north. At this time, it is unknown whether this lamprophyre is related to the Prairie Lake activity.

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