

Article

Columbite-Group Minerals from New York Pegmatites: Insights from Isotopic and Geochemical Analyses

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Received: 11 April 2018; Accepted: 3 May 2018; Published: 9 May 2018



Abstract: Columbite crystals from niobium-yttrium-fluorine (NYF) pegmatites lacking zircon or containing metamict cyrtolite were analyzed for major and minor elements (Electron Microprobe (EMP)), trace elements (Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS)), and U-Pb geochronology (Laser AblationMulti-Collector-Inductively Coupled Plasma-Mass Spectrometry (LA-MC-ICP-MS)). All four pegmatite localities sampled are hosted by the Proterozoic Fordham gneiss and/or Paleozoic Bedford gneiss (Columbite-(Fe); Kinkel and Baylis localities) and the Manhattan Schist of Lower Paleozoic age (Columbite-(Mn); Fort George and Harlem River Drive localities) and yield Neoacadian ages. The weighted average U-Pb ages are 372.2 ± 8.2 Ma (Baylis Quarry), 371.3 ± 7.3 and 383.4 ± 8.9 Ma (Kinkel Quarry); 383 ± 15 Ma (185th St. and Harlem River Drive); and 372 ± 10 Ma (Fort George). A partial metamict zircon ("cyrtolite") from the Kinkel Quarry yielded a weighted average U-Pb age of 376.9 ± 4.3 Ma. The Neoacadian ages obtained agree with those determined by thermal ionization mass spectrometry (TIMS) for zircon from Lithium-Cesium-Tantalum (LCT) pegmatites from Connecticut and Maine. No pegmatites temporally associated with the Taconic orogeny were found. The size, lack of common Pb, uniform U concentrations across crystal cross-sections, sufficient but moderate uranium concentrations, lack of metamictization, and consistency in U-Pb isotopic ratios for columbite samples BCB-COL, NYSM #25232, and NYSM #525.8 suggests they show promise as potential standards for oxide mineral LA-MC-ICP-MS geochronological analyses, however, additional characterization using ID-TIMS would be necessary to develop as such.

Keywords: NYF pegmatites; columbite-(Fe); columbite-(Mn); Bedford; Manhattan; Neoacadian; U-Pb columbite geochronology

1. Introduction

Columbite (designated the columbite-group within) has the general formula AB₂O₆ where the "A" site is occupied mainly by Fe, Mn, and Mg and the "B" site by Nb and Ta. Three end-members, columbite-(Fe), columbite-(Mn), and columbite-(Mg), are known to occur in nature. Columbite-(Fe) is the most common, whereas columbite-(Mg) is rare [1]. The columbite minerals occur in magmatic deposits of W, Sn, and rare earth elements (REE) [2], alkaline and carbonatitic intrusions [3],



and pegmatites [4]. Coltan, a dark ore of columbite-group minerals, is an important source for the strategic elements niobium and tantalum and, for this reason, ignited and funded armed conflicts in some African countries [5].

Despite relatively low uranium concentrations, columbite-group minerals can be used for high resolution U-Pb geochronology because they have sufficient uranium concentrations and low common Pb content [2,6–8]. Dating columbite-group minerals is an important geochronological tool for rocks that lack zircon, rocks in which zircon is metamict or inherited, and for fingerprinting of conflict minerals [9]. Isotope dilution-thermal ionization mass spectrometry (ID-TIMS) was the first method used to date columbite [2,6,7,10–12], followed LA-MC-ICP-MS [8], and LA-ICP-MS [13–17]. In these studies, monazite and zircon were used as external standards because of the absence of a columbite standard and developing a matrix matched standard is central to further the utility of columbite geochronology and the study of its trace-element geochemistry.

This study characterizes the columbite-group minerals from niobium-yttrium-fluorine (NYF-type) pegmatite occurrences in southern New York (Figure 1) [18].



Figure 1. Location diagram, geological contacts, and sample locations for this study. The inset shows the location of the study area with respect to New York State.

We present major and trace element concentrations by electron microprobe (EMP) and LA-ICP-MS, respectively. In addition, U-Pb ages determined by LA-MC-ICP-MS are presented for columbite-(Fe) from two pegmatites from Westchester County, southern New York (Kinkel and Baylis) and columbite-(Mn) from Fort George and Harlem River Drive in New York City (Figure 1). Co-existing

high-U and Hf zircon ("cyrtolite") from the Kinkel pegmatite was also analyzed for comparison purposes. This work further validates the use of columbite as a geochronometer and is a crucial step towards development of a matrix- matched columbite standard.

2. Geological Setting

NYF-type pegmatites are known in southern New York and New York City where they intrude rocks metamorphosed to amphibolite facies conditions such as the Precambrian Fordham gneiss, the Paleozoic Bedford gneiss (southern New York), and the Paleozoic Manhattan Schist (New York City) (Figure 1) [18,19].

The ca. 1170 Ma Fordham gneiss is the oldest recognized rock unit underlying New York City [20]. It is composed of interlayered felsic and mafic units of meta-sedimentary and meta-igneous rocks [21,22]. The Ordovician Bedford gneiss is a biotite-quartz-plagioclase gneiss with interlayered amphibolite [22]. In places, andesine and microcline form "augen", a characteristic feature of the gneiss [21,23]. The pegmatites intruding the Bedford gneiss were mined for feldspar in several quarries from 1878 to 1949, when they closed [24], and in 1962 and 1963 the sites were developed for residential purposes [19].

Geological information on two of the main pegmatite bodies, Kinkel and Baylis, is found in several references [23,25–28]. The 133-m long and 67-m wide pegmatite body mined at the Baylis Quarry displayed a border, wall, outer and inner intermediate, and core zones [19]. No zonation was reported for the 200 m long and 100 m wide main Kinkel pegmatite body. The complex mineral composition of the Kinkel and Baylis pegmatites are reported in many sources [18,19,29–31]. The exact location of columbite in the Baylis pegmatite is uncertain. The occurrence of columbite is described as at "the point between the feldspar and the country rock" [29] (p. 46) or from the inner intermediate zone of the pegmatite body [19].

The Manhattan Schist (Cambrian-Ordovician) is a coarse-grained schist and gneiss containing biotite, muscovite, quartz, and plagioclase with rare occurrences of sillimanite, kyanite, tourmaline, and almandine. The columbite-(Mn) crystals used for this study were from two small pegmatite bodies intruding the Manhattan Schist at the intersection of 185th Street with Harlem River Drive and at Fort George (Figure 1). The mineral associations are simple, quartz, microcline, and beryl (185th Street with Harlem River Drive pegmatite) and quartz, microcline, almandine, and muscovite (Fort George pegmatite).

3. Analytical Methods

The columbite samples analyzed in this paper are from the New York State mineral collection and include columbite-(Fe) NYSM #25232 and #22361 (Kinkel), #BCB-COL (Baylis) and columbite-(Mn) NYSM #525.7 (185th Street and Harlem River Drive) and #525.8 (Fort George). Sample locations are shown on Figure 1. The identity of each sample was confirmed by X-ray diffraction at St. Lawrence University (Figure 2).



Figure 2. Representative X-ray diffractogram for Columbite-(Fe) sample from the Kinkel pegmatite.

3.1. Major Elements

Centimeter- to millimeter-sized fragments of columbite-group minerals were mounted in epoxy, polished, and coated with carbon under vacuum and then analyzed using a CAMECA SX 100 electron microprobe at the Department of Earth and Environmental Sciences, Rensselaer Polytechnic Institute, Troy, NY. The analysis of major elements included Nb, Ta, Fe, Mn, and Ti. Mg and Ca were also included in the analysis, although high concentrations of these elements were not found (Table 1).

Oxide	NYSM 22361	NYSM 25232	BCB-COL	NYSM 525.8	NYSM 525.7
CaO	0.02	udl	udl	0.03	0.10
FeO	14.18	14.18	14.12	6.24	6.26
MnO	6.38	6.33	6.32	13.64	12.73
MgO	0.14	0.06	0.13	udl	0.03
Nb_2O_5	71.50	71.53	71.74	67.85	59.89
Ta ₂ O ₅	6.35	7.93	6.93	12.78	20.43
TiO ₂	1.62	0.82	1.69	0.45	0.64
Total	100.19	100.85	100.93	100.99	100.08
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Ca ²⁺	nd	nd	nd	nd	0.01
Fe ²⁺	0.68	0.68	0.67	0.30	0.32
Mn ²⁺	0.31	0.31	0.30	0.67	0.66
Mg ²⁺	0.01	0.01	0.01	0	nd
Nb ⁵⁺	1.85	1.85	1.84	1.79	1.65
Ta ⁵⁺	0.10	0.12	0.11	0.20	0.34
Ti ⁴⁺	0.07	0.04	0.07	0.02	0.03
Mn/(Mn+Fe)	0.31	0.31	0.31	0.69	0.67
Ta/(Ta+Nb)	0.05	0.06	0.06	0.10	0.17

Table 1. Electron microprobe data of the columbite-group minerals from southern New York (wt. %).

(10 analyses on each crystal); udl-under the limit of detection; nd-not determined.

To avoid potential problems that could influence U-Pb dating, such as the presence of tiny uraninite inclusions or other U-rich minerals, we screened both columbite-(Fe) and columbite-(Mn) in back scattered electron mode and produced X-ray maps (Figure 3) for U, Nb, Ta, Fe, Ti and Mn.



Figure 3. (**A**) Back-scattered electron image of columbite-(Mn) sample NYSM #525.7 from the corner of 185th Street and Harlem River Drive in New York City; X-ray maps: (**B**) Nb; (**C**) Ta; (**D**) Fe; (**E**) Mn; and (**F**) Ti. Field of view is 300 microns in each picture.

No inclusions were found and none of the columbites displayed zoning. Only sample NYSM #525.7 displays compositional variation in Nb, Ta, Fe, and Mn (Figure 3), but is homogeneous in Ti and U (not shown).

All elements were analyzed at 15 keV accelerating voltage and a 60 nA beam current, using integral PHA mode. Due to the high concentration of niobium (~50 wt. %), the Nb 2nd order (La2) line was used to suppress the high-count rate (measured on the TAP crystal) and reduce dead time correction. The remaining elements measured were Ta L α 1 (on LLIF), Fe K α and Mn K α (on LLIF), Ti K α and Ca K α (on LPET), Mg K α (on TAP), and O K α (on PC1). All elements were background corrected using traditional two-point off-peak background interpolation. The oxygen K α peak was free of significant high-order interferences from major elements. Background selection on the high-energy side of the oxygen peak avoided potential interferences such as Mn Ll and Ln (1st order), Ta M α (3rd order), and Nb L α (4th order). An interference correction was applied for the tail overlap of Mn K β with Fe K α (0.39 cps/nA). Standard reference materials included niobium metal for Nb (C. M. Taylor), tantalum metal for Ta (C. M. Taylor), synthetic fayalite for Fe (RPI), tephroite for Mn (Smithsonian), rutile for Ti (Harvard collection), diopside for Ca (Geophysical Lab) synthetic forsterite for Mg (RPI) and quartz for O (Smithsonian). The niobium metal was found to contain a significant oxidation layer resulting in apparent Nb excess in unknown materials. Therefore, columbite from the Kinkel Quarry (NYSM #22361) was chosen as an internal reference material for Nb based on the low concentration of trace elements. Ideal Nb concentration was calculated by difference from Ta (assuming these were the only two elements in the B-site).

3.2. Trace Elements

Trace elements in columbite were measured by LA-ICP-MS on a Photon Machines Analyte193 G1 short-pulse eximer laser coupled to Varian 820 quadrupole inductively coupled plasma mass spectrometer (Tables 2 and 3) at RPI.

Table 2. Trace elements in columbite and "cyrtolite" by LA-ICP-MS and LA-MC-ICP-MS (U) (ppm) (five analyses on each crystal).

Sample	Zr	Y	Sn	Sc	W	Hf	Pb	U	Th
BCB-COL	4670	170	487.2	53.8	7050	480	580.8	620.5	8.7
NYSM 22361	4500	223.9	499.5	72.7	8391.6	476.8	882.5	647.1	10.9
NYSM 25232	4524	307.4	368.8	30.4	2088	556.4	392.8	315.0	2.4
NYSM 525.7	500.4	3930	97.7	35.2	1726	71.9	238.6	170.1	13.9
NYSM 525.8	2622	2104	386.8	8.6	4496	406	736	500.2	20.7
CYR	-	1948.2	-	118.7	-	54,100	1678.2	2327	16.9

Table 3. Rare earth elements in columbite and "cyrtolite" by LA-ICP-MS (ppm) (five analyses on each crystal).

Sample	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Но	Er	Tm	Yb	Lu	Y
BCB-COL	0.07	0.72	0.35	3.89	26.14	0.05	75.88	23.8	78.84	4.12	4.11	0.32	1.59	0.13	170
22361	11	16	2	10	33	0.07	99	30	105	6	6	0.6	3	0.22	223.85
25232	0.02	0.3	0.2	2	20	0.03	82	31	127	10	11	1	5	0.35	307.4
525.7	2.76	8	2	20	76	2	264	112	824	144	397	70	574	75	3930
525.8	0.16	3	2	14	66	1	191	86	534	64	138	23	180	23	2104
CYR	1.49	1.95	0.35	1.88	10.29	0.11	97.09	48.92	301.75	29.95	50.99	7.23	54.13	7.91	1948.2

All trace elements were calibrated using NIST standard glasses (#610, primary; and #612, secondary). Laser parameters included 360 shots at 6 Hz repetition rate per ablation, at 58% laser power attenuation, 6.5 J/cm^2 fluence using 20-micron square spot. Mass spectrometer acquisitions were 140 s windows each, including 60 s ablation, 20 s washout, and 60 s background acquisition. Masses analyzed by LA-ICP-MS (with millisecond dwell times in parentheses) included Ca-43 (30),

Sc-45 (10), Ti-49 (1), Mn-55 (0.2), Fe-57 (1), Y-89 (10), Zr-90 (10), Sn-118 (10), La-139 (30), Ce-140 (30), Pr-141 (30), Nd-146 (30), Sm-149 (20), Eu-153 (20), Gd-157 (20), Tb-159 (20), Dy-163 (10), Ho-165 (10), Er-166 (10), Tm-169 (10), Yb-172 (10), Lu-175 (10), Hf-178 (10), W-182 (10), Pb-206 (10), Th-232 (20), and U-238 (30). The total quadrupole scan time was 465 ms per cycle, resulting in >120 cycles within each 60 s ablation event. Each columbite sample was ablated five times in distinct locations and standards were reanalyzed every five ablations. Data were processed using the Iolite software's trace element data reduction scheme using Ti as internal standard (as measured by EPMA).

3.3. Geochronology

U-Pb columbite geochronology was carried out at the Arizona Laserchron Center, University of Arizona. Analyses by LA-MC-ICP-MS were conducted as described for zircon [32]. Ablation of columbite was done with a Photon Machines Analyte G2 DUV193 Excimer laser using spot diameters of 30 microns. The ablated material was carried with helium gas into the plasma source of a Nu Instruments HR ICPMS equipped with a flight tube of sufficient width that U, Th, and Pb isotopes can be measured simultaneously. All measurements were made in static mode, using Faraday detectors for ²³⁸U, ²³²Th, and ²⁰⁸⁻²⁰⁶Pb, and discrete dynode ion-counters for ²⁰⁴Pb, and ²⁰²Hg. Ion yields are typically ~1 mv per ppm. Each analysis consists of one 15 s integration on peaks with the laser off (for backgrounds), fifteen 1-s integrations with the laser firing, and a 30 s delay to purge the previous sample and prepare for the next analysis. The ablation pit is ~15 microns in depth.

For each analysis, the errors in determining ²⁰⁶Pb/²³⁸U and ²⁰⁶Pb/²⁰⁴Pb result in a measurement error of ~1% (at 2σ level) in the 206 Pb/ 238 U age. The errors in measurement of 206 Pb/ 207 Pb and 206 Pb/ 204 Pb also result in ~1% (2 σ) uncertainty in age for grains that are >1.0 Ga, but they are substantially larger for younger grains due to the low intensity of the ²⁰⁷Pb signal. For most analyses, the crossover in precision of ²⁰⁶Pb/²³⁸U and ²⁰⁶Pb/²⁰⁷Pb ages occurs at ca. 1.0 Ga. The ²⁰⁶Pb/²³⁸U ages are reported here. Common Pb correction is accomplished by using the measured ²⁰⁴Pb and assuming an initial Pb composition [33], with uncertainties of 1.0 for ²⁰⁶Pb/²⁰⁴Pb and 0.3 for ²⁰⁷Pb/²⁰⁴Pb. The measurement of ²⁰⁴Pb is unaffected by the presence of ²⁰⁴Hg because backgrounds are measured on peaks (thereby subtracting any background ²⁰⁴Hg and ²⁰⁴Pb), and because very little Hg is present in the argon gas. Interelement fractionation of Pb/U is generally ~20%, whereas apparent fractionation of Pb isotopes is generally <2%. In-run analysis of fragments of a large zircon crystal (generally every fifth measurement through the course of analyses) with known age of 564 ± 4 Ma (2σ error) is used to correct for this fractionation. The uncertainty resulting from the calibration correction is generally $\sim 1\%$ (2σ) for both 206 Pb/ 207 Pb and 206 Pb/ 238 U ages. The analytical data are summarized in Table 4 and reported in full in the Table S1A–F. Uncertainties shown in these tables are at the 1σ level and include only measurement errors. The reported ages were calculated using Isoplot (Figures 4 and 5) [34].

Table 4. Summary of the U-Pb columbite/cyrtolite geochronological data.

Sample		U (ppm)	²⁰⁶ Pb/ ²⁰⁴ Pb	U/Th	Concordant Age (Ma)	MSDW	PROB	Weighted Mean (Ma)	MSDW	PROB	n
NYSM BCB-COL	Mean SD	620.1 26.7	28,730.2 1405.3	117.0 3.2	372.2 3.4	0.04	0.84	372.2 8.2	0.15	1.00	20
NYSM 25232	Mean SD	315.0 6.1	92,970.4 9769.9	352.3 6.0	372.3 2.8	0.27	0.60	371.3 7.3	0.13	1.00	20
NYSM 22361	Mean SD	647.1 80.1	77,805.3 41,412.8	128.1 12.0	383.6 3.0	0.02	0.88	383.4 8.9	0.37	0.98	15
NYSM CYR	Mean SD	2230 525	238,925 164,168	239 36	376.8 1.2	0.05	0.83	376.9 4.3	0.64	0.73	8
NYSM 525.7	Mean SD	165.5 49.5	106,213.2 72,993.9	32.7 8.7	382 6.4	0.31	0.58	383.0 15	0.15	1.00	14
NYSM 525.8	Mean SD	500.2 4.5	28,854.1 5479.9	80.5 2.5	372.4 3.9	0.03	0.86	372 11	0.35	0.97	12



Figure 4. Weighted averages for columbite samples and cyrtolite analyzed during this study: (**A**) Baylis (NYSM #BCB-COL); (**B**) Kinkel (NYSM #25232); (**C**) Kinkel (NYSM #22361); (**D**) Kinkel (Cyrtolite); (**E**) Harlem River Drive (NYSM #525.7); and (**F**) Fort George (NYSM #525.8). All were analyzed by LA-MC-ICP-MS at University of Arizona in Tucson.

Concordia ages are given for comparison on Tera–Wasserberg diagrams (Figure 5) and are the same as weighted averages within error limits.

Final weighted average age diagrams (Figure 4) show two sigma uncertainties. The smaller uncertainty (labeled Mean) is based on the scatter and precision of the set of 206 Pb/ 238 U or 206 Pb/ 207 Pb ages, weighted according to their measurement errors (shown at 2 σ). The larger uncertainty (final age), which is the reported uncertainty of the age, is determined as the quadratic sum of the weighted mean error plus the total systematic error for the set of analyses. The systematic error, which includes contributions from the standard calibration, age of the calibration standard, composition of common Pb, and U decay constants, is generally ~1–2% (2 σ).



Figure 5. Tera-Wasserberg Concordia diagrams for columbite samples and cyrtolite analyzed during this study: (**A**) Baylis (NYSM #BCB-COL); (**B**) Kinkel (NYSM #25232); (**C**) Kinkel (NYSM #22361); (**D**) Kinkel (Cyrtolite); (**E**) Harlem River Drive (NYSM #525.7); and (**F**) Fort George (NYSM #525.8). All were analyzed by LA-MC-ICP-MS.

Analyses were conducted on large columbite grains or grain fragments mounted in epoxy plugs and polished to yield a significant cross-section through the grain. As noted below, the grains were analyzed in back scattered electron mode and x-ray mapping to find and avoid inclusions and zoning, if present (Figure 3). The sampling strategy involved analyzing transects across each grain from edge to edge, passing through the center, to check for inconsistencies that might arise from zoning, cores, or Pb-loss from rims. Cracks, fractures, inclusions, or other heterogeneities were avoided. Except where noted below, the grains gave concordant analyses which overlapped within uncertainty regardless of where the ablation pit was located.

4. Results

4.1. Major Elements

Electron microprobe (Table 1) and X-ray diffraction data (Figure 2) show that the analyzed columbite-group minerals are columbite-(Fe) and columbite-(Mn). Both species display low Ca and Mg contents and low Ti with exception of NYSM #22361 and #BCB-COL (1.62 and 1.69 Ti, respectively, all in wt. %). The fractionation discrimination ratios [35] of Mn/(Mn+Fe) is 0.31 for the columbite-(Fe) and 0.67–0.69 for columbite-(Mn) and Ta/(Ta+Nb) is 0.05–0.06 for columbite-(Fe) and 0.10–0.17 for columbite-(Mn).

4.2. Trace Elements

Table 2 shows the composition in trace elements determined by LA-ICP-MS in the columbite-group minerals from the pegmatites from southern New York. These minerals are enriched primarily in Zr, W, and U (thousands of ppm), followed by Sn, Pb and Hf (hundreds of ppm). Scandium and especially Th were detected at low concentrations. In general, Zr, Sn, W, Hf, Pb and U are at the lowest concentration in NYSM #525.7. Sc ranges from 8.56 to 72.68 ppm. It has a higher concentration in columbite-(Fe) (30.48 to 72.68 ppm) than in columbite-(Mn) (8.56 to 35.18 ppm). Tin content varies between 97.74 and 499.5 ppm and Pb between 238.6 and 882.5 ppm.

Columbite-group minerals seem to be significant carriers of Zr and Hf, especially in pegmatites where zircon is scarce or very rare; however, only a few studies have measured Zr concentrations in the columbite-group minerals [36]. The same authors reported Hf amounts in columbite minerals from three pegmatites from Canada and one from Sweden. In the samples we analyzed, Zr is found at a higher concentration in columbite-(Fe) (4500 to 4670 ppm) and less in columbite-(Mn) (500.4 to 2622 ppm); Hf follows almost the same trend, 556.4 to 480 ppm in columbite-(Fe) and 71.92 to 406 ppm in columbite-(Mn). The Zr/Hf ratio is 8–10 for columbite-(Fe) and 6–7 for columbite-(Mn).

The results for the REE and Y are in Table 3. Y varies between 170 and 307.4 ppm in columbite-(Fe) and 2104 and 3930 ppm in columbite-(Mn). The light rare earth elements (LREE) in both columbite species are at low concentrations and the middle (MREE) and heavy rare earth elements (HREE) are more abundant with Gd (75.88–264 ppm) to Dy (78.84–824 ppm) group prevalent over Ho (4.12–144 ppm) to Lu (0.13–75 ppm). Columbite-(Mn) is enriched in HREE compared to columbite-(Fe). The incorporation and occurrence of W in columbite-group minerals is not well documented. W is present in significant concentrations, 1726 to 8391.6 ppm, in both columbite-(Fe) and columbite-(Mn) from the New York pegmatites.

4.3. Geochronology

The age of the Bedford pegmatites was determined previously using the Pb/U ratio of "cyrtolite" to be 373 and 381 Ma [37–39]. Similar ages, 360–380 Ma, were obtained by K-Ar and Rb-Sr techniques [38,40]. A summary of the U-Th-Pb columbite ages is presented in Table 4.

4.3.1. NYSM #BCB-COL

This columbite-(Fe) comes from the Baylis quarry and was ca. 5 mm in size. Twenty spots were analyzed and yielded from 578 to 655 ppm uranium. The mean ratio of U/Th was 117. The mean ratio of 206 Pb/ 204 Pb was 28,730. The weighted mean age is 372.2 ± 8.2 Ma (Figure 4A). Results produced a Concordia age of 372.2 ± 3.4 Ma (MSWD = 0.04) (Figure 5A).

4.3.2. NYSM #25232

The specimen analyzed is a 3 mm fragment of columbite-(Fe) from the Kinkel Quarry. Analysis of 20 spots yielded uranium contents between 307 and 331 ppm, a mean U/Th ratio of 352.6 and mean

 206 Pb/ 204 Pb ratio of 92,970. The weighted mean age is 371.3 \pm 7.3 Ma (Figure 4B). The Concordia age obtained is 372.3 \pm 2.8 Ma with MSWD 0.27 and 0.60 probability of concordance (Figure 5B).

4.3.3. NYSM #22361

Fifteen spots from a second columbite-(Fe) fragment, from a different crystal, was analyzed from the Kinkel quarry. The crystal analyzed has uranium contents ranging between 480 and 685 ppm and the mean of the U/Th ratios is 128.14. The mean of the 206 Pb/ 204 Pb ratios was 77,805.4. The weighted mean age is 383.4 \pm 8.9 Ma (Figure 4C). The Concordia age was 383.6 \pm 3.0 Ma with MSWD of 0.02 and 0.88 probability of concordance (Figure 5C).

4.3.4. Zircon- "Cyrtolite" (CYR)

The metamict zircon sample comes from the Kinkel quarry. Uranium content is between 1539 and 3104 ppm, U/Th ranges from 182.7 to 261.7 and the mean ratio of 206 Pb/ 204 Pb is 273,977. The weighted mean age is 376.9 ± 4.3 Ma (Figure 4D). The Concordia age obtained from eight analyses is 376.8 ± 1.2 with a MWSD of 0.05 and probability of concordance of 0.83 (Figure 5D).

4.3.5. NYSM #525.7

A single, small 4 mm crystal of columbite-(Mn), was analyzed from a quartz-microcline-beryl pegmatite sample collected from the intersection of 185th Street and Harlem River Drive. The sample also contained an unknown U-mineral. The area we analyzed contained between 115 and 272 ppm uranium and had a mean U/Th ratio of 32.7. The mean 206 Pb/ 204 Pb was 106,213 for 14 analyses. The weighted mean age is 383 ± 15 Ma (Figure 4E). The Concordia age is 382 ± 6.4 Ma with MSWD 0.31 and 0.58 probability of concordance (Figure 5E).

4.3.6. NYSM #525.8

A 5 mm columbite-(Mn) crystal, was separated from a quartz-microcline-almandine-muscovite pegmatite sample from Fort George. The crystal contained between 494 and 510 ppm uranium with a mean ratio of U/Th of 80.53. The mean of the 206 Pb/ 204 Pb ratios was 76,726 for 12 analyses. The weighted mean age is 372 ± 11 (Figure 4F). The Concordia age is 372.4 ± 3.9 Ma, with MSWD of 0.03 and probability of concordance of 0.86 (Figure 5F).

5. Discussion

Columbite-group minerals have the general formula AB_2O_6 where Fe, Mn, Mg, Nb, and Ta are the main constituents and the significant range of substitutions between these components contributes to the occurrence of the three species of the group mentioned above. The substitutions of Mn for Fe and Ta for Nb are used to define the fractionation trend in the rare-element granitic pegmatites. High Mn/(Mn+Fe) and Ta/(Ta+Nb) ratios characterize the more fractionated pegmatites [40]. The calculated ratios (Table 1) show that the pegmatites from New York City are somewhat more fractionated compared with those from Bedford.

The trace elements Sc, Zr, Hf, and REEs are incorporated into the columbite structure in different amounts by coupled substitutions. Scandium is incorporated through the coupled euxenite-type substitution, $Sc^{3+} + (Ti,Sn)^{4+} = (Fe,Mn)^{2+} + (Nb,Ta)^{5+}$. Scandium resides in the A-site where it substitutes preferentially for Fe because of their closer charge and ionic radius. The other two components of the coupled substitution, Sn and Ti, partition into the B-site [41]. Zr and Hf occur in significant concentrations in both New York City and Bedford pegmatites and Zr/Hf ratio is medium (9.73 in NYSM #22361) to low (6.95 in NYSM #525.7) which is common for less evolved NYF pegmatites lacking zircon. The enrichment of Zr and Hf in columbite is typical for the highly fractionated pegmatites of the lithium-cesium-tantalum (LCT) family [35]. The metamict zircon, "cyrtolite", occurs in the Kinkel pegmatite and displays 54,100 ppm Hf. The incorporation of relatively significant amounts of Zr and Hf in the columbite-group minerals we analyzed could be the result of: (a) little appreciable difference in the partitioning of these elements in zircon or columbite-minerals [35]; or, possibly, (b) columbite and zircon ("cyrtolite") formed from different melt batches. Unfortunately, a thorough description of the occurrence of these two minerals is missing from literature and New York State Museum database and remains unresolved.

The REEs substitute in six-fold coordination and are incorporated into the columbite-group minerals by two types of coupled substitutions: (a) euxenite-type $A^{2+} + B^{5+} = Ln^{3+} + Ti^{4+}$; and (b) samarskite-type $2A^{2+} + B^{5+} = 3(La + Fe)^{3+}$ [35,42]. The REE/chondrite diagrams (Figure 6) display three types of patterns for columbite-(Fe) and columbite-(Mn).



Figure 6. Chondrite-normalized rare earth element plots for columbite samples analyzed: (**A**) Baylis (NYSM #BCB-COL); (**B**) Kinkel (NYSM #25232); (**C**) Kinkel (NYSM #22361); (**D**) Kinkel (Cyrtolite); (**E**) Harlem River Drive (NYSM #525.7); and (**F**) Fort George (NYSM #525.8). Red line on each diagram is average REE concentrations for Kinkel cyrtolite for comparison.

The first type represented by the REE pattern for columbite-(Fe) shows an ascending plot line for the LREE_N from La to Sm, strong negative Eu anomaly, a "dome" of the middle REE (MREE_N) and a descending trend for the HREE_N (Figure 6A–C). The MREE_N are higher than the HREE_N. The second type of REE pattern is shown by columbite-(Mn), NYSM 525.7 (Figure 6E). It is like that of "cyrtolite" (Figure 6D) displaying an ascending trend for the LRRE_N, negative Eu anomaly and MREE_N slightly dominating over the HREE_N. NYSM 525.8 shows an ascending trend from La to Sm,

negative Eu anomaly, and another ascending trend for the $HREE_N$ (Figure 6F) that dominate over the $MREE_N$. These different REE patterns probably describe the degree of evolution of the pegmatites [42], thought to be relatively low due to the small concentrations of LREEs. However, LREEs may also be preferentially excluded from lattice sites in the columbite-group minerals due to their greater size. The "cyrtolite"/chondrite diagram (Figure 6D) shows the LREE_N at low concentrations with an almost flat plateau between Ce and Nd. Other characteristics include positive Sm anomaly, negative Eu anomaly suggesting a significant plagioclase crystallization in the parent melt, and a dome for the group Gd to Ho. The Ho- to Lu group is on a flat plateau.

As shown in Table 4, the U-Pb columbite geochronology displays a narrow range of weighted mean ages: 372.2 ± 8.2 Ma for the Baylis Quarry, 371.3 ± 7.3 and 383.4 ± 8.9 Ma for the Kinkel Quarry, and 383 ± 15 and 372 ± 11 Ma for New York City pegmatites. In addition, "cyrtolite" yielded a U-Pb weighted mean age of 376.9 ± 4.3 Ma. Although two samples of columbite and one of cyrtolite from the Kinkel Quarry differ in age by 12 million years (371.3-383.4 Ma), the data are not precise enough to determine if this age range represents true analytical error or two pegmatite intrusion events. This range of ages indicates that emplacement of the pegmatites occurred during the Neoacadian orogeny (395 to 360 Ma) [43]. The age of the southern New York pegmatites is consistent with the older group of LCT-type pegmatites along the Appalachians [44,45]. The LCT pegmatites display two groups of ages: (a) 371 Ma; and (b) 274–264 Ma [44]. We consider the pegmatites to be related to the Neoacadian magmatism known in the northern Appalachians. The New York pegmatites appear to represent the southernmost expression of the Neoacadian orogeny in New England.

Several characteristics suggest some columbite crystals may have potentially as a U-Pb isotopic standard for oxide mineral analysis. Columbite-group minerals have a simple formula with limited solid solution and often form large chemically and isotopically homogeneous crystals. In terms of U-Pb geochronology, columbite excludes common-Pb during crystallization (high 206 Pb/ 204 Pb ratios) and has sufficient uranium concentrations to accumulate radiogenic Pb over geologic time, even within the late Paleozoic samples analyzed here. In fact, the variation in U-content determined by LA_MC-ICP-MS in some samples is quite limited (Table 4). For example, twelve analyses of sample #525.8 yields a uranium concentration and standard deviation of 500.2 ± 4.5 ppm. Further work defining the extent of chemical and isotopic variation, metamictization, and blocking temperatures will determine the limits of columbite's use in geochronological and isotopic studies.

6. Conclusions

The NYF-pegmatites from southern New York were intruded into Manhattan Schist of Lower Cambrian or Upper Proterozoic age and Bedford gneiss of probable Ordovician age. The two columbite species, columbite-(Fe) and columbite-(Mn), do not show significant differences in their trace element composition and, according to the discriminant fractionation ratios, Mn/(Mn+Fe) and Ta/(Ta+Nb), the pegmatites containing columbite-(Mn) seem to be slightly more fractionated than those containing columbite-(Fe). U-Pb columbite geochronology by LA-MC-ICP-MS yields a narrow range of ages (371.3 \pm 7.3 to 383 \pm 15 Ma). This indicates emplacement during the Neoacadian orogeny rather than the Taconic orogeny, and is consistent with ages from LTF pegmatites from the Appalachians. The U concentration, common Pb content, and internally homogeneous chemistry of columbite are favorable for using columbite in radiometric dating when zircons are lacking or metamict or for fingerprinting of conflict minerals.

Supplementary Materials: The following are available online at www.mdpi.com/xxx/s1, Figure S1: Weighted averages for columbite samples and cyrtolite analyzed during this study, Table S1: Detailed U-Pb geochonological data.

Author Contributions: M.V.L. provided the samples, analyzed them for U-Pb geochronology with J.R.C. and S.P.R., acquired EMP and LA-ICP-MS data with J.W.S., and wrote the article. J.R.C. wrote with M.E.P. the geochronology part, corrected and edited the article and provided the images. J.W.S. wrote the EMP and LA-ICP-MS methods.

Funding: This work was funded by the New York State Museum (M.V.L.), the James Street Fund at St. Lawrence University (J.R.C.), and by the National Science Foundation NSF for support of the lab at Arizona Laserchron Center (NSF-EAR #1649254).

Acknowledgments: The authors thank the staff at the Arizona Laserchron Center for their help with sample preparation and analysis, Ryan McAleer for internal USGS review, two anonymous reviewers for their helpful suggestions, and the Assistant Editor that handled the manuscript throughout the editorial process.

Conflicts of Interest: The authors declare no conflict of interest.

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