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**DIAGENETIC APATITE CHARACTER AND IN-SITU ION MICROPROBE U-Pb AGE, KEESEVILLE
FORMATION, POTSDAM GROUP, NEW YORK STATE.**

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ABSTRACT

An occurrence of diagenetic fluorapatite cement is documented within the Cambro-Ordovician Keeseville Formation, Potsdam Group, near Chateaugay in New York State. The fluorapatite cement occurs as stratiform layers within ephemeral fluvial quartz arenites, which have been reworked by aeolian processes prior to burial. The paragenetic sequence includes: compaction of dust-rimmed grains → quartz cementation → minor kaolinite → fluorapatite cementation followed by secondary dissolution porosity and telogenetic hematite cementation. Mesogenetic illitization of kaolinite may have taken place prior to or following fluorapatite cementation. The fluorapatite occurs as elongated bladed crystals that characteristically contain ladder-like, inclusion-rich cores running parallel to crystal length, surrounded by clearer rims, and larger blocky crystals towards the middle of interstices. In-situ SHRIMP analyses of blocky fluorapatite crystals yield a U-Pb age of 486 ± 29 Ma, indicating that the cement formed during mesogenetic burial processes and/or during fluid flow driven by Taconic orogenic events. There is no obvious source of phosphorous for the fluorapatite cement within the Potsdam Group but phosphorous-rich lithologies are known from the adjacent basement of the Adirondack Dome. Phosphorous-rich fluids may have been derived from these basement lithologies. The occurrence of the rare fluorapatite cement in the Keeseville Formation adjacent to the Chateaugay Lake Fault raises the possibility that alkaline phosphatic fluids were focused within the fault and migrated laterally away from the fault into the host Keeseville Formation to form stratiform fluorapatite cement in the sandstone.

Key Words: Fluorapatite , Diagenetic , Keeseville Formation , U-Pb age

INTRODUCTION

The siliciclastic Lower Cambrian to Lower Ordovician Potsdam Group and its attendant stratigraphic subdivisions, including the Keeseville Formation, has been the focus of numerous studies for at least 170 years (from Emmons 1838, to Sanford and Arnott 2010). The majority of these studies have focussed on the stratigraphy, correlation and depositional paleoenvironment of the Potsdam Group. There have been relatively few studies, however, documenting Potsdam Group diagenesis (Selleck 1978, 1993, 1997; Salad Hersi et al. 2002) and, more particularly, diagenetic apatite cement in the siliciclastic Keeseville Formation. Recent work by Lowe et al. (2015) in the Keeseville Formation of northern New York has identified apatite cement that had not been previously noted within the Potsdam Group. Selleck (2005) noted hydrothermal conduits and carbonate, sulphide, oxide and phosphate (including apatite) alteration minerals in the Potsdam Group within the Richville Shear Zone, Adirondack Lowlands.

Phosphate cements are most commonly described in Ediacaran-Cambrian and younger Phanerozoic marine sedimentary rocks (more commonly in shales and carbonates than in coarser siliciclastics), less so in terrestrial sedimentary rocks, typical of the Keeseville Formation, and are uncommon in the Proterozoic (McKelvey 1973; Cook and McElhinney 1979; Glenn et al. 1994; chapters in Bentor 1980; Notholt et al. 1989). However, a few occurrences of apatite cement in terrestrial arenites have been documented, predominantly in Proterozoic units (e.g., Chandler 1988; Rainbird et al. 2003; Gall and Donaldson 2006). Although apatite is not a common diagenetic cement, it typically has elevated uranium and radiogenic lead contents that

make it useful for dating the time of diagenesis in the hosting strata (e.g., Chandler and Parrish 1989; Harrison et al. 2002; Davis et al. 2011).

This study addresses three facets of the Potsdam Group Keeseville Formation in northern New York State which have not been previously described to any great extent: (1) diagenesis in the terrestrial quartz arenites; (2) the characteristics of the apatite cement; and (3) the age of diagenetic apatite cement. The focus of the study is documenting the unusual apatite cement morphologies, the apatite composition and the age of the apatite cement based on in-situ ion microprobe U-Pb geochronology analyses.

REGIONAL AND LOCAL GEOLOGIC SETTINGS

Regional

The Potsdam Group is interpreted to have been deposited between the Late Cambrian and Early Ordovician (Landing et al., 2009; Lowe and Arnott, 2016) on the flanks of Precambrian highlands in the central part of the more extensive northeast-trending St. Lawrence Platform (Poole et al. 1970) following the tectonic breakup of southeastern Rodinia (Laurentia) and the formation of the Iapetus Ocean. In the central part of the St. Lawrence Platform, at least 630 m (Lowe 2016) of Potsdam Group sandstones and conglomerates were deposited in the Quebec Basin and, to the west, in the Ottawa Embayment (Fig. 1). The Potsdam Group is primarily comprised of conglomerates and sandstones, which unconformably overlie Mesoproterozoic metamorphic and igneous terranes of the Grenville Province, and are overlain by interbedded sandstones and dolostones of the various Early Ordovician Beekmantown Group stratigraphic

units. The Potsdam Group generally records terrestrial to marine deposition within the Sauk Megasequence (Sloss 1963, 1988; Bally 1989; Lavoie 2008; Lowe 2016; Low and Arnott 2016).

The Potsdam Group consists of a number of formations assigned different names depending on their geographic location. Of concern in this paper is the stratigraphic nomenclature for northern New York State (Fig. 2). According to the stratigraphic framework of Selleck (1993), Landing et al. (2009), Sanford and Arnott (2010) and recent stratigraphic revision by Lowe et al. (in press), the Potsdam Group in northeastern New York State is comprised of the lowermost Ausable Formation and overlying Keeseville Formation. The Ausable consists of pebbly arkose and pebble to boulder orthoconglomerate with an arkose matrix unconformably overlying the various Mesoproterozoic lithologies of the Central Metasedimentary Belt of the Grenville Province. Near the base of the Ausable Formation in the eastern part of the Ottawa Embayment and in the Quebec Basin are intertonguing, bioturbated arkose, mudstone, siltstone and biolaminated dolostone of the Altona Member. Yet to be identified in the eastern Ottawa Embayment and Quebec Basin is quartz arenite of the Hannawa Falls Formation which, elsewhere, overlies the Ausable Formation. The uppermost unit of the Potsdam Group is the Keeseville Formation, consisting of subordinate basal conglomerate and more extensive quartz arenite that unconformably rest on the Ausable Formation and, locally, Grenville Province lithologies. Abundant but low diversity trace fossils have been identified in the Keeseville Formation (Lowe 2016) as well as minor pebble conglomerate, silty mudstone and rare dolostone. The Keeseville Formation is conformably or unconformably overlain by interbedded and bioturbated dolomite-cemented sandstone and silica-cemented sandstone of the Theresa Formation (Beekmantown Group).

Lowe et al. (in press) recognized three unconformity-bound units (Fig. 2, their allostratigraphic units) corresponding with distinct episodes of regional sedimentation. Episode 1, comprised of the Ausable and Hannawa Falls formations, reflects Early Cambrian terrestrial sedimentation in fault-bounded sub-basins temporarily interrupted by marine transgression in the east (Altona Member). Episodes 2 (Middle Cambrian to Early Ordovician) and 3 (Early Ordovician) are, respectively, represented by transgression-regression and then transgression sequences in the overlying Keeseville Formation.

These Potsdam Group stratigraphic units can be correlated, in part using the aforementioned unconformity-bound units, with similar units along the St. Lawrence Platform (e.g., Williams 1991; Lavoie et al. 2003; Sanford and Arnott 2010; Lowe et al, in press). However, of specific interest here is that the Keeseville Formation in New York State is correlated with the lithologically similar and age-equivalent Nepean Formation in eastern Ontario and the Cairnside Formation in western Québec. Recently, Lowe et al. (in press) proposed that the Canadian formation names (Nepean and Cairnside) be abandoned and replaced by the Keeseville Formation. These predominantly siliciclastic formations were deposited in shallow marine, shoreline, aeolian and fluvial environments (Wolf and Dalrymple 1985; McRae and Johnson 1986; Selleck 1997; Hagadorn et al. 2011; Sanford and Arnott 2010; Lowe et al. 2015, Lowe and Arnott 2016). Redeposited deep-marine equivalents (Karmouraska Formation) have been identified recently by Malhame and Hesse (2015) in eastern Québec.

The base of the Keeseville Formation in northern New York might be slightly older than equivalent formations elsewhere in the Ottawa Embayment, as deposition of the Potsdam

Group is believed to be progressively older from north to south (Hagadorn and Belt 2008; Sanford and Arnott 2010; Lowe 2016; Lowe and Arnott 2016). Epoch 3 Cambrian trilobites (representing the *Crepicephalus* and *Cedaria* Zones) were collected near the base of the Keeseville Formation (Flower 1964; Landing et al. 2007, 2009). Upper Cambrian trilobites were collected from strata higher in the Keeseville Formation (Fisher 1968) in New York State. A Late Cambrian paleopole was obtained by Seguin et al. (1981) from equivalent Cairnside Formation sandstone near Montreal. Finally, earliest Ordovician (Tremadocian stage) conodonts were collected from the Rivière Aux Outardes Member by D. Lowe and B. Arnott (Nowlan 2013; Lowe 2016). Based on the Geologic Time Scale 2012 (Gradstein et al. 2012), the Keeseville Formation was deposited between Epoch 3 Cambrian (509.0 to 497.0 Ma; Peng et al. (2012)) and Early Ordovician (Tremadocian, 485.4 to 477.7 Ma; Cooper and Sadler (2012)).

Local

Within New York State, the Keeseville Formation varies from 8.8 m (Blind Bay area) to about 180 m (Ausable Chasm area) in thickness going west to east (Sanford and Arnott 2010; Lowe 2016). It generally consists of white to light grey mature quartz arenite, primarily composed of quartz grains surrounded by quartz cement with little to no finer detrital or authigenic material; and was deposited in both terrestrial and marine environments (Hagadorn and Belt 2008; Sanford and Arnott 2010; Lowe et al. 2015; Lowe 2016). Quartzite framework conglomerate with quartz arenite matrix occurs locally (Lowe et al. 2015; Lowe and Arnott 2016). Paleocurrent indicators and detrital zircon chronology indicate the majority of the Keeseville Formation was derived from local and distal Grenville Province highlands to the

(present day) south, west and northwest (Adirondack Dome – Frontenac Arch - Central Metasedimentary Belt) and even further to the west and north (Central Gneiss Belt terranes), as well as reworking of the underlying Ausable Formation (Chiarenzelli et al. 2010; Lowe et al. 2015; Lowe 2016).

Detailed Keeseville Formation stratigraphy in the Chateaugay area, New York State, by Lowe et al. (2013, 2015), Lowe (2016) and Lowe and Arnott (2016), have identified a 12 m sequence of planar stratified sandstone containing inverse-graded wind ripples and coarse deflation lags, interlayered with low-angle cross-stratified sandstone with scoured bases recording the migration of supercritical bedforms (antidunes, chutes-and-pools and cyclic steps) under high-energy sheetflood conditions. Lowe (2016) and Lowe and Arnott (2016) include this sequence within their facies association 2 (FA2), which they describe as sheet flood dominated ephemeral fluvial deposits. FA2 likely represents mainly ephemeral fluvial sheetflood deposits (terminal splays) reworked by aeolian deflation within a semi-arid terrestrial environment. The apatite-bearing sandstone samples collected for this study are from the FA2 sequence. Although not exposed in the sampling area, the FA2 succession overlies FA1 cross-bedded braided fluvial sandstones exposed 200 m up-river at the Chateaugay High Falls. Furthermore, Lowe (2016) and Lowe and Arnott (2016) have placed the sample site in the upper part of the Keeseville Formation within the Potsdam Group unconformity-bound unit 3 (Fig. 2).

SAMPLE DESCRIPTION

The Keeseville Formation samples are from continuous outcrop along the Chateaugay River, approximately 5 km south of Chateaugay, New York State. They were collected from a

steep river-side outcrop on the west side of the river just a few hundred metres north of where Pulp Mill Road crosses the river (Fig. 3; UTM 572037E 4973136N NAD 83 zone 18). The outcrop consists of light grey, planar bedded arenite with common inversely graded wind ripple lamination and deflation lags. The apatite cement occurs as planar stratiform layers, ≤ 4 cm thick, that tend to follow bedding for many metres before pinching out within a sandstone bed (Figs. 4a and 4b). Hand samples of the apatite-cemented arenite (Fig. 4c) have a medium beige fresh colour and a light pinkish-brown weathered colour.

For the arenite in general (lacking apatite cement), grain size varies from fine to coarse sand with subordinate scattered granule-size grains. The grains are rounded to well-rounded, and generally well sorted within individual layers. Point count data (minimum of 130 points on nine thin sections) reveals a mineralogy of: quartz (range 63.1% to 75.6%; 7.7% polycrystalline 92.3% monocrystalline), orthoclase ($\leq 2.4\%$), quartz cement (range 8.7% to 23.7%), kaolinite / illite (range 0.7% to 11.0%), hematite cement (range 1.5% to 6.3%) and trace amounts ($<1\%$) of zircon, tourmaline, garnet and biotite grains are also present. None of the samples contained distinct lithic fragments; although many of the polycrystalline quartz grains containing a shear fabric or foliation suggesting that they may have been eroded from Mesoproterozoic lithologies in the Adirondack Dome (supported by local paleocurrent data and detrital zircon ages documented by Lowe et al. (2013), Lowe (2016) and Lowe and Arnott (2016)). All samples plot within the quartz arenite field of Gilbert (in Williams et al. 1982).

Paragenesis

The paragenetic sequence developed in the terrestrial Keeseville Formation samples from this study is shown in Fig. 5. This sequence is based on petrographic observation of overlapping or cross-cutting mineral relationships in the study samples. Detrital grains of monocrystalline and polycrystalline quartz exhibiting faint “dust rims” of hematite and/or undistinguishable clays, and primarily concavo-convex with fewer tangential grain-grain contacts. The quartz grains are commonly overgrown by syntaxial quartz cement that can occlude all interstitial space (Fig. 6a). The scarcity of diagenetic kaolinite makes its relative paragenesis equivocal; however, in a few places, it appears to have grown across the quartz cement boundaries (Fig. 6b). Fibrous illite replaces some kaolinite (Fig. 6c), and fills microfractures in the quartz grains. Fluorapatite cement (first bladed then blocky) is superimposed on grain boundaries, “dust rims”, quartz cement and illitized kaolinite. The fluorapatite cementing fluids had the ability to corrode grains and replace earlier diagenetic minerals. Both the quartz and fluorapatite cements are overprinted by late hematite cement (Fig. 8c).

As described, where apatite cement does not obscure the grain-grain contacts, most are concavo-convex with minor tangential contacts. There are many more grain-grain contacts in apatite-poor layers; whereas in apatite-rich layers the apatite cement has corroded and surrounded the grains to the extent that they appear to be suspended in the apatite cement (Figs. 7a and 7b). The contacts between the apatite-rich and apatite poor layers are abrupt and parallel to local bedding (Figs. 4c and 8a).

Up to 15% intergranular dissolution secondary porosity was identified in the quartz arenite samples. Most of the secondary porosity occurs within the apatite-poor layers (64% to 78%) primarily due to quartz cement dissolution but also, to a lesser extent, due to quartz grain dissolution. A lesser minor amount of secondary porosity (22% to 36%) occurs within the apatite-rich layers due to apatite cement dissolution (Fig. 8b). These relationships indicate that secondary porosity developed after apatite cementation, but primarily due to quartz cement dissolution.

Apatite cement

Generally, the apatite is colourless in thin section and has a typical first order grey birefringence. Two forms of apatite crystals were recognized by microscopic examination, cathodoluminescence (CL) and back-scattered electron (BSE) imaging. The first crystal form is referred to as bladed and the second as blocky, and the transition between the crystal forms is gradational. All samples contained both crystal morphologies, but some samples contain more of one crystal morphology than the other. From the SEM-BSE and CL imaging, individual bladed or blocky apatite crystals show no apparent internal zoning, however it is obvious that darker bladed crystal cores were overgrown by blocky forms exhibiting lighter shade.

Bladed crystals (Figs. 7c and 7d) are elongated and often contain ladder-like dark cores running parallel to crystal length, surrounded by a clearer / lighter rim. The majority appear to have nucleated on and grown perpendicular to grain boundaries. Overall, near grain edges, the bladed crystals tend to be smaller and increase in size away from the grains (e.g., Figs. 7b and 7c). Bladed crystals can reach up to 150 μm in length and average 15 μm in width.

Blocky crystals (Figs. 7d and 7e) are nearly equidimensional. Those close to grain boundaries are small (5 μm minimum) and are often mingled with bladed morphologies. Large blocky crystals are commonly found away from grain edges towards the middle of the interstices. These blocky cements can reach up to 170 μm in diameter, and proved to be better targets for the in-situ ion microprobe analyses.

ANALYTICAL METHODS

Electron microprobe

The JEOL 8230 electron microprobe at the University of Ottawa was used in wavelength dispersive mode to collect 50 apatite cement analyses. Operating conditions included: an acceleration voltage of 20kV, a beam current of 10 nA and a defocused analytical beam diameter of 10 μm . Durango apatite was used as a primary standard. Additionally, the University of Ottawa's JEOL 6610LV and the Geological Survey of Canada's EVO50 scanning electron microscopes were used in cathode luminescent and back-scatter electron modes to image the apatite cement's textural variations, to detect zoning and to guide in-situ ion microprobe analyses.

Ion Microprobe

The SHRIMP ii at the J.C. Roddick Ion Microprobe Laboratory, Geological Survey of Canada, was used to collect U-Pb isotopic data. Three polished thin sections of apatite-cemented sandstone were prepared and areas of interest identified by SEM were cored and mounted together with a reference apatite BR5 ($^{206}\text{Pb}^*/^{238}\text{U}$ age= 2040 Ma; A. Kennedy pers. comm.). Mount surfaces

were evaporatively coated with 10 nm of high-purity Au. Analyses were conducted using an $^{16}\text{O}^-$ primary beam, projected onto the surface at 10 kV. The sputtered area used for analysis was ca. 20 μm in diameter with a beam current of ca. 4 nA. Count rates at nine masses were sequentially measured over 7 scans with a single electron multiplier and a pulse counting system with dead time of 25 ns. The instrument was tuned to achieve a mass resolution of ~ 5500 (1%) and no isobaric interferences were noted over the Pb mass range (e.g., Sano et al. 1999). Off-line data processing was accomplished using SQUID2.5 with the U-Pb calibration based on the linear relationship between $\ln[^{206}\text{Pb}^*/^{254}\text{UO}]$ and $\ln[^{270}\text{UO}_2/^{254}\text{UO}]$ with a slope of 2. The unknown samples analysed have different compositions relative to the standard used (higher uranium, lower Th), and a small matrix effect may be indicated by differences in measured average $^{270}\text{UO}_2/^{254}\text{UO}$ between samples and standard. The 1σ external errors of $^{238}\text{U}/^{206}\text{Pb}$ ratios incorporate a $\pm 1.0\%$ error determined for the reference mineral. No fractionation correction was applied to the Pb-isotope data. As the proportion of common Pb in the analyses is quite large (14-80%) the Total Pb/U-Isochron method (Ludwig, 1998) based on three-dimensional regression of the measured $^{207}\text{Pb}/^{206}\text{Pb}$, $^{238}\text{U}/^{206}\text{Pb}$ and $^{204}\text{Pb}/^{206}\text{Pb}$ ratios and uncertainties was used to determine the age of the apatite (Isoplot v. 3.00; Ludwig 2003). The error ellipses on the Tera-Wasserburg concordia diagram are reported at 2σ .

RESULTS

Electron Microprobe Analyses

Fifty analyses (23 bladed- and 27 blocky-crystals), evenly distributed between four polished thin sections, were collected on apatite cement crystals (Table 1 and supplemental

data). The analyses show little variation in composition and yield fluorapatite for both crystal forms. As seen in Table 1, the fluorapatite contains approximately 4 wt% fluorine and extremely low to no detectable chlorine. On average CaO, P₂O₅ and F make up 99.83 wt% of the blocky morphologies and 98.61 wt% of the bladed morphologies. The bladed fluorapatite cement contains more impurities on average than blocky fluorapatite cement. The most significant differences are the higher SiO₂, Al₂O₃, FeO and K₂O concentrations in the bladed fluorapatite than the blocky fluorapatite. These oxides can be present in significant amounts, but always below 0.5 wt%, and are likely inclusions of precursor material. Rare earth elements in both crystal morphologies are below analytical detection limit.

Ion Microprobe Analyses

U-Th-Pb isotopic data are presented in Table 2. U and Th contents of the apatite cements were not quantitatively determined, however based on variable U count rates the cements have variable U content but uniformly low Th.

Seventeen analyses yield a range of isotopic compositions with the proportion of common Pb varying from 14% to 80%. Owing to the very large common Pb corrections, calculated ages for individual analyses are very sensitive to the composition of common Pb in the analyses. As there is no independent estimate of the common Pb value the data were evaluated using the Total Pb/U-Isochron method (Ludwig, 1998), which uses a three-dimensional linear regression of the measured ²⁰⁷Pb/²⁰⁶Pb, ²³⁸U/²⁰⁶Pb and ²⁰⁴Pb/²⁰⁶Pb ratios. In addition to determining the age from the intersection of the three-dimensional regression with the Concordia curve, this method also determines the composition and uncertainty of the

common Pb. The data define a three-dimensional linear array with a concordia intercept age at 486 ± 29 Ma (MSWD = 1.6) and calculated common $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ values of 19.6 ± 2.6 and 16.1 ± 1.6 , respectively (Fig. 9). The calculated common Pb value is within uncertainty of the Stacey-Kramer (1975) model composition at that age, indicating that the common Pb value has average crustal values and is not anomalous. A similar age of 491 ± 36 Ma is determined using the SemiTotal-Pb/U isochron approach anchored at the Stacey and Kramers (1975) model $^{207}\text{Pb}/^{206}\text{Pb}$ ratio for 500 Ma. The 486 ± 29 Ma age is taken as the best estimate for the time of diagenetic apatite cementation in the rock.

DISCUSSION

The apatite cement described in this paper is notable for a couple of reasons. First, at the basin scale in general, phosphatic minerals in sedimentary rocks are most commonly associated with marine phosphorite deposits (chapters in: Bentor 1980; Burnett and Riggs 1986; Glenn et al. 2000; Nelson et al. 2010), lacustrine deposits (Swirydczuk et al. 1981; Stamatakis and Koukoulzas 2001), guano deposits (Cook 1984) and weathering profiles (Nriagu 1976; Flicoteaux and Lucas 1984; Dahanayake and Subasinghe 1989); not with terrestrial quartz arenites as documented here. Furthermore, the fluorapatite cement within the Keeseville Formation is rare and, to the authors' knowledge, has not been previously documented within the Potsdam Group.

At the microscopic level, the dark-cored (inclusion-rich) bladed morphology of the apatite in the Keeseville Formation is uncommon, with the only other similar occurrence described by Gall and Donaldson (2006), and dated by Davis et al. (2011), in the Proterozoic

Thelon Formation, Nunavut (Fig. 7f). Interestingly, the fluorapatite cement in both the Keeseville and Thelon formations formed within terrestrial quartz arenites and the fluorapatite morphologies (ladder- bladed followed by blocky cements) and paragenesis (post-quartz cementation) are similar. In the Keeseville Formation occurrence, the bladed fluorapatite has dark, ribbed cores with elevated elemental Si, Al, Fe and K surrounded by a rim of clear fluorapatite which, in turn, is overgrown by blocky, limpid pure fluorapatite. In the Thelon Formation occurrence, early bladed fluorapatite contains dark, ribbed cores with elevated elemental C, S and Cl, followed by blocky, limpid pure fluorapatite. In both occurrences, early bladed fluorapatite cement appears to have engulfed minor amounts of matrix material as it grew from the grain boundaries into the interstices in these matrix-poor quartz arenites. Once the scarce matrix was entombed within the bladed fluorapatite, the cement morphology changed to a blocky, pure fluorapatite. A similar explanation for a change in apatite cement morphology has been used by Hollocher et al. (2005) to account for brown bladed and radiating masses of apatite in coprolite from the Upper Triassic Ischigualasto Formation. They attribute the apatite colour to inclusion of organic material as the bladed apatite grew. Other apatite cement in the Ischigualasto Formation is nearly colourless and blocky.

Paragenesis

The fluorapatite cement is found within mineralogically- and texturally-mature matrix-poor quartz arenite; part of a succession that Lowe (2016) and Lowe and Arnett (2016) ascribe to a semi-arid ephemeral fluvial depositional environment reworked by aeolian processes (their facies assemblage FA2). Apart from the fluorapatite cement, the diagenetic mineral

paragenesis (quartz cement → kaolinite → illite → hematite cement) is common in sandstones deposited in semi-arid terrestrial environments and reflects time-temperature changes in fluid compositions from high silica, low-pH modified meteoric burial fluids, to deeper alkaline mesogenetic fluids and, finally, late telogenetic oxidized fluids (e.g., McBride 1989; Worden and Burley 2003; Worden and Morad 2003).

In one of the very few descriptions of Potsdam sandstone diagenesis in New York, Selleck (1993) also recognized early quartz cementation followed by illite and kaolinite formation and late hematite cement. Salad Hersi et al. (2002) identified telogenetic pendant and chalcedonic quartz cement in the equivalent Cairnside Formation sandstone in the northern part of the Ottawa Embayment and the Quebec Basin; but this style of quartz cement was not found in the samples from the Chateaugay area of New York State.

Although kaolinite is a common eogenetic clay formed in warm and wet environments by meteoric fluids, the Keeseville Formation kaolinite appears to post-date quartz cementation. Two plausible explanations exist: (a) that booklets of eogenetic kaolinite were redistributed interstitially during mesogenetic quartz cementation; or (b) kaolinite formed from detrital feldspar in adjacent strata during meteoric water influx from ephemeral rivers (Worden and Morad 2003) and illuvial processes carried it into the FA2 strata. This later explanation fits with Lowe and Arnett's (2016) FA2 depositional environment model. Illitization of kaolinite is also common in late-stage burial diagenesis, and is often attributed to an influx of potassic (alkaline) fluids (e.g., Dunoyer de Segonzac 1970; Hower et al. 1976; Hancock and Taylor 1978; Nesbitt and Young 1989). The presence of minor illitized kaolinite within the Keeseville Formation

followed, more locally, by fluorapatite cement, suggests that the evolved mesogenetic fluids affecting the silica-cemented FA2 quartz arenites had become more alkaline. Stability studies of fluorapatite (e.g., Antignano and Manning 2008; Bengtsson et al. 2009; Zhu et al. 2009) and detrital apatite in North Sea sandstones by Nickel (1973), Morton (1986) and Walderhaug and Porten (2007), suggest that apatite and, by inference the Keeseville Formation fluorapatite cement, could have formed from pH 8 mesogenetic fluids and could have been stable over a large range in burial depths (i.e., once the quartz arenite was removed by burial from the near-surface meteoric groundwater eogenetic realm). It is possible that illitization of the kaolinite did not precede fluorapatite cementation but, in fact, followed fluorapatite cementation (hence “?” in Fig. 5).

Interestingly, Selleck (1993) suggests that the illite and hematite in the lower Potsdam sandstone are Early Carboniferous, or Late Paleozoic, based on K-Ar dates (illite) and paleomagnetic data (hematite) and, furthermore, that late tectonic disturbances (Acadian-Alleghanian) may have triggered craton-ward diagenetic brine flow. Dating of authigenic illite from Potsdam sandstone in northwestern New York by Reynolds and Thomson (1993) yielded ages of ca. 360 Ma and 392 Ma. Subsequent studies by Ziegler and Longstaffe (2000a, 2000b) also indicate that the secondary illite in Paleozoic strata of SW Ontario and the Ottawa Embayment could have formed from the influx of low temperature (40-55°C) meteoric water from the Algonquin and Frontenac arches respectively, in conjunction with potassic brine migration activated by Appalachian orogenic pulses to the east. We cannot rule out that the illitization of kaolinite in samples from this study occurred after fluorapatite cementation. However, based on physical relationships alone (overprinting or cross-cutting diagenetic

mineral phases), the illitized kaolinite identified in the Keeseville Formation from this study appear to pre-date the Late Cambrian - Early Ordovician fluorapatite cement and the late-stage hematite cement.

Monazite and xenotime overgrowths on detrital monazite and zircon within basal sandstone of the Potsdam Formation have been identified and dated by Allaz et al. (2013). The formation of the overgrowths is attributed to local dissolution and reprecipitation of detrital phosphates (monazite) by diagenetic or low-grade metamorphic fluids. Diagenetic apatite with low REE content was not documented. Allaz et al. (2013) proposed five discrete monazite and xenotime overgrowth events at 505, 460, 420, 370, and 225 Ma, which they attributed to early diagenesis (505 Ma), followed by four episodic paleo-fluid-flow events driven by Appalachian orogenic events to the east. Two of their sample sites (EC and LM) are close to the Chateaugay fluorapatite occurrence. Monazite overgrowths from these sites are dominated by the 420 and 370 Ma age groups (Salinic to Acadian), however distinctly older ages are also documented at 505 and 460 Ma. The older events were ascribed to early diagenetic processes (505 Ma) and to a later fluid flow event driven by Taconic loading to the east. Owing to relatively large uncertainties in the ages reported by Allaz et al. (2013) and this study, it is not possible to discriminate the timing of these proposed events from the 486 ± 29 Ma age reported for the fluorapatite cement in the Keeseville Formation. As such the fluorapatite may relate to mesogenetic burial processes and/or to fluid flow driven by Taconic orogenic events.

An important consideration is the close proximity of the Chateaugay fluorapatite cement occurrence to the northwest-trending Chateaugay Lake Fault, which is interpreted as a

normal fault. Fluorapatite cement is not noted to be widely distributed in the basin and therefore its occurrence along the Chateaugay River section may be related to more local fluid processes focused by and along the fault zone. The coincidence of the rare fluorapatite cement occurrence in the Keeseville Formation and the fault raises the possibility that alkaline phosphatic fluids were focused within the fault and then migrated laterally away from the fault into the host Keeseville Formation where they formed statiform fluorapatite cement in the sandstone. The timing of fault development is not well constrained; however mapping by Lowe (2016) show that the Chateaugay Lake Fault also dissects the younger Beekmantown Group strata. In order to test this hypothesis more work is required to determine if other fluorapatite occurrences exist in areas where faults dissect the Keeseville Formation. If verified, then it may be more appropriate to refer to the fluids which generated the fluorapatite cement as hydrothermal rather than mesogenetic. The occurrence of apatite-bearing hydrothermal alteration and structures in the Adirondack Lowlands (Selleck, 2005) supports this possibility. Davis et al. (2011) have also noted that some of the fluorapatite-cemented Thelon Formation occurrences are also proximal to regional faults in the Thelon Basin, Nunavut.

Phosphorous source

There is no obvious source for the phosphorous and fluorine in the Keeseville Formation fluorapatite. To date, no sedimentary phosphorite deposits have been identified near or within the Ottawa Embayment Potsdam Group from whence the critical elements needed in fluorapatite formation could have been derived. A few black collophane-bearing gravel-size clasts have been identified in the Keeseville Formation approximately 40 km east of the study

area in the Altona Flat Rock area (J. Chiarenzelli, personal communication, 2017). However, their genetic link to the fluorapatite cement, if any, has yet to be established. The phosphate dissolution and reprecipitation described by Allaz et al. (2013) appear to document local redistribution of phosphate within a rock volume, although more widespread redistribution cannot be ruled out. Selleck (1993) noted fragments of phosphatic inarticulate brachiopods (Linguliformea) in the upper Potsdam Group and overlying mixed siliciclastic / carbonate Theresa Formation. However, thin section and hand sample inspection of brachiopod-rich rocks shows that the bioclasts are scattered and composed of cryptocrystalline collophane, not well-crystallized fluorapatite. This suggests that the Keeseville Formation fluorapatite is not diagenetically linked to the brachiopod-rich strata.

In the predominantly terrestrial setting envisioned for the Keeseville Formation (Sanford and Arnott 2010; Lowe et al. 2013; Lowe and Arnott 2016), the source for phosphorous and other critical elements would more likely be from the paleoweathering and dissolution of phosphate minerals in underlying basement rocks. Although apatite-bearing lithologies are abundant in the Grenville Province Central Metasedimentary Belt to the west and northwest (e.g., Sabina, 1965), the metamorphic Adirondack Dome and the Oka-Beauharnois Arch are considered the predominant sources for the study site Keeseville Formation detritus based on proximity, paleocurrent indicators and detrital zircon provenances (Chiarenzelli et al. 2010; Sanford and Arnott 2010; Lowe et al. 2013; Lowe 2016). Within the Adirondack Dome, there are significant Kiruna-type magnetite-apatite deposits (McKeown and Klemic 1956; Valley 2013), which, conceivably, could be a source for P-bearing meteoric fluids. Some of these are geographically close to the Keeseville Formation fluorapatite occurrence. The Lyon Mountain

granite gneiss, for example, is approximately 24 km to the SSE of the diagenetic fluorapatite occurrence. The 1.06-1.05 Ga Lyon Mountain granite gneiss intruded the Adirondack highlands and, through a combination of hydrothermal and magmatic processes, produced the apatite- and magnetite-rich deposits which are also enriched in REE (Valley 2013). There are other significant apatite- and LREE-rich deposits in the Adirondack Dome basement in the form of nelsonite intrusions (Darling and Florence 1995). However, these deposits are further away from the occurrence (177 km to the SW). Generally, the chemical weathering of these Proterozoic lithologies in the Adirondack Dome may have yielded the critical elements which concentrated in basinal fluids and led to the formation of diagenetic fluorapatite in the FA2 strata of the Keeseville Formation. As noted by Lowe and Arnott (2016), the FA2 succession was deposited in a subdued paleotopography (compared with FA1 succession) and, eventually, covered local Precambrian hills. The semi-arid ephemeral fluvial (reworked by aeolian processes) FA2 sequences are comprised of low-angle sheet-like deposits, along which the phosphatic fluids could migrate during burial diagenesis. The apatite-rich sandstone layers are thin (≤ 4 cm), stratiform and concordant with local sheet-like stratification (rather than discordant). It is clear that the early quartz cement is corroded by the later, stratiform fluorapatite cement.

CONCLUSIONS

To date, the diagenetic fluorapatite in the Keeseville Formation sandstone near Chateaugay, New York, is the only documented occurrence of apatite cement in the Potsdam Group anywhere in the Ottawa Embayment. Future investigations of the Potsdam Group,

perhaps adjacent to faults, may reveal more occurrences. The stratiform zones of fluorapatite cement documented in this paper occur in undeformed, mineralogically- and texturally-mature quartz arenite deposited in a semi-arid ephemeral fluvial environment. During burial diagenesis, the fluorapatite crystallized after the formation of pervasive quartz cementation and minor illitized kaolinite and before the formation of secondary porosity and late-stage (telogenetic) hematite cement. The fluorapatite initially crystallized as micron-scale bladed crystals that are elongated and often contain ladder-like dark cores running parallel to crystal length, surrounded by a clearer rim, and then as slightly larger blocky crystals commonly found towards the middle of the interstices. The bladed fluorapatite morphology has been rarely documented in geological literature; here it is felt that it is a result of initial engulfment of minor amounts of matrix material as it grew from the grain boundaries into the interstices in these matrix-poor quartz arenites. Once the scarce matrix was entombed within the bladed fluorapatite, the cement morphology changed to a blocky, pure fluorapatite.

Deposition of the Keeseville Formation is biostratigraphically constrained between the beginning of the upper Middle Cambrian (ca. 509.0 Ma) and the end of the Early Ordovician (ca. 477.7 Ma). The U-Pb isotopic age fluorapatite cement of 486 ± 29 Ma overlaps with these depositional constraints, suggesting that the cement formed during burial diagenesis. Alternatively the apatite cement may be as much as 20 to 30 million years younger than the depositional age and be related to fluid flow driven by Taconic orogenic events.

There are no obvious sources for phosphorous within either the terrestrial-marine Potsdam Group or overlying marine Theresa Formation. The favoured ultimate phosphorous

source is weathering of phosphorous-rich lithologies within the nearby Adirondack Dome, which was a highland source for the Keeseville Formation detritus. During burial diagenesis of the Keeseville Formation, alkaline and slightly basic mesogenetic fluids appear to have evolved locally and led to the dissolution of pre-existing quartz cement and precipitation of fluorapatite. It is possible that alkaline phosphatic fluids emanated from the nearby Chateaugay Lake Fault and migrated laterally along the pre-existing silica-cemented Keeseville Formation sandstone beds.

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CAPTIONS

Figure 1. Regional geology in and surrounding the Ottawa Embayment and Quebec Basin.

The study sample site within the Potsdam Group is located. CLF = Chateaugay Lake Fault.

Figure 2. Regional geology stratigraphic column highlighting the placement of the Keeseville Formation within the Potsdam Group. Numbers depict the stratigraphic position of the Potsdam Group unconformity-bound units as defined by Lowe et al. (in press).

Figure 3. Google Earth image showing sample site location 5 km south of Chateaugay beside the Chateaugay River, New York.

Figure 4. (a) Up to 20-cm thick zones of stratiform, pink apatite-cemented Keeseville Fm. quartz arenite (Between arrows. Hammer handle length = 21 cm.). (b) Lateral pinching out of fluorapatite-cemented quartz arenite. (c) Coarsening-upward bedding containing apatite-rich and apatite-poor layers. Smallest scale divisions are millimetres.

Figure 5. Paragenetic sequence for the Keeseville Formation fluorapatite-bearing quartz arenite.

Figure 6. (a) Photomicrograph of ambient quartz arenite (i.e., lacking apatite cement) showing monocrystalline and polycrystalline quartz grains with convex-concave grain-grain contacts, dust rims (DR) and syntaxial quartz overgrowths (arrows). (b) Illitized kaolinite (arrows) post-dating quartz overgrowths (QO). (c) Interstitial illitized vermiform macrokaolinite (arrows).

Figure 7. (a) Rounded and corroded quartz grains suspended in fluorapatite cement. Cored ion microprobe sample, SEM BSE mode image. (b) Same view as (a) but in CL mode which accentuates bladed fluorapatite cement. (c) CL mode image of framed area in (b) showing bladed fluorapatite with dark cores and luminescent rims. (d) SEM BSE mode image of bladed fluorapatite cement (a few are arrowed) with ladder-like dark cores. Blocky fluorapatite (BA) occupy a more central interstitial position. (e) Blocky fluorapatite (BA) occupy a central interstitial position compared to darker grain-rimming bladed fluoapatite. (f) SEM CL mode image of Thelon Formation bladed fluorapatite with dark, laddered cores and more luminescent rims.

Figure 8. (a) Photomicrograph of abrupt contact between quartz-cemented quartz arenite (bottom half) and apatite-cemented quartz arenite (top half). Dark interstitial apatite cement has dissolved pre-existing quartz cement and corroded grain boundaries. (b) Secondary cement dissolution porosity (blue) developed in both quartz-cemented and apatite-cemented (dark brown) quartz arenite. (c) Interstitial and quartz-grain corroding bladed fluorapatite cement (Ap and arrows) overprinted by late-stage opaque hematite cement.

Figure 9. $^{207}\text{Pb}/^{206}\text{Pb}$ vs $^{238}\text{U}/^{206}\text{Pb}$ plot of 17 blocky fluorapatite analyses. Regression parameters are calculated from Isoplot (Ludwig 2003).

Table 1. Electron microprobe analyses of average bladed and blocky fluorapatite.

Table 2. U-Th-Pb isotopic data.

Supplemental data

Electron microprobe analyses of Keeseville Formation fluorapatite

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Figure 1. Regional geology in and surrounding the Ottawa Embayment and Quebec Basin. The study sample site within the Potsdam Group is located. CLF = Cateaugay Lake Fault.

181x109mm (300 x 300 DPI)

Figure 2. Regional geology stratigraphic column highlighting the placement of the Keeseville Formation within the Potsdam Group. Numbers depict the stratigraphic position of the Potsdam Group allounits as defined by Lowe (2016).

86x156mm (300 x 300 DPI)

Figure 3. Google earth image showing sample site location 5 km south of Chateaugay beside the Chateaugay River, New York.

247x135mm (300 x 300 DPI)

Figure 4. (a) Up to 20-cm thick zones of stratiform, pink apatite-cemented Keeseville Fm. quartz arenite (Between arrows. Hammer handle length = 21 cm.). (b) Lateral pinching out of fluorapatite-cemented quartz arenite. (c) Coarsening-upward bedding containing apatite-rich and apatite-poor layers. Smallest scale divisions are millimetres.

86x193mm (300 x 300 DPI)

Figure 5. Paragenetic sequence for the Keeseville Formation fluorapatite-bearing quartz arenite.

182x120mm (300 x 300 DPI)

Figure 6. (a) Photomicrograph of ambient quartz arenite (i.e., lacking apatite cement) showing monocrystalline and polycrystalline quartz grains with convex-concave grain-grain contacts, dust rims (DR) and syntaxial quartz overgrowths (arrows). (b) Illitized kaolinite (arrows) post-dating quartz overgrowths (QO). (c) Interstitial illitized vermiform macrokaolinite (arrows).

86x194mm (300 x 300 DPI)

Figure 7. (a) Rounded and corroded quartz grains suspended in fluorapatite cement. Cored ion microprobe sample, SEM BSE mode image. (b) Same view as (a) but in CL mode which accentuates bladed fluorapatite cement. (c) CL mode image of framed area in (b) showing bladed fluorapatite with dark cores and luminescent rims. (d) SEM BSE mode image of bladed fluorapatite cement (a few are arrowed) with ladder-like dark cores. Blocky fluorapatite (BA) occupy a more central interstitial position. (e) Blocky fluorapatite (BA) occupy a central interstitial position compared to darker grain-rimming bladed fluorapatite. (f) SEM CL mode image of Thelon Formation bladed fluorapatite with dark, ladder-like cores and more luminescent rims.

215x279mm (200 x 200 DPI)

Figure 8. (a) Photomicrograph of abrupt contact between quartz-cemented quartz arenite (bottom half) and apatite-cemented quartz arenite (top half). Dark interstitial apatite cement has dissolved pre-existing quartz cement and corroded grain boundaries. (b) Secondary cement dissolution porosity (blue) developed in both quartz-cemented and apatite-cemented (dark brown) quartz arenite. (c) Interstitial and quartz-grain corroding bladed fluorapatite cement (Ap and arrows) overprinted by late-stage opaque hematite cement.

86x198mm (300 x 300 DPI)

Figure 9. $^{207}\text{Pb}/^{206}\text{Pb}$ vs $^{238}\text{U}/^{206}\text{Pb}$ plot of 17 blocky fluorapatite analyses. Regression parameters are calculated from Isoplot (Ludwig 2003).

182x145mm (300 x 300 DPI)

Table 1. Electron Microprobe Analyses of Keeseville Fm. fluorapatite.

Oxide Wt%	CaO	K2O	SO3	F	P2O5	Cl	SrO	UO2	ThO2	PbO
BLADED FLUORAPATITE EMP ANALYSES (n=23)										
Average	53.65	0.04	0.10	4.21	40.75	0.03	0.08	0.05	0.04	0.06
Std. Dev.	0.73	0.05	0.00	0.29	0.94	0.03	0.03	0.00	0.01	0.01
BLOCKY FLUORAPATITE EMP ANALYSES (n=27)										
Average	54.06	0.02	0.10	4.47	41.31	0.03	0.07	0.04	0.04	0.06
Std. Dev.	0.55	0.01	0.02	0.51	0.77	0.04	0.02	0.01	0.01	0.00
MDL Ox. Wt%	0.0213	0.0102	0.0714	0.0522	0.024	0.0102	0.0375	0.0288	0.0306	0.0351

Oxide Wt%	FeO	Ce2O3	La2O3	Nd2O3	Tm2O3	Yb2O3	Lu2O3	Na2O	SiO2	Al2O3	Total
BLADED FLUORAPATITE EMP ANALYSES (n=23)											
Average	0.12	0.05	0.06	0.04	0.04	0.05	0.04	0.02	0.17	0.09	99.71
Std. Dev.	0.15	0.01	0.01	0.01	0.01	0.02	0.01	0.00	0.16	0.10	
BLOCKY FLUORAPATITE EMP ANALYSES (n=27)											
Average	0.04	0.04	0.07	0.04	0.04	0.04	0.04	0.02	0.02	0.01	100.05
Std. Dev.	0.03	0.00	0.04	0.01	0.01	0.01	0.01	0.00	0.02	0.00	
MDL Ox. Wt%	0.0129	0.0327	0.0369	0.0288	0.0285	0.0285	0.0285	0.0114	0.012	0.0042	

Table 2. U-Th-Pb Isotopic data.

Spot Name	^{206}Pb cps	^{206}Pbc (%)	$^{238}\text{U}/$ ^{206}Pb	% err	$^{207}\text{Pb}/$ ^{206}Pb	% err	$^{204}\text{Pb}/$ ^{206}Pb	% err	$^{208}\text{Pb}/$ ^{206}Pb	% err
11622-003.1	16	32	7.284	3.3	0.3579	3.5	0.0177	18	0.79	4.4
11622-003.4	35	54	6.623	8.1	0.5163	4.2	0.0296	14	1.26	2.8
11620-001.1	47	43	6.752	7.1	0.4062	7.3	0.0232	9	1.07	18.7
11620-001.2	5	80	5.096	6.7	0.5620	6.9	0.0435	22	1.16	8.7
11620-001.3	12	31	9.138	5.4	0.3169	4.6	0.0176	19	0.63	5.8
11620-001.4	29	20	9.898	3.4	0.2778	7.5	0.0113	17	0.54	11.8
11620-001.5	15	42	6.772	3.7	0.4211	6.8	0.0233	16	0.94	4.8
11621-002.2	109	71	2.251	20.3	0.6036	7.4	0.0385	17	1.48	7.9
11621-002.3	7	27	8.442	9.3	0.2874	10.5	0.0144	27	0.52	11.9
11621-002.4	25	34	7.756	4.6	0.3837	6.0	0.0183	14	0.79	8.3
11622-003.5	28	51	6.650	4.7	0.4630	2.8	0.0284	10	1.15	6.7
11622-002.1	17	61	5.073	6.3	0.4908	3.2	0.0343	13	1.18	3.8
11622-003.2	22	40	8.028	3.0	0.3814	5.3	0.0222	13	0.89	3.6
11622-003.3	21	33	8.013	2.4	0.3070	3.2	0.0177	16	0.65	4.1
11622-003.4a	19	24	11.085	2.3	0.1982	8.0	0.0132	19	0.35	9.4
11620-003.1	18	38	6.969	3.2	0.3790	3.2	0.0211	15	0.89	4.0
11620-003.2	36	14	9.934	3.4	0.1838	2.8	0.0079	17	0.26	8.0

Spot name refers to three individual thin sections identified as 11620 to 11622 from the same sample site.

All ratios are reported uncorrected for common Pb; $^{238}\text{U}/^{206}\text{Pb}$ ratio calibrated relative to apatite reference material BR5 (2040 Ma; A. Kennedy pers comm. 2016)

^{206}Pbc (%) = per cent common Pb in analysis based on ^{204}Pb

All errors are at 1 sigma level

SUPPLEMENTAL DATA: Electron microprobe analyses of Keeseville Fm. fluorapatite.**BLADED FLUORAPATITE EMP ANALYSES**

CaO	K ₂ O	SO ₃	F	P ₂ O ₅	Cl	SrO	UO ₂
54.11	BDL	BDL	4.05	40.76	BDL	0.15	BDL
53.60	0.02	BDL	4.15	41.44	BDL	0.04	BDL
52.01	0.02	BDL	3.94	37.78	0.07	BDL	BDL
53.21	BDL	BDL	4.22	39.50	BDL	BDL	BDL
53.26	0.03	BDL	3.95	40.02	0.01	BDL	BDL
54.15	BDL	BDL	4.50	41.51	0.02	0.04	BDL
53.98	0.01	BDL	4.12	40.71	BDL	0.14	BDL
53.61	BDL	BDL	4.49	40.77	BDL	0.04	BDL
54.22	BDL	BDL	4.50	41.32	BDL	0.08	BDL
54.20	BDL	BDL	4.22	41.81	BDL	0.13	BDL
53.36	0.02	0.10	4.62	40.50	BDL	0.06	0.04
54.37	BDL	BDL	4.39	41.69	BDL	0.07	BDL
51.67	BDL	BDL	3.65	39.40	0.02	0.05	BDL
53.14	BDL	BDL	3.93	40.69	BDL	0.05	BDL
53.87	BDL	BDL	3.83	40.38	BDL	0.07	0.05
54.20	BDL	BDL	4.72	41.12	BDL	BDL	BDL
53.42	BDL	BDL	4.34	40.78	BDL	0.09	BDL
52.72	0.13	BDL	3.96	40.54	BDL	0.11	0.04
53.98	BDL	BDL	4.40	42.30	BDL	0.05	BDL
53.79	BDL	BDL	4.29	41.33	BDL	0.08	BDL
54.42	BDL	BDL	4.04	40.60	BDL	0.06	BDL
54.16	BDL	BDL	3.91	41.23	BDL	BDL	BDL
54.39	BDL	BDL	4.71	41.06	BDL	0.09	BDL
Average	53.65	0.04	0.10	4.21	40.75	0.03	0.05

BLOCKY FLUORAPATITE EMP ANALYSES

CaO	K ₂ O	SO ₃	F	P ₂ O ₅	Cl	SrO	UO ₂
54.26	BDL	BDL	3.70	41.87	BDL	BDL	0.06
53.93	BDL	BDL	4.61	39.96	0.03	BDL	0.03
54.59	BDL	BDL	4.77	41.43	0.01	0.05	BDL
53.84	0.01	BDL	4.61	40.43	BDL	0.07	0.03
53.85	BDL	BDL	5.14	41.85	BDL	0.06	BDL
54.07	BDL	BDL	4.75	41.61	BDL	0.04	BDL
54.35	BDL	0.08	4.35	41.56	BDL	0.10	0.04
53.80	BDL	BDL	5.18	41.79	BDL	0.09	0.03
54.18	BDL	BDL	4.93	41.82	BDL	BDL	BDL
54.25	BDL	BDL	4.16	42.00	BDL	0.04	BDL
54.25	BDL	BDL	3.66	42.09	BDL	0.10	BDL
54.34	BDL	BDL	4.19	42.14	BDL	BDL	BDL
54.41	BDL	BDL	4.05	42.31	BDL	BDL	BDL
54.59	0.01	BDL	4.54	41.36	0.01	BDL	BDL
51.71	0.02	0.11	3.47	38.96	0.11	0.06	BDL

	54.76	BDL	BDL	3.83	40.86	BDL	0.05	BDL
	54.31	BDL	BDL	5.60	41.10	BDL	0.07	BDL
	54.04	BDL	0.10	4.00	41.12	BDL	BDL	0.04
	54.02	BDL	BDL	4.56	40.96	0.01	BDL	BDL
	53.69	BDL	BDL	3.93	41.70	BDL	0.07	BDL
	54.03	BDL	BDL	4.40	41.02	BDL	0.08	BDL
	54.17	BDL	BDL	4.76	41.97	BDL	BDL	BDL
	53.99	BDL	BDL	4.70	40.23	BDL	0.12	BDL
	54.34	BDL	BDL	4.83	41.29	0.02	BDL	BDL
	53.38	BDL	BDL	4.22	40.67	BDL	0.05	BDL
	54.17	BDL	BDL	4.88	41.20	BDL	BDL	0.04
	54.23	BDL	BDL	4.77	42.08	BDL	0.10	BDL
Average	54.06	0.02	0.10	4.47	41.31	0.03	0.07	0.04

Oxide Weight Percent

BDL = Below Detection Limit

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ThO2	PbO	FeO	Ce2O3	La2O3	Nd2O3	Tm2O3	Yb2O3	Lu2O3
BDL	BDL	0.02	0.06	0.07	BDL	BDL	0.05	BDL
BDL	BDL	BDL	BDL	BDL	BDL	0.03	BDL	BDL
0.04	BDL	BDL	BDL	0.08	BDL	BDL	0.07	BDL
0.05	BDL	0.41	BDL	0.04	BDL	BDL	0.04	0.04
BDL	0.06	0.50	BDL	BDL	0.03	0.04	BDL	BDL
BDL	BDL	0.06	BDL	BDL	BDL	0.05	BDL	BDL
BDL	BDL	0.03	BDL	BDL	BDL	BDL	BDL	BDL
BDL	0.05	0.16	BDL	BDL	BDL	BDL	BDL	BDL
BDL	0.06	BDL	0.05	BDL	BDL	BDL	BDL	BDL
BDL	BDL	0.02	BDL	BDL	BDL	BDL	BDL	BDL
BDL	BDL	0.34	BDL	BDL	0.05	BDL	BDL	BDL
0.04	BDL	BDL	BDL	BDL	BDL	0.05	BDL	BDL
BDL	BDL	0.16	0.05	0.07	BDL	BDL	BDL	BDL
BDL	BDL	0.06	BDL	BDL	BDL	0.03	BDL	BDL
BDL	0.06	0.06	0.06	BDL	0.04	BDL	BDL	BDL
BDL	BDL	0.02	BDL	BDL	BDL	BDL	BDL	BDL
BDL	BDL	0.05	BDL	BDL	BDL	BDL	BDL	0.03
BDL	BDL	0.05	0.05	BDL	BDL	BDL	BDL	BDL
BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
BDL	BDL	0.05	BDL	BDL	BDL	BDL	BDL	BDL
BDL	0.07	BDL	BDL	BDL	BDL	0.06	BDL	BDL
BDL	BDL	0.02	0.06	0.06	0.03	BDL	BDL	BDL
BDL	0.05	BDL	BDL	BDL	BDL	BDL	BDL	BDL
0.04	0.06	0.12	0.05	0.06	0.04	0.04	0.05	0.04

ThO2	PbO	FeO	Ce2O3	La2O3	Nd2O3	Tm2O3	Yb2O3	Lu2O3
BDL	BDL	0.02	BDL	BDL	BDL	BDL	BDL	BDL
0.04	BDL	0.04	0.03	BDL	BDL	BDL	BDL	0.05
BDL	BDL	0.02	BDL	BDL	BDL	BDL	BDL	0.03
0.03	BDL	0.12	BDL	BDL	BDL	BDL	0.03	0.06
BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
BDL	0.06	0.02	BDL	BDL	BDL	0.03	BDL	BDL
BDL	BDL	BDL	BDL	0.06	BDL	BDL	BDL	BDL
BDL	BDL	BDL	BDL	0.05	0.03	BDL	BDL	BDL
BDL	BDL	0.02	BDL	BDL	BDL	BDL	BDL	BDL
BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.03	BDL
BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
BDL	BDL	0.04	BDL	BDL	BDL	BDL	0.04	BDL
BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
BDL	BDL	BDL	BDL	BDL	BDL	0.04	BDL	BDL
BDL	BDL	0.10	0.04	BDL	BDL	BDL	BDL	BDL

BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
BDL	BDL	0.05	BDL	0.04	BDL	BDL	BDL	0.04
BDL	BDL	BDL	BDL	BDL	BDL	0.05	0.04	BDL
BDL	BDL	0.06	BDL	BDL	BDL	BDL	BDL	BDL
BDL	BDL	0.03	0.04	BDL	0.04	BDL	BDL	BDL
BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
BDL	BDL	BDL	BDL	BDL	0.04	BDL	BDL	BDL
BDL	BDL	0.02	BDL	BDL	BDL	BDL	0.03	BDL
BDL	BDL	BDL	BDL	0.12	BDL	BDL	0.05	BDL
0.06	BDL	0.02	BDL	BDL	BDL	BDL	BDL	BDL
BDL	BDL	0.05	0.04	BDL	BDL	BDL	BDL	BDL
BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
0.04	0.06	0.04	0.04	0.07	0.04	0.04	0.04	0.04

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Na2O	SiO2	Al2O3	Total	Sample
BDL	BDL	BDL	99.26	QD-1 2-1
BDL	0.04	0.05	99.38	QD-1 2-2
BDL	0.30	0.03	94.34	QD-1 2-3
BDL	0.03	0.05	97.59	QD-1 3-1
BDL	0.17	0.18	98.25	QD-1 3-2
BDL	BDL	BDL	100.32	QD-4 3-2
BDL	BDL	BDL	99.00	QD-4 1-3
BDL	0.07	0.07	99.26	QD-4 2-2
BDL	BDL	BDL	100.23	QD-4 2-3
BDL	BDL	0.02	100.41	QD-2 2-2
BDL	0.06	0.05	99.21	QD-2 1-3
BDL	BDL	BDL	100.61	QD-2 3-1
BDL	0.47	0.21	95.75	QD-2 3-3
BDL	BDL	0.03	97.94	QD-2 4-1
BDL	BDL	0.01	98.43	168-D 2-1
BDL	BDL	BDL	100.06	168-D 2-2
0.02	BDL	0.03	98.76	168-D 2-3
BDL	0.24	0.34	98.19	168-D 1-1
BDL	BDL	BDL	100.73	168-D 1-2
BDL	BDL	BDL	99.54	QD-1 1-4
BDL	BDL	BDL	99.26	QD-1 2-4
BDL	BDL	BDL	99.48	QD-4 1-5
BDL	BDL	BDL	100.30	QD-4 2-7
0.02	0.17	0.09	99.71	

Na2O	SiO2	Al2O3	Total	Sample
BDL	BDL	BDL	99.93	QD-1 1-1
BDL	0.01	0.01	98.86	QD-1 3-3
BDL	BDL	0.01	100.97	QD-4 3-1
BDL	BDL	BDL	99.25	QD-4 3-3
BDL	BDL	BDL	100.98	QD-4 1-1
BDL	BDL	BDL	100.69	QD-4 1-2
BDL	BDL	BDL	100.59	QD-4 2-1
BDL	BDL	BDL	100.99	QD-2 2-1
BDL	BDL	BDL	101.05	QD-2 2-3
BDL	BDL	BDL	100.54	QD-2 1-1
BDL	BDL	BDL	100.14	QD-2 1-2
BDL	BDL	BDL	100.89	QD-2 3-2
BDL	BDL	0.01	100.85	QD-2 4-2
BDL	BDL	BDL	100.64	QD-2 4-3
0.02	BDL	BDL	94.64	QD-2 5-1

0.02	BDL	BDL	99.57	QD-2 5-2
BDL	BDL	0.01	101.27	QD-2 5-3
BDL	BDL	BDL	99.50	QD-2 5-4
BDL	BDL	BDL	99.67	QD-1 1-3
BDL	BDL	BDL	99.58	QD-1 1-5
BDL	BDL	BDL	99.59	QD-1 2-5
BDL	BDL	BDL	101.06	QD-1 2-6
BDL	BDL	BDL	99.15	QD-4 1-4
BDL	BDL	BDL	100.74	QD-4 2-4
BDL	0.04	BDL	98.57	QD-4 2-5
BDL	BDL	BDL	100.45	QD-4 2-6
BDL	BDL	BDL	101.27	QD-4 2-8
0.02	0.02	0.01	100.05	

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