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Microprobe analysis and dating of monazite from the Potsdam Formation, NY: A progressive record of chemical reaction and fluid interaction

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Abstract

It has been recognized for several decades that REE-phosphates (monazite and xenotime) can grow during diagenesis and low-grade metamorphism. Growth of REE-bearing accessory phases at low-grade conditions commonly involves pervasive fluid-rock interaction, dissolution of detrital grains, transportation, and precipitation of REEs, typically facilitated by an increase in temperature. The occurrence of low-grade REE-phosphate offers a rare opportunity to date a crystallization/mineralization and possibly fluid percolation.
We report here the results of in situ dating by electron microprobe of Paleozoic authigenic and low-grade monazite and xenotime overgrowths on detrital monazite and zircon, respectively. Samples are from the Potsdam Formation, a basal sandstone deposited uncomfortably on Proterozoic basement of the Adirondack Mountains of New York State. This study also focuses on the textural and chemical relationships of these REE-bearing accessory phases. Textures include rounded and fractured detrital monazite and zircon, which contrast with new sub-euhedral REE-phosphate overgrowths. Monazite overgrowths are enriched in LREE and depleted in HREE compared to detrital cores. The U and Th concentrations are low, typical of low-grade metamorphic conditions.

Monazite core ages yield Proterozoic ages between 1.17 and 0.90 Ga (Shawinigan and Ottawa orogeny). Monazite overgrowth and xenotime ages indicate four to five major overgrowth events between ca. 500 Ma (shortly after the time of deposition) and ca. 200 Ma. As these ages are relatively young and the actinide content is low ($\Sigma < 2$ wt.%), the radiogenic Pb content of monazite overgrowths and xenotime is low (< 400 ppm). Therefore, EPMA dates have relatively large uncertainties. Nevertheless, the ages determined broadly correlate with major Paleozoic orogenic events recorded in the Appalachian Orogen to the East (Taconic, Salinic, Acadian, Neo-Acadian and Alleghanian). Fluid percolation, driven by orogenic loading, may induce dissolution of detrital monazite and zircon. Subsequent precipitation of new monazite and xenotime probably results from changes in fluids or metamorphic conditions. This study demonstrates the power of the EMPA technique to resolve the fluid-related growth history of REE-phosphates in low-grade metasediments.

**Introduction**
Fluids play an important role in the evolution of sedimentary rocks from early diagenesis and lithification to alteration, low-grade metasomatism, and even ore mineralization (e.g. Putnis and Austrheim 2010). Fluids may be derived locally, during compaction and dewatering, or they may be derived from underlying rocks or from deeper parts of the sedimentary basin during burial or tectonic loading. Fluid-rock interaction can fundamentally modify the original mineral assemblage(s), bulk composition, and mechanical properties, thus obscuring the record of depositional environments and sedimentary provenance. However, fluid-rock interaction can also leave an interpretable record of stages in the evolution of a sedimentary basin and of depositional and tectonic events in other parts of the basin. It is important to identify and characterize the spatial, temporal, and compositional nature of fluid-rock interaction events, but this has proven to be challenging because of the relatively low metamorphic grades and the heterogeneity of fluid pathways through many sedimentary rocks.

Analysis and dating Rare Earth Element (REE) phosphate, i.e. monazite and xenotime, is a promising approach for characterizing past fluid interaction events in sedimentary rocks. Monazite (LREE-phosphate) and xenotime (HREE-phosphate) are common detrital minerals in a variety of sedimentary rocks (Overstreet 1967). Further, they are susceptible to dissolution and precipitation, and it has been recognized for several decades that authigenic monazite can overgrow detrital monazite during diagenesis (Burnotte et al. 1989; Evans and Zalasiewicz 1996; Evans et al. 2002; Tomkins and Ross 2005), and also during low-grade metamorphism (Cabella et al. 2001; Rasmussen et al. 2001; Rasmussen and Muhling 2007; Wan et al. 2007; Wilby et al. 2007). The broad compositional range of monazite and xenotime, including an array of trace elements and REE, make them very suitable geochemical monitors. Further, both monazite and xenotime can incorporate significant amounts of Th and U, with little common Pb, which makes them datable by
isotopic or elemental chemical analysis. Therefore, they provide an opportunity to monitor
the geochemical evolution through time of sedimentary basins (e.g. Burnotte et al. 1989;
Evans et al. 2002; Wilby et al. 2007; Mahan et al. 2010).

This paper presents results of an investigation of the evolution of REE-phosphates in
the Upper Cambrian Potsdam Formation (NY, USA). Several generations of monazite and
xenotime overgrowths are associated with detrital monazite and zircon, respectively. The
presence of these overgrowths provides an opportunity to date and characterize the diagenesis
and low-grade burial metamorphism in the Potsdam Formation. Here, we use the electron
microprobe to reveal variation of composition and U-Th-Pb age in situ, that is, on mineral
grains and overgrowths exposed in thin sections of the sedimentary rocks. Results indicate
that several distinct events, possibly linked to Appalachian orogenic pulses, have triggered
the dissolution and precipitation of REE-minerals.

**Geological setting and sample description**

The Potsdam Formation was deposited during Middle to Upper Cambrian (510-490 Ma;
Fisher 1977; Landing et al. 2009). It ranges from feldspar-rich arkose (basal Aussable
Member) to nearly pure quartzite (Keeseville Member). Sedimentary facies analysis indicates
a progressive change from terrestrial to shallow marine deposition (Fisher 1968). The
Potsdam Formation was unconformably deposited on Grenvillian metamorphic rocks of the
Adirondack massif (NY, USA; Ontario and Québec, Canada).

Samples were collected from six localities near the margins of the Adirondack massif
in New York State (Fig. 1). The sandstones consist of quartz and K-feldspar, with a matrix of
Fe-rich chlorite, quartz, illite, minor kaolinite and local carbonate (Selleck 2008). Heavy
minerals, including monazite, xenotime and zircon, are commonly concentrated along thin placer laminae in coarse pebbly sandstone. Aside from late fracturing, no obvious deformation features are visible in these samples.

Authigenic REE-minerals (monazite, xenotime), sulfides (pyrite, galena, sphalerite), fluorite and barite suggest that hydrothermal fluids circulated through permeable basal sands in the Potsdam Formation, causing alteration of susceptible minerals such as biotite, hornblende, garnet, ilmenite, and plagioclase. Fluid inclusion data (homogenization and melting temperatures) from Collins-Waite (1987) on vein quartz and carbonate suggest that metamorphic temperatures were in excess of 200°C with high salinity, near halite saturation.

Methodology

Nine samples were selected for petrographic examination and microprobe analysis. Textural and compositional relationships between detrital and authigenic minerals were examined. Identification of zircon, monazite, and xenotime was performed by acquiring full-thin-section Wavelength Dispersive Spectroscopy (WDS) maps of Zr Lα, Ce Lα and Y Lα on a CAMECA SX-50 microprobe at the University of Massachusetts, following the method of Williams and Jercinovic (2006). Then, high-resolution WDS maps of Th Mα, U Mβ, Y Lα, Ca Kα and one REE (Nd Lα, Pr Lα or Sm Lα) were acquired from numerous monazite grains in each polished section. For xenotime, Y Lα, Th Mα, U Mβ, Dy Lα and Gd Lα x-ray maps were generated; Zr Lα was occasionally used to highlight the zircon on which xenotime grew.

Quantitative analyses were acquired on the CAMECA SX-100 “Ultrachron” microprobe at the University of Massachusetts, following methods described in Williams et al. (2006) and Jercinovic et al. (2008) for monazite, and in Hetherington et al. (2008) for
xenotime. In addition to the interference corrections described in these papers, a correction for the interference of Pr Lβ2,15 on Eu Lα was included. Acquisition time for U (600 s), Th (500 s) and Pb (700 s, integrating counts from two spectrometers equipped with VLPET crystals) were optimized to improve precision and accuracy, while minimizing diffusion effects. Background intensities for U, Th, and Pb were regressed from high-resolution WDS scans (see Williams and Jercinovic 2006).

Standardization and age calculations were checked before and after each analysis session using the following consistency standards: (a) Moacyr monazite (TIMS 207Pb/235U 506.7 ± 1.4 Ma and 208Pb/232U 506.4 ± 1.8 Ma; B. Davis, pers. comm. 2005) and (b) GSC-6413 xenotime (TIMS 207Pb/206Pb 996.7 ± 0.8 Ma and 206Pb/238U 993.8 ± 0.7 Ma; Stern and Rayner 2003). In addition to U, Th and Pb, monazite and xenotime analyses include Si, P, S, Ca, As, Y and REE (La to Nd and Sm to Yb). Results are presented in Table 1, and the complete set of analysis is available in Table DR1 in the Data Repository. U-Th-Pb dates were calculated based on the age equation from Montel et al. (1996) and decay constants from Steiger and Jäger (1977). We distinguish an analysis (single point measurement) from a date, obtained by averaging 3 to 12 single point analyses in a homogeneous compositional domain. Errors associated with dates are given at the 2σ level and include counting statistics and a 10% relative error on the background regression.

The CAMECA SX-100 “Ultrachron” is optimized for U, Pb and Th acquisition. However, the low actinide content and the Paleozoic age of these grains result in low total Pb, typically between 22 and 392 ppm. This is close to the detection limit of the electron microprobe at the optimum analytical conditions used here; the detection limit for Pb is ca. 10 ppm on a 5-point average. Longer counting time or higher current would improve this, but the risk of inaccuracy due to beam damage would become unacceptable (see Jercinovic et al. 2012). Therefore, dating results show large variability even within single homogeneous
domains, and errors are typically larger than ±25 Ma (2σ). When Th and Pb concentration are
greater than 1.2 wt% and 250 ppm respectively, errors are less than ±20 Ma (ca. 5% relative).
There is no correlation between the calculated dates and Pb- or Th-content (Fig. 2a), but a
correlation exists between the relative error and the Pb- or Th-content (Fig. 2b).

Results

**Detrital monazite**

Monazite grains exposed in thin section are typically greater than 50 µm in size, and are
commonly concentrated on bedding planes with other heavy minerals (e.g. oxides, zircon).
On backscattered electron (BSE) images, most monazite grains have distinct bright cores and
darker rims. The cores are typically rounded and fractured. They commonly have patchy
zoning (Fig. 3f-l, n-q), but are typically rich in Th (3.5 to 22.0 wt-% ThO₂) and Y (0.1 to 4.2
wt-% Y₂O₃; Table DR1). Most cores have a significant component of cheralite (Chr;
CaTh(PO₄)₂) and thorite/huttonite (Thr; (Th,U)SiO₄), with up to 30-40% Thr+Chr in grain
m1 of sample EC-3, and 10-15% in all other samples (Fig. 4a). REE spectra vary from
sample to sample and within a single sample (Fig. 5b; Fig. DR1). Dates fall into a number of
sub-populations but are constrained between 1005 and 1162 Ma with errors between 5 and 13
Ma (2σ; Tables 1, DR1; Fig. 6).

**Monazite overgrowths**
Monazite overgrowths commonly surround detrital monazite cores. The overgrowths are typically 50-100 µm in apparent thickness, resulting in very large (for accessory minerals) composite grains, up to 200-300 µm. Smaller overgrowths of 5-50 µm are also observed. When present, the overgrowths represent 30 to 70% of the total grain area. They are typically in optical continuity with the detrital cores (Fig. 3d). The overgrowths are texturally distinct from the rounded and locally fractured cores. They typically have subeuhedral crystal shapes, but they can also fill cracks and grain interfaces. Apatite, ThSiO$_4$, and/or xenotime commonly occur along the core-rim interface or along fractures in cores.

Some overgrowths are incomplete or asymmetric in their distribution around detrital cores. Many are preferentially developed towards pore space, or susceptible minerals such as plagioclase or K-feldspar. Textural analysis further suggests a preferential replacement of K-feldspar by monazite relative to other matrix phases, as shown in Figure 7a,b; the overgrowth contains inclusions of K-feldspar, whereas the overgrowth is much thinner or absent when adjacent to quartz or other less soluble minerals.

Overgrowths typically display multiple concentric layers, each with a distinct composition (e.g. Fig. 3). Successive rim analyses are identified with by number; “rim1” being the innermost, nearest to the core (Table DR1). WDS compositional mapping of Nd $\alpha$ notably reveals distinctive compositional textures. The innermost overgrowth typically has a fibrous or floweret texture, with fibers radiating from the core-overgrowth interface (e.g. Fig. 3a,e). Monazite “fibers” are also rarely found as overgrowths on zircon (Fig. 7c). The next successive overgrowth generation typically fills the spaces between the rim1 fibers (Fig. 3a-c). Subsequent generations occur in concentric layers. Up to 4 layers have been distinguished in a single grain (e.g. LM-11 m1 in Fig. 3a-c). Up to 5 compositionally distinct layers have been identified among several grains in a single sample.
REE spectra from monazite overgrowths are distinctly different from those of the cores (Fig. 5). Although absolute values differ from grain to grain, all rims are depleted in Th, U, Y, Ca, Si and HREE compared to cores, and slightly enriched in light REE (LREE; La to Eu; Table DR1; Figs 3,4b). A positive correlation between Nd, Pr, Sm, Gd, Eu and Tm is observed, while La and Ce are anti-correlated with these elements. These observations are independent of sample locality, with the exception of the PC samples, which tend to yield the highest La-contents and also higher La/Nd ratios relative to other samples. Whereas all detrital monazite cores show a negative Eu-anomaly, most overgrowths do not (Fig. 5). U concentrations are typically below detection limit (< 50-60 ppm), while Th and Y are low (0.22 to 1.73 wt-% Th; 0.08 to 0.51 wt-% Y). Samples WNR-1 and WNR-3 contain sulfates (barite, anhydrite/gypsum), and a significant amount of sulfur is detected in monazite, especially in rims (cores: 0.18-0.43; rims: 0.22-0.70 wt-% SO₂).

Dating results are represented graphically using a single Gaussian probability curve for each homogeneous compositional domain, identified from high-resolution WDS maps (as per Williams et al., 2006). Results for monazite range from 550 Ma to 320 Ma, with a few outliers as young as 221 Ma (sample WFR-14 only) and as old as 745 Ma (Table DR1). Four major peaks are visible in the combined data set for all samples: 505, 460, 420 and 370 Ma (Fig. 8a). Consistent with the concentric growth patterns, dates become progressively younger from internal rims (500-400 Ma) to external rims (400-300 Ma). Figure 3a-d shows an example with four compositional domains: (a) internal rim at 507±26 Ma, (b) two intermediate domains at 418±20 Ma and 348±22 Ma, and (c) an external rim at 321±22 Ma. Another spectacular overgrowth (m7 in sample PC-2A) has an internal rim at 528±26 Ma and an external rim at 359±37 Ma (Table DR1). Some other rims only record one or two events (e.g. PC-6 m3, one event: 436±30 and 402±61 Ma; Fig. 3e-g).
There is a noticeable difference in overgrowth geochronology between samples from different geographic localities. Maxima for the northern (LM, EC; Fig. 1) and southern (WNR; Fig. 1) samples occur at 420, 370 and 325 Ma, whereas maxima for eastern samples (PC, WFR occur at 505, 460 and 420 Ma (Fig. 1). Further, even within a single sample, contemporaneous (based on the age results) rims do not tend to have identical compositions, although this could result from the large error on age, and the relatively small number of grains analyzed. Several vague trends are apparent. With decreasing age:

- Y increases and Ce decreases (EC-3, LM-11, WFR-14 and WNR-3);
- Pr decreases (LM-12 and WFR-14);
- Eu and Gd slightly increase (LM-11, WFR-14 and WNR-3).

Interestingly, Th concentrations are highest in monazite with ages around 500-400 Ma for several samples (Fig. 2a). The relatively high Th abundance also corresponds to relatively high Ca, Sr and Y content (EC-3 and PC-2A).

**Xenotime**

Xenotime preferentially occurs as 10-30 µm-wide rims on detrital zircon grains. The overgrowths are locally detached and separated from the zircon core, with the gaps primarily filled with chlorite, illite and/or quartz (Fig. 9). Several minute grains up to 10 µm in diameter also occur at the boundary between detrital monazite cores and overgrowths or within fractures in monazite cores (Fig. 3c,e). 10-20 µm crystals occur more rarely in pore spaces, between detrital quartz and feldspar. High-resolution WDS mapping and compositional analysis reveals only subtle compositional zonation, particularly in Th, Y, Gd, Dy, Er and Yb (e.g. Fig. 9 inset). Th-content is similar to monazite rims or slightly greater.
(0.41 to 2.29 wt-% ThO$_2$), whereas U-content is significantly greater (0.12 and 0.30 wt-% UO$_2$). Four age peaks are visible in the combined xenotime dataset: ca. 395, 370, 325, and 225 Ma (Fig. 8c). In contrast to monazite overgrowths, there are no xenotime dates in the range of 505 and 460 Ma.

**Discussion**

**Monazite cores**

Monazite cores are rounded, consistent with erosion and transport. REE patterns are strongly variable from sample to sample and within a single sample (Fig. 5), reflecting their different source regions or host rocks. Several monazite cores have patchy zoning indicative of fluid-related alteration (e.g. Fig. 3f-l, n-q). Xenotime and ThSiO$_4$ (thorite or huttonite) are present in cracks and on core to rim boundaries (Fig. 3g-h,o,p,s-t). Age results for some pristine cores (Table DR1; Fig. 3a,r) demonstrate the usefulness of detrital monazite dating to illuminate the origin of sediments (e.g. Hietpas et al. 2010). Most dates fall between 1.06 and 1.00 Ga, characteristic of the Ottawan phase of the Grenville Orogeny (Wong et al. 2011). One core yields 0.91±0.01 Ga (PC-6 m1, core 2; Fig. 6), and likely represents a later event following the Ottawan Orogeny such as late granite intrusion, or retrograde metamorphism after the Rigolet Orogeny (1005-980 Ma; McLelland et al. 2010). Two other cores yield 1.10 (LM-11 m1, core) and 1.16 Ga (PC-2A m2, core2; Fig. 6), which may be related to the Hawkeye granite in LM samples (1100-1095 Ma) and to mangerite-charnockite intrusions in PC samples (1160-1145 Ma; McLelland et al. 2010).
Monazite overgrowths

Monazite core-rim textures can be interpreted in terms of several different processes. They might represent replacements (by metasomatism or alteration) of the outer parts of detrital grains. Alternatively, they could result from precipitation of new monazite on precursor grains. Both processes would indicate some degree of fluid-rock interaction, and both are certainly enhanced at higher temperature. Several lines of evidence point to dissolution-precipitation of new monazite overgrowths in our samples. First, a subeuhedral habit and well-defined concentric zoning are visible on some compositional maps (e.g. Fig. 3i,r). This texture, similar to magmatic monazite, is commonly observed in low-grade monazite (Burnotte 1989; Shandl and Gorton 2004). Second, if monazite overgrowths were formed by alteration/replacement (a pseudomorphic reconstruction mechanism), one would expect the grain shape to preserve the original rounded and fractured shape of detrital grains and the inner boundary to be more of an irregular reaction front (e.g. Petrik and Konecný 2009; Hetherington et al. 2010), which is not the case. Third, monazite overgrowths are locally developed on other detrital minerals, such as plagioclase and K-feldspar (e.g. Fig. 7a,b).

The presence of fluid circulation in the Potsdam Formation after deposition is indicated by the presence of hydrous minerals (chlorite, clay) replacing feldspar and other susceptible minerals. Fluid inclusion studies (Collins-Waite 1987; Lim et al. 2005), the presence of chlorite and illite (Reynolds and Thomson 1993; Selleck 2008) and the conodont alteration index of ca. 4 (Repetski et al. 2008) all document low-grade metamorphism and metasomatism in the Potsdam Formation at ca. 250 °C. Further, zircon fission track dating from the Potsdam and Galway Formations yield peaks at 540, 780 and 1200 Ma (Montario
and Garver 2009), i.e. older than the deposition time. This suggests that the sediments were not heated above 200-300°C for extended periods. Peak pressures were on the order of 0.2 GPa, based on estimates of overlying sediment thickness (<7 km; Friedman 1987). At these low-grade PT-conditions, volume diffusion is too sluggish to explain the observed metamorphic reactions (e.g. chloritization of ferromagnesian silicate, sericitization of feldspar). K-Ar modeling in K-feldspar suggests at least three thermal peaks at 470, 450 and 300 Ma (Heizler and Harrison, 1998). The low-grade reactions, and the growth of Paleozoic REE-phosphates are thus interpreted to reflect fluid-rock interaction and dissolution-precipitation (Putnis and Austrheim 2010). In addition, episodic fluid percolations are likely to bring heat from deeper units, thereby increasing the reaction rate.

Monazite and xenotime results indicate a multiphase crystallization history. Based on composition and U-Th-Pb dating, at least five discrete overgrowth generations were identified, suggesting a minimum of five crystallization events. However, significant questions include: the nature of the reactions involved in the formation of these REE-phosphates, the possible source(s) for the REE, the origin and composition of the fluids responsible for their growth, and finally, the possible causes of the fluid influx events. These will be discussed in subsequent sections.

**Interpretation of Age Peaks**

Monazite and xenotime overgrowth ages are summarized in cumulative age probability diagrams built from the summing of Gaussian probability curves for each set of analyses (Fig. 8). The peaks for monazite (Fig. 8a,b) suggest five discrete pulses at 505, 460, 420, 370, and 225 Ma. These pulses can be grouped in three main categories: (a) diagenetic (i.e. close
to the deposition time at 510-490 Ma), (b) older (470-420 Ma) and (c) younger ages (410-320 Ma). Only two samples yield even younger ages around 250-200 Ma (EC-3, WFR-14). The results are consistent with results from Storm and Spear (2002), who report monazite rim ages between 505 and 395 Ma, and allanite rim ages at 353 and 144 Ma in pelitic samples from the southern Adirondack Mountains.

The peak distribution of monazite dates is different depending on the sample location (Fig. 8b). The distribution of the older age group (470 to 420 Ma) is higher in the PC area (E-side of the Adirondacks) than in the LM or EC areas (NE-side), while younger ages at 410 and 320 Ma are more common in the LM and EC areas. This suggests that crystallization of REE-phosphate was more significant between 470 and 420 Ma in the E-flank of the Adirondacks. Later generations, younger than 420 Ma, are more abundant in samples from the northeastern flank of the Adirondacks.

Most xenotime dates correspond with the younger monazite groups, with two major pulses around 350 and 225 Ma (Fig. 8c). Interestingly, xenotime overgrowths are detached and separated from their original zircon substrate in some samples, and the space is filled with metamorphic minerals (chlorite and illite; Fig. 9). The youngest xenotime with this feature is 320±50 Ma (Fig. 8c). We conclude that low-grade metamorphic conditions persisted or were reestablished periodically until 320 Ma. The late occurrence of xenotime compared to monazite remains difficult to explain without precise fluid composition and metamorphic conditions achieved during each event. We can only speculate that the level of enrichment in HREE required for xenotime crystallization was higher during later events.

The problem of excess $^{230}$Th (an intermediate decay product of $^{238}$U; Schärer 1984; Parrish 1990) cannot be addressed, because the isotope ratios are unknown in our data set. Excess Th can be important in young monazite (< 500 Ma) with a high Th/U ratio. This will induce an excess $^{206}$Pb, which results in abnormally old microprobe dates. Although it is
impossible to estimate the magnitude of this effect, we suspect that it is within the large analytical error for our samples.

Orogenic loading and monazite crystallization

REE-phosphates from the Potsdam Formation record four to five distinct crystallization events (Fig. 8). Although some of the dissolution/precipitation events may have been triggered by thermal pulses alone (with fluid derived from dehydration reactions), it seems likely that crystallization was enhanced by the infiltration of external fluids (fluid pulses) that would not only contribute heat, but also the necessary conditions for dissolution/precipitation (pH, salinity…). The ages shown in Figure 8 broadly correlate with the age of diagenesis and with the age of major orogenic events recorded in the Appalachian Belt to the east: diagenesis (510-490 Ma; Fisher, 1977; Landing et al., 2009), Taconic (480-455 Ma), Salinic (445-420 Ma), Acadian (420-400 Ma), Neo-Acadian (380-350 Ma; van Staal et al. 2009), and Alleghanian (310-250 Ma; Rast 1984; Wintsch et al. 2003; Walsh et al. 2007). We suggest that each event recorded in monazite (after diagenesis) may be related to orogenic loading to the east in the Appalachians Mountains, each of these loading events being accompanied by a thermal pulse as suggested in Heizler and Harrison (1998), and a fluid pulse, also suggested by fluid inclusion data (Table 2 and reference therein; see also discussion on dissolution-reprecipitation). The youngest ages around 250-200 Ma from sample EC-3 and WFR-14 may further reflect fluid flow and distal deformation associated with the breakup of Pangea.

Existing geochronologic constraints on orogenic loading in the Potsdam Formation are rare. Beside data from Storm and Spear (2002), only illite K/Ar ages from the Potsdam Formation around Alexandria Bay are available. Data from Reynolds and Thomson (1993)
yield 360 ± 9 Ma and 392 ± 9 Ma, and an unpublished K/Ar date by Selleck yields 355 ± 12 Ma. These also might suggest that low-grade metamorphism may be distally related to the Neo-Acadian orogeny (395-350 Ma; van Staal et al. 2009). However, considering the range of ages from monazite and xenotime preserved here, and the likelihood of several burial-exhumation events between 500 Ma and 200 Ma around the Adirondack Mountains (e.g. Heizler and Harrison 1998), another explanation may be the effect of mixed ages. The occurrence of several illite generations or partial resetting of K-Ar is likely, and would result in the observed distribution of K/Ar ages.

We also observe that older ages are more common in monazite from PC samples (Fig. 8b). These observations are consistent with studies on extensional structures in and around the Taconic allochthon near Whitehall (Goldstein et al. 2005; Lim et al. 2005): Taconic veins (480-455 Ma) are more common than Acadian or later ones (younger than 420 Ma), and most Taconic faults were not reactivated during the Acadian orogeny. Moreover, homogenization temperatures of fluid inclusion are lower in Acadian veins compared to Taconic veins. The close proximity of PC samples to the Taconic frontal thrust may explain this difference. Other samples, situated north and south of the Adirondack Mountains, are further from the Taconic frontal thrust. Although there are no detailed studies of fault distribution and timing in the northern area near the LM and EC samples, several large scale faults are known to have been reactivated during the Acadian orogeny (Jacobi 2002), and could have induced fluid flow in sediments lying on the NE-side of the Adirondacks, thus promoting the growth of younger monazite.

Source of REE
All monazite overgrowths in the Potsdam samples studied here are characterized by enrichment in LREE, depletion of HREE, Y, and actinides, and also have a higher Eu concentration compared to the detrital cores (Table DR1; Fig. 4). Studies on authigenic and low-grade monazite have suggested several possible sources of REE: (a) REE adsorbed on clay minerals (Burnotte et al. 1989; Milodowski and Zalasiewicz 1991), (b) liberation of REE during the reduction of Fe-oxides and hydroxide (Milodowski and Zalasiewicz 1991; Lev et al. 1998), (c) degradation of organic matter (Evans and Zalasiewicz 1996; Lev et al. 1998), and (d) dissolution of existing REE-rich minerals such as allanite, monazite, or xenotime (Janots et al. 2008; Rasmussen and Muhling 2009). Cases (a) and (b) are likely to occur during the early growth of REE-phosphate, i.e. during burial and diagenesis. However, case (b) remains uncertain because the observed mineralogy suggests a slightly oxic environment; Fe- and Ti- (hydr-) oxides are present together with sulfate, whereas sulfides are only present in the basal layers of the Potsdam Formation. Case (c) seems unlikely due to the absence of significant organic matter in the Potsdam samples. Textures in the Potsdam samples suggest that the most plausible explanation is that detrital monazite is the major source of REE during low-grade metamorphism (case d). Therefore, we suggest that growth of Paleozoic monazite in the Potsdam Formation involves mainly the dissolution of detrital monazite, followed by transportation, and later precipitation. The following non-stoichiometric reaction is suggested:

\[ \text{Mnz}_1 + \text{Fsp} \pm \text{Ap} \pm \text{Grt} \pm \text{Zrn} + \text{Fluid}_1 \rightleftharpoons \text{Mnz}_2 + \text{Xnt} + \text{Thr} \pm \text{Ap} \pm \text{Chl} \pm \text{clay} + \text{Fluid}_2 \] (1)
This reaction involves the dissolution of detrital monazite (Mnz$_1$) and feldspar (Fsp), which releases P and LREE into the solution. The general increase of Eu anomaly (Eu/Eu*)$^1$ between detrital and overgrowth monazite is attributed essentially to feldspar breakdown, especially plagioclase. Eu/Eu* values increase dramatically between detrital monazite (ca. 0.1-0.2) and monazite overgrowths (0.55-1.45 Eu/Eu*; Table DR1). Eu/Eu* is higher for LM samples and for some WNR monazite, which is consistent with the presence of strongly sericitized plagioclase, particularly in LM samples, that may have released Eu into the fluid. Garnet (Grt), zircon (Zrn) and other susceptible minerals potentially provide additional HREE in the fluid.

Once saturated in REE or upon a change in fluid conditions, new monazite enriched in LREE (Mnz$_2$) is precipitated. Detrital apatite (Ap) could provide an additional source of P, and could also re-precipitate later when the solution becomes undersaturated in REE. The REE budget is balanced by the growth of xenotime taking most of the Y+HREE (Fig. 3h,p,t), and also ThSiO$_4$ for the actinides (±Y; Fig. 3g,o,s), both minerals crystallizing mainly around and in fractures of detrital cores. Although no well-constrained analyses were obtained from ThSiO$_4$, due to the fine grain size (typically a few micron or less), analysis of grains in PC-6 reveals a maximum of 1-2 wt% U. Because new monazite and xenotime are poor in actinides, ThSiO$_4$ is the main secondary phase that contains most of the actinides released by the dissolution of detrital monazite. However, the Th/U ratio in ThSiO$_4$ is higher than that of several monazite cores, suggesting that some U remains in solution (see concluding remarks).

The breakdown of feldspar and other silicates is balanced by the growth of chlorite (Chl) and clay minerals (illite or illite/smectite). Other silicates might also be involved in this reaction (e.g. amphibole, mica, oxide, hydroxide). The difficulty of accurately determining

$^1$ Eu/Eu* = Eu$_{CI}$/(Sm$_{CI}$ * Gd$_{CI}$)$^{0.5}$; CI = normalization to carbonaceous chondrite from McDonough and Sun 1995).
the modal abundance of accessory phases prevents an accurate mass balance calculation. Moreover, the relative transport distance of the REE-enriched fluid remains unknown, and the system is likely to have been open.

Fluid-mediated reactions seem most likely (e.g. Putnis and Austrheim 2010), because the metamorphic conditions never exceed lower greenschist facies, and diffusion rates are expected to have been low. This is also supported by the presence of hydrous phases replacing plagioclase and K-feldspar (e.g. chlorite, illite), and more indirectly by the occurrence of hydrothermal veins interpreted to be related to Paleozoic orogenies (e.g. Collins-Waite 1987; Goldstein et al. 2005; Lim et al. 2005). The precise conditions of dissolution-transport-precipitation are difficult to assess, but REE-phosphate chemistry, fluid inclusion studies, and studies on REE speciation in low-grade fluids are helpful. In the following section, we speculate on the possible fluid composition (Fluid_1) associated with each growth phase.

The composition of monazite overgrowth generations varies slightly from sample to sample. Further, correlations between LREE (Ce, La, Nd) and MREE (Pr, Sm, Gd) may reflect a change in pressure, temperature, or fluid conditions (composition, pH, eH). Composition of co-genetic monazite (based on age data) even in a single sample is variable from grain to grain (Table DR1). If the composition of an infiltrating fluid was the dominant control on the composition of new monazite, one would expect it to be homogeneous throughout a specific sample. Instead, the variation seems to suggest local derivation of REE from detrital monazite, which in turn, influences the fluid composition. A strong effect of local rock composition, and thus, partial disequilibrium and lack of homogenization at the thin section scale, is indeed expected for low-grade metamorphism, especially for REE (e.g. Carlson 2002; Vidal et al. 2006).
Dissolution-precipitation of REE-phosphates

The oldest monazite overgrowths in the Potsdam Formation yield ages close to the time of deposition (ca. 510-490 Ma; Fisher 1977; Landing et al. 2009). These overgrowths are usually thinner compared to younger ones. In a few grains, such as m1 in LM-11 (rim1: 507±26 Ma), finger-like or floweret structures are visible in Nd and Sm maps (Fig. 3a,e). A similar fibrous texture is also observed in a monazite overgrowth on zircon (e.g. Fig. 7c). This habit suggests that the precursor of monazite may have been rhabdophane (hydrophosphate), a diagenetic mineral that commonly occurs in fibrous aggregates (e.g. Milodowski and Zalasiewicz 1991; Lev et al. 1998; Čopjaková et al. 2011). However, Akers et al. (1993) suggested that rhabdophane is unlikely to be the precursor of monazite. Schatzmann et al. (2009) observed floweret crystals of LaPO₄ precipitating from La(NO₃)₆H₂O and phosphoric acid reaction at low temperature, so this texture may be common to early monazite growth during low-temperature diagenesis.

Early burial could also have caused an increase in temperature during diagenesis, but in the absence of constraints on the early burial history of the Potsdam Formation in the area studied, this hypothesis remains to be tested. Fluids may have played a more important role in the early precipitation of monazite; studies on low-grade "authigenic" monazite have suggested that the release of pore water, the dehydration of clay minerals, and/or the infiltration of meteoric water could have induced the initial precipitation of monazite at ca. 510-490 Ma (e.g. Milodowski and Zalasiewicz 1991; Evans and Zalasiewicz 1996; Rasmussen et al. 2001; Čopjaková et al. 2011). In contrast to black shale and mud rock (e.g. Evans et al. 2002; Wilby et al. 2007), the Potsdam Formation has very little organic matter, and the presence of hydrocarbon is unlikely at this stage in the burial history. No xenotime of
this age has been identified. This suggests that (a) xenotime was unstable during early burial, (b) the fluid was mostly saturated in LREE, or (c) the amount of xenotime produced was too small to be identified and/or that it was dissolved during a later event.

The presence of hydrous minerals (chlorite, illite), together with calcite, sulfate and other diagenetic minerals in the Potsdam Formation suggests low-grade metamorphism reaching a maximum of 250°C. Fluid-inclusion studies, summarized in Table 2, provide some constraints on the possible fluid composition and temperature (Collins-Waite 1987; Elliott and Aronson 1987; Whitney and Davin 1987; O’Reilly and Parnell 1999; Goldstein et al. 2005; Lim et al. 2005). Fluids associated with thrusting during the Taconic orogeny yield low salinity and variable homogenization temperatures pointing to maximum temperature between 170 and 280°C (Lim et al. 2005; Goldstein et al. 2005). These fluids are likely to have originated from the dehydration of clay minerals (e.g. Milodowski and Zalasiewicz 1991; Lev et al. 1998; Goldstein et al. 2005). Variable salinity in the range 5-12% NaCl equivalent is observed in samples close to the carbonate platform due to the mixture of water-rich fluid with saline fluid from the carbonate platform (Lim et al. 2005). During the Acadian and Neo-Acadian orogenies (420-350 Ma), fluid temperature decreased to 145-225°C and salinity increased up to 21% equivalent NaCl due to the possible reflux of Silurian evaporite brines (Collins-Waite 1987). Finally, during the Alleghanian orogeny (310-250 Ma), highly saline and medium-warm (70-130°C) fluids induced further clay transformation in the southern Appalachians (illitization; Elliott and Aronson 1987). This is possibly accompanied by hydrocarbon enrichment (O’Reilly and Parnell 1999).

REE speciation
Several studies have investigated the speciation of REE in sediments at variable temperature, pH, eH, and fluid composition (McLennan 1989; Haas et al. 1995; Lewis et al. 1997; Lev et al. 1998, 1999; Gimeno Serrano 2000; Smith et al. 2000). Fluoride, chloride and hydroxide create REE complexes at low, neutral and high pH, respectively (Haas et al. 1995). There is no evidence in the literature for F-rich fluid percolating in the Potsdam Formation and other Paleozoic units, and therefore it is likely that Cl-content in fluid and pH play a major role in REE speciation. From the fluid-inclusion data presented above, an increase in fluid salinity was observed between Taconic and Neo-Acadian orogenies (i.e. from 510 to 350 Ma; Table 2). In addition, fluids were significantly hotter around PC and WFR samples, up to 280°C (Collins-Waite 1987; Lim et al., 2005); these warmer and more saline fluids would have enhanced REE-dissolution, which is consistent with the prominence of Taconic ages in monazite overgrowths from PC and WFR samples (warmer fluid) and of Acadian or Neo-Acadian ages in those from EC and LM samples (higher fluid salinity; Fig. 8b). The formation of carbonate complexes may further enhance the dissolution of REE in the form of bicarbonate (REE-HCO$_3$) or carbon trioxide (REE-CO$_3$) depending on pH (Haas et al. 1995). A slightly higher La/Nd ratio in monazite overgrowths from PC and WFR samples further suggests interaction with carbonate-bearing fluid (e.g. Smith et al. 2000).

The larger volume of monazite overgrowths compared to xenotime, and the depletion of HREE in monazite overgrowths compared to cores can be further explained by the presence of Cl, which preferentially creates complexes with LREE (Haas et al. 1995). This may also explain the scarcity of xenotime compared to monazite. REE can also be dissolved through interaction with sulfate complexes (Lewis et al. 1997; Gimeno Serrano 2000). This is likely the case for WNR samples, where sulfates are present, and monazite shows a significant amount of S (Table DR1). Finally, hydrocarbon-rich fluids are likely to release additional REE into fluids (e.g. Lev et al. 1998), and to further induce new monazite
crystallization during the Alleghanian orogeny (310-250 Ma) where hydrocarbon-rich fluids have been documented (O’Reilly and Parnell 1999). More details on fluid REE-enrichment and precipitation necessitate more accurate fluid composition data. Another unknown is the exact pH of these fluids; a lower pH might have enhanced the dissolution of REE-minerals (Lewis et al., 1997), but in the absence of specific fluid composition data this remains elusive. Despite the limited knowledge of fluid composition, we conclude that the solubility of REE in the Potsdam Formation is essentially triggered by an increase in temperature and fluid salinity, whereas a decrease of temperature during (partial) exhumation would induce precipitation. Locally, sulfur-, carbonate- or hydrocarbon-rich fluids are potential candidates for enhancing dissolution of detrital monazite.

The role of feldspar

Finally, some monazite rims appear to grow into K-feldspar (thickest rim adjacent to K-feldspar; Fig. 7a,b). This disequilibrium texture further implies a strong interaction with a fluid that promotes metasomatism and dissolution-precipitation as described in Putnis and Austrheim (2010). Plagioclase is also altered, and participates in the monazite forming reactions through the release of Eu in fluid and the enrichment in Eu in monazite overgrowths compared to cores (Fig. 5). These features suggest that (a) monazite rims preferentially grow toward susceptible minerals, and (b) the dissolution of alkali in fluids could enhance the process of monazite dissolution and precipitation. The latter has been demonstrated experimentally at both low and high PT-conditions (Chisca et al. 2009; Harlov et al. 2011).

The dissolution of K-feldspar or plagioclase is expected to increase the alkali-content in solution, inducing a local increase of pH. Experiments on REE-speciation at different pH
demonstrate a strong diminution of REE-solubility at near-neutral conditions (e.g. Lewis et al. 1997; Oelkers and Poitrasson 2002; Poitrasson et al. 2004). A sudden neutralization of fluid acidity through K-feldspar dissolution could induce the precipitation of REE-minerals. However, clays (e.g. illite) also locally replace the feldspar, and this reaction would tend to buffer the pH and the fluid alkalinity. Dissolution and precipitation may reflect the local balance of conflicting influences on fluid pH and fluid composition.

Concluding remarks

The study of accessory phases, notably REE-phosphate, in low-grade sediments has a great potential not only to date but also to provide a qualitative and quantitative characterization of fluid infiltration in sedimentary units. Obviously, more work is required on this subject and is beyond the scope of this paper. The electron microprobe offers high-spatial resolution in situ dating of these micrometer-sized overgrowths. However, the technique has its limitations, notably in terms of precision and accuracy, dictated by the detection limits of U, Th, and Pb measurements, and by the potential for excess $^{230}$Th (Schärer 1984; Parrish 1990) particularly in younger monazite. Laser ablation or isotope dilution techniques could potentially overcome this issue, but these techniques will likely yield mixed ages, because most of the monazite grains have multiple narrow (5-10 µm) overgrowth domains with relatively complex geometry.

The process of dissolution-precipitation of REE-phases is still subject to several unknowns. It is crucial to have a better knowledge of fluid conditions (temperature, pH, $eH$, composition) associated with the process of dissolution-precipitation, and in this sense, fluid inclusion data could be extremely useful (e.g. Smith et al. 2000). Although no fluid inclusion
data have been collected for our samples, the composition of REE-phases can be used as a qualitative indicator of fluid conditions. The REE-pattern of monazite indicates Y, HREE, Th, and U depletion, compensated by LREE enrichment. Xenotime is also typically poor in actinides, although slightly richer in Th and U compared to monazite in these samples; the REE-budget is dominated by HREE. These results imply that the REE-pattern of a sedimentary rock can be strongly affected by fluid percolation, which calls into question the use of REE-patterns as indicators of sediment provenance (McLennan 1989). To assess the precise conditions of leaching in sedimentary environments, further investigations combining bulk-rock geochemistry, fluid inclusion data, and modeling of REE-speciation under variable fluid conditions is required.

Finally, the results of the study have implications for the use of phosphates in nuclear waste storage. REE-phosphates are thought to be candidates for nuclear waste storage (e.g. Ewing and Wang 2002; Oelkers and Montel 2008; Chisca et al. 2009), as they can contain significant amounts of actinides, are resistant to metamictization, and have a fast recovery from damage induced by alpha particles. However, several studies at lower PT-conditions have demonstrated that alkali-rich fluid, notably KOH fluids, can potentially alter monazite to an amorphous phase, as can HCl and humic acid commonly found in soil (e.g. Chisca et al. 2009; Polyakov et al. 2010). Our study and other field studies have highlighted the potential for hydrothermal alteration or dissolution-reprecipitation of REE-phosphates under geological conditions that would approach those of long-term storage for nuclear waste (e.g. Poitrasson et al. 1996, 2000; Read et al. 2002). Although the exact timing for such reactions remains largely unknown, the rapid rate of experimental reactions showing dissolution-reprecipitation of monazite at 300-500 °C (e.g. Harlov et al. 2007; Williams et al. 2011) suggests that reaction progress under natural conditions could be very rapid. An important point is that newly formed monazite in the fluid rich diagenetic environment is poor in
actinides relative to associated and partially dissolved detrital monazite. Whereas most of the
Th from detrital monazite appears to reprecipitate as ThSiO$_4$, the fate of U remains less
certain. Both ThSiO$_4$ (Th/U = 20-718) and monazite overgrowths (Th/U = 34-620) in sample
PC-6 yield higher Th/U ratios compared to monazite cores (Th/U = 5.5-90), which would
suggest that U partly remains in solution. This observation is further supported by
experiments at high pH, which progress eventually to the reprecipitation of Th minerals, and
U enrichment of the fluid (Clavier and Dacheux 2006). Monazite is certainly better than a
glass matrix for actinide storage (Oelkers and Montel 2008), but further research regarding
the short-term (laboratory time scale) and long-term (natural field time scale) behavior of
monazite under hydrogeological conditions is clearly warranted.

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References


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Figure captions

Figure 1: Simplified geological map highlighting the Adirondack massif and the Potsdam Formation. Sample locations are Ellenburg, NY (EC: 44.8693 N / 73.8146 W); Laphams Mills, NY (LM: 44.5873 N / 73.5001 W); Putnam Center, NY (PC: 43.7546 N / 73.4071 W); Wright's Ferry Road, NY (WFR: 43.7992 N / 73.3865 W); Erin, NY (core sample from Olin #1 well; WNR: 42.1734 N / 76.1855 W).

Figure 2: (a) Age versus Th-content in monazite rims. (b) Exponential relation between error on age, and Pb- or Th-content.

Figure 3: WDS compositional mapping in monazite from samples (a-c, e) LM-11 grain m1, (f-i) PC-2A grain m3, (j-l) EC-3 grain m2, (n-q) WNR-1 grain m6, and (r-u) WNR-3 grain m6. Green dots in (a), (f), (k), (n) and (r) indicate analyzed area and dates in Ma (2σ error). (d) Cross-polarized microphotograph of monazite grain in LM-11. (m) Plan-polarized microphotograph of monazite grain in EC-3. The monazite grains in (d) and (m) are contoured with a red line, and the detrital core with a dashed red line.

Figure 4: Ternary diagrams (LREE) – (HREE+Y) – (thorite/huttonite+cheralite) for (a) monazite detrital core, (b) rim, and (c) xenotime.

Figure 5: REE spectra for (a) detrital cores and (b) rims of monazite normalized to “Moacyr” (Brazilian monazite reference material). Grey area represents the range of variation (a) for
rims and (b) for cores. An average composition of 3 to 12 analyses is used for each spectrum.

(c,d) Chondrite normalization using the CI chondrite from McDonough and Sun (1995). A strong negative Eu-anomaly is visible in all monazite cores, but is absent or only weakly negative for monazite rims and xenotime.

**Figure 6:** (a) Summary of age results for detrital monazite cores. Error (2σ) is equal or less than symbol size. (b) Same results using Gaussian probability curve.

**Figure 7:** WDS element mapping of U Mβ in grains (a) m1 and (b) m4 of sample PC-6 showing the relation between monazite overgrowths and K-feldspar (Kfsp). K-rich phase is visible on these element maps because the peak position of K Kα overlaps that of U Mβ. Kfsp inclusions are restricted to the monazite overgrowth, and the monazite rim preferentially overgrows Kfsp. (c) BSE image highlighting the growth of “fibrous” monazite on a detrital zircon in sample EC-1A.

**Figure 8:** Cumulative probability plots obtained by summing the Gaussian probability curves, and normalizing to the number of samples considered (n). (a) All data (monazite rims and xenotime), (b) monazite rims, and (c) xenotime. In (b) and (c) data have been split according to the sample location relative to the Adirondack Mountains: northeast (LM, EC), east (PC, WFR) and southern area (WNR). D: deposition time (diagenesis); T: Taconic orogeny; S: Salinic orogeny; Ac: Acadian orogeny; nAc: Neoacadian orogeny; Al: Alleghenian orogeny.
Figure 9: Xenotime overgrowth on zircon in sample PC-6. A late crack has appeared between this overgrowth and the zircon, and is now sealed by chlorite, mixed-clay-interlayer (possibly illite/smectite) and quartz. Inset: WDS compositional map of Th Mα.

Table captions

Table 1: Typical quantitative analysis (average on 4 to 8 points) for core and rim monazite in sample LM-11 and PC-6, and for one xenotime in sample PC-6.

Table 2: Synthesis of fluid inclusion studies in the Appalachian region during the Taconic, Acadian, Neo-Acadian and Alleghanian orogenies.

Data repository

Table DR1: Complete set of averaged analysis for monazite and xenotime. For rims, row “position” refers to the internal (in), middle (mid) or external (out) rim. 3 to 12 analyses points are averaged in each homogeneous domain. Points showing an obvious difference of chemistry were dismissed. Error on age results is given at 2σ. Eu* and Ce* are respectively Eu- and Ce-anomaly, normalized to chondrite CI (see text).
Figure 1
Figure 2
Figure 3
Figure 4
Figure 5
Figure 6

(a) Age [Ga]

Age: 0.9 to 1.2

- EC-1a
- EC-3
- LM-11
- PC-2A
- PC-6
- WNR-1
- WNR-3

1. Shawinigan orogeny
2. Late granite dykes
3. Ottawan orogeny

(b) Age [Ga]

Age: 0.9 to 1.2

0.00 to 0.10

Probability

Hawkeye granite

Late granite dykes
Figure 7
**Figure 8**

(a) Distribution of ages for Mnz (n=45) and Xnt (n=24) minerals.

(b) Distribution of ages for EC+LM (n=16), PC+WFR (n=20), and WNR (n=9) mineral groups.

(c) Distribution of ages for LM-12 (n=5), EC-3 (n=3), PC-2A & PC-6 (n=16) mineral groups.
Figure 9
### Table 1

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<td>Condition</td>
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<td>Taconic (480-450 Ma)</td>
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<td>Low salinity, 5-12% NaCl equivalent, maximum close to carbonate platform</td>
<td>Lim et al. (2005)</td>
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<td>170°C (Swanton) to 280°C (Albany, Whitehall)</td>
<td>Lim et al. (2005)</td>
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<td>Elliott and Aronson (1987)</td>
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<td>Northern Appalachian</td>
<td>Saline fluid Hydrocarbon enrichment</td>
<td>O’Reilly and Parnell (1999)</td>
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