Re–Os depositional age for Archean carbonaceous slates from the southwestern Superior Province: Challenges and insights

G. Yang, J.L. Hannah, A. Zimmerman, H.J. Stein, A. Bekker

1. Introduction

Since early work by Ravizza and Turekian (1989), a number of studies have utilized Re–Os geochronology to determine the time of deposition for carbonaceous shales. Re and Os in carbonaceous shales are mainly of hydrogenous origin because both Re and Os are fixed by reduction with organic matter at or below the sediment–water interface in anoxic environments (Ravizza et al., 1991; Ravizza and Esser, 1993; Cohen et al., 1999; Jaffe et al., 2002). The \(^{187}\text{Re}–^{187}\text{Os}\) isotopic system with its long half-life (\(\lambda^{187}\text{Re} = 1.666 \times 10^{-11}\); Smoliar et al., 1996; Shen et al., 1996) can provide highly precise depositional ages for carbonaceous sedimentary rocks. Early methods for digestion of shales, however, introduced significant uncertainty in the ages. In particular, the common method of digestion in Carus tubes using inverse aqua regia, dissolves or leaches the entire rock, including non-hydrogenous detritus. Mixing of Re and Os from both hydrogenous and non-hydrogenous sources reduces the overall accuracy and precision of the isochron age and initial \(^{187}\text{Os}/^{188}\text{Os}\) ratio \((O_{187})\). Hannah et al. (2004) circumvented this problem by analyzing syndepositional sulfides, establishing a highly precise age for Paleoproterozoic shales. In many cases, however, sulfides have exchanged Re and Os with fluids or organic material during recrystallization, and therefore yield post-depositional or spurious ages (Hannah et al., 2006). Selby and Creaser (2003) recommended
H$_2$SO$_4$-CrO$_3$ as the digestion reagent to release mainly hydrogenous Re and Os from organic matter in carbonaceous shales. This new method yields significantly less scatter around $^{187}$Re/$^{188}$Os isochrons and, therefore, more accurate and precise age and Osi data (Kendall et al., 2004; Hannah et al., 2006).

Os, in the hydrogenous fraction of carbonaceous shale reflects the Os isotopic composition of seawater at the time of deposition (Ravizza and Turekian, 1989, 1992; Cohen et al., 1999). Because Re and Os compounds are remarkably insoluble when reduced, but mobilized under oxidizing conditions, radiogenic Os can be delivered to the oceans only by oxidative weathering and transport from the continents. In the anoxic Archean environment, therefore, seawater Os was dominated by chondritic sources, such as mid-ocean ridge hydrothermal systems and dissolution or leaching of cosmic dust (Hannah et al., 2004). Thus, we can anticipate a chondritic Osi in Archean carbonaceous shales. Several recent studies of Archean shales, however, have produced sub-chondritic Osi (Anbar et al., 2007; this study; AIRIE, unpublished data). Here we propose that recent oxidation of reactive materials with high Re/Os ratios, such as mafic tuffs, during exposure to meteoric groundwater can release Re which is then reduced and incorporated into adjacent carbonaceous shales. This shifts the isochron to higher $^{187}$Re/$^{188}$Os ratios and produces a spuriously low Osi intercept.

For this study, we focus on Neoarchean rocks of the Deer Lake greenstone belt near Bigfork, Minnesota, in the western Wawa subprovince of the Superior Province (Fig. 1). This belt comprises the Thistledew Lake sequence of Fe-rich tholeiitic basalt flows, rare clastic rocks, and hypabyssal sills, the overlying Joy Lake sequence of supracrustal strata with intercalated mafic and felsic tuff layers, and the intrusive peridotite–pyroxenite–gabbro sills of the Deer Lake Complex (Jirsa, 1990; Severson and Jirsa, 2005; Fig. 2). There are no age constraints on the deposition of Neoarchean supracrustal successions in northern Minnesota, although broadly correlative successions to the east in the Wawa subprovince of Canada are well dated (Corfu and Stott, 1998). In the Shebandowan greenstone belt (Fig. 1), the oldest Greenwater assemblage includes ca. 2720 Ma ultramafic to felsic volcanic rocks, peridotitic, gabbroic, and anorthositic intrusions, and volcanogenic massive sulfide deposits. The unconformably or structurally overlying ca. 2695 Ma Kashabowie assemblage contains felsic volcanic and volcaniclastic rocks intruded by felsic plutons. The youngest ca. 2692–2689 Ma unconformably overlying Timiskaming-type Shebandowan assemblage contains calc-alkaline to alkaline volcanic and coarse-grained sedimentary rocks deposited in pull-apart basins. This assemblage was intruded by tonalites and syenites at ca. 2690 Ma. Subsequent deformation during the 2685–2680 Ma Shebandowan phase of the Kenoran Orogeny, related to collision of the Wabigoon and Wawa volcanic arcs, is expressed by the regional D$_2$ event (Fralick et al., 2006; Percival et al., 2006; Fig. 1).

Poor exposure and lack of geochronologic data for supracrustal sequences of northern Minnesota hinder construction of a geologic framework for the western part of the Wawa subprovince. This compromises correlation and metallogenetic comparison with other sedimentary successions in the Wawa subprovince and Superior Province. The Deer Lake Complex was the target of Cu–Ni exploration during the late 1960s and early 1970s (Ripley, 1983). Although exploration did not define economic ore deposits in the Deer Lake Complex, the drill cores provide access to intercalated supracrustal rocks of the Joy Lake sequence (Severson and Jirsa, 2005). In this study, H$_2$SO$_4$-CrO$_3$ digestion is used to acquire the depositional age of the Joy Lake sequence. Our Re-Os ages for the Joy Lake sequence permit correlation with other supracrustal sequences in the Superior Province, constrain timing of the dominant regional deformation event, and provide a maximum emplacement age for the Deer Lake Complex. In addition, the data point to a possible cause for spuriously low Osi determined from isochrons for Archean carbonaceous shales.

2. Geologic setting

The Joy Lake sequence is confined to the Deer Lake greenstone belt, which resembles and is likely broadly correlative with the classic Neoarchean greenstone sequence in the Vermillion district to the east (Sims, 1972). Supracrustal volcanic and sedimentary rocks are bordered on the northwest by poorly studied undifferentiated granitic

![Fig. 1. Subprovinces of the southern Superior Province (from Card, 1990 and Percival et al., 1994) with locations of the areas referred to in the text shown.](image-url)
rocks and on the south by the syenite of the Coon Lake pluton. Early deformation of the supracrustal rocks produced nappe-like isoclinal folds whose overturned limbs are currently exposed at the surface (Jirsa et al., 1992). The \( \text{F}_1 \) folds, associated \( \text{D}_1 \) cleavage, and axial planar veins were refolded during the dominant \( \text{D}_2 \) deformation and accompanying greenschist facies metamorphism. Subsequent deformation (\( \text{D}_3 \)) generated brittle structures and a NE-trending fabric in syntectonic plutonic rocks.

Severson and Jirsa (2005) divide the supracrustal rocks into two sequences. The lower Thistledew Lake sequence consists of high-Fe tholeiitic metabasalts and marks the stratigraphic base in this area. Although strongly deformed in the study area, exposures to the east show well-developed flows with massive bases, pillowed interiors, and fragmented tops. The overlying Joy Lake sequence comprises sedimentary and volcanic units, some of which may be contemporaneous with the Thistledew Lake sequence and are mapped as its lateral equivalents. The sedimentary unit at the top of the sequence includes interbedded slate and graywacke, with lesser amounts of carbonaceous slate (the focus of this study), felsic tuff, mafic tuff, and chert. All units display a well-developed cleavage attributed to the \( \text{D}_2 \) deformation. Sparse development of \( S_1 \) cleavage in these units suggests that \( \text{D}_2 \) occurred at least partly prior to consolidation of sedimentary units, leading Jirsa et al. (1992) to propose an accretionary wedge setting for deposition and deformation. The graywackes comprise turbiditic Bonna A units, suggesting a relatively proximal environment. The adjacent volcanic unit consists of dacite, andesite, quartz latite tuff and breccia, with sparse hornblende andesite tuff and amygdaloidal flows, locally interbedded with volcanioclastic graywacke and conglomerate (Severson and Jirsa 2005). These rock types suggest a depositional setting proximal to a volcanic arc, in part subaerial, with local deeper-water sediment-starved basins accumulating carbonaceous muds in an anoxic Archean environment.

The supracrustal rocks are intruded by the Deer Lake Complex, a series of interfingered mafic and ultramafic sills (Berkley et al., 1978; Ripley, 1979; Ripley et al., 1982; Ripley, 1983; Jirsa, 1990; Severson and Jirsa, 2005). The intrusive rocks include layered peridotite–pyroxenite–gabbro sills, a gabbroic body with an unexposed basal section, and ultramafic lenses. As a result of greenschist facies metamorphism, olivine is extensively serpentinized, pyroxene is altered to amphibole, and plagioclase is saussuritized. The Deer Lake Complex as defined by Severson and Jirsa (2005) also includes a unit of ultramafic and mafic volcanic rocks comprising high-Mg tholeiitic, komatiitic, and ultramafic flows, some with spinifex-textured bases, along with common lenses of carbonaceous argillite. Olivine and pyroxene in these flows are largely pseudomorphed by talc and actinolite. Both the supracrustal rocks and the Deer Lake Complex are cut by the NW-trending Kenora-Kabetogama diabase dike swarm (equivalent to the Fort Frances dikes in Canada), which yields a baddelyite U–Pb age of 2.076 ± 0.05 Ga (Southwick and Day, 1983; Buchan et al., 1996).

3. Sampling and analytical procedures

The sampled drill holes both angle about 45° to the northwest through an overturned section (Fig. 3). The intersected units consistently show nearly vertical dips and tops down hole (NW), as indicated by graded bedding, spinifex textures, and pillowowed flows. The carbonaceous slates, which comprise up to 25% by volume of supracrustal rocks in drill cores, range from 0.3 to 300 m in thickness and contain up to 10% pyrite, occurring as nodules, concretions, disseminated crystals, and bedding-parallel seams (Ripley and Nicol, 1981; Severson and Jirsa, 2005). Both drill holes intersected intervals of carbonaceous slate in the Joy Lake sequence. Contrasting contact relationships are exhibited by the two cores, however (Fig. 3). In DH26503, the sampled interval is bracketed by massive gabbroic sills...
of the Deer Lake Complex, including a shear zone at the lower contact and a chilled margin at the upper (down hole) contact. In DH26506, the sampled interval is not adjacent to intrusive rocks. The upper (down hole) contact is with volcaniclastic lithic wacke and siltstone of the Joy Lake sequence, which typically includes intercalated felsic and mafic tuffs. The lower (up hole) contact is with mafic volcanic rocks of the Deer Lake Complex.

Pyrite, confined to finely laminated carbon-rich layers, occurs as nodules, disseminated grains, and laminated seams within the carbonaceous slate. Local folding of the pyrite seams is attributed to the Joy Lake sequence, which typically includes intercalated felsic and mafic tuffs. The lower (up hole) contact is with mafic volcanic rocks of the Deer Lake Complex.

Pyrite was sampled over short drill core intervals (≤2 m) to minimize potential temporal variations in the Os ratio (Hannah et al., 2004). For DH26503, about 500 mg of powder was produced by micro-drilling, using a new diamond drill bit for each sample. We have tested several lot of drill bits by wearing them down on pure quartz and analyzing the resulting grey powder; near blank levels of Re and Os were found. Nevertheless, care is taken that diamonds are not badly worn during drilling, and that the metal does not contact the rock. For DH26506, clean chips weighing less than 1 g were manually pulverized with a corundum mortar and pestle. Replicate analyses were made on adjacent chips, pulverized and dissolved separately. Inclusion of sulfide and calcite veins was minimized by micro-drilling under a microscope or by selection of carefully inspected chips.

For dissolution, a CrO3·H2SO4 solution was made by dissolving 0.2 g CrO3 per ml of 4N H2SO4. About 500 mg of the whole rock powder were accurately weighed and loaded into Cairius tubes with 187Re and 186Os spikes and 15 ml of the CrO3·H2SO4 solution, then digested at 240 °C for 36 h, following the procedure outlined in Selby and Creaser (2003). Os was measured and purified by CHCl3 solvent extraction and micro-distillation. After Os extraction, SO2 gas was bubbled through the remaining Re-bearing solution for 3 min to reduce Cr(III) completely to Cr(II). Rhenum was then separated by anion exchange chromatography with 1 g Eichrom 1×8 100–200 mesh CI-form resin. Rheun was purified further by single bead anion extraction.

Purified Re and Os were loaded onto Pt filaments and isotope ratios were determined using Negative Thermal Ionization Mass Spectrometry (NTIMS) in peak-hopping mode on the NBS mass-spectrometer at the AIRIE laboratory, Colorado State University. Measured isotopic ratios of Re and Os were corrected for isobaric oxygen interferences, mass fractionation of Os (182Os/188Os = 0.08271, Brandon et al., 1999), and blank contributions. Re–Os isochrons were constructed with Isotop 3.0 (Ludwig, 2003), using a 187Re decay constant of 1.666 × 10−11 year−1 (Smoliar et al., 1996) and calculated 2σ uncertainties.

### Table 1

<table>
<thead>
<tr>
<th>Depth in Core</th>
<th>Re, ppb</th>
<th>Os, ppb</th>
<th>187Re/188Os</th>
<th>187Os/188Os</th>
<th>Rho</th>
</tr>
</thead>
<tbody>
<tr>
<td>304.8–305.4</td>
<td>5.439 (4)</td>
<td>0.1967 (4)</td>
<td>659 (2)</td>
<td>30.38 (12)</td>
<td>0.60</td>
</tr>
<tr>
<td>304.8–305.4</td>
<td>4.738 (4)</td>
<td>0.1656 (3)</td>
<td>800 (2)</td>
<td>36.97 (14)</td>
<td>0.59</td>
</tr>
<tr>
<td>304.8–305.4</td>
<td>6.024 (4)</td>
<td>0.2135 (3)</td>
<td>505 (1)</td>
<td>23.33 (8)</td>
<td>0.57</td>
</tr>
<tr>
<td>306.3</td>
<td>15.12 (1)</td>
<td>0.5139 (10)</td>
<td>770 (2)</td>
<td>35.22 (12)</td>
<td>0.58</td>
</tr>
<tr>
<td>306.9</td>
<td>12.80 (1)</td>
<td>0.4150 (9)</td>
<td>1343 (4)</td>
<td>61.74 (31)</td>
<td>0.61</td>
</tr>
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<td>305.4</td>
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</tr>
</tbody>
</table>

### 4. Results

Samples from drill core DH26503 yield a 5-point isochron with a Model 1 age of 2695 ± 14 Ma, Os of 0.15 ± 0.16, and MSWD of 0.80 (Table 1, Fig. 4A). Re and Os concentrations range from 4.7 to 12.8 ppb and 0.166 to 0.532 ppb, respectively. Samples from drill core DH26506 yield an 8-point errorchron with a Model 3 age of 2684 ± 16 Ma, Os of −0.29 ± 0.20, and MSWD of 3.8 (Table 1, Fig. 4B). Re and Os concentrations range from 12.6 to 24.9 ppb and from 0.423 to 0.836 ppb, respectively. The isochron age for samples from drill core DH26503 is consistent with that for samples from drill core DH26506 within the uncertainties. If the results from the two drill holes are combined on a single 13-point errorchron, the result is a Model 3 age of 2679 ± 40 Ma, Os of −0.23 ± 0.55, and MSWD of 49 (Fig. 4C). The age is consistent with the broad regional age constraints on this sequence. The high errors and MSWD, however, clearly indicate real geologic scatter in the
5. Discussion

5.1. Precision and accuracy of the ages

The statistics on the isochron for DH26503 are excellent, and the age therefore likely reflects the depositional age. In our experience and in published Re-Os results for shales, post-depositional disturbance increases both the isochron uncertainties and the MSWD. While the isochron age may reflect isotopic closure after compaction and perhaps early diagenesis, it is highly unlikely that these processes extended for more than the 14 m.y. uncertainty on the age. There are no reported instances of a fully reset isochron (e.g., by metamorphism or hydrothermal alteration) without significant scatter of the data. Moreover, as discussed below, the age of ca. 2695 Ma is consistent with the existing regional geochronology.

Although the isochron for DH26506 also has an uncertainty of only 0.6% for the age, the MSWD is slightly elevated (3.8), suggesting minor disturbance. The analytical uncertainties for these data reflect the best measurement capabilities of the NBS mass-spectrometer used in the study. Instrumental uncertainties for isotopic ratio measurements are less than 0.04% for $^{187}\text{Re}^{188}\text{Os}$, 0.24% for $^{187}\text{Os}^{188}\text{Os}$, and 0.12% for $^{185}\text{Os}^{188}\text{Os}$, although fully propagated analytical uncertainties, including error magnification, are up to an order of magnitude greater. The calculated MSWD decreases as analytical uncertainties increase, and slightly higher analytical uncertainties for DH26506 would result in a Model 1 age with MSWD < 1. Furthermore, if the data for DH26506 are forced into a Model 1 regression, none of the parameters—age, initial ratio, uncertainties, or MSWD—change significantly. Thus, while we base our conclusions on the more reliable isochron age for DH26503, the two ages are statistically indistinguishable, and there is no reason to doubt the validity of either one.

Quality of results may be dependent upon the amount of material homogenized prior to sub-sampling for dissolution (e.g., Kendall et al., in press). Small-scale decoupling of parent and daughter isotopes by transport or diffusion after deposition can introduce heterogeneities in Os, thereby causing scatter on the isochron diagram. To overcome this, samples must be large enough to capture the potential isotopic migration. At the same time, if too much material is homogenized, there may be no variation in $^{187}\text{Re}^{188}\text{Os}$, which also compromises quality of the isochron. Because our results were achieved by homogenizing less than 1 g of material, we suggest that for very old samples the errors introduced by parent and daughter decoupling are smaller than the uncertainties caused by other factors (e.g., ~0.31% uncertainty on the decay constant).

5.2. Secular variations in Re and Os concentrations

Re and Os concentrations in seawater reflect input from seafloor hydrothermal activity, meteoritic dust, and continental weathering. Because Re and Os are both redox-sensitive elements, their dissolution and transport in surface environments depend on the redox state of the atmosphere. Under anoxic atmospheric conditions such as inferred for the Archean, seawater is expected to have low concentrations of both Re and Os, and Os sources dominated by chondritic compositions (Yang et al., 2002; Hannah et al., 2004; Anbar et al., 2007). The low initial Os for DH26503, although imprecise, is consistent with a chondritic composition for seawater Os. Re and Os concentrations and $^{187}\text{Re}^{188}\text{Os}$ ratios are significantly higher than those of the average continental crust (Esser and Turekian, 1993; see Fig. 5) indicating larger Re and Os fluxes with higher $^{187}\text{Re}^{188}\text{Os}$ ratios than those expected from simple recycling of Re and Os from continental crust on the Archean anoxic Earth. The Re and Os concentrations and $^{187}\text{Re}^{188}\text{Os}$ ratios are also comparable to those cited by Anbar et al. (2007) for the stratigraphic interval that provides evidence for “a whiff of atmospheric oxygen” prior to the early Paleoproterozoic Great Oxidation Event (Holland, 2002; Bekker et al.,

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Fig. 4. Re-Os isochrons for the Joy Lake carbonaceous slates: (A) data for DH 26503, (B) data for DH 26506, and (C) all data combined. Symbols are larger than analytical uncertainties. Insert shows the plot of weighted residuals. A positive value indicates a point above the isochron; a negative value indicates a point below the isochron.

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The impossible, negative Osi ratio in Fig. 4B likely documents open-system behavior that has shifted the data points to the right (higher $^{187}\text{Re}^{188}\text{Os}$ and/or lower $^{187}\text{Os}^{188}\text{Os}$) with minimal impact on the isochron age, as discussed below.
Formation from Selby and Creaser (2003) are the (unpublished data; see Hannah et al., 2008) are analyses of shungite, a unique analytical method, although there is no reason to doubt their accuracy. Data from AIRIE organic carbon. See text for details.

Paleoproterozoic "migrated pyrobitumen" that contains more than 50% organic carbon. See text for details.

Concentrations in individual samples are dependent upon a number of factors, including total organic carbon contents, sulfur concentrations, sedimentation rates, dilution by carbonate, uptake mechanism, and analytical procedures. As none of these factors are fully constrained in the comparisons made here, further pursuit of the argument is not warranted. To demonstrate a short-term excursion in Re and Os concentrations, a detailed stratigraphic profile of concentrations in a single section is required, as was done for Re by Anbar et al. (2007).

While absolute concentrations are controlled by the above mentioned factors, we might expect the $^{187}\text{Re}/^{188}\text{Os}$ ratios to be higher in Archean shales. This is because Archean seawater was dominated by hydrothermal sources with relatively high $^{187}\text{Re}/^{188}\text{Os}$ ratios. Fig. 5 shows that indeed the two Archean data sets have the highest values, but range to relatively low values. We infer that Re and Os concentrations as well as $^{187}\text{Re}/^{188}\text{Os}$ ratios in these two shale sets may reflect enhanced hydrothermal circulation that accompanied ca. 2.7 and 2.5 Ga mantle plume breakout events that are also responsible for a global peak in mafic-ultramafic magmatism, sea-level rise, deposition of organic matter-rich sulfidic shales, enhanced continental weathering, and banded iron formations (Condie et al., 2001; Barley et al., 2005). Furthermore, we suggest that fine-grained sediments deposited during time intervals when surface environments were not influenced by mantle plume breakout events will have lower Re and Os concentrations and $^{187}\text{Re}/^{188}\text{Os}$ ratios reflecting larger relative contributions of Re and Os from recycled continental crust. A much broader sampling of both Archean and younger shales is needed to explore these hypotheses and to document a statistically significant difference.

5.3. Challenges in defining initial $^{188}\text{Os}/^{188}\text{Os}$ ratios

The Os ratios given by isochrons for both DH26503 and DH26506 drill cores have large uncertainties. In addition, within 2σ uncertainty, the Os for DH26506 is impossibly low, below the chondritic value at 2.69 Ga (0.0186). The high uncertainties could be caused by (1) inadequate sampling or poor analytical uncertainties, (2) the long projection to the intercept from high $^{187}\text{Os}/^{188}\text{Os}$ ratios of the data points, or (3) post-depositional disturbance. Small analytical uncertainties, good precision and apparent accuracy of the isochrons, and minimal change in results with exclusion of some data points all argue against the first possible cause.

The most likely cause of the poor precision for the Os in both cases is the long projection from high measured $^{187}\text{Os}/^{188}\text{Os}$ ratios. A survey of recent literature illustrates this anticipated problem. Reported absolute uncertainties for Os, for samples with measured $^{187}\text{Os}/^{188}\text{Os}$ less than ten are typically in the second decimal place (generally <0.05; Hannah et al., 2004; Kendall et al., 2004; Selby and Creaser, 2005; Kendall et al., 2006), whereas those for samples with measured $^{187}\text{Os}/^{188}\text{Os}$ of 20 to 100 or more are commonly in the first decimal place (generally <0.1; Bierlein et al., 2006; Morelli et al., 2007; Anbar et al., 2007). High measured $^{187}\text{Os}/^{188}\text{Os}$ may be the result of high $^{187}\text{Re}/^{188}\text{Os}$ ratios (Morelli et al., 2007) and/or great age (this study; Anbar et al., 2007).

The Os of DH26506 presents a more complex case, as it shows not only a large uncertainty, but also a nominally negative $^{187}\text{Os}/^{188}\text{Os}$ ratio. As noted above, the age for DH26506 is within analytical uncertainty of that for DH26503, and the analytical uncertainties for individual measurements are excellent. A Model 3 regression was required for DH26506, however, and the MSWD is slightly elevated (3.8), suggesting that some geologic factor introduced scatter and contributed to the low ratio. The low apparent Os can be explained by a process that offsets the isochron toward the right (lower $^{187}\text{Os}/^{188}\text{Os}$ and/or higher $^{187}\text{Re}/^{188}\text{Os}$). This requires either loss of $^{187}\text{Os}$, addition of $^{187}\text{Re}$, or both, long after deposition so that the Os ratio is reduced but the isochron age is minimally affected.

Loss of $^{187}\text{Os}$ is an unlikely explanation. Re is mobilized more easily than Os during oxidative weathering of carbonaceous sedimentary rocks (Pierson-Wickmann et al., 2002; Jaffe et al., 2002; Dalai et al., 2002). In other words, the loss of Os should normally be accompanied by even greater loss of Re. The result would be to shift the isochron to the left instead of right, and to increase rather than decrease the Os.
Furthermore, all of the drill core samples from DH26506 are fresh and clean, with no evidence of oxidation.

Relatively recent addition of $^{187}\text{Re}$ offers an alternative explanation. The mafic and ultramafic rocks that occur in and adjacent to the Joy Lake sequence are a potential source (Fig. 1). These rocks are likely to contain high concentrations of Re and Os, with mafic rocks contributing relatively high Re/Os ratios. Re is mildly incompatible during mantle melting, and is enriched in mantle-derived melts relative to highly compatible Os (Shirey and Walker, 1998). That is, crustal rocks typically have high Re/Os ratios relative to mantle material. For example, the $^{187}\text{Re}/^{188}\text{Os}$ ratio for fertile mantle is about 0.4, whereas the same ratio in komatiites is greater than 1, and in MORB and OIB ranges from 20 to 5000 (Shirey and Walker, 1998). Consequently, the average presently eroding continental crust has a $^{187}\text{Re}/^{188}\text{Os}$ ratio of ~50 (Esser and Turekian, 1993). Mafic rocks, such as the mafic tufts and basalts found in the Joy Lake sequence, represent moderate degrees of partial melting, and therefore contain relatively high concentrations of Re and Os, and also relatively high $^{187}\text{Re}/^{188}\text{Os}$ ratios. Thus, significant concentrations of Re and Os are locally available adjacent to the Joy Lake slates, and the potential contaminants most likely have $^{187}\text{Re}/^{188}\text{Os}$ ratios comparable to or higher than average continental crust.

To test our hypothesis, we can calculate the amount of Re that must be added to each sample to offset the Os from chondritic to the isochron value of ~0.29 (see derivations in Supplementary material). For this calculation, we assume that the isochron age remains unchanged. For simplification, we assume that only Re is added to the slate; the amount of $^{188}\text{Os}$ remains unchanged. The amount of additional $^{187}\text{Re}$ required for each point on the isochron is given by:

$$
\left( ^{187}\text{Re} \right)_c = \left( ^{187}\text{Re} \right)_S \left( e^{\lambda t} - e^{\lambda t_e} \right) \frac{\left( ^{188}\text{Os} \right)_M}{\left( ^{188}\text{Os} \right)_S}
$$

where $\left( ^{187}\text{Re} \right)_c$ is the amount of $^{187}\text{Re}$ added after deposition by contaminating fluids, $\left( ^{188}\text{Os} \right)_S$ is the amount of $^{188}\text{Os}$ measured in the sample, $\left( ^{188}\text{Os} \right)_S$ is the Os determined from the isochron, $\left( ^{188}\text{Os} \right)_S$ is the true Os, $t_t$ is the time of deposition of the slate, and $t_e$ is the time when Re was added to the slate. We assume that $\left( ^{188}\text{Os} \right)_S$ is chondritic (0.1086 at 2695 Ma), $t_t = 2695$ Ma, and that the contamination was recent ($t_e = 0$). The calculated amounts of $^{187}\text{Re}$ required to offset the Os from chondritic to $-0.29$ range from 0.07 to 0.25 ppb, or from 0.9 to 2.4% of the measured $^{187}\text{Re}$ concentrations. That is, the amount of Re contamination is small and has minimal impact on the precision of the isochron. Note, however, that the required change increases as $t_e$ increases.

If the isochron age is unaffected by the contamination, the $^{187}\text{Re}$ addition must be proportional to the $^{188}\text{Os}$ concentration of each sample. Small deviations from this proportionality, however, result in only minor increases in the scatter, and thus in the uncertainties and MSWD. Indeed, the amount of added $^{187}\text{Re}$ required to offset the isochron in the disturbed drill core is small, and the MSWD is slightly higher. Moreover, to avoid any change in the age, proportionally more Re must be added to the samples with higher $^{188}\text{Os}$ concentrations. If insufficient Re is added to the samples with high $^{188}\text{Os}$ concentrations, the result will be an apparent decrease in the age. Indeed, the age is nominally younger (though within uncertainty) for the disturbed drill core. Of course, the assumption that no Os is added is almost certainly not true. Because the contaminant source certainly had a much lower $^{188}\text{Os}$ than the shales at the time of contamination, however, addition of Os would complement rather than counter the addition of Re. Our purpose is not to suggest a unique process or explanation for the data. Rather, we show with relatively simple calculations that minor contamination by a fluid with moderately high $^{187}\text{Re}/^{188}\text{Os}$ ratios occurring relatively recently can significantly shift the apparent Os in old samples with little impact on the isochron age.

Another obvious question arises. Why was DH26506 disturbed while DH26503 was not? Fig. 3 shows that the samples from DH26506 were taken from a slate section at a shallow depth (about 70 m below the present surface in an inclined drill hole) bound by graywackes and volcaniclastic rocks. These units include mafic tufts, volcanic flows, and volcaniclastic rocks, which are relatively permeable and fine grained, and, therefore, reactive. As the section was exhumed and eroded to its present shallow depth, oxidizing groundwater could readily attack the more permeable rocks, releasing Re and lesser amounts of Os. The highly reducing environment of the adjacent carbonaceous slate offers a ready sink for the mobilized, redox-sensitive elements (Siebert et al., 2005). In contrast, Fig. 3 shows that the samples from DH26503, which are undisturbed, were taken from a slate section at a greater depth (about 220 m below the present surface in an inclined drill hole) bound by gabbro with a recognized chilled margin at one contact. Not only do gabbros normally have lower concentrations of Re and Os than mafic tufts, but they also have very low permeability. It is therefore less likely that recently introduced oxidizing groundwater could readily infiltrate through the gabbro at >200 m depth and impact the adjacent slate.

In the nearby Mesabi Iron Range, Minnesota, quartz- and kaolinite-rich profiles were generated by oxidation and intense chemical weathering from the Late Jurassic through Early Cretaceous under a wet, subtropical climate (Tyler and Bailey, 1961; Morey, 1983; 1999). This event may also have caused oxidation of mafic and ultramafic volcaniclastic rocks in the Joy Lake sequence, releasing Re for uptake by adjacent shales. The required amount of Re that must be introduced at 100 Ma is statistically indistinguishable from the amount required for recent contamination (0.9 to 2.6% at 100 Ma vs. 0.9 to 2.4% at 0 Ma). For much earlier contamination, however, the required Re addition is much larger, and varies much more for each data point (e.g., 3.5 to 9.4% at 2000 Ma). The more Re addition required, the greater the probability that the age, Os, and MSWD will be significantly disturbed. Therefore, we favor a relatively recent contamination event.

Nominally low Os initial ratios have been reported, both formally and informally, for several Archean examples (this study; Anbar et al., 2007; Selby and Creaser, 2005; Kendall et al., 2006; Hannah et al., 2006, 2007; Creaser and Stasik, 2007; Turgeon et al., 2007; Selby, 2007). Far more Re must be added to these samples to offset the isochron to a sub-chondritic value similar to that observed in this study (Fig. 6); it is therefore less likely. The
increased scatter because of non-proportional addition of Re will be far greater with large Re additions, so that the isochron is likely to be discounted as disturbed. A small decrease in the measured Os, might be easily overlooked; a small Re addition will simply shift the Os, to a slightly lower, but still reasonable value. Finally, Archean terranes commonly contain reactive, high-Re/Os mafic rocks, a ready source for contamination that is less abundant in post-Archean sections.

5.4. Regional significance of geochronology

The 2695 ± 14 Ma isochron age for samples from drill core DH26503 is the oldest reported Re–Os age for carbonaceous slate or shale and the first depositional age for the Neoarchean supracrustal sequences in the western part of the Wawa subprovince in USA. It provides a robust age for sedimentation in the Deer Lake greenstone belt, and potentially places a minimum age constraint on mafic and ultramafic volcanism and a maximum age on the Deer Lake intrusive complex.

Multiple models have been proposed for crustal thickening in the Superior Province, including amalgamation of arc terranes (Langford and Morin, 1976; Percival and Williams, 1989; Card, 1990; Thurston and Chivers, 1990; Kimura et al., 1993; Kerrich and Polat, 2006) and a global mantle reorganization (Rey et al., 2003). Recent models incorporate both of these scenarios into a model of complex and long-lived interaction between collisional processes in a subduction setting and mantle plume breakout events (Ayer et al., 2002). Most models for the Superior Province suggest that the D2 compressional event was roughly contemporaneous with deposition of arc volcanic and associated sedimentary rocks, and centered around 2695 Ma (Corfu and Stott, 1998). The ca. 2695 Ma Re–Os age for carbonaceous slates from the Joy Lake sequence links their deposition to this event and permits correlation with sequences of similar age to the east in the Wawa and Quetico subprovinces (Fig. 1).

Throughout much of the Wawa and Quetico subprovinces, the ca. 2695 Ma sequences are dominated by volcaniclastic and felsic volcanic material, sited unconformably or in fault contact with ca. 2720 Ma volcanic and sedimentary sequences, and are intruded by felsic plutons (Corfu and Grunsky, 1987; Mueller et al., 1996; Corfu and Stott, 1998; Zaleski et al., 1999; Davis et al., 2000). The sedimentary part of the Joy Lake sequence is supposed to be a deeper-water (and/or locally starved basin) time equivalent of the turbiditic graywackes of the Quetico subprovince and McKellar Harbour Formation, which overlies the carbonaceous and pyritiferous Kingdom Slate in the northern part of the Wawa-Abitibi subprovince between Schreiber and Hemlo (Fralick et al., 2006). In contrast to the correlative successions further east in the Wawa and Quetico subprovinces (Schreiber-Hemlo area), the Joy Lake sequence is interlayered with mafic and ultramafic volcanic rocks and intruded by mafic and ultramafic intrusions. Two alternatives can be put forward to reconcile this difference in associated magmatism and, likely, tectonic settings: (1) imbrication of terrigenous and oceanic materials of variable ages in an accretionary setting (Kimura et al., 1993), or (2) on-going distal arc volcanism at ca. 2695 Ma outboard of, but simultaneous with northward-directed subduction under the Wabigoon subprovince in a more proximal part of the Superior Province.

In accretionary settings, imbrication of terrigenous sediments and sliced oceanic crust can generate allochthonous rather than autochthonous contacts between units of different ages representing different tectonic settings. This has been already demonstrated in the Malartic and Larder areas in the southern Abitibi subprovince and in the Beardmore-Geraldton area of the southeastern Wabigoon Subprovince (Kimura et al., 1993). Although similar relationships seem applicable to the Deer Lake greenstone belt, we note that some mafic and ultramafic intrusions have well-documented chilled zones, arguing against tectonic contacts. Furthermore, the intrusions lack penetrative deformation (Severson and Jirsa, 2005), suggesting that they post-date the D2 event, and therefore, the Joy Lake sequence. It bears noting, however, that some of these intrusions have a sheared contact with the Joy Lake sequence (see Fig. 3). If some units are indeed allochthonous, then mafic and ultramafic volcanic units of the Thistledew Lake and Joy Lake sequences could be older than the dated sedimentary rocks, and, perhaps, correlative with ca. 2720 Ma ultramafic to felsic magmatism in the Schreiber-Hemlo area farther east in the Wawa subprovince of Canada. This implies a ca. 25 Ma time gap between terrigenous and volcanic units in the Deer Lake greenstone belt, similar to that documented in the Manitouwadge greenstone belt to the east (Zaleski et al., 1999; Fig. 1).

The alternative and our preferred interpretation is that the sedimentary and magmatic rocks in the Deer Lake greenstone belt are autochthonous, with either depositional or intrusive contacts locally disturbed by faulting. If so, the ca. 2695 Ma age applies to both the sedimentary and associated mafic to ultramafic volcanic rocks. A similar relationship was indeed documented in the Newton greenstone belt of the adjacent western part of the Vermillion district in Minnesota, where felsic and mafic volcanic rocks, volcaniclastic rocks, graywacke, iron formation, and impure marble are interlayered, and the supracrustal sequence is intruded by diabasic gabbro and differentiated mafic to ultramafic sills (Schulz, 1980; Southwick et al., 1996). Lithologically similar 2700–2687 Ma sequences (Corfu et al., 1989; Mueller and Donaldson, 1992) in the southern Abitibi subprovince contain deep-water facies (turbiditic graywacke, carbonaceous shales, and banded iron formations), are closely associated with ultramafic-mafic and felsic volcanic rocks, and are proximal to major east–west trending fault zones with gold mineralization. These sequences are confined to the southern (external) part the Abitibi greenstone belt, which is the eastern extension of the Wawa subprovince across the Kapuskasing uplift. Together, the Deer Lake, Vermillion, and southern Abitibi greenstone belts may reflect on-going distal arc volcanism in the distal part of the Wawa-Abitibi subprovince during its collision with the Wabigoon arc along the southern margin of the Superior Province (Fig. 1). This interpretation, if correct, would explain the apparent differences in metallogeny between the Deer Lake greenstone belt and the ca. 2720 Ma successions in the Wawa-Abitibi subprovince. Specifically, the supracrustal succession lacks volcanogenic massive sulfide deposits and the ultramafic–mafic intrusions lack economic NiS mineralization, both common in the older successions. Further geochronologic work and careful documentation of contact relationships is needed to discriminate between these two alternatives, as they have significant implications for the metallogenic potential of this belt.

The D2 event represents the collision between the Wawa and Wabigoon greenstone belts of the Shebandowan phase of the Kenoran Orogeny, which impacted the entire Superior Province (Card, 1990; Percival et al., 2006; Fig. 1). In Minnesota, to the east of our study area, dating of two phases of the Giant Range batholiths brackets the D2 event between 2685 and 2669 Ma (Boerboom and Zartman, 1993). Ages from the Shebandowan greenstone belt farther to the east of the Deer Lake Complex place the D2 transgressive event at 2685 to 2680 Ma (Corfu and Stott, 1998), and stitching granitoids along the Wawa-Quetico subprovince boundary in the Manitouwadge greenstone belt bracket the D2 event between 2687 and 2680 Ma (Zaleski et al., 1999). The 2695 Ma age for deposition of the Joy Lake sequence provides a maximum age for the D2 event in the Deer Lake greenstone belt, complements other age constraints for this event, and extends age constraints for the D2 event to the western limit of the Wawa subprovince. Because the intracrustally interlayered mafic and ultramafic sills of the Deer Lake Complex lack a penetrative fabric and show chilled, intrusive contacts with the deformed Joy Lake supracrustal rocks, they must have been emplaced after D2 deformation (Severson and Jirsa, 2005), potentially at the same time as post-orogenic ca. 2668 Ma composite ultramafic to felsic intrusions in the Gamitaga and Batchawana greenstone belts on the east shore of Lake Superior (Fig. 1; Krogh and Turek, 1982; Corfu and Grunsky, 1987).
Mueller et al. (1996) propose two distinct evolutionary phases in the Abitibi greenstone belt: (1) arc–arc collision between 2697 and 2690 Ma, and (2) arc fragmentation between 2689 and 2680 Ma with D2 deformation. The volcanosedimentary supracrustal succession of the Deer Lake greenstone belt may be correlative with similar successions to the east in the Wawa subprovince and southern Abitibi belt. Together, these sequences may represent on-going distal arc volcanism along the southern margin of the Superior Province during collision of the more proximal part of the Wawa arc with the Wabigoon arc. The mafic and ultramafic sills of the Deer Lake Complex intruded and interfingered with the supracrustal rocks of the Joy Lake sequence during arc fragmentation in the aftermath of D2 event.

6. Conclusions
We report here the oldest Re–Os isochron age for carbonaceous slate or shale to date. The 2695 ± 14 Ma Joy Lake carbonaceous slate was deposited during or after D1, but before D2 deformation. The volcanosedimentary supracrustal succession of the Deer Lake greenstone belt may be correlative with similar successions to the east in the Wawa subprovince and southern Abitibi belt. Together, these sequences may represent on-going distal arc volcanism along the southern margin of the Superior Province during collision of the more proximal part of the Wawa arc with the Wabigoon arc. The mafic and ultramafic sills of the Deer Lake Complex post-date deposition of the Joy Lake carbonaceous slate. The negative Os and apparently slightly younger isochron age of the DH26506 may result from addition of Re derived from mafic and ultramafic rocks during exhumation and oxidation.

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