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## Re-Os isotopic variations in carbonaceous pelites hosting the Duluth Complex: Implications for metamorphic and metasomatic processes associated with mafic magma chambers

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**Abstract**—Previous mineralogic and isotopic studies of sulfide mineralization in the 1.1 Ga Duluth Complex have suggested that sulfur, and possibly metals, have been derived from Proterozoic sedimentary country rocks. The Re-Os isotopic system offers great potential in the evaluation of crustally derived metals in magmatic ore-forming processes, but an understanding of the mechanisms that could cause isotopic variations in country rock contaminants is a prerequisite. A suite of sulfidic and carbonaceous pelitic rocks of the Virginia Formation (country rock to the Duluth Complex), ranging from unmetamorphosed through strongly recrystallized and partially melted xenoliths, have been analyzed for their Os isotopic composition. Sulfide mineral separates (mainly pyrrhotite), kerogen-graphite isolates, and whole rocks, were analyzed. Whole rocks, kerogen, and graphite from metamorphosed samples plot between 1.85 Ga and 1.1 Ga chondritic reference isochrons. Sulfide separates from all metamorphosed samples plot nearer the chondritic 1.1 Ga reference isochron and require exchange with a fluid or melt characterized by a chondritic Os isotopic composition (potentially derived from the Duluth Complex). Devolatilization and partial melting may perturb isotopic systematics when accompanied by the loss of Re- and Os-bearing fluids. These processes could in part explain the scatter in isotopic values found in kerogen and metamorphosed whole rocks. However, metasomatic addition of Os via interaction with a fluid or melt is required to explain the sulfide isotopic ratios and is consistent with sulfide minerals being more susceptible to Os exchange with a fluid than kerogen. The relative ease with which pyrrhotite may be reset during fluid interaction, as well as the variable degrees of exchange shown by kerogen/graphite, suggest that a knowledge of the petrologic and isotopic evaluation of country rocks is necessary before a meaningful assessment of the isotopic variations found in igneous rocks or associated ore deposits can be undertaken. Copyright © 2001 Elsevier Science Ltd

### 1. INTRODUCTION

Several recent studies (e.g., Keays, 1995; Leshner and Stone, 1996; Lambert et al., 1998a, 1998b, 1999a; Ripley et al. 1998, 1999; Naldrett, 1999) have highlighted the importance of country rock contamination in the generation of magmatic Cu-Ni-PGE deposits. Both stable and radiogenic isotopic studies have proven particularly valuable in evaluating the degree of contamination of magmas, although distinct isotopic systems may give results that differ as a result of fractionation or resetting during metamorphism, assimilation, and magma crystallization, or later hydrothermal alteration. Because of their potential for detecting crustal contamination of mafic magmas in general and because they offer a direct measurement of metals involved in magmatic ore genesis, Re/Os isotopic studies have become a standard tool in the evaluation of magmatic sulfide deposits (e.g., Lambert et al., 1998b, 1999b). Leshner and Stone (1996), Lambert et al. (1998b, 1999a), and Leshner and Burnham (2001) have discussed the importance of R values (silicate/sulfide magma ratios; Campbell and Naldrett, 1979) and mixing properties to Os isotopic compositions in contaminated mafic magmas. Because Os is more chalcophile than Re (Os D values [concentration in sulfide/concentration in silicate] exceed those

for Re; Lambert et al., 1998b, 1999b), a sulfide liquid that separates from a silicate melt will be characterized by a higher Os/Re ratio and will evolve independently from the silicate in terms of Re-Os isotopic compositions. Mixing of Re and Os from distinct sources can likewise lead to variations in sulfide and silicate systems that augment effects due to the R factor.

To properly assess Re-Os isotopic effects in magmatic sulfide systems, it is of fundamental importance to understand potential isotopic variations that may accompany processes such as devolatilization and partial melting of country rock contaminants. For example, dehydration of a sedimentary rock during contact metamorphism may liberate a fluid with a Re/Os ratio that is much different than the unmetamorphosed source rock. Incorporation of the fluid in an H<sub>2</sub>O-undersaturated magma may lead to a considerably different isotopic evolution relative to a magma that totally digested the source rock or the dehydrated residue. Partial melting of country rock may also fractionate Re from Os, and magma contamination by the partial melt will lead to a different isotopic evolution relative to bulk assimilation or incorporation of a fluid phase.

The aim of this study was to trace the evolution of the Re/Os system in carbonaceous, sulfidic pelitic rocks of the ~1.85 Ga Virginia Formation during contact metamorphism by the ~1.1 Ga Duluth Complex (Fig. 1). Previous studies have shown that the most common xenoliths in troctolitic to gabbroic rocks of the Complex are from the Virginia Formation. The Virginia Formation overlies the Biwabik Iron Formation, which has also locally served as a contaminant of the mafic magmas (see

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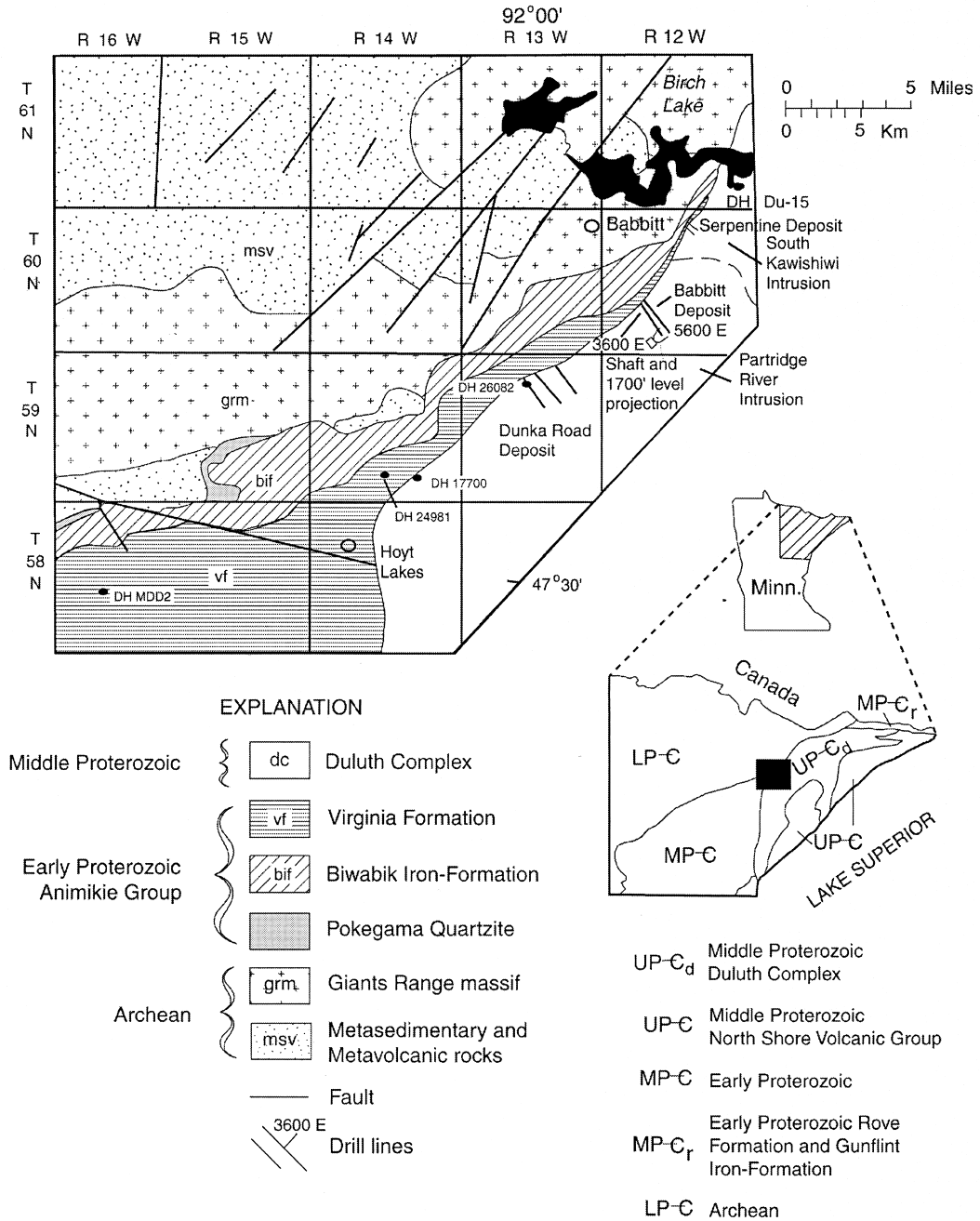


Fig. 1. Regional geologic map of northeastern Minnesota showing locations of samples used in this study. Unmetamorphosed Virginia Formation is from core MDD2, whereas slightly metamorphosed samples are from core 24981. Footwall (cores B1-354, 10134, and 214-1978) and xenolith (core B1-127) samples are from the Babbitt deposit, located in the northeastern portion of the map area. Drill holes at Babbitt are located along NW-SE lines exemplified by those labelled 3600E and 5600E.

below). Our sampling strategy included analyses of unmetamorphosed and slightly recrystallized pelitic rocks outside of or at the margin of the contact aureole, as well as highly recrystallized footwall hornfels and partially melted xenoliths. Although our hypothesis was that Re-Os fractionation would accompany the process of devolatilization and partial melting, results indicate that metasomatism of the country rocks by

fluids potentially related to the Duluth Complex was the most important control on their Os isotopic compositions.

## 2. REGIONAL AND LOCAL GEOLOGIC SETTING

The Duluth Complex of northeastern Minnesota is composed of a series of intrusive rocks that comprise the principal plu-

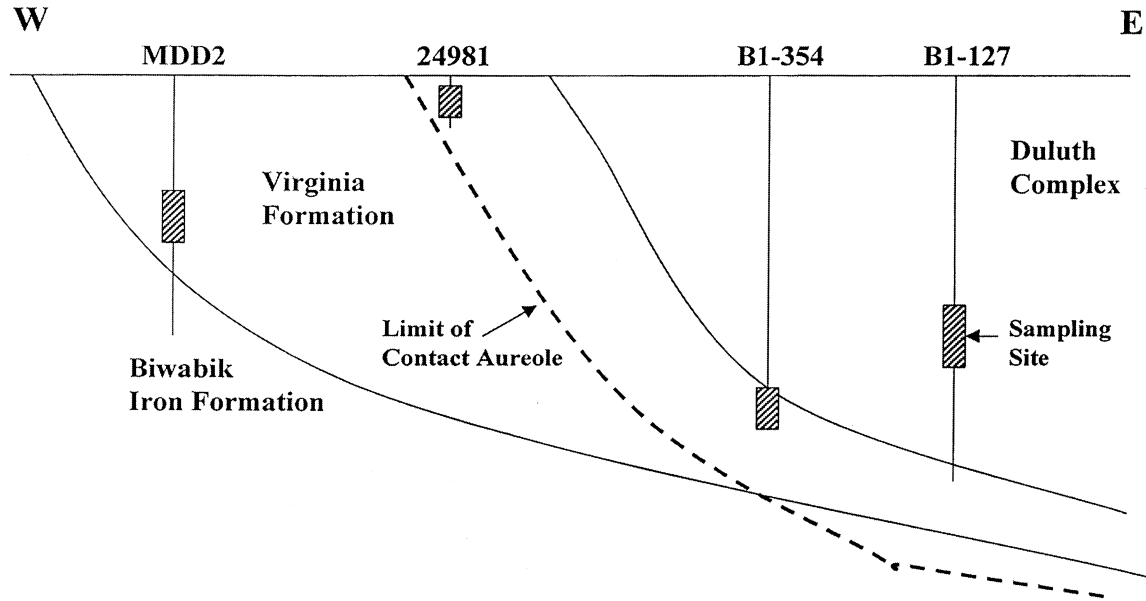


Fig. 2. Schematic cross section illustrating relative positions of drill core samples in this study. Core MDD2, unmetamorphosed; core 24981, slightly metamorphosed; core B1 to 354, strongly recrystallized footwall; core B1 to 127, partially melted xenolith. The approximate distance between drill holes B1 to 127 and MDD2, projected to the common cross section line, is 25 km.

tonic component of the Middle Proterozoic (Keweenaw) Midcontinent Rift System (Miller and Ripley, 1996). Volcanic rocks associated with the  $\sim 1.1$  Ga rifting event extend from Ontario as far southward as Kansas (at depths of  $\sim 200$  m). In the Lake Superior area the thickness of volcanic rocks is estimated to locally be in excess of 20 km (Cannon et al., 1989; Allen et al., 1994). The volcanic rocks were erupted onto a peneplained crust composed of Early Proterozoic graywacke, shale, and iron-formation and Archean granite-greenstone terrain. Country rocks of the Duluth Complex include Archean volcano-sedimentary and plutonic rocks to the north and meta-sedimentary rocks of the Proterozoic Animikie Group to the south (Fig. 1). The Animikie Group is composed of the Pokegama quartzite, a relatively thin basal sandstone, overlain by the Biwabik Iron Formation and the Virginia Formation. Lucette and Morey (1983) have divided the Virginia Formation into two informal members. An upper lithosome is dominated by siltstone and fine-grained graywacke, whereas the lower lithosome is primarily carbonaceous, locally sulfidic, shale and argillite. Unmetamorphosed to weakly recrystallized argillite of the Virginia Formation is composed of chlorite, muscovite, quartz, plagioclase, potassium-feldspar, and variable percentages of pyrite and organic matter (kerogen). Thickness of the Virginia Formation is poorly constrained but is in excess of 500 m. The Virginia Formation has not been precisely dated but is thought to be  $\sim 1.8$  Ga in age based on dating of underlying dike rocks and overlying volcanics (Morey and Van Schmus, 1988) and U-Pb zircon ages obtained from correlative units in Wisconsin and Michigan (Sims and Carter, 1996). The Biwabik Iron Formation consists of interbedded silicate-rich and magnetite-rich units that have been divided into "slatey" and "cherty" members. In general, slatey members contain in excess of 40% thin-bedded, silicate-rich layers, and cherty mem-

bers contain less than 10 to 50% thin-bedded material and are magnetite-rich (Morey et al., 1972). Although sulfide minerals are present in the iron formation, a much larger sulfur reservoir exists in the Virginia Formation, and hence it has received most attention with respect to its role in the formation of sulfide mineralization in the Duluth Complex.

Intrusion of the Duluth Complex has resulted in a relatively narrow contact aureole, especially when considered in relation to the overall size of the Complex. Visible recrystallization of the Biwabik Iron Formation may be found at surface distances of  $\sim 4800$  m from the intrusive contact (French, 1968), but recrystallization of the Virginia Formation is restricted to surface distances less than  $\sim 1500$  m. Because the intrusive contact cuts downward to the east, the thickness of the preserved Virginia Formation is less than 150 m (Figs. 1 and 2). The difference in degree of recrystallization is in part due to mineralogical differences between the rock types and may in part be related to the highly reduced nature of fluids present in the carbonaceous Virginia Formation (i.e., low element solubility in  $H_2$ - $CH_4$ -rich fluids). The thickness of the contact aureole is thought to be due to the growth of the Complex by intrusion of relatively thin sheets of magma (e.g., Lee and Ripley, 1996). Petrochemical and isotopic aspects of contact metamorphism of the Biwabik Iron Formation have been studied by Perry and Bonnicksen (1966), French (1968), Bonnicksen (1969, 1975), Morey et al. (1972), and Perry et al. (1973). Labotka et al. (1981, 1984) described and modeled dehydration reactions that accompanied the contact metamorphism of the Rove Formation, equivalent to the Virginia Formation, in the northern portion of the Complex. Andrews and Ripley (1989), Ripley and Taib (1989), Ripley et al., (1992), and Arcuri and Ripley (1998) have investigated mineralogic and stable isotopic aspects of the contact metamorphism of the Virginia Formation.

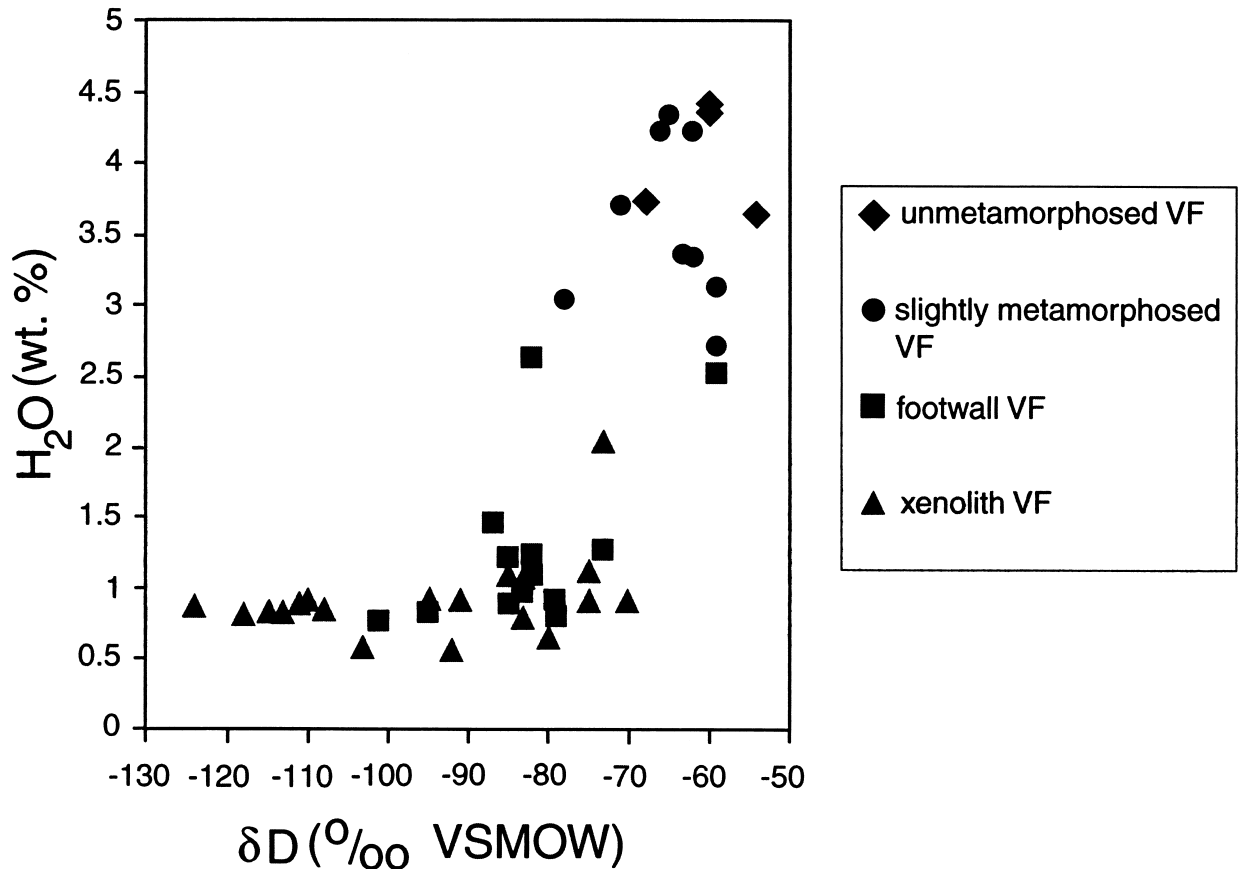


Fig. 3.  $\delta D$  vs. H<sub>2</sub>O content for various grades of Virginia Formation (from Ripley et al., 1992).

The sheetlike intrusive style of much of the Duluth Complex has led to delamination of footwall rocks. Blocks of country rocks, some as large as  $40 \times 100$  m, have been incorporated as xenoliths during intrusion. Many of the xenoliths have undergone extensive partial melting (Ripley and Alawi, 1988).

Most information concerning the Virginia Formation has been obtained by the study of drill cores because outcrop is limited near the contact with the Duluth Complex. Highly recrystallized Virginia Formation is found in most of the cores obtained by exploration drilling for Cu-Ni sulfide occurrences along the basal intrusive contact (e.g., Fig. 1; Serpentine deposit, Babbitt deposit, Dunka Road deposit). Less strongly recrystallized Virginia Formation is found in drill core 24981 (Figs. 1 and 2), whereas apparently unmetamorphosed Virginia Formation is found in a series of drill cores to the west of the intrusive contact, with core MDD2 (Figs. 1 and 2) located nearest the intrusive contact. Samples from core MDD2 contain chlorite, muscovite, quartz, plagioclase, potassium-feldspar, ilmenite, pyrite, and kerogen. Chlorite and muscovite occur in subequal amounts and together account for most of the volume of the argillites. It is clear that the original clay minerals in the Virginia Formation have been recrystallized either during diagenesis or during a very low-grade metamorphic event. However, because these rocks show no evidence of dehydration or recrystallization related to spatial proximity to the Duluth Complex, they are referred to as unmetamorphosed. The mineralogy

of drill core 24981 is similar to that of core MDD2, but some pyrrhotite occurs at the expense of pyrite, and chlorite and muscovite are characterized by sharper and narrower X-ray diffraction peaks. Strongly metamorphosed samples have a hornfelsic texture and contain quartz, plagioclase, biotite, cordierite, potassium feldspar, locally orthopyroxene, and minor amounts of pyrrhotite, graphite, apatite, and zircon (e.g., Andrews and Ripley, 1989).

Chemical changes in the protoliths were due primarily to devolatilization until the onset of partial melting. Figure 3 shows the H<sub>2</sub>O contents of Virginia Formation relative to  $\delta D$  values. Ripley et al. (1992) found large changes in  $\delta D$  values of the Virginia Formation as a result of the devolatilization process. Partial melting is restricted to rocks located very near the intrusive contact and to those that occur as xenoliths. Virginia Formation xenoliths typically show the loss of SiO<sub>2</sub>, Na<sub>2</sub>O, K<sub>2</sub>O, and Al<sub>2</sub>O<sub>3</sub> and relative enrichment in FeO (Ripley and Alawi, 1988) and appear to follow the scheme of partial melting reactions determined by Hoffer and Grant (1980).

Andrews and Ripley (1989) suggested that the initial mineralogical transitions during prograde metamorphism were the graphitization of organic matter and production of pyrrhotite from pyrite. Both of these reactions have clearly progressed before dehydration of chlorite and muscovite. The main phase of dehydration, signaled by the appearance of biotite and cordierite, occurred between 500 and 600°C (Labotka et al., 1981,

## 3. SAMPLING METHODOLOGY

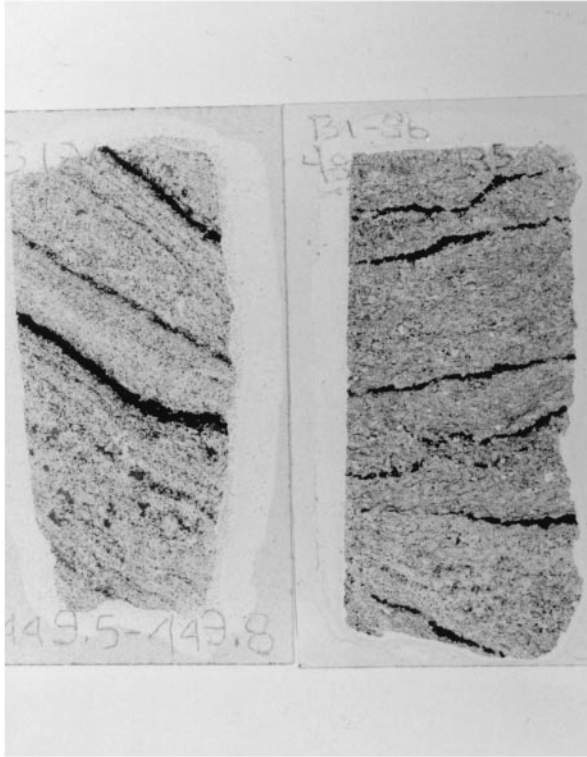


Fig. 4. Photographs of thin sections showing pyrrhotite beds and laminae (black) in highly recrystallized Virginia Formation footwall. The thin sections are  $4 \times 1.7$  cm. In unmetamorphosed samples, the sulfides are pyrite rather than pyrrhotite.

1984; Andrews and Ripley, 1989). A contact temperature of  $\sim 630$  to  $660^\circ\text{C}$  was calculated by Andrews and Ripley (1989) and is consistent with the occurrence of orthopyroxene only in xenoliths or very near the contact in footwall rocks. Partial melting, primarily of xenoliths, is thought to have commenced at temperatures in excess of  $700^\circ\text{C}$  (Hoffer and Grant, 1980), although this value is dependent on  $P(\text{H}_2\text{O})$ , which may have been considerably lower than  $P_f$  because of the presence of graphite and carbonic species in the fluid.

Samples for this study were carbonaceous and sulfidic and ranged from partially melted xenoliths through argillite. Drill cores sampled were MDD2 (unmetamorphosed), 24981 (slightly metamorphosed), B1-354, 10134, and B1-214 (footwall hornfels from the area of the Babbitt Cu-Ni deposit with cordierite, biotite, and locally orthopyroxene), and B1-127 (xenolith from the Babbitt deposit;  $\text{SiO}_2$ -depleted with biotite-cordierite and orthopyroxene). Three samples from cores MDD2, 24981, B1-354, and B1-127 were selected for Re-Os isotopic analysis. For all samples kerogen or graphite was isolated, and for all samples other than those from MDD2, sulfide separates were also collected. Pyrite in the shales from MDD2 proved to be too fine-grained for concentration. Sulfide minerals in all other samples were found as laminae or thin beds, in addition to finely disseminated grains (Fig. 4). A composite whole rock, in addition to the sulfide and kerogen separates, was analyzed for each sample. For cores 10134 and B1-214, only whole rock samples were analyzed.

The sample types were chosen to match as closely as possible the probable protoliths and their metamorphosed equivalents. Samples from drill cores 24981, B1-354, and B1-127 all contain distinctive sulfide laminae and beds. In footwall sequences Severson et al. (1994) has demonstrated that the sulfide-bearing intervals are laterally continuous and have referred to the package as the "bedded pyrrhotite unit." Stable isotopic data from each sample, along with S/C ratios, are given in Table 1. Figure 3 illustrates variations in  $\text{H}_2\text{O}$  content and  $\delta\text{D}$  values. The lack of well-defined differences in  $\delta^{34}\text{S}$ ,  $\delta^{13}\text{C}$ , and  $\delta^{18}\text{O}$  between the sample types is in line with all previous studies of the Virginia Formation. In brief, sulfur isotopic fractionation does not accompany the conversion of pyrite to pyrrhotite (e.g., Ripley and Snyder, 2000), carbon isotopic fractionation is balanced by the liberation of both  $\text{CH}_4$  and  $\text{CO}_2$  in the metamorphic volatile phase, and insufficient oxygen is liberated in the fluid to impact significant oxygen isotopic differences between unmetamorphosed and metamorphosed samples.  $\delta\text{D}$  values (see Fig. 3) show pronounced differences as a result of fractionation accompanying dehydration and fluid liberation.

Table 1. Elemental and stable isotopic data for Virginia Formation samples used in this study.

Sample No.	Type	$\delta^{13}\text{O}$ (% SMOW)	$\delta^{34}\text{S}$ (% VCDT)	$\delta^{13}\text{C}$ Kerogen (% VPDB)	Sulfur (wt.%)	Carbon (wt.%)	S/C
MDD2 1424	Unmetamorphosed	11.8	19.1	-31.6	1.34	0.38	3.41
MDD2 1421	Unmetamorphosed	12.2	14.8	-32.0	0.88	1.55	0.57
MDD2 1366	Unmetamorphosed	11.8	6.7	-31.5	0.22	0.91	0.25
24981 210.7	Slightly metamorphosed 3	13.4	11.2	-30.2	1.67	0.84	1.98
24981 213.5	Slightly metamorphosed 3	12.8	11.3	-30.5	1.18	0.88	1.34
24981 212.5	Slightly metamorphosed 3	13.2	10.9	-29.3	0.88	0.80	1.10
B1-354 322	Footwall	12.7	18.2	-32.3	2.48	1.48	1.68
B1-354 323.8	Footwall	12.8	19.7	-33.6	2.66	0.98	2.71
B1-354 319.8	Footwall	12.7	19.1	-32.9	2.91	0.95	3.05
B1-127 1042.5	Xenolith	11.7	15.3	-31.5	7.08	1.70	4.17
B1-127 1045	Xenolith	11.7	7.6	-31.6	1.21	1.70	0.71
B1-127 1032	Xenolith	11.8	16.5	-29.2	3.15	2.26	1.39

Table 2. Results of Re-Os isotopic analyses of the Virginia Formation.

Sample No.	Type	Os ppb	Re ppb	$^{187}\text{Os}/^{188}\text{Os}$	$^{187}\text{Re}/^{188}\text{Os}$	$\gamma_{\text{Os}}^{1.85}$	$\gamma_{\text{Os}}^{1.1}$
MDD2-136	Whole rock unmet.	0.116	0.82	1.2917 ± .0031	42.86 ± 0.43	-124	
MDD2-1421	Whole rock unmet.	0.244	4.92	4.1831 ± .0063	149.28 ± 1.49	-426	
MDD2-1424	Whole rock unmet.	0.280	4.95	3.5349 ± .0067	123.68 ± 1.24	-339	
24981-210.7	Whole rock slightly met	0.192	6.05	7.7767 ± 0.143	305.15 ± 3.05	-1514	1754
24981-212.5	Whole rock slightly met	0.302	11.02	9.7214 ± 0.34	399.50 ± 4.00	-2352	1944
24981-213.5	Whole rock slightly met	0.092	2.82	4.9873 ± .0292	259.00 ± 2.59	-2706	157
24981-223	Whole rock slightly met	0.481	11.99	9.6859 ± 0.596	300.10 ± 9.00	284	3424
24981-186.3	Whole rock slightly met	0.798	6.15	1.4454 ± .0110	44.55 ± 0.45	-36	429
10134-124	Whole rock footwall	0.666	7.34	2.1594 ± .0072	68.45 ± 0.68		662
214-1978	Whole rock footwall	0.590	5.59	1.7547 ± 0.365	56.42 ± 1.43		507
B1-354-319.8	Whole rock footwall	0.927	33.75	12.841 ± .0193	468.37 ± 4.69		3501
B1-354-322	Whole rock footwall	0.635	24.09	12.288 ± .0537	478.73 ± 4.75		2882
B1-354-323.8	Whole rock footwall	0.752	27.28	10.509 ± .0172	413.51 ± 4.13		2388
B1-127-1032	Whole rock xenolith	3.998	101.29	5.3950 ± .0124	229.67 ± 2.30		913
B1-127-1042.5	Whole rock xenolith	1.969	27.13	6.0580 ± .0091	248.82 ± 2.49		1176
B-127-1045	Whole rock xenolith	2.283	56.85	5.1640 ± .0079	199.51 ± 2.00		1178
MDD2-1366	Kerogen unmet.	0.479	4.71	1.8500 ± .0092	58.85 ± 0.59	-68	
MDD2-1421	Kerogen unmet.	4.852	103.60	5.70080 ± .0177	179.63 ± 1.89	45	
MDD2-1424	Kerogen unmet.	5.690	90.42	3.3496 ± .0063	108.92 ± 1.09	-104	
24981-210.7	kerogen slightly met.	17.994	685.02	12.0443 ± .1309	524.16 ± 5.24	-3675	1988
24981-212.5	kerogen slightly met.	8.359	226.38	7.7904 ± .0188	246.57 ± 3.06	69	2656
24981-213.5	kerogen slightly met.	19.381	768.29	16.7580 ± .0340	611.68 ± 6.12	-1916	4593
B1-354-319.8	graphite footwall	12.736	455.17	12.8719 ± .0193	468.84 ± 4.69		3520
B1-354-322	graphite footwall	11.512	417.26	13.0649 ± .0196	474.88 ± 4.75		3589
B1-354-323.8	graphite footwall	12.835	442.63	9.9105 ± .0149	379.82 ± 3.80		2401
B-127-1032	graphite xenolith	19.642	270.51	6.8737 ± .0103	264.07 ± 2.64		1625
B1-127-1042.5	graphite xenolith	15.857	536.10	7.7004 ± .0116	324.71 ± 3.25		1393
B1-127-1045	graphite xenolith	30.414	617.59	4.0832 ± .0061	148.92 ± 1.49		1045
24981-210.7	sulfide slightly met.	0.074	1.76	2.1160 ± .0120	148.69 ± 1.49		-593
24981-212.5	sulfide slightly met.	1.338	52.76	5.7670 ± .0180	355.74 ± 3.66		-691
24981-213.5	sulfide slightly met	0.078	2.41	2.8730 ± .0024	219.78 ± 2.20		-1041
B1-354-319.8	sulfide footwall	0.712	37.74	17.1911 ± .0169	837.33 ± 8.37		1526
B1-354-322	sulfide footwall	0.606	28.66	11.9481 ± .0298	585.57 ± 5.86		975
B1-354-323.8	sulfide footwall	0.450	19.14	8.9848 ± .0152	466.88 ± 4.47		305
B1-127-1032	sulfide xenolith	3.818	160.18	8.8294 ± .0153	432.53 ± 4.33		697
B1-127-1042.5	sulfide xenolith	2.988	102.26	6.7885 ± .0144	327.18 ± 3.29		594
B1-127-1045	sulfide xenolith	2.632	86.33	7.3956 ± .0148	356.66 ± 3.56		653

unmet: unmetamorphosed.

met: metamorphosed.

#### 4. ANALYTICAL METHODS

Kerogen and graphite from unmetamorphosed and metamorphosed Virginia Formation was isolated using the HF-BF<sub>3</sub> method of Robl and Davis (1993). Neoformed fluorides were removed from residual kerogen using AlCl<sub>3</sub> · 6H<sub>2</sub>O (Wedeking et al., 1983) and gravitational methods. Isolated carbonaceous matter was reacted with 60 mL of CrCl<sub>2</sub> and concentrated HCl to dissolve any remaining sulfide minerals following the general procedure of Canfield et al. (1986). Sulfide minerals were separated from whole rock using a combination of magnetic methods and hand picking. Purity of the organic and sulfide fractions was in excess of 99%.

To avoid potential Re contamination from steel and tungsten carbide crushing equipment, all whole rock powders were prepared using a ceramic jaw crusher and an agate TEMA mill. The jaw crusher and mill were thoroughly cleaned by crushing multiple aliquots of clean quartz and precontaminated with an aliquot of sample. The contaminated sample was discarded before preparation of a clean aliquot of rock powder. All reagents used in the following procedures were purified by subboiling distillation in Teflon or quartz and diluted to the

specified concentration with 18.2 mol/L-ohm Millipore water, except where specified. Hydrochloric acid was produced from UHP HCl gas bubbled through Millipore water.

Re and Os concentrations and Os isotopic compositions were measured using the Carius tube isotopic dilution procedure employed at Monash University, which is similar to that developed by Shirey and Walker (1995). For Re-Os isotopic analysis, sample powders of whole rock, sulfide, and organic matter were accurately weighed and spiked with <sup>185</sup>Re and <sup>190</sup>Os. Re and Os were extracted from ~0.5 g of whole rock, ~0.1 g of sulfide, and 0.2 g of organic matter using solvent extraction and microdistillation techniques. During this study, total chemistry and mass spectrometry blanks were 6 pg for Re and 2 pg for Os, with a <sup>187</sup>Os/<sup>188</sup>Os of 0.183. Blank corrections were insignificant for all samples analyzed in this study. Analyses over a period of 3 years of an Os isotopic mass spectrometry standard provided by the Carnegie Institution of Washington, Department of Terrestrial Magnetism (DTM), made using Johnson-Matthey ammonium hexachlorosmate batch 5.56870-A, yielded a mean <sup>187</sup>Os/<sup>188</sup>Os = 0.17367 ± 0.00058 (external reproducibility at the 2s level, n = 24), within error of

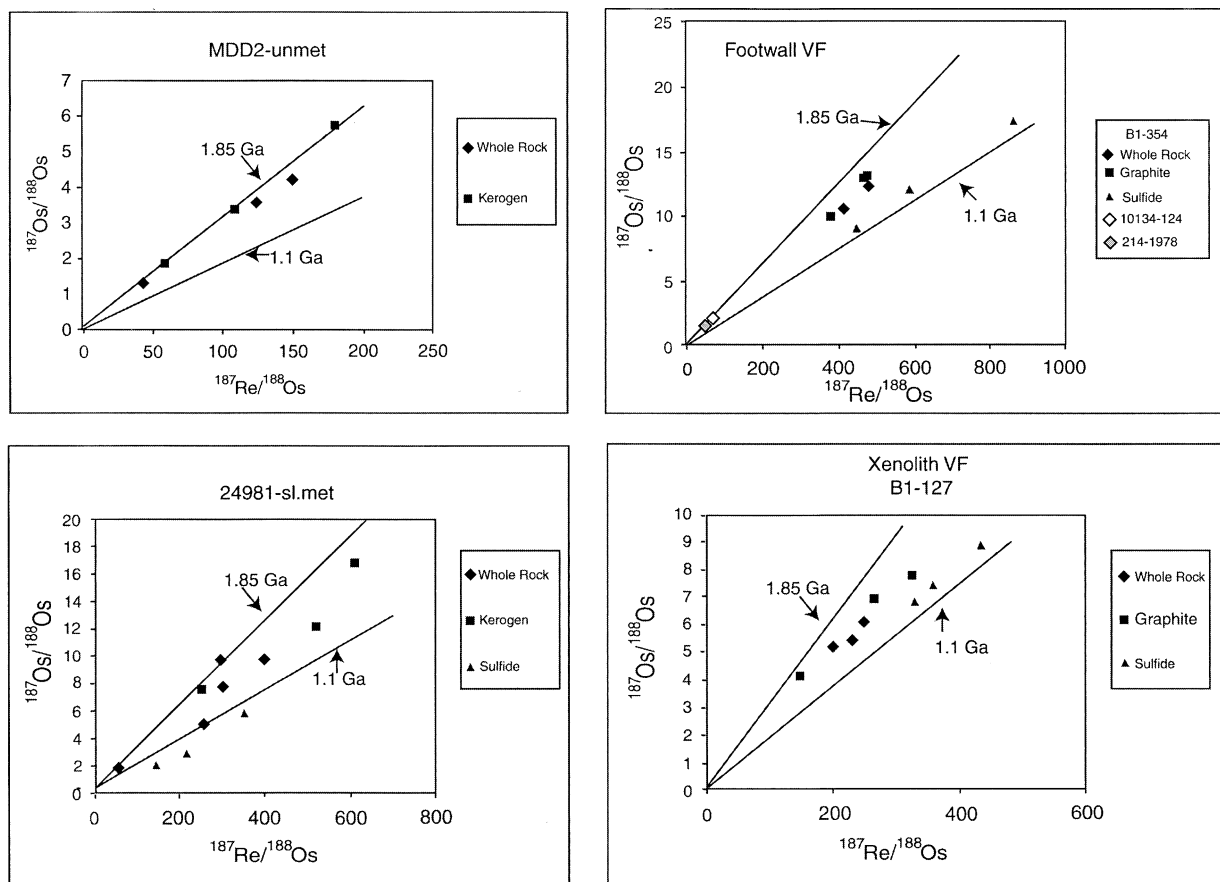


Fig. 5.  $^{187}\text{Os}/^{188}\text{Os}$  vs.  $^{187}\text{Re}/^{188}\text{Os}$  for unmetamorphosed through xenolith Virginia Formation.

the DTM value of  $0.17429 \pm 0.00055$  (Shirey, 1997; Lambert et al., 1998a). Thus, there is no measurable bias introduced into the data from our mass spectrometer (Finnigan MAT 262 *N*-TIMS) relative to DTM. Comparable external reproducibility was obtained on measured  $^{189}\text{Os}/^{188}\text{Os}$  and  $^{190}\text{Os}/^{188}\text{Os}$  for all samples after spike subtraction and blank correction. Moreover, no bias in Os isotope ratios was observed between the SEM collector (peak hopping mode) and the Faraday cups (static mode; Lambert et al., 1998a).

At present, there is no accepted international rock standard for Re and Os concentrations and Os isotopic composition to permit laboratories to monitor overall analytical accuracy. We have attempted to assess our analytical accuracy by measuring Re and Os concentrations and Os isotopic composition in the proposed peridotite PGE standard "WPR-1" provided by the Canadian Certified Reference Materials Project. Our average concentrations are 16.8 ppb Os and 11.7 ppb Re, and our measured  $^{187}\text{Os}/^{188}\text{Os} = 0.14599 \pm 0.00073$  (external reproducibility at the 2s level,  $n = 7$ ). Our Os isotopic result compares well with the limited number of published Re-Os isotopic analyses available for WPR-1:  $^{187}\text{Os}/^{188}\text{Os} = 0.14543 \pm 0.00018$  ( $n = 3$ ; Cohen, 1996) and  $^{187}\text{Os}/^{188}\text{Os} = 0.14549 \pm 0.00018$  ( $n = 6$ ; G. Pearson data from DTM, quoted in Cohen, 1996).

## 5. RESULTS

Analytical results are presented in Table 2 and Figures 5 and 6. Re and Os abundances in whole rocks range from 0.82 to 101 ppb and 0.116 to 3.998 ppb, respectively. Values are highest in the more strongly metamorphosed footwall and xenolith samples. Values in both kerogen and sulfide separates are considerably higher than those of the whole rock, with Re concentrations as high as 768 ppb in kerogen from sample 24981-213.5 and Os as high as 31.8 ppb in kerogen from xenolith sample B1-127-1045. The uptake of Re and Os by pyrrhotite (discussed more fully below) is clearly seen in sample 24981-212.5. In this sample the sulfide laminae are composed primarily of pyrite, but the majority of sulfide is finely disseminated and has been converted to pyrrhotite. The Re and Os contents of the sulfide fraction of this sample (1.338 ppb Os, 52.76 ppb Re) are much higher than those from samples 24981-210.7 and 24981-213.5 where pyrite is dominant. In contrast, the Re and Os contents of kerogen in these two samples are considerably higher than that of kerogen in sample 24981-212.5 (Table 2).

Kerogen samples from core MDD2 plot near a 1.85 Ga chondritic reference isochron on a  $^{187}\text{Os}/^{188}\text{Os}$  vs.  $^{187}\text{Re}/^{188}\text{Os}$  diagram (Fig. 6;  $\gamma_{\text{Os}} = 45$  to  $-104$ , Table 2). Whole rocks, kerogen, and sulfide from the other sample types exhibit more complex relationships, which will be discussed below. Of par-

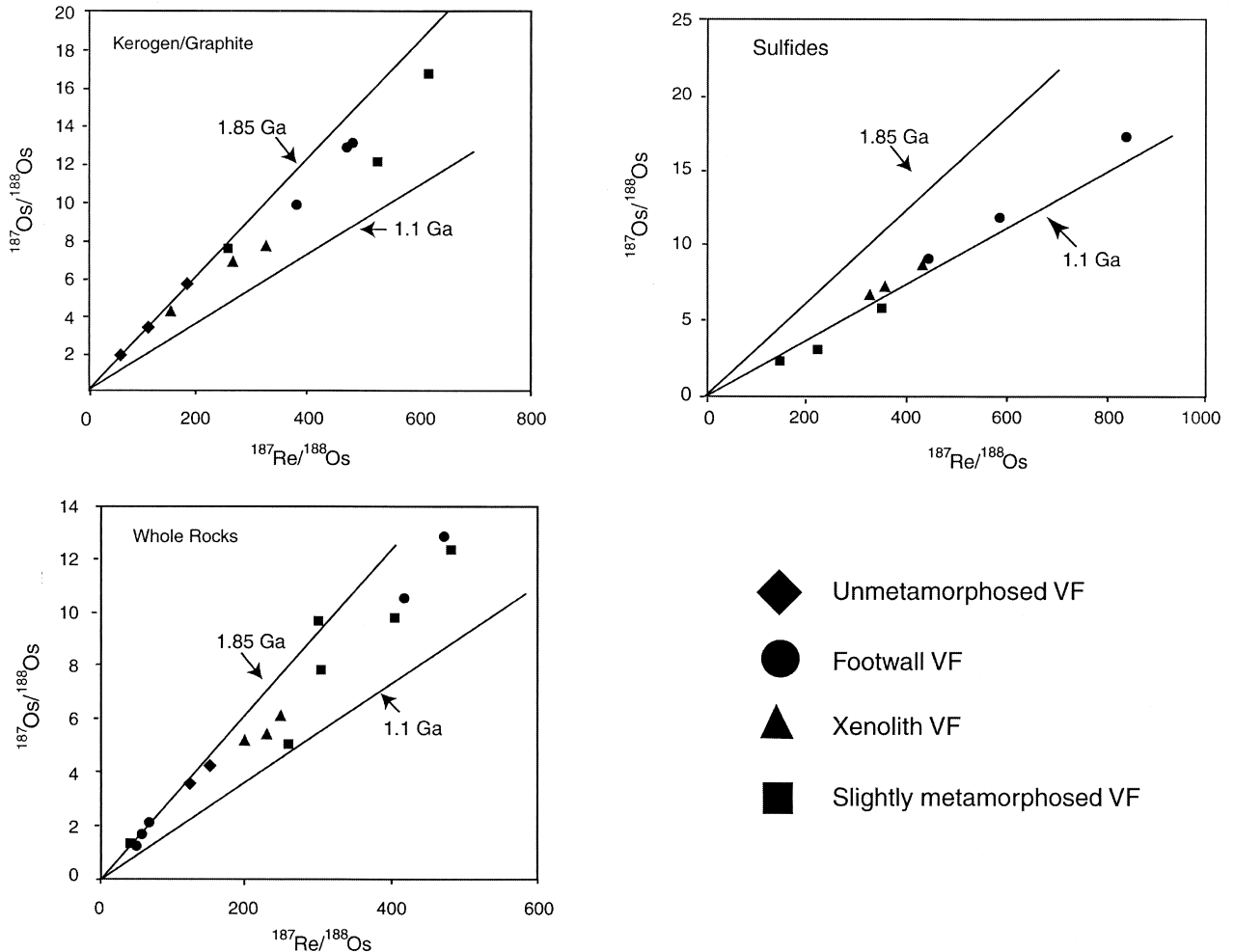


Fig. 6.  $^{187}\text{Os}/^{188}\text{Os}$  vs.  $^{187}\text{Re}/^{188}\text{Os}$  for Virginia Formation whole rocks, kerogen-graphite separates, and sulfide minerals.

tical significance is that most samples do not lie on the 1.85 Ga isochron and that for all sample types the sulfide separates show  $^{187}\text{Os}/^{188}\text{Os}$  ratios that suggest sulfide recrystallization accompanied by fluid mobility at  $\sim 1.1$  Ga.

## 6. DISCUSSION

Before discussing the observed results from the Virginia Formation, we review some general processes that could affect metamorphic rocks. Closed system, thermally driven isotopic homogenization could affect minerals in a whole rock (Fig. 7). Although the whole rock would not change isotopic composition, minerals could be reset to the whole rock  $^{187}\text{Os}/^{188}\text{Os}$  value via diffusion. The effectiveness of this process depends on the scale of diffusion and hence may be restricted to spatially localized areas. In this manner several new initial  $^{187}\text{Os}/^{188}\text{Os}$  values could be produced in a spatially restricted area (Fig. 7).

A second process that could alter isotopic systematics is devolatilization. If the liberated fluid does not differ in Re/Os ratio from the residual rock, then no change occurs in the isotopic systematics. If the fluid is either enriched or depleted

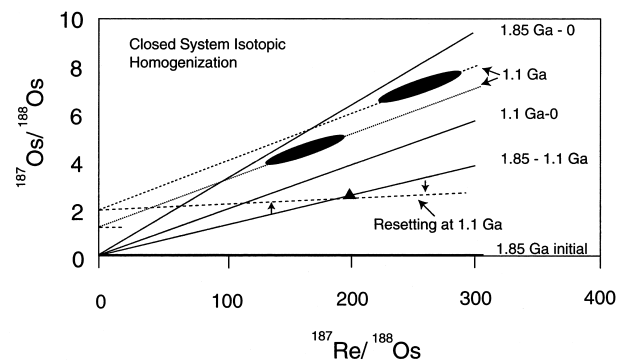


Fig. 7.  $^{187}\text{Os}/^{188}\text{Os}$  vs.  $^{187}\text{Re}/^{188}\text{Os}$ , illustrating the internal homogenization of osmium isotopic ratios at 1.1 Ga to a value greater than the initial ratio at 1.85 Ga. A series of reset, homogenized values could occur on local scales as a function of mineral assemblages and variations in Re and Os diffusivity. The shaded ellipsoids illustrate potential data clusters along secondary isochrons that fall below the 1.85 to 0 reference isochron. Hence, radiogenic decay from 1.1 Ga to the present could account for the values now observed in the whole rocks and kerogen samples but cannot explain the sulfide values that require initial Os isotopic ratios to be very close to those at 1.85 Ga.



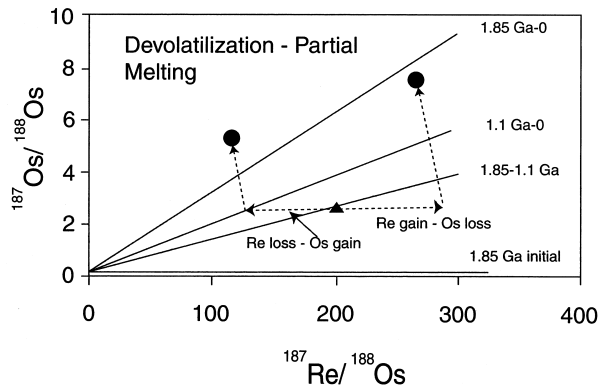


Fig. 8.  $^{187}\text{Os}/^{188}\text{Os}$  vs.  $^{187}\text{Re}/^{188}\text{Os}$ , illustrating possible consequences of fluid or melt loss from the Virginia Formation. Evolution of a relatively Re-rich fluid or melt at 1.1 Ga produces a low Re/Os residue. Decay from 1.1 Ga to the present will produce some samples with isotopic ratios that plot above the 1.85 Ga-0 reference isochron. Loss of a relatively Os rich fluid or melt leaves a high Re/Os residue. Decay since 1.1 Ga may lead to values that plot beneath the 1.85 Ga reference isochron, similar to the whole rock and kerogen values observed from the metamorphosed Virginia Formation.

in Re relative to Os then  $^{187}\text{Os}/^{188}\text{Os}$  values in the rock will evolve along a different trajectory (Fig. 8). Continued decay until the present will result in isotopic ratios that exceed or are below those of the isochron for the age of the rock at the initial  $^{187}\text{Os}/^{188}\text{Os}$  ratio (Fig. 8). Partial melting of a protolith could produce results similar to those of devolatilization, depending on the partitioning of Re and Os between partial melt and residual phases.

Interaction of a rock with a Re- or Os-bearing fluid or melt, resulting in metal addition either by precipitation or exchange, is treated as a mixing process. Depending on the Os isotopic and elemental composition of the fluid, as well as mixing proportions, a much different initial  $^{187}\text{Os}/^{188}\text{Os}$  ratio may result, which will affect today's values, produced as a result of decay since the time of mixing.

Samples from drill core MDD2 show little evidence for recrystallization, and all previous researchers (e.g., Lucente and Morey, 1983; Rao and Ripley, 1983; Ripley and Alawi, 1988; Abrajano et al., 1991) have regarded the core as being unaffected by contact metamorphism. However, constraining possible temperatures to less than  $\sim 350^\circ\text{C}$  is difficult. The assemblage chlorite + muscovite + quartz does not readily recrystallize in the absence of a water-rich fluid at temperatures below  $\sim 400^\circ\text{C}$  (Winkler, 1967). The kerogen Re/Os isotopic values plot near a 1.85 Ga isochron, in excellent agreement with the proposed depositional age of the Virginia Formation (Morey and Van Schmus, 1988). Two of the whole rock samples do not plot on the isochron, suggesting some Re-Os mobility. The three kerogen data points are insufficient to describe a statistically valid isochron. However, the data from core MDD2 suggest near closed system behavior for the Re-Os isotopic system in kerogen, even if temperatures near  $400^\circ\text{C}$  were attained.

Metamorphosed Virginia Formation samples from drill cores 24981, B1-127, and B1-354 illustrate isotopic systematics that differ from those of unmetamorphosed samples. With the exception of sulfide minerals from core 24981, all samples fall

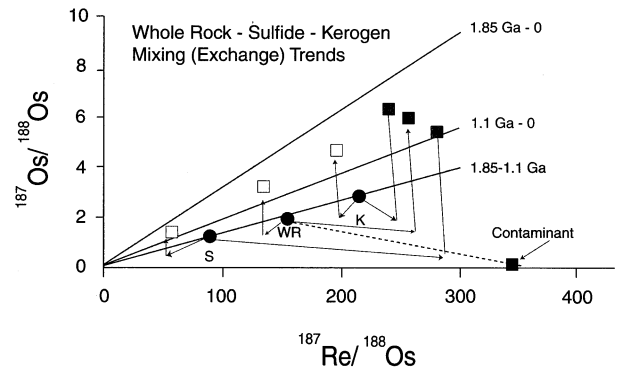


Fig. 9.  $^{187}\text{Os}/^{188}\text{Os}$  vs.  $^{187}\text{Re}/^{188}\text{Os}$ , illustrating possible mixing trajectories resulting from interaction between the Virginia Formation and a low  $^{187}\text{Os}/^{188}\text{Os}$ , high  $^{187}\text{Re}/^{188}\text{Os}$  contaminant. Enhanced reactivity of sulfides relative to kerogen leads to sulfide fractions that plot nearer the 1.1 Ga chondritic reference isochron. Resulting whole rock values plot between the final sulfide and kerogen values. Preferential uptake of Os from the contaminant, or exchange with a low Re/Os contaminant, may produce sulfides with a lower  $^{187}\text{Re}/^{188}\text{Os}$  ratio than found in coexisting kerogen (open symbols). This relative Re/Os order is similar to that found in mildly metamorphosed samples from core 24981, suggesting that the fluid that interacted with these rocks was distinct from the fluid or melt that interacted with footwall and xenoliths.

between 1.85 Ga and 1.1 Ga chondritic reference isochrons. Internal, closed system homogenization could produce such values if resetting resulted in only very low initial  $^{187}\text{Os}/^{188}\text{Os}$  values (Fig. 7). Resetting to  $^{187}\text{Os}/^{188}\text{Os}$  ratios in excess of  $\sim 1$  should produce some values that plot above, or to the left of, the 1.85 Ga-0 reference isochron (Fig. 7). The abundance of samples with high  $^{187}\text{Os}/^{188}\text{Os}$  indicates that resetting to low initial  $^{187}\text{Os}/^{188}\text{Os}$  ratios would have been very unlikely. Alternatively, a series of secondary 1.1 Ga isochrons could be produced if isotopic resetting varied on a local scale (Fig. 7). This process is feasible only if Re/Os ratios varied spatially in such a manner that systematic differences in initial  $^{187}\text{Os}/^{188}\text{Os}$  ratios resulted. For example, if at 1.1 Ga a high Re/Os location in the Virginia Formation was reset to an elevated  $^{187}\text{Os}/^{188}\text{Os}$  ratio, continued decay of the high Re/Os subset would result in  $^{187}\text{Os}/^{188}\text{Os}$  ratios today that could plot below the 1.85 Ga chondritic isochron. This is a highly speculative scenario that, when taken together with information given below, renders closed system isotopic homogenization in the Virginia Formation very unlikely. For core 24981 two whole rocks and one kerogen sample plot along the 1.85 Ga reference isochron. These samples lend evidence to the hypothesis that isotopic resetting at the margin of the contact aureole was spatially variable and that these samples were not reset. However, it is also possible that these data points represent low Re/Os samples along a secondary 1.1 Ga isochron. The same is true for Virginia Formation footwall samples 10134-124 and 214-1978 (Fig. 6). These low Re/Os samples plot very near the 1.85 Ga reference isochron and appear to have escaped being reset at 1.1 Ga.

There is no doubt that footwall samples from core B1-354 and the xenolith samples have experienced dehydration. This is not apparent for samples from core 24981 (Fig. 3). Loss of a high Re/Os fluid is not indicated because all values fall below the 1.85 Ga reference isochron (Fig. 5). The loss of a low Re/Os

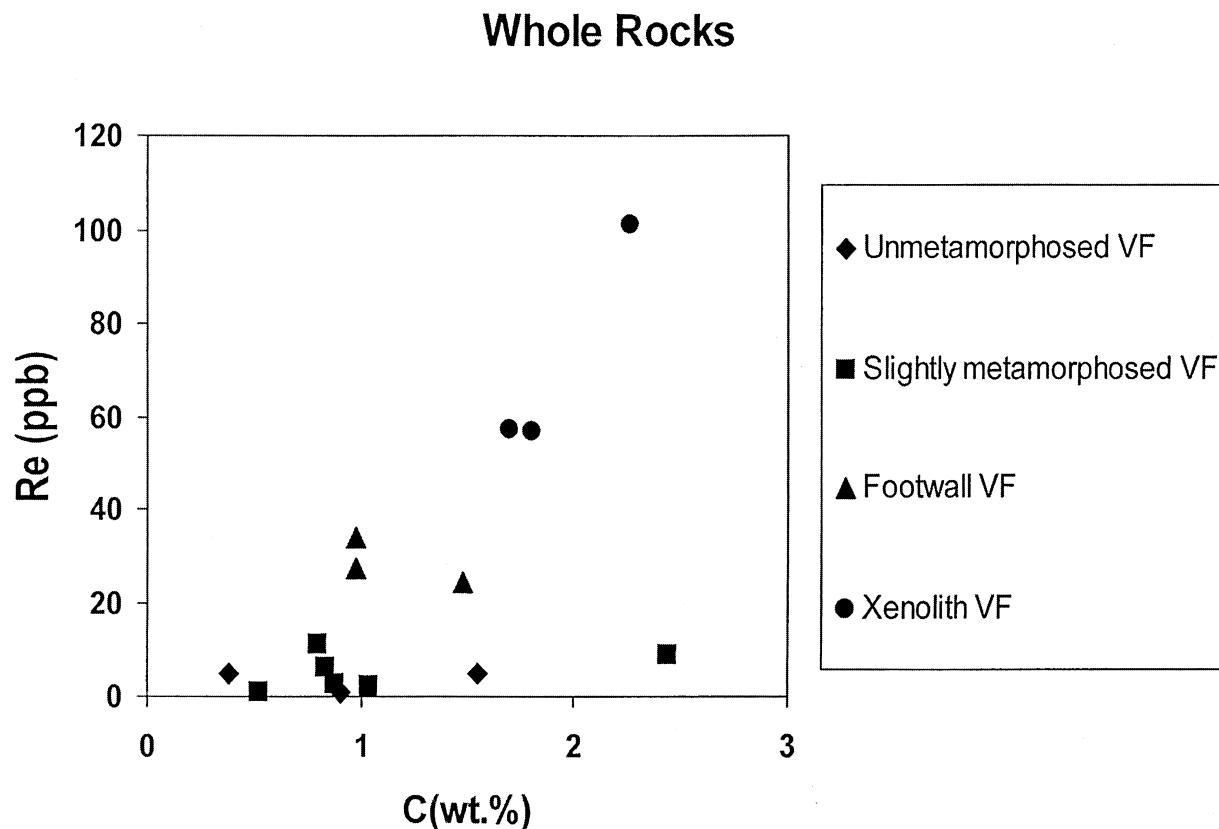


Fig. 10. Carbon abundance versus Re concentration for samples from the Virginia Formation.

fluid is possible because today's values would fall below the 1.85 Ga isochron (Fig. 8). Although this process appears feasible, the  $^{187}\text{Os}/^{188}\text{Os}$  values of the sulfide separates (near the 1.1 Ga chondritic reference isochron) are difficult to explain by this mechanism. In addition, recent experimental studies by Wood and Xiong (2000) indicate that under all conditions thus far examined, Re is more soluble than Os.

The effects of partial melting of the xenoliths are difficult to evaluate because both kerogen/graphite and sulfide separates are characterized by a wide range of Re/Os ratios. However, in many samples the organic fraction is characterized by higher Re/Os ratios than the sulfides. Preferential melting of either organic matter or sulfide could result in significant isotopic shifts. Textural or chemical evidence for the melting of either pyrrhotite or graphite in the Virginia Formation is weak, and hence the partitioning of Re and Os between these phases and a siliceous partial melt would be expected to control isotopic systematics. If the partial melt were Re-enriched, the results would be similar to those of Re-loss via dehydration (Fig. 8), and today's values do not support such a mechanism.

Of the possible processes that could give rise to Os isotopic variability in the Virginia Formation, only mixing, or mass transfer, can readily explain the sulfide isotopic values. Such a mechanism is also consistent with the kerogen/graphite and whole rock data. All of the sulfide minerals fall near a 1.1 Ga reference isochron with a chondritic initial Os isotopic ratio. A closed system process cannot account for the "resetting" of sulfides only to such low Os isotopic ratios at 1.1 Ga. Rather,

the data indicate that open system processes, exchange or mixing with a fluid or melt related to the intrusion, have been responsible for the isotopic resetting. Decreasing of initial Os isotopic ratios could be accomplished by mixing or exchange with a fluid of lower  $^{187}\text{Os}/^{188}\text{Os}$  ratio but with variable Re/Os ratio. However, the spread of observed Re/Os ratios in the metamorphosed rock types, along with the abundance of samples with high Re/Os ratios, suggests that the fluid was characterized by Re/Os ratios that were as elevated, or more so, than those of unmetamorphosed Virginia Formation. The sample values suggest that the degree of openness to exchange and addition was variable but that sulfides were much more reactive than kerogen (see Fig. 9). In fact, the sedimentary sulfides appear to have been totally reset to near chondritic initial ratios, suggesting that their Os budget was dominated by that of the external reservoir. It appears that the fluid or melt was characterized by chondritic initial Os isotopic ratios and hence may have been related to emplacement of the mantle-derived mafic melts of the Duluth Complex that would have had near-chondritic Os isotopic ratios at 1.1 Ga (Shirey, 1997; Ripley et al., 1998). In the case of the xenolith the contaminant may have been the surrounding melt, but because such interaction is somewhat more difficult to envision for the footwall rocks and virtually impossible for the rock of core 24981, we propose that a fluid phase interacted with the rocks near the margins of the intrusion. Figures 10 and 11 plot C abundance versus Re in Virginia Formation samples. It is clear that the xenolith samples, and to a lesser extent footwall from core B1-354, are

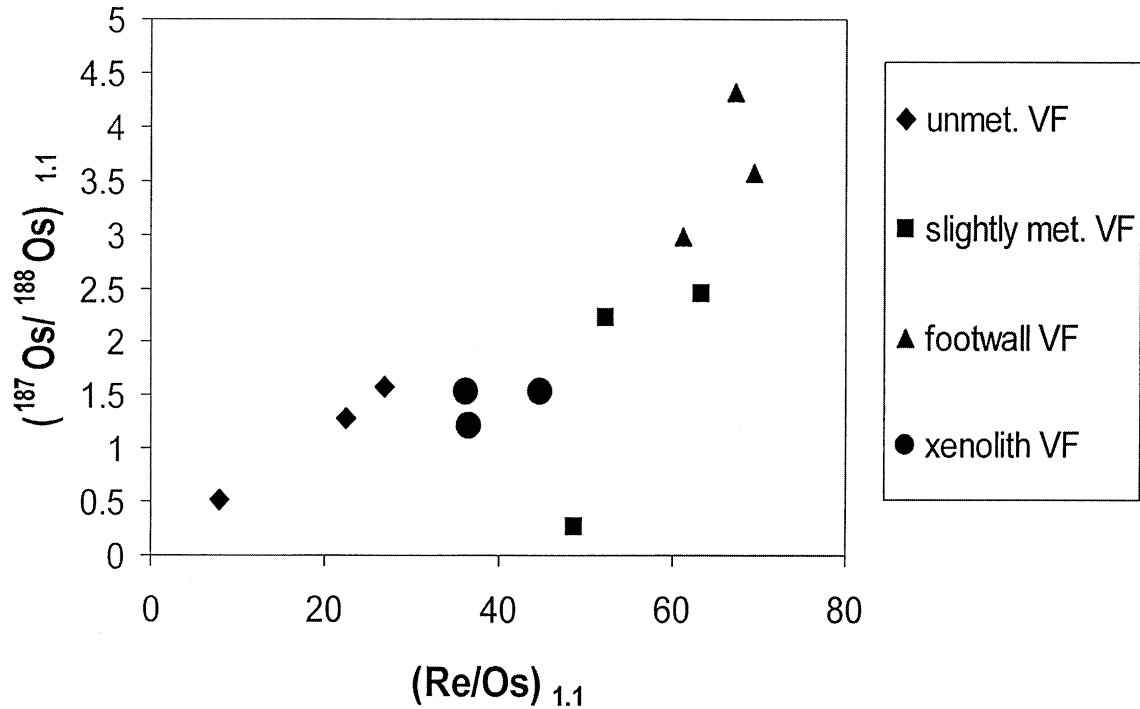


Fig. 11. ( $^{187}\text{Os}/^{188}\text{Os}$ )<sub>1.1</sub> versus (Re/Os)<sub>1.1</sub>. The positive trend suggests that the unmetamorphosed Virginia Formation must be characterized by a larger range in Re/Os values than those shown by the samples analyzed in this study. Mixing with a contaminant characterized by chondritic  $^{187}\text{Os}/^{188}\text{Os}$  values at 1.1 Ga should produce lower values than the unmetamorphosed Virginia Formation. For this reason, the protoliths to the metamorphosed Virginia Formation samples are thought to have had higher Re/Os values and  $^{187}\text{Os}/^{188}\text{Os}$  values.

enriched in metals. This is not the case for footwall material from core 214 (Ripley, 1990) or slightly metamorphosed samples from core 24981. Isotopic anomalies associated with the xenolith samples or core B1-354 footwall are more easily linked to metal enrichment due to magma- or fluid-rock interaction than are those from samples of core 24981.

Figure 12, a plot of Re/Os at 1.1 Ga versus  $^{187}\text{Os}/^{188}\text{Os}$  at 1.1 Ga, suggests that a wider range in Virginia Formation Re/Os ratios may exist than that indicated by the unmetamorphosed samples analyzed in this study. If this were not the case, mixing of the Virginia Formation and a Re + Os-bearing fluid or melt with a chondritic isotopic ratio could not produce  $^{187}\text{Os}/^{188}\text{Os}$  values of the Virginia Formation greater than  $\sim 1.5$  at 1.1 Ga (Fig. 11). The fact that the xenolith is very enriched in both Re and Os, yet its Re/Os ratio is lower than that of the footwall also suggests either initial Re/Os variability in the Virginia Formation, or variability in the composition of the fluid or melt that interacted with the rocks. The lower Re and Os contents of the slightly metamorphosed samples from core 24981, coupled with their variable isotopic ratios, suggests that Os and Re concentrations must have been very low in the protoliths and that only small amounts of exchange with a Re- and Os-bearing fluid was sufficient to strongly modify isotopic systematics.

Evidence for the involvement of a fluid at the margin of the contact aureole is found within some samples from core 24981. Several quartz-rich stringers have been found that are concentrated along bedding planes, particularly along pyrite-silicate contacts. The quartz stringers or veinlets contain abundant

pyrrhotite (10–15%), and lesser amounts of chalcopyrite, cubanite, bornite, pentlandite, and sphalerite. The sulfide assemblage is very similar to that found in the magmatic sulfide mineralization in the Duluth Complex. Fluid inclusions in the quartz of the veinlets homogenize at 300 to 380°C (Butler, 1989), indicating that moderately high-temperature fluids did interact with rocks of core 24981, even though mineralogical evidence for recrystallization is minor.

Many researchers have proposed the existence of fluids associated with crystallization and mineralization of the Duluth Complex. Mogessie et al. (1991) proposed that PGE accumulations in the complex have resulted from fluid transport and deposition. Ripley (1990) illustrated that Au, Pt, and Pd have been mobilized from the massive sulfides, most likely by late-stage fluids. Pasteris et al. (1995) documented the importance of both magmatic and externally derived fluids in the alteration of the troctolitic and gabbroic rocks of the Duluth Complex based on fluid inclusion studies. Ripley et al. (1993) showed via oxygen and hydrogen isotopic data that three fluids have been involved in the alteration of the Duluth Complex. One fluid has been derived from dehydration of the Virginia Formation, one is of meteoric origin, and one represents deuteric fluids from the crystallizing intrusion. All of these studies highlight the potential importance of a magmatic fluid phase. Pasteris et al. (1995) stress that, due to the high salinity of fluids derived from a mafic melt, metals would be efficiently scavenged and transported. Reaction with a Re- and Os-rich fluid derived from the Duluth Complex can most easily explain the isotopic charac-

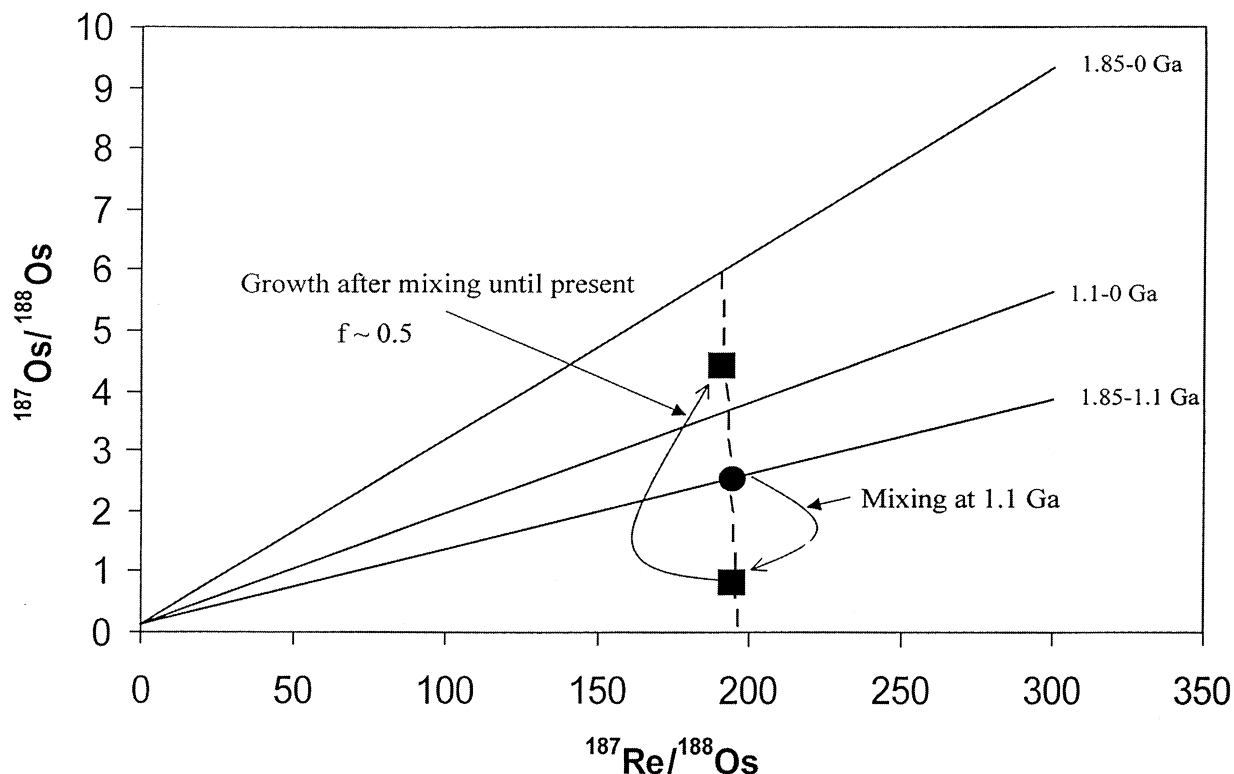


Fig. 12.  $^{187}\text{Os}/^{188}\text{Os}$  vs.  $^{187}\text{Re}/^{188}\text{Os}$  showing the result of mixing of a fluid component with the following characteristics at 1.1 Ga: Os = 1.50 ppb,  $^{187}\text{Os}/^{188}\text{Os}$  = 0.1198 and Virginia Formation with Os = 0.15 ppb and  $^{187}\text{Os}/^{188}\text{Os}$  = 2.5. Mixing with  $f$  (fractional abundance of Virginia Formation) values between 0.5 and 0.8 yields Os isotopic ratios in the mixture between 0.336 and 0.800. With a present-day  $^{187}\text{Re}/^{188}\text{Os}$  = 195, growth since 1.1 Ga produces Os isotopic values similar to those of the whole rocks and kerogen. Sulfide minerals are more open to exchange and Os addition, and hence the initial (1.1 Ga) Os isotopic ratios are closer to those produced at  $f$  values less than 0.5.

teristics of the metamorphosed Virginia Formation. The sulfide mineralogy of the veinlets found in drill core 24981 is similar to that of the magmatic mineralization and also suggests that a derivation from the magma is likely. The exact nature and composition of this fluid is poorly constrained, but data from the metamorphic rocks indicate that the fluid Re/Os ratio would have been similar to or higher than that which characterizes unmetamorphosed Virginia Formation, and the  $^{187}\text{Os}/^{188}\text{Os}$  would have been near chondritic.

A simple mixing calculation illustrates the possible result of the interaction between a magmatic fluid and the Virginia Formation. Given Os concentrations of 0.15 ppb for the Virginia Formation and 1.50 ppb for the fluid,  $^{187}\text{Os}/^{188}\text{Os}$  ratios of 2.5 and 0.1198 respectively, and a  $^{187}\text{Re}/^{188}\text{Os}$  ratio of the Virginia Formation today of  $\sim 195$ ,  $^{187}\text{Os}/^{188}\text{Os}$  ratios of the mixture today at  $f$  (fractional abundance of Virginia Formation) values between 0.5 and 0.8 vary from 3.98 to 4.40 (Fig. 12). Because of the variability in the isotopic composition of the Virginia Formation at 1.1 Ga, and because of the uncertainty in the isotopic composition of the fluid component more precise mixing computations are tenuous. However, it is clear that mixing of this type can easily explain the whole rock and kerogen isotopic data. Figure 12 also illustrates that the sulfide separate data require initial  $^{187}\text{Os}/^{188}\text{Os}$  values to be near chondritic. For this to occur, the sulfide minerals must have been much more open to interaction with the fluid than were

kerogen or other whole rock components. Using the concentrations given above,  $f$  values less than  $\sim 0.4$  are required to generate the sulfide isotopic compositions.

Metasomatism of the Virginia Formation has not been previously suggested based on petrochemical studies. Although devolatilization of footwall hornfels and partial melting of the xenoliths have definitely occurred, later interaction with a fluid or melt has controlled Os isotopic systematics in the metasedimentary rocks. Exchange and mixing involving the magma and xenoliths is easily envisioned, but footwall samples located as far as 1.5 km from the contact suggest that the Re-Os isotopic system was perturbed via interaction with a fluid without affecting silicate mineralogy or major element chemistry.

## 7. CONCLUSIONS

Metasomatism of the pelitic rocks in the contact aureole of the Duluth Complex and xenoliths in the intrusion has strongly modified Re-Os isotopic systematics. The distribution of Re-Os isotopic values in whole rocks and kerogen can be explained by thermal resetting at the time of intrusion (1.1 Ga), although the variability of isotopic ratios requires that the internal homogenization varied on a local scale. Dehydration and partial melting have affected footwall and xenolith material, but loss of an Os-rich fluid or melt is required to explain the whole rock and kerogen isotopic values. Alternatively, open system exchange

processes offer a more reasonable explanation for the observed isotopic variability. Exchange or mixing with a Re-rich fluid characterized by a near chondritic  $^{187}\text{Os}/^{188}\text{Os}$  ratio can explain the kerogen and whole rock data, as well as that from the sulfide separates. Sulfide minerals in the metamorphosed Virginia Formation plot near a 1.1 Ga chondritic reference isochron. Infiltration of the Virginia Formation by a magmatically derived fluid, coupled with high reactivity of the sulfide minerals relative to kerogen and other mineral fractions, is consistent with all of the Re-Os isotopic data. Isotopic resetting of rocks such as those from core 24981 that have interacted with moderate temperature fluids (300–400°C), but that show little mineralogical recrystallization, suggests that extreme care should be taken in the application of the Re-Os system to low-grade metamorphic or hydrothermally altered rocks.

The results of this study are in strong agreement with the recent experimental work of Brenan et al. (2000). Results of their diffusion studies suggest that pyrrhotite exchanges Os much more readily than does pyrite. Brenan et al. (2000) calculated a diffusive time scale for “core retention” in pyrrhotite of  $\leq 0.5$  Ma at 500°C. Oxygen isotopic studies of diffusion profiles in sills within the contact aureole of the Duluth Complex by Park et al. (1999) indicate that isotopic exchange in the presence of a fluid may have extended from tens of thousands to 1.4 Ma. It is clear that pyrrhotite in the metamorphosed Virginia Formation acquired Os from an external reservoir within a relatively short time period. Results from this study are also consistent with those of Lambert et al. (2000), who reported the Os isotopic resetting of sulfide minerals in the magmatic ores of the Voisey’s Bay Intrusion as a result of hydrothermal activity associated with the younger Grenville orogeny.

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