Sm-Nd and Rb-Sr dating of an Archean massive sulfide deposit: Kidd Creek, Ontario

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ABSTRACT

Highly altered felsic metavolcanics associated with the Kidd Creek, Ontario, Cu-Zn massive sulfide deposit show a large range of Sm/Nd ratios and yield a Sm-Nd isochron of 2674 ±40 Ma (initial ratio ϵ_{Nd} = 1.55 ± 0.30), which represents the time of rare-earth-element redistribution during intense hydrothermal alteration. That the Sm-Nd age is consistent with age constraints on ore deposition provided by precise U-Pb zircon data indicates contemporaneity of ore deposition, hydrothermal alteration, and rare-earth mobility. The age is therefore interpreted as a minimum age of ore deposition. In contrast, the Rb-Sr age of the altered rocks, as well as the metavolcanic rocks outside the alteration zone, has been reset at 2576 ±26 Ma, most likely as a result of widespread low-temperature metasomatism unrelated to ore deposition. Our results suggest that Sm-Nd dating could be a useful tool in the study of ore deposits and, potentially, in the study of a wide range of mineralizations.

Initial $\epsilon_{Nd}(T)$ values for massive ore, altered felsic volcanics, and their weakly altered precursors are identical, indicating derivation and redistribution of light rare-earth elements within the altered footwall volcanics. These data suggest that the footwall volcanics have also supplied part of the base metals to the stratiform ore.

INTRODUCTION

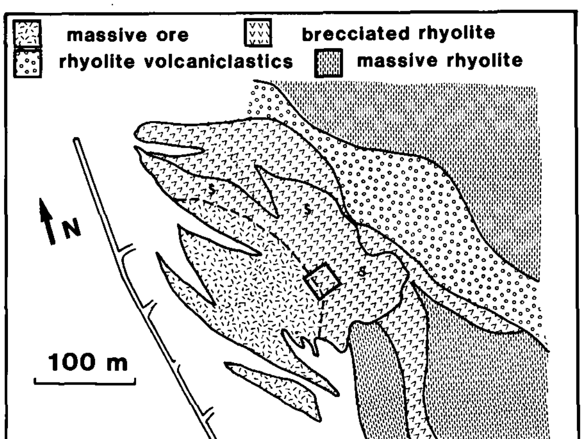
Rare-earth elements (REE) are immobile under most geologic conditions, but they may become mobile in zones of intense alteration associated with some ore deposits (Graf, 1977; Kerrich and Fryer, 1979). For example, Campbell et al. (1984) reported extreme REE mobility from the large Kidd Creek Cu-Zn massive sulfide deposit in Ontario and suggested that hydrothermal alteration of footwall volcanics during ore formation was responsible for fractionation of REE. We show that Sm-Nd whole-rock dating can be used to determine the time of REE fractionation and to obtain useful information on its relationship to ore deposition. This approach has potential in a variety of ore-forming environments and may be valuable in the study of ore deposits. The Sm-Nd data are compared with Rb-Sr isotopic data to evaluate their relative resistance to subsequent disturbance.

Initial $^{143}Nd/^{144}Nd$ ratios for altered host rocks and stratiform sulfide ore are used to constrain the source of mobile Nd within the alteration system. This can give information on the source or pathway of the hydrothermal solutions precipitating Nd and can complement data on ore fluid sources obtained from other methods.

GEOLOGIC SETTING AND SAMPLES

The Kidd Creek deposit—one of the world's largest Cu-Zn mines—is an Archean, volcanics-hosted, massive sulfide deposit (Franklin et al., 1981). It is located in an overturned volcano-sedimentary sequence near the boundary between Lower and Upper Supergroup of the western part of the Abitibi greenstone belt, 45 km north of Timmins, Ontario. Massive stratiform sulfides occur within rhyolitic volcaniclastics, and they are stratigraphically underlain by a conformable, lobate-shaped blanket of stringer-Cu mineralization located within a crackle-brecciated massive rhyolite (Coad, 1985). The mineralized sequence is sandwiched by pillowed metabasalts (hanging wall), and rhyolitic volcaniclastics and subvolcanic sills of massive rhyolite (footwall), which have a U-Pb zircon age of 2717 ±4 Ma (Nunes and Pyke, 1981). Several ultramafic and felsic stocks occur in the mine area, but field relations are unclear because of structural complexity and pervasive alteration. Felsic volcanics in the alteration zone associated with the mineralization contain quartz ± chlorite ± sericite ± calcite assemblages typical of many volcanics-hosted, massive sulfide deposits (Walker et al., 1975). There ore-related alteration features contrast with the low-grade assemblages associated with burial metamorphism and include distinct changes in major and trace elements (Campbell et al., 1984) and unusual oxygen isotopic characteristics (Beaty et al., 1980).

Samples for Nd and Sr isotopic analyses were taken from both within and outside the alteration zone to represent the compositional range from nonmineralized, weakly altered volcanics, through altered and highly altered volcanics, to massive chalcopyrite ore. Weakly altered felsic volcanics (WFV) were collected from massive footwall rhyolites about 300 m below the Cu-stringer ore zone; they are probably geochemically similar to pre-ore mine sequence volcanics (Campbell et al., 1984). Sample locations for altered felsic volcanics (AFV) and massive stratiform Cu ore are shown in Figure 1. Major- and trace-element data for most of the samples are reported in



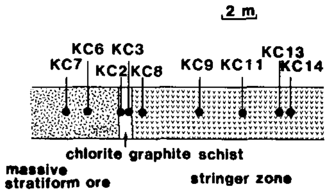


Figure 1. Left: Schematic geologic map of mine level 2400 ft showing relative position of samples with prefix KC from crosscut 26-600 on 2600-ft level (quadrangle). Right: Details of sample locations in crosscut 26-600. Modified after Coad (1984).

Campbell et al. (1984) who demonstrated spectacular REE mobility within the alteration zone at the stringer zone–massive ore contact. In essence, intense hydrothermal alteration, probably associated with ore formation, produced zones of depletion in light REE and middle REE, as well as zones of light REE enrichment within AFV (Fig. 2). This zoning resulted in a large spread of Sm/Nd ratios in AFV which makes these rocks amenable to Sm-Nd isotopic dating. Furthermore, AFV exhibit a wide range in Rb/Sr ratios, which allows precise Rb-Sr dating.

TIME OF RARE-EARTH FRACTIONATION AND ORE DEPOSITION: Sm-Nd ISOTOPES

The Sm-Nd isotopic data (Table 1) show a large range in $^{147}Sm/^{144}Nd$ for AFV and massive ore (0.09 to 0.27) compared to the very limited range in WFV. The most altered AFV from the lower part of the alteration zone have the highest $^{147}Sm/^{144}Nd$ compared to AFV closer to stratiform ore which have values lower than WFV. Massive, stratiform sulfide ore has the lowest $^{147}Sm/^{144}Nd$.

The AFV and ore data define a 2674 ±40 Ma isochron (95% confidence limit [C.L.]; model 4, McIntyre et al., 1966) with an initial ratio of ϵ_{Nd} (T) = 1.55 ± 0.30 (Fig. 3a). Inclusion of the WFV data does not effect significant changes in either age or initial ratio. Although the data show some scatter beyond analytical uncertainty (see inset Fig. 3a), both age and initial ratio are surprisingly well defined considering the strong alteration of the samples. The age is regarded as the time when REE in AFV and stratiform ore were mobilized and fractionated as a result of hydrothermal alteration (Campbell et al., 1984).

The 2674 ±40 Ma age is identical within error to the 2640 ±60 Ma Pb-Pb isochron age for Kidd Creek sulfides and whole rocks which has been interpreted as the age of sulfide ore deposition (Bugnon et al., 1979). It is, however, somewhat younger than the U-Pb zircon age of 2717 ±4 Ma for massive rhyolites underlying stratiform ore which represents a maximum age for ore deposition (Nunes and Pyke, 1981). A similarly precise U-Pb zircon age of 2703 ±3 Ma for a rhyolite higher up in the stratigraphic sequence from elsewhere in the Timmins area (Nunes and Pyke, 1981) sets a minimum age for ore formation, which is within error of the Sm-Nd age.

It is not clear whether the small difference between the 2717 Ma zircon age and the Sm-Nd age is real or the result of minor disturbance of the Sm-Nd isotopic system. The field relations strongly suggest a broadly syngenetic origin of the ore (Walker et al., 1975) consistent with modern concepts for ore genesis in volcanics-hosted, massive sulfide deposits (Franklin et al., 1981). On the other hand, the close association of argillic, carbonaceous sedimentary rocks with the stratiform ore at Kidd Creek suggests a break in volcanic activity (Walker et al., 1975). In addition, U-Pb zircon data and regional mapping indicate a temporal relationship of base metal and gold mineralization in the Abitibi belt with a paraconformity between Lower and Upper Supergroup (Nunes and Pyke, 1981). However, any delay between eruption of the footwall rhyolites and ore deposition did not exceed ~15 m.y., based on the 2703 ±3 Ma zircon age for rhyolites at the top of the Upper Supergroup, which is separated from the mine sequence by several thousand metres of volcanics. It is therefore more probable that the Sm-Nd age is marginally too young, possibly because of post-ore metamorphic or metasomatic disturbance which may be responsible for some of the data scatter seen in Figure 2a. The same process could have disturbed the U-Pb isotopic systems of Kidd Creek whole rocks and resulted in the low Pb-Pb isochron age of the sulfides (Bugnon et al., 1979). Alternatively, the presence of systematic differences in initial $^{143}Nd/^{144}Nd$ could also affect the age. However, without a priori reasons for sample rejection, we accept 2674 ±40 Ma as a minimum estimate for the time of ore deposition.

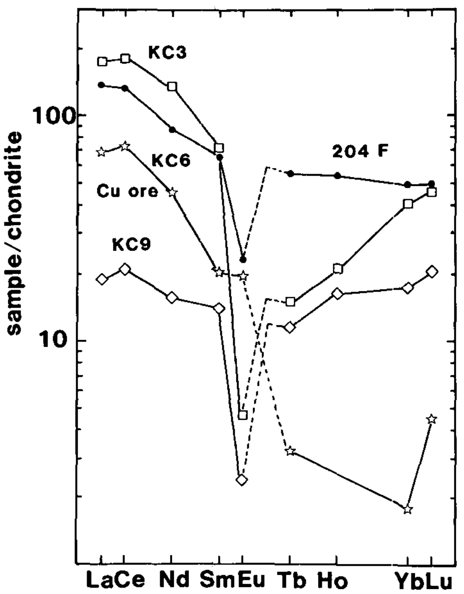


Figure 2. Chondrite-normalized REE patterns for Kidd Creek weakly altered volcanics, altered felsic volcanics from stringer zone, and stratiform Cu ore, illustrating REE mobility within alteration zone (REE data from Campbell et al., 1984, and unpublished analyses). Normalizing values are those of Evensen et al. (1978) × 1.5. Solid circles = weakly altered felsic volcanics; squares and diamonds = altered felsic volcanics; stars = stratiform, massive Cu ore.

TABLE 1. Sm-Nd AND Rb-Sr ANALYTICAL RESULTS FOR KIDD CREEK FELSIC VOLCANICS AND MASSIVE SULFIDES

Sample	Rock	Sm	Nd	Rb	Sr	$^{147}Sm/^{144}Nd$	$^{143}Nd/^{144}Nd$	$\epsilon_{Nd}(T)$*	$^{87}Rb/^{86}Sr$	$^{87}Sr/^{86}Sr$
Weakly altered felsic volcanics										
204 F	WFV	15.57	62.91	75.43	22.50	0.1497	0.511105 ± 18	+2.2	10.0313	1.07881 ± 6
204 G	WFV	32.48	128.01	222.11	26.05	0.1535	0.511133 ± 22	+1.4	27.0464	1.71515 ± 8
204 H	WFV	19.24	75.49	61.54	39.89	0.1542	0.511211 ± 32	+2.7	4.5277	0.87619 ± 4
204 J	WFV	9.36	38.19	86.85	20.50	0.1482	0.511045 ± 24	+1.6	12.7933	1.17721 ± 8
Altered felsic volcanics										
KC 2	AFV	21.19	129.69	14.94	15.73	0.0988	0.510174 ± 18	+1.8	2.7691	0.80767 ± 4
				15.79	16.51				2.7610	0.80739 ± 9
KC 3	AFV	16.85	99.19	14.21	8.09	0.1027	0.510260 ± 30	+2.2	5.1623	0.89758 ± 16
KC 8	AFV	6.80	29.32			0.1403	0.510948 ± 12	+2.4		
		6.87	29.79	48.67	32.78	0.1395	0.510940 ± 24	+2.4	4.3576	0.86848 ± 6
KC 9	AFV	3.19	11.23	28.08	20.16	0.1717	0.511488 ± 24	+2.0	4.0815	0.85687 ± 6
KC 11	AFV	4.81	13.43	25.91	12.52	0.2167	0.512235 ± 16	+0.8	6.1100	0.93329 ± 3
		4.96	14.03			0.2139	0.512171 ± 14	+0.5		
KC 13	AFV	2.26	9.17	18.51	8.47	0.1491	0.511093 ± 22	+2.2	6.4545	0.94675 ± 7
				19.70	8.95				6.5032	0.94596 ± 9
KC 14	AFV	2.35	8.68	35.26	14.63	0.1637	0.511308 ± 20	+1.3	7.1376	0.97145 ± 6
KCZ 6	AFV	2.66	7.02	29.07	17.12	0.2306	0.512516 ± 28	+1.4	4.9917	0.89131 ± 3
KCZ 11	AFV	7.79	17.67	43.13	18.91	0.2668	0.513167 ± 24	+1.5	6.7448	0.95403 ± 6
		7.74	18.13			0.2581	0.513000 ± 22	+1.4		
KCZ 14	AFV	6.00	19.49	35.72	13.46	0.1837	0.511680 ± 20	+1.4	7.8799	0.99777 ± 11
Massive sulfides										
KC 6	ore	4.73	32.64	2.83	2.01	0.0877	0.509990 ± 26	+2.1	4.0465	0.85009 ± 23
KC 7	ore	6.99	44.99	1.31	1.70	0.0940	0.510115 ± 28	+2.4	2.2366	0.78830 ± 61

Note: Procedures for sample preparation and mass-spectrometry as in McDonough et al. (1985).
Nd isotopic composition normalized to $^{146}Nd/^{142}Nd$ = 0.636151.
$^{143}Nd/^{144}Nd$ for BCR-1 is 0.511833 ± 10 (n=7), $^{87}Sr/^{86}Sr$ for NBS 987 is 0.71022 ± 2 (n=7).
All errors quoted are 2 σ_M.
Present-day reference values are $(^{143}Nd/^{144}Nd)_{CHUR}$ = 0.511836,

$(^{147}Sm/^{144}Nd)_{CHUR}$ = 0.1967; $\lambda = 6.54 \times 10^{-12}\ yr^{-1}$.

$^{143}Nd/^{144}Nd^T_{INIT}$: measured ratio in the rock corrected for decay since time of crystallization, i.e. 2717 Ma.

Discrepancies between some repeat analyses are due to sample heterogeneities which were particularly severe in the case of Rb-Sr analyses on the massive ore samples KC 6 and KC 7. These analyses were repeated 4 times each and the weighted averages were used in the calculations. Inclusion of repeat analyses in the isochron calculations did not cause significant changes in isochron parameters.

$$* \epsilon_{Nd}(T) = [(^{143}Nd/^{144}Nd)^T_{INIT}/(^{143}Nd/^{144}Nd)^T_{CHUR} - 1] \times 10^4,$$

$$\text{where } (^{143}Nd/^{144}Nd)^T_{CHUR} = (^{143}Nd/^{144}Nd)^0_{CHUR} - (^{147}Sm/^{144}Nd)^0_{CHUR}\,(e^{\lambda T} - 1).$$

POST-ORE DISTURBANCE: Rb-Sr ISOTOPES

The pooled Rb-Sr isotopic data for AFV, stratiform ore, and WFV (Table 1) define a 2576 ±26 Ma isochron (95% C.L., model 3) with an initial $^{87}Sr/^{86}Sr$ of 0.7047 ±24 (Fig. 3b). The pooling of all data appears justified in view of their colinearity on the isochron diagram and only small differences in ages and initial ratios obtained from regressing the data sets for AFV and WFV individually. The significance of the 2576 Ma age is uncertain. Resetting of Rb-Sr isotopic systems between 2600 and 2400 Ma is a common feature throughout most of the Superior province and may be attributed to one or more phases of the Kenoran orogeny (Turek et al., 1982; Davis et al., 1982). Jolly (1978) assigned an age of 2400 to 2600 Ma to Kenoran events that involved north-south compression, emplacement of granitoid diapirs, and contact metamorphic overprinting of earlier burial metamorphic assemblages in the volcanics. However, precise U-Pb zircon ages for granitoids cutting deformed metavolcanics in the western part of the Abitibi belt indicate that major metamorphism and tectonism in this area occurred shortly after termination of the volcanic activity and was completed, at least at crustal levels occupied by the metavolcanics, before about 2685 Ma (Percival and Krogh, 1983); therefore, contact metamorphism is eliminated as the reason for isotopic resetting of Kidd Creek rocks at 2576 ±26 Ma.

Brooks (1980) suggested widespread low-temperature metasomatism as the process responsible for resetting of the Rb-Sr age of the Chibougamau batholith and surrounding metavolcanics. Similar processes may have been active at Kidd Creek where WFV show signs of low-temperature alteration (Coad, 1985), although AFV may have had a more complex history, as indicated by the trace-element data of Campbell et al. (1984). We propose a two-stage model for Sr isotopic evolution in AFV and ore which involves alteration of initial $^{87}Sr/^{86}Sr$ ratios and Rb-Sr redistribution during reaction with hydrothermal solutions and ore deposition, followed by more widespread isotopic resetting during a low-temperature metasomatic event affecting both WFV and AFV. The poorly defined initial $^{87}Sr/^{86}Sr$ of 0.7047 ±0.0024 lies above the range of 0.7011 to 0.7020 for 2400 to 2600 Ma magmatic rocks (Hart and Brooks, 1977) and is probably a consequence of multi-stage isotopic resetting.

Nd ISOTOPES AND IMPLICATIONS FOR BASE METAL SOURCES

The origin of base metal sulfides in volcanics-hosted, massive sulfide deposits has long been debated (Franklin et al., 1981). Proposed metal sources include the host volcano-sedimentary pile, subvolcanic intrusions, and underlying basement. Isotopic tracing methods using Pb, Sr, and Nd isotopes can help constrain possible metal sources. The isotopic composition of hydrothermal minerals should reflect the isotopic composition of the hydrothermal solution forming the minerals and thereby give direct information about the source(s) of Pb, Sr, and Nd. In sulfide-generating systems on the sea floor, the Nd isotopic composition of the hydrothermal solution is a sensitive indicator of the pathway of the solution to the discharge site, because the low Nd concentration in seawater (<80 pg/g) makes it insensitive to seawater contamination (Piepgras and Wasserburg, 1985). In addition, it may be possible to identify magmatic or metamorphic fluid sources at depth if they are isotopically different from the wallrocks closer to the discharge site and contribute a substantial portion of the total Nd carried by the fluid.

At Kidd Creek there is clear evidence for REE mobility related to ore deposition. This evidence offers the opportunity to use the Nd isotopic data for ore and AFV to trace the Nd isotopic composition of the ore-forming hydrothermal solution near the sea floor–seawater interface. The determination of this parameter might help explain the unusual enrichment in ^{18}O in Kidd Creek alteration zone rocks (Beaty et al., 1980) which contrasts with the lowered $\delta^{18}O$ values commonly associated with volcanics-hosted, massive sulfide deposits. Although the origin of the high $\delta^{18}O$ fluid inferred to have caused this isotopic anomaly is not known, the anomaly may be related to the large size of the Kidd Creek deposit.

As shown earlier, the Sm-Nd isotopic data for AFV and ore define an isochron indicating very limited scatter in initial $^{143}Nd/^{144}Nd$ ratios. WFV plot on or close to this isochron. Furthermore, we have alluded to possible post-ore isotopic disturbance of Sm-Nd isotopic systems. Nevertheless, we feel that calculation of ϵ_{Nd} (T) values at 2717 Ma, the maximum age for ore deposition, can give qualitative information on the isotopic variation between WFV, AFV, and stratiform ore at that time.

Initial ϵ_{Nd} (T) values in AFV range from 0.8 to 2.4, and between 2.1 and 2.4 for stratiform sulfide ore (Table 1), very similar to the range of 1.4 to 2.7 observed in WFV. The small variation between WFV, AFV, and ore suggests REE redistribution and isotopic homogenization within the sampled volume of the stringer and ore zones. Apparently, REE contributions from sources isotopically different from the footwall volcanics have been absent or were insignificant, in accordance with Campbell et al. (1984), who, on the basis of systematic changes in REE patterns with stratigraphic position in the alteration zone, argued for light-REE transport from the stringer zone to the stratiform ore. This argument is supported by a mass balance calculation for Nd which indicates that all Nd in stratiform ore (10–40 ppm in ~100 ×

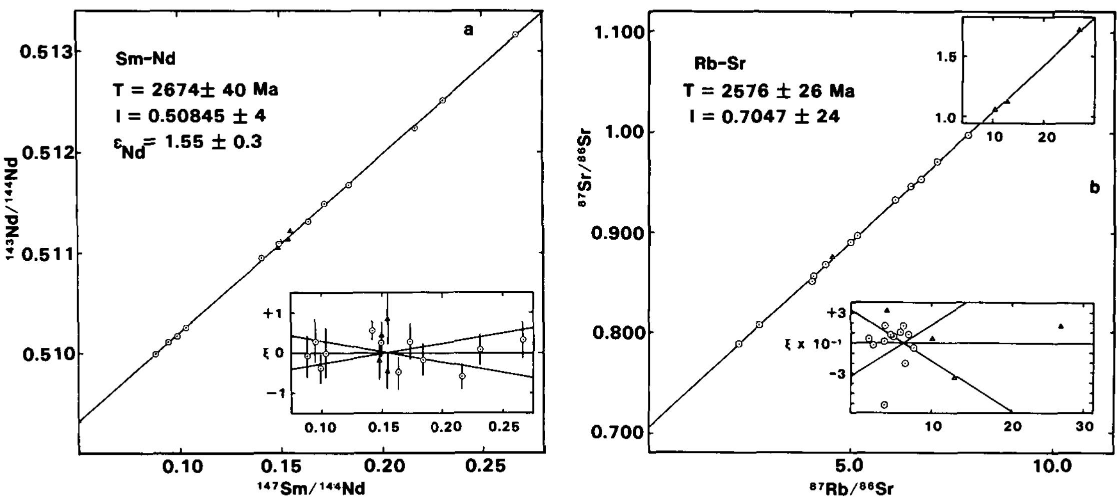


Figure 3. a: Sm-Nd evolution diagram for Kidd Creek altered felsic volcanics and stratiform ore. Weakly altered felsic volcanics are shown for comparison; they were not included in isochron calculations. Altered felsic volcanics show large spread in $^{147}Sm/^{144}Nd$ ratios as result of REE mobility associated with ore deposition. Inset shows deviations in parts per 10^4 of samples from model 4 isochron. b: Rb-Sr evolution diagram for same samples. Weakly altered felsic volcanics were included in calculations. Inset shows deviations in parts per 10^3 of samples from model 3 isochron. Observed scatter is most likely a result of multiple and possibly heterogeneous isotopic resetting subsequent to ore deposition. All isochron parameters were calculated by using modified version of McIntyre et al. (1966); results are given on 95% confidence limit. Triangles = weakly altered felsic volcanics; circles = altered felsic volcanics and stratiform ore.

10^6 tonnes) could be derived from a source volume of ≤ 0.03 km^3, if an average decrease in Nd in AFV from 60 to 19 ppm (Campbell et al., 1984) is used. This volume corresponds to roughly three times the volume of the stringer zone and is clearly smaller than the ~ 100 km^3 source volume for base metals (using a source/ore tonnage ratio of 1 km^3/10^6 tonnes; MacGeehan, 1978). It is easily contained in the upper part of the alteration zone within the footwall volcanics where REE mobility was particularly strong (Campbell et al., 1984). In such a scenario, locally derived Nd would mask any externally derived Nd in the hydrothermal solution, and we would expect to see only the Nd isotopic signature of the footwall volcanics, thought to be represented by WFV.

A possible exception—although at the limit of analytical reproducibility—is sample KC 11 from the stringer zone which has a somewhat lower ϵ_{Nd} (T) of 0.8 (Table 1). It is not clear if KC 11 is anomalous or an expression of isotopic heterogeneity in AFV precursors. If the low ϵ_{Nd} (T) is the result of interaction with the hydrothermal fluid, a fluid source with low, possibly negative ϵ_{Nd} (T) is implied. One possible source having negative ϵ_{Nd} (T) is the granitoid basement underlying the Abitibi volcanics, or sediments derived from it. The influence of the basement on the composition of igneous and sedimentary rocks in the greenstone belt has been demonstrated in several studies (Gariepy et al., 1984; Gariepy and Allegre, 1985; Lajoie and Ludden, 1984), but its contribution to base-metal deposition is unknown.

In general, however, our data suggest buffering of the ^{143}Nd/^{144}Nd ratio in the hydrothermal fluid by local footwall volcanics wall rocks. This implies that at least part of the base metals are also derived from these rocks, an implication consistent with results by other workers (Franklin et al., 1981). At the moment we can only speculate on further base metal sources, but there is some indication (Beaty et al., 1980) that isotopic traces of a deep-seated ore fluid are preserved at deeper levels of the alteration zone. Further work on rocks from that area and other parts of the stratiform orebody will show whether the Nd isotopic tracer is sufficiently sensitive to characterize the origin of this deep-seated fluid and help constrain base-metal sources at Kidd Creek.

CONCLUSIONS

Despite the small difference between zircon and Sm-Nd age, Sm-Nd whole-rock dating appears to have considerable potential in the dating of alteration and mineralization events, provided they were associated with REE mobility efficient enough to produce a suitable spread in Sm/Nd ratios. Although this does not seem to be the case in other, smaller massive sulfide deposits in the Canadian Superior province (Campbell et al., 1984), suitable REE mobility is known from the base metal deposits of New Brunswick, Canada (Graf, 1977). Detailed Sm-Nd isotopic studies could provide valuable constraints on the time of formation of numerous hydrothermal vein deposits, U deposits (Fryer and Taylor, 1984; Maas et al., in prep.), skarn deposits, and other types of mineralization where REE mobility has been demonstrated. The advantage of Sm-Nd dating over Rb-Sr and K-Ar dating is its far greater resistance to isotopic disturbance during subsequent metamorphic overprinting.

The Nd isotopic data indicate that the ^{143}Nd/^{144}Nd ratio of the ore-forming hydrothermal solution at the stringer zone–stratiform ore zone contact was controlled by Nd derived from the footwall volcanics. This suggests that part of the base metals in the ore was derived from the host rhyolitic sequence. Further work is in progress to fully evaluate the potential of the Nd isotopic tracer at Kidd Creek and other massive sulfide deposits.

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