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Closure temperatures of the Sm–Nd system in metamorphic garnets

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ABSTRACT

Garnet–whole rock and garnet–mineral isochrons were determined on granulite facies gneisses and amphibolites from the Archean Pikwitonei Granulite Domain of the Superior Province, and the Proterozoic Central Gneiss Belt and Adirondack Highlands of the Grenville orogen. The Sm–Nd ages obtained from Archean garnets 0.1–0.5 cm in length are 30–110 Ma younger than the U–Pb ages obtained on the same garnets and also younger than the time of the last regional metamorphism, as determined by the growth ages of the youngest metamorphic garnets and zircons. Similarly, the Sm–Nd ages obtained from Proterozoic garnets with a diameter of 0.1–5 cm are younger than the time of the last regional metamorphism and similar or younger than cooling ages obtained on sphenes from the same sample or from the same geologic setting. Only the core of a garnet with a diameter of ca. 30 μ m and without abundant inclusions may record the time of garnet growth. Comparison of the Sm–Nd ages with other geochronologic data and temperature estimates leads to the conclusion that the closure temperature for the Sm–Nd system in garnets analyzed in this study is ca. $600 \pm 30^\circ\text{C}$. Only garnets with radii much larger than 5 cm may record Sm–Nd growth ages in upper amphibolite facies rocks from slowly cooled terranes. Garnets from higher grade terranes yield cooling ages that define the retrograde history of metamorphic terranes.

1. Introduction

Garnet is the single most important mineral for obtaining information on pressures and temperatures in medium to high grade metamorphic rocks [e.g., 1,2]. Garnet is also an important mineral in many isogradic reactions and is one of the most widely used minerals for determining metamorphic P – T paths [e.g., 3–9]. In addition, garnet can be used to obtain geochronological information with the Sm–Nd [e.g., 10–15], U–Pb [16,17] and Rb–Sr [18] decay schemes. Thus, garnet is the only major rock-forming mineral in metamorphic rocks that can yield high precision ages and, at the same time, provide information on P – T conditions during its formation. In this respect dating of garnet has the potential to pro-

vide a better understanding of metamorphic processes than dating of accessory minerals. This information is critical for the construction of quantitative P – T – t paths and to obtain information on rates of metamorphic processes. P – T – t paths are essential for constraining important tectonothermal processes involved in the evolution of metamorphic terranes and thus large parts of the continental crust.

In order to utilize garnet chronometers meaningfully it is necessary to obtain ages which are highly precise and to evaluate whether an age represents the time of mineral growth or some time along the cooling path. As a result of advances in geochronological techniques, including sample preparation and mass spectrometry, it is now possible to obtain high precision Sm–Nd ages that have an uncertainty of less than 1% for most Proterozoic and Archean samples. Such precision is essential for defining events within a single metamorphic episode. Currently the major problem in the interpretation of mineral ages is

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the evaluation of whether these dates represent growth ages or record the time at which the system cooled below a certain closure temperature (T_c) [19]. Therefore, it is necessary to have relevant information on the diffusion behavior of the parent–daughter system. Only if T_c is known would it be possible to use the mineral ages, combined with pressure and temperature estimates, to determine variations in the pressure and temperature conditions of metamorphism as a function of time, thus refining the understanding of P – T – t paths.

2. Sm–Nd systematics of garnets

As a consequence of their identical charge and similar ionic radii, Sm and Nd are not fractionated sufficiently in any rock-forming mineral to obtain an age from a single mineral without significant correction for inherited Nd. The Sm–Nd system can thus be used only if an isochron is constructed from at least two minerals or one mineral and the corresponding whole rock. The precision obtainable for a two-point isochron is, to a large extent, a function of the spread in the Sm/Nd ratio of the two points. Garnet is one of the few rock-forming minerals that strongly prefers the heavy over the light rare earth elements, and it is the only common major rock-forming mineral in metamorphic rocks that discriminates sufficiently between Sm and Nd so that ages with a precision better than 1% can be obtained (at least on Precambrian samples). Such precision is comparable to that obtainable with the K–Ar and U–Pb systems. The use of U–Pb geochronology on garnets is, in general, only successful in evolved igneous, meta-igneous or metasedimentary rocks [16]. Most intermediate to mafic rocks have U concentrations that are too low to yield reliable age information. In addition, datable U-rich minerals, such as zircon or monazite, are extremely rare or absent in mafic and ultramafic rocks. Therefore, Sm–Nd geochronology is often the system chosen for garnet-bearing rocks to obtain a dating when it is difficult to obtain geochronologic information by other methods. Therefore, the Sm–Nd decay scheme has frequently been used to obtain mineral isochrons from garnet-bearing mafic and ultramafic rocks [e.g., 11,12,15].

3. Closure temperatures

Closure temperatures must be known in order to relate the ages obtained from minerals to geologic processes and events. The T_c cannot be calculated from first principles and therefore has to be determined empirically. This can be done through experiments [20–22] or in geologic settings where the thermal history can be evaluated using a variety of minerals with different known T_c 's [e.g., 17,23,24].

The T_c of the parent–daughter system, and ideally its dependence on composition, cooling rate, grain size and geometry, for each phase is requisite knowledge for the interpretation of mineral isochrons. In addition, it is important to evaluate with which other phase(s) the mineral under consideration was in isotopic equilibrium at the time recorded by the isochron. Some of the ambiguities of multi-mineral isochrons can be removed by constructing a two point whole-rock–mineral isochron. The interpretation of such an isochron is based on the assumption that the whole rock represents a closed system and is equivalent to the last assemblage with which the mineral equilibrated.

It is possible to assess the T_c for the Sm–Nd system in garnets by comparing the garnet Sm–Nd age with ages obtained from other minerals with known T_c in the same rock or same geologic unit and the maximum temperature achieved in these rocks, as determined by careful thermometry. Therefore, samples for this study were chosen so that comparisons with the regional metamorphic grade and other thermochronometric information already available (U–Pb data on zircon, sphene, monazite, rutile and allanite; K–Ar and $^{40}\text{Ar}/^{39}\text{Ar}$ data on hornblende, phlogopite, muscovite, biotite and Kfeldspar) would allow estimates of T_c and/or growth temperatures of the Sm–Nd systems in garnets of different compositions.

Humphries and Cliff [25] concluded that the T_c for the Sm–Nd system in garnets is in the range 500–700°C; based on the extrapolation of high-temperature experimental diffusion data by Harrison and Wood [26]. However, due to the design and the high temperatures of the experiments, the diffusion data derived is questionable [27]. In a recent study on coronitic anorthosite granulites from Norway, Cohen et al. [14] suggested that

garnets preserve their Sm–Nd systematics up to 900°C. This high temperature is consistent with the proposed T_c of > 850°C for the system garnet–clinopyroxene from an eclogite xenolith studied in detail by Jagoutz [14]. However, in both cases no other geochronologic information from systems with known diffusion behavior was available that would allow an assessment of whether the Sm–Nd system records the time of garnet growth or some later date when the garnets closed to diffusion.

4. Sampling

The garnets selected for this study are from the Archean Pikwitonei Granulite Domain in Manitoba, Canada [16,28] and the Proterozoic Grenville orogen in Ontario, Canada and New

York, USA, [e.g. 29,30]. The metamorphic history (P – T – t path) for the Pikwitonei Granulite Domain was studied using geothermobarometry [28] and geochronology on zircon, garnet, rutile and sphene [16,17,31]. Mineral ages on zircon, garnet, sphene, monazite, rutile, hornblende and biotite are available for the Adirondacks [e.g., 32–34]. For the Central Gneiss Belt mineral ages were determined on zircon, baddeleyite, monazite, sphene, hornblende and biotite [e.g., 30,35–38]. The conditions for peak metamorphism of the Grenville orogen are summarized by Bohlen et al. [7] for the Adirondacks and by Anovitz and Essene [39] for the Grenville orogen in Ontario. The available geochronological data provide a detailed picture of the T – t paths above 400°C for all three areas from which samples were chosen for this study. Thus, the critical information

TABLE 1

Compilation of radiometric ages (in Ma)

Sample	Sm–Nd age	Other ages	Mineral	System	Age	References
Pikwitonei Granulite Domain						
<i>Cauchon Lake</i>						
217	2576 ± 5	same sample	garnet	U–Pb	2687 ± 1	16
			rutile	U–Pb	2430 ± 2	17
64	2605 ± 9	same sample	garnet	U–Pb	2637 ± 5	16
		same area	zircon	U–Pb	2695–2598	31
			garnet	U–Pb	2984–2591	16
			rutile	U–Pb	2430	17
Grenville Orogen						
<i>Central Gneiss Belt</i>						
CHF2	1019 ± 3	same sample	sphene	U–Pb	1039 ± 2	38
			hornblende	$^{40}\text{Ar}/^{39}\text{Ar}$	1006 ± 4	30
		same area	zircon	U–Pb	1170, 1060	36, 37
			baddeleyite	U–Pb	1170, 1060	36, 37
			monazite	U–Pb	1100, 1074	38
			sphene	U–Pb	1075	38
			hornblende	$^{40}\text{Ar}/^{39}\text{Ar}$	1005–930	30
			biotite	$^{40}\text{Ar}/^{39}\text{Ar}$	918–869	30
			muscovite	$^{40}\text{Ar}/^{39}\text{Ar}$	870	30
<i>Adirondacks (Gore Mountain)</i>						
CCL	1051 ± 4					
GM (rim)	1029 ± 3					
GM (core)	1018 ± 7					
		same area	zircon	U–Pb	1156, 1150	33
			garnet	U–Pb	1154, 1064	34
			monazite	U–Pb	1033	34
			sphene	U–Pb	1033–991	34
			rutile	U–Pb	911, 885	17
			hornblende	$^{40}\text{Ar}/^{39}\text{Ar}$	950–900	32
			biotite	$^{40}\text{Ar}/^{39}\text{Ar}$	853–810	32

needed for evaluation of the T_c for the Sm–Nd system in garnets is available.

4.1. *Pikwitonei Granulite Domain*

4.1.1. *Cauchon Lake area*

The zircons and garnets in this Archean high grade terrane yielded U–Pb ages that indicate that this terrane had undergone three different metamorphic episodes at about 2740 Ma, 2700–2687 Ma and 2660–2640 Ma [16,31]. The last metamorphism reached peak temperatures of 750°C and pressures of ca. 7 kbar. Pegmatites and minimum melt granites intruded at ca. 2600–2590 Ma, indicating that the area had reached < 650°C at this time [28]. Subsequently, the terrane cooled further and reached ca. 430°C, the T_c for the U–Pb system in rutile [17,28] at 2430 Ma (Table 1). In this study the following samples from the Pikwitonei Granulite Domain were used:

217: Garnet–biotite–plagioclase–K-feldspar–quartz–sillimanite–cordierite–ilmenite–spinel–rutile–graphite–monazite–zircon. The garnets in this sample 0.1–0.5 cm in length were dated by the U–Pb technique and yielded an age of 2687 ± 1 Ma [16]. The rock was overprinted by a subsequent metamorphic episode that reached ca. 750°C at 2640 Ma. Rutile from this sample yielded a U–Pb age of 2430 Ma [17].

64: K-feldspar–quartz–garnet. The garnets 0.1–0.3 cm in length yielded a K-feldspar–garnet Pb–Pb age of 2637 ± 5 Ma [16]. This age is consistent with other garnet and U–Pb zircon ages from this area [16,31] and dates garnet growth during the last regional metamorphic episode.

4.2. *Grenville orogen*

4.2.1. *Central Gneiss Belt*

From the Grenville orogen the following amphibolite samples were selected:

CHF2: Hornblende–plagioclase–K-feldspar–biotite–garnet–sphene. The garnets in this amphibolite had a diameter of 0.1 to 0.2 cm. A U–Pb sphene age of 1039 ± 2 Ma was obtained for this sample. Other sphenes and monazites from this part of the Grenville orogen yielded ages from 1100 to 1074 Ma [38]. The $^{40}\text{Ar}/^{39}\text{Ar}$ system yielded an age of 1006 ± 4 Ma for hornblende from the same sample and ages ranging

from 1005 to 930 Ma for other hornblendes from the same area [30].

4.2.2. *Adirondack Highlands*

The following samples were selected from the Adirondack Highlands:

GM, CCL: Garnet–hornblende–plagioclase–hypersthene–biotite–ilmenite–rutile–apatite–pyrrhotite–pyrite–zircon. The samples were chosen because they contained large garnets (up to 50 cm). Most garnets from this locality (Gore Mountain) have only minor amounts of inclusions. From one of these garnets an isochron was obtained using material from the core of the garnet and amphibole from the matrix (sample CCL with a diameter of 30 cm). Some rare samples have a core consisting of garnet–hypersthene–plagioclase–biotite–ilmenite and a rim that has only trace amounts of biotite and rutile inclusions. Such a garnet, with a diameter of 14 cm, was chosen in order to obtain separate Sm–Nd isochrons for the core and the rim assemblage. For the rim isochron hornblende and plagioclase from the matrix immediately adjacent to the garnet rim were taken. Due to the large grain size of the minerals, particularly the garnet, it was not feasible to obtain a representative whole-rock sample for isotope analysis.

No direct age information was available for the Gore Mountain garnet, but U–Pb zircon, garnet, sphene and rutile ages have been determined previously in this area and indicate that this section of the Adirondack Highlands underwent metamorphism at ca. 1150 Ma and at 1100–1050 Ma [33,34]. The last regional metamorphism reached temperatures of ca. 700°C [29] in the area of Gore Mountain. Subsequently, the terrane cooled and reached ca. 430°C at 900 Ma, as indicated by U–Pb ages obtained on rutile [17] (Table 1).

5. Composition of the garnets

The end-member compositions of the garnets are given in Table 2. The garnets from the metapelite (sample 217) and meta-rhyolite (sample 64) are predominantly almandine–pyrope solid solutions with minor spessartine and grossular components. Both samples are homogeneous with respect to their major element composition and

show only a thin rim (ca. 30 mm) with an elevated Fe/Mg ratio [28]. The garnets from the amphibolites are almandine–pyrope–grossular solid solutions with minor spessartine component. All these garnets show significant major element zoning within individual grains and in the garnets from Gore Mountain, even within individual segments used for the isotope study. The garnets from Gore Mountain exhibit pronounced prograde zoning, with a marked increase in pyrope and grossular components from core to rim and a corresponding decrease in the almandine and spessartine components (Table 2).

6. Analytical techniques

The minerals were separated from crushed rocks using heavy liquids and a Frantz Isodynamic separator. High purity separates were subsequently handpicked under a binocular microscope. From the garnet sample GM a slab about 1 cm thick was cut through the center of the crystal. A piece about 2 cm wide was cut through the center of this slab. This piece was cut again into seven segments about 1 cm wide from core to rim. One piece from the core and the rim were crushed and the different phases were picked under the binocular microscope. The minerals were washed in warm, ca. 2 M HCl for several hours to remove surface contamination. Prior to dissolution the garnets were crushed to < 0.5 mm. The whole rock powders were obtained by repeated crushing and splitting from 1 to 5 kg samples. The garnets were digested in a mixture of concentrated HF, HNO₃ and H₂SO₄. The hornblende and plagioclase separates, as well as the whole rock powders were dissolved in a mixture of concentrated HF and HNO₃. All samples

were digested in 3 ml screw-top Teflon PFA® vials inside Krogh-style Teflon® bombs or Parr® bombs at 210°C for up to 1 week. Subsequent to drying down, the samples were redissolved in 6 M HCl. The addition of H₂SO₄ to the garnets at the digestion step has the advantage that dissolution of the fluorides in HCl can be achieved more readily than in cases where no H₂SO₄ is used. However, if there was still any trace of residue, the clear solution was removed and saved. The residue was treated again in the same manner as the original sample. After complete dissolution was achieved, the solutions were combined and then aliquoted for spiking. One part of the solution was spiked with a mixed ¹⁴⁹Sm–¹⁵⁰Nd tracer and rehomogenized on a hot plate for 1 day. Subsequently, the samples were dried and then redissolved for cation exchange column chemistry. The REE were separated as a group using BioRad AG50W-X8 (200–400 mesh) and Sm and Nd were separated using HDHP–PTFE columns. For analysis Sm and Nd were loaded separately on Ta–Re triple filaments and run as metal. Analyses were performed in the Radiogenic Isotope Geochemistry Laboratory at the University of Michigan using two VG Sector mass spectrometers. All Nd isotope ratios were normalized to ¹⁴⁶Nd/¹⁴⁴Nd = 0.7219. During the course of this study the value obtained for La Jolla Nd-standard was 0.511858 ± 10 (2σ). For all isochron calculations in this paper a minimum uncertainty of ± 0.0020% (2σ_m) was assumed for the measured ¹⁴³Nd/¹⁴⁴Nd ratios, based on the reproducibility of the standard. If the standard error of an analysis was higher than ± 0.0020% (2σ_m), the higher value was used. The uncertainty for the Sm/Nd ratio was taken as 0.15%. The total procedural blank for Nd was < 20 pg. Since ca. 100–200 ng

TABLE 2

End-member composition of garnets

Mineral	Sample		Gore Mountain			CGB
	Pikwitonei		GM1	GM7	CCL	CHF2
	64	217				
Almandine (%)	70	62	54–58	41–45	48–49	57–64
Pyrope (%)	22	34	31–34	38–43	38–40	12–13
Grossular (%)	4	2	9–11	12–17	11	21–29
Spessartine (%)	4	3	2– 2	1	1	2– 3

of Nd were used for an individual isotope analysis the procedural blank was negligible.

7. Results

The Sm and Nd concentrations and the isotopic composition of Nd from the minerals and whole-rock samples measured for this study are given in Table 3. The reproducibility of the $^{147}\text{Sm}/^{144}\text{Nd}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios of the garnets are well outside analytical uncertainty but reproduce well for the plagioclase. Despite this poor reproducibility of the ratios in garnet, the data points lie on the respective isochrons. This indicates that there is substantial zoning in the Sm and Nd concentrations in the garnets and it is essential to obtain concentrations and isotopic ratios from the same homogeneous aliquot. For

this reason all samples used in this study were split after a completely clear solution of the material was obtained.

The two garnet–whole rock isochrons for the samples from the Pikwitonei Granulite Domain yielded ages of 2605 ± 9 Ma (Fig. 1a) and 2576 ± 5 Ma (Fig. 1b). These ages are significantly younger than the time of last metamorphism, which lasted from about 2660–2640 Ma [16,31]. Based on two-feldspar thermometry, combined with U–Pb ages from zircons and garnets, peak temperatures of about 750°C were reached in the Cauchon Lake area during the last peak of regional metamorphism at ca. 2640 Ma. Since the Sm–Nd ages are significantly younger, this temperature is an upper limit for the T_c of the Sm–Nd system in garnet. Comparison of the Sm–Nd with the U–Pb age for sample 217 also indicates that the Sm–Nd

TABLE 3
Analytical results

Sample	Sm (ppm)	Nd (ppm)	$^{147}\text{Sm}/^{144}\text{Nd}$	$^{143}\text{Nd}/^{144}\text{Nd}^a$
Pikwitonei Granulite Domain				
<i>Cauchon Lake</i>				
217 wr ^b	2.521	15.27	0.09975	0.510819 ± 5
217 ga	4.589	3.249	0.8562	0.523669 ± 6
64 wr	1.323	8.421	0.09493	0.510559 ± 5
64 ga/3	6.647	1.921	2.108	0.545211 ± 7
64 ga/2	6.381	1.883	2.064	0.544327 ± 18
Grenville Orogen				
<i>Central Gneiss Belt</i>				
CHF2 wr	10.98	78.69	0.1392	0.512156 ± 5
CHF2 ga/1	4.571	2.744	1.009	0.517989 ± 4
CHF2 ga/2	4.592	2.587	1.075	0.518374 ± 15
CHF2 hbl/1	45.32	161.9	0.1692	0.512380 ± 6
CHF2 hbl/2	46.45	168.2	0.1669	0.512350 ± 5
<i>Adirondack Highlands</i>				
GM1 ga/1	1.066	0.5413	1.193	0.519451 ± 7
GM1 ga/2	1.050	0.4899	1.298	0.520103 ± 6
GM1 ga/3	1.034	0.4758	1.316	0.520268 ± 6
GM1 hyp	4.299	15.65	0.1661	0.512571 ± 12
GM1 plag	0.1620	1.507	0.06498	0.511991 ± 20
GM7 ga/1	0.7166	0.4966	0.8735	0.517379 ± 9
GM7 ga/2	0.8599	0.5650	0.9213	0.517710 ± 19
GM7 plag	0.06461	0.7945	0.04915	0.511829 ± 14
GM8 plag	0.06126	0.7548	0.04906	0.511814 ± 11
GM8 hbl	4.289	16.09	0.1611	0.512565 ± 5
CCL ga	0.5440	0.4652	0.7076	0.516315 ± 8
CCL hbl	2.936	11.81	0.1503	0.512472 ± 5

^a normalized to $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$, errors are $2\sigma_m$.

^b ga = garnet; hbl = hornblende; hyp = hypersthene; plag = plagioclase; wr = whole rock.

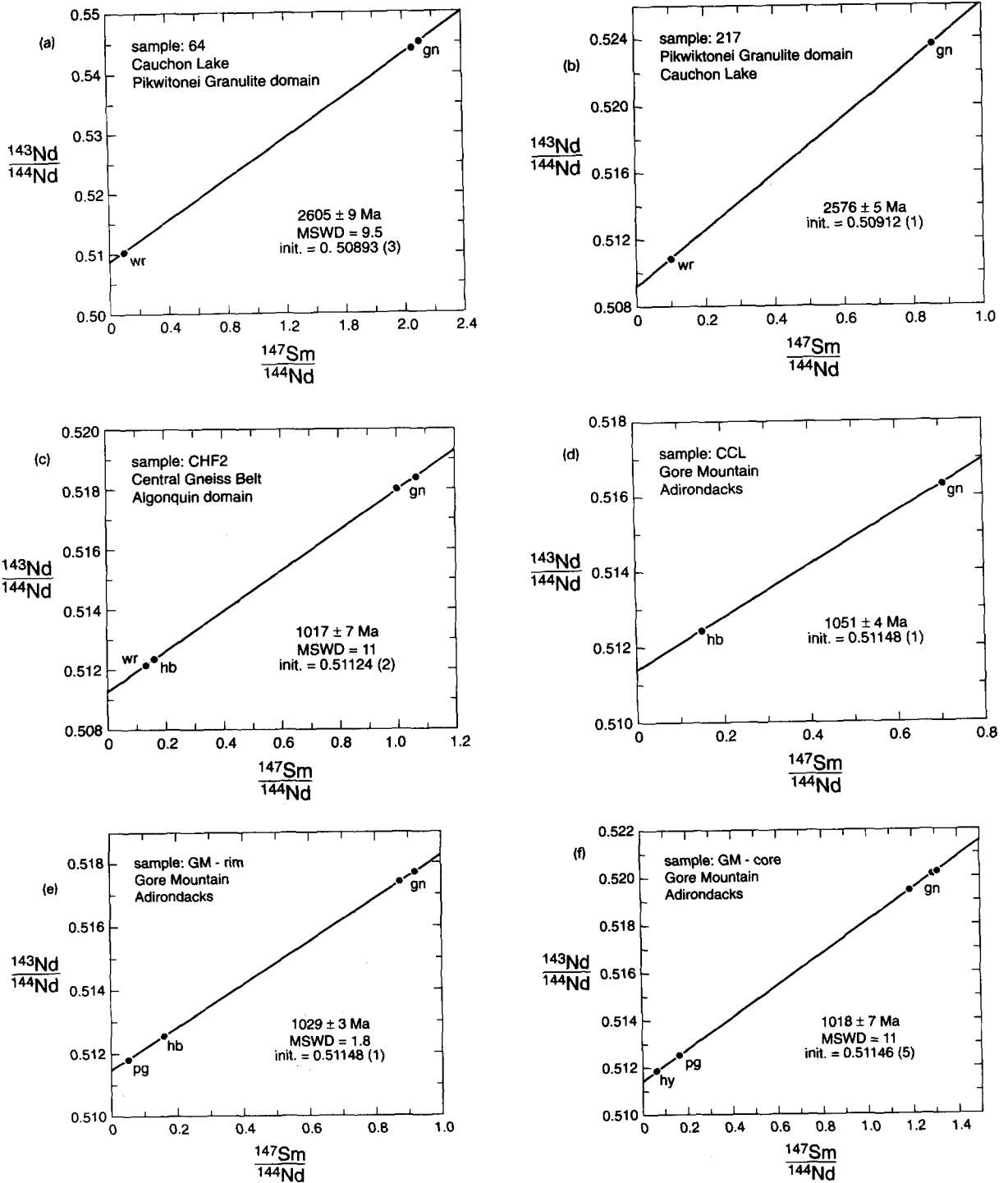


Fig. 1. (a) Sm-Nd isochron diagram with analyses of garnet (gn) separates and whole rock (wr) sample 64 from the Pikwitonei Granulite Domain. (b) Sm-Nd isochron diagram with analysis of gamet separates and whole rock sample 217 from the Pikwitonei Granulite Domain. (c) Sm-Nd isochron diagram with analyses of gamet, hornblende (hbl) separates and whole rock sample CHF2 from Central Gneiss Belt of the Grenville orogen. (d) Sm-Nd isochron diagram with analyses of garnet and hornblende separates from sample CCL from Gore Mountain, Adirondack Highlands. (e) Sm-Nd isochron diagram with analyses of garnet, plagioclase (pg) and hornblende separates from the rim of sample GM from Gore Mountain, Adirondack Highlands. (f) Sm-Nd isochron diagram with analysis of garnet and hypersthene (hy) separates from the core of sample GM from Gore Mountain, Adirondack Highlands. If the plagioclase analysis is included the minerals yield an age of 1011 ± 11 Ma (MSWD = 42.4).

systematics in this garnet were completely reset during the last regional metamorphism whereas the U–Pb systematics survived this high grade metamorphism (Table 1). Comparison of the Sm–Nd ages obtained in this study with the T – t path for these samples (Fig. 2a) [28] indicates that the T_c for the Sm–Nd system in these almandine–py-

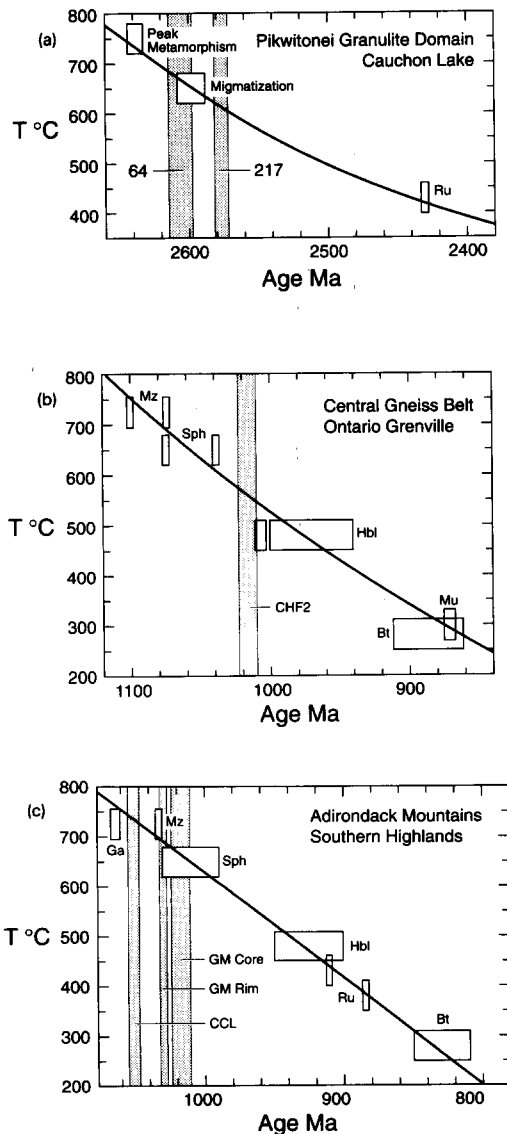


Fig. 2. Temperature–time paths for (a) the Pikwitonei Granulite Domain; (b) the Central Gneiss Belt of the Grenville orogen; and (c) the southern Adirondack Highlands. Shaded bars = the Sm–Nd ages for the different samples; *Bt* = biotite; *Ga* = garnet; *Hbl* = hornblende; *Mu* = muscovite; *Mz* = monazite; *Ru* = rutile; *Sph* = sphene.

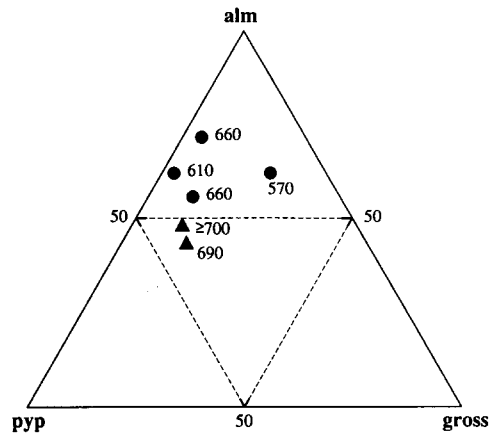


Fig. 3. This ternary diagram shows the average composition of the garnets used in this study (Table 2) combined with the closure temperatures derived from the cooling histories (Fig. 2). Dots = garnets with a diameter of 0.1–0.5 cm; solid triangles = the large garnets with a diameter of 5 cm (sample GM rim) and 30 cm (sample CCL). Since the estimated uncertainties for T_c are at least 30°C, there is no significant correlation between the estimated T_c and garnet composition. The apparently higher T_c obtained for the large garnets is most likely a size, not a composition, effect.

rope dominated garnets from a meta-rhyolite and a meta-pelite is about 600–650°C.

Amphibolite sample CHF2 from the Central Gneiss Belt of the Grenville orogen yields a Sm–Nd hornblende–garnet–whole rock age of 1017 ± 7 Ma (Fig. 1c). This area experienced peak metamorphic temperatures of about 780°C [39]. Sphene from the same rock yielded a concordant U–Pb age of 1039 ± 2 Ma. Assuming that this sphene closed for the U–Pb system at ca. 600–650°C [34], and that the terrane cooled at a rate of 2–4°C/Ma [30] this yields a T_c of 610–520°C for the Sm–Nd system in this garnet (Fig. 2b). This range of T_c values is consistent with the $^{40}\text{Ar}/^{39}\text{Ar}$ hornblende age of 1006 Ma ($T_c = 480^\circ\text{C}$) obtained on the same sample by Cosca et al. [30]. Although the major element composition of this garnet is very different from the garnets from the Pikwitonei domain there does not seem to be a significant difference in the T_c for Ca-poor garnets from the Pikwitonei domain and the Ca-rich garnets from the Central Gneiss Belt (Fig. 3).

The peak temperature for the last regional metamorphism experienced by the garnets from Gore Mountain was about 700°C [29] and was reached at 1100–1050 Ma [34]. The core of the

garnet sample CCL (30 cm long) with a hornblende from the matrix yields an age of 1051 ± 4 Ma (Fig. 1d), which corresponds to the late stages of the regional metamorphism. This age is similar to the Sm–Nd isochron age of 1059 ± 19 Ma obtained on plagioclase, hornblende and garnet from the same outcrop by Basu et al. [40]. However, these authors do not give any information on the size of the garnets nor the location of the material within these garnets used to obtain the isochron. Therefore, a direct comparison with the results presented here is not possible. Since no other age information on the samples from Gore Mountain is available, the age of 1151 Ma can either be interpreted as a growth age or it may date very early cooling. In contrast, the rim and core of sample GM yielded significantly younger ages and therefore must record cooling following this last regional metamorphism. The core yields a garnet–hypersthene age of 1018 ± 7 Ma (Fig. 1e) and, if the plagioclase analysis is included, 1011 ± 11 Ma (MSWD = 42.4). The age for the rim is 1029 ± 3 Ma (Fig. 1f). The slightly younger Sm–Nd age for the core compared to the rim indicates that re-equilibration in the core continued at lower temperatures than in the rim. This surprising observation can be explained by differences in the grain size of garnet. Due to the large amount of hypersthene, plagioclase and biotite inclusions, the size of individual pieces of garnet in the core is ca. 0.5 cm. In contrast, the rim consists of ca. 5 cm wide solid garnet with only minor inclusions. The correlation of grain size in samples GM and CCL with the Sm–Nd ages suggests that equilibration of the Sm–Nd system is probably caused by volume diffusion.

The interpretation of the garnet Sm–Nd ages from sample GM as cooling ages is consistent with the observation that sphene from the nearby Snowy Mountain dome yielded a U–Pb age of 1033 Ma [34]. This age is most likely a cooling age because peak metamorphism reached at least 700°C in this area [29], well above the T_c of 600–650°C characteristic for sphene [34].

8. Discussion

The T_c proposed in this study for the Sm–Nd system in garnet is in the range suggested by Humphries and Cliff [25] but significantly lower

than that proposed by Cohen et al. [14] and Jagoutz [15]. In order to evaluate whether the T_c derived in this study is consistent with other data, Sm–Nd ages of garnets from other studies have to be considered. For this evaluation only the Sm–Nd ages of garnets for which other reliable age constraints and temperature information on the same samples, or samples from the same general area, are available can be used.

Ashwal and Wooden [41] obtained two isochrons for a garnet-bearing mafic gabbro dike and a sample from the layered ultramafic sequence in the Mt. Marcy anorthosite massif in the central Adirondacks, which is located to the north of Gore Mountain. The ages of 995 ± 19 Ma and 973 ± 19 Ma are based on mineral isochrons that include a whole rock analysis. Basu et al. [40] used garnet, wollastonite and diopside (their sample GWD1) from the Lewis Mine (Central Adirondacks) to obtain a Sm–Nd isochron with an age of 1010 ± 10 Ma. The ages obtained are similar or younger than the U–Pb sphene ages of 1033–991 Ma from this part of the Adirondacks [34]. This relationship supports a T_c for the Sm–Nd system in garnet that is similar to or slightly lower than T_c for the U–Pb system in sphene. In contrast, a Sm–Nd garnet–plagioclase–whole rock isochron determined by Basu and Pettingill [42] for an anorthositic sample from the Snowy Mountain dome in the central Adirondacks yielded an age of 1095 ± 7 Ma. This age indicates that the Sm–Nd system in this sample survived a later granulite facies metamorphism that reached temperatures of up to 700°C [29]. This is the only sample found that seems to show evidence of a T_c in excess of 700°C for garnets with a grain size of < 0.5 cm.

In granulites from southern Calabria (Italy) Schenk [43] obtained a Sm–Nd garnet age that is 75 Myr younger than the U–Pb monazite ages but 35 Myr older than the K–Ar hornblende ages. The T_c for the U–Pb system in monazite is ca. 725°C [45] and T_c for the K–Ar system in slowly cooled hornblende is about 480°C [20]. Assuming a constant cooling rate, the T_c for the Sm–Nd system in this garnet is 560°C. A significant number of Sm–Nd mineral ages have been obtained from crustal eclogites [e.g., 11,44]. However, since no age information on metamorphic minerals with a T_c above 600°C is available for

almost all of these eclogites, these studies cannot be used to constrain T_c for the Sm–Nd system in garnets.

The data presented here, together with the data from studies where temperature and other relevant age information are available, are consistent with a T_c for garnet of approximately 600°C. This value is significantly lower than the T_c proposed by Cohen et al. [14] and Jagoutz [15]. In both of these studies [14,15] no independent age constraints were available for comparison. It was also assumed that the temperature obtained through geothermometers could be correlated with the time given by the Sm–Nd isochron. Since different cations exhibit different diffusion behavior in the same mineral [e.g., 46] the geothermometers are expected to record temperatures that do not necessarily correspond to the time given by the chronometer. In addition, in the studies by Cohen et al. [14] and Jagoutz [15] the metamorphic temperatures were estimated using a garnet–clinopyroxene thermometer and the temperatures obtained with this thermometer may not be reliable [2]. This problem is particularly serious since the clinopyroxenes contain an appreciable amount of Al, which makes it difficult to calculate the activities for the various end-member components unambiguously.

Thin pigeonite lamellae found in some clinopyroxenes from the Norwegian coronites [47], have been used to suggest that the mineral assemblages found in these rocks formed at temperatures in excess of 900°C. The presence of these pigeonite lamellae, however, cannot be used in support of high metamorphic temperatures as such lamellae are most probably metastable features that developed significantly below the stability temperatures of coarse pigeonite [e.g., 48].

The preservation of major and trace element zoning in garnets up to apparently 900°C was used by Cohen et al. [14] as an argument that Sm and Nd should also have preserved their prograde distribution. As shown in this study (Table 3) the Sm/Nd ratios in different aliquots of garnet from the same sample show significant variability that is well outside analytical error. In addition, the garnets from Gore Mountain preserve prograde zoning in the major element compositions (Table 2). Despite this well-preserved zoning, the garnets record cooling ages, and

therefore reached isotopic equilibrium, some time after they grew. This observation supports evidence that isotope heterogeneities can be erased much more easily than concentration gradients [e.g., 49]. For this reason, chemical diffusion data can only be used as an approximation and upper limit for the calculation of T_c for the corresponding isotope systems. Studies in regional metamorphic terranes show that major element zoning in garnet (ca. 0.1–1 cm) is only preserved up to upper amphibolite conditions [50] and there is no evidence that garnets from terranes which experienced temperatures in excess of 700°C preserve significant, prograde, major element zoning. This finding is consistent with recent experimental studies which indicate complete rehomogenization of major elements in garnets at ca. 700°C during a regional metamorphic episode [51]. It is expected that, at about 900°C, even garnets several centimeters in length will have lost their prograde, major element zoning. Therefore, we argue that the temperature estimates for the formation of the Norwegian coronites are too high, as is consequently, the proposed T_c for the Sm–Nd system in these garnets.

Within the compositional range investigated in this study (Table 2; Fig. 3), the T_c for all metamorphic garnets 0.1–0.5 cm in length is ca. 600°C. Comparison of the major element chemistry of the garnets with the corresponding cooling curves indicates a slight increase in the T_c with increasing Mg/Fe. However, since the uncertainties in the T_c of the various minerals used to construct the cooling curves are at least 30°C, the uncertainties in these curves are large. Therefore, the possible correlation of the derived T_c with composition is not considered to be significant. A T_c of ca. 600°C allows one to obtain prograde information on garnets using the Sm–Nd system up to mid-amphibolite facies conditions. In high grade metamorphic terranes Sm–Nd garnet ages obtained on typical grain sizes can yield information only on the cooling history. If it is desired to obtain prograde information on higher grade garnets using the Sm–Nd system it would be necessary to obtain garnets that are several centimeters in diameter.

The T_c for the Sm–Nd system in garnets proposed in this study is consistent with the commonly observed phenomenon that garnets from

upper mantle xenoliths yield ages close to the time of the eruption rather than the age of formation of the garnet [e.g., 10,52–54]. There may be an exception to this if the rock consists only of garnet and clinopyroxene. Since clinopyroxenes have a T_c (at least for Sm) that may be as high as 800°C for slowly cooled rocks [55], the garnets in such bi-mineralic rocks cannot exchange after the pyroxene has closed to diffusion. In these rocks it might be possible to obtain a reliable age for the temperature of equilibration [15]. However, to test this hypothesis it would be necessary to find garnet–clinopyroxene rocks from areas where other temperature and age information is available. Since the concentrations of rare earth elements in pyroxenes are much higher than in garnet, it may be sufficient if only the rims of the pyroxene equilibrate with the garnet and lead to a much lower T_c . Another case where garnets may provide information on high-temperature processes are diamondiferous mantle xenoliths. As shown by Richardson et al. [56], garnets that grew in the mantle can preserve their Sm–Nd systematics if they are included in diamond. However, in this case, diffusion is limited by the diamond and is independent of the behavior of Sm–Nd in garnet.

The results in this study imply that the Sm–Nd systematics in metamorphic garnet record cooling rather than mineral growth in most cases. Only very large and inclusion-free garnets may record prograde information in upper amphibolite facies or higher grade rocks. Nevertheless, this technique can provide important information on the early cooling history of mafic, high grade metamorphic rocks for which it is difficult to obtain age information with any other chronometer. In addition, the technique can be used to obtain prograde information for lower amphibolite facies rocks.

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