Rates of Tectonometamorphic Processes from Rubidium and Strontium Isotopes in Garnet

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Measurement of the radial variation of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in a single crystal from a metamorphic rock can be used to determine the crystal's growth rate. That variation records the accumulation of $^{87}\text{Sr}$ from radioactive decay of $^{87}\text{Rb}$ in the rock matrix from which the crystal grew. This method can be used to study the rates of petrological processes associated with mountain building. It is applied to garnet crystals in rocks from southeast Vermont that were metamorphosed about 380 million years ago. The average growth rate measured for three garnets is 1.4 ± 0.2 millimeters per million years and the average time interval of growth is 10.5 ± 4.2 million years. Garnet and its mineral inclusions show a sequential record of temperature change, strain, and chemical reactions during metamorphism; therefore, the technique offers the potential for determination of the rates of those processes as well. The growth interval and observed amount of rotation recorded by inclusion trails in one garnet indicate that the mean shear strain rate during garnet growth was $2.4 \times 10^{-14}$ per second.

Fundamental to an understanding of metamorphism is knowledge of the rates of concurrent processes affecting the rocks such as heating, increasing in pressure, devolatilization, deformation, and recrystallization. Quantitative measurement of these rates has proved elusive because continued metamorphism acts to overprint or to erase earlier metamorphic phenomena. We have overcome this difficulty by measuring the growth rate of a widespread metamorphic mineral, garnet, that commonly resists overprinting. We determine the growth rate by precisely measuring the radial variation of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio (1) in single crystals of garnet. This variation reflects the rate of accumulation of $^{87}\text{Sr}$ in the rock matrix caused by radioactive decay of $^{87}\text{Rb}$ during the time of growth of the garnet crystal.

We chose garnet because it grows by dehydration reaction during metamorphism in common rocks, because it preferentially incorporates Sr relative to Rb, and because its low catonic diffusivity (2) helps to preserve the isotope record. Garnet also preserves other information important in characterizing metamorphism. For example, there is the possibility of estimating the pressure and temperature history of the rock during garnet growth from mineral inclusions in garnet (3, 4), oxygen-isotope thermometry (5), and chemical zoning profiles (6). Garnet can also record progressive deformation of its surrounding matrix (7, 8) because it is rigid, equant, and commonly inclusion-bearing. Thus measurement of growth rates of metamorphic garnet may provide a direct measure of rates of temperature-pressure change, chemical reaction, dehydration, and deformation during metamorphism.

Determination of the growth interval of a mineral by our method requires that (i) the mineral had a much lower $^{87}\text{Rb}/^{86}\text{Sr}$ ratio than the matrix from which it grew; (ii) changes in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the matrix were due solely to in situ decay of $^{87}\text{Rb}$ in the matrix and were not significantly influenced by infiltrating fluid or exchange with neighboring rock units with contrasting $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{87}\text{Rb}/^{86}\text{Sr}$ ratios; (iii) the local source matrix sampled by the growing mineral was homogeneous with respect to $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{87}\text{Rb}/^{86}\text{Sr}$ ratios during growth; (iv) Sr diffusion in the mineral was sufficiently slow; (v) the crystal grew at a constant rate as it emplaced; and (vi) Sr diffusion in the mineral was sufficiently slow.

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given by:

\[ S_g = \frac{R_g S_m - R_m S_g}{R_g - R_m} \]  

where \( S_{\text{g}} \) and \( S_{\text{m}} \) are the \( 87\text{Sr}/86\text{Sr} \) ratios of garnets (9). Typical \( 87\text{Rb}/86\text{Sr} \) ratios of garnet-bearish schists are between 1 and 100.

We analyzed three garnets (GA, GB, and GD) collected in southeast Vermont near the base of the late Cambrian (?) Ottauquechee Formation on the west side of the Athens dome. These garnets were chosen for their large size, relative paucity of inclusions, and because they preserve a record of deformation related to the Acadian Orogeny (8). Peak metamorphic temperatures in the rocks were about 500°C (staurolite zone). During the orogeny, the rocks were first transported to the west in a series of large nappe (11); they were later arched upward by a number of mantled gneiss domes including the Athens and Chester domes (8).

The garnets are large (3 cm) crystals in a schist containing paragonite, muscovite, chlorite, quartz, and plagioclase. Quartz, ilmenite, minor tourmaline, and small (≤10 mm) clinozoisite inclusions are present in the garnets (12). The garnets have narrow alteration rims of muscovite, paragonite, and chlorite. Electron microprobe traverses of GB and GD indicate that the crystals are normally zoned in MnO, MgO, and FeO and that Mn is not enriched at the rims. There is no significant zoning in CaO in GB and GD except for a small decrease within 1 mm of the garnet edge. Rim samples were taken inward of this zone. In one of the analyzed garnets (GA), the inclusions are arranged (Fig. 2, inset) in a sigmoidal spiral in a cross section. The pattern indicates that the garnet rotated during growth; rotation is inferred to have taken place during nappe formation (10).

### Table 1. Results of Rb and Sr analyses. Reported errors of the measured \( 87\text{Sr}/86\text{Sr} \) ratios are \( 2 \) SD of the mean of 20 to 30 sets of data, each set consisting of ten measurements of the \( 87\text{Sr}/86\text{Sr} \) ratio. The errors of the \( 87\text{Rb}/86\text{Sr} \) ratio of the garnet segments are based on the error of the concentrations derived from the isotopic analyses. The error of the \( 87\text{Rb}/86\text{Sr} \) ratio is a small contribution to the total error of the calculated time intervals (10); \( 87\text{Sr}/86\text{Sr} \) values are calculated ratios at the time of segment formation for matrix (Eq. 2).

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \text{Sr} ) (ppm)</th>
<th>( \text{Rb} ) (ppm)</th>
<th>( 87\text{Sr}/86\text{Sr} )</th>
<th>( 87\text{Rb}/86\text{Sr} )</th>
<th>( 87\text{Sr}/86\text{Sr} )</th>
</tr>
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<tbody>
<tr>
<td>GA-8</td>
<td>15.06</td>
<td>0.406</td>
<td>0.07810 ± 0.0714635 ± 20</td>
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<tr>
<td>GA-6</td>
<td>13.74</td>
<td>0.453</td>
<td>0.0955 ± 0.0714792 ± 22</td>
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<tr>
<td>GA-4</td>
<td>26.56</td>
<td>0.407</td>
<td>0.08403 ± 0.0714585 ± 19</td>
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</tr>
<tr>
<td>GB-7</td>
<td>14.58</td>
<td>0.488</td>
<td>0.0968 ± 0.0714545 ± 26</td>
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<td></td>
</tr>
<tr>
<td>GB-10</td>
<td>14.99</td>
<td>0.524</td>
<td>0.1012 ± 0.0714648 ± 22</td>
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<tr>
<td>GD-6</td>
<td>19.11</td>
<td>0.666</td>
<td>0.1009 ± 0.0714397 ± 25</td>
<td></td>
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<tr>
<td>GD-11</td>
<td>11.53</td>
<td>0.442</td>
<td>0.1110 ± 0.0714593 ± 47</td>
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</tr>
<tr>
<td>Matrix I</td>
<td>246.1</td>
<td>69.47</td>
<td>0.8178 ± 0.718922 ± 22</td>
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<tr>
<td>Matrix II</td>
<td>268.5</td>
<td>96.65</td>
<td>1.0432 ± 0.719498 ± 20</td>
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</table>

### Fig. 1. Hypothetical plot of \( 87\text{Sr}/86\text{Sr} \) ratio versus age for a mineral growing continuously between times \( t_1 \) and \( t_2 \) from a matrix with a much higher \( 87\text{Rb}/86\text{Sr} \) ratio than that of the mineral. Shown are evolution lines for mineral core, mineral rim, and matrix. Slopes of evolution lines are proportional to their \( 87\text{Rb}/86\text{Sr} \) ratios. The \( 87\text{Rb}/86\text{Sr} \) ratio of the matrix and the difference in \( 87\text{Sr}/86\text{Sr} \) ratios of the core and rim determine time interval of growth.

### Fig. 2. Positions of analyzed segments (shaded) and unanalyzed segments for garnets GA, GB, and GD. Segments were approximately 5 mm tall. Inset: sketch, showing S-shaped arrangement of inclusions in garnet GA (S1), indicating about 4 radians rotation during growth; \( S_n \) is the plane of foliation in the matrix.
emplacement (8). A mineral age of 376 ± 5.5 Ma (million years ago) \(^{40}\text{Ar}^{39}\text{Ar}\) total fusion, amphibole) has been obtained from nearby amphibolite (13). Another mineral age of 380 ± 2 Ma \(^{40}\text{Ar}^{39}\text{Ar}\), incremental heating, amphibole) has been obtained from an amphibolite that was collected 50 m from our garnet sample location (14).

A disk was cut and polished through the center of each garnet perpendicular to a rotation axis (where determined) from oriented samples. A diameter-parallel prism was cut from each disk and wire-sawed into 2- to 3-mm-long segments for isotopic analysis (Fig. 2). The data (15) are thus an average for each segment, but because the garnets are large (~3 cm in diameter), the segments are short relative to garnet diameter. Garnets GB and GD were separated by ~3 cm. Sample GA was collected ~1 m distant from GB and GD parallel to the strike. We have analyzed core and rim segments from GB, GD, and GA and an intermediate segment from GA (Fig. 3). We also analyzed portions of matrix associated with GB and GD. Matrix I is a 6-g sample within 5 cm of GB and GD, and matrix II is a 100-g slab taken adjacent to the garnets. No unweathered matrix for GA was available.

The Sr concentrations in the analyzed garnet segments ranged from 11.5 to 26.5 ppm (Table 1); there was no consistent relation to radial position in the garnets. Concentrations of Sr in the matrix were 10 to 20 times as great as those in the garnets; Rb concentrations were up to 200 times as great. Growth of garnet in the schist therefore had little effect on the \(^{87}\text{Sr}^{86}\text{Sr}\) ratio of the matrix, satisfying the fifth condition above. The \(^{87}\text{Rb}^{86}\text{Sr}\) values are ~1, which places the specimens at the low end of the range of time resolution. The \(^{87}\text{Rb}^{86}\text{Sr}\) ratios of the garnet segments are less than 0.1 times that of the matrix fulfilling the first condition.

For each garnet, there was a measurable difference in the \(^{87}\text{Sr}^{86}\text{Sr}\) ratio between core and rim. For GB and GD, the \(^{87}\text{Rb}^{86}\text{Sr}\) ratios of the core and rim segments are nearly equal, whereas for GA, the \(^{87}\text{Rb}^{86}\text{Sr}\) ratios are more variable (Fig. 3). The measured isotopic difference in \(^{87}\text{Sr}^{86}\text{Sr}\) between the core and rim segments is \(1.0 \times 10^{-4} \pm 3 \times 10^{-5}\) for GB and \(2 \times 10^{-4} \pm 5.3 \times 10^{-5}\) for GD. The difference at an age of 380 Ma is \(9.0 \times 10^{-5} \pm 3 \times 10^{-5}\) for GB and \(1.6 \times 10^{-4} \pm 5.3 \times 10^{-5}\) for GD. For sample GA, the \(^{87}\text{Rb}^{86}\text{Sr}\) ratios of the segments are sufficiently different that the measured \(^{87}\text{Sr}^{86}\text{Sr}\) ratios do not increase from core to rim, but the age-corrected (~380 Ma) ratios do.

The calculated growth time intervals between the analyzed segments are 6.0 ± 2.6 m.y. for GB and 10.6 ± 4.1 m.y. for GD, for matrix II (Fig. 4). These time intervals correspond to average growth rates of 1.5 \pm 0.3 mm/m.y. for GB and 1.1 \pm 0.7 mm/m.y. for GD. Assuming constant radial growth rates and using the total radii of the garnets, we obtained total growth times of 10.0 ± 4.3 m.y. for GB and 12.7 ± 4.8 m.y. for GD. Using a model matrix that averages the \(^{87}\text{Rb}^{86}\text{Sr}\) ratios of matrix I and matrix II and setting the \(^{87}\text{Sr}^{86}\text{Sr}\) evolution line such that the age of the GA core is 380 Ma, we calculated that the time interval between GA-8 (core) and GA-4 is 6.6 ± 2.1 m.y. (Fig. 4). This gives an average growth rate of 1.7 ± 0.3 mm/m.y. and, extrapolated to the rim, a total growth time of 8.8 ± 3.6 m.y. The interval between GA-6 and GA-4 is 1.3 ± 2.2 m.y. The data for GA, although consistent with a constant radial growth rate within the uncertainties, hint that the outer portion of the garnet may have had a greater radial growth rate than the inner portion.

The apparent ages of the garnets calculated from segment-matrix pairs vary. The data imply that the garnets decrease in age in the order GD, GB, GA, with little overlap in growth interval (Figs. 4 and 5). The differences in calculated age either could be real or could result if the \(^{87}\text{Sr}^{86}\text{Sr}\) values of the matrix samples do not reflect precisely those from which the garnets actually grew. We prefer the latter interpretation because (i) it seems unlikely, although not inconceivable (16), that garnet crystals GB and GD, of similar diameter and separated by ~6 cm, would have nucleated 10 m.y. apart, and (ii) all of the absolute ages appear low in comparison with the nearby \(^{40}\text{Ar}^{39}\text{Ar}\) ages of 380 Ma, which may record a later stage in metamorphism. Most likely, GB and GD were in isotopic equilibrium with slightly different Sr reservoirs, and the analyzed matrix samples represent neither reservoir perfectly. It is also possible that matrix domains specific to individual garnets underwent differential modifications after garnet growth. The distance between GD and GB approximates the scale of Sr isotopic communication in the matrix during garnet growth. This isotopic variability apparently does not increase with increasing distance between samples because the initial isotopic difference between GB and GD cores (6-cm separation) is as great as that between GB and GA cores (1-m separation). This heterogeneity in the \(^{87}\text{Sr}^{86}\text{Sr}\) ratio may be an inherited variation of \(^{87}\text{Sr}^{86}\text{Sr}\) or \(^{87}\text{Rb}^{86}\text{Sr}\) ratios, or both, from the...
sedimentary protolith.

As discussed above, the three remaining conditions (ii, iii, and iv) must be met for the determined growth intervals to be valid. The small scale of isotopic communication argues that the \(^{87}\text{Sr}/^{86}\text{Sr}\) ratio of the matrix was not significantly influenced by infiltrating fluid, because that would be expected to cause isotopic homogenization on larger scales. The apparent small scale of isotopic communication casts doubt on whether a single garnet crystal, with a diameter of 3 cm, could be expected to sample a homogeneous reservoir during its growth. All the garnets, however, have initial \(^{87}\text{Sr}/^{86}\text{Sr}\) ratios that increase from core to rim and that yield similar growth intervals and rates, suggesting satisfaction of the third requirement (17). Regarding the fourth condition, we estimate that the characteristic diffusive length scale for Sr in garnet for 10 m.y. at 500°C and a diffusivity of 10\(^{-20}\) cm\(^2\)/s (18) is about 3.5 \(\times 10^{-2}\) mm, which is negligible relative to the diameters of the crystals. Diffusive effects would be important for small (millimeter-sized) garnets or garnets that were subjected to higher temperatures for a significant period of time.

The average growth rate of the three garnets (1.4 \(\pm 0.3\) mm/m.y.) compares well with the range 10\(^{3}\) to 1 mm/m.y. in growth rate estimated by Cashman and Ferry (19) for regional metamorphic garnets of south-central Maine using crystal size distributions and assumed reaction kinetics. The estimated total growth time for the small (\(<0.1\) mm) garnets of that study was in the range 100 to 40,000 years, much shorter than that for GA, GB, and GD (average growth time = 10.5 \(\pm 4.2\) m.y.). In addition to the different sizes, the contrasting growth times may also reflect differing thermal histories; the proper conditions for garnet growth persisted for a longer period of time in the Vermont samples.

The average growth time allows calculation of average rates of deformation and heating during the growth of the garnets as the peak temperatures of metamorphism were approached. The spiral ("snowball") inclusion trails in GA indicate that it rotated \(-4\) radians during growth. For a simple shear approximation, the magnitude of the shear strain is twice the rotation angle (7) or \(-8\) over the growth time of the garnet. Growth of GA over an interval of 10.5 \(\pm 4.2\) m.y. leads then to an average shear strain rate of 2.4 \(\pm 0.5\) \(\times 10^{-14}\) s\(^{-1}\). For an estimated shear stress of approximately 3 bars (8), the calculated strain rate corresponds to a viscosity of \(10^{20}\) poise.

For calculation of a heating rate, we estimate that the temperature of garnet nucleation was \(-425\)°C on the basis of saturation compositions of both calcite coexisting with dolomite and muscovite coexisting with paragonite (20) for the rocks at the lowest temperature appearance of garnet in the area. The peak temperature was \(-500\)°C on the basis of the CaAl\(_2\)Si\(_2\)O\(_8\) content of plagioclase feldspar in a nearby sample (7, 21). This interval gives a heating rate of 5 to 10°C/m.y. during garnet growth, consistent with thermal modeling of orogenic belts (22).

Emplacement of the gneiss domes noted above folded the nappes while they were still hot. Sleep (23) used a thermal model for the relaxation of folded isotherms to constrain the duration of doming to \(-1\) m.y. The garnets we analyzed grew during the earlier nappe stage of deformation, whereas other garnets in different structural positions record both nappe- and dome-stage deformations (8). The doming event is recorded only in the outer 1 to 2 mm of these garnets. If a growth rate of 1.5 mm/m.y. also applies to the outer parts of these garnets, it implies that the dome stage deformation occurred on a time scale of \(-1\) m.y., in accord with Sleep's estimate (23). The total growth time of the analyzed garnets, which record nappe-stage deformation, constrains the total time allowed for the entire Acadian orogeny to be at least 10 m.y. This time span is a significant fraction of the \(-30\) m.y. between sedimentation and the end of Acadian deformation (24).

Our results suggest that this method may be generally applicable to rate studies in metamorphic terranes. Possible problems with the method concern the scale of isotopic homogeneity in the rock matrix and the size of the matrix volume sampled; furthermore, the volume sampled by a mineral will change during its growth. If further studies bear out the applicability of the method, it should allow study of the kinetics of mineral growth and the determination of the timing and duration of deformation and heating at different structural levels of orogenic belts.

**Fig. 5.** \(^{87}\text{Sr}/^{86}\text{Sr}\) evolution lines for cores of garnets GB, GD, and GA and, for reference, both matrix I and matrix II. Garnets GB and GD were \(-3\) cm apart, and garnet GA was \(-1\) m distant from the other two specimens.
Purification and Reconstitution of Chloride Channels from Kidney and Trachea

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Chloride channels mediate absorption and secretion of fluid in epithelia, and the regulation of these channels is now known to be defective in cystic fibrosis. Indanol-oxyacetic acid 94 (IAA-94) is a high-affinity ligand for the chloride channel, and an affinity resin based on that structure was developed. Solubilized proteins from kidney and trachea membranes were applied to the affinity matrix, and four proteins with apparent molecular masses of 97, 64, 40, and 27 kilodaltons were eluted from the column by excess IAA-94. A potential-dependent 36Cl⁻ uptake was observed after reconstituting these proteins into liposomes. Three types of chloride channels with single-channel conductances of 26, 100, and 400 picoamperes were observed after fusion of these liposomes with planar lipid bilayers. Similar types of chloride channels have been observed in epithelia.

Chloride channels are present in the plasma membrane of most cells. In epithelia these channels act together with other ion transporters, such as the Na⁺,K⁺,2Cl⁻ cotransporter and the Na⁺ and K⁺-dependent adenosine triphosphatase, to mediate absorption or secretion of NaCl (1). Characterization of the channels has been limited to analysis of electrophysiological properties such as single-channel conductance, voltage dependence, and the effect of second messengers on channel opening. In airway epithelia the opening of a channel with a conductance of 40 to 50 pS and a rectifying current-voltage (I-V) relation was stimulated by the adenosine 3',5'-monophosphate-dependent protein kinase (A-kinase) (2). The inability of A-kinase to stimulate channel opening in excised apical membrane patches of secretory cells is thought to reflect the pathogenetic defect in cystic fibrosis (2). Similar Cl⁻ channels are present in fibroblasts and lymphocytes, and here too their opening is defective in cystic fibrosis (3).

We have developed high-affinity ligands for the Cl⁻ channel by screening inhibitors of 36Cl⁻ transport in bovine kidney cortex microsomes (4). An indanol-oxyacetic acid, IAA-94 (Fig. 1), was the most potent inhibitor with an inhibition constant (Kᵢ) of 1 μM, and [¹H]IAA-94 bound to these microsomes with a dissociation constant (Kₐ) of 0.6 μM. Similar results were seen in apical membranes from bovine trachea. The rank order of potency for inhibition of 36Cl⁻ transport for several inhibitors correlated with that for displacement of [¹H]IAA-94, suggesting that IAA-94 binds to the Cl⁻ channel. We describe here the purification of the solubilized channel by chromatography on an affinity matrix based on the IAA structure. Reconstitution of the purified proteins into planar bilayers revealed the presence of Cl⁻ channels.

To purify Cl⁻ channels from bovine kidney cortex vesicles and from apical membranes of bovine trachea, we first solubilized these preparations in n-octyl glucoside. A final detergent concentration of 1.4% solubilized 60% of the protein and 20% of the [¹H]IAA-94 binding sites (5). The addition of 10% glycerol preserved the number of solubilized binding sites after freezing at −70°C or incubation at 4°C for 24 hours. The concentration of IAA-94 required to displace 50% of the specifically bound [¹H]-labeled ligand (IC₅₀) from the solubilized proteins was 2 μM, similar to the value obtained for intact vesicles. Potential-driven 36Cl⁻ uptake was observed when the solubil...