

the outer ~60 km of the silicates. Even with complete serpentinization of this region, an H₂O abundance consistent with Europa's density implies an outer water/ice layer many tens of kilometres thick.

If solid state convection could occur in the ice shell, heat transport rates would be sufficient to freeze the underlying water¹⁸ rapidly. Using an ice activation energy constant of $E/kT_{\text{melting}} = 26$ rather than the value of 18 used previously⁶, solid state convection could only occur for ice crusts thicker than about 30 km, however. The larger value is favoured by Weertman¹⁹, and is consistent with observations of crater relaxation on icy satellites²⁰. Again taking a thermal conductivity appropriate for solid ice ($3.4 \times 10^5 \text{ erg cm}^{-1} \text{ K}^{-1}$), we expect a thin (<30 km) shell of ice underlain by liquid water to exist at present if the surface heat flow has never been lower than $\sim 20 \text{ erg cm}^{-2} \text{ s}^{-1}$.

These calculations are sensitive to parameter uncertainties, particularly because the heat flux is comparable in magnitude with that required to maintain a liquid layer. Our parameter estimates are consistent with the presence of such a layer. For confirmation we must look to the observational evidence.

The paucity of craters on Europa implies a mean retention time for 10 km craters of only 3×10^7 yr based on an impact flux calculated from the expected collision rate with comet nuclei²¹. Using appropriate relationships for relaxation of topography with temperature dependent viscosity²² and a geothermal gradient given by our calculated heat flow, and making the very conservative assumption that a crater will become 'invisible' once its floor rebounds by a factor of $1/e$, this retention time implies a surface viscosity corresponding to a temperature of ~ 140 K. This value is much higher than the mean solar equilibrium temperature of ~ 92 K, and actually must be higher still to relax crater rims. To allow high near-surface temperatures, even for very high heat flows, an insulating blanket at the surface is required. Fracturing of a thin ice crust over liquid water could provide such a blanket. Water exposed by fracturing would not flood the surface, due to the buoyancy of the crust, but would boil, producing vapour that would condense as frost over a large area. Frosts typically have very low densities and thermal conductivities, and could provide the insulation required. An insulating layer could also result in an average crustal thickness much less than the mean value of ~ 16 km calculated for conduction in solid ice alone.

There is evidence for such a frost layer. First, the photometric function of Europa requires much more homogeneous scattering than produced by ejecta deposits of equal albedo on Ganymede and Callisto⁴. The difference is probably textural, and is consistent with a more tenuous structure than produced by impacts. Second, deposits of sulphur, evidenced by a UV absorption feature³, are only present on the trailing hemisphere. This feature is attributed to S–O bonds, and a sulphur column density of $2 \times 10^{16} \text{ cm}^{-2}$ is inferred. Estimated values for the flux of S ions into Europa's trailing hemisphere predict that this column density would be deposited in only ~ 7 yr. These observations were interpreted to require equilibrium between deposition of S ions and escape of SO₂ molecules by charged particle sputtering, since H₂O escapes more readily than SO₂ (ref. 23). Recent measurements²⁴ have shown that SO₂, which is more volatile than H₂O at thermal energies, is more easily sputtered than H₂O by high-energy particles. As SO₂ also has a lower escape rate, such a model would imply higher abundances on the leading hemisphere where sputtering is much less severe, contrary to observations. Assuming instead that the observed column density is a result of uniform addition of S ions to a surface on which a much larger amount of H₂O is continually deposited, an estimate of the minimum H₂O deposition rate can be obtained. For a UV measurement depth of 5,000 Å, this rate would be $\sim 0.1 \mu\text{m yr}^{-1}$.

The appearance of Europa is consistent with this model. Vapour released from fractures will travel large distances, while particulate matter such as salts or organic material would be preferentially deposited near an open active surface. Such

material could also undergo radiation darkening²⁵, creating a pattern of darker features on a bright surface. Stresses sufficient to fracture the crust could be generated by tidal flexure^{6,26}, or by membrane stresses induced by rotation of the ice shell over Europa's tidal bulge. The crust would in reality be inhomogeneous in thickness, and fractures would form preferentially in thinner regions. Continuing or repeated deformation would cause repetitive activation of pre-existing fractures. If large resurfacing events are frequent on Europa they might be observable as transient increases in the thermal IR flux or as clouds of vapour and condensate visible to the Galileo orbiter.

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Metamorphic fluids in the deep crust: evidence from the Adirondacks

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Unusual mineral assemblages of tremolitic hornblende + diopside + enstatite + quartz have been examined to estimate the temperature (T) and water fugacity ($f_{\text{H}_2\text{O}}$) at the time of the granulite facies metamorphism in the Adirondacks. The pyroxenes are closely represented by the system CaO–MgO–SiO₂ allowing application of experimental data¹ with only small corrections for reduced values of activities. Tremolite equilibria² buffered $\log f_{\text{H}_2\text{O}} = 3.0 \pm 0.1$, equivalent to 0.9 kbar of water pressure ($P_{\text{H}_2\text{O}}$) at 7 kbar, 710 °C. Nearby marbles contain wollastonite + calcite + quartz and buffered $P_{\text{CO}_2} = 1.1$ kbar, consistent with $P_{\text{H}_2\text{O}} \leq 5.9$ kbar. Inferred local gradients in fluid compositions suggest that deep crustal fluid conditions are complex and heterogeneous indicating that fluid movements, whether of mantle³ or deep crustal origin, are channelized rather than pervasive. Thus some granulite facies rocks were wholly or partly closed systems with respect to externally derived fluids permitting localized buffering of fluid compositions. Recognition of restricted fluid-mixing limits theories that call for massive amounts of pervasive fluid flow to facilitate melting, cause metasomatism, or to stabilize granulite facies mineralogy.

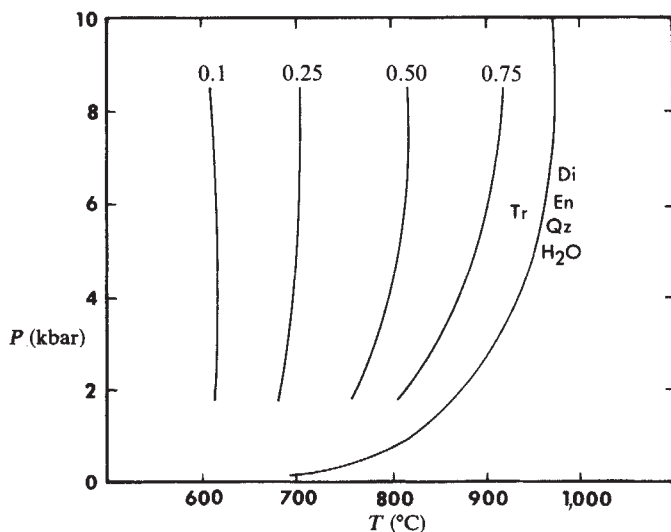


Fig. 1 Dehydration equilibria for synthetic tremolite² for $X_{\text{H}_2\text{O}} = 0.1, 0.25, 0.50, 0.75$ and 1.0.

We have found a series of metasediments containing enstatite and diopside located at Wolf Hill (JM/TRD) and Burnham Mountain (ST14) in the south-east Indian Lake Quadrangle in the Adirondack Mountains, New York, USA. These localities are 2–4 km from the contact of the Oregon Dome, a major anorthosite outlier of the Mt Marcy anorthosite massif⁴. Detailed mapping and structural analysis show the upper contact of the Oregon Dome to dip shallowly beneath these metasediments⁴, suggesting the possibility of early contact metamorphism. While this may have occurred, the equilibria now preserved are consistent with P - T conditions at the peak of regional metamorphism during the 1,000-Myr Grenville orogeny. Any contact aureole that formed during intrusion of the anorthosite has thus been overprinted by the subsequent granulite facies metamorphism. This is supported by textural relationships, showing undeformed, poikiloblastic grains of enstatite and diopside growing across well-defined planes of foliation. This foliation is regional and occurs throughout the nearby anorthosite⁴; which, therefore, predates the assemblages under consideration. This conclusion is consistent with radiometric dates that suggest anorthosite intrusion some 100–200 Myr before regional metamorphism^{5,6}.

The P - T conditions of granulite facies metamorphism in the Adirondacks are well known from several studies. Isotherms have been contoured using temperature estimates from re-integrated feldspar and oxide compositions⁷. These temperatures are in good agreement with those estimated from silicate reactions^{8,9}. Pressures have been estimated from the common occurrences of sillimanite¹⁰ and rare kyanite^{11,12}, from ferrosilite and fayalite-quartz assemblages¹³, from a rock containing akermanite-monticellite-wollastonite⁹, and from various garnet assemblages^{14,15}. Taken together, these data from differing rock types and widely spaced localities are self-consistent and indicate that $T = 710 \pm 30$ °C and $P = 7 \pm 1$ kbar for the peak of regional metamorphism in south-east Indian Lake Quadrangle.

Minerals were analysed by electron microprobe using standard procedures for analysis, data reduction and cation normalization⁸. Representative analyses are given in Table 2. The pyroxenes are remarkably close to the diopside-enstatite join with 1–2% Al_2O_3 as their greatest impurity. Enstatites contain 92–97 mol % MgSiO_3 and diopsides contain 88–94 mol % $\text{CaMgSi}_2\text{O}_6$. Phlogopites are slightly peraluminous with 13.1 wt % Al_2O_3 . Approximate whole-rock chemical analyses (Table 2) were calculated from modes (Table 1), the mineral analyses and estimated densities.

The solvus between enstatite and diopside has been experimentally reversed at various P - T (ref. 1), but none of the experimental data is greatly restrictive below 15 kbar and

Table 1 Mineralogy and modal analysis (1,000 points)

	JM/TRD-2	ST-14-1
Quartz	56.8	3.4
Diopside	11.2	54.5
Enstatite	1.0	21.8
Amphibole	31.0	—
Phlogopite	—	14.1
Pyrrhotite	—	2.6
Apatite	—	0.1
Plagioclase	—	3.5

850 °C. Margules formulations have been fit to the pyroxene data with a maximum discrepancy of 18 °C between model and experiment¹⁶. Application of these equations to the pyroxene pairs, using the Wood-Banno model¹⁷ for distributing minor cations, yields $T = 278$ – 625 °C (Table 3). In this temperature range the solvus is steep and very sensitive to small analytical, experimental or thermodynamic errors. Routine errors in microprobe analysis alone could account for the discrepancy between these values and the inferred metamorphic T suggesting that the pyroxene solvus, as applied here, is not precise enough to be useful for metamorphic thermometry. Alternatively, it could be proposed that these temperatures accurately represent retrograde reequilibration of pyroxenes, but our data do not resolve this.

The calculated rock analyses (Table 2) are unusual with high Mg, $\text{Mg} > \text{Ca}$, low Fe and variable Si. Talc-tremolite-quartz schists near Balmat in the north-west Adirondacks have similar chemistry and are associated with halite and anhydrite-bearing marbles that are clearly metaevaporites¹⁸. The samples of this study may thus represent isochemical metamorphism of evaporites or they may have been metasomatized, possibly by nearby anorthosite.

Many reactions can be written for the dehydration of a complex natural amphibole to a pyroxene-bearing assemblage. The simplest end-member reaction that has been experimentally calibrated² is:



Our sample, JM/TRD, contains this H_2O -buffering assemblage. Figure 1 shows this reaction calculated for various values of $X_{\text{H}_2\text{O}}$. Reaction positions were calculated from the equilibrium point at $P_{\text{H}_2\text{O}} = 2$ kbar, $T = 875$ °C (ref. 2) using the computer program EQUIL⁸. To apply reaction (1) to the assemblage of JM/TRD a correction must be made for the effects of solid solution in both the amphibole and pyroxenes. In the absence of calibrated activity versus composition relations this correction can be approximated using an ideal ionic model^{8,17}. This results in a change of Gibbs energy of reaction (1) of -4.8 to -6.8 kJ due primarily to fluortremolite and tschermakite solid solution in amphibole. The range of energies derives from different amphibole models with variable order-disorder on various cation sites and extends the stability of amphibole 75–100 °C, consistent with experiments on tschermakite¹⁹. At 7 kbar, 710 °C these compositions thus buffer $X_{\text{H}_2\text{O}} = 0.11$ – 0.14 or $\log f_{\text{H}_2\text{O}} = 3.0 \pm 0.1$ (Fig. 1). A larger uncertainty in the application of these experiments arises from results showing that some synthetic tremolites decompose more than 100 °C below natural tremolite, possibly due to crystal defects accounting for up to 8 kJ change in Gibbs energy²⁰. In extreme cases, a correction for the effect of crystal defects in the experimental charge would shift estimated $X_{\text{H}_2\text{O}}$ from 0.11 to 0.05 while high contact metamorphic temperatures of 850 °C would shift estimated $X_{\text{H}_2\text{O}}$ from 0.11 to 0.29. Low $P_{\text{H}_2\text{O}}$ is indicated in any case.

Considerable controversy exists as to the significance of low $P_{\text{H}_2\text{O}}$ values in high grade metamorphic rocks. It has been proposed that low $P_{\text{H}_2\text{O}}$ results from dilution of a fluid phase by deep-seated CO_2 (refs 3, 21) or CH_4 (ref. 22) of either crustal or mantle origin or that alternatively there was no free fluid phase²³. A traditional alternative view regards

Table 2 Electron microprobe analyses of minerals and calculated rock analyses

	JM/TRD-2				ST-14-1			
	Opx	Cpx	Amph	Rock	Opx	Cpx	Phlg	Rock
SiO ₂	58.81	54.55	53.00	80.99	59.97	55.79	42.07	52.19
TiO ₂	<0.05	0.17	0.71	0.27	<0.05	0.12	2.79	0.40
Al ₂ O ₃	1.54	1.99	7.29	2.50	0.87	2.01	13.10	3.58
Fe ₂ O ₃ *	0.00	0.76	0.00	—	0.08	0.00	0.00	—
FeO*	2.63	0.00	0.78	0.39	0.74	0.24	0.35	3.25
MnO	0.18	0.07	<0.05	0.01	0.20	0.12	<0.05	0.11
MgO	36.73	18.84	21.01	10.09	39.54	17.40	27.13	21.05
CaO	0.23	24.91	12.91	4.41	0.17	24.64	<0.05	13.54
Na ₂ O	<0.05	0.21	0.82	0.31	<0.05	0.45	0.23	0.45
K ₂ O	ND	ND	0.75	0.26	ND	ND	10.22	1.25
H ₂ O*	ND	ND	1.85	0.63	ND	ND	3.46	0.41
F	ND	ND	0.69	0.24	ND	ND	1.72	0.20
Cl	ND	ND	<0.05	<0.01	ND	ND	<0.05	<0.01
Total†	100.12	101.50	99.52	100.00	101.57	100.77	100.35	100.00‡
Si	1.996	1.934	7.325	—	1.982	1.997	2.935	—
Al	0.004	0.066	0.675	—	0.018	0.003	1.065	—
Al	0.056	0.017	0.510	—	0.016	0.081	0.012	—
Ti	<0.002	0.005	0.073	—	<0.002	0.003	0.146	—
Fe ³⁺ *	0.000	0.020	0.000	—	0.002	0.000	0.000	—
Fe ²⁺ *	0.074	0.000	0.090	—	0.020	0.007	0.020	—
Mn	0.006	0.002	<0.006	—	0.006	0.003	<0.006	—
Mg	1.858	0.998	4.327	—	1.950	0.928	2.821	—
Ca	0.008	0.946	1.912	—	0.006	0.945	<0.003	—
Na	<0.003	0.014	0.220	—	<0.003	0.031	0.031	—
K	ND	ND	0.132	—	ND	ND	0.909	—
Cl	ND	ND	<0.006	—	ND	ND	<0.003	—
F	ND	ND	0.300	—	ND	ND	0.381	—
OH [†]	—	—	1.700	—	—	—	1.619	—

ND, not determined. * Calculated from normalized formula. † Adjusted for Fe₂O₃, F = 0 and H₂O. ‡ Includes 3.61 SO₃, 0.04 P₂O₅.

Table 3 Calculated activities of MgMgSi₂O₆ and CaMgSi₂O₆ in pyroxenes and calculated equilibrium T[†]

	JM/TRD	ST-14
* $\alpha_{\text{MgMgSi}_2\text{O}_6}^{\text{opx}}$	0.863	0.951
* $\alpha_{\text{CaMgSi}_2\text{O}_6}^{\text{opx}}$	0.007	0.006
* $\alpha_{\text{MgMgSi}_2\text{O}_6}^{\text{cpx}}$	0.037	0.018
* $\alpha_{\text{CaMgSi}_2\text{O}_6}^{\text{cpx}}$	0.907	0.860
† T _A (°C)	451	278
† T _B (°C)	557	625

* From ref. 17.

† Using equations A and B of ref. 16.

low $P_{\text{H}_2\text{O}}$ values as anomalous and assumes that in general $P_{\text{H}_2\text{O}} = P_{\text{lithostatic}}$.

The samples of this study occur in proximity to granulite facies, wollastonite-bearing marbles that buffered metamorphic fluids to low P_{CO_2} . Sample SP202-1 was also collected from Burnham Mountain, 1 km on strike from ST-14 and contains the assemblage wollastonite + calcite + quartz + grossular + sphene + apatite⁸. Grossular (Gr₈₈) + quartz in this sample limits temperature to below 815 °C at 7 kbar (ref. 9), further arguing against high temperature contact metamorphism. The assemblage wollastonite + calcite + quartz buffers P_{CO_2} to 1.1 kbar. Similar low values of P_{CO_2} are inferred for 30 other wollastonite localities that are known in the Adirondacks including the mines near Willsboro, New York that account for most of the world wollastonite production^{8,9,12,24}.

If the fluids of granulite facies metamorphism are pervasive and migrate in sufficient quantity to control buffering reactions^{3,21}, then the fluid compositions inferred in marbles should be similar to those in the nearby two-pyroxene rocks. This

would indicate that both $P_{\text{H}_2\text{O}}$ and P_{CO_2} were low during Adirondack metamorphism requiring large quantities of some other fluid diluent in the lower crust. Alternatively, we believe that $P_{\text{H}_2\text{O}}$ and P_{CO_2} can be highly variable in marbles and sharp gradients in fluid composition can exist⁸. Such a model suggests great complexity in fluid compositions of the deep crust that is not generally recognized. Locally high $P_{\text{H}_2\text{O}}$ and low P_{CO_2} in marbles can stabilize wollastonite while nearby rocks might have low $P_{\text{H}_2\text{O}}$ stabilizing the two-pyroxene assemblages reported here. Recognition of complex fluid conditions would indicate that generalities should be made with caution as to the composition of fluids in the granulite facies. Such fluid movement as exists in the deep crust may largely be channelized and restricted to zones of weakness, structural misfit or permeable lithologies.

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