# Old radiocarbon ages in the southwest Pacific Ocean during the last glacial period and deglaciation

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Marine radiocarbon (<sup>14</sup>C) dates are widely used for dating oceanic events and as tracers of ocean circulation, essential components for understanding ocean-climate interactions. Past ocean ventilation rates have been determined by the difference between radiocarbon ages of deep-water and surface-water reservoirs, but the apparent age of surface waters (currently  $\sim$ 400 years in the tropics and  $\sim$ 1,200 years in Antarctic waters<sup>1</sup>) might not be constant through time<sup>2</sup>, as has been assumed in radiocarbon chronologies<sup>3,4</sup> and palaeoclimate studies<sup>5</sup>. Here we present independent estimates of surface-water and deep-water reservoir ages in the New Zealand region since the last glacial period, using volcanic ejecta (tephras) deposited in both marine and terrestrial sediments as stratigraphic markers. Compared to present-day values, surface-reservoir ages from 11,900<sup>14</sup>C years ago were twice as large (800 years) and during glacial times were five times as large (2,000 years), contradicting the assumption of constant surface age. Furthermore, the ages of glacial deepwater reservoirs were much older (3,000-5,000 years). The increase in surface-to-deep water age differences in the glacial Southern Ocean suggests that there was decreased ocean ventilation during this period.

Surface ocean reservoir ages reflect a balance between equilibration with the atmosphere, radioactive decay, and the input of deep waters to the mixed layer of the ocean<sup>6</sup>. Whereas subtropical surface waters remain at the surface long enough to be in steady state with atmosphere<sup>6</sup>, thermohaline circulation removes surface water in the North Atlantic, isolating it from contact with the atmosphere. This causes its <sup>14</sup>C age to increase until the water outcrops in the Southern Ocean. There it partially re-equilibrates with the atmosphere before leaving the surface again; it forms Antarctic deep-water masses flowing northward, with initial radiocarbon ages of  $\sim$ 700 years for intermediate waters and  $\sim$ 1,400 years for bottom waters<sup>7</sup>. Subsurface return flow from the north in the Pacific causes the oldest reservoir ages of  $\sim$ 1,500–2,000 years to occur at mid-depths<sup>7</sup>. Past changes in atmospheric <sup>14</sup>C levels that are not caused by changes in cosmogenic production are assumed to be owing to changes in ocean-atmosphere partitioning; these may be caused by changes in vertical mixing, ventilation of thermocline and deep waters, and changes in residence times related to changes in thermohaline circulation associated with colder, glacial-type climate conditions.

Unlike benthic-planktonic <sup>14</sup>C difference estimates of apparent ventilation ages<sup>5,8</sup>, our approach to determining past reservoir ages uses tephras as stratigraphic marker beds to reference surface- and deep-water <sup>14</sup>C ages directly to the atmosphere using terrestrial <sup>14</sup>C (ref. 2). Volcanic eruptions on the North Island of New Zealand have produced tephras deposited on land with datable organic

matter incorporated within or bracketing the tephras9 and in adjacent ocean basins associated with planktonic and benthic foraminifera<sup>9,10</sup> (Fig. 1). Marine ages were determined for this study by accelerator mass spectrometry radiocarbon (AMS <sup>14</sup>C) dating of foraminifera directly above and below the ashes in marine cores from the Bay of Plenty and the Chatham Rise (Fig. 1 and Table 1). The tephras in this study form layers 1–7 cm thick of nearly pure ash grains and contain features which indicate minimal bioturbation: sharp basal contacts below layers of nearly 100% ash, fining upwards of grains, and/or shower-bedding features characteristic of airfall deposition<sup>11</sup>. The existence of pure tephra layers above a sharp contact indicates that the ash falls capped the sediments and although the sediments above and below the layers are clearly bioturbated, these layers remained separated by the ash. Differences between <sup>14</sup>C dates above and below the tephras confirm minimal mixing through the ash layers (Table 1). We use previously established mean terrestrial <sup>14</sup>C dates as reference ages for the tephras<sup>9</sup>. The surface-reservoir ages are the difference between planktonic foraminiferal and terrestrial <sup>14</sup>C ages, and the deep-water ages (or apparent ventilation ages) are the differences between benthic foraminiferal and terrestrial ages.

During the Holocene (Whakatane, 4,830<sup>14</sup>C yr BP; Mamaku, 7,250<sup>14</sup>C yr BP; and Rotoma, 8,530<sup>14</sup>C yr BP tephras), surface-reservoir ages in the subtropical Bay of Plenty are indistinguishable from pre-bomb values of 400–470 years (ref. 12; Tables 2 and 3; Fig. 2). At 4,830<sup>14</sup>C yr BP the apparent ventilation age at 1,675 m was 1,520 years. This is similar to modern deep-water radiocarbon





Table 1 Ash lay	er dates				
Depth (cm)	Tephra layer	Sample	Lab code	<sup>14</sup> C age	<sup>14</sup> C error
H209 37° 09.5' S		······		<u> </u>	
57-58		GL inflata	CAMS 4172	4 960	
57–58		Gl. inflata	CAMS 41743	4,880	40
58-60	Whakatane (4,830 ± 20)				
60-61		Gl. inflata	CAMS 41744	5,520	50
70,00		Gi. Initiata	CAMO 47197	10,000	40
79-80 80-81		GI. Inflata GI. inflata	CAMS 47 187 CAMS 41746	13,280	60 50
81-82	Rotoma (8,530 ± 10)*	Ci. Inidia	07.000 417 40	10,100	00
171-172		Gl. inflata	CAMS 40462	12,730	50
171-172		GI. inflata	CAMS 40461	12,650	70
171-172	Multiples (11.050 ± 00)	Mixed benthics	CAMS 41747	13,710	60
172-176	Waiohau (11,850 $\pm$ 60)	GL inflata	CAMS 10163	12.640	50
176–177		Gl. inflata	CAMS 40464	12,720	50
176–177		Mixed benthics	CAMS 41748	13,280	50
H211 37° 18.2' S	177°21.5′ E 1,500 m				
		Gl. inflata	CAMS 39603	12,130	50
90-95	Waiohau (11,850 ± 60)			,	
95-96		Gl. inflata	NZA 6668	12,750	160
95-96 95-96		GL inflata	CAMS 39604 CAMS 39605	12,650	70 50
158_161		GL inflata	CAMS 41749	14,800	50
158-161		Gl. inflata	CAMS 41749 CAMS 41750	14,720	50
159-161		GI. inflata	NZA 6665	14,740	130
167-170	Rerewhakaaitu (14,700 $\pm$ 110)			15.000	(50
172-173		GI. inflata	NZA 6666	15,330	150
H213 37° 02.5' S	177°10.5′E2,065m				
60-61		Gl. inflata	CAMS 41751	3,650†	40
61-62	Whakatane (4,830 $\pm$ 20)	CL inflata	CAMS 41752	5 100	50
62-63		Gl. inflata	CAMS 41752	5,120	40
62-63		Mixed benthics	CAMS 52010	6,350	80
240-243		Mixed benthics	CAMS 41779	26,500	160
241-242		Gl. inflata	CAMS 41756	24,240	130
241-242		Gl. inflata	CAMS 41757	24,530	120
242-243	Kawakawa (22 590 + 230)	GI. INIIAIA	CAIMS 41754	24,370	150
248-249	1 awarawa (22,000 = 200)	Gl. inflata	CAMS 41755	24,770	150
248–251		Mixed benthics	CAMS 41778	25,610	140
H214 36° 55.5' S	177°26.5′ E 2,045 m				
75–77		Gl. inflata	NZA 6654	7,640	90
76-77		Gl. inflata	CAMS 39597	7,540	40
77-78	Mamaku (7,250 ± 20)	OL inflata	CAME 20508	7.610	40
78-79		Gl. inflata	CAMS 39590	7,010	40
94_96		GL inflata	CAMS 39600	8 800	30
96-97	Rotoma (8,530 ± 10)	Ci. Inidia		0,000	00
97–98		Gl. inflata	CAMS 39602	8,960	40
97–98		Gl. inflata	CAMS 39601	9,130	40
151-153		Gl. inflata	NZA 6655	12,820	110
153-159	Waiohau (11,850 $\pm$ 60)	GL inflata	NZA 6662	12 010	140
160-161		Gl. inflata	CAMS 40465	12,940	70
202-203		GL inflata	CAMS 40466	14 980	70
203-205		Gl. inflata	NZA 6663	14,980	120
205-206	Rerewhakaaitu (14,700 ± 110)				
206-208		Gl. inflata	NZA 6664	15,350	160
208-209		Gl. inflata	CAMS 40467 CAMS 40468	14,910	70
1 1938 45° 04 5' S	179°29 9′ F 2 700 m			,	
107 101	Kowakowa (22 500 ± 220)				
131-133	nawanawa (22,090 ± 200)	GL inflata	CAMS 41778	24.390	120
130-134		G. bulloides	CAMS 50998	23,880	220
130-134		Mixed benthics	CAMS 50996	27,410	220
130–134		Mixed benthics	CAMS 50997	27,820	200
U939 44° 29.7' S	179°30' E 1,300 m				
76-83	Kawakawa (22,590 ± 230)				
84.5-85		Gl. inflata 110 µg	CAMS 40472	24,810	510
84.5-85		Uvigerina 170 u.a	CAMS 40473	24,070	380
Disal to al			Devel Directored and All Cl	Here Dies Die 11 1 1	-14-0
Hanktonic and ben	unic ioraminiteral Alvis "C results. Samples were taken	urectly above and below tephras in the	Bay of Pienty and south of the Cha	unam Hise. Planktonic foramin	illeral Cages were

generated on monospecific samples of Globourotalia inflata and in one sample on Globigerina bulloides (U939 84.5–85 cm; CAMS 40473). Both species are known to calcity in surface waters<sup>26</sup>. Benthic foraminiferal <sup>14</sup>C ages are based on mixed species. All samples were taken within 3 cm of the tephra, except above the Rerewhakaaitu in H211. Dates are conventional <sup>14</sup>C ages based on a half life of 5,568 ± 30 years (ref. 1). Analyses were made at the Rafter Radiocarbon Laboratory, New Zealand (NZA) and the Centre for Accelerator Mass Spectrometry (CAMS), Lawrence Livermore National Laboratory, California, USA. Sub-optimal target weights are given in micrograms of carbon where necessary. Duplicates generally agree within the reported errors. There is no significant difference between the dates from Rafter Radiocarbon Laboratory and those from Lawrence Livermore National Laboratory, although Rafter errors are larger. Tephra identifications were based on relative position in the core, identification of the ferromagnesian assemblage and the chemical variations within the titanomagnetites.<sup>11</sup>, with the exception of the tephras at 90–95 cm in core H211 was only tentatively identified.<sup>11</sup> as Rotoma. A re-identification of this ash as Waiohau (also from the Okataina volcanic centre and of similar mineralogy to the Rotoma<sup>9</sup>) is based on a re-examination of the ferromagnesian assemblage and is in agreement with its stratigraphic position in the core. Similarly, the ash at 77–78 cm in H214 is re-identified as the Mamaku. It was originally identified as the Whakatane<sup>11</sup>. A re-examination of the ferromagnesian assemblage indicates it is the Manaku (of similar interaction of the Whakatane, and from the Okatane acentre), which is consistent with its stratigraphic position in the core. The Rotoma is identified as the tephra lying below this ash in this core<sup>9</sup> and is known to be present in this locality<sup>30</sup>. If these two ashes are excluded from our discussion, it does not affect the reservoir calculations for any time slice. \* Dates on this tephra are out of sequence indicating disturbance in this core. These ages are not included in averages for this study. † This data is younger than the terrestrial <sup>14</sup>C age for the tephra indicating disturbance above the tephra. This data is not included in the average for this tephra.

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ages (Table 3), indicating Holocene ocean circulation conditions similar to today. During the early deglaciation, at 14,700<sup>14</sup>C yr BP (Rerewhakaaitu tephra) the surface-reservoir age was 310 years, similar to modern values, within errors. Lower atmospheric CO<sub>2</sub> in the glaciation and early deglaciation would have decreased the <sup>14</sup>C of the ocean at this time<sup>6</sup>; thus the low reservoir age at 14,700<sup>14</sup>C yr BP indicates that the return to modern circulation by this time was strong enough to more than counter this effect.

At about 11,850 <sup>14</sup>C yr BP (Waiohau tephra) we estimate a surfacereservoir age of 800 years (twice the modern value), a ventilation age at 1,675 m of 1,650 years (similar to the modern value), and an equivalent surface-to-deep-water age of 850 years (about 500 years younger than modern; Table 3, Fig. 3b). These results are consistent with previous benthic-planktonic foraminiferal <sup>14</sup>C differences indicating reduced benthic-planktonic ages relative to present at around 12,000 <sup>14</sup>C yr BP (refs 5 and 13).

Our data from the Waiohau indicates that surface-reservoir ages in the subtropical Pacific were older at the time of the Antarctic Cold Reversal but that deep-reservoir ages were unchanged, indicating that shallow, not deep, circulation was affected. Ocean circulation changes associated with brief climate variations such as the Younger Dryas can alter atmospheric <sup>14</sup>C levels<sup>2-4,14</sup>. At about 11,700 <sup>14</sup>C yr BP a smaller, but similar change in atmospheric <sup>14</sup>C levels has been determined<sup>4</sup>. This is just after melt-water peak 1A and the reinitiation of NADW flux<sup>15</sup>, coincident with both the Antarctic Cold Reversal<sup>4,16,17</sup> and the deposition of the Waiohau tephra. If the resulting increased ages of the subtropical surface water were not the result of atmospheric <sup>14</sup>C variations as a consequence of the deglaciation process<sup>4</sup> they may have been associated with changes in subantarctic shallow-watermass<sup>18</sup> production<sup>14</sup>. Older surfacereservoir ages could have been translated to South Pacific subtropical thermocline waters as a transient effect caused by increased leakage of subantarctic surface waters across the subtropical convergence.

During the last glaciation (Kawakawa tephra 22,590<sup>14</sup>C yr BP)<sup>9</sup> the

surface-reservoir age in the Bay of Plenty was 1,990 years. The Kawakawa tephra is also found south of the Chatham Rise<sup>10</sup> (Fig. 1), allowing us to estimate the glacial reservoir ages of subpolar waters. Subpolar surface ages during the glaciation were 1,970 years, the same as regional subtropical waters. Modern subtropical and subpolar surface ages differ by 100–200 years (ref. 12). Thus, subtropical and subpolar surface ages were 4–5 times modern values (Table 1). Such large increases in subtropical surface-reservoir ages contradict box model calculations which indicate that subtropical surface-reservoir ages are insensitive to ocean circulation changes<sup>6,8</sup>.

The Kawakawa tephra was associated with sufficient benthic foraminifera to obtain apparent ventilation ages from three cores at 1,300, 2,065 and 2,700 m water depth. Deep-reservoir ages increase with increasing depth yielding apparent ventilation ages of 3,000, 3,470 and 5,040 respectively, which are 1,500–3,000 years greater than today (Table 3; Fig. 3c). In contrast, owing to the old surface-reservoir ages, the benthic-planktonic (surface-to-deepwater) age of 1,030 in our shallowest core is similar to today (Table 3), and consistent with previous benthic-planktonic age studies, indicating that glacial radiocarbon age of Pacific deep waters were only 100–500 years greater than today<sup>5,8,13</sup>. Significantly, this indicates that during the glaciation, although the surface-todeep-water age contrast changed minimally, deep-water ages were 2-3 times larger than modern. Additionally, ventilation ages increase nearly twofold between 2,000 and 2,700 m (Fig. 3c).

The large ventilation ages and <sup>14</sup>C vertical structure during the glaciation bear directly on conflicting reconstructions of Southern Ocean deep-water palaeocirculation. Benthic foraminiferal  $\delta^{13}$ C (refs 15,19,20) and carbonate dissolution<sup>21</sup> indicate a gradient between 'older' poorly ventilated deep waters and better ventilated 'younger' intermediate waters. Authigenic uranium also suggests more poorly ventilated Southern Ocean deep waters<sup>22</sup>. In contrast, trace-metal indices in benthic foraminifera<sup>23,24</sup> and U-series tracers<sup>25</sup> suggest similar rates of ventilation for the Holocene and glacial

Table 2 Modern samples	le 2 Modern samples					
Location	Collection date	Sample	Lab Code	<sup>14</sup> C age	Error	
Waitangi Beach, Chatham Is.	1933	Gastropod 1*	CAMS 40758	690	40	
Waitangi Beach, Chatham Is.	1933	Gastropod 2	CAMS 40759	540	40	
Waitangi Beach, Chatham Is.	1933	Gastropod 3A†	CAMS 40760	550	40	
Waitangi Beach, Chatham Is.	1933	Gastropod 3B†	CAMS 40761	560	50	
Waitangi Beach, Chatham Is.	1933	Gastropod 4	CAMS 40852	590	40	
Awanui Bay, East Cape, NZ	1924	Bivalve 1A‡	CAMS 40762	470	40	
Awanui Bay, East Cape, NZ	1924	Bivalve 1B‡	CAMS 40763	460	40	

\* Gastropod 1 (CAMS 40758) was a fragment with bio-erosion, probably not alive at time of collection (not used in pooling for averages).

† 3A and 3B are sub-samples of the same gastropod. ± 1A and 1B are two values from one articulated bivalve.

‡1A and 1B are two values from one articulated bivalve

Modern sample results presented in conventional ages. Reported ages have been age corrected for the date of collection, which for all samples is pre-bomb. Analyses were made at the Centre for Accelerator Mass Spectrometry (CAMS), Lawrence Livermore National Laboratory, California, USA.

Table 3 Tephra ages and ocean reservoir estimates									
Location	Terrestrial <sup>14</sup> C age	Planktonic foraminiferal <sup>14</sup> C age	Surface reservoir age	Benthic foraminiferal <sup>14</sup> C age	Apparent ventilation age	Modern ventilation age	Past surface to deepwater age difference	Modern surface to deepwater age difference	Water depth (m)
Bay of Plenty									
Modern	0	470 ± 40	470 ± 40						
Whakatane	4,830 ± 20	$5,190 \pm 50$	$360 \pm 50$	6,350 ± 80	1,520 ± 80	~1,800	1,160 ± 90	~1,330	2,065 (H213)
Mamaku	$7,250 \pm 20$	$7,610 \pm 60$	$360 \pm 60$						
Rotoma	8,530 ± 10	8,920 ± 40	390 ± 40						
Waiohau	$11,850 \pm 60$	$12,650 \pm 90$	800 ± 110	$13,500 \pm 60$	$1,650 \pm 80$	~1,500	850 ± 130	~1,030	1,675 (H209)
Rerewhakaaitu	14,700 ± 110	$15,010 \pm 110$	$310 \pm 160$						
Kawakawa	$22,590 \pm 230$	24,580 ± 140	$1,990 \pm 270$	$26,060 \pm 150$	$3,470 \pm 270$	~1,800	$1,480 \pm 210$	~1,330	2,065 (H213)
Chatham Rise									
Modern	0	$560 \pm 40$	560 ± 40	25,590 ± 380	$3,000 \pm 440$	~1,300	$1,030 \pm 540$	~740	1,300 (U939)
Kawakawa	22,590 ± 230	24,560 ± 320	1,970 ± 390	27,630 ± 210	5,040 ± 310	~1,400	3,070 ± 440	~840	2,700 (U938)

Summary of the terrestrial<sup>9</sup> and marine <sup>14</sup>C ages of the tephras and ocean reservoir estimates in this study. The marine age for each tephra was obtained by: (1) forming weighted averages, using reported errors on AMS<sup>14</sup>C dates (1/*a*<sup>2</sup>) as weights, of the radiocarbon dates above and below the tephra respectively; (2) taking the mean of the weighted averages from above and below the tephra obtained in step (1), providing core-specific tephra ages; and (3) taking the mean of core-specific tephra ages for identical tephras. The error associated with the marine <sup>14</sup>C ages of tephras is a pooled estimate of the standard deviation using individual reported errors. Errors for reservoir ages, ventilation ages and surface-to-deep water ages, are calculated from the tephra uncertainties using gaussian error propagation. All error estimates in this table are rounded to the nearest 10-year interval.

Southern Ocean. Our results support longer residence times for Southern Ocean deep waters in the glaciation and are consistent with a strong gradient between 'older' poorly ventilated deep waters and better ventilated 'younger' intermediate waters.

The large reservoir ages we observe in the early glaciation are likely to represent short-lived transients, as  $CO_2$  exchange dynamics<sup>6,14</sup> tend to re-equilibrate atmospheric and oceanic <sup>14</sup>C reservoirs on short timescales<sup>6</sup>. An increase in <sup>14</sup>C production or

changes in atmosphere–ocean partitioning associated with large circulation changes could account for the enhanced gradient. However, cosmogenic production rates are an unlikely cause because estimates of <sup>14</sup>C production rates during the late glaciation are nearly constant<sup>26,27</sup>. The existence of an atmospheric <sup>14</sup>C plateau near about 25,000 <sup>14</sup>C yr BP (ref. 28) and our vertical hydrographic <sup>14</sup>C profile (Fig. 3c) occurring shortly thereafter leads us to speculate that these may be connected by a significant change in ocean



**Figure 2** Surface-reservoir ages for subtropical and subpolar waters. During the Last Glacial Maximum surface-reservoir ages were  $\sim$ 2,000 years in both subtropical and subpolar surface waters. At 11,850 <sup>14</sup>C yr BP, surface-reservoir ages in subtropical waters were  $\sim$ 800 years. Comparison of marine and terrestrial <sup>14</sup>C ages for the Waiohau tephra in cores H209, H211 and H214 show significant variation between the three cores; the surface-reservoir age estimate at 11,850 <sup>14</sup>C yr BP is  $\sim$ 1,030 years in H214,  $\sim$ 840 years

in H209 and ~530 years in H211. The smaller surface-reservoir age estimate in H211 may be due to higher bioturbation intensity associated with lower sedimentation rates above the Waiohau tephra in that core (5.8 cm kyr<sup>-1</sup> above versus 25.3 cm kyr<sup>-1</sup> below). In cores H214 and H209 the <sup>14</sup>C ages above and below the tephra differ by no more than 100 years, whereas in core H211 the ages differ by ~550 years. We therefore consider the surface-reservoir age estimates from cores H209 and H214 to be more reliable.



**Figure 3** Surface and deep reservoir ages in the southwest Pacific for three time slices. **a**, Modern carbonate samples from the Bay of Plenty and Chatham Islands (solid circles). The modern profile is from GEOSECS station 303 (38° S, 170° W) and includes radiocarbon ( $\Delta^{14}$ C, and equivalent <sup>14</sup>C age; grey circles) and salinity (solid line). Major water masses are labelled: Antarctic Intermediate Water (AAIW), North Pacific Deep Water (NPDW) Antarctic Bottom Water (AABW) / Circumpolar Deep Water (CPDW). (We note that the horizontal scale changes for this modern profile, which is plotted with the palaeo- $\Delta^{14}$ C estimates for reference in **b** and **c**. **b**, Deglacial period, Waiohau (11,805<sup>14</sup>C yr BP, solid triangles). **c**, Last glaciation, Kawakawa (22,590<sup>14</sup>C yr pp; Bay of Plenty core, solid triangles; Chatham Rise cores, solid squares). Palaeo- $\Delta^{14}$ C estimates were calculated using the respective foraminifera age relative to the atmosphere. During the Waiohau,  $\Delta^{14}$ C at 1,675 m is similar to modern pre-bomb values, whereas the surface-reservoir age is older. During the Kawakawa, surface-reservoir ages and apparent ventilation ages are significantly older than today. The sharp increase in apparent ventilation ages with water depth supports interpretations of a strong gradient between 'older' poorly ventilated deep waters and 'younger' better ventilated intermediate waters.

circulation during the onset of full glaciation. A reduction in deepocean ventilation before about 25,000 <sup>14</sup>C yr BP, as the climate system came into full glacial conditions (at or about the stage 3/2 boundary), followed by a return to more modestly reduced production later in the glacial period could explain the large apparent ventilation age, acknowledging that the exact timing of the <sup>14</sup>C plateau<sup>28</sup> is somewhat uncertain. Such a transient effect would have produced older deep water that continued to work its way through the deep ocean at about 22,590 <sup>14</sup>C yr BP.

Our results have important implications for marine <sup>14</sup>C chronologies which assume a constant reservoir correction. For example, greater-than-modern surface-reservoir ages in the Southern Hemisphere would cause synchronous events to appear artificially earlier in the south than elsewhere. Our data provide constraints for models of the radiocarbon cycle which seek to explain atmospheric <sup>14</sup>C changes in terms of ocean dynamics<sup>4,28</sup>, provide diagnostics of glacial thermohaline circulation, and address mechanisms for reduced glacial atmospheric  $p_{CO_2}$ .

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# Multiple seismic discontinuities near the base of the transition zone in the Earth's mantle

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The seismologically defined boundary between the transition zone in the Earth's mantle (410-660 km depth) and the underlying lower mantle is generally interpreted to result from the breakdown of the  $\gamma$ -spinel phase of olivine<sup>1</sup> to magnesiumperovskite and magnesiowustite<sup>2</sup>. Laboratory measurements of these transformations of olivine have determined that the phase boundary has a negative Clapeyron slope and does indeed occur near pressures corresponding to the base of the transition zone<sup>2,3</sup>. But a computational study has indicated that, because of the presence of garnet minerals, multiple seismic discontinuities might exist near a depth of 660 km (ref. 4), which would alter the simple negative correlation of changes in temperature with changes in the depth of the phase boundary. In particular, garnet minerals undergo exothermic transformations near this depth, acting to complicate the phase relations<sup>5-9</sup> and possibly effecting mantle convection processes in some regions9. Here we present seismic evidence that supports the existence of such multiple transitions near a depth of 660 km beneath southern California. The observations are consistent with having been generated by garnet transformations coupling with the dissociation of the yspinel phase of olivine. Temperature anomalies calculated from the imaged discontinuity depths—using Clapeyron slopes determined for the various transformations<sup>4</sup>—generally match those predicted from an independent P-wave velocity model of the region.

Non-olivine components in upper mantle chemistry may be significant in the nature of the transition zone and mantle convection<sup>4,10</sup>. Ringwood<sup>10</sup> suggests that subduction materials are likely to accumulate 660 km below delamination and transformation of former oceanic crust. This process may generate a 'garnetite' layer near a depth of 660 km, which possibly impedes penetration of subducted oceanic lithosphere. This layering may effectively hinder whole-mantle convection at some locations. In Ringwood's model, relatively young and thin oceanic slabs may be too buoyant to penetrate the pre-existing garnetite layer and may therefore be trapped above the 660-km discontinuity, becoming part of the transition zone. This implies that lateral heterogeneity in transition-zone chemistry might occur. These variations in mantle chemistry would most probably cause lateral variations in velocity contrasts across the base of the transition zone.