40. HYDROTHERMALLY ALTERED FELSIC ROCKS OF THE TONGA FOREARC¹

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ABSTRACT

A felsic volcanic series (605-825 mbsf) overlain by upper Eocene shallow-water sediments (500-605 mbsf) and basalticandesitic sills that intruded into sediments of Holocene to Miocene age (0-500 mbsf) was drilled in the forearc region of the Lau Basin at a water depth of 4810 m. The volcanic sequence at Site 841 includes altered and mineralized calc-alkaline rhyolites and dacites, dacitic tuffs, lapilli tuffs, flow breccias, and welded tuffs. These rocks formed subaerially or in a very shallow-water environment suffering a subsidence of >5000 m since Eocene times. Calculations of gains and losses of the major components during alteration show most pronounced changes in the uppermost 70 m of the volcanic sequence. Here, Al, Fe, Mg, and K are enriched, whereas Si and Na are strongly depleted. Illite, vermiculite, chlorite, and hematite predominate in this part of the hole. Throughout the section, quartz, plagioclase, kaolinite, and calcite are present. Sulfide mineralization (up to 10 vol%) consisting mainly of disseminated pyrite (with minor pyrrhotite inclusions) and marcasite together with minor amounts of chalcopyrite is pervasive throughout. Locally, a few sulfide-bearing quartz-carbonate veins as well as Ti-amphibole replacement by rutile and then by pyrite were observed. Strong variations in the As content of sulfides (from 0 to 0.69 wt%) from the same depth interval and local enrichments of Co, Ni, and Cu in pyrite are interpreted to result from fluctuations in fluid composition. Calculations of oxygen and sulfur fugacities indicate that fO₂ and fS₂ were high at the top and lower at the bottom of the sequence. Sulfur isotope determinations on separated pyrite grains from two samples give δ^{34} S values of +6.4‰ and +8.4‰, which are close to those reported from Kuroko and Okinawa Trough massive sulfide deposits and calc-alkaline volcanic rocks of the Japanese Ryukyu Island Arc. Calculated chlorite formation temperatures of 265°-290°C at the top of the sequence are consistent with minimum formation temperatures of fluid inclusions in secondary quartz, revealing a narrow range of 270°-297°C. Chlorite formation temperatures are constant downhole and do not exceed 300°C. The presence of marcasite and 4C-type pyrrhotite indicates a formation temperature of ≤250°C. At a later stage, illite was formed at the top of the volcanic series at temperatures well below 200°C.

INTRODUCTION

Drilling at Ocean Drilling Program (ODP) Site 841 in the Tonga forearc had two principal objectives: (1) to recover a section of volcaniclastic sediments in order to examine the evolution of arc volcanism in the Tonga region, and (2) to identify the age and composition of the forearc basement. Unexpectedly, a series of hydrothermally altered and mineralized dacitic to rhyodacitic volcanics were drilled between 605 and 825 m below seafloor (mbsf).

Eruptive complexes rich in SiO_2 are unusual in intraoceanic island arcs, although recent field and experimental studies have suggested that tonalitic melts can be generated in the subducted slab, in particular during the early stages of subduction. Silica-rich volcanics were also recently drilled in the Mariana forearc and the backarc basin of the Japan Sea (Fryer, Pearce, et al., 1990; Ingle, Suyehiro, et al., 1990). Detailed studies of alteration and mineralization in these rocks, however, have not been conducted so far.

The purpose of this study is to describe alteration and sulfide mineral assemblages in felsic rocks of Hole 841B and to document the processes responsible for the formation of these phases during development of the Tonga forearc.

LITHOLOGY AND PETROGRAPHY

Hole 841B is located approximately 55 km west of the axis of the Tonga Trench and 60 km east of the crest of the Tonga Ridge at a water depth of 4810 m (Fig. 1). The hole intersects two major igneous sequences: (1) a series of nine thin (7 cm to 17 m) basaltic andesite sills within upper Miocene volcaniclastic siltstones and sandstones (Unit 1, 324.76–497.68 mbsf), and (2) a series of altered and mineralized dacites, dacitic tuffs, lapilli tuffs, flow breccias, and welded

tuffs (Fig. 2). The dacitic volcaniclastic rocks recovered from the lower part of Hole 841B were first intersected at 605.05 mbsf where shallow-water limy sandstones of upper Eocene age (approximately 38 Ma) are faulted against dacitic fragments. The volcanic sequence can be identified to at least 825 mbsf and thus has a minimum thickness of 220 m. Core recovery was relatively poor, averaging 11.6%. Unit designations exist only throughout the recovered interval in Section 135-841B-69R-CC (815.20 mbsf). The last core (Section 135-841B-70R-CC; 824.60 mbsf) revealed a single clast of altered basalt (greenstone with pyrite and digenite mineralization) of unknown origin.

Five units (Units 2-6) were distinguished within the silicic volcanic complex (Table 1). Unit 2 consists of 49.15 m of highly phyric, vitreous quartz-plagioclase dacites and poorly welded pumice breccias. It is separated from the overlying upper Eocene sandstone by a dacitic fault gouge and sheared dacitic breccias (Subunit 2A). Two other subunits were identified as mixed dacite and pumice breccia (Subunit 2B) and poorly welded dacitic pumice breccia (Subunit 2C). Unit 3, about 93 m thick, is divided into four subunits and consists of a generally upward-fining sequence of dacitic breccias (Subunit 3D), laminated crystal tuffs and lapilli tuffs (Subunit 3C), welded tuffs (Subunit 3B), and dacitic tuffs and lapilli tuffs (Subunit 3A). Unit 4, 10.2 m thick, comprises a well-defined welded dacitic lapilli tuff that is sheared at the base and quickly grades into the underlying unit. It contains lenticular pumice fragments and abundant dacite lithic clasts. Unit 5 is an intensely sheared breccia with an estimated thickness of 18.8 m. Total recovery was only 1.3 m. Unit 6 is at least 39 m thick and consists largely of clasts and fragments mixed with drilling rubble. The fragments recovered are welded dacitic lithic lapilli tuffs containing strongly deformed altered pumice lenticles, lapilli tuffs, and fragments of mafic greenstone.

ANALYTICAL TECHNIQUES

Rock samples were analyzed by quantitative X-ray fluorescence (XRF) spectrometry for major and trace element compositions using a Philips PW 1400 spectrometer with an on-line Philips PM 851

¹ Hawkins, J., Parson, L., Allan, J., et al., 1994. Proc. ODP, Sci. Results, 135: College Station, TX (Ocean Drilling Program).

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Figure 1. Location of Leg 135 drill sites showing the major geological features of the Tonga Trench and the Lau Basin arc and backarc system. Site 841 is located in the forearc region between the Tonga Ridge and the Tonga Trench. MTJ = Mangatolu Triple Junction, CLSC = Central Lau Spreading Center, ELSC = Eastern Lau Spreading Center, VF = Valu Fa Ridge, Z = Zephyr Shoal, U = Upolu, NF = Niuafo'ou, V = Vava'u, T = Tongatapu, E = 'Eua, and A = 'Ata. Depths are in kilometers.

computer. Major element analyses refer to dried (110°C) and ignited (1000°C) material that was fused with a flux/sample ratio of 10:1. Trace elements were determined on pressed powder pellets. All rock samples were analyzed by instrumental neutron activation analysis (INAA) for rare earth elements, bromine, and gold. X-ray diffraction (XRD) analyses were conducted on powdered samples with a scanning speed of 0.5° 20/min between 2° and 72° on a Siemens D500 diffractometer, using Cu-K\alpha radiation. For clay mineral identification, selected samples were reanalyzed after glycolation. Mineral chemistry was determined employing a five-channel ARL SEMQ electron microprobe. Operating conditions were 25-kV accelerating voltage and 20-nA specimen current on a polished brass sample, and 10–30

s counting time for sulfide and 4–12 s at 15 kV/20 nA for oxide analyses. Fluid inclusion microthermometry was performed following the procedures described by Roedder (1981) on double-sided, polished thin sections using a Chaixmeca MTM heating stage. For sulfur isotope determinations, SO₂ was extracted from hand-picked pyrite grains. The ³⁴S/³²S ratio is reported in the conventional δ notation relative to Cañon Diablo troilite with a precision of ±0.2%. Estimations of temperature, oxygen, and sulfur fugacity at the time of chlorite formation are based on chlorite composition as determined by electron microprobe and were calculated according to Walshe (1986), Kranidiotis and MacLean (1987), and Jowett (1991). Gains and losses of major components (Si, Ti, Al, Fe, Mn, Mg, Ca, Na, and K) during



Figure 2. Schematic section across the Tonga Ridge and the Tonga Trench with the location of Site 841 and a simplified stratigraphy of Hole 841B. Depth and vertical dimensions are not to scale.



Figure 3. Classification diagram of Nb/Y vs. Zr/TiO_2 ratios (after Winchester and Floyd, 1977). Most of the Site 841 samples (605–825 mbsf) plot into the rhyodacite and dacite field.

alteration were quantitatively determined using the method described by MacLean and Kranidiotis (1987) and are expressed as oxides.

RESULTS

Geochemistry

Seventeen samples out of the silicic sequence were selected for major, trace, and rare earth element analyses including loss on ignition (LOI). The SiO₂ and low K contents of the least altered samples and the SiO₂ and K contents of volcanic glass (Table 2) indicate affiliation to calc-alkaline rocks of andesitic to rhyolitic composition. Ratios of Nb/Y vs. Zr/TiO₂ largely exhibit a dacitic to rhyodacitic composition (cf. Winchester and Floyd, 1977) (Fig. 3).

Most samples are extremely poor in Cu, Co, and Ni, rarely reaching the detection limit. Barium, Rb, and Br seem to be slightly enriched in samples from the top of the sequence (Table 2). The same samples reveal the highest losses on ignition. Gold higher than the detection limit of 5 ppb could only be detected in four samples, where it reaches a maximum concentration of 41 ppb (Table 2).

Rare earth element profiles are typically flat and contain about 10–20 times chondrite but generally reveal two different Eu patterns.

Table	1. Division	of silicic	units	and	petrography
in Hol	le 841B.				

Unit	Depth (mbsf)	Thickness (m)	Petrography
2	605.05	49.15	Highly phyric, vitreous quartz-plagioclase dacites and poorly welded pumice breccias.
3	654.20	93.00	Dacite, welded, and lapilli tuffs; dacitic breccias; laminated crystal tuffs.
4	747.20	10.20	Welded dacitic lapilli tuff with lenticular pumice fragments and dacite lithic clasts.
5	757.40	18.80	Dacitic breccias.
6	776.20	>39.00	Fragments of welded dacitic, lithic lapilli tuffs with altered pumice lenticles, lapilli tuffs, and mafic greenstone.

Some samples are depleted in Eu, others show a normal Eu distribution, although the samples have experienced a similar degree of alteration (Fig. 4). A single analysis of fresh glass from this sequence (J. Hergt, pers. comm., 1992) (Table 2) also exhibits a prominent Eu depletion.

Mineralogy

Most of the dacitic lava clasts are very uniform in mineralogy and texture. Phenocryst phases are quartz (1%-12% relative amount; 0.1–2.5 mm in diameter; equant euhedral to anhedral crystals occasionally showing partial resorption), plagioclase (1%-15%); up to 2.5 mm in diameter; euhedral to subhedral crystals with prominent oscillatory zoning), traces of euhedral to subhedral prismatic clinopyroxene and orthopyroxene, and magnetite (<1%; up to 0.4 mm in diameter; commonly enclosed in plagioclase phenocrysts). Apatite and zircon are additional but rare primary accessory minerals. The groundmass is a microcrystalline mosaic of quartz, plagioclase, and interstitial alkali feldspar. A common textural feature is the development of irregular

Table 2. Major, trace, and rare-earth-element	contents and gold contents o	f bulk samples from the silicic se	equence of Hole 841B.

Core, section:	47R-2	47R-2	47R-CC	51R-3	52R-2	53R-2	54R-1	55R-1	55R-1	57R-1	57R-CC	58R-1	59R-1	60R-1	61R-1	62R-CC	64R-CC	70R-CC	Glass
Depth (mbsf):	605.34	605.34	607.18	644.41	652.84	662.79	670.88	679.89	679.97	699.14	700.68	54-57 709.14	718.11	727.86	737.54	750.28	766.50	824.60	631.76
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SiO ₂	58.76	87.36	67.30	67.50	68.12	59.58	75.38	78.59	79.17	79.65	80.32	80.64	77.74	78.67	80.54	80.19	80.41	56.05	78.63
TiO ₂	0.63	0.09	0.37	0.33	0.32	0.41	0.28	0.20	0.23	0.24	0.24	0.23	0.23	0.22	0.22	0.12	0.23	1.29	0.16
Al_2O_3	15.29	4.13	14.16	13.67	13.20	19.50	10.63	11.77	11.56	11.43	10.78	10.55	11.17	10.90	11.21	11.20	11.46	13.73	12.31
Fe ₂ O ₃	8.12	3.49	5.36	2.94	3.09	6.68	2.54	2.41	2.24	0.67	2.49	2.05	2.00	2.20	1.88	2.10	1.08	13.10	1.87*
MnO	0.10	0.00	0.06	0.05	0.05	0.02	0.04	0.02	0.00	0.01	0.01	0.01	0.00	0.02	0.00	0.01	0.00	0.24	0.09
MgO	7.72	0.31	4.22	2.01	1.97	2.37	1.20	0.44	0.55	0.53	0.54	0.24	0.35	0.53	0.27	0.46	0.60	5.55	0.21
CaO	0.30	0.11	0.37	2.93	2.96	2.40	2.02	1.55	1.59	2.13	1.51	1.81	1.51	2.16	1.64	1.19	1.92	2.20	1.59
Na ₂ O	0.26	0.25	0.41	3.39	3.39	4.19	2.82	3.79	3.22	2.45	2.13	3.65	3.70	3.72	3.96	4.59	4.16	4.51	4.31
K ₂ O	1.99	0.93	2.33	0.91	1.14	1.05	1.32	0.56	0.39	0.23	0.43	0.46	0.51	0.55	0.57	0.56	0.48	0.07	0.82
P_2O_5	0.08	0.01	0.07	0.06	0.04	0.07	0.05	0.02	0.03	0.01	0.02	0.05	0.03	0.03	0.02	0.01	0.03	0.08	0.00
LOI	6.64	4.16	5.20	6.01	6.34	5.72	3.60	1.50	2.26	3.83	2.78	1.73	2.06	1.64	1.38	0.91	0.79	4.15	
Total	99.92	100.87	99.87	99.81	100.63	102.00	99.91	100.86	101.26	101.20	101.26	101.43	99.32	100.66	101.70	101.36	101.18	101.06	99.99
Au	6	17		_	_		-	41		10		-		-			_		ND
Ni	44	2	8	2	0	6	2	8	1	1	2	_	1	3	4	4	9	14	ND
Zn	126	14	103	71	49	160	28	34	15	17	15	15	16	29	14	57	22	115	ND
As	21		19			7	9		6		2	1	3					100 million (100 m	ND
Rb	22	9	29	9	9	8	7		3	3	4	2	4	6	1	0	0		10.97
Sr	11	7	16	85	88	128	56	54	54	33	41	59	53	78	57	65	63	61	70
Y	55	13	54	33	37	95	43	48	51	50	45	40	47	39	43	46	49	13	60.4
Zr	156	61	171	168	150	278	148	142	163	156	148	146	158	150	144	145	147	52	160.8
Nb	4	3	3	3	4	4	3	4	3	4	4	3	4	3	3	4	4	3	1.2
Ba	271	129	318	71	68	135	199	71	78	44	100	92	83	76	78	105	79	19	178.6
La	7.1	1.2	6.5	2.7	3.4	1.9	5.2	4.1	3.8	5.0	3.1	3.3	3.9	3.2	3.5	4.0	3.6	2.0	4.23
Ce	23	5	24	17	15	14	19	20	16	19	14	14	15	15	15	16	14	6	12.95
Nd	17		14	8	8	8	11	10	10	14	9	9	15	7	13	13	10	1000	12.61
Sm	5.0	0.9	4.5	2.6	3.2	4.0	3.7	3.6	3.4	4.3	3.1	2.7	3.6	2.3	3.3	3.6	3.1	1.6	4.96
Eu	0.8	0.2	0.8	0.6	0.8	1.4	1.0	1.4	0.7	0.9	0.7	0.9	0.8	0.9	1.2	1.0	1.2	0.9	1.12
Tb	1.3	-	1.2	0.9	0.8	1.4	0.9	1.1	1.0	0.9	0.8	0.8	1.0	0.9	0.9	0.9	1.0		1.12
Yb	5.6	1.3	5.4	3.3	3.8	8.5	4.4	5.2	5.0	4.8	4.6	4.7	5.0	4.7	4.6	5.0	5.0	1.6	6.23
Lu	0.86	0.22	0.85	0.54	0.60	1.37	0.73	0.83	0.78	0.77	0.73	0.74	0.80	0.79	0.73	0.80	0.83	0.23	1.12
Co	18	10	5	15	25			6	12			13	-	3	6	4	7	33	ND
Cu	25	151	53			10	10	29	25	-	-	~	0	_	-	-	-	126	ND
Br	10	э	14	23	25	10	10	1	5	1	0	0	2	4	3	2	0	5	ND

Notes: Major elements in wt%, trace and rare-earth elements in ppm, and gold in ppb. Dash (--) = below detection limits, ND = not detected, and asterisk (*) = expressed as FeO.



Figure 4. Selected chondrite-normalized (Nakamura, 1974), rare-earth-element plots showing typical patterns for Eu-depleted and Eu-undepleted dacites from Site 841. Although both dacites have experienced a similar degree of alteration, an Eu depletion only occurs in Sample 135-841B-55R-1, 17–20 cm. Note that fresh rhyodacitic glass also exhibits an Eu depletion. An asterisk (*) indicates that sample values have been reduced by a factor of 5 for better illustration.

quartz-feldspar symplectitic intergrowths enclosing some of the quartz and plagioclase phenocrysts (Fig. 5A).

All samples have experienced a certain degree of alteration ranging from weakly to strongly altered with the rocks becoming soft and soapy. Disseminated pyrite aggregates are scattered throughout the groundmass and at the most come up to 10 vol%. Rare amphibole phenocrysts are pseudomorphed by prismatic rutile (Fig. 5B) and subsequently replaced by pyrite. Other secondary minerals are clay minerals, chlorite, calcite, albite, and quartz. Locally, quartz-calcite (Mn-rich) veins with marcasite grains were observed (Sample 135-841B-54R-1, 68–70 cm) and in fresher specimens, small (<0.2 mm) interlacing pyrite veins occur (e.g., Sample 135-841B-59R-1, 1–3 cm). At the very top of the sequence (605.34 mbsf), Fe-hydroxide (hematite) is a common secondary mineral, indicating oxidizing conditions.

The depth distribution and relative abundance of X-ray detected minerals is summarized in Table 3. With the exception of the uppermost 5 m where feldspar is totally replaced by illite and chlorite, quartz and plagioclase are the major constituents of the altered rocks. In addition, kaolinite, calcite, and pyrite were detected in different proportions in most of the samples. A nonexpandable 14-Å mineral occur-







100 µm

Figure 5. **A.** Irregular symplectitic quartz-feldspar intergrowth enclosing a quartz phenocryst (Sample 135-841B-59R-1, 1–3 cm; 718.11 mbsf). **B.** Amphibole crystal pseudomorphed by prismatic rutile (gray) and surrounded by pyrite (white) (Sample 135-841B-59R-1, 1–3 cm; 718.11 mbsf).

ring in samples from about 640 to 675 mbsf was identified as belonging to vermiculite.

Microprobe Data for Ore Minerals

Rutile

В

Microprobe analyses of rutile pseudomorphs (Fig. 5B) yield nearly stoichiometric TiO₂ (Table 4). Only minor amounts of Fe (0.34–2.52 wt% FeO; N = 23) and Al (0.10–1.84 wt% Al₂O₃) could be detected.

Table 3. Distribution and relative abundance of mineral phases detected by XRD in felsic rocks of Hole 841B.

Core, section	Depth (mbsf)	Quartz	Feldspar	Kaolinite	Illite	Vermiculite	Chlorite	Calcite	Pyrite
135-841B-									
47R-2 ^a	605.34	+++++		+++++	+	_	+++		+
47R-2 ^b	605.34	+++++		+	+		+		+
47R-CC	607.18	+++++		+	+	—	+		+++
51R-3	644.41	+++	++++			+		+	
52R-2	652.84	+++	+++	+++		+		+	+
53R-2	662.79	+++++	+++++	+++		+	+	+	+
54R-1	670.88	+++++	+++++	+	_	+		+	+
55R-1, 9 cm	679.89	+++++	+++++	+		_		-	+
55R-1, 17 cm	679.97	+++++	+++++	+	-			+	+
57R-1	699.14	+++++	+++++	++++	-			+	
57R-CC	700.68	+++++	+++++	+++	-	\sim		+++	+
58R-1	709.14	++++	++++	+				+	+
59R-1	718.11	+++++	+++++	+		· · · · ·			+
60R-1	727.86	+++++	+++++	+	_	-		+	+
61R-1	737.54	+++++	+++++	+	_		1	+	+
62R-CC	750.28	+++++	+++++	+	-	_		+	+
64R-CC	766.50	+++++	+++++	+	-	_			+
70R-CC	824.60	++++	++++	<u> </u>	-		++++	+	+

Notes: Dash (----) = not detectable, + = rare, ++ = few, +++ = common, ++++ = abundant, and +++++ = major component.

^aHematitic.

^bSilicified.

Core, section:	55R-1	59R-1	59R-1	59R-1	61R-1	61R-1	61R-1	61R-1	61R-1	61R-1
Depth (mbsf):	679.89	718.11	718.11	718.11	737.54	737.54	737.54	737.54	737.54	737.54
TiO ₂	99.03	98.32	97.45	96.24	96.67	98.73	98.44	97.71	96.67	96.06
FeO	0.34	0.61	0.99	1.49	1.29	1.05	1.26	1.46	1.36	1.46
Cr ₂ O ₂	0.01	0.00	0.02	0.00	0.01	0.04	0.00	0.00	0.01	0.00
MgO	0.02	0.05	0.09	0.04	0.00	0.01	0.00	0.01	0.03	0.01
MnO	0.02	0.03	0.00	0.01	0.00	0.05	0.00	0.02	0.00	0.33
Ta ₂ O ₅	0.00	0.06	0.03	0.00	0.00	0.03	0.02	0.02	0.00	0.00
Nb ₂ O ₅	0.00	0.01	0.00	0.04	0.00	0.02	0.00	0.02	0.00	0.00
V202	0.00	0.00	0.04	0.00	0.00	0.00	0.00	0.05	0.03	0.00
CuO	0.00	0.00	0.02	0.01	0.00	0.01	0.04	0.00	0.00	0.02
Al ₂ O ₂	0.25	0.11	0.13	0.17	0.27	0.34	0.14	0.16	0.19	0.31
Total	99.67	99.19	98.77	98.00	98.24	100.28	99.90	99.45	98.29	98.19

Table 4. Selected microprobe analyses (wt%) of rutile, Hole 841B.

Concentrations of Nb, Ta, Mn, Mg, Cr, V, and Cu do not exceed the detection limit. High Ti and low Fe and Al contents and the lack of trace elements support the microscopic observation that the formation of rutile is caused by the alteration of Ti-bearing mafic minerals such as amphibole and/or pyroxene.

Sulfides

Microprobe analyses have been conducted on pyrite and marcasite, on pyrrhotite inclusions in pyrite, and on a few chalcopyrite grains. Selected data (totals in the range between 98 and 102 wt%) are given in Tables 5, 6, and 7. All sulfides are of stoichiometric composition. At about 690 and 750 mbsf, individual pyrite grains are enriched in Co (up to 8.88 wt%) and Ni (up to 1.58 wt%). Copper concentrations seem to increase towards the bottom of the sequence, reaching a maximum of 1.78 wt% at 750 mbsf. Arsenic is strongly varying in concentration ranging from 0 to 0.69 wt% in pyrite and marcasite from the same depth interval, but is uniformly distributed downhole (Fig. 6). Other elements such as Au, Ag, and Sb are well below detection limits.

Chalcopyrite reveals a Cu:Fe ratio of 1.025 but a Me:S ratio of 0.97 on average, indicating a slight metal (Fe) depletion assuming 2 sulfur atoms in the chalcopyrite structure. As in pyrite and marcasite, As is erratically distributed in chalcopyrite, reaching a maximum content of 0.44 wt% (Fig. 6).

A range of 0.08–0.52 wt% As was detected in pyrrhotite. Copper and Ni reach 0.32 and 0.05 wt% on average. Gold, Ag, Co, and Sb contents are below detection limits. The Me:S ratio of pyrrhotite covers a range of 0.86–0.91 with a mean of 0.88, which is close to the formula Fe₇S₈. The low Cu content and an average Fe content of 46.47 atomic% implies the presence of the 4C-type pyrrhotite with a maximum thermal stability of 254°C (Nakazawa and Morimoto, 1971; Kissin and Scott, 1982).

Microprobe Data for Chlorite

Chlorite from three different samples (135-841B-47R-2, 124–127 cm; -55R-1, 1–3 cm; and -70R-CC, 0–3 cm) was analyzed by electron microprobe. Average compositions and Mg numbers are given in Table 8. After Hey (1954), chlorite in a sample from the top of the sequence at 605.34 mbsf is clinochlore (Mg# = 83.6), whereas pycnochlorite (Mg# = 55.0–57.2) occurs in samples from 679.81 and 824.60 mbsf.

Thermodynamic calculations on the basis of chlorite composition (cf. Walshe, 1986) can yield temperature as well as oxygen and sulfur fugacities for the time of chlorite formation, provided that the system is buffered by Fe-sulfides. Thin-section petrography of our samples revealed a direct contact of pyrite and chlorite, suggesting coprecipitation of both minerals. Using Walshe's equations for a pressure of 1 kbar, the average chlorite formation temperature comes up to 270°C at the top of the sequence and decreases to 200°C with increasing depth (Table 8). Applying the chlorite geothermometers of Kranidiotis and MacLean (1987) and Jowett (1991), a temperature decrease downhole does not occur. Furthermore, these geothermometers yield much narrower temperature ranges from 265° to 285°C and from 270° to 300°C (Table 8). Calculated oxygen and sulfur fugacities for clinochlore at 605.34 mbsf ($fO_2 = 10^{-29.7}$ atmosphere [atm], $fS_2 = 10^{-8.6}$ atm) are much higher than for pycnochlorite at 679.81 and 824.60 mbsf ($fO_2 = 10^{-40.4}$ and $10^{-44.2}$ atm, $fS_2 = 10^{-14.5}$ and $10^{-16.5}$ atm). In a temperature vs. log fO_2 diagram, clinochlore data indicate oxidizing conditions whereas pycnochlorite data point to a more reducing environment (Fig. 7).

Sulfur Isotopes

Sulfur isotope ratios were measured for two hand-picked pyrite concentrates from Samples 135-841B-47R-CC, 8–11 cm (607.18 mbsf), and -53R-2, 69–73 cm (662.79 mbsf). The resulting δ^{34} S values are +6.4‰ and +8.4‰, respectively.

Illite Crystallinity

The formation of illite in a SiO₂-rich environment mainly occurs at a high water/rock ratio (Cathelineau, 1988). A characteristic feature of illite is an increasing K interstratification with increasing temperature, resulting in a higher degree of crystallinity. The temperature dependence of crystallinity is usually expressed as crystallinity index Δ (named Kubler index; Kubler, 1967). The Kubler index decreases with increasing crystallinity (i.e., increasing temperature).

Illite crystallinity was determined for separates from Samples 135-841B-47R-2, 124–127 cm (605.34 mbsf), and -47R-CC, 8–11 cm (607.18 mbsf), with 0.845° and 0.705° Δ 2 Θ , respectively, indicating an illite formation temperature well below 200°C (cf. Krumm, 1990).

Fluid Inclusion Microthermometry

Fluid inclusions in secondary quartz were found in a single sample (135-841B-47R-2, 124–127 cm) from the top of the sequence at 605.34 mbsf, where quartz is intergrown with hematite and clinochlore. Small, probably secondary inclusions $(1-2 \,\mu\text{m})$ are found in trails unsuitable for homogenization and freezing experiments. Some larger, isolated inclusions vary in size from 5 to 10 μ m. According to the criteria given by Roedder (1981), these inclusions are considered as primary. They are all two-phase, consisting of an aqueous fluid and a small vapor bubble. Daughter crystals do not occur. The mean homogenization temperature amounts to 281°C with a range from 270° to 297°C for individual inclusions. Because of the small size of inclusions, freezing reactions could not be observed.

Mass Gains and Losses

Gains and losses of elements during alteration (expressed as oxides) were calculated by the method described by MacLean and Kranidiotis (1987), using rhyodacitic glass (Sample 135-841B-50R-1, 16–18 cm) as a standard and assuming immobility of Zr. Plots of

Table 5. Selected microprobe analyses (wt%) of pyrite and marcasite, Hole 841B.

Core, section:	54R-1	55R-1																			
Interval (cm):	35-37	35-37	35-37	35-37	35-37	35-37	35-37	35-37	35-37	97-99	97-99	97-99	1-3	1-3	1-3	1-3	1-3	1-3	1-3	1-3	1-3
Depth (mbsf):	670.55	670.55	670.55	670.55	670.55	670.55	670.55	670.55	670.55	671.17	671.17	671.17	679.81	679.81	679.81	679.81	679.81	679.81	679.81	679.81	679.81
Fe	46.59	46.59	46.39	46.76	46.59	46.75	46.48	46.56	46.06	45.61	46.03	45.68	46.63	46.55	46.86	46.99	46.80	46.98	47.05	45.91	46.15
S	53.68	53.44	53.60	53.22	53.12	52.90	53.28	53.06	52.10	52.52	52.03	52.04	52.52	52.40	52.93	53.72	54.03	53.82	53.95	53.72	52.91
Co	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.46	0.08
Ni	0.02	0.02	0.00	0.02	0.02	0.00	0.02	0.03	0.03	0.03	0.07	0.05	0.03	0.00	0.02	0.01	0.00	0.02	0.01	0.03	0.03
As	0.00	0.11	0.01	0.00	0.01	0.00	0.22	0.04	0.15	0.47	0.32	0.42	0.00	0.00	0.20	0.00	0.41	0.00	0.00	0.35	0.00
Au	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.09	0.03	0.07	0.06	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cu	0.00	0.01	0.01	0.00	0.01	0.00	0.00	0.01	0.30	0.03	0.03	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.01
Ag	0.00	0.02	0.00	0.00	0.03	0.02	0.00	0.00	0.00	0.02	0.00	0.00	0.05	0.00	0.02	0.00	0.03	0.03	0.00	0.00	0.03
Sb	0.00	0.00	0.00	0.00	0.01	0.00	0.01	0.01	0.00	0.01	0.03	0.03	0.01	0.00	0.00	0.00	0.03	0.00	0.00	0.00	0.03
Total	100.29	100.18	100.01	100.00	99.80	99.66	100.02	99.73	98.63	98.78	98.54	98.35	99.30	98.95	100.03	100.71	101.30	100.85	101.01	100.50	99.25
Me:S	0.50	0.50	0.50	0.50	0.50	0.51	0.50	0.50	0.51	0.50	0.51	0.51	0.51	0.51	0.51	0.50	0.50	0.50	0.50	0.50	0.50

Table 5 (continued).

Core, section:	55R-1	56R-1	56R-CC	56R-CC	56R-CC	56R-CC	56R-CC	59R-1	59R-1	62R-1	62R-1	62R-1	62R-1	62R-1	62R-1						
Interval(cm):	1-3	1-3	1-3	1-3	1-3	1-3	1-3	0-3	0-2	0-2	0-2	0-2	0-2	8-12	8-12	23-27	23-27	23-27	23-27	23-27	23-27
Depth (mbsf):	679.81	679.81	679.81	679.81	679.81	679.81	679.81	689.40	690.90	690.90	690.90	690.90	690.90	718.18	718.18	747.43	747.43	747.43	747.43	747.43	747.43
Fe	45.70	46.21	46.50	46.19	45.94	46.60	46.70	46.25	45.79	41.22	43.38	39.70	46.46	46.18	46,12	45.88	45.19	45.49	45.94	45,72	45.75
S	53.14	53.45	52.52	52.71	52.23	52.55	52.77	51.63	52.39	52.34	52.03	52.03	51.18	51.72	51.93	52.37	52.20	52.39	52.52	52.39	52.38
Co	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.13	1.24	6.26	3.57	8.88	0.19	0.00	0.00	0.00	0.08	0.00	0.00	0.01	0.01
Ni	0.01	0.02	0.02	0.02	0.03	0.01	0.02	0.01	0.02	1.58	0.85	0.03	0.05	0.01	0.01	0.06	0.03	0.04	0.04	0.04	0.01
As	0.00	0.04	0.14	0.34	0.19	0.15	0.41	0.08	0.26	0.11	0.00	0.01	0.06	0.14	0.00	0.12	0.47	0.47	0.14	0.20	0.32
Au	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.00	0.00	0.00	0.00	0.06
Cu	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.07	0.02	0.02	0.02	0.00	0.07	0.01	0.03	0.12	0.09	0.13	0.04	0.08	0.13
Ag	0.00	0.00	0.11	0.00	0.00	0.00	0.03	0.00	0.03	0.05	0.00	0.00	0.00	0.00	0.00	0.08	0.00	0.03	0.03	0.00	0.02
Sb	0.01	0.03	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.01	0.04	0.03	0.03	0.03	0.00
Total	98.86	99.77	99.28	99.26	98.40	99.31	99.93	98.16	99.75	101.57	99.85	100.64	98.02	98.07	98.10	98.67	98.10	98.58	98.74	98.47	98.68
Me:S	0.49	0.50	0.51	0.51	0.51	0.51	0.51	0.52	0.52	0.54	0.53	0.53	0.53	0.51	0.51	0.51	0.50	0.50	0.50	0.50	0.51

Table 5 (continued).

Core, section:	62R-2	62R-2	62R-2	62R-2	62R-2	62R-2	62R-2	62R-CC	66R-1	66R-1	70R-CC	70R-CC	70R-CC	70R-CC							
Interval(cm):	16-20	16-20	16-20	16-20	113-116	113-116	113-116	29-31	29-31	39-31	29-31	29-31	29-31	29-31	29-31	24-27	24-27	2-4	2-4	2-4	2-4
Depth(mbsf):	748.86	748.86	748.86	748.86	749.83	749.83	749.83	750.49	750.49	750.49	750.49	750.49	750.49	750.49	750.49	786.14	786.14	824.62	824.62	824.62	824.62
Fe	46.20	46.44	45.72	46.02	45.79	45.76	45.04	45.06	45.64	45.25	42.77	42.93	41.57	41.83	41.81	45.97	46.31	45.85	45.80	45.34	45.73
S	52.70	52.97	52.19	52.68	51.90	52.73	52.74	52.91	52.39	52.31	53.54	53.82	53.61	53.43	53.91	53.61	54.93	53.06	53.10	53.14	52.42
Co	0.02	0.01	0.01	0.03	0.03	0.00	0.53	0.11	0.03	0.12	1.22	1.05	2.78	2.45	1.48	0.00	0.00	0.00	0.00	0.00	0.01
Ni	0.04	0.05	0.00	0.02	0.03	0.00	0.03	0.08	0.00	0.07	0.27	0.26	0.59	0.49	0.38	0.00	0.00	0.02	0.00	0.02	0.02
As	0.11	0.00	0.13	0.37	0.52	0.34	0.59	0.01	0.48	0.00	0.28	0.44	0.69	0.44	0.21	0.00	0.00	0.49	0.00	0.18	0.08
Au	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00
Cu	0.19	0.11	0.22	0.02	0.05	0.53	0.09	0.76	0.08	0.76	1.69	1.78	1.33	1.22	1.27	0.01	0.00	0.13	0.27	ND	ND
Ag	0.03	0.05	0.06	0.00	0.03	0.05	0.02	0.00	0.03	0.00	0.00	0.00	0.06	0.06	0.03	0.02	0.05	0.00	0.00	0.00	0.00
Sb	0.00	0.00	0.01	0.00	0.00	0.03	0.03	0.00	0.01	0.01	0.05	0.04	0.01	0.03	0.00	0.01	0.03	0.00	0.00	0.00	0.00
Total	99.28	99.63	98.34	99.15	98.36	99.44	99.07	98.93	98.65	98.53	99.83	100.31	100.64	99.95	99.09	99,64	101.32	99.55	99.17	98.68	98.27
Me:S	0.51	0.51	0.51	0.51	0.51	0.51	0.50	0.50	0.51	0.51	0.49	0.49	0.50	0.50	0.48	0.49	0.48	0.50	0.50	0.49	0.50

Note: Me:S = metal:sulfur ratio; ND = not determined.

Table 6. Selected microprobe analyses (wt%) of pyrrhotite, Hole 841B.

Core section	50R-1	50R-1	50R-1	50P-1	51R-3	51P-3	55P-1
Interval (cm)	14-17	14-17	14-17	14-17	80-01	89-91	1-3
Depth (mbsf)	631.74	631.74	631.74	631.74	645.19	645.19	679.81
Fe	58.91	59.19	59.34	60.06	58.51	59.35	59.75
S	39.19	38.90	38.84	37.94	39.08	40.10	38.37
Co	0.00	0.00	0.00	0.01	0.00	0.00	0.00
Ni	0.08	0.06	0.05	0.06	0.02	0.05	0.02
As	0.41	0.20	0.19	0.04	0.39	0.52	0.08
Au	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cu	0.21	0.16	0.24	0.28	0.83	0.54	0.00
Ag	0.00	0.00	0.00	0.01	0.00	0.00	0.03
Sb	0.00	0.00	0.00	0.00	0.00	0.00	0.01
Total	98.81	98.51	98.66	98.41	98.83	100.55	98.27
Me:S	0.87	0.88	0.88	0.91	0.87	0.86	0.90

Note: Me:S = metal:sulfur ratio.

Table 7. Selected microprobe analyses (wt%) of chalcopyrite, Hole 841B.

Core, section:	56R-CC	56R-CC	62R-1	62R-1	62R-1	62R-1	62R-2	62R-2
Interval (cm):	0-2	0-2	23-27	23-27	23-27	23-27	16-20	16-20
Depth (mbsf):	690.90	690.90	747.43	747.43	747.43	747.43	748.86	748.86
Fe	30,13	30.16	29.52	29.07	28.77	28.52	29.31	28.92
S	34.59	34.16	35.93	35.77	35.26	35.60	36.03	35.83
Co	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ni	0.00	0.04	0.05	0.00	0.02	0.03	0.02	0.01
As	0.00	0.44	0.31	0.00	0.10	0.09	0.22	0.35
Au	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cu	33.61	34.21	33.43	34.78	34.24	34.30	34.07	34.48
Ag	0.01	0.01	0.03	0.03	0.04	0.00	0.03	0.01
Sb	0.00	0.03	0.03	0.00	0.00	0.04	0.00	0.04
Total	98.35	99.06	99,30	99.65	98.43	98.57	99.68	99.64
Me:S	0.99	1.02	0.95	0.96	0.96	0.95	0.95	0.95
Cu:Fe	0.98	1.00	1.00	1.05	1.05	1.06	1.02	1.05

Note: Me:S = metal:sulfur ratio.



Figure 6. Variation in As concentration in sulfides (pyrite, chalcopyrite, and pyrrhotite; N = 89) from the dacitic sequence of Site 841.

Core, section:	47R-2	55R-1	70R-CC
Interval (cm):	124-127	1-3	0-3
Depth (mbsf):	605.34	679.81	824.60
N:	8	9	7
SiO	29.48 ± 0.47	27.95 ± 0.36	28.14 ± 0.81
Al2Ő3	20.48 ± 0.29	21.06 ± 0.34	17.68 ± 0.31
CaÕ	0.05 ± 0.03	0.10 ± 0.03	0.07 ± 0.03
FeO	9.22 ± 2.62	21.44 ± 1.57	24.10 ± 1.31
MnO	0.28 ± 0.04	0.06 ± 0.01	0.65 ± 0.02
MgO	26.57 ± 2.60	16.05 ± 1.03	16.17 ± 0.88
TiO ₂	0.05 ± 0.02	0.10 ± 0.07	0.02 ± 0.01
Total	86.14	86.77	86.82
Mg#	83.6	57.2	55.0
Log fO ₂ (atm)	-29.7	-40.4	-44.2
Log fS ₂ (atm)	-8.6	-14.5	-16.5
Temperature (°C) ^a	267.7	221.0	200.5
Temperature (°C)b	265.6	284.7	268.9
Temperature (°C) ^c	290.6	298.2	272.7
-			

Note: The average composition is equivalent to the weight percent ± 1 standard deviation (SD). N = number of analyses. Formation temperatures calculated after a = Walshe (1986), b = Kranidiotis and MacLean (1987), and c = Jowett (1991).

mass changes of the major elements vs. the degree of alteration (i.e., LOI content) show the mobility or immobility of individual components (Fig. 8).

The upper 70 m of the sequence is characterized by a strong depletion in SiO_2 , a somewhat weaker depletion in Na_2O , and an enrichment in Al_2O_3 , Fe_2O_3 , MgO, and K₂O. Farther downhole, the rocks are enriched in SiO_2 and slightly depleted in K₂O. Here, Fe_2O_3 and MgO do not seem to be affected by alteration. CaO exhibits a somewhat diffuse distribution, with the highest losses occurring in illite-bearing samples. An unusual behavior is recognized for MnO. This element is depleted in less altered samples and reaches its original concentration in the sample richest in LOI. As expected, TiO₂ (not shown in Fig. 8) does not show any significant mobility. Generally, gains and losses smooth down with increasing depth.

DISCUSSION

Felsic volcanic rocks and tuffs of pre-Eocene age were recovered between 605.05 and 824.60 mbsf (Units 2–6) from Hole 841B in the forearc region of the Lau Basin. The evidence of welding in some of the dacitic clasts and tuffs, the complete absence of interbedded sediments and fossil marine flora and fauna, and the coexistence of dense clasts and highly vesicular pumice suggest a subaerial to very shallowwater emplacement of this sequence, which subsequently has experienced a subsidence of about 5400 m during forearc development.

Based on their primary igneous SiO₂ and Na₂O + K₂O contents, the rocks are andesitic to rhyolitic in composition and exhibit a distinct calc-alkaline affinity. In addition, immobile element ratios (Zr/TiO2 vs. Nb/Y) have been used to characterize the rocks as being dacites and rhyodacites. It is not clear if these rocks represent an early phase of Lau Ridge volcanism (and thus an early stage in the development of the Melanesian proto-arc) or if they are part of an exotic terrane of some older, far distant plate margin (e.g., Lord Howe Rise). Rhyolitic rocks of the upper Cretaceous Lord Howe Rise were recovered 3200 km west of the Lau Basin during Deep Sea Drilling Project (DSDP) Leg 21 at Site 207 (Burns, Andrews, et al., 1973). Compositionally, these rocks are characterized by a higher K2O and lower TiO2 and CaO contents than the rocks studied in this paper. So far, no trace element data have been published on Lord Howe Rise volcanism, thus preventing a comparison with the trace element spectra of the volcanics from the Lau Basin. In any case, Site 841 rocks exhibit an arc-like signature (Bloomer et al., this volume) and constitute a part of the igneous basement on which the Lau Ridge and the Tofua Arc are constructed.



Figure 7. Temperature vs. log fO_2 plot calculated for average compositions of chlorite in samples from Site 841 using different chlorite geothermometers (Walshe [1986] = filled squares; Kranidiotis and MacLean [1987] = diamonds; Jowett [1991] = crosses). Clinochlore from the top of the sequence appears to have formed in a more oxidizing environment, whereas pycnochlorite from farther down in the hole formed under more reducing conditions. Hm = hematite and Mt = magnetite.



Figure 8. Gains (+) and losses (-) of major components relative to a rhyolitic glass standard (horizontal line) vs. LOI (loss on ignition) in wt%. Open symbols indicate samples from the uppermost 70 m of the sequence, and filled symbols represent samples from 675 to 767 mbsf.

-	T	:	100	
		1	m	e

Recrystalliza	ation			
Amphibole - Biotite -> v	-> rutile vermiculite			
	Silicification			
	Secondary qu	Jartz		
	Chloritization			
	Clinochlore, p	ycnochlorite		
		Mineralization		
		Pyrite, marcasite, chalcopyrite, pyrrhotite		
			Illitization,	kaolinization
			Illite, kaol	inite

Figure 9. Schematic diagram showing the alteration history for volcanic rocks in Hole 841B.

All recovered samples are altered and mineralized to a certain degree. Alteration comprises the presence of secondary quartz, illite, chlorite, kaolinite, vermiculite, calcite, hematite, and rutile. This mineralogy is typical for altered felsic rocks and indicates alteration at somewhat elevated temperatures. The distribution and relative abundance of alteration minerals partly varies with depth; for example, illite is restricted to the top of the sequence (605-610 mbsf), whereas feldspar is totally missing and vermiculite occurs only between 640 and 675 mbsf. Below 675 mbsf neither illite nor vermiculite are present. The depth distribution of alteration minerals is accompanied by a slight enrichment of Ba, Rb, and Br in the uppermost 70 m of the sequence. Here, the highest losses on ignition indicate a higher degree of alteration. Calculations of gains and losses also point to higher element mobility in the uppermost 70 m. With increasing depth, element gains and losses smooth down, likely reflecting a decreasing water/rock ratio, less extensive recrystallization, and thus more restricted element mobility.

Prominent Eu depletions in some of the samples and especially in a single glass analysis may be the result of a fractionation effect rather than alteration. Fractionation of large amounts of (Eu-bearing) plagioclase from a parent magma source (i.e., calc-alkaline basalt, arc tholeiite, etc.) may cause Eu depletion in the evolved lavas (J. Allan, pers. comm., 1992).

Symplectitic quartz-feldspar intergrowths enclosing quartz and plagioclase phenocrysts and rutile pseudomorphs after Ti-amphibole are interpreted as having developed during groundmass recrystallization. Vermiculite is thought to be the product of biotite alteration whereas clay minerals, quartz, and quartz-calcite veins are likely the result of hydrothermal activity. The poor crystallinity of illite $(0.845^{\circ}-0.705^{\circ}\Delta 2\Theta)$ is attributed to a formation temperature presumably well below 200°C, indicating a late stage of formation, which is also assumed for kaolinite. Although this temperature is very reasonable, care must be taken in the application of this geothermometer as illite crystallinity may have been influenced by kinetic effects occurring during burial metamorphism and subsequent heating.

Sulfur isotope values for pyrite (+6.4‰ and +8.4‰ δ^{34} S) are substantially higher than those for seafloor sulfide deposits at the midocean ridges, but they are comparable to the general range of +5% to +8‰ for volcanogenic Kuroko-type massive sulfide deposits (Kajiwara et al., 1981), sulfide-sulfur of Quaternary volcanic rocks from the Japanese Ryukyu Island Arc (+5.1% to +7.3%; Ueda and Sakai, 1984), and pyrite from Okinawa Trough massive sulfides (+6% to +8‰; Halbach et al., 1989). Mid-ocean ridge hydrothermal deposits have δ^{34} S values averaging about +3‰ (Herzig, unpubl. data), which is attributed to the addition of 10% to 20% of a reduced seawater sulfur component (+21‰; Rees et al., 1978) to MORB sulfur (+0.1‰; Sakai et al., 1984). The same process may have occurred in the Tonga forearc regardless whether the original $\delta^{34}S$ value of the rocks was MORB (+0.1‰) or more arc-like (about +5‰; Ueda and Sakai, 1984). Speculating that the original 834S value was MORB-like, an incorporation of unusually high amounts of reduced seawater sulfur (30%-40%) is required to produce the observed δ^{34} S values. Consequently, one can assume that the higher $\delta^{34}S$ values of the pyrites are caused by an arc sulfur component that has been mixed with seawater sulfur.

Local enrichments of Co (up to 8.88 wt%), Cu (up to 1.78 wt%), and Ni (up to 1.58 wt%) in pyrite likely result from distinct fluctuations in fluid composition, as might also be indicated by the strong variation of the As content in the sulfides (up to 0.69 wt%). An average of 46.5 atomic% Fe implies the presence of the 4C-type pyrrhotite with a maximum thermal stability of 254°C (Nakazawa and Morimoto, 1971; Kissin and Scott, 1982). The formation of marcasite is restricted to a temperature of <240°C and a pH of <5 (Murowchick and Barnes, 1986), thus placing the formation for these sulfides to a temperature of \leq 250°C.

À decrease in oxygen and sulfur fugacities with increasing depth is indicated by systematic variations in chlorite composition. Clinochlore occurring together with hematite at the top of the sequence points to an oxidizing environment, whereas pycnochlorite further downhole has likely been formed under more reducing conditions. The calculated oxygen and sulfur fugacities for clinochlore formation ($fO_2 = 10^{-29.7}$ atm, $fS_2 = 10^{-8.6}$ atm) are quite similar to published values of hot springs at the East Pacific Rise at 21°N ($fO_2 = 10^{-29.8}$ atm, $fS_2 = 10^{-9.6}$ atm; Janecky and Seyfried, 1984).

According to thermodynamic equations given by Walshe (1986), calculated formation temperatures of chlorite decrease from 270°C at the top of the sequence to 200°C in the lowermost part. Because decreasing temperatures downhole are unlikely and difficult to explain, chlorite formation is rather assumed to have taken place in a narrow temperature interval ranging from 265° to 300°C, as indicated by the chlorite geothermometers by Kranidiotis and MacLean (1987) and Jowett (1991), which contain a correction for Fe/Fe+Mg. However, the average formation temperature given by all three geothermometers for clinochlore in the top sample at 605.34 mbsf (265°C, 270°C, and 290°C) is in good agreement with fluid inclusion homogenization temperatures (i.e., minimum formation temperatures) of coexisting quartz ranging from 270° to 297°C.

Changing chlorite composition with depth (clinochlore to pycnochlorite) might have also been effected by changes in fluid composition. Magnesium-rich chlorites (i.e., clinochlore) preferably form in an environment with a high water/rock ratio, whereas Fe-rich chlorites are known to precipitate from more evolved Fe-bearing fluids that likely have circulated in the deeper part of the sequence (Edmond et al., 1982; Michard et al., 1984). A high water/rock ratio is assumed for the top of the sequence (see discussion of element mobility above) where Mg-rich chlorite is present. Chlorites intermediate in composition such as those at 679.81 and 824.60 mbsf may have been formed at a reduced water/rock ratio and/or precipitated from an Fe-bearing fluid.

SUMMARY

The volcanic sequence at Hole 841B probably represents an early stage of island arc evolution in the Tonga region. Once in a nearsurface position, the silicic rocks have subsided more than 5000 m since Eocene times. Summarizing the observations and data for alteration and mineralization, the following processes may have taken place in subsequent succession (Fig. 9): (1) recrystallization of amphibole to rutile, and biotite to vermiculite, and formation of symplectitic quartz-feldspar intergrowths; (2) mobilization, transport, and redeposition of silica and formation of chlorite (Mg-fixation) at a temperature of about 30°C; (3) pyritization and formation of marcasite in quartz-calcite veins (T $\leq 250^{\circ}$ C); and (4) late-stage illitization (K-fixation) and kaolinization at temperatures well below 200°C.

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