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[1] Hydrogen peroxide (H_2O_2) is a reactive oxygen intermediate involved in the cycling of metals and dissolved organic matter. Because little is known of its distribution in the North Pacific Ocean, we determined H_2O_2 in surface waters continuously and obtained vertical profiles at nine stations during a cruise from Japan to Hawaii. Surface water H_2O_2 varied from less than 10 to more than 250 nmol dm^{-3}. A diel cycle in surface water H_2O_2 ($\sim$25 nmol dm^{-3}) was observed only on one day during the monthlong cruise. This is contrary to expectations based on the usual assumption of photo-production as the dominant input of H_2O_2. Experiments were also conducted during the cruise to examine both photo-production and dark decay. The net rate of photo-production at a station near Hawaii was determined to be 8 nmol dm^{-3} h^{-1}, similar to rates reported for the central Atlantic Ocean and Antarctic. However, this maximum estimate of photo-production is also similar to probable rates of H_2O_2 input by other mechanisms (biological production and rain). The pseudo-first-order rate constant for dark decay varied from 0.1 to 0.2 d^{-1}, which is toward the low end of previous reports of H_2O_2 decay rates, and was observed to increase proportionately to the dissolved organic carbon concentration. Taken together, these results suggest that photo-production of H_2O_2 in open ocean waters may be less important than previously thought and therefore H_2O_2 is likely less of an indicator of the photo-chemical reactivity of surface waters than hoped for. Furthermore, we observed that the H_2O_2 inventory for the upper 200 m of the water column has a maximum at midlatitudes. We suggest that this results from diminished inputs at high latitude as well as increased decay rates at low latitudes.

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Theme: Biogeotracers in the Northwest Pacific Ocean
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1. Introduction

[2] Hydrogen peroxide (H_2O_2) is a relatively stable reactive oxygen intermediate [*Stumm and Morgan*, 1996]. It reacts with and can be significantly involved in the cycling of various trace metals [*Millero and Sotolongo*, 1989; *Moffett and Zika*, 1987; *Pettine and Millero*, 1990; *Voelker and Sulzberger*, 1996; *Zepp et al.*, 1992] and dissolved organic substances [*Cooper and Zika*, 1983; *Draper*

and Crosby, 1983; *Voelker and Sulzberger*, 1996]. The steady state concentration of hydrogen peroxide is very low, however, with concentrations typically less than 100 nmol dm^{-3} in ocean surface waters [*Zika et al.*, 1985; *Johnson et al.*, 1989; *Moore et al.*, 1993; *Miller and Kester*, 1994; *Sarthou et al.*, 1997; *Price et al.*, 1998; *Yocis et al.*, 2000; *Yuan and Shiller*, 2001; *Hanson et al.*, 2001; *Brooks Avery et al.*, 2005].

[3] There are several sources of hydrogen peroxide in natural waters. Hydrogen peroxide can be produced by photochemical excitation of dissolved organic matter which then transfers electrons to dissolved O_2 [*Cooper and Zika*, 1983; *Draper and Crosby*, 1983; *Cooper et al.*, 1988; *Zuo and Hoigne*, 1993; *Abele-Oeschger et al.*, 1997; *Herut et al.*, 1998]. This has generally been viewed as the dominant mechanism of hydrogen peroxide input to surface waters and has led to the common thought that hydrogen peroxide is a relatively easily measured parameter indicating the photochemical reactivity of surface waters. However, hydrogen peroxide can also be generated through biological processes associated with aerobic organisms [*Palenik et al.*, 1987; *Zepp et al.*, 1987; *Palenik and Morel*, 1988; *Cooper and Lean*, 1992; *Wong et al.*, 2003]. Additionally, hydrogen peroxide can be produced through chemical oxidation of some reduced metals [*Cooper and Lean*, 1992]. Finally, rainfall input of hydrogen peroxide to ocean surface waters can be significant in some circumstances [*Cooper et al.*, 1987; *Yuan and Shiller*, 2000].

[4] There are two basic mechanisms by which hydrogen peroxide decays in natural waters: biological/enzymatic removal and abiotic chemical reaction. The enzymes peroxidase and catalase are produced by most organisms to scavenge this potent oxidizer/reductant. *Moffett and Zafiriou* [1990] used isotopic tracer methods to demonstrate that these enzymes are responsible for most hydrogen peroxide decay, at least in the coastal setting they studied. Other evidence for a biological decay mechanism includes culture and natural water studies showing that various bacteria and phytoplankton can enhance the decay of hydrogen peroxide [*Zepp et al.*, 1987; *Cooper et al.*, 1994; *Lean et al.*, 1994; *Herut et al.*, 1998; *Wong et al.*, 2003]. Inorganic processes, such as oxidation of metal ions, may also be a factor in hydrogen peroxide decay, though probably not a dominant one in open oceanic surface waters [*Cooper and Lean*, 1992; *Zepp et al.*, 1992; *Moffett and Zafiriou*, 1993]. Our own previous work indicated that colloidal material can enhance the rate of hydrogen peroxide decomposition, though whether this results from oxidation of colloidal material or the presence of enzymes in the colloidal-sized material is unknown [*Yuan and Shiller*, 2001].

[5] Apart from an earlier study in an inland sea [*Fujiwara et al.*, 1993] and a recent study of the equatorial Pacific [*Hanson et al.*, 2001], the distribution of hydrogen peroxide in the North Pacific Ocean is not well documented. Recently, we conducted studies of hydrogen peroxide in the northwest Pacific Ocean from Osaka, Japan to Honolulu, Hawaii during the 2002 Intergovernmental Oceanographic Commission (IOC) Contaminant Baseline Expedition. Deep-water hydrogen peroxide results from this cruise are presented elsewhere [*Yuan and Shiller*, 2004]. Here, we discuss surface water variations, shallow water profiles, and rate measurements from this cruise as part of an effort to better understand the distribution of hydrogen peroxide in the marine environment as well as the factors that affect its production and decay.

2. Methods

[6] Seawater samples were collected during the IOC Baseline Expedition from Osaka, Japan to Honolulu, Hawaii in May and June of 2002 (Figure 1). Surface water was pumped aboard continuously while the ship was underway and its concentration of hydrogen peroxide was determined approximately every 4 minutes. A shallow water vertical profile of hydrogen peroxide was determined at each of the nine stations. Hydrogen peroxide was determined using a luminol chemiluminescence flow injection analysis method [*Yuan and Shiller*, 1999]. Triplicate determinations were conducted on each of the samples and the mean values are reported here. The relative standard deviation of triplicate determinations was usually less than 3%. The instrument was calibrated for seawater by making standard additions of hydrogen peroxide. A stock hydrogen peroxide solution was calibrated for stability at the beginning and end of the cruise using UV absorbance at 240 nm [*Huang and Dasgupta*, 1985]. Working standards of hydrogen peroxide were made by a series of dilutions.

[7] A photo-production experiment was conducted on a clear day at station S9 (i.e., station ALOHA). Replicates of seawater from 10 m at station S9 were collected in six 250 cm^3 round-bottom quartz

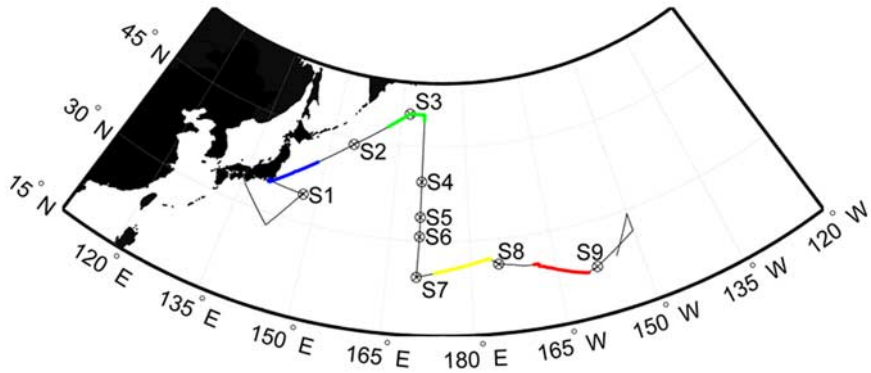

Figure 1. Cruise track of the IOC 2002 Baseline Expedition in the northwest Pacific Ocean. Profiles of hydrogen peroxide were obtained at each of the stations. The rate constant of hydrogen peroxide decay was determined at S2 to S9; net hydrogen peroxide photo-production was determined at S9; diel variations of hydrogen peroxide in shallow waters presented in four subplots of Figure 4 were obtained at four sections of colored tracks (Figure 4a, blue; Figure 4b, green; Figure 4c, yellow; Figure 4d, red).

flasks. All the flasks were sealed and placed upside down in a deck-top incubator that was maintained at ambient temperature (~25°C) by circulating surface seawater. One flask was covered with aluminum foil and used as a dark control. One replicate was used for determining the concentration of hydrogen peroxide every hour. The mean rate of photo-production is presented here which was derived from a linear regression of the first four hours of incubation. Because the decay and dark production of hydrogen peroxide were not eliminated in this incubation experiment, the rate of production thus determined was the net result of photo-production, minus possible dark and photo-decay, plus possible dark production, and will hereafter be called net photo-production. UV A + B radiation reaching the incubator was recorded hourly during the incubation experiment (G. Cutter unpublished data). At the end of the experiment, the hydrogen peroxide concentration of the dark control was also determined.

[8] A series of dark decay experiments were also conducted during the cruise. At stations S2, S3, S4, S5, S6, S7, S8, and S9, an unfiltered shallow water sample was collected in a 500 cm^3 acid-washed high-density polyethylene bottle and placed in the dark at room temperature (~21°C). A subsample of ~15 cm^3 was taken from these shallow water samples for the determination of hydrogen peroxide daily for at least 4 days.

[9] A shallow water vertical profile of hydrogen peroxide was determined at each of the stations. Hydrogen peroxide inventory was calculated by integrating vertical profiles from the surface to 200 m. Two integration methods were used. These are based on assumptions that the concentration of hydrogen peroxide at a particular depth represents its concentration in (1) the layer between the depth and the depth of the next shallower sample and (2) the layer between the depth and the depth of the next deeper sample. Dissolved organic carbon (DOC) was determined by high-temperature catalytic oxidation using a Shimadzu 5050A TOC analyzer (W. Landing, unpublished data). Chl *a* data were obtained from K. Selph et al. (Microbial community composition and growth rates in the NW Pacific during spring 2002, submitted to *Geochemistry, Geophysics, Geosystems*, 2005).

3. Results and Discussion

3.1. Dark Decay Experiments

[10] The rate constant of dark decay of hydrogen peroxide in shallow waters was determined at most of our stations in the northwest Pacific Ocean (Table 1). Since the reaction mechanism of hydrogen peroxide decay is not known and the decay fits a first-order reaction model, the rate constant of dark decay thus derived will be called the pseudo-first-order rate constant. The rate constant varied from 0.10 ± 0.01 d^{-1} at S2 to 0.22 ± 0.02 d^{-1} at S4. These rate constants imply a hydrogen peroxide half-life of from 3 to 7 days in shallow waters of the northwest Pacific Ocean.

[11] The reported rate constants of hydrogen peroxide decay in seawater vary by more than an order of magnitude. Data from *Moore et al.* [1993] indicate a hydrogen peroxide decay rate constant of from 0.13 to 2.9 d^{-1} in seawater of the Orinoco River plume and the Eastern Caribbean Sea.

Table 1. Comparison of Surface Concentration, Water Column Inventory, and Surface Decay Rate Constant of Hydrogen Peroxide

Station	Date	Local Time	Latitude, °N	Longitude, °	Water Column H_2O_2 Inventory, mmol m^{-2}	Shallow Water H_2O_2, nmol dm^{-3}	Decay Rate Constant, d^{-1}
S1	5/6/2002	12:13	34.43	147.09	2.8 ± 0.5	33	
S2	5/12/2002	19:24	44.00	155.00	2.1 ± 0.4	33	0.10 ± 0.02
S3	5/15/2002	14:35	50.00	167.00	2.7 ± 0.4	26	0.16 ± 0.02
S4	5/18/2002	20:32	39.32	170.56	3.2 ± 0.7	108	0.22 ± 0.02
S5	5/19/2002	2:01	33.76	170.58	3.3 ± 0.7	69	0.20 ± 0.01
S6	5/20/2002	10:49	30.50	170.58	5.1 ± 1.4	120	0.17 ± 0.02
S7	5/22/2002	8:52	24.25	170.33	5.0 ± 0.9	77	0.14 ± 0.02
S8	5/26/2002	22:20	26.00	−175.00	5.7 ± 1.0	92	0.21 ± 0.06
S9	5/30/2002	10:32	22.75	−158.00	3.0 ± 0.5	54	0.12 ± 0.04

Petasne and Zika's [1997] work indicates decay rate constants of from 0.14 to 1.4 d^{-1} in seawater from South Florida to the Gulf Stream. In both of these studies, the highest decay rate constants were observed in coastal waters. We reported a rate constant of 0.13 ± 0.01 d^{-1} for surface water of the Central Atlantic Ocean [*Yuan and Shiller*, 2001]. Therefore the hydrogen peroxide decay rate constants determined here for shallow waters of the northwest Pacific Ocean are at the low end of the range of previous reports but generally similar to the decay rate constants reported for other open ocean near-surface waters.

[12] As discussed in the introduction, biological/enzymatic processes appear to dominate the decay of hydrogen peroxide in shallow ocean waters. For our experiments, we observed no significant relationship between the rate constant of hydrogen peroxide decay and chlorophyll-a (Figure 2, top). However, the rate constant does significantly correlate with DOC (Figure 2, bottom). The lack of correlation with chlorophyll-a may reflect both the fact that this parameter accounts for only one type of organism as well as the fact that even among species of phytoplankton, the rate constant for hydrogen peroxide decay varies significantly [*Wong et al.*, 2003]. The correlation between decay constant and DOC may be due to extra-cellular catalase and/or peroxidase in the DOC pool.

3.2. Photo-production Experiment

[13] The photo-production incubation began at 12:00 PM local time on a clear day. Integrated UV A + B radiation increased gradually from 1004 to 1708 kJ m^{-2} during the incubation (Figure 3). The concentration of hydrogen peroxide increased in all six incubation flasks relative to the beginning concentration (Figure 3). The mean net rate of hydrogen peroxide production during the first four hours of the experiment was 8 nmol dm^{-3} h^{-1}. There was also a 15 nmol dm^{-3} increase of hydrogen peroxide in the dark control by the end of the experiment. Because the dark control was not replicated, we are uncertain whether this dark increase resulted from experimental error or from dark production of hydrogen peroxide. In any event, the 8 nmol dm^{-3} h^{-1} net production rate appears to be a maximum estimate of the rate of photo-production.

[14] The net photo-production of hydrogen peroxide determined at station S9 is similar to rates reported for other open ocean regions. For example, *Yocis et al.* [2000] reported midday photo-production rates of 2 to 10 nmol dm^{-3} h^{-1} for the surface waters of the Antarctic. We previously reported a photo-production rate of 8 nmol dm^{-3} h^{-1} for the surface waters of the central Atlantic Ocean [*Yuan and Shiller*, 2001]. A wide range of photo-production rates (5 to ~550 nmol dm^{-3} h^{-1}) was reported for the waters of the Orinoco River plume and the Eastern Caribbean Sea (see Table 1 of *Moore et al.* [1993], assuming UV irradiance of 40 W-h m^{-2}].

[15] It has been shown that the photo-production rate of hydrogen peroxide increases with both UV radiation and DOC concentration [*Cooper and Zika*, 1983; *Scully et al.*, 1996]. Because subtropical regions (i.e., station S9) receive more solar UV insolation than the Caribbean Sea in summer [*Kirk*, 1983], a difference in UV radiation probably does not explain the difference in production rate of hydrogen peroxide between station S9 and stations in Caribbean Sea. However, the shallow water DOC concentration of station S9 (77 μM; Landing unpublished data) was likely lower than that of the Orinoco River plume and the Eastern Caribbean Sea given that DOC fluorescence and absorbance were high for those waters [see *Moore et al.*, 1993, Tables 1 and 3]. Therefore the difference in DOC concen-

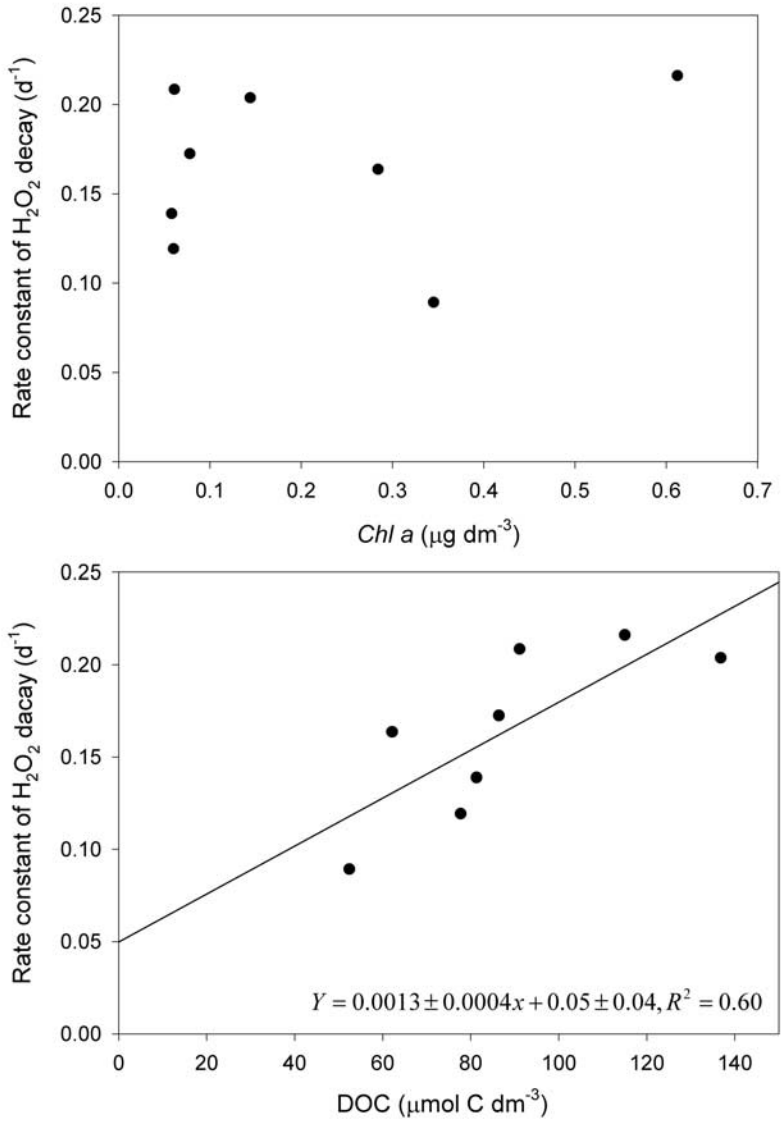

Figure 2. The variation of the decay rate constant of hydrogen peroxide (at 21°C) versus (top) chlorophyll-a and (bottom) DOC.

tration may be the dominant cause of the difference in the production rate of hydrogen peroxide between station S9 and stations in Caribbean Sea.

3.3. Variation of Hydrogen Peroxide in Surface Waters

[16] The concentration of hydrogen peroxide in surface waters varied from less than 10 to more than 250 nmol dm^{-3} along the cruise track (Figure 4). With a sampling frequency of approximately once every 4 minutes, it appears that hydrogen peroxide varied on a spectrum of frequencies from less than 1 d^{-1} to 0.25 min^{-1}. On a typical day, the ship traveled about 500 km; thus the low-frequency variations reflect both the temporal and spatial variations of hydrogen peroxide on 1 day and a 500 km scale or larger. Regarding high-frequency hydrogen peroxide variability, the ship travels about 1.5 km in every sampling interval of 4 minutes. Thus the high-frequency variations reflect temporal and spatial variations of hydrogen peroxide on timescales of 4 minutes to 1 day and spatial scales 1.5 to 500 km.

[17] The hydrogen peroxide diel cycle (i.e., 1 d^{-1} frequency) is of particular importance and is generally regarded as evidence for photo-production

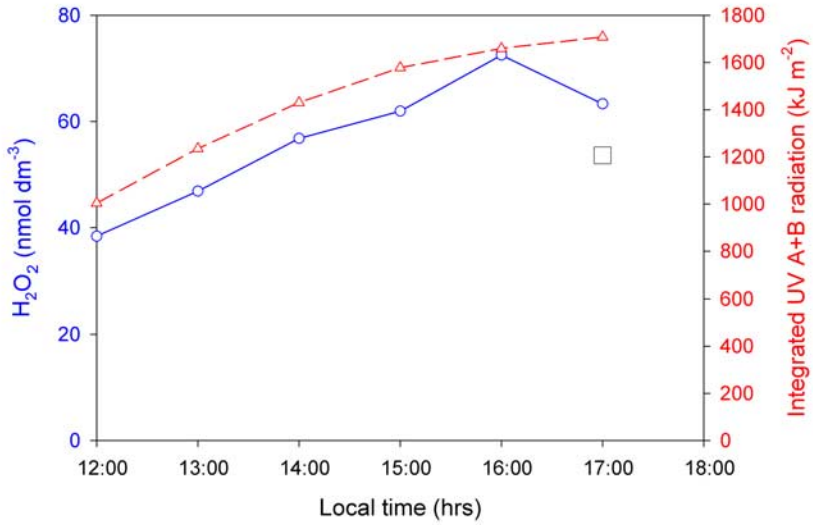

Figure 3. The concentration of hydrogen peroxide (blue circles) and integrated UV A+B radiation (red triangles) during the photo-incubation experiment at station S9. One of six replicates was used for hourly peroxide determination. Dark control is shown as an open square.

being the dominant source of hydrogen peroxide. However, during the cruise a diel cycle of hydrogen peroxide was observed clearly only on 9 May (Figure 4a). On 25 May, 29 May, and two other days (Figures 4c, 4d, and other data not shown) there was arguably an increase in hydrogen peroxide during the day. On other days of the cruise, diel cycles were not recognizable (Figure 4b and other data not shown). For the 9 May cycle, hydrogen peroxide increased with the increase of Photosynthetically Available Radiation (PAR) in the local morning; and with a slight delay, hydrogen peroxide decreased with the decrease of PAR in the local afternoon. Although hydrogen peroxide appeared also to have covaried with PAR on both 25 and 29 May, this variation was superimposed on much larger temporal and spatial variations and was not very prominent (Figures 4c and 4d). In these diel cycles, the magnitude of the diel variations was $\sim$25 nmol dm^{-3}.

[18] The magnitude of our one clearly observed hydrogen peroxide diel cycle ($\sim$25 nmol dm^{-3}) was similar to those reported for several other oceanic regions. A diel cycle of $\sim$25 nmol dm^{-3} was observed on two studies of the Central and South Atlantic Ocean [*Yuan and Shiller*, 2001]. *Zika et al.* [1985] observed diel cycles of $\sim$25 and $\sim$40 nmol dm^{-3} in surface waters of two Gulf of Mexico stations. *Miller and Kester* [1994] revealed a diel cycle of $\sim$25 nmol dm^{-3} in surface waters of Sargasso Sea after removing a long term spatial trend. Recently, *Brooks Avery et al.* [2005] observed a diel cycle of 30 to 50 nmol dm^{-3} at the Bermuda Atlantic Time Series Station (BATS).

[19] As noted above, several processes can produce hydrogen peroxide in aquatic environments. These include photochemical activation of dissolved organic matter, biological activity, certain metal redox reactions, and wet deposition [*Cooper and Lean*, 1992]. For fresh and coastal waters, reported photo-production rates (>100 nmol dm^{-3} h^{-1}) are more than an order of magnitude higher than the production rates through other processes [*Abele-Oeschger et al.*, 1997; *Cooper and Zika*, 1983; *Cooper et al.*, 1988; *Draper and Crosby*, 1983; *Herut et al.*, 1998; *Moore et al.*, 1993; *Scully et al.*, 1996; *Zuo and Hoigne*, 1993]. Thus photochemical production appears to be dominant in fresh and coastal waters. For open ocean seawater, the reported rate of photo-production varies from 5 to 40 nmol dm^{-3} h^{-1} [*Moore et al.*, 1993; *Yocis et al.*, 2000; *Yuan and Shiller*, 2001; *Brooks Avery et al.*, 2005; this work], and is on the same level of the rate of biological production of $\sim$10 nmol dm^{-3} h^{-1} [*Palenik and Morel*, 1988] and possible wet deposition [*Yuan and Shiller*, 2000; *Yuan and Miller*, 2002].

[20] Apart from photo-production and biological production, there are two additional sources of hydrogen peroxide: abiotic chemical reactions and wet deposition. For abiotic chemical reactions,

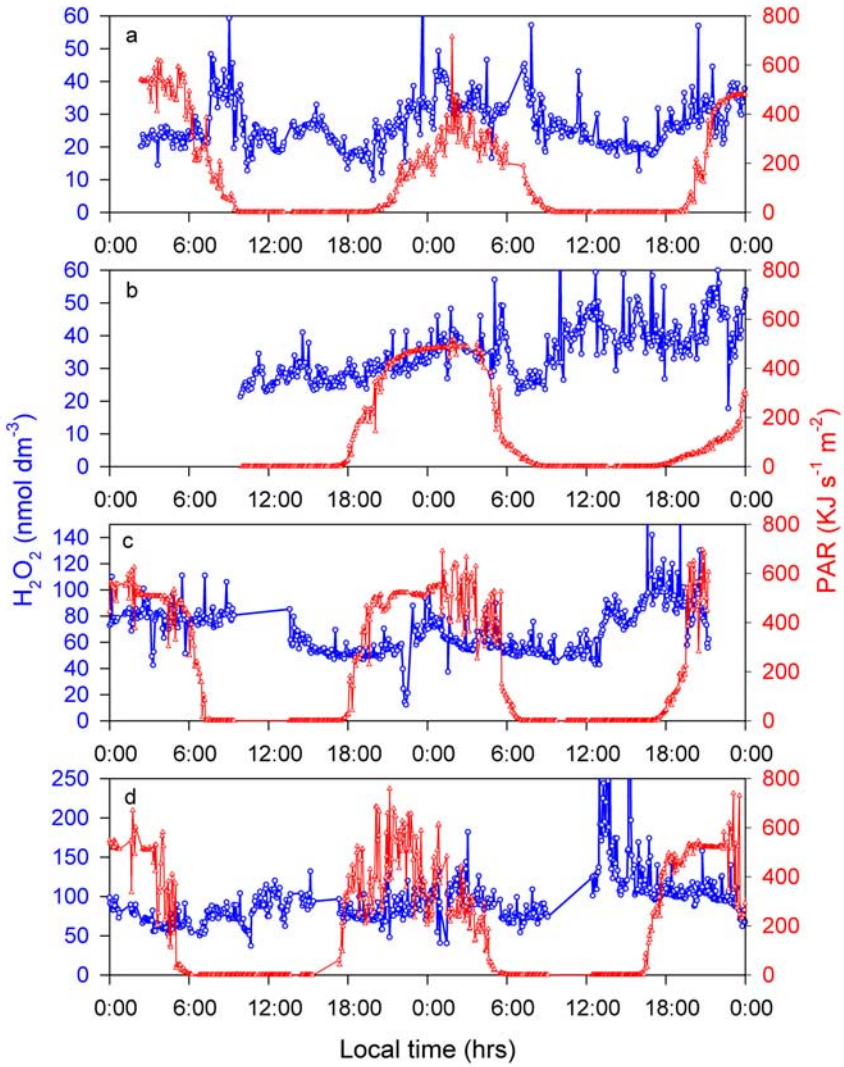

Figure 4. Variations of hydrogen peroxide in shallow waters (blue circles) and surface Photosynthetically Available Radiation (PAR, red triangles) for selected days: (a) 8 and 9 May, (b) 14 and 15 May, (c) 24 and 25 May, and (d) 28 and 29 May. Transect locations as shown in Figure 1.

the mechanisms as well as relative contributions to hydrogen peroxide production are poorly known. Input from rainfall is likely to be important only in selected regions (i.e., intertropical convergence zone, south Pacific convergence zone, and temperate wet regions) [*Yuan and Miller*, 2002] or immediately after a rainfall [*Yuan and Shiller*, 2000]. Recently, it has been shown that at some times wet deposition and at other times photo-production controls the hydrogen peroxide distribution at the Bermuda Atlantic Time series Study (BATS) station [*Brooks Avery et al.*, 2005]. When photo-production controls the hydrogen peroxide distribution, surface water diel cycles were observed [*Brooks Avery et al.*, 2005]. The fact that diel cycles were rarely observed on our cruise (despite mostly clear days) suggests that photo-production is not the dominant process affecting the cycling of hydrogen peroxide in surface waters of the North Pacific Ocean. Again, this is supported by our low observed photo-production rate relative to what little is known about biological and rain inputs.

3.4. Vertical Profiles of Hydrogen Peroxide

[21] A vertical profile of hydrogen peroxide was obtained at each of the stations during this cruise (Figures 5, 6, and 7). Reported hydrogen peroxide profiles can be classified into three categories: surface maximum, surface mixed, and subsurface

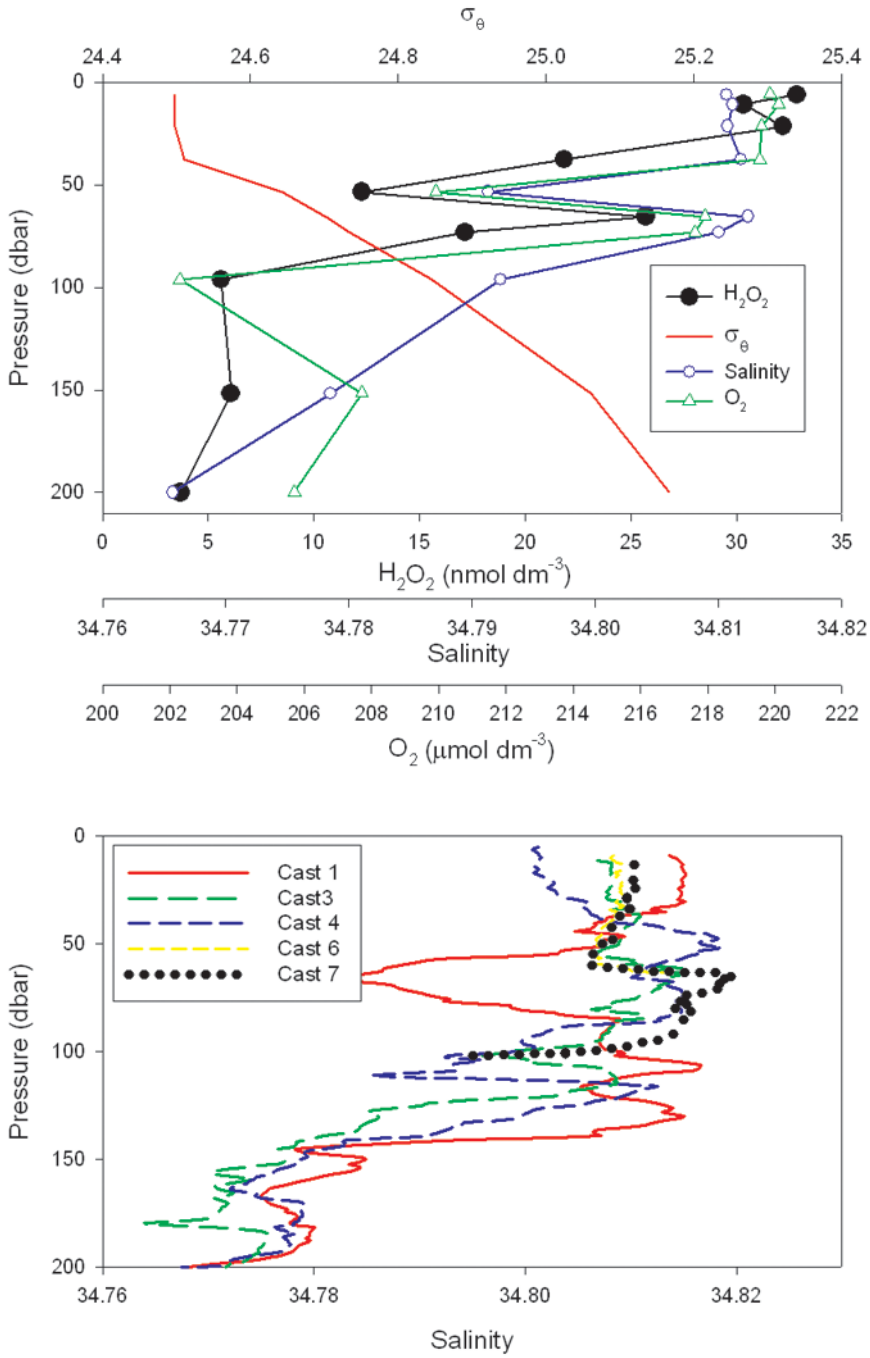

Figure 5. (top) Profiles of hydrogen peroxide (solid black circles), potential density (dotted red line), salinity (open blue circles), and dissolved oxygen (open green triangles) obtained at Station 1 Cast 1. (bottom) Profiles of salinity recorded by the CTD at the Station 1. These casts were conducted over the course of 14 hours on station.

maximum [*Yuan and Shiller*, 2001]. With the exception of station S1, the hydrogen peroxide profiles observed during this cruise were surface maximum profiles.

[22] At station S1 a subsurface maximum was observed (Figure 5, top). This station was nominally sited within the Kuroshio Current (Figure 1). Concurrent variations in bottle salinity and oxygen from the same cast (i.e., cast 1) suggest that the back-and-forth nature (interleaving) of this profile was a real feature (Figure 5). Interestingly, the CTD salinity profiles for the various bottle casts at this station showed great variability in the upper 200 m (Figure 5, bottom) indicating that this station was in a particularly dynamic region. Sim-

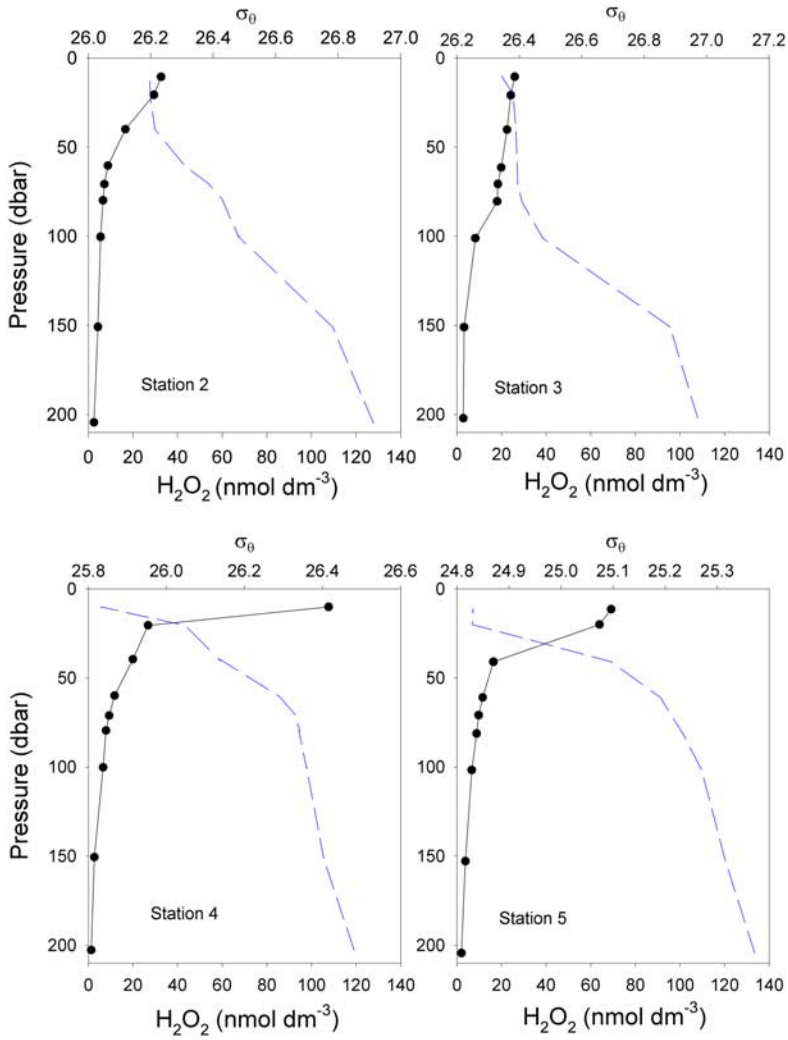

Figure 6. Profiles of hydrogen peroxide (solid line) and potential density (dotted line) at stations S2, S3, S4, and S5 in the North Pacific Ocean.

ilar interleaving of shallow waters has previously been reported at the Kuroshio Front [e.g., *Teague et al.*, 1994]. Because of the short life-time of hydrogen peroxide, the observation of concurrent hydrogen peroxide variation in this feature further emphasizes that the interleaving is occurring on short (less than a week) timescales.

[23] Surface maximum profiles were obtained at all the other stations (Figures 6 and 7). Although there was a well-developed mixed layer at some of these stations (S2, S3, S5, and S7), the concentration of hydrogen peroxide decreased gradually with the depth. At other stations (S4, S6, S8, and S9) where the mixed layer was not well developed, the concentration of hydrogen peroxide decreased more rapidly with the depth.

[24] There were large variations in shallow water concentrations of hydrogen peroxide between different stations (Figures 6 and 7). Low shallow water concentrations (~30 nmol dm^{-3}) were observed at stations S2 and S3, and high concentrations (>100 nmol dm^{-3}) were observed at stations S4 and S6. These concentrations are within the range of past observations of near surface hydrogen peroxide from other regions of the ocean [e.g., *Zika et al.*, 1985; *Johnson et al.*, 1989; *Moore et al.*, 1993; *Miller and Kester*, 1994; *Price et al.*, 1998; *Yuan and Shiller*, 2001]. Many of the higher oceanic concentrations reported in the past are from river plumes and coastal areas [e.g., *Zika et al.*, 1985; *Yuan and Shiller*, 2001] or regions with high wet deposition [*Brooks Avery et al.*, 2005]. All the stations

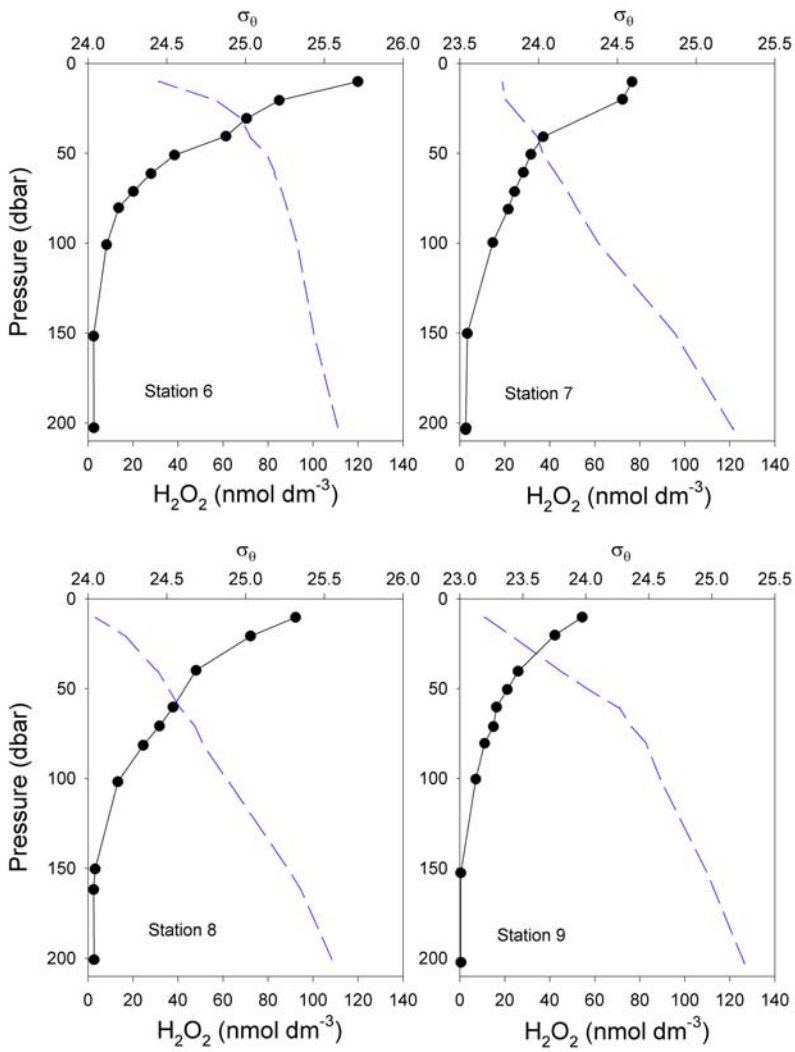

Figure 7. Profiles of hydrogen peroxide (solid line) and potential density (dotted line) at stations S6, S7, S8, and S9 in the North Pacific Ocean.

for this cruise were open ocean stations. At present there is no simple explanation for the variation in open ocean near-surface hydrogen peroxide concentrations. This is not surprising given the various factors that can affect these concentrations (e.g., sunlight, biological activity, horizontal advection, recent rainfall, and mixing with hydrogen peroxide-depleted waters from below).

3.5. Shallow Water Inventory of Hydrogen Peroxide

[25] Although the main sources of hydrogen peroxide, photo-production and wet deposition, tend to be most effective for surface waters, these processes can also affect the distribution of hydrogen peroxide in subsurface waters. First, light absorption (and therefore light penetration) can differ greatly in different aquatic environments [*Mobley*, 1994]; therefore photochemical production of hydrogen peroxide should extend to different depths accordingly. Additionally, photo-produced chemical species can be transported to different depths by vertical mixing [*Doney et al.*, 1995]. Consequently, vertical profiles of hydrogen peroxide can take different shapes [*Yuan and Shiller*, 2001]. To evaluate the effect of various photo and meteorological processes on shallow water hydrogen peroxide, the inventory of hydrogen peroxide needs to be calculated.

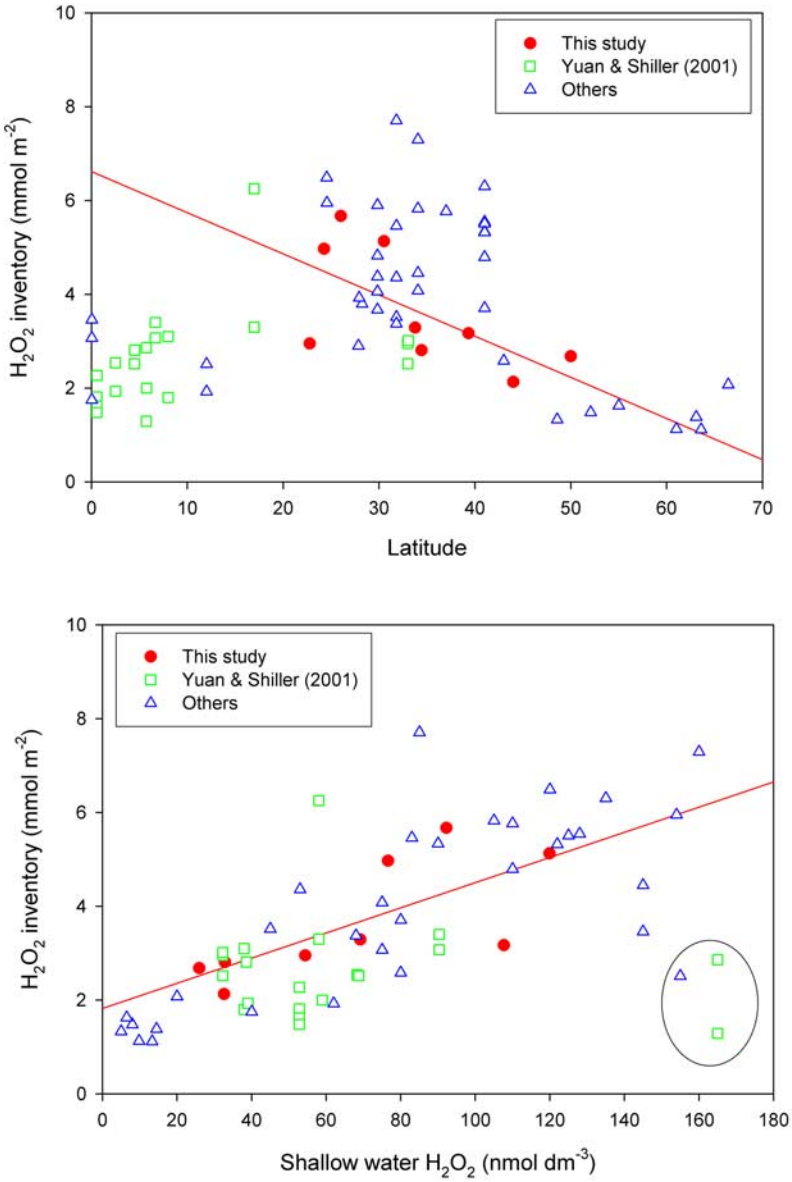

Figure 8. Variations of hydrogen peroxide inventory with the variation of (top) latitude and (bottom) hydrogen peroxide in shallow water. These graphs are based on three sets of data: this study (red circles), *Yuan and Shiller* [2001] (green squares), and others (blue triangles). The others include our integration of open ocean profiles reported by *Zika et al.* [1985], *Johnson et al.* [1989], *Moore et al.* [1993], *Miller and Kester* [1994], *Sarthou et al.* [1997], *Price et al.* [1998], *Hanson et al.* [2001], and *Brooks Avery et al.* [2005]. The profiles obtained in the Amazon [*Yuan and Shiller*, 2001] and Orinoco [*Moore et al.*, 1993] plumes are marked with an ellipse.

[26] The shallow (i.e., surface to 200 m) inventory of hydrogen peroxide varied from 2.1 to 5.7 mmol m^{-2} in the northwest Pacific Ocean (Table 1). Relatively high inventory of hydrogen peroxide (5.0 to 5.7 mmol m^{-2}) was observed at three stations (S6, S7, and S8), and relatively low inventory was observed at the other stations. The inventory of hydrogen peroxide of the northwest Pacific is within the range of previously reported hydrogen peroxide inventories [*Yuan and Shiller*, 2001].

[27] On the basis of a synthesis of previous studies, it appears that there is a maximum in the hydrogen peroxide inventory at midlatitudes (Figure 8, top). Seasonal bias in sampling does not appear to contribute to this trend. Because both solar radiation and wet deposition generally decrease toward

the pole from the middle latitudes [*Yuan and Miller*, 2002], the poleward hydrogen peroxide inventory decrease is understandable. However, the equatorward decrease of the hydrogen peroxide inventory is puzzling given that solar radiation, wet deposition, and biological production (i.e., the three main sources of hydrogen peroxide) all increase toward the equator. We speculate that there may be a general increase of the decay rate toward the equator due to the increase in temperature and biomass.

[28] On the basis of the data from the northwest Pacific stations, the water column inventory of hydrogen peroxide increases (P-value = 0.03) with increasing hydrogen peroxide concentrations in near surface waters (Figure 8, bottom). For every 10 nmol dm^{-3} increase of hydrogen peroxide in near surface waters, there is ~0.5 mmol m^{-2} increase of hydrogen peroxide inventory. An analysis of reported hydrogen peroxide profiles indicates that except for a few coastal ocean profiles (in the ellipse at low right side in Figure 8 bottom), the linear correlation between water column inventory and near surface water hydrogen peroxide appears to be a general trend. Near surface water concentrations of hydrogen peroxide can be determined at very high spatial resolution with towed continuous sampling device coupled with flow injection analysis systems [*Yuan and Shiller*, 1999]. Therefore the correlation between near surface water concentrations and its inventory can be useful for estimating the inventory of hydrogen peroxide.

4. Conclusions

[29] Surface water H_2O_2 was continuously determined on a cruise through the northwest Pacific Ocean. A diel cycle in H_2O_2 was generally not observed during the ~30-day study, suggesting that photo-production is not the dominant process controlling H_2O_2 distribution in these open ocean surface waters. The pseudo-first-order rate constant for dark decay varied from 0.1 to 0.2 d^{-1} and was observed to increase proportionately to the dissolved organic carbon concentration. The net photo-production determined on a clear day at S9 was 8 nmol dm^{-3} hr^{-1}. Because open ocean photo-production rates are similar to the reported dark biological H_2O_2 production rate [*Palenik and Morel*, 1988] and because rain input of H_2O_2 can also be occasionally important [*Cooper et al.*, 1987; *Yuan and Shiller*, 2000; *Brooks Avery et al.*, 2005], these processes can also affect the open ocean hydrogen peroxide distribution significantly. Hydrogen peroxide may therefore be less of an indicator of the photo-chemical reactivity of surface ocean waters than previously assumed. On the basis of this study and previous reports, the H_2O_2 inventory for the upper 200 m was found to vary linearly with the surface water H_2O_2 concentration, except in some coastal waters. Globally, the H_2O_2 inventory shows a maximum at midlatitudes. We suggest that this results from diminished inputs at high latitude as well as increased decay rates at low latitudes. Important questions for further study relating to H_2O_2 include the effect of temperature on dark decay rates, further determination of dark production rates and the factors influencing it, and the extent to which surface water H_2O_2 concentrations correlate with changes in the concentration or speciation of redox-sensitive metals such as iron.

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