rotation (the five rates of Table 1) can be directly tested for with the extensive series of solar surface maps in the light of H_α constructed by McIntosh (*19*). The published sequence (*19*) of maps, superposed at epochs of 27.3 days for the years 1965 to 1974, dramatically shows the persistence of large-scale patterns whose rotation periods can be accurately measured if they are in the approximate range of 23 to 32 days. There are 11 prominent cases where the rotation period is constant for at least 1 year. Of these, four cluster about a rotation period of 30.3 days with a 3% spread from lowest to highest, closely corresponding to the family $\ell = 4$ in Table 1. Six others form a broader cluster (6% spread) centered on a 27.8-day period, agreeing with *H* in Table 1. The eleventh period, at 32 days, was hardest to measure accurately and agreed with nothing in the model. Thus, these maps contain good evidence for at least two preferred longitudes simultaneously rotating at different, constant rates agreeing with theory. Replotting the maps at longer epochs would allow testing for the lower ℓ families.

In summary, global *r*-modes appear to have a strong influence on the outer layers of the sun. More than half the variance in irradiance at periods of 13 to 85 days could be attributed to *r*-mode families. Since only a single free parameter (ν_s) determines the value of all theoretical frequencies plotted on Fig. 2, the statistical significance of the agreement is rather high. This agreement confirms a preliminary detection (*14*) of two *r*-mode families in this century's sunspot area records. Also, evidence shows that *r*-modes with $\ell > 3$ cause persistent longitudes for large-scale surface features. By inference, *r*-modes have forced their periodicities onto convection, perhaps by assisting the initial growth. If this is true, a modification of convection theories on rotating bodies would be needed. If our identification of *r*-modes is correct, it determines a mean sidereal rotation rate for the sun's convective envelope of $\nu_s = 455 \pm 5$ nHz during the 3 years after 16 November 1978. This rate corresponds to a sidereal rotation period of 25.4 days (=27.3 days, synodic), and the above 1.1% uncertainty is the maximum deviation over which the agreement on Fig. 2 still holds.

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Correlation of Volcanic Activity with Sulfur Oxyanion Speciation in a Crater Lake

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The Yugama crater lake at Kusatsu-Shirane volcano, Japan, contains nearly 2200 tons (2800 parts per million) of polythionate ions ($S_nO_6^{2-}$, where $n = 4$ to 9). Analytical data on lake water sampled before and during eruptions in 1982 showed that the concentrations of polythionates decreased and sulfate increased in response to the preeruption activities of the subaqueous fumaroles. These changes were observed 2 months before the first phreatic explosion on 26 October 1982. The monitoring of polythionates and sulfate in crater lake water is a promising means of anticipating potential volcanic eruption hazards.

AS EMPHASIZED BY VERHOOGEN (*1*), it has been difficult to forecast volcanic eruptions because of many unknown factors controlling the time, place, and character of eruptions. Investigators have accumulated statistical records of volcanoes as well as their day-to-day vital signs in terms of earthquakes, surface deformation, temperature, and gas emissions. This report deals with dynamic formation and decomposition of sulfur oxyanions such as polythionates and sulfate ions in a crater lake in Japan. These anions exhibit sharp responses to the preeruption activities of the volcano. This reaction suggests that monitoring of the oxyanions can aid in forecasting possible volcanic hazards such as the disastrous mud streams that were triggered by a lake-bottom eruption, which killed more than 5000 people and damaged 104 villages, at Mount Kelud on Java Island in 1919 (*2*).

Kusatsu-Shirane is an active volcano located 153 km northwest of Tokyo. Many people visit the area for sight-seeing or skiing throughout the year. The volcano has three active craters, Mizugama, Yugama, and Karagama, from northeast to southwest (Fig. 1). A sequence of phreatic explosions at these craters has been recorded since 1805 (*3–5*). The central crater, Yugama, contains a lake, which has an average diameter of 270 m and is 27 m at the deepest point. Almost no vertical temperature variation was noted in the lake water (*6*). Molten sulfur was found at subaqueous fumarole vents where volcanic gases are violently discharged. The bottom temperatures at these gas vents have therefore exceeded 116°C (maximum observed temperature was 140°C) (*7*).

The lake water contains a variety of salts, fine particles of sulfur, and hydrochloric and sulfuric acids whose total acidity is almost 0.1*M* (Table 1). Major anions that have been detected in the water include chloride and sulfate. In analyses of the lake water, unidentified sulfur-containing anions have been expressed as equivalent to total sulfate after oxidation by hydrogen peroxide. Data for no. 1 of Table 1 show such an analysis with total equivalent sulfate (*8*).

In order to identify unknown sulfur compounds in the crater water, the water was analyzed by liquid chromatographic techniques. Detailed analytical conditions are described in the legend of Fig. 2. All the water analyzed was sampled at the fixed site on the lake shore without any pretreatment. No distinct difference in concentrations of the oxyanions has been detected among the samples taken at four to six other sites along the lake shore, but slightly higher concentrations of sulfur oxyanions were observed

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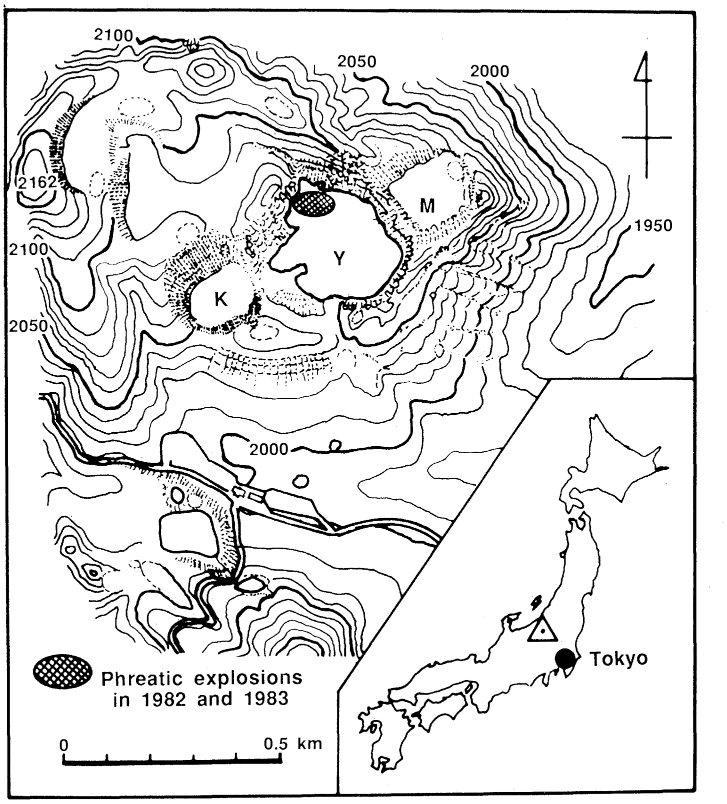

Fig. 1. Topographic map of Kusatsu-Shirane volcano. K, M, and Y indicate the craters Karagama, Mizugama, and Yugama, respectively. Since 1805, 15 phreatic explosions around the craters have been recorded. Yugama crater lake contains several effervescent zones (six occurred in October 1982). Temperatures of the surface water at periods of repose range from 0°C in winter to 18°C in summer.

around an effervescent zone on the lake. The containers for the water samples were thick-walled 250- to 1000-ml polyethylene bottles with tightly sealed lids. They were stored in a cabinet at room temperature after the samples were taken.

Determination of the oxyanions in the crater lake water began on 10 August 1984. Since then the acidic (*p*H 1 to 1.5) samples listed in Table 1 showed no serious decomposition of polythionates during the periodic redeterminations (*9*). It was also found that a 0.1*M* hydrochloric acid solution of synthesized polythionates that was kept in a volumetric flask for more than 2 years showed almost no change in concentration ($S_4O_6^{2-}$ was 520 and 444 ppm, and $S_5O_6^{2-}$ was 305 and 304 ppm on 11 August 1984 and 11 July 1986, respectively). The samples taken before 1982 would not contain less polythionate than those shown in Table 1 because polythionates do not form again once they have decomposed to elemental sulfur and sulfate in the container. No thiosulfate and sulfite ions except polythionates were detected in the lake water beyond the detection limit of the methods (10 ppm for both ions). This finding was also confirmed by microbore high-performance liquid chromatography (HPLC) with an ultraviolet (UV) detector.

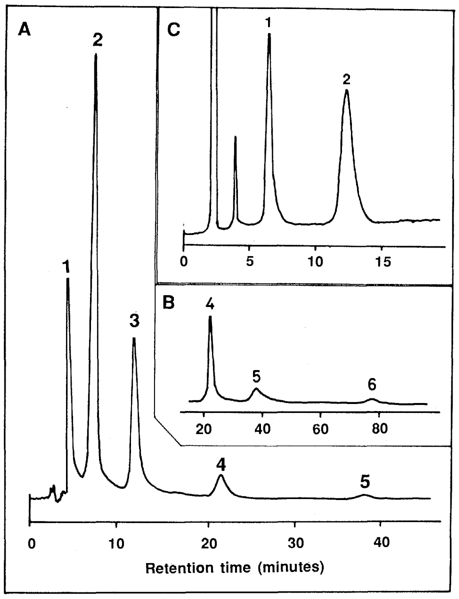

Fig. 2. Microbore column HPLC (A and B) and ion chromatogram (C) of the Yugama crater lake water. (**A**) Column Spherisorb ODS, 1 by 100 mm; particle size, 3 μm; temperature, 30°C; mobile phase CH_3CN/aqueous phase is 3/7 (v/v); aqueous phase is 0.1*M* KH_2PO_4 + 0.1% tetrabutylammonium hydroxide (TBAOH) (v/v) (*p*H = 3.5); flow rate, 25 μl/min; UV detector at 220 nm; peaks are as follows: 1, $S_4O_6^{2-}$; 2, $S_5O_6^{2-}$; 3, $S_6O_6^{2-}$; 4, $S_7O_6^{2-}$; and 5, $S_8O_6^{2-}$. (**B**) Extended chromatogram of (A); peak 6, $S_9O_6^{2-}$. (**C**) Column Shodex IC I-613, 6 by 150 mm; mobile phase is 1 m*M* phthalic acid + 0.5 m*M* TBAOH + 3.3% tetrahydrofuran (v/v) (*p*H = 3.5); flow rate, 1.5 ml/min; peaks are as follows: 1, $S_4O_6^{2-}$; and 2, $S_5O_6^{2-}$.

The chromatograms obtained by the microbore HPLC and ion chromatographic techniques used in this study are shown in Fig. 2. Both tetrathionate ($S_4O_6^{2-}$) and pentathionate ($S_5O_6^{2-}$) were clearly identified in the ion chromatogram (Fig. 2C). Hexathionate was detected by HPLC together with tetra- and pentathionates (Fig. 2A). Further scrutiny of the microbore HPLC chromatograms revealed that other, higher homologs of polythionates above hexathionate may be present. As shown in Fig. 2B, some minor UV-absorbing substances were eluted out after hexathionate. Indirect evidence showed that they may be hepta- ($S_7O_6^{2-}$), octa- ($S_8O_6^{2-}$), and nona- ($S_9O_6^{2-}$) thionates (*10*).

The polythionates in this volcanic water system are known as the minor constituents of Wackenroder's solution, which is prepared by passing hydrogen sulfide slowly and intermittently into a solution of sulfurous acid over a period of days (*11*). Yugama crater, from the floor of which hydrogen sulfide and sulfur dioxide gases (gas composition collected from samples at one of the effervescent zones of the lake: CO_2, 40.3%; H_2S, 0.59%; SO_2, 0.44%) are being actively released (*12*), could be described as a huge reaction vessel for preparing a "natural" Wackenroder's solution. By using complicated classical techniques of wet chemical analysis, MacLaurin claimed that pentathionate was detected in the water from a lake on White Island, New Zealand, the island being the summit of an active volcano (*13*). That claim was the first but partial confirmation of polythionates in volcanic water.

Since 1959, when the most recent eruption was recorded at Yugama crater, no conspicuous volcanic activity had been observed except for a small steam eruption at the adjacent crater, Mizugama. However, on 26 October 1982, the north portion of Yugama crater exploded suddenly (hatched area in Fig. 1). At least 2 months before the explosion (26 August 1982), the levels of polythionates in the lake water fell below the analytical detection limit (Table 1). Analyses of the waters sampled at regular intervals during intense fumarole emissions and ash deposition in 1982 and 1983 after the first explosion showed that the level of polythionates varied frequently, responding to the volcanic activities (which included four eruptions and swarming earthquakes with no eruption) at the bottom of the crater lake (Table 1). Several people witnessed the ejection of water columns rising a few meters above the surface of the lake in late October 1982. Without doubt, polythionates had been degraded almost completely by the increasing volcanic activities at the lake floor just before the explosion. Polythionate degradation yielded elemental sulfur and sulfate ions as products in the lake water. Even though the reactions responsible for yielding such sulfur species are more complicated than the following equations, they can be summarized as follows:

$$SO_2 + H_2O \rightarrow HSO_3^- + H^+ \qquad (1)$$

$$S_nO_6^{2-} + (3n - 7)HSO_3^- \rightarrow (2n - 3)SO_4^{2-} + (2n - 4)S + (n - 1)H^+ + (n - 3)H_2O \qquad (2)$$

where $n > 3$. These reactions illustrate the sulfitolysis of polythionates (*14*), which is followed by disintegration of resulting sulfur oxyanions. As expected from Eq. 2, a rapid increase in sulfate was observed in the crater water when polythionates disappeared from the solution (nos. 5, 6, and 8 in Table 1). Moreover, SO_2 gas that was intentionally bubbled into the Yugama water sample ($S_4O_6^{2-}$ at 950 ppm; $S_5O_6^{2-}$ at 1430 ppm; and $S_6O_6^{2-}$ at 490 ppm) almost completely decomposed the polythionates within 30 hours at room temperature (*15*). Therefore, as illustrated by Eqs. 1 and 2, increasing SO_2/H_2S ratio of the fumarole gases is likely to be the most probable factor controlling the level of $S_nO_6^{2-}$ in the lake water.

Magmatic gas of usually high SO_2 and HCl content may be responsible directly for the increase in the value of the SO_2/H_2S ratio, but it is ruled out for the Kusatsu-Shirane volcano because the level of chloride ions in the lake water was virtually constant during the explosion and also because measurements at the fumaroles around the lake showed low temperatures (less than 100°C) and high water concentrations (98%) (*16*). Magmatic resurgence, however, could be the case for other volcanic lake systems. The rate of fumarolic gas release also may change the sulfur oxyanion chemistry of the lake water because SO_2 is more soluble than H_2S, resulting in an increase in the SO_2/H_2S ratio of the water. Change in the gas release rate beneath the volcanic lake is ordinarily linked to the change in gas temperature. Increase in the gas temperature is one of the major signs of increasing volcanic activities. This increase causes a suspected increase in the value of the SO_2/H_2S ratio in the fumarole gases before the explosion through, for example, the rapid shift of the following reaction to the right (*17*):

$$H_2S + 2H_2O = SO_2 + 3H_2 \qquad (3)$$

At some volcanoes, impending magmatic activities may be associated with the release of substantially more hydrogen sulfide (*18*) than sulfur dioxide. If such a gas release occurs beneath a crater lake, the level of polythionates is likely to increase. An increase in polythionates from 225 to 1250 ppm and ensuing swarms of volcanic earthquakes were observed at the Kusatsu-Shirane volcano when hydrogen sulfide from the submerged fumaroles increased in May 1986. Therefore, a rapid increase in the polythionate content of crater lake water may also be connected with increasing volcanic activity.

The effect of the ephemeral rise in water temperature on the degradation of polythionates during the explosion would be small: the half-life of tetra- and pentathionates is about 20 days at 60°C (*15*), and hot water (55°C) erupting from newly opened explosion vents in the walls of the crater raised the lake surface by 1 m, below which the water remained near 25°C (*5*). Three days later the hot water flowed back into the same vent, as in the draining back of basaltic lava observed in the Kilauea Iki crater, Hawaii (*19*). The climatic effects (dilution by precipitation or concentration by evaporation) on the water compositions can be removed by monitoring the variations relative to chloride ions: the 1982 and 1983 eruptions added no substantial amount of chloride to the lake water.

In conclusion, the variation in the concentration levels of polythionates and sulfate ions, observed in the Yugama crater lake water, is likely to be a sensitive indicator of impending disastrous activity in volcanoes with crater lakes in the region of the Ring of Fire around the Pacific Ocean, for example, at Kawah Idjen and Kelud in Java, Indonesia (*20*), Taal in Luzon, Philippines (*21*), Ruapehu in New Zealand (*22*), Poás in Costa Rica (*22*), and El Chichón, in Mexico (*23*). The method proposed in this report is a type of volcanic gas monitoring, with techniques much simpler and easier than direct fumarole gas monitoring for both sampling and analyzing collected samples.

Table 1. Analytical results (in milligrams per liter) of the Yugama crater lake water at Kusatsu-Shirane volcano, Japan.

No.*	*p*H	Na^+	K^+	Mg^{2+}	Ca^{2+}	Fe^{2+}	Al^{3+}	Cl^-	SO_4^{2-}	$S_4O_6^{2-}$†	$S_5O_6^{2-}$†	$S_6O_6^{2-}$‡
1	1.0	58	22		255	320		5010	5349			
2	1.0	20	16	16	173	150	171	4010	3770	880	1510	430
3	1.1	16	12	10	110	100	116	2820	2550	1260	1060	520
4	1.4	12	11	7.4	83	113	111	1960	1900	640	710	
5	1.3	12	11	6.6	98	113	105	1940	4130	<10	<10	<1
6	1.3	30	24	36	413	147	131	2120	5730	<10	<10	<1
7	1.5			46	458		203	1970	3160	170	440	
8	1.5			40	419		186	1880	3940	<10	<10	
9	1.5	50	21	67	440	204	219	1820	2450	140	180	45
10	1.5							2060	2770	52	106	52

*Results were sampled (S) and determined (D) as follows: 1. Data from (*8*); S, 17 December 1949. 2. S, 23 October 1969; D, 7 September 1984. 3. S, 7 October 1977; D, 11 August 1984. 4. S, 14 October 1981; D, 15 August 1984. 5. S, 26 August 1982; D, 7 November 1984. 6. S, 27 October 1982, a day after the first phreatic explosion started; D, 7 November 1984. 7. S, 31 July 1983; D, 7 November 1984. 8. S, 29 October 1983; D, 7 November 1984. 9. S, 19 July 1985; D, 22 July 1985. 10. S, 2 March 1986; D, 5 March 1986. †By ion chromatography. ‡By microbore column HPLC, using a UV detector.

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