Reports

Deep-Seated Gas Emission Induced by the Earth Tide: A Basic Observation for Geochemical Earthquake Prediction

Abstract. Variations of the helium/argon ratio of gas bubbles in a mineral spring along a fault zone coincide with fluctuations of areal dilation induced by the earth tide. This observation suggests that deep-seated gases characterized by higher helium/argon ratios are squeezed out by stress preceding an earthquake.

Geochemical parameters of ground water have attracted considerable attention in studies of seismic phenomena. A change in radon content was observed before the 1966 Tashkent earthquake (1). Other observations of this kind in various countries have been published. These empirical studies inferred that fluids such as radon and helium in the ground are expelled before earthquakes by stresses at depth. Significant amounts of hydrogen were observed in soil gas collected along active faults and were discussed in relation to fault activity (2). However, little evidence directly connecting stress with gas quality change has been reported. Such evidence could provide a sound basis for identifying geochemical earthquake precursors.

I have pointed out (3) the utility of the He/Ar ratio in fault gas for earthquake prediction and observed some correlation between earthquakes and changes in this ratio. As a geochemical parameter the He/Ar ratio has several advantages: (i) its value in lithospheric gas (~ 10) is 2×10^5 times higher than that in the atmosphere (6×10^{-5}) and hence it can be used to measure the emission of lithospheric gas from depth, (ii) it does not

change through such processes as dilution by other gases, and (iii) it can be rapidly measured with a gas chromatograph. In the work reported here, I used this parameter to examine the possibility that lithospheric gas can be driven by stress at depth.

Fluctuations of the ground water level caused by ocean tides, earthquakes, passing trains, and other sources of stress in the ground were observed as early as the beginning of this century. Earth tides produced by the attraction of the moon and the sun also cause water level fluctuations in wells (4); the tidal attraction allows a slight dilation of the aquifer, which in turn reduces the pressure and causes the water in the well to drop. Likewise, one could expect the ground water in fissures and crystal boundaries of minerals to be squeezed out by stress in the ground. If this occurs, the gas dissolved in the waters of deeper origin should have a higher He/Ar ratio and the alternate compression and expansion of the crust produced by the earth tide would cause a periodic variation of the ratio.

To test this inference, I made a series of measurements of the He/Ar ratio of



Fig. 1. Location map showing the observation point and other areas. By. fault represents Byobu-San fault; CMO denotes the site of the Inuyama Crustal Movement Observatory, where the extensometer data were obtained. Dashed lines represent the main active faults in central Japan.

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gas bubbles in the mineral water at Byakko Spa, Mizunami, Japan. This mineral spring is located along an active fault, the Byobu-San fault, which crosses an area of thin Miocene sediments and underlying granites (Fig. 1). The mineral water and gas bubbles issue from many locations at the bottom of a pond about 100 m^2 in area; the flow rate cannot be accurately measured but is estimated as 0.4 ton/min. Water temperature remains constant at 25°C. The mineral water contains radon (as much as 30×10^{-10} Ci/ liter) and the gas bubbles contain helium (up to 840 ppm). This indicates emission of lithospheric gas produced from radioactive elements in the ground.

Gas was collected and analyzed every 3 hours. A funnel 1 m in diameter was placed upside down on a part of the bottom from which many bubbles were issuing. Gas samples were collected from the tube of the funnel and analyzed by gas chromatography according to the following procedure (5). Tank oxygen was used as the carrier gas. Helium, argon, nitrogen, and methane were separated with a molecular sieve 5A column, 4 m long, at 35°C; the four peaks representing these gases appeared on a recorder chart and the relative areas under the peaks indicated the relative volumes of the gases in the sample. The ratios of these gases were determined by use of a composite gas reference standard under the same conditions. The standard deviation of repeated measurements of one sample was less than 1 percent.

The measurements showed a periodic variation of the He/Ar ratio. The causes of this change were examined. (i) Since the distance from this pond to the ocean is about 60 km and the altitude of the pond is 190 m (Fig. 1), there should be no connection between ocean water and the mineral water: hence the variation of the ratio cannot be caused by the ocean tide. (ii) A variation of 1°C in the temperature of the mineral water corresponds to a change of only 0.002 in the He/Ar ratio of the bubbling gas; since the water temperature remains constant at 25°C, the observed variation of 0.12 to 0.15 is too large to be attributed to any change in the water temperature. (iii) A comparison of the variation of strain in the ground resulting from the earth tide with the observed fluctuation of the ratio shows a good correlation between the strain variation and the ratio fluctuation.

The temporal variation at this location $(137^{\circ}17'16''E, 35^{\circ}23'47''N;$ elevation, 190 m) predicted for a laterally homogeneous solid earth was computed from published formulas (6). Since actual tidal data are sometimes different from theoretical val-

ues owing to crustal inhomogeneity, the tidal strain computed for this location was compared with extensometer data from the Inuyama Crustal Movement Observatory, Nagoya University, which is about 21 km west (Fig. 1). As shown in Fig. 2, the theoretical and observed wave forms are similar, although the amplitudes are not identical. The theoretical curve does, therefore, represent relative variations of the actual tidal strain.

When the observed He/Ar ratio of the gas is compared with the theoretical tidal strain expressed as areal dilation, the period of the variation of the ratio coincides with that of the strain, but the phase of the former is somewhat delayed. If the curve for the gas is moved forward about 4 hours, both curves coincide fairly well (Fig. 3). Figure 3 represents observations made in two different seasons. If the ratio variation were diurnal, the phases of the curves obtained for different seasons would coincide. As shown in Fig. 3, the phases observed in August and December do not coincide.

Figure 3 also shows the variations of atmospheric pressure and temperature. In August each maximum of the atmospheric temperature curve appears to correspond to a minimum of the He/Ar curve. In December, however, the temperature variation is not correlated with the ratio variation. The well-known fluctuation of atmospheric pressure influenced by the earth tide also appears in Fig. 3. In December each minimum pressure approximately corresponds to each maximum ratio, while in August there is no correlation between them. Thus Fig. 3 shows that the fluctuation of the He/Ar ratio is more closely related to the tidal strain than to atmospheric pressure and temperature.

Several aspects of Fig. 3 are related to the emission of lithospheric gas from depth. The He/Ar ratio increases at the time of tidal compression with a phase lag. Because the He/Ar ratio of lithospheric gas is high at this site, we can infer that the gas dissolved in mineral water at depth is squeezed out of fissures under the tidal compression and rises to the surface through the fault zone. Laboratory studies showed that He is expelled more easily than Ar on fracture of rocks (7). This behavior of He and Ar may make the ratio even higher in gas from greater depths. The gas dissolved in the deep water separates from the water as bubbles near the surface. As the compressive stress decreases, the partial pressure of lithospheric gas in the mineral water becomes lower and air (with a lower He/Ar ratio) contaminates the 12 JUNE 1981



bubbles. This interpretation of the fluctuation of gas quality resembles that of the level of ground water, but the time of maximum emission of lithospheric gas appears somewhat later than the time of maximum compressive stress. This suggests that it takes some time for the lithospheric gas in mineral water at depth Fig. 2. Comparison of the observed strain records measured with the extensioneter at Inuyama with the theoretical tidal strain at Byakko Spa; *Cont.* and *Ext.* represent contraction and extension, respectively.

to travel through fissures and reach the surface. It also implies that the bubbles in mineral water gather gas from a voluminous rock body at depth (8).

The strain produced by the earth tide amounts to only about 10^{-7} , whereas the ultimate crustal strain resulting in an earthquake is estimated to be about 10^{-5} (9). The observations at Byakko Spa show that the He/Ar ratio in fault gas is affected by tidal strains much smaller than the crustal strains that cause earthquakes. The He/Ar ratio of fault gas can thus be used as a strain gauge for the



Fig. 3. Observed variation of the He/Ar ratio and related geophysical data. (Circles) Fluctuation of the He/Ar ratio in gas bubbles in the mineral spring water at Byakko Spa; (dotted curve) theoretical tidal strain expressed as areal dilation; (solid curve) fluctuation of atmospheric pressure; and (dashed curve) fluctuation of atmospheric temperature. All are shown for (a) August 1979 and (b) December 1979.

crust. Continuous observation of gas quality at a location geochemically sensitive to stresses at depth could therefore be meaningful for earthquake prediction. **Ryuichi Sugisaki**

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References and Notes

- M. A. Sdovsky, I. L. Nesesov, S. K. Nigatul-laev, L. A. Latynina, A. A. Lukk, A. M. Semenov, I. G. Simbireva, V. I. Ulmov, *Tecton-ophysics* 14, 295 (1972).
 R. Sugisaki, H. Anno, M. Adachi, H. Ui, *Geo-chem. J.* 14, 101 (1980); H. Wakita, Y. Naka-mura, I. Kita, N. Fujii, K. Notsu, *Science* 210, 188 (1980)
- 188 (1980)
- 3. R. Sugisaki, Nature (London) 275, 209 (1978).

- 4. T. W. Robinson, Trans. Am. Geophys. Union Y. W. Roomson, Trans. Am. Geophys. Union 20, 656 (1939).
 R. Sugisaki, Bull. Am. Assoc. Pet. Geol. 48, 85
- K. Sugisaki, Bull. Am. Assoc. Per. Geol. 40, 85 (1964).
 I. M. Longman, J. Geophys. Res. 64, 235 (1959); T. Mikumo and M. Kato, Disaster Prev. Res. Inst. Kyoto Univ. Bull. 26, 71 (1976).
 K. Honda, K. Kurita, Y. Hamano, Abstr. Pap. Geochem. Soc. 152 (1979).
- According to H. Yamamoto and A. Masuda (in preparation), rare earth elements in the mineral water show an La-depleted pattern normalized by chondrite. This suggests that the water originates at depth. T. Rikitake, Tectonophysics 26, 1 (1975)
- I am grateful to A. Yamamoto for providing the computer program for calculating the earth tide, to R. Shichi and M. Furumoto for providing extensometer data at Inuyama and for valuable comments, and to Y. Isobe for technical assistance

15 December 1980

and less sensitive to the fluorescence free in solution resulting from the unbound tagged molecules and the natural fluorescence of the specimen.

Consider a homogeneous sample with two fluorescent species: one consists of free molecules, each with one unit of fluorescence, and the other suspended beads, with n units of fluorescence (ntagged molecules bound to the bead). If the average fluorescent free molecules and beads per sampling volume are $N_{\rm f}$ and $N_{\rm b}$, respectively, the contribution to S from each species (2) is given by

 $S = S_{\rm f} + S_{\rm h}$

and *i* a constant having the units of

intensity. The average fluorescent inten-

sities from each of the two species are

 $I_{\rm f} = iN_{\rm f}$

 $I_{\rm b} = iN_{\rm b}n$

 $I = I_{\rm f} + I_{\rm b}$

In this model we have assumed that the

fluorescent efficiencies of bound and un-

Under appropriate conditions there

are two reasons why S is dominated by

 $S_{\rm b}$. First, bright fluorescent objects con-

tribute more strongly to S than they do to

I. This is seen by forming the following

 $\frac{S_{\rm b}}{S_{\rm f}} = \frac{N_{\rm b}n^2}{N_{\rm f}} = \left(\frac{I_{\rm b}}{I_{\rm f}}\right) \quad n$

From Eq. 5 we see that if n is large

enough, it is possible for $S_{\rm b} \gg S_{\rm f}$ even

with $I_f > I_b$. For example, suppose the

bead structure and reagent concentra-

tions are such that an assay is performed

with *n* varying between 10^3 and 10^4 . To

determine S_b with 1 percent accuracy

from a measurement of S, we want

 $S_{\rm b}/S_{\rm f} \ge 100$. From Eq. 5 we see that at the low end in the range of n, we would

The second reason for the relative

insensitivity of S to the free fluorescence

is the relative diffusion rates of large and

small particles. Since the fluorescent in-

tensity fluctuations are due to particle

number fluctuations, these fluctuations

come and go as the particles diffuse in

and out of the sampling volume. Because

large particles diffuse slowly, large-parti-

thus contribute more strongly to the cor-

still be able to tolerate $I_{\rm f} = 10 I_{\rm b}$.

bound molecules are equal.

ratios from Eqs. 1 and 3,

 $\frac{I_{\rm b}}{I_{\rm f}} = \frac{N_{\rm b}n}{N_{\rm f}}$

$$S_{\rm f} = i^2 N_{\rm f}$$
$$S_{\rm b} = i^2 N_{\rm b} n^2 \qquad (1)$$

(2)

(3)

(4)

(5)

with

with

Abstract. A fluorescent immunoassay based on the correlation of fluctuations in particle number measures the amount of tagged species bound to micrometer-sized beads and is insensitive to background fluorescence. Without separation steps, a competitive assay can resolve 1 nanogram of gentamicin per milliliter from a total sample volume of only 10 microliters.

New trends in instrumentation in clinical chemistry (1), such as automated immunoassays, are simplifying clinical procedures. An example is an immunoassay that works with homogeneous samples; the technique does not require the separation of bound from free unknown and is insensitive to background sources naturally present in the sample. We developed a fluorescent immunoassay (2) and report data that demonstrate the sensitivity of this assay without the conventional separation steps.

The fluorescence from a small sampling volume (~ 10^{-6} ml) is detected by a photomultiplier. The detected signal fluctuates in time because of fluctuations in the number of fluorescent particles in the sampling volume. A microprocessor calculates the temporal autocorrelation function of this fluctuating signal. To improve the sampling statistics, the sampling volume is periodically scanned through the specimen, and the microprocessor computes the correlation function at a time equal to the scanning period. This ensures that each sampling volume is periodically measured with the same period for all sampling volumes. Fluctuations in the detected signal that are not correlated over this scanning period contribute only to the baseline of the correlation function. However, a fluctuation in the signal from a specific sampling volume due to a fluctuation in fluorescent particle numbers that persists beyond the scanning period drives the correlation function above its baseline. The microprocessor determines the correlation peak height S above the baseline averaged over the number of sampling intervals.

In the competitive assay the unknown (U) competes with a tagged mimic (U^*) for a limited number of binding sites (\tilde{U}) that are attached to beads suspended in the sample. Our technique is not limited to such competitive assays. For example, a sandwich assay is possible in which the complexes \overline{U}^* -U- \overline{U} are formed on the bead. The usual procedure would be to separate out the beads by centrifugation and measure the bead fluorescence. To eliminate the separation steps requires a measurement highly sensitive to the fluorescence bound to beads



Fig. 1. The correlation peak height S in arbitrary units is plotted as a function of $I_{\rm b}/I_{\rm f}$ for Dow fluorescent spheres plus rhodamine. If S were sensitive to the rhodamine in the measured range of $I_{\rm b}/I_{\rm f}$, S would deviate from the 45° diagonal and settle to a constant value determined by the fixed concentration of rhodamine.

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