On the CO$_2$-bubbling extraction of dissolved He, Ne, H$_2$, Ar, N$_2$ and CH$_4$ in waters for their gas chromatographic determinations

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ABSTRACT

The CO$_2$-bubbling method for extracting gases dissolved in water samples has been reexamined in order to apply it to monitoring of dissolved gases in groundwaters. Dissolved He, Ne, Ar and N$_2$ in water equilibrated with the atmospheric air in a temperature range of 13–31°C were extracted by the method, and gas chromatographically determined. The measured values for dissolved atmospheric He, Ne, Ar and N$_2$ show temperature variations in parallel with the calculated ones from their solubilities, but they are systematically higher than the calculated values by 18% for He, 11% for Ne, 6% for Ar and 8% for N$_2$. Although the CO$_2$-bubbling method is effective and convenient for extracting the dissolved gases in the field, appreciable amounts of blanks are associated with it. The blank sources of He, Ne, Ar and N$_2$ are the dissolved air in HCl and NaOH solutions used in the method and the direct air contamination. The extracted gas by the method contains H$_2$ and CH$_4$ from fluid inclusions of the marble dissolved in the extraction process to generate CO$_2$ for stripping. The blank H$_2$ and CH$_4$ depend on the nature of inclusions in the used marble and on the amount of the marble dissolved. We also found that the fine marble grains and particles formed by crushing and grinding retain significant amounts of tribochemically produced H$_2$. Such fine marble grains and particles should be removed completely from granular marble used in the extraction. When the CO$_2$-bubbling extraction is applied to routine analyses of dissolved gases in groundwaters, it is important to minimize such blank gases and to make reliable corrections for them.

INTRODUCTION

The CO$_2$-bubbling extraction of dissolved gases in water samples is a convenient method for collecting dissolved gases of N$_2$, O$_2$, Ar, He, H$_2$ and CH$_4$ in field and laboratory (Sugawara et al., 1937; Oana, 1957; Sugisaki, 1961; Koyama

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and Tomino, 1967; Motojima et al., 1973). We have intended to use the CO_2-bubbling method for seismo-geochemical monitoring of dissolved gas compositions in artesian groundwaters from deep bore-hole wells (Kawabe, 1984/85, 1987). This extraction method does not need any vacuum lines or tank gas for stripping. The apparatus consists of only several glass wares that can easily be assembled even in the field (Fig. 1). This feature is suitable for our
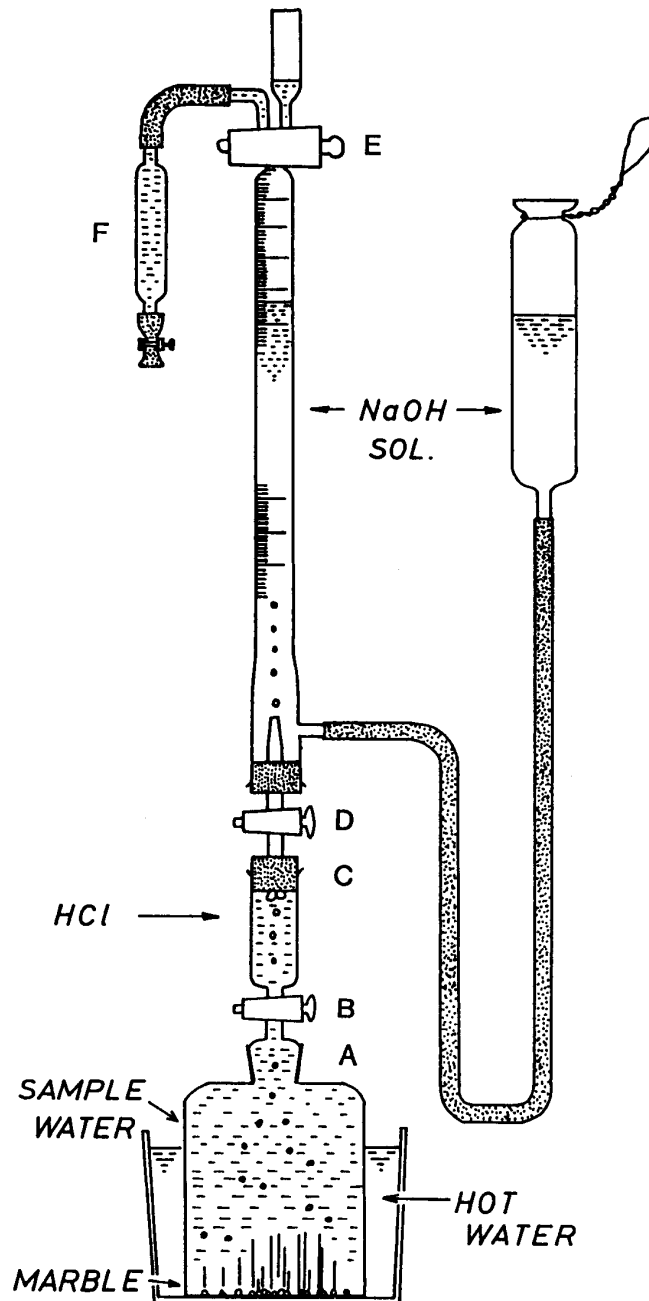

Fig. 1.   The apparatus for extraction of dissolved gases in water by the CO_2-bubbling method. A: a sample bottle, B: a stopcock with a funnel, C and D: a joint with a stopcock, E: a stopcock of a gas burette, and F: a glass sample tube.

purpose. We have reported gas chromatographic determinations of atmospheric He, Ne and H$_2$ without any pre-purification and enrichment procedures (Kawabe et al., 1985). Hence the CO$_2$-bubbling extraction enables us to analyze gas chromatographically He, Ne and H$_2$ dissolved in water as well as Ar, N$_2$ and CH$_4$. This is a simple and inexpensive method for analyzing dissolved gases, unlike the other methods including mass-spectroscopic ones.

Despite the simplicity of the CO$_2$-bubbling extraction, however, the solutions of HCl and NaOH and marble for producing CO$_2$ used in it are potential sources of blank gases. Little attention has been paid on this point previously, in particular, for the cases of He, Ne, H$_2$ and CH$_4$ analyses. We have gas chromatographically determined He, H$_2$, Ne, Ar and N$_2$ in the extracted gas from water equilibrated with the atmospheric air at temperatures of 13 to 31°C by this method. The measured values were compared with calculated ones from the Bunsen solubility coefficients for He, Ne, Ar and N$_2$ in water and their atomospheric abundances. We have also examined possible effects due to CH$_4$ and H$_2$ derived from fluid inclusions of the marble used in it. We will report our examinations, and discuss the feasibility of this method and the precautions as to blank gases inherent in the convenient extraction method.

EXPERIMENTAL

The apparatus shown in Fig. 1 was used to extract dissolved air in water. The water saturated with atmospheric air was prepared as followed: Before setting the apparatus as in Fig. 1, the glass bottle (A of Fig. 1) was filled with the distilled water (280 ml), where granular marble (5.0 g) and a spin bar for magnetic stirrer were immersed. The water was aerated by the magnetic stirrer for more than fifteen minutes. After stirring was stopped, water temperature was measured as well as atmospheric pressure and temperature. After setting the apparatus and the sample water as in Fig. 1, the stopcock (B) was opened to react granular marble in the sample water with 6M HCl and to generate CO$_2$. Bubbles of CO$_2$ strip dissolved gases in the water, and they rise to the gas burette filled with NaOH solution. CO$_2$ in the bubbles is absorbed in the alkaline solution, but stripped gases unabsorbed in the alkaline solution remain in the gas burette. The collected gas volume was measured by the burette, and then it was transferred into a glass tube via the rubber tube connection in replacing the alkaline solution filling the sample tube initially. The gas sample was analyzed gas chromato-graphically with the carrier gas of O$_2$ (Kawabe, 1984/85; Kawabe et al., 1985) for He, Ne, H$_2$, Ar, N$_2$ and CH$_4$. The aliquot volume of usually 1.5 ml was injected into a gas chromatograph by a gas-tight syringe.

For determining the amount of dissolved marble in the extraction, the water in the bottle after the extraction was filtered to separate suspending small grains of marble. The concentration of Ca^{2+} in the filtrate was determined by complexometric titration with EDTA. In some runs, trace

components of Mg and Fe in the filtrate were also analyzed by ICP-AES. From the measured Ca^{2+} concentration, the amount of dissolved marble in the extraction was calculated.

We have used three different marbles to ensure gas components from fluid inclusions in the marbles. One is a "reagent marble" from Katayama Chem. Com. The others are Ouge-jima marble and Natori one collected from Ouge-jima, Ochi-gun, Ehime Pref. and Natori, Sada-Misaki Pen., Ehime Pref, respectively. Each marble was crushed and ground, and then grains with the size of 8/14 mesh were selected by sieving. After being washed with water they were partly reacted with HCl solution to remove adherent finer grains and to clean grain surfaces.

RESULTS AND DISCUSSIONS

(1) CH_4 and H_2 derived from marbles

Figures 2-a, b and c show our results on the relationship between the amount of dissolved marble and the measured volume of each gas component when the CO_2-bubbling method was applied to distilled water equilibrated with air at room temperature. The results of Figs. 2-a, b and c have been obtained by using the "reagent marble", Ouge-jima marble and Natori marble, respectively. They indicate that the measured volumes of CH_4 increase with the increasing amounts of dissolved marbles even after the complete extraction of dissolved air. This suggests the presence of CH_4 derived from dissolved marbles. The increase rate of the measured CH_4 volume with increasing amount of dissolved "reagent marble" in Fig. 2-a is about twenty times as much as that in the case of Natori marble of Fig. 2-c. Significant parts of the measured CH_4 here must be derived from fluid inclusions in the respective marbles dissolved in the extractions. For routine analysis of CH_4 dissolved in groundwater samples, marbles having low CH_4 in their fluid inclusions are to be selected. The Natori marble is the best among the three, because it gives rise to the least amount of CH_4 blank.

The results of Figs. 2-a, b and c also suggest that the measured volumes of H_2 include significant amounts of H_2 derived from the dissolved respective marbles just like those of CH_4. However, the increase rate of H_2 in each case is by no means constant unlike CH_4. It appears that H_2 is released at faster rates in early dissolutions than in the later ones. In order to see the behavior of H_2 in the extraction process, we made the following series of experiments; the extraction of dissolved air in distilled water was repeated four times by using Natori marble, in which the same aliquot of granular marble was used throughout the four successive extractions despite its weight-loss due to repeated dissolution. The results are summarized in Table 1. The excess H_2 per unit weight of marble dissolved in the first run is 40% larger than the constant value in later three runs. In the case of CH_4, the excess volumes of CH_4 in the first and second runs are smaller than those measured in the third and fourth runs by 30 and 20%, respectively. Chemical analyses of Fe and Mg in the
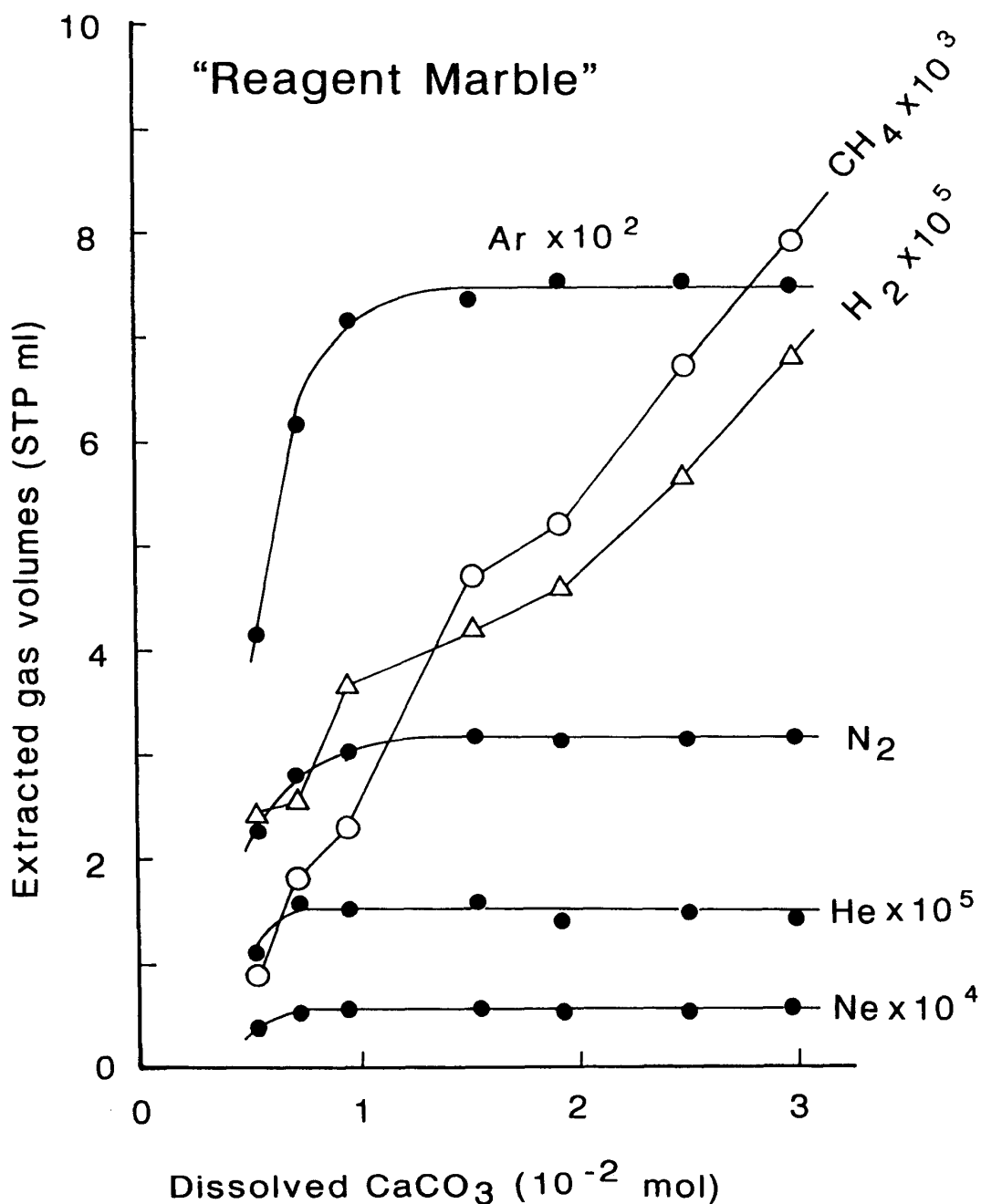
Fig. 2-a.   Extracted gas volumes by the CO_2-bubbling method from distilled
water of 280 ml equilibrated with the air at 30°C and 1 atm. Gas chro-
matographic analyses are plotted against the amount of dissolved
marble in the extraction. The "reagent-marble" purchased from
Katayama Chem. Com. is used in all the runs.

filtrates of sample waters after gas extractions do not indicate any dissolution
of contaminated metals at crushing and sieving the marble.

In the successive use of the granular marble, very fine marble particles ad-
herent to surfaces of granular grains dissolve at very beginning, and surface
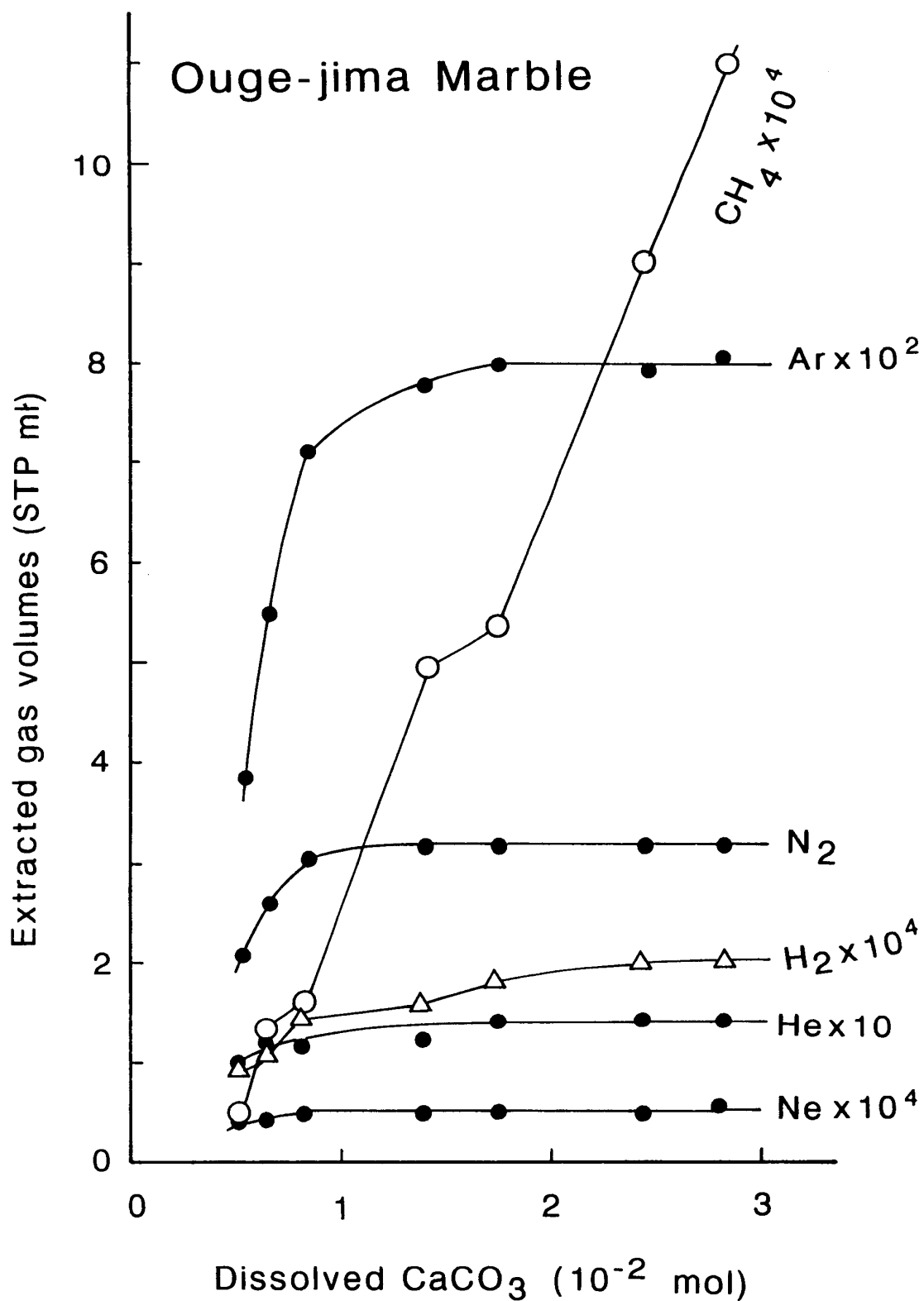
Fig. 2-b. Extracted gas volumes by the CO_2-bubbling method from distilled water of 280 ml equilibrated with air at 29°C and 1 atm. Gas chromatographic analyses are plotted against the amount of dissolved marble in the extraction. The Ouge-jima marble is used in all the runs.
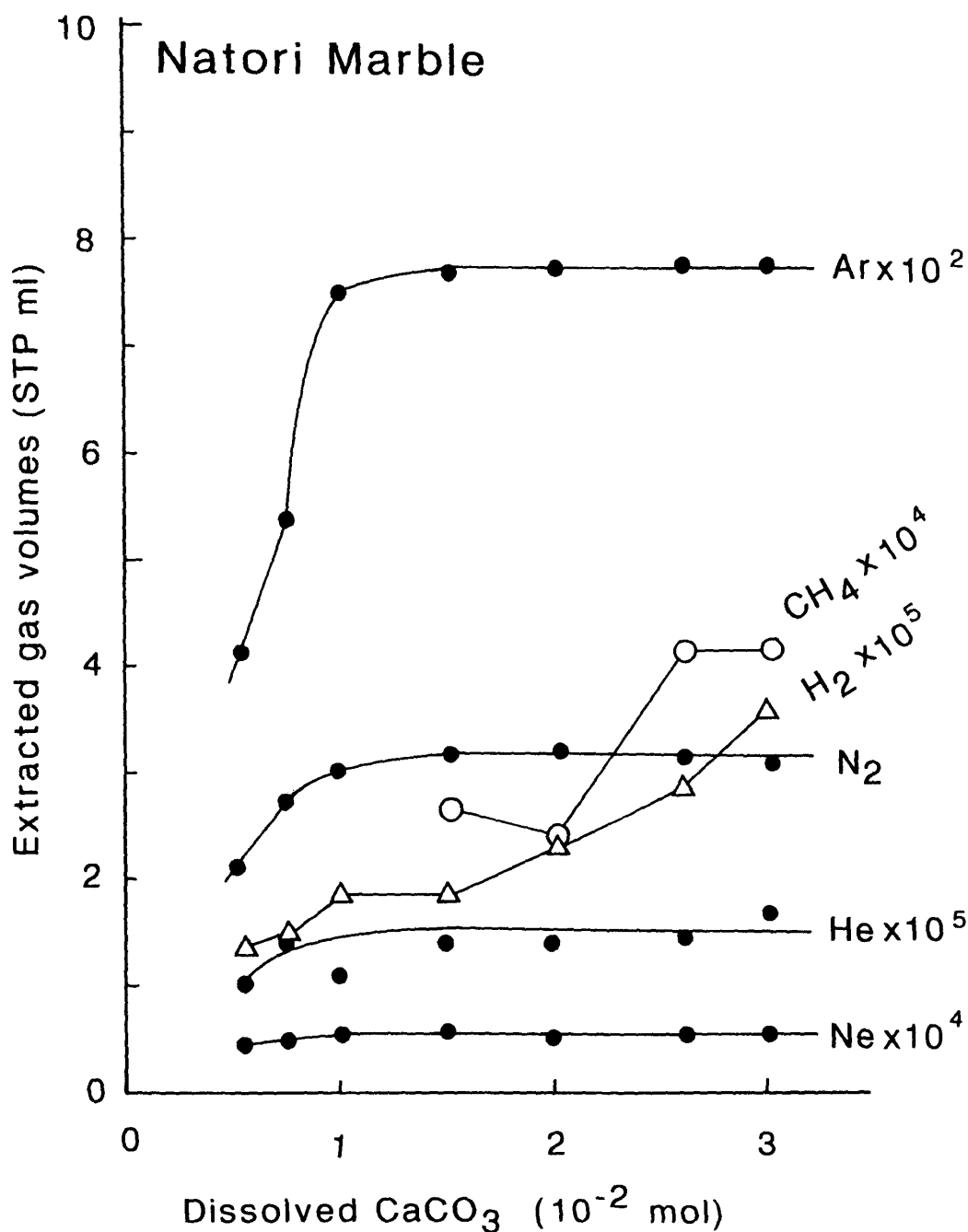
Natori Marble

Fig. 2-c. graph: Extracted gas volumes (STP ml) vs Dissolved CaCO$_3$ (10^{-2} mol), with curves labeled $Ar \times 10^2$, $CH_4 \times 10^4$, $H_2 \times 10^5$, N_2, $He \times 10^5$, $Ne \times 10^4$.

Fig. 2-c.   Extracted gas volumes by the CO$_2$-bubbling method from distilled water of 280 ml equilibrated with air at 29°C and 1 atm. Gas chromatographic analyses are plotted against the amount of dissolved marble in the extraction. The Natori marble is used in all the runs.

parts of granular grains are etched, and lastly their interiors. We used Natori marble of 8/14 mesh which was washed with water and partly reacted with HCl before use. However, it is not easy to remove all the fine particles and grains adherent to surfaces of sieved grain as well as their damaged surfaces formed at crushing and grinding. Hence, the results of Table 1 may suggest

Table 1.   Successive extractions of dissolved air from distilled water samples by the CO_2-bubbling method using the same aliquot of granular Natori marble*.

	No.1	No.2	No.3	No. 4
Dissolved marble				
Ca (mg)	325	313	399	374
Mg (mg)	0.66	0.58	0.75	0.67
Fe (mg)	0.042	0.042	0.067	0.043
Extracted H_2 and CH_4				
H_2 (10^{-5} STP ml)	1.14	0.86	0.97	0.95
CH_4 (10^{-5} STP ml)	4.3	4.4	6.0	5.9
Excess H_2 and CH_4**				
H_2 (10^{-5} STP ml)	0.72	0.44	0.55	0.53
CH_4 (10^{-5} STP ml)	2.6	2.7	4.3	4.2
Excess H_2 and CH_4 per diss. Ca				
H_2/Ca (10^{-5} STP ml/g)	2.0	1.4	1.4	1.4
CH_4/Ca (10^{-5} STP ml/g)	7.4	8.6	11	11

*   The distilled water of 280 ml are equilibrated with the atmospheric air at 17°C and 1 atm.
** Atmospheric H_2 and CH_4 dissolved in distilled water of 280 ml at 17°C and 1 atm are corrected for the measured values. Corrections of dissolved atmospheric H_2 and CH_4 are estimated to be 0.42×10^{-5} and 1.7×10^{-5} STP ml, respectively. They are based on their Bunsen solubility coefficients (Croizer et al., 1974 for H_2; Yamamoto et al., 1976 for CH_4) and atmospheric abundances (Kawabe et al., 1985 for H_2; Rasmussen and Khalil, 1981 for CH_4).

that the average gas composition of fluid inclusions in fine grains and/or in surface parts of granular marbles is altered from the original one during mechanical crushing and grinding. If fluid inclusions in finer grains and in surface parts of granular ones are partly opened by crushing and grinding, their gas contents are lower than their interiors of granular marble grains. The results of CH_4 in Table 1 are compatible with this idea, however, the H_2 data do not favor it. The enrichment of H_2 in readily soluble parts of the marble may imply the presence of tribochemically produced H_2 at crushing and grinding. Cress et al. (1987) reported that the atomic hydrogen Balmer series alpha line and H_2 gas molecular bands were identified in the spectrum obtained when various rocks including marbles immersed in water were uniaxially fractured.

(2) Tribochemical H_2 retained by crushed and ground marble

In order to examine the possible tribochemical H_2, another series of successive extractions have been made using the finer grains of Natori marble. The grains which passed the 14 mesh sieve were used. They are residuals after selection of 8/14 mesh grains for usual use. They are neither washed with water nor reacted with HCl before use. The results are shown in Fig. 3. The amounts of extracted H_2 in the first and second runs are indeed 60 and 20 times as much as that in the last run, respectively. The H_2 extracted in the last run in this series is almost the same as the constant value in the last
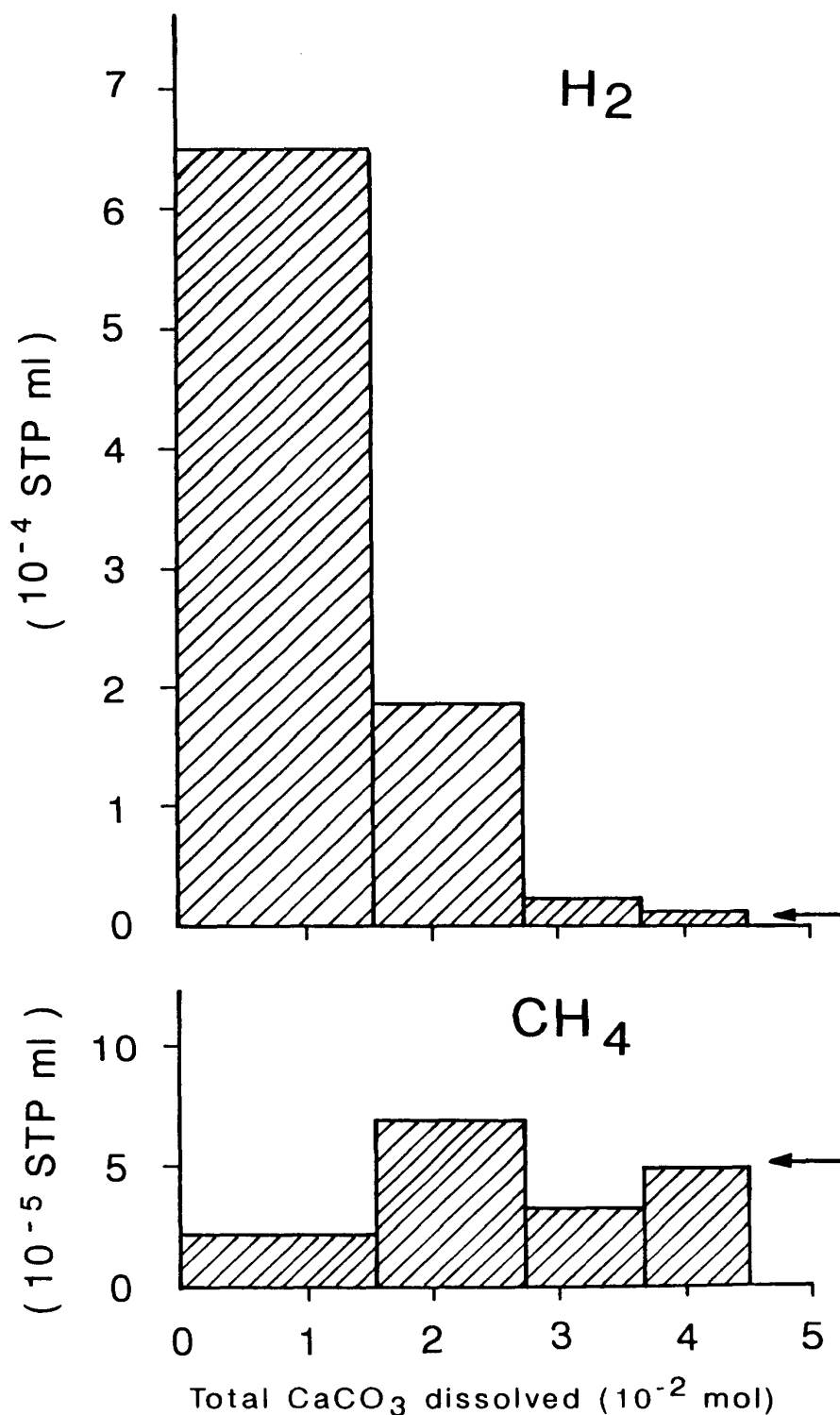
Fig. 3.   H$_2$ and CH$_4$ in the extracted gases from distilled waters of 280 ml equilibrated with air by using the Natori marble of fine grains smaller than 14 mesh. These grains are not subjected to any treatments other than crushing, grinding and sieving. The extractions were repeated four times by using the same aliquot of marble grains left after preceding extraction runs. The arrows indicate the averaged results summarized in Table 1 using the washed and cleaned granular grains of Natori marble.

three runs in the first series using the washed and cleaned granular marble.

The results concerning H_2 in the two series of successive extractions suggest that the extracted H_2 includes (i) H_2 in the fluid inclusions in the dissolved marble, (ii) the atmospheric H_2 dissolved in water of 280 ml, and (iii) the tribochemically produced H_2. The third component of tribochemical H_2 is retained preferentially by finer particles formed by crushing and grinding. The puzzling results of H_2 in Figs. 2-a, b and c are attributed to incomplete removal of such fine grains and particles adherent to granular marble grains. In order to realize the constant blank of H_2 only due to the H_2 from fluid inclusions, fine grains and particles adherent to the granular grains should be removed as completely as possible by cleaning them thoroughly with HCl solution. As in the case of CH_4, we must select marbles that gives rise to low and constant H_2 blanks in routine analysis of dissolved H_2 in groundwater samples.

(3) Temperature variations of atmospheric He, Ne, Ar and N_2 dissolved in waters

Figure 4 shows the extracted gas volumes of He, Ne, Ar and N_2 from distilled waters equilibrated with the air at water temperatures from 13 to 31°C. The solid curves are the least-squares fittings of our data to the following equation for temperature dependence of the air solubility (Weiss, 1970);

$$\ln C^* = A_1 + A_2(100/T) + A_3 \ln(T/100), \tag{1}$$

where C^* is the solubility for each atmospheric gas component expressed by the volume of the gas (STP) absorbed from water saturated air at 1 atm, per unit volume of the water at the absolute temperature of T. A_i's are constants determined from experimental data. Each dashed curve is the calculated moist air solubility for the component from its Bunsen solubility coefficient and atmospheric abundance (Weiss, 1970, 1971). Figure 5 shows the temperature variation of the extracted total gas volume determined by the gas burette. The solid and dashed curves in Fig. 5 are the least-squares fitting of our measurements to eq. (1) and the calculated total air solubility, respectively.

Temperature dependence of air solubility for the total gas or for each constituent gas is well determined by the CO_2-bubbling method combined with gas chromatographic analysis. Each solid curve, however, is slightly displaced to higher values from the corresponding dashed curve, although they are almost in parallel with each other. The difference between each pair of solid and dashed curves in Figs. 4 and 5 corresponds to the blank for the total or each gas in the present method. Such a difference in the total gas seen in Fig. 5 gives the blank value actually for N_2 plus O_2, since the other components are much less abundant than the two components.

The blank value for N_2 plus O_2 is evaluated to be (0.22 ± 0.05) STP ml for the water sample of 280 ml from the comparison in Fig. 5. On the other hand, the blank for N_2 itself estimated from the differences between measured and calculated ones in Fig. 4 is (0.25 ± 0.04) STP ml. This blank value for N_2 is
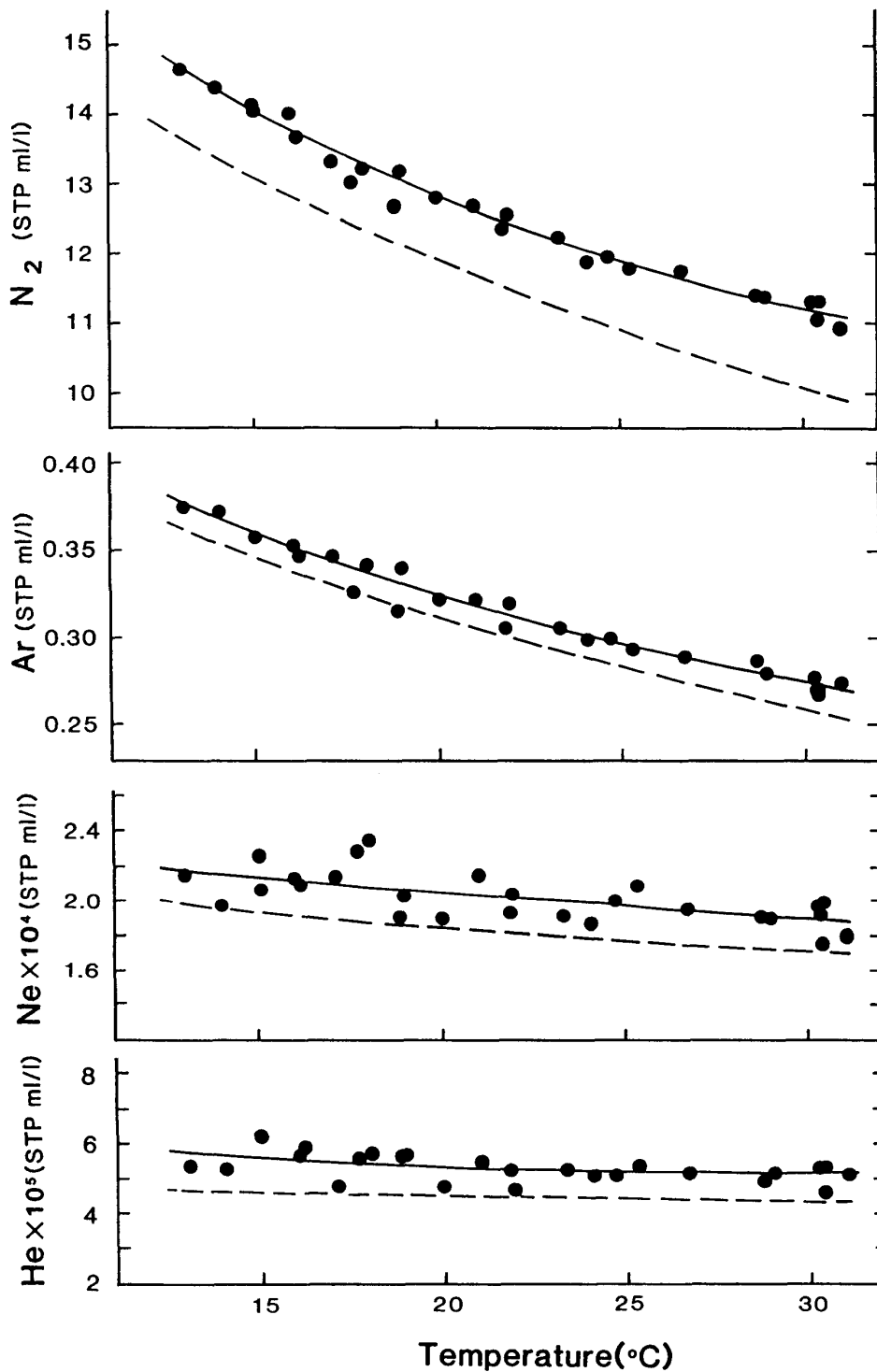
Fig. 4.   Air solubility for N$_2$, Ar, Ne or He in distilled water as a function
of temperature of its equilibrium dissolution. Filled circles are
determined values by CO$_2$-bubbling extraction followed by gas
chromatographic analysis in this study, in which no blank correc-
tions are made. The solid curves are the least-squares fittings of
the measured values to eq. (1). The dashed curves are the calcu-
lated values from Bunsen solubility coefficients and atmospheric
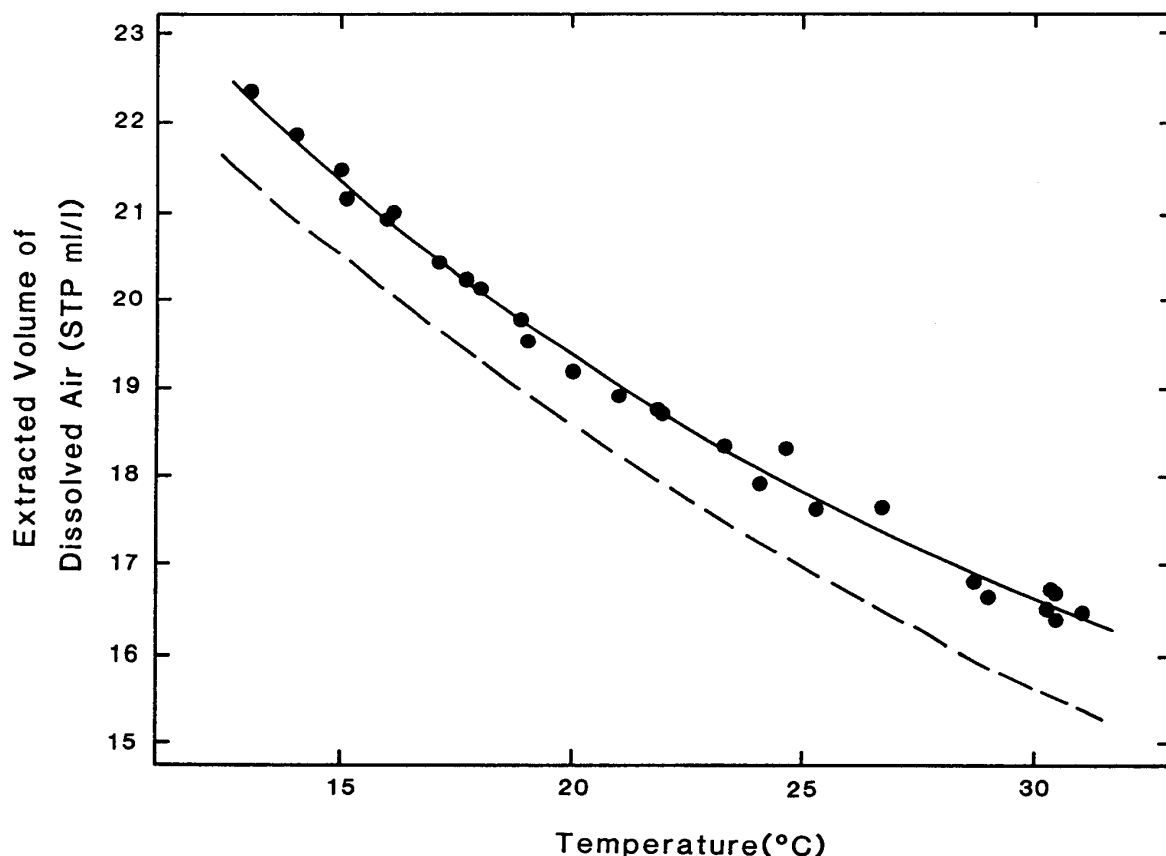abundances of respective gases.

Fig. 5.   Total gas volumes extracted from distilled waters equilibrated with the air at different temperatures. They are the residual gas volumes determined by the burette in the CO_2-bubbling extraction method. The solid and dashed curves are, respectively, the least-square fitting of the data to eq. (1) and the calculated curve from solubilities and atmospheric abundances of constituent gases.

even greater than that for N_2 plus O_2. This suggests that air contamination is occurring in the procedures of transferring the extracted gas in burette into a gas sample tube and in the subsequent gas chromatographic analysis. The blank value for N_2 plus O_2 is corresponding to the extracted air from HCl and NaOH solutions used in the method.

(4) Blank sources of He, Ne, Ar and N_2

Figure 6 shows the plots of measured He/Ar and N_2/Ar ratios against the measured Ne/Ar ratio in the extracted air dissolved in waters. The plots are based on the same data as shown in Fig. 4. The plotted ratios are all normalized by the respective ratios of the atmospheric air. If the sample of dissolved air is contaminated with the atmospheric air, the sample is plotted on a mixing line connection between the dissolved air and the air itself. In Fig. 6, the averaged values for such ratios of the extracted air (larger filled circles with error bars) are indeed displacing from the respective ratios calculated from the air solubilities to the air along their mixing lines. From the displacements, we have estimated that the air of (0.17 ± 0.02) STP ml, on the average,
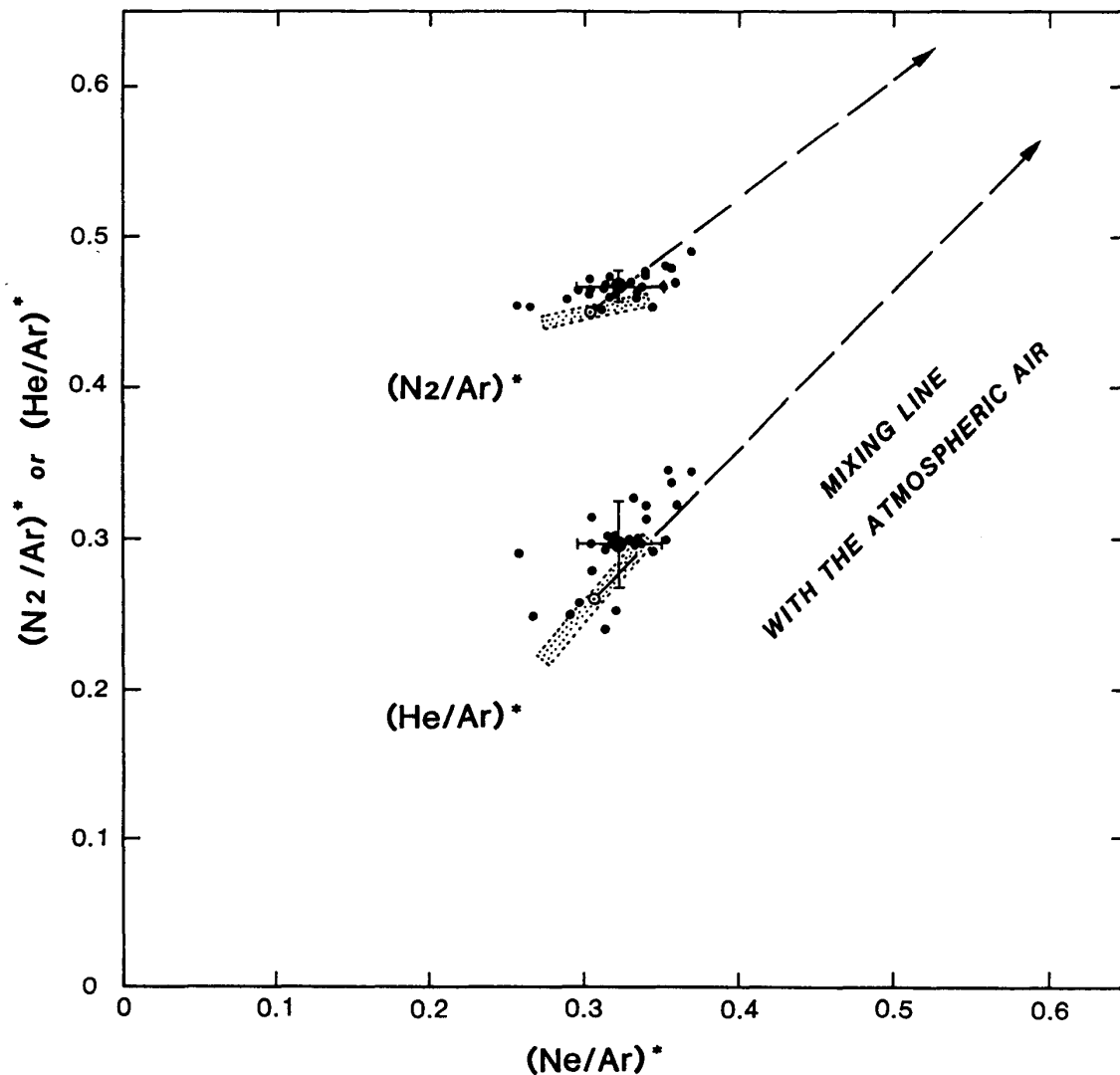
Fig. 6. Relationships among measured N_2/Ar, He/Ar and Ne/Ar ratios for gas samples of dissolved air by the CO_2-bubbling method. Plotted data are the same as in Fig. 4, and their averages are shown by larger filled circles with error bars. The stippled area correspond to ratios from air solubility for the temperature range of 13—31°C, and the averaged ratios are shown by open circles. The asterisks indicate that the ratios are normalized by the air.

contaminates each extracted gas sample of dissolved air from 280 ml of water. In this estimation, we assumed that extracted air from HCl and NaOH solutions has the same composition as the air dissolved in distilled water. A small amount of the atmospheric air may have remained inside of the rubber tube connecting the gas sample tube (F) and the stopcock (E) in Fig. 1, even though we carefully filled them with NaOH solution in every run. The dead volume of the syringe we used in gas chromatographic analysis may also contribute to the air contamination. But the dead volume is measured to be 2 μl, so that its contribution may be negligibly smaller than the remaining atmospheric air inside of the rubber tube.

The blanks for N_2 and Ar found in Fig. 4, when they are corrected for the direct air contamination of (0.17 ± 0.02) STP ml, give their blanks due to the extracted air from HCl and NaOH solutions. The atmospheric air composed of non-electrolyte gases is less soluble in concentrated acid or alkaline solutions than in distilled water owing to the salting-out effect. We have calculated the water volume that can absorb the air equivalent to the extracted atmospheric N_2 and Ar from HCl and NaOH solutions at 22°C. The assumed temperature is the average water temperature of our extraction experiments. Such an effective water volume is calculated to be (10.6 ± 3.0) ml, which can also give estimates for the Ne and He blanks due to the extracted air from HCl and NaOH solutions. The total blank air from HCl and NaOH solutions is estimated to be (0.18 ± 0.05) STP ml. This is in a reasonably good agreement with the estimated blank value of (0.22 ± 0.05) STP ml for N_2 plus O_2 in Fig. 5. These calculations and the estimated blank values for N_2, Ar, Ne and He are summarized in Table 2.

The blanks found as the differences between solid and dashed curves for respective gases in Fig. 4 are composed of the direct air contamination and the extracted air from HCl and NaOH solutions. The blank gases from the dissolved marble are unimportant for He, Ne, Ar and N_2 analyses, when Natori marble is used in the extraction. The radiogenic He derived from the dissolved marble is a potential blank source for He, although we could not make sure the presence of radiogenic He beyond our detection limit of He.

Table 2.   Estimated blank N_2, Ar, Ne and He in the CO_2-bubbling extraction of dissolved air in distilled water of 280 ml followed by their gas chromatographic analysis.

	(A)* $V_{obs} - V_{calc}$ (STP ml)	(B)** Direct air Contamination (STP ml)	(C)† Dissolved air from HCl and NaOH solutions (STP ml)	(D) (B) + (C) (STP ml)
N_2	0.25 ± .04	0.13 ± .02	0.12 ± .02	0.25 ± 04
Ar ($\times 10^{-3}$)	5 ± 2	1.6 ± .1	3.1 ± .9	4.7 ± .9
Ne ($\times 10^{-6}$)	5 ± 3	3.1 ± .3	1.9 ± 4	5.0 ± .3
He ($\times 10^{-6}$)	2 ± 1	0.89 ± .08	0.5 ± .1	1.4 ± .1
O_2	—	0.034 ± .004	0.06 ± .02	0.10 ± .02
$N_2 + O_2$	0.22 ± .05††	0.17 ± .02‡	0.18 ± .05‡	0.35 ± .05‡

*   Averaged differences between measured and calculated values for the distilled waters of 280 ml for temperatures of 13–31°C.
**   The air contamination is estimated from the mixing ratios indicated as in Fig. 5 and total gas volumes extracted.
†   Estimated from the following steps: First, the extracted N_2 and Ar from HCl and NaOH solutions are estimated from the respective differences between the values in (A) and (B). Next, the pure water volume that can dissolve these amounts of the atmospheric N_2 and Ar is calculated to be (10.6 ± 0.3) ml, and then from the pure water volume the dissolved air from HCl and NaOH solutions is estimated.
††   Averaged differences between measured gas volumes by burette and calculated ones as in Fig. 5.
‡   The sum of N_2 and O_2 in the column.

CONCLUSIONS

(1) The marble, which is used in this extraction method to generate CO$_2$ for stripping, is the blank source of CH$_4$ and H$_2$ analyses. They are present in fluid inclusions in the marble. The blank values for CH$_4$ and H$_2$, when Natori marble is used, are estimated to be 4×10^{-5} STP ml and 5×10^{-6} STP ml, respectively.

(2) The marble of granular grains used in the extraction should be washed with HCl as completely as possible before its use. This removes fine marble particles adherent to granular grains and damaged surface layers of the granular grains. Such fine particles retain significant amounts of H$_2$ formed tribochemically when the marble was crushed and pulverized.

(3) Temperature dependence of air solubility for the total gas or for each constituent gas (He, Ne, Ar or N$_2$) is well determined by the CO$_2$-bubbling method combined with gas chromatographic analysis, but they are affected by two blank sources. One is the dissolved air in HCl and NaOH solutions used in the extraction method. The blank air from the solutions amounts to (0.18 ± 0.05) STP ml. Another blank source is the atmospheric air. We evaluated that the air of (0.17 ± 0.02) STP ml contaminates the extracted gas sample.

These precautions are important for routine analysis of dissolved gases in groundwaters by the simple method of CO$_2$-bubbling extraction followed by gas chromatographic analysis of He, Ne, H$_2$, Ar, N$_2$ and CH$_4$.

ACKNOWLEDGEMENTS

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