

2007年度の予定

	嶋田グループ
H17	東京、ソウル
H18	大阪(東京)、バンコク、台北(ジャカルタ)
H19	東京、バンコク、ジャカルタ
H20	東京、大阪、バンコク、ジャカルタ
H21	大阪、ソウル、ジャカルタ
H22	必要に応じて国内・国外

	嶋田グループ
H17	海外パートナーからの現地地下水データ検討、海外現地調査(ソウル)、CFC,Kr 85手法検討、東京でのシミュレーション着手
H18	CFC法分析立上、Kr85分析立上、同採水法検討、大阪(東京)・バンコク、ジャカルタ現地調査、
H19	CFC法、Kr85法現地適応調査、(東京、バンコク)、ジャカルタ現地地下水調査、
H20	ジャカルタでのサンプリングライン調査、バンコクの補足調査と解析、大阪でのサンプリングライン調査
H21	ソウルサンプリングライン調査、大阪・ジャカルタサンプリングライン調査補足、
H22	補足調査、成果の解析と取りまとめ、

(1) H19年度研究計画(調査日程・人数・観測項目などを含む)

現地調査 BKK 7-8月(10-14日程度)

嶋田・辻村・山中・筑波大院生2名 (計 5名)

- ・同位体項目補足(含14C)
- ・地下水ポテンシャルデータ収集
- ・CFC予備調査

現地調査 JAK 9月 (10日程度)

嶋田・山中・熊大院生 1名 (計3名)

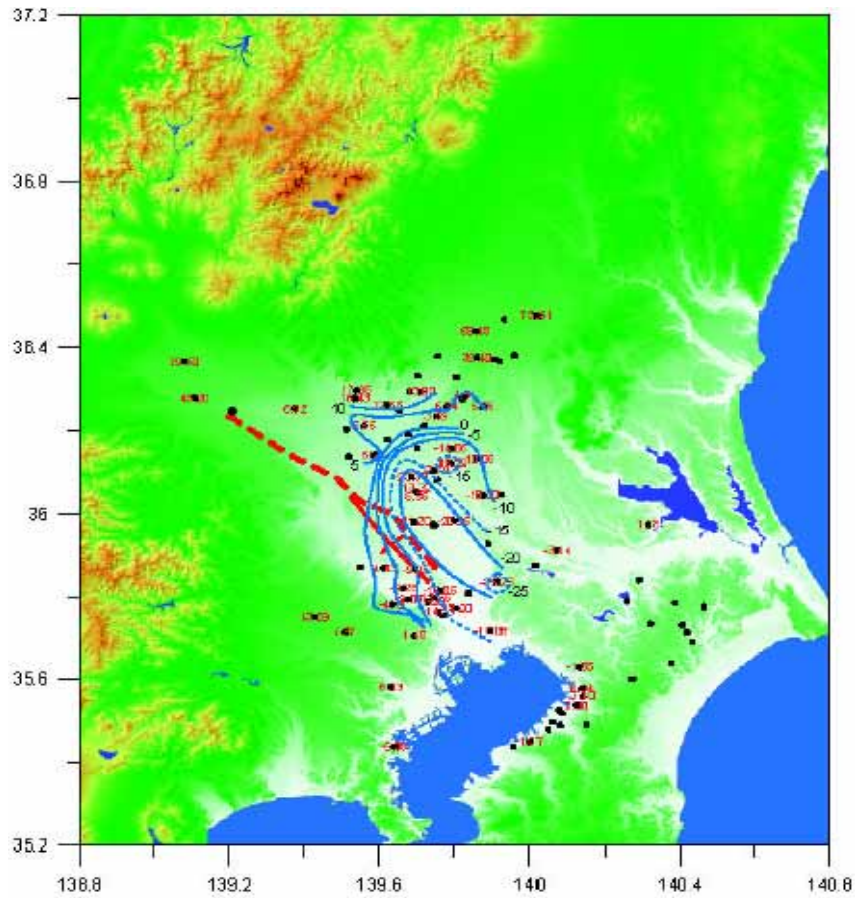
- ・同位体項目補足(含14C)
- ・地下水ポテンシャルデータ収集

現地調査 関東地区 K85 予備調査あるいはCFC2次調査

12-03月 (1週間程度)

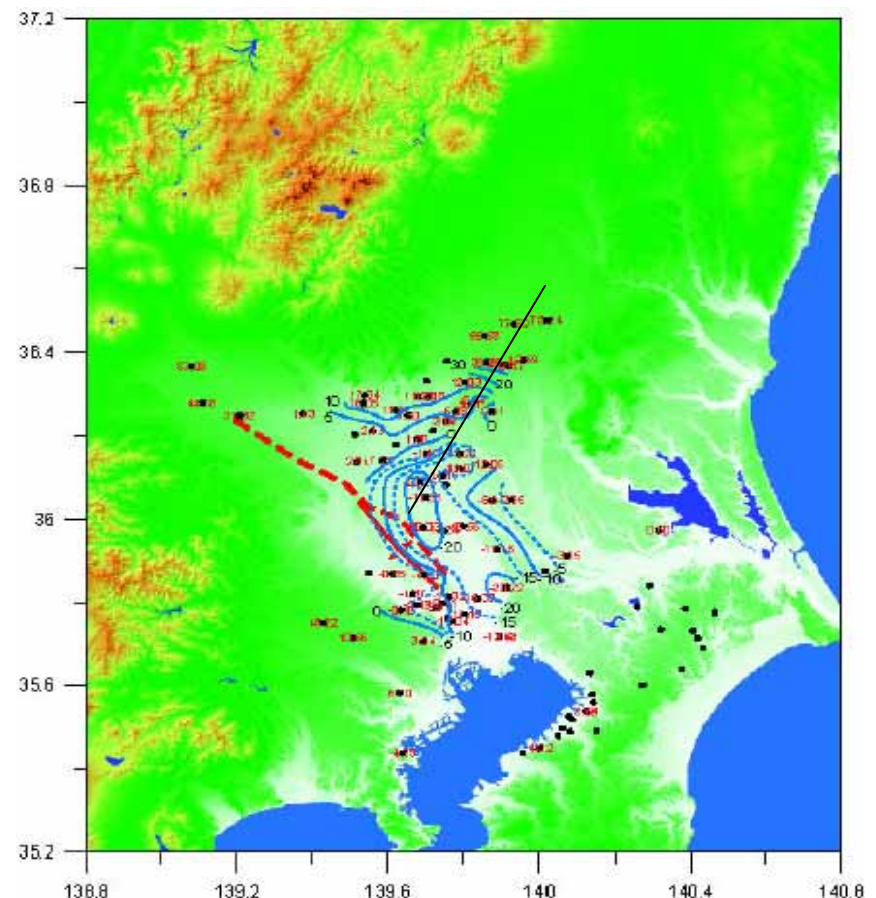
嶋田・馬原・林・辻村・筑波大院生2名 (計6名)

関東平野の地下水ポテンシャル変化



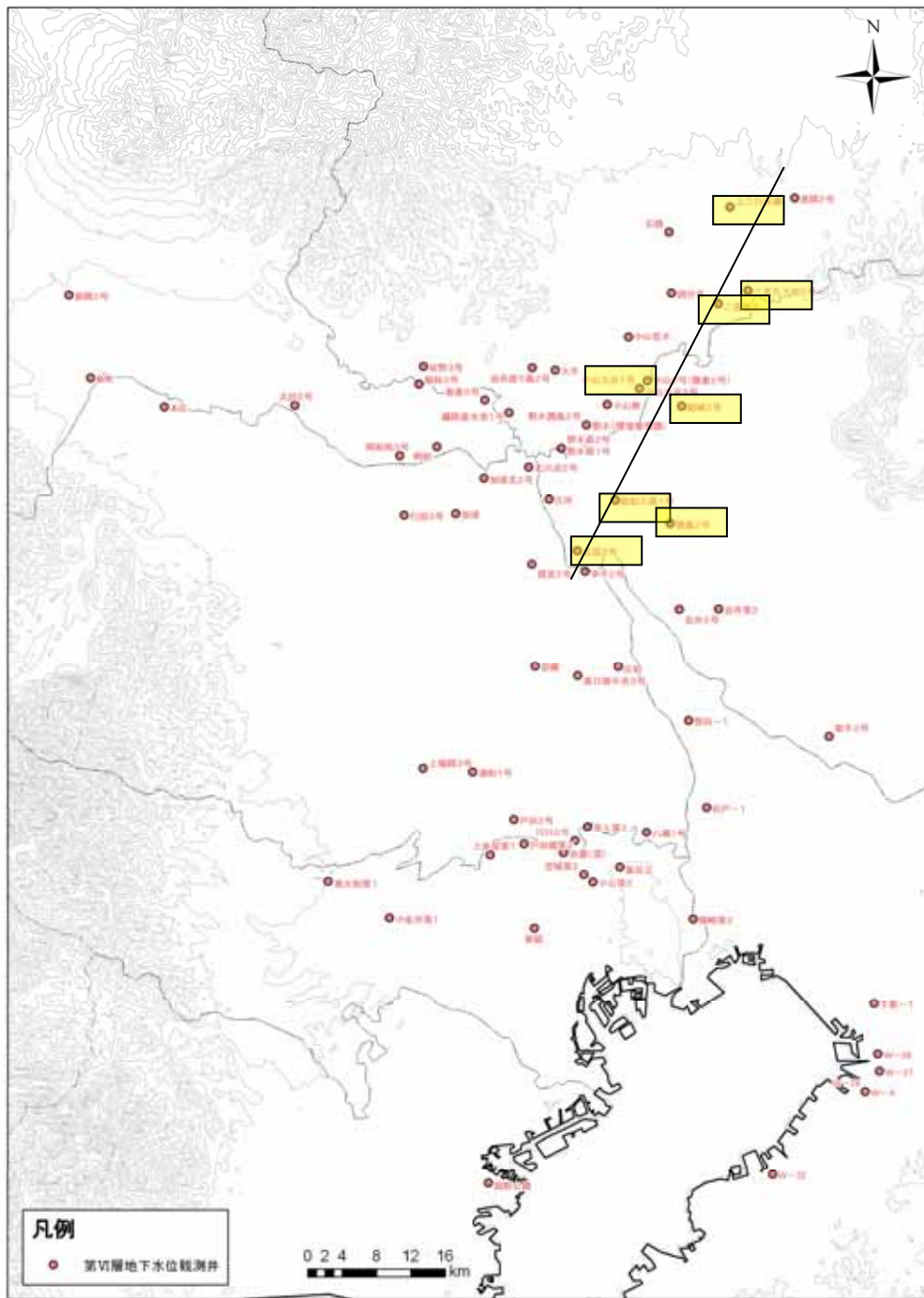
VI層

1985



VI層

1995



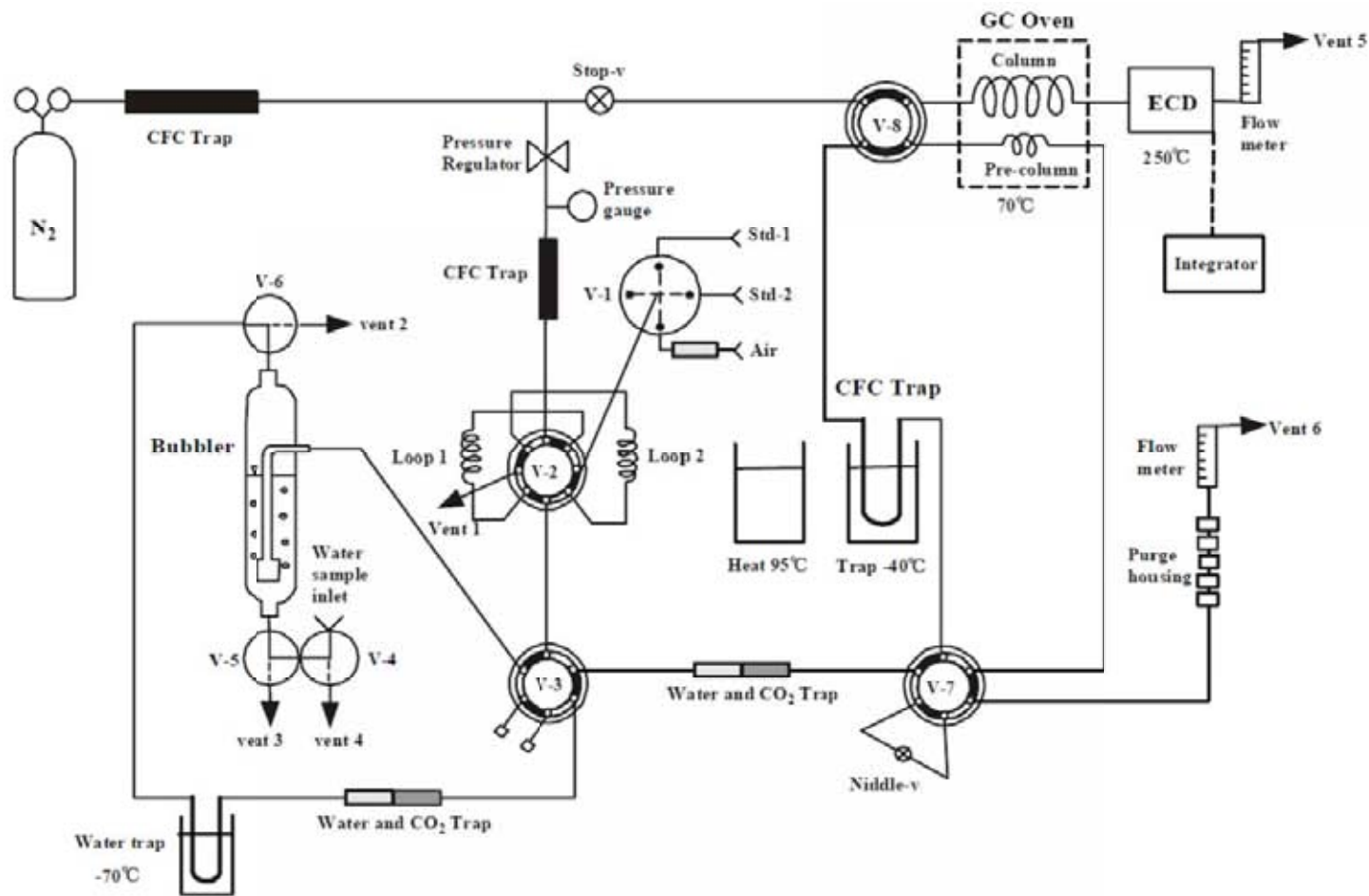
2007.03 CFC予備調査

(3) 中間評価(2008年3月1日)までの目標とそれ以降の研究計画

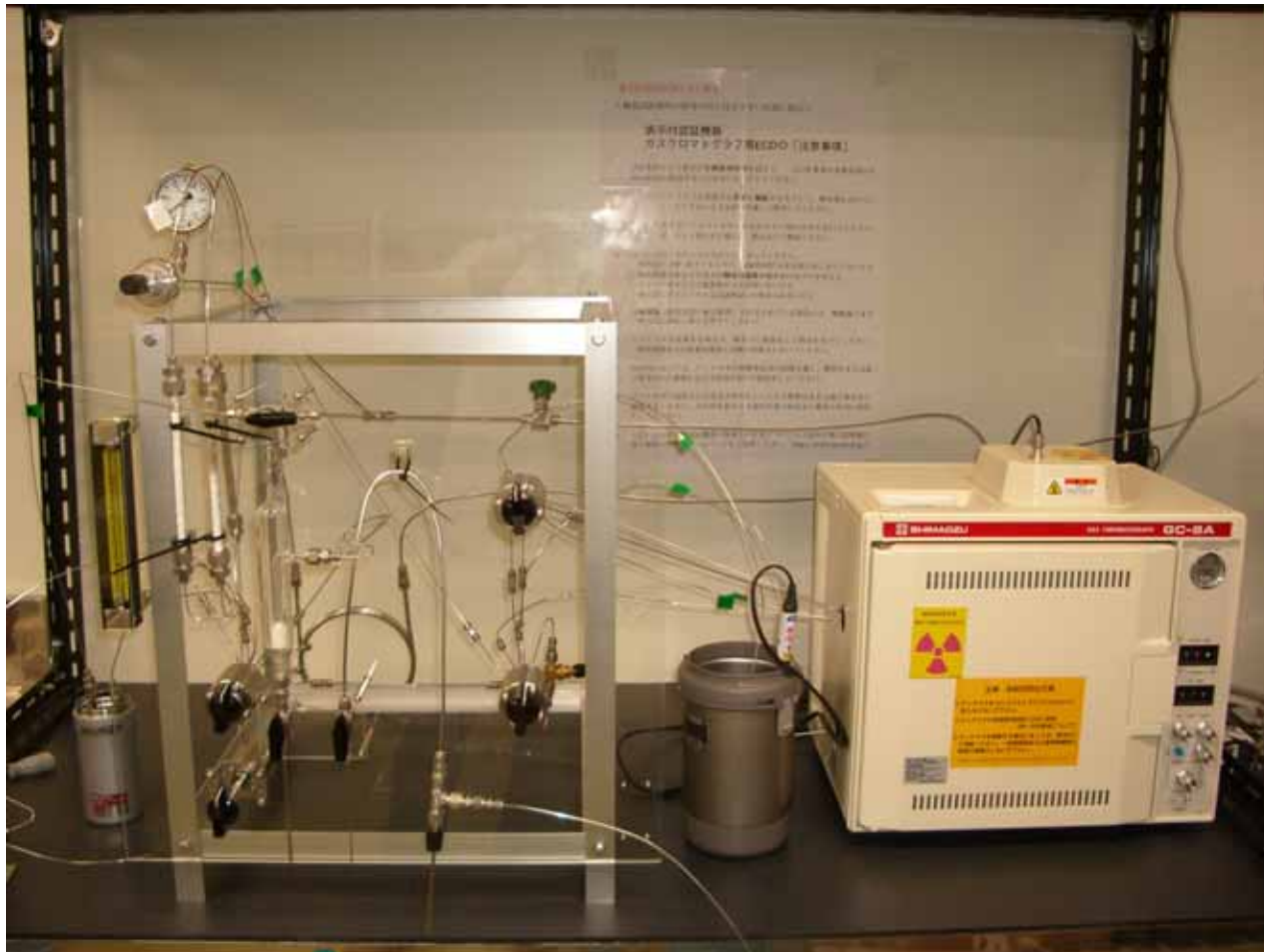
- CFC法 (2006年度立上げ) 筑波大辻村研
3月末でほぼ手法として確立
関東地域で予備調査実施(2006.後期)
バンコック地域での予備調査(2007.前期)
- Kr85法 (2006年度立上げ) ガス分離と液シンによる
放射性クリプトン測定(九州大 百島研)
大気による測定法検討(2007前期)
地下水からの溶存ガス抽出法の開発
(京大 馬原研)
抽出システムの設計と発注(2006)
水道水からのクリプトンガスの抽出(2007前期)

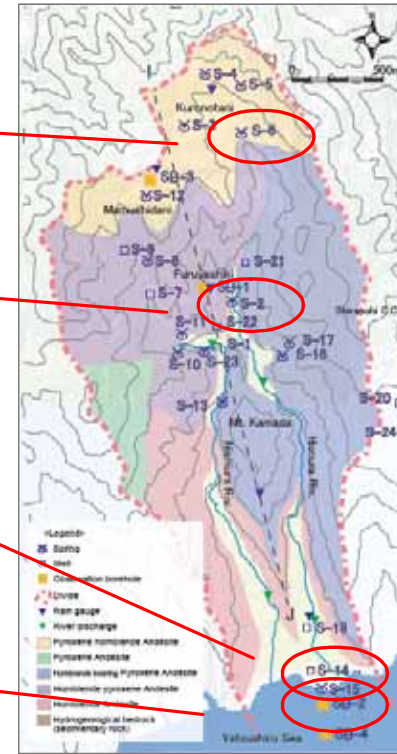
双方のシステムの統合化(2007後期)と現地予備調査(200712-03月)

CFC 分析ライン(筑波大・辻村研)



CF C 分析システム





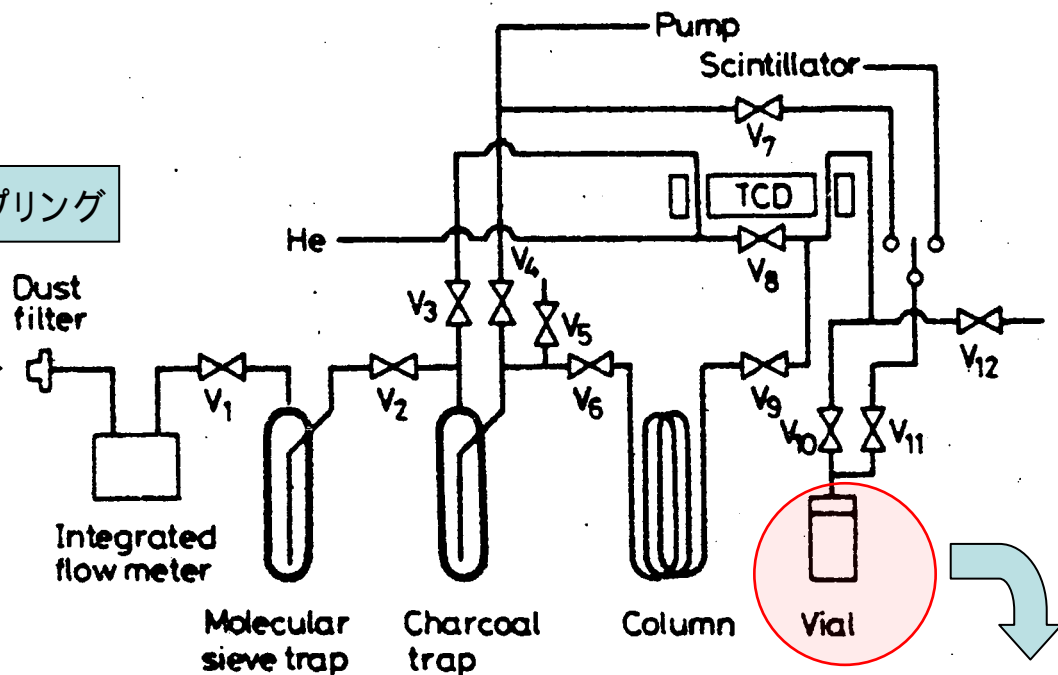
Sample	Type	Environment	Concentration (pg/kg)			Dating by CFC	³ H (TU)	EC (mS/m)
			CFC12	CFC11	CFC113			
S-6	Spring	Headwater	218.35	427.72	52.66	15	2.0	11.7
S-2	Spring	Midstream region	139.66	244.25	33.97	25	2.3	13.8
S-15	Spring	Coastline	27.22	60.83	-	> 50	2.2	19.2
SB-2D	Deep borehole	Coastline	23.85	29.78	-	> 50	0.1	19.2

Kr-85分離系

分離系の構成

- ・活性炭トラップ
- ・分離カラム
- ・熱伝導度検出器 (TCD)
- ・Kr回収バイアル

フィールドサンプリング



地下水中のKrはパージガス (N₂, He等) で取り出す

パージガス (Kr) をKr-85分離系に導入

活性炭トラップでパージガスを粗分離

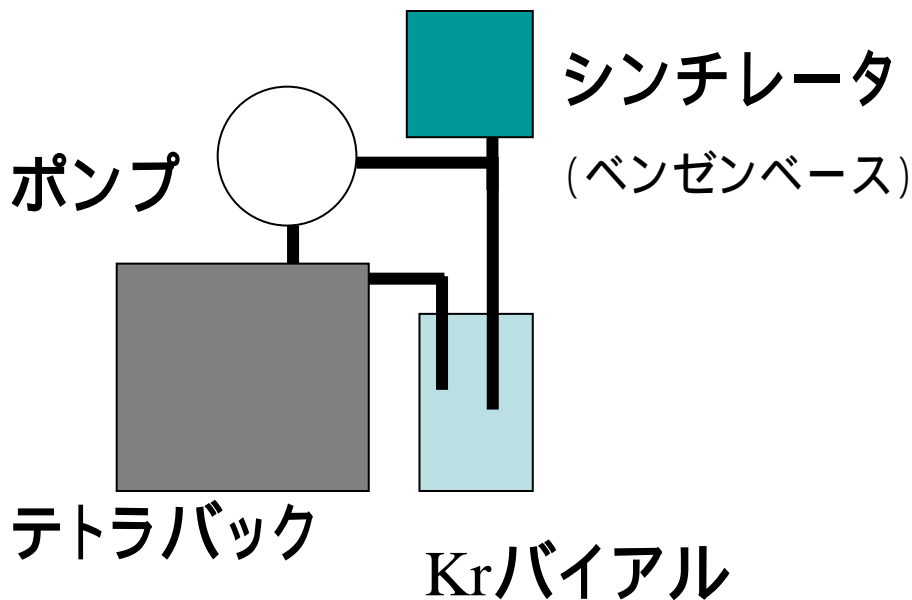
分離カラムでKrと他ガスを精密分離

ガスクロ (TCD) でKrのピークを確認し、Kr回収系へ導入

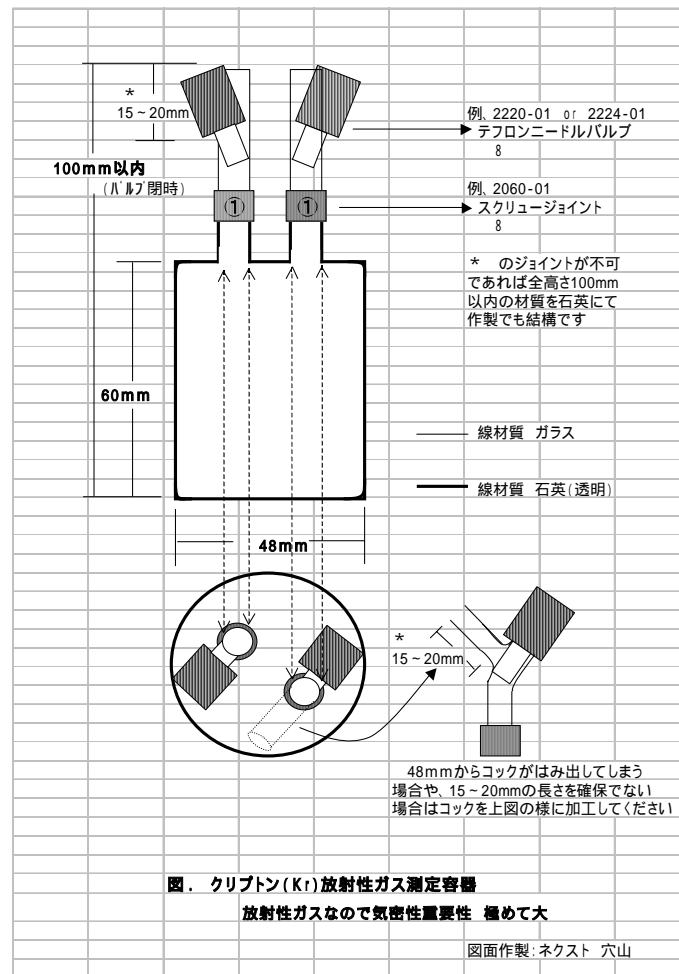
LL液シンへ

Kr回収系

- ・精密分離カラムからKrをテトラバッグへ移す
- ・KrバイアルにKrを回収 (Heキャリアー、液体窒素)
- ・シンチレータをKrバイアルへ入れ密閉する



テフロン製Krバイアル(100ml)



マイクロバルブで機密性を確保、
大容量を確保



Method for Extraction of Dissolved Gases From Groundwater for Radiokrypton Analysis

H41B-0414



Peter C. Probst, Reika Yokochi and Neil C. Sturchio
University of Illinois at Chicago, Earth and Environmental Sciences (MC-186), 645 W. Taylor St., Chicago, IL 60607 USA

Introduction

Two indicative isotopes of krypton (^{81}Kr and ^{84}Kr) suitable environmental tracers having practical applications (such as, determining groundwater residence times, water circulation and mixing rates, and ages of ground ice. ^{81}Kr $t_{1/2} = 223,000$ yr) is an ideal tracer for the 100 to 100,000 year scale. ^{84}Kr $t_{1/2} = 10.8$ yr) is ideal for tracing processes in the 100 yr range. The natural analysis uses the Atom Trap Trace Analysis (ATTA) apparatus developed by Z.-T. Lu and colleagues at Argonne National Laboratory. This apparatus uses filtered photo lasers to hold and count individual Kr atoms of with complete isotopic selectivity in a magneto-optical trap (Chen et al. 1998; Du et al. 2000). ATTA analysis currently requires ~ 100 μL of Kr , which is the amount contained in ~ 100 L of air-saturated water. The yield of this ^{81}Kr analysis has recently dated groundwater from a Italian aquifer in the Western Desert of Egypt to be as old as 107 years. The results of the ATTA analysis showed agreement to ^{14}C data and marked the first use ATTA was used to determine groundwater residence time (Sturchio et al. 2004). We developed a new, high-volume, gas-extraction system, EDGAR (Extraction of Dissolved Gases for Analysis of Radiokrypton) that provides a simple and robust method for obtaining high-volume samples suitable for delivery of micromolar amounts of radioactive trace gases for isotopic analysis.

Method

The key component of EDGAR is a hydrophobic semi-permeable membrane interface (Membrane Cap). This extracts dissolved gases from water with efficiency approaching 90%. Water flows through the inner surface of the membrane and a vacuum is applied to the outer surface of the membrane. Vacuum is provided with the compressor that compresses the extracted gas into a standard gas cylinder. The extraction apparatus is contained in a rigid frame (Fig. 1). EDGAR weighs about 180 kg and is powered by a 120VAC, 20-amp power source. Electronic pressure monitors the membrane vacuum, sample tank pressure, water temperature and total water flow. A 288 kg bagger records the entire flight. A schematic of EDGAR is shown in Fig. 2.



Figure 1. Picture of extraction cap being deployed in the field.



Figure 2. Schematic diagram of EDGAR.

Gas	V_{gas} (mL)	n_{gas} (moles)	$n_{\text{gas}}/V_{\text{water}}$ (mM)	Total gas volume per analysis (L)
N_2	0.367	5.46×10^{-6}	1.26×10^{-4}	14.8
CH_4	0.225	3.40×10^{-6}	8.10×10^{-5}	9.3
CO_2	1.790	2.69×10^{-5}	6.72×10^{-4}	7.8
O_2	0.220	3.20×10^{-6}	7.90×10^{-5}	9.2
Ar	0.800	1.19×10^{-5}	2.97×10^{-4}	3.4
Kr	0.000	0.00×10^{-6}	0.00×10^{-4}	0.0
Xe	0.000	0.00×10^{-6}	0.00×10^{-4}	0.0

Table 1. Estimated gas sample composition for quantitative extraction from 100 L of air-saturated water at 37°C. $P_{\text{H}_2\text{O}}$ is water vapor pressure in atmosphere and $n_{\text{H}_2\text{O}}$ is solubility of gas in water at 37°C. n_{gas} is molar concentration of gas in 1 L of air-saturated water. Targeted amount of Kr is 100 molecules.

Testing

Initial testing of membrane extraction efficiency was conducted using Chicago tap water. Dissolved O_2 (DO) was measured in water before and after O_2 passed through the membrane (Fig. 3) at flow rates ranging from 4 to 34 L/min. DO dropped from 12 to 18 mg/L (before) to 1.6 to 3.7 mg/L (after), indicating O_2 extraction efficiency of 67 to 88% at a flow rate of 4 to 5 L/min. The DO extraction efficiency decreased with membrane vacuum pressure and with flow rate (Fig. 4), but was insensitive to water pressure in the range 1,000 to 3,000 torr.

Field testing of EDGAR was performed on a groundwater well in Oswego, IL. The compositions of dissolved and extracted gases were measured using a quadrupole mass spectrometer. The concentration of O_2 was at blank level in these samples, indicating negligible atmospheric contamination. Nitrogen in extracted gas was enriched by $\sim 18\%$ and Kr was depleted by $\sim 21\%$ relative to Ar (Fig. 5). The correlation between DO -extraction efficiency (E_{DO}) and membrane vacuum pressure suggests that water and gas partials across the membrane are in solubility equilibrium. Consequently, extraction efficiencies of other gas species (E_{gas}) can be estimated as a function of their activities (a_{gas}) from:

$$\frac{E_{\text{gas}}}{(1-E_{\text{gas}})} = \frac{S_{\text{gas}} E_{\text{DO}}}{(1-E_{\text{DO}})}$$

According to this model, E_{gas} values for N_2 , CH_4 , Ar , and Kr are expected to be 0.89, 0.78, 0.79 and 0.69 respectively for $E_{\text{DO}} = 0.8$ at ambient temperature (0 to 20°C). Nitrogen and Kr should then be fractionated relative to Ar by +18% and -17%, respectively, which is roughly in agreement with the observation.

References

- Chen C.-Y., Lu Y.M., Bailey K., O'Connor T.P., Young L., Lu Z.-T. 1998. Ultra-sensitive photo-trace analysis with a magneto-optical trap. Science 280, 1139-1141.
- Du X., Pultschert R., Bailey K., Lehmann B.E., Lorenz R., Lu Z.-T., Mueller P., O'Connor T.P., Sturchio N.C., Young L. 2000. A new method for measuring ^{81}Kr and ^{84}Kr abundances in environmental samples. Geophysical Research Letters 27, No. 20, pp. 2008.
- Sturchio N.C., Du X., Pultschert R., Lehmann B.E., Sultan M., Patterson L.J., Lu Z.-T., Müller P., Sigler T., Bailey K., O'Connor T.P., Young L., Lorenz R., Becker N., El Aily C., El Kallouby B., Dawood T., and Abdallah A.M.A. 2004. One million year old groundwater in the Sahara revealed by ^{81}Kr and ^{14}C . Geophysical Research Letters 31, L05303.

Acknowledgements

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Figure 3. Extraction membrane cross-section.

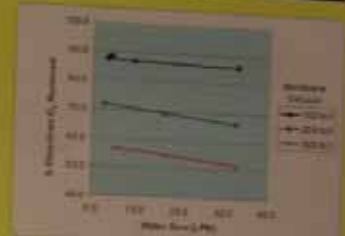


Figure 3. Lab testing with Chicago tap water. Extraction efficiency for O_2 increases significantly with increasing membrane vacuum pressure and with water flow rate.

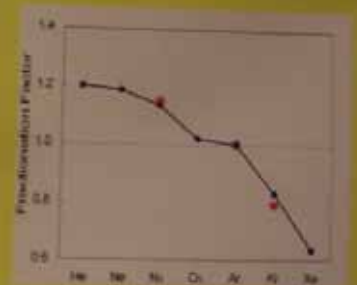


Figure 5. Approximation of extracted gases relative to Ar . Extraction efficiencies are higher for less-soluble gases (e.g., N_2 and Kr) and Kr .

シカゴ大の Kr 85 抽出システム (AGU2006)

2008年度以降の予定

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H21	大阪、ソウル、ジャカルタ
H22	必要に応じて国内・国外

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H19	CFC法、Kr85法現地適応調査、(東京、バンコク)、ジャカルタ現地地下水調査、
H20	ジャカルタでのサンプリングライン調査、バンコクの補足調査と解析、大阪でのサンプリングライン調査
H21	ソウルサンプリングライン調査、大阪・ジャカルタサンプリングライン調査補足、
H22	補足調査、成果の解析と取りまとめ、