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Noble gases in common rocks and their bearing on
noble gas occurrences in the hydrological cycle

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Abstract

Thermal and cold water sources in the French Massif Central were selected as targets for the present work. In this area waters issue in both igneous and sedimentary terrain. A comparison of the noble gases in these different rocks was aimed to allucidate amounts and nature of noble gases contributed by country rocks as opposed to atmospheric noble gases brought in by recharged water. No previous information was available on the noble gas contents in the area and the data obtained are, therefore, important by themselves.

Field collection was done in collaboration with Prof. G. Michard and Dr. C. Fouillac of the Laboratoire de Geochimie des Eaux, Universite de Paris, who made also the chemical analyses.

The analytical work lasted much longer than anticipated, mainly due to the enormous amounts of reactive gases that accompanied the studied sources. These dictated special cleaning procedures and time-consuming separations prior to the mass spectrometric analyses.

No difference in the noble gas contents was found between waters issuing in igneous rocks to those issuing in sedimentary rocks. In both, significant variations in the contents of atmospheric and radiogenic noble gases were found.

Radiogenic helium has been found to reveal a positive correlation to the contents of atmospheric Ne, Ar, and Kr. This indicates water recharge into the deep part of the systems, mixing with radiogenic He and Ar flushed from igneous and sedimentary rocks, and subsequent partial gas loss.

Loss of gas is evident from the observed low noble gas contents. These losses have been accompanied by a "reversed" retention pattern of

Ne > Ar > Xe

This reversed retention pattern can not be an artifact of sampling nor can it result by partial steam loss. A new pattern, has thus been observed to occur, not known so far from other areas of thermal water activity.

Lack of isotopic oxygen "shifts" is taken as an indication of lack of elevated temperatures at depth.

Much more work on noble gases in waters issuing in different rock types is needed.

Introduction

The Massif Central is rich in springs and wells of cold and warm (up to 82°C) mineral waters, which are often extremely rich in gases (mainly CO₂).

Many of these waters are encountered in igneous terrains and others occur in sedimentary rocks. Hence, waters of two major types of aquifers may be studied and compared in regards to their chemical and isotopic composition. Previous geochemical studies of waters of the Massif Central included parts of these aspects (Michard et al., 1976).

In the present study representative springs and wells of mineral and thermal waters in the Massif Central (Table 1 and Fig. 1) were studied for their noble gases and ionic and isotopic composition.

Techniques

The samples were collected for noble gases in 10 cm³ pyrex tubes with high quality spring loaded stopcocks at the ends. These tubes were pre-evacuated and tested for leaks. Sample/collection was done by flushing the vessels with the sampled water and closing of the stopcocks. The gases were extracted within one month since collection and transferred into He-tight glass tubes with breakseals. Subsequently were the samples cleaned over a hot Ti getter. He and Ne were separated by an activated charcoal trap at liquid nitrogen temperature. Argon was released from the trap at -120°C and Kr at +80°C.

The gases were let into a 4.5" 60° Reynold's type glass mass spectrometer (Nuclides Co.). A liquid nitrogen trap was applied at the inlet, trapping hydrocarbons (but also xenon).

Sampling reproducibility for noble gases

Many of the waters were extremely rich in gases, appearing as real "sprinkle water". This caused variations in the size of the gas bubble present in each collection vessel. In most cases this bubble was 0.5-1.0 cm³ in the 10 cm³ vessels (except No. F-6, which contained 7.9 cm³ gas and only 1.2 cm³ water). Thus, significant variations were seen in the concentration of the noble gases in duplicate samples (Table 2). However, the relative abundances and the isotopic compositions were well reproducible (Tables 2 and 3).

Results and discussion

The data are given in Tables 2 and 3. The following patterns emerge:

1. In part of the cases significant amounts of He were observed, in excess over the 5×10^{-8} cc STP/cc water that may be expected from dissolved air alone (Fig. 2). This excess helium is regarded to be radiogenic, i.e. from the radioactive decay of uranium and thorium present (in common concentrations) in the aquifer rocks. Radiogenic helium is often observed in thermal and mineral waters (Mazor, 1977).

No correlation between radiogenic helium content and observed temperature is seen in the five Vichy samples (Table 2).

2. In several cases (Table 3) the $^{40}\text{Ar}/^{36}\text{Ar}$ ratios are above the atmospheric value of 295.6, indicating the presence of a non-atmospheric ^{40}Ar excess. This is attributed to radioactive decay of ^{40}K in the

aquifer rocks. In most of these cases the total argon content was, however, low and only in sample F-6 of Vichy a significant amount of radiogenic argon was observed (2.3×10^{-5} cc STP/cc water).

The radiogenic helium and argon, coming from the aquifer rocks, thus serve as deepseated tracers and their correlation to the atmospheric noble gases will be discussed below. It is only of interest to note that the He rad/Ar rad ratio in the F-6 sample is 4.4, i.e. well in the range of 1 to 6, observed in similar waters in other parts of the world (Mazor, 1977).

3. The isotopic composition of the observed Ne and Kr was found to be atmospheric (Table 3). Hence, three atmospheric tracers, Ne, Ar atm. (atmospheric fraction, calculated via ^{36}Ar) and Kr are at hand (Table 2).

4. The atmospheric Ne, Ar and Kr vary in their concentrations in the various waters studied but they are positively correlated (Fig. 3), indicating they originate from one type of gases (derived from the atmosphere, but modified).

5. The amount of radiogenic helium varies much between the studied waters. Yet, the concentrations of the radiogenic helium values are positively correlated to the concentrations of the three atmospheric noble gases (Fig. 4).

This indicates that the atmospheric gases were carried down with the recharging water and were mixed with the deep-seated radiogenic helium and most probably also with the CO_2 and other reactive gases. Variations of the gas/water ratio must have occurred subsequently, either because

losses into a separating steam phase or due to pressure release during ascent to the surface.

Positive correlations between the atmospheric and radiogenic noble gases have been previously observed in the geothermal systems of Larderello in Italy (Mazor, 1979) and in the Lassen Volcano National Park, U.S.A. (non published data). Such a correlation may indicate that all recharged water penetrated deep into the aquifers and mixing with shallow water (devoid of the radiogenic tracers) is negligible. This seems to be well supported by the low tritium values observed (Table 5).

6. The observed concentrations of the atmospheric noble gases are compared in Fig. 2 to the original amount, expected in the recharging water (assuming an average annual temperature of 10°C (Hertzberg and Mazor, 1979) and average intake elevation 2000m, (i.e. applying a correction factor of 1.27 (Mazor, 1977)).

The concentrations of the atmospheric noble gases are seen to be in general lower than the values expected to be in the recharging waters. Thus, part of the atmospheric noble gases were lost prior sampling. In light of the positive correlation between the atmospheric noble gases and the radiogenic helium (Fig. 4) one may conclude that part of the original radiogenic helium was lost as well. Part of the reactive gases must have been similarly lost prior sampling. The atmospheric noble gas concentrations may be applied to calculate the deep-seated concentration of other gases in the waters, i.e. prior to the losses. This topic will be discussed further on.

8. The retention percentages of atmospheric noble gases are given in Table 4 and Fig. 5. The following general pattern of retention is seen:



This is in contrast to the pattern prevailing at Yellowstone (Mazor and Fournier, 1973). There, the explanation was that a steam and gas phase had been separated. The lighter gases are expected to escape in such cases more efficiently than the heavier ones and the residual liquids will have a retention pattern of:



Such a "reversed" relation exists in the separated steam and gas phase. There, the lighter gases will accumulate more than the heavy ones. The pattern in Fig. 5 resembles, thus, a separating gas phase and not a residual liquid. The meaning of this pattern in terms of a geochemical model is still to be worked out.

Gas losses at the surface, prior or during sampling, would produce liquids with a "normal" fractionation pattern of the atmospheric noble gases. Hence, the observed "reversed" pattern can not be an artifact caused by sampling.

Stable hydrogen and oxygen isotopes

The δD and $\delta^{18}\text{O}$ values are reported in Table 5 and Fig. 6.

No "oxygen shifts" or evaporational shifts are observed. This seems to indicate that:

(a) No partial steam phase was separated.

(b) Temperatures at depth were relatively low, in contrast to the "classical" geothermal fields.

Thus, the stable isotope data seem to exclude partial steam losses as an explanation for the observed noble gas depletions, a conclusion that agrees with the fact that the observed fractionation patterns are not "normal".

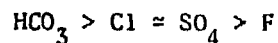
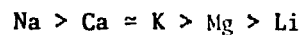
Tritium

The observed tritium data (Table 5) are low, excluding intermixing with significant amounts of surface, or near-surface, waters. This is in good agreement with the positive correlation observed between the contents of radiogenic helium and atmospheric neon, argon and krypton (Fig. 4).

Dissolved ions

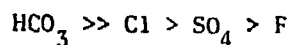
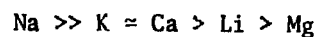
The chemical data are given in Table 6. The following groups emerge:

(a) Low total dissolved ion contents (Neris, Evaux, Mont Dore, Chaudes Aigues) with 27-45 milimoles/l. The relative abundances in this group are:



This pattern seems to typify the igneous aquifers.

(b) High total dissolved ion contents (Vichy, St. Yorre, St. Nectaire) with 162-186 milimole/l. The relative abundances are:



This group differs, thus, from the previous one by higher contents of the various ions, especially of Na and HCO_3 . This group is associated with sedimentary aquifers of

(c) A separate case of high total dissolved ion contents is presented by Ceysat, with 177 milimole/l and a relative abundance pattern of:

$\text{Mg} > \text{Ca} > \text{Na} > \text{Li}$

$\text{HCO}_3 \gg \text{Cl} > \text{SO}_4 > \text{F}$

The terrain is built of alluvial sediments.

It seems, as a general trend, that the waters issuing in igneous terrain are low in dissolved ions as compared to those issuing in sedimentary rocks. No similar correlation is observed in the radiogenic or atmospheric noble gases.

Future work recommended

1. The results turned out to be of high interest to the study of the Massif Central Thermal water systems. More sites should be studied but an effort should be done to collect samples at the bottom of wells to avoid gas losses.

2. Other terrains, with waters that do not contain so high amounts of reactive gases should be selected for further rock-water-noble gas studies.

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Table 1 : Sample data

No.	Source	type	flow lit/min	°C	country	rock	total dissolved* ions, meq/l	T, (T.U.)*	Remarks
F-1	Noris, Cesar	well	1580	53	granite		33.3	1.7±0.7	
F-2	Evaux, Cesar	well		62	granite		39.5	1.3±0.7	
F-3	Evaux, St. Marie	well		45	granite		40.4		
F-4	Vichy, Source de Dome	well	20	62	alluvium on Oligocen, sediments		176.3	0.9±0.7	travertine rich
F-6	Vichy, Boussanges	well (220m)	255	42	" "		184.9	0.3±0.7	high CO ₂ content
F-7	Vichy, Grand Grille	spring	56	41	" "		182.1		
F-8	Vichy, L'hospital	spring	72	34	" "		185.6		
F-9	Vichy, Genereuse	well	20	25	" "		169.2		
F-10	St. Yorre, Prof. L. Blanquet	well	79	15	" "		162.3	< 0.4	high gas content
F-17	Ceyssat	spring		11	?		177.2	1.2±0.7	
F-20	Mont Dore, St. Jean			42	?		44.7	< 0.6	sampled in Etabiliation Thermal, after gas was partially released.
F-21	St. Nectaire, Mont Cornadore			38	granite and diorite ?		175.8	0.8±0.7	
F-22	Chudes Aigues, Moulin du Bon			45	granite		28.7	0.3±0.7	
F-23	Chaudes Aigues, Forage du Bon	well	91	75	granite		27.3		
F-24	Chaudes Aigues, Source du Par	spring	273	82	granite		28.7	0 ±0.7	

* C. Fouillac and G. Michard, Laboratoire de Geochimie des Eaux, Paris.

Table 2: Noble gases, cc STP gas/cc STP water*

No.	Source	*C	Run No.	He x 10 ⁻⁸	Ne x 10 ⁻⁸	Ar tot x 10 ⁻⁴	Ar ^{**} atm x 10 ⁻⁴	Ar ^{**} rad x 10 ⁻⁴	Kr x 10 ⁻⁹
F-1	Neris, Cesar	53	486	3360+420	4.9+0.4				
			502	1630+200	1.1+0.1	1.30+0.16	1.29+0.16	n.d.	19.4 +1.9
			504	3780+470	6.8+0.6				
F-2	Evaux, Cesar	62	506	10540+1300	20.5+1.8	2.81+0.35	2.75	0.06	14.3 +1.4
F-3	Evaux, St. Marie	45	507	6500+800	22.3+2.0	2.17+0.27	2.11	0.06	20.3 +2.0
F-4	Vichy, Dome	62	488		3.5+0.3				
			493	17+5	2.9+0.3				
F-6 ^{***}	Vichy, Boussanges	42	508	10170+1300	13.9+1.2	1.79+0.20	1.56	0.23	18.2 +1.8
F-7	Vichy, Grand Grille	41	501	9+5	2.6+0.2				
F-8	Vichy, L'Hopital	34	498	14+5	0.8+0.07				
F-9	Vichy, Genereuse	25	500	1+3	1.0+0.1				
F-10	St. Yorre, Blanquet	15	484		3.6+0.3				
			509	320+40	2.1+0.2	0.38	0.32	0.05	1.93+0.19
F-17	Ceyssat	11	483		2.6+0.2				
F-20	Mont Dore, St. Jean	42	495	< 5 ^{****}	< 0.5				
			503	5+3	0.5+0.3				
F-21	St. Nectaire, M.C.	38	485		2.8+0.3				
			492	15+4	1.1+0.1	0.10+0.01	0.09	n.d.	2.44+0.24
F-22	Chaudes Aigues, M. d. Bon	45	494	77+10	9.7+0.9				
			500	72+9	10.6+0.9	1.94+0.24	1.93	n.d.	16.4 +0.16
			510	24+3	11.0+1.0	0.81+0.10	0.80	n.d.	11.1 +1.1
F-23	Chaudes Aigues, F. d. Bon	75	499	48+6	1.9+0.2				
F-24	Chaudes Aigues, Par	82	497	60+8	1.1+0.1				
	Air saturated water, (at 2200 m)	10		3.7	16		2.9		71

* STP stands for 0°C and 760 mm Hg. The data of gas and water values in each sample collected are given in Table 1.

** Calculated from Ar total, applying the measured ⁴⁰Ar/³⁶Ar ratio reported in Table 3 and using the common atmospheric value of 295.6. n.d. - non detectable; i.e. 0.01 x 10⁻⁴ cc STP Ar rad/cc STP water or less.

*** Note the high amount of gas in the sample (Table 1).

**** Sample was collected at the Etaliation Thermale at which the water was accumulated in a room, so a gas phase was formed. We sampled the remaining water phase.

Table 3: Isotopic compositions

No.	Source	Run No.	$^{20}\text{Ne}/^{22}\text{Ne}$	$^{40}\text{Ar}/^{36}\text{Ar}$	$^{82}\text{Kr}/^{84}\text{Kr}$	$^{83}\text{Kr}/^{84}\text{Kr}$	$^{86}\text{Kr}/^{84}\text{Kr}$
F-1.	Neris, Cesar	496	10.28				
		502	10.0	298.1	0.189	0.182	0.286
		504	10.27				
F-2	Evaux, Cesar	506	10.10	302.2			
F-3	Evaux, St. M.	507	10.20	304.5			
F-4	Vichy, Dome	488	10.55		0.204	0.202	0.301
		493	10.69				
F-6	Vichy, Bous	508	10.62	339.0			
F-7	Vichy, G. G.	501	10.31				
F-8	Vichy, Hopital	498					
F-9	Vichy, Gen.	500	10.70				
F-10	St. Yorre, B.	484	10.75		0.200	0.176	0.300
		509		347.8	0.188	0.197	0.274
F-17	Ceyssat	483	10.48		0.190		0.288
F-20	Mont Dore, S. J.	495					
		503					
F-21	St. Mectaire, M. C.	485	10.55				
		492	11.50	291.1	0.198	0.195	0.290
F-22	Ch. Aigues, M. d. B.	494	10.50				
		505	10.50	297.8			
		510	10.26	300.6	0.198	0.191	0.293
F-23	Ch. Aigues, F. d. B.	459	10.68				
F-24	Ch. Aigues, Par	497	10.80				
	Atmospheric values		10.31	295.5	0.203	0.203	0.305

Table 4 : Percent retention of atmospheric noble gases, assuming recharge at 15°C at 2200 m

No.	Source	°C	Run No.	Ne	Au atm	Kr
				1.6	2.9	71
F-1	Nerris, Cesar	53	496	26		
			502	6	38	24
			504	36		
F-2	Evau, Cesar	62	506	108	81	18
F-3	Evau, St. Marie	45	507	117	62	25
F-4	Vichy, Dome	62	488	18		
			493	15		
F-6*	Vichy, Boussanges	42	508	75	46	23
F-7	Vichy, Grand Grille	41	501	14		
F-8	Vichy, L'Hopital	34	498	4		
F-9	Vichy, Genereuse	25	500	5		
F-10	St. Yorre, Blanquet	15	484	19		
			509	11	9	2
F-17	Ceyssat	11	483	14		
F-20	Mont Dore, St. Jean	42	495	< 3		
			503	3		
F-21	St. Nectaire, M.C.	38	485	15		
			492	6	3	3
F-22	Chaudes Aigues, M. d. Bon	45	494	51		
			505	56	57	21
			510	58	24	14
F-23	Chaudes Aigues, F. d. Bon	75	499	10		
F-24	Chaudes Aigues, Par	82	497	6		
	Air saturated water at 2200 m	10		100	100	100

Table 5 : Isotopic composition and dissolved ions

No.	Source	δD ‰	$\delta^{18}O$ ‰	T, T.U.	Cl meq/l	TDI meq/l
F-1	Neris, Cesar	-58.1	-8.40	1.7±0.7	3.7	33.3
F-2	Evaux, Cesar	-57.6	-8.25	1.3±0.7	3.2	39.5
F-3	Evaux, St. Marie	-57.0	-8.15		3.3	40.4
F-4	Vichy, S. d. Dome	-62.0	-9.30	0.9±0.7	9.8	176.3
F-6	Vichy, Bousanges	-62.0	-9.45	0.3±0.7	10.0	184.9
F-7	Vichy, G. Grille	-62.5	-9.50		10.2	182.1
F-8	Vichy, L'Hopital	-58.0	-9.15		9.9	185.6
F-9	Vichy, Genereuse	-64.2	-9.70		9.7	169.2
F-10	St. Yorre, Blanquet	-60.5	-9.05	< 0.4	8.9	162.3
F-17	Cyssat	-58.7	-9.40	1.2±0.7	13.7	177.2
F-20	Mont Dore, St. Jean	-61.3	-9.40	< 0.6	6.3	44.7
F-21	St. Nectaire	-59.0	-8.85	0.8±0.7	40.0	175.8
F-22	Chaudes Aigues, M. d. B.	-60.0	-9.10	0.3±0.7	2.1	28.7
F-23	Chaudes Aigues, F. d. B.	-60.7	-9.05		1.9	27.3
F-24	Chaudes Aigues, Par	-61.1	-9.20	0 ±0.7	2.1	28.7

Table 6 : Dissolved ions (10^{-4} moles/liter)

No.	source	°C	aquifer	pH	Ca	Mg	K	Na	Li	Cl	SO ₄	HCO ₃	SiO ₂	F	Σ _{i+}	Σ _{i-}	Al%	Σ _i
F-1	Neris, Cesar	53	igneous	6.96	0.93	0.035	0.43	13.6	0.27	3.7	2.57	7.80	1.80	0.36	16.3	17.0	4.0	33.3
F-2	Evaux, Cesar	62	"	6.79	0.99	0.079	0.50	17.2	0.39	3.2	5.80	5.50	2.06	0.39	20.2	19.3	5.0	39.5
F-3	Evaux, St. Marie	45	"	6.83	1.00	0.081	0.49	17.5	0.34	3.3	5.30	5.60	1.92	0.40	20.5	19.9	3.0	40.4
F-20	Mont Dorc, St. Jean	48	?	5.90	2.02	1.29	1.09	14.2	0.19	6.3	0.38	15.5	2.92	0.036	22.1	22.6	2.1	45.0
F-22	Chaudes Aigues, M. du Bon	45	igneous	6.72	0.57	0.29	0.76	12.0	0.12	2.1	0.29	11.2	1.43	0.18	14.6	14.1	3.7	29.0
F-23	Chaudes Aigues, F. du Bon	72	"	6.30	0.55	0.26	0.70	11.5	0.12	1.9	0.25	10.2	1.30	0.16	13.9	13.4	4.0	27.0
F-24	Chaudes Aigues, Par	82	"	6.20	0.57	0.26	0.75	12.0	0.12	2.1	0.30	11.2	1.47	0.18	14.6	14.1	3.5	29.0
F-4	Vichy, S. du Dome	62	sedimentary	7.93	1.28	0.42	2.68	80.6	0.79	9.8	2.04	74.5	0.83	0.44	87.5	88.8	1.5	176
F-6	Vichy, Bousanges	42	"	6.66	3.43	0.45	2.48	80.8	0.80	10.0	2.10	78.5	0.82	0.41	91.8	93.1	1.4	185
F-7	Vichy, Grand Grille	41	"	6.23	2.59	0.45	2.45	82.2	0.79	10.2	2.00	76.0	0.83	0.45	91.5	90.6	1.0	182
F-8	Vichy, L'Hopital	34	"	6.78	3.93	0.49	2.52	80.8	0.79	9.9	1.92	78.5	0.69	0.44	92.9	92.7	0.3	186
F-9	Vichy, Genereuse	25	"	6.46	1.00	0.38	2.35	78.4	0.77	9.7	1.87	71.0	1.22	0.50	84.3	84.9	0.8	169
F-10	St. Yorre, Blanquet	15	"	6.22	2.02	0.42	2.84	73.0	0.72	8.9	1.77	68.0	0.26	0.47	81.4	80.9	1.0	162
F-21	St. Nectaire, Corradore	38	?	6.49	4.07	3.12	4.05	66.9	1.57	40	0.91	47.0	1.80	0.042	86.9	88.9	2.2	176
F-17	Ceyssat	11	?	6.31	18.8	21.2	0.71	9.2	0.27	13.7	8.62	56.0	1.28	0.023	90.2	87(?)	4	177

Figure Captions

1. Map of studied samples.
2. Noble gas abundances (sample numbers are indicated). A.S.W. 15°C - air saturated water at 15°C, at 2200 m altitude - representing average recharge conditions. High He excesses are observed.
3. Correlation between atmospheric Ne and Ar, and Ar and Kr. A positive correlation is observed.
4. Correlation of atmospheric Ne, Ar and Kr as a function of radiogenic He. Positive correlations are seen.
5. Percent retention of noble gases, i.e.:

$$\frac{\text{observed concentration}}{\text{expected concentration in recharge water}} \times 100$$

A "reversed" pattern is seen, i.e. the heavier gases are less retained than the lighter ones.

6. Isotopic composition of stable hydrogen and oxygen. No oxygen shifts or evaporation trends are seen.
7. Chemical composition (Table 6). The Vichy and St. Yorre samples (right group), issuing in sedimentary terrains are higher in dissolved ion contents than the igneous terrains waters (Neris, Evaux, Mt. Dore and Chaudes Aigues), the major enrichment being in $\text{Na}(\text{HCO}_3)$ (left group).

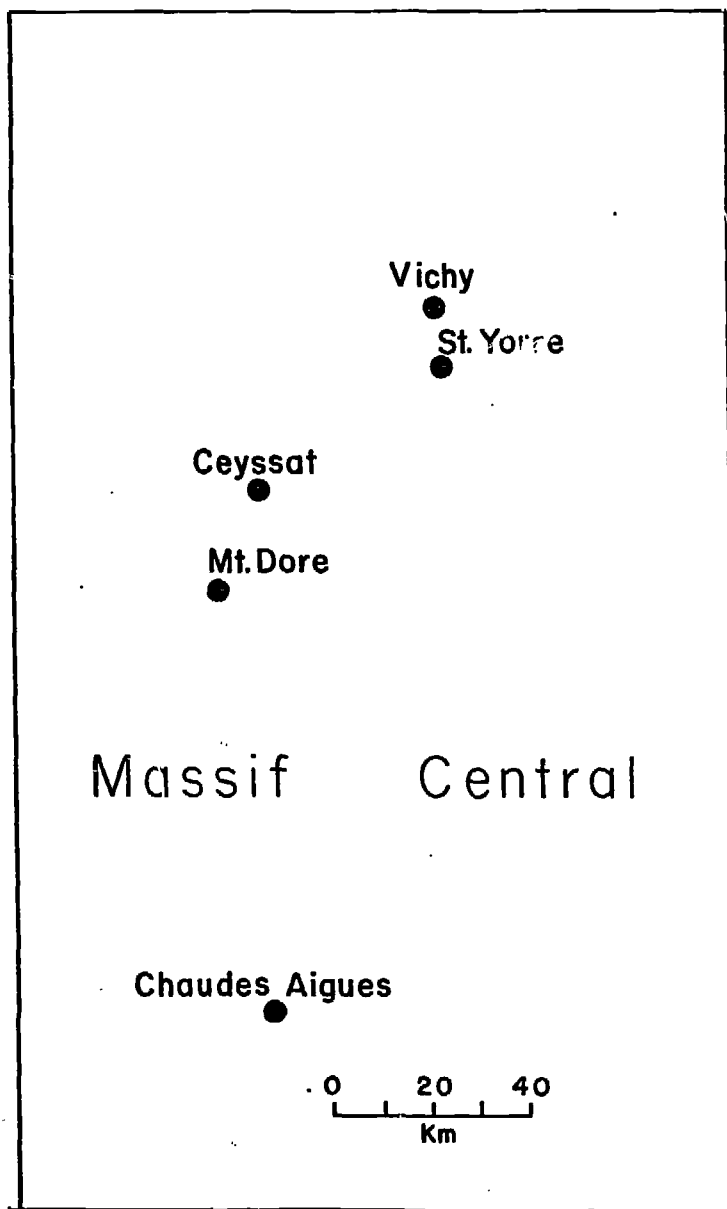


Fig. 1

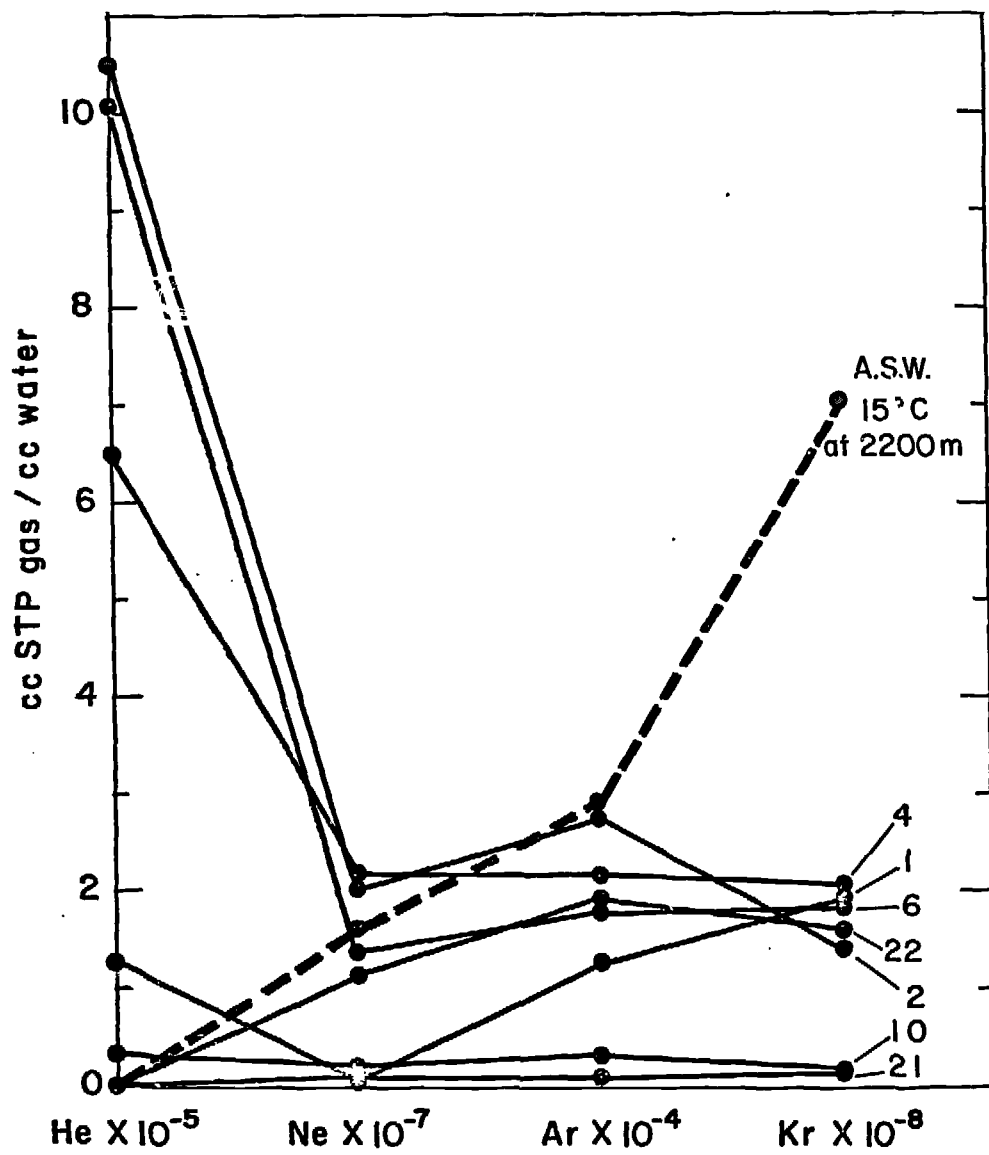


Fig. 2

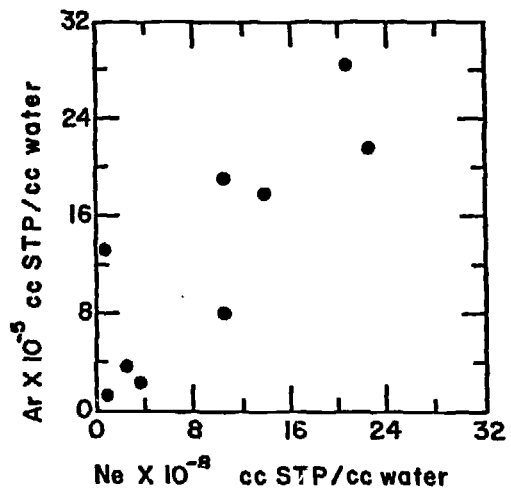
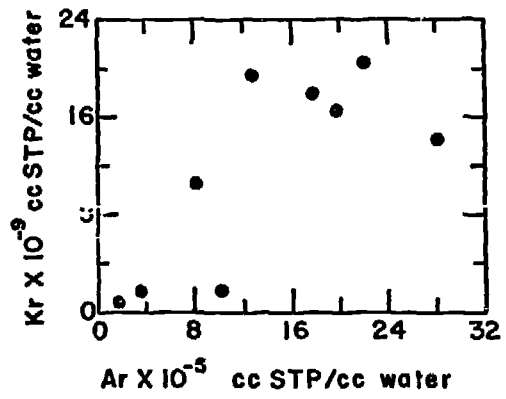


Fig. 3

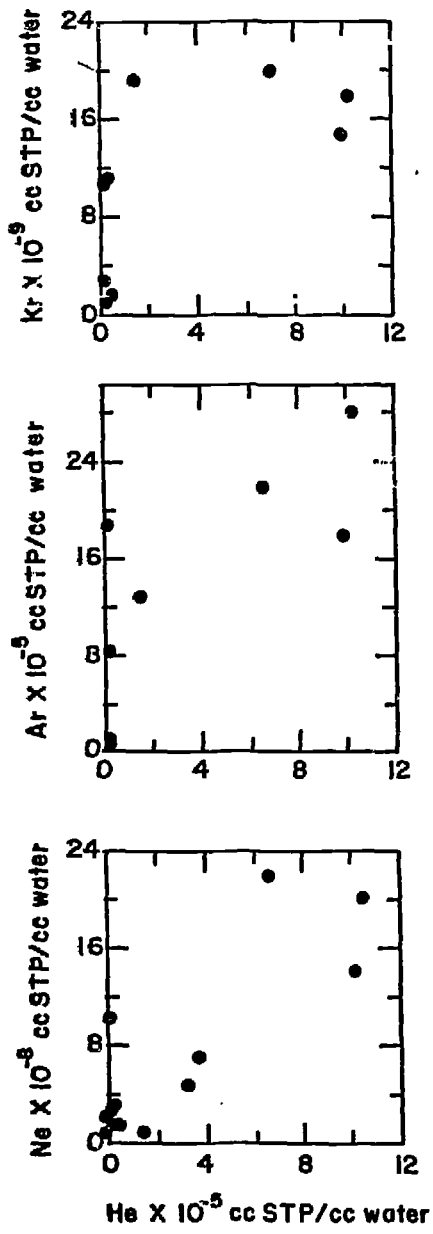


Fig. 4

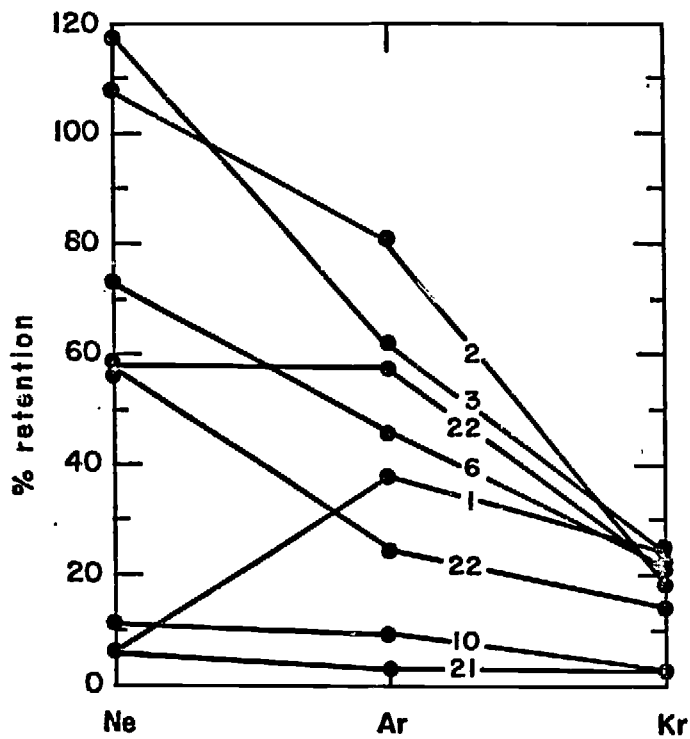


Fig. 5

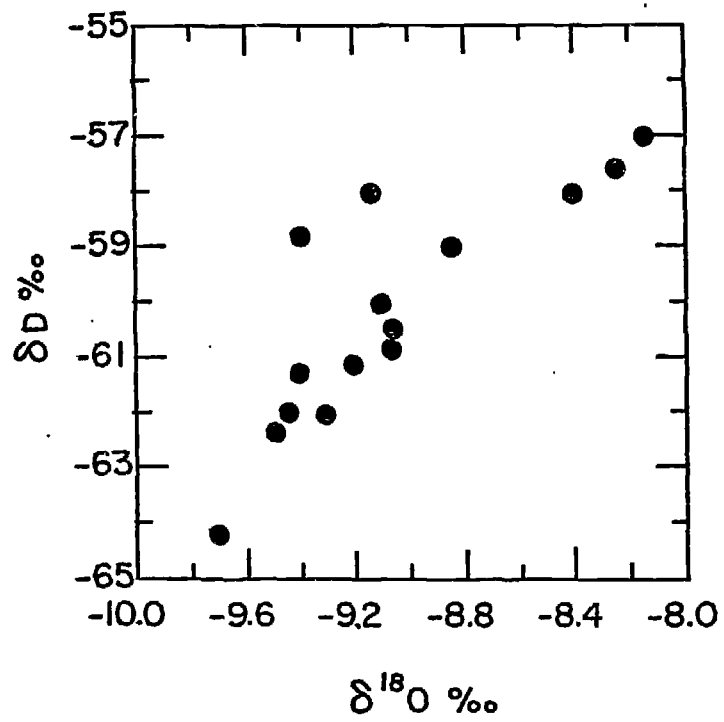


Fig. 6

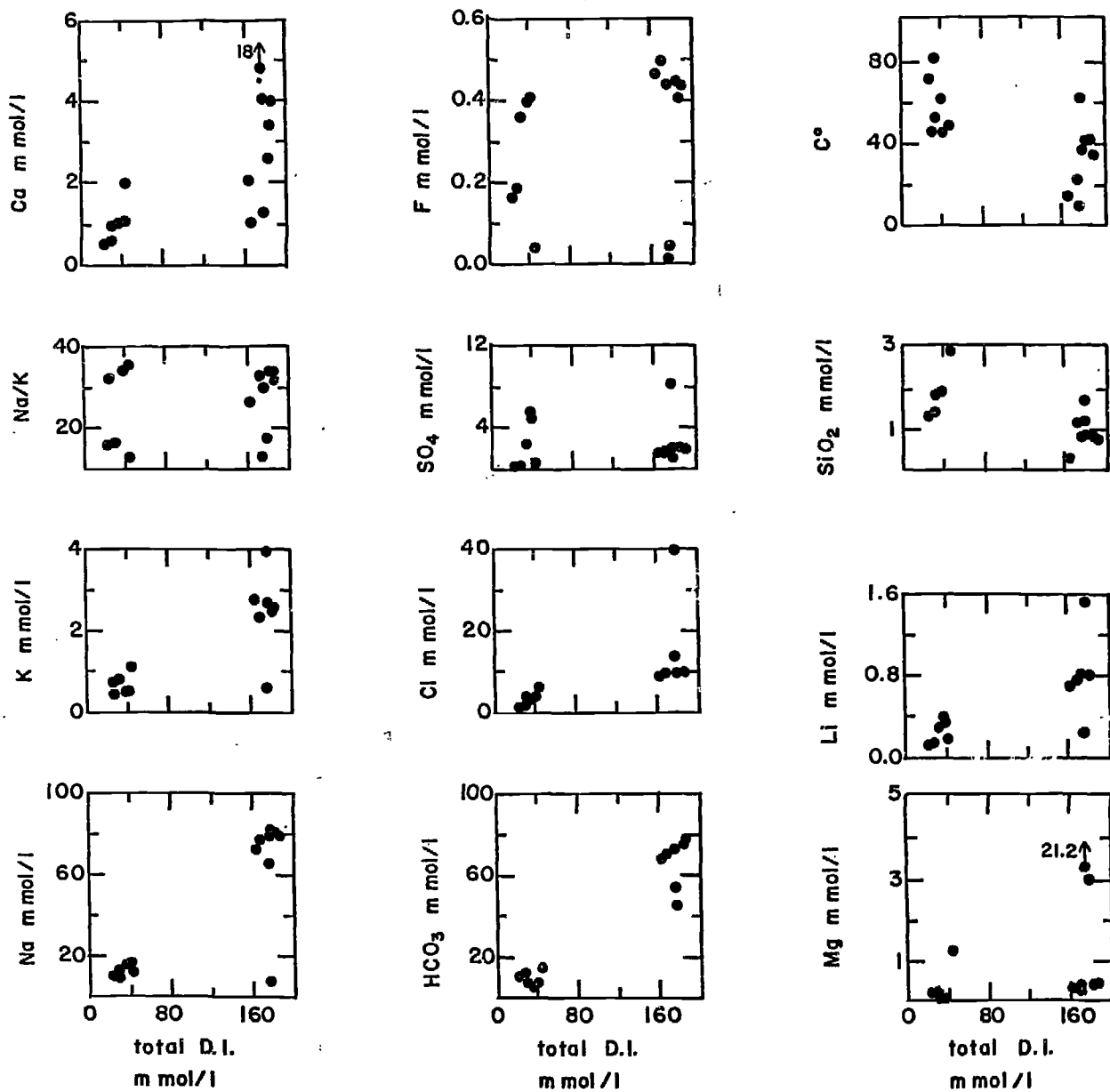


Fig. 7

