

Chlorine Isotopes Potential as Geo-chemical Tracers

P. V. Shirodkar, Umesh Kumar Pradhan and R. Banerjee

*National Institute of Oceanography, Dona Paula, Goa – 403 004,
INDIA*

Introduction

Here, the potential of chlorine isotopes as tracers of geo-chemical processes of earth and the oceans is highlighted based on systematic studies carried out in understanding the chlorine isotope fractionation mechanism, its constancy in seawater and its use as a tracer of hydrothermal activity.

Chlorine isotopic fractionation between solid and liquid phases was studied in hyper saline, evaporative salt lakes of Qaidam Basin, China. The $d^{37}\text{Cl}$ measured by +ve TIMS from brines and deposited saline minerals from 23 salt lakes showed lower values of -2.05 to $+1.01\%$ for brines and higher of -0.53 to 1.2% for the deposited saline minerals, indicating enrichment of ^{37}Cl in solid phase relative to ^{35}Cl . The highly evaporative salt lakes showed reverse isotopic fractionation of chlorine during quick salt deposition, wherein ^{35}Cl remained enriched in solid phase relative to ^{37}Cl .

Knowledge of the $d^{37}\text{Cl}$ value of seawater is very important for elucidating the crust-mantle processes operating deep within the oceans, because the resulting $d^{37}\text{Cl}$ signature reflects a mixture of seawater value, oceanic crust and the mantle value. The $d^{37}\text{Cl}$ values of crust (0%) and mantle ($+4.7\%$) are specific and different from each other. To evaluate constancy in $d^{37}\text{Cl}$ values of seawater, chlorine isotopic measurements were made from 51 surface seawater samples from 4 major oceans – Indian, Atlantic, Pacific and Southern Ocean, which indicated a variation in $d^{37}\text{Cl}$ from -0.76 to $+0.74$ (av. $0.039 \pm 0.04\%$). Q-mode factor and multiple regression analyses applied to air-sea fluxes and $d^{37}\text{Cl}$ values, showed 4 distinct zones, each with a different $d^{37}\text{Cl}$ variability, indicating that the air-sea fluxes control 38 to 78% of $d^{37}\text{Cl}$ variation in these zones. The observed $d^{37}\text{Cl}$ variability in 4 zones when tested with ANOVA indicated no significant difference, suggesting constancy in $d^{37}\text{Cl}$ values of seawater.

To trace the presence of hydrothermal activity at 3 locations – Vema (10° 43.23'S and 66° 36.5'E), Vityaz – VT4 (5° 39.55'S and 68° 03.77'E) and Vityaz – VT6 (5° 38.83'S and 67° 27.39'E) in the Central Indian Ridge (CIR), the $d^{37}\text{Cl}$ values were measured from seawater column at selected depths. The measured $d^{37}\text{Cl}$ values showed distinct differences between the upper 300m layer and the layer below it at VT6 relative to those at VM and VT4. The observed difference corroborated well with geological findings on serpentinization observed very near VT6 (within 1°), which led to the suspected presence of hydrothermal activity at VT6.

Two chlorine isotopes, ^{35}Cl and ^{37}Cl , with a relative abundance of 24.22% and 75.78%, respectively are highly mobile and fractionate (Xiao et al 2000, Eastoe et al, 1989 and Desaulniers et al, 1986). During the past few decades, chlorine isotopes had limited applications. Recent improvement in measurement precision and better understanding of fractionation mechanisms, helped in using these isotopes for understanding major processes of the earth and oceans, such as subduction that trigger tsunami waves; mantle-crust recycling; hydrothermalism; origin of salt lakes; in mineral exploration etc. The important factor which govern these processes is the chlorine isotopic fractionation associated with (i) solid-liquid phase and (ii) gas – liquid phase, which is more prevalent during high temperature hydrothermal processes of the earth. The constancy in chlorine isotopic compositions ($d^{37}\text{Cl}$) of seawater plays a significant role in unraveling these processes. Various studies involving chlorine isotopic fractionation mechanism, constancy in $d^{37}\text{Cl}$ of seawater and its use as a tracer, carried out in the past are detailed here, highlighting its potential as excellent geo-chemical tracer.

Material and methods

Isotopic fractionation mechanism was better studied in the hypersaline environment where isotopic fractionations are markedly evident. So, brine and chloride minerals (halite) were collected from 23, highly saline, evaporative salt lakes of Qaidam Basin, China (Fig.1), during July 1992. pH and density of brines were measured during sampling and the samples were processed for chlorine extraction by ion exchange method for isotopic measurements.

Constancy in $d^{37}\text{Cl}$ of seawater was evaluated by collecting surface seawater samples from 51 stations at various locations in 4 major world oceans –

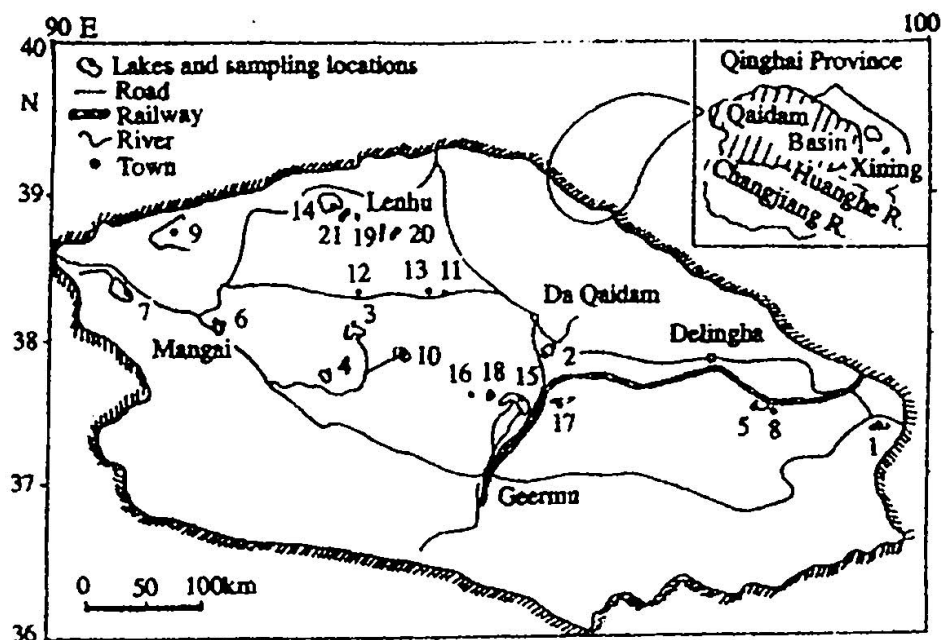


Fig. 1 The sampled locations of salt lake brine in Qaidam Basin

Indian, Atlantic, Pacific and Southern Ocean during the 9th Antarctic Scientific Expedition of the Third Institute of Oceanography, China from November 1992 to April 1993. The temperature and salinity were obtained from the CTD whereas; air-sea fluxes were downloaded from HOAPS Atlas using satellite data (Grassl et al, 2002). The collected seawater samples were ion exchanged for chlorine extraction for isotopic

Measurements

For tracing the presence of hydrothermal activity in the CIR, seawater samples were collected from selected depths in 2000m water column at 3 stations - VM3 (10° 43.23'S and 66° 36.5'E), VT4 (5° 39.55'S and 68° 03.77'E) and VT6 (5° 38.83'S and 67° 27.39'E) transform fault areas (Fig.2), during ORV Sagar Kanya cruise 125 (July – August 1997). Chlorine was extracted from each of these samples by ion exchange for isotopic measurements.

Extraction of Chlorine

Nearly 20 to 40 mg of chloride mineral (halite) was dissolved in 0.5 to 1.0 ml of water and 0.5 gm each of dry Ba-form resin (Shanghai 732) provided with Ba(NO₃)₂ solution to remove SO₄²⁻ ions and the dry H-form resin (Dowex 50 W x 8) were successively added to the above solution and allowed to stand for 5 min. Thereafter the resins were discarded and the clear solu-

tions containing chloride were adjusted to pH 3 - 4 by adding Cs_2CO_3 solution. The resulting test solution was 5 - 10 mg/ml of Cl. In case of brine, about 2.5 ml of brine was taken and 3 - 5 ml of seawater was exchanged the same way as above.

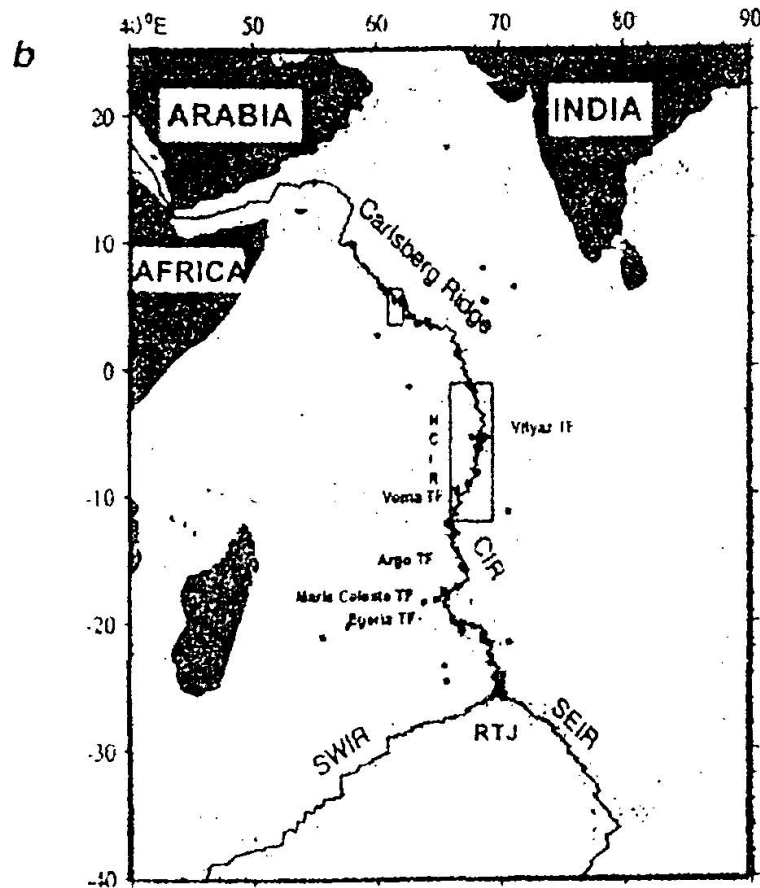


Fig.2: Seawater sampling area in the CIR

Finally, the sample was passed through cesium type resin bed (Dowex 50W x 8) column provided with CsOH solution to convert Cl^- ions to CsCl . The test sample (eluate), which is CsCl was collected for isotopic measurements of chlorine.

Chlorine isotopic measurements in the extracted samples were carried out at the Institute of Salt Lakes, China by +ve thermal ionisation mass spectrometry of Cs_2Cl^+ ion, using a VG 354 model TIMS (Xiao and Zhang, 1992, Xiao et al, 1995). The measured isotopic ratios were

$$\delta^{37}\text{Cl} (\text{‰}) = \left[\frac{(^{37}\text{Cl}/^{35}\text{Cl})_{\text{Sam.}}}{(^{37}\text{Cl}/^{35}\text{Cl})_{\text{ref.}}} - 1 \right] \times 1000$$

expressed as δ values relative to their standard reference materials and were calculated as follows;

The standard used for chlorine isotopic measurement was the ISL 354 NaCl, provided by the Institute of Salt Lakes, Xining, China, with an average chlorine isotopic ratio of 0.3189296 ± 0.000083 .

Results and Discussion

Low $d^{37}\text{Cl}$ values of brines ranged from -2.05 to 1.01‰ , with a mean of -0.45‰ relative to those of solids (-0.53 to 1.2‰ , av. 0.08‰). This indicated isotopic fractionation of chlorine, where the heavier isotope, ^{37}Cl remains associated with solids and is a normal process of chlorine isotopic fractionation in the environment. This variation was related to pH, density and chloride concentration of brines in such a way that the $d^{37}\text{Cl}$ values decreased with the decrease of pH and increase of chloride cons. The evaporation of brine caused the decrease of pH and increase of density and Cl^- cons. Consequently, the $d^{37}\text{Cl}$ values decreased with decreasing pH and increase of density during evaporation.

However, the quickly deposited solids from highly evaporative salt lakes and those from artificial brines, obtained by boiling and quick cooling in the laboratory, indicated a decrease in ^{37}Cl , suggesting a reverse isotopic fractionation process. In this case, the lighter isotope ^{35}Cl remains associated with solids relative to ^{37}Cl . This gave low a value below 1.0, which gradually increases with standing time, suggesting that the equilibration time is very important for isotopic fractionation of chlorine in nature. Normally, a molecule with heavy isotope has a low zero point energy and the bond of the molecule with heavy isotope is not easily broken when the molecule is dissolved (Zhang 1983). In chemical reactions, the molecule containing lighter isotope react more easily compared to those with heavy isotope. The isotopic equilibrium between the salt and coexisting brine is attained during slow deposition of salt, during which, the ^{37}Cl preferentially enters into the solid phase due to different bonding energies of ^{37}Cl and ^{35}Cl with Na and K ions to form NaCl and KCl. Therefore, the saline minerals tend to be enriched in ^{37}Cl . However, the Cl^- ions in solution are present as hydrated ions $[\text{Cl}-\text{H}_2\text{O}]$, which react with Na, K or other ions to form NaCl, KCl etc. during evaporation of brine to a saturated state.

So, the $^{35}\text{Cl}-\text{H}_2\text{O}$ should react preferentially with Na or K ions to form solids. The ^{35}Cl is therefore enriched in the solid phase in the salt being crystallized. Salt crystallization and dissolution occurs simultaneously when salt is slowly crystallized and since Na^{35}Cl or K^{35}Cl dissolves faster to Na^{37}Cl or K^{37}Cl , it causes enrichment of ^{37}Cl in solid phase during slow deposition or deposition over longer time period.

$\delta^{37}\text{Cl}$ variation in seawater from 4 major world oceans was observed from -0.76 to $+0.74\text{‰}$ with a mean of $0.039 \pm 0.04\text{‰}$. The surface temperature of water in these oceans showed large variation from -1.25 to 29.4°C with higher temperatures ($>20^\circ\text{C}$) beyond 100°E meridian within 40°N and 40°S of the equator. Similarly, the salinity ranged from 33.31 to 35.25 psu., with a difference of 2.5 psu units. The high salinity was evident within the high temperature zone beyond 100°E meridian.

The data indicated that the measured $d^{37}\text{Cl}$ values belong to the areas experiencing evaporation, precipitation or condensation, which gave rise to large variation in $d^{37}\text{Cl}$. As these variables are the air sea fluxes, for a better understanding, 7 air-sea flux variables pertaining to each sampling area were downloaded from HOAPS atlas and regressed with $d^{37}\text{Cl}$ values using multivariate and univariate statistical techniques. The Q-mode factor analyses showed 3 principle factors providing information of sample variance of about 81%. Further statistical analyses of the data yielded 4 different Zones, each with a different $d^{37}\text{Cl}$ variability along with significant air-sea flux variables.

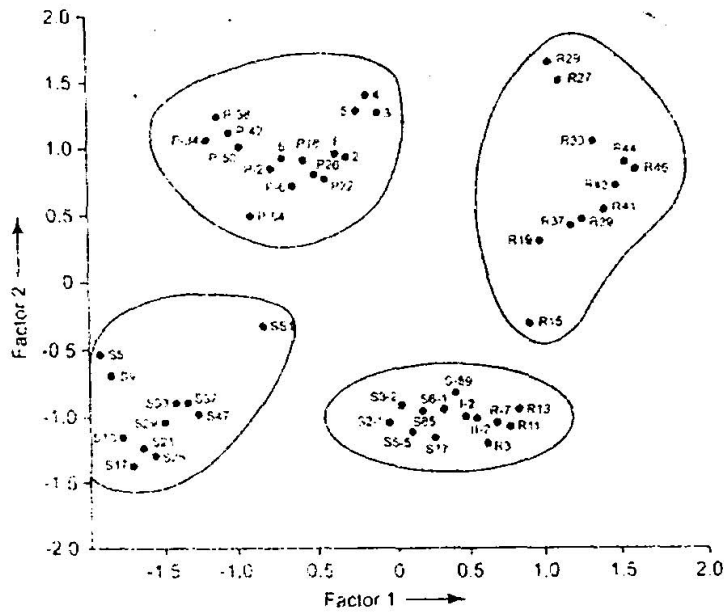


Fig.3. Factor analysis plot shows 4 Zones of significant air-sea flux variables.

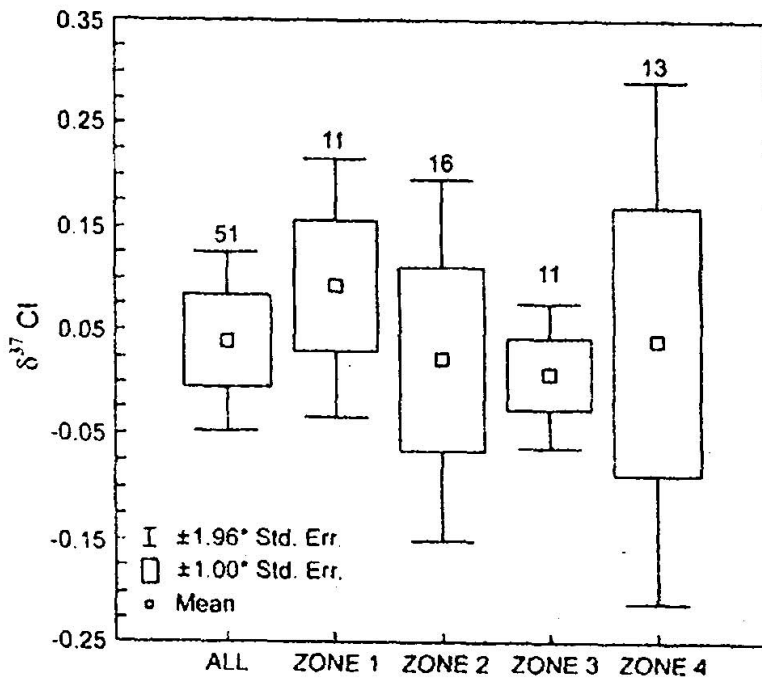


Fig. 4. Box Plot- mean \pm SE in $\delta^{37}\text{Cl}$ in 4 zones

Each of these 4 zones showed different chlorine isotopic variability, which was confirmed for their similarity or dissimilarity using ANOVA. It is a conservative test and is applied to confirm significant differences in $d^{37}\text{Cl}$ values between 4 groups. The 4 groups though indicated different $d^{37}\text{Cl}$ variability (Fig. 4); ANOVA indicated no significant difference in $d^{37}\text{Cl}$ values of each of these groups. This showed that $d^{37}\text{Cl}$ of seawater are constant.

The variation in $\delta^{37}\text{Cl}$ of seawater at 3 stns. in the CIR is given in Table 1. Large variability in $d^{37}\text{Cl}$ is shown by VT6 stn. from 300m to 2000m depth. The average values calculated for 3 stns. showed significantly low $d^{37}\text{Cl}$ value of -0.37‰ at VT6 as compared to stn. VT4 (av. $+0.25\text{‰}$) and VM ($+0.21\text{‰}$). This significant difference suggested some sort of process going on deep below in the ocean at VT6.

Bonifacie et al, (2005) indicated that at hydrothermal sites in MOR areas, the interaction of seawater with wall rock in a convection cell is associated with mineralisation and phase separation processes, both at sub critical (low T & P) and supercritical conditions (high T & P). During phase separation, volatile chlorides partition into vapour phase and non-volatile elements into condensed phase. At subcritical separation, circulating seawater is associated with small vapour with lower chlorinity separated from large amount of seawater enriched in salts and depleted in volatile species. During supercritical separation, vapour phase is associated with seawater like liquid accompanied by brine of high salinity, high metal content and low volatiles. During chlorine isotopic fractionation in this case, chlorine is chemically transferred from aqueous chloride ion to gaseous molecule (NaCl , HCl & Chlorine) or incorporated into solids.

The chlorine isotopic fractionation factor between aqueous chlorine and HCl ($a_{\text{aq-Chlorine-HCl}}$) and that between vapour and liquid or between seawater and brine ($a_{\text{vapour-liquid}}$) is from 0 to 1‰ for temperatures of 300 to 450°C . This suggested low salinity vapour phase to have $d^{37}\text{Cl}$ from 0 to $+1\text{‰}$ and conjugate high salinity phase to have $d^{37}\text{Cl}$ from -1 to 0‰ . In an extreme case of HCl and Cl_2 coexistence, the $a_{\text{HCl-Cl}_2}$ is less than 0.30‰ at temperature $>200^\circ\text{C}$ and the $d^{37}\text{Cl}$ values are $-ve$ to $+1\text{‰}$.

Eastoe and Guilbert (1992) indicated that $d^{37}\text{Cl}$ vary from -1 to 0.5‰ in hydrothermal fluids from ore forming systems. The $d^{37}\text{Cl}$ measured in hydrothermal fluids from fast spreading MOR areas showed values of -0.03‰

(Bonifacie et al, 2005). These values are obtained from the real hydrothermal fluids collected from actual hydrothermal sites, however, our values were measured from seawater collected much above the seafloor from VM, VT4 and VT6 areas. The observed $d^{37}\text{Cl}$ value at VM is of +0.25‰, at VT4 it is +0.21‰ while at VT6, the value is -0.37‰. The stations VT4 and VT6 are very close to each other while station VM is 5° S apart from both VT4 and VT6 stations, despite this, the station VT4 and VM show similar $d^{37}\text{Cl}$ values and the value at VT6 is different and significantly lower, falling within the hydrothermal fluid values observed by Eastoe and Guilbert (1992). This indicated that there must be a presence of hydrothermal activity at or near VT6 transform fault in the CIR. The low temperature serpentinization of peridotites was observed within 1° of VT6 stn., which further supports the presence of hydrothermal activity at or nearby VT6.

Table 1: The hydro-chemical characteristics and $\delta^{37}\text{Cl}$ values of seawater at Stations

Depth (mtr.)	VM3				VT4				VT6			
	Temp (°C)	Sal.(psu)	pH	$d^{37}\text{C}$ ‰	Temp. (°C)	Sal.(psu)	pH	^{37}C ‰	Temp. (°C)	Sal.(psu)	pH	$d^{37}\text{C}$ ‰
0	25.96	35.24	8.18	-	27.48	35.29	8.19	0.82	27.42	35.26	8.28	0.94
25	25.96	35.25	8.18	0.59	27.46	35.29	8.20	0.84	27.42	35.26	8.29	0.77
50	25.97	35.26	8.19	0.49	27.45	35.29	8.20	0.87	27.43	35.26	8.29	0.69
100	21.36	35.28	8.12	0.53	18.6	35.3	8.09	0.75	18.9	35.26	8.10	0.94
200	13.88	34.86	7.97	0.42	13.21	35.06	8.00	0.12	13.48	35.1	8.03	0.87
300	11.72	35.02	8.09	0.57	11.05	34.94	7.98	0.11	11.01	34.94	8.00	0.76
500	8.41	34.72	7.94	0.10	9.08	34.82	7.96	0.33	9.17	34.83	7.98	-0.36
750	6.63	34.71	7.89	0.30	7.1	34.8	7.93	0.39	7.39	34.81	7.93	-0.19
1000	5.14	34.68	7.9	0.29	5.94	34.79	7.94	-0.03	6.03	34.8	7.95	-0.53
1250	4.31	34.69	7.99	0.10	4.95	34.77	7.95	0.59	5.31	34.81	7.95	-0.53
1500	3.39	34.72	7.96	0.41	4.06	34.75	7.96	-0.02	4.12	34.76	7.98	-0.19
1750	2.81	34.73	7.98	0.27	-	-	-	-	-	-	-	-
2000	-	-	-	-	2.8	34.74	7.99	0.49	2.66	34.73	8.05	-0.43

Acknowledgement

The authors express their sincere thanks to Director NIO for his encouragement in this study. They also thank Prof. Xiao Yingkai and his group, ISL,

China for their help in isotopic measurements of chlorine by mass spectrometry.

References

1. Bonifacie, M., Charlou, J. L., Jendrecejewski, N., Agrinier, P. and J.P. Donval . *Chemical Geol.* **221** (2005) 279.
2. Desaulniers, D.D., Kaufmann, R.S., Cherry, J. A. . *Geochim Cosmochim Acta* **50** (1986) 1757.
3. Eastoe, C. J., Guilbert, J. M., Kaufmann, R. S. *Geology* **17** (1989) 285.
4. Eastoe, C. J. and Guilbert, J. M. *Geochim Cosmochim Acta* **56** (1992) 4247.
5. Grassl, H., Jost, V., Ramesh Kumar, M. R., Schulz, J. Bauer, P., Schluessel, P. *HOAPS Report*, vol. 312, Germany: Max-Plank Institute for Meteorology (2002) 130.
6. Xiao, Y. K. and Zhang, C. G. *Int. J. Mass Spectrom. Ion Process*, **116** (1992) 183.
7. Xiao Y. K., Zhou, Y.M., Liu, W.G. *Anal. Lett.* **28** (1995) 1295.
8. Xiao, Y.K., Liu, W.G., Zhou, Y.M., Wang, Y. H., Shirodkar, P. V. *Chinese J. Oceanol Limnol.* **182** (2000) 169.
9. hang, W. M. The application of stable nuclides. Science Press, Beijing (1983) 10s.