

Pakistan J. Sci. Ind. Res., 12, 506-507 (1970)

### DETERMINATION OF ZINC IN INTERSTITIAL WATERS BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

SYED A. ALI\* and DAVID C. BURRELL

*Institute of Marine Science, University of Alaska College, Alaska, U.S.A.*

(Received June 17, 1969)

The trace transition metals occur in sediment interstitial fluids in concentrations greater than in the overlying water column.<sup>1</sup> The transition metal group presents a greater complexity in terms of both determination and characterization. Table I shows the average abundances of these metals in sea water. It can be noted that the mean value of these metals fall below the detection limits of currently available instruments. Since these metals play an important role in the chemical diagenetic sequence, development of a highly sensitive, yet accurate and rapid, analytical technique is mandatory. Atomic absorption spectrophotometry, together with a simple pre-analysis concentration step, would appear highly suitable.

TABLE I.—ABUNDANCE, DETECTION LIMITS AND OPTIMUM WORKING RANGE OF SELECTED TRACE METALS IN SEA WATER.

Element	Sea water concentration (mg/l)	Detection limits (mg/l)	Optimum working range (mg/l)
Sr	8.0	0.01	2—20
Li	0.17	0.005	0.5—5
Rb	0.12	0.015	2—20
Mn	0.002	0.01	2—20
Fe	0.01	0.06	2—20
Cu	0.003	0.01	2—20
Zn	0.01	0.005	0.2—3
Co	0.0001	0.07	4—40
Ni	0.002	0.10	2—25

\*Present address: Department of Geology, Rensselaer Polytechnic Institute, Troy, New York, U. S. A.

Chelation and subsequent solvent extraction of the complexed metal offers an advantageous pre-analysis concentration technique for many trace metals present in sea water.<sup>2,3</sup> However, since this method is better suited to relatively large volumes of solution, application to interstitial fluid analysis is limited and a simple concentration using commercially available chelating resin, as advocated for sea water by Riley and Taylor,<sup>4</sup> appears to offer great promise.

This preliminary report demonstrates the application of these techniques to the analysis of the trace zinc content of interstitial fluids taken from recent glacial sediments from Glacier Bay National Monument, Southeast Alaska.

### Methods

*Sample Collection.*—A sequence of long piston cores was collected in Queen Inlet, Glacier Bay, Alaska on R/V ACONA Cruise 069 in July, 1968. The polybutyrate core liners were sectioned into 1-ft lengths and the sediments extruded and squeezed in the metal-free nitrogen activated squeezer designed by Reeburgh.<sup>5</sup> The pore water thus obtained was stored in acid washed, sealed polyethylene bottles prior to the pre-analysis concentration process.

*Resin Column Preparation.*—The procedure employed for the preparation of the concentration column closely parallels that described by Riley and Taylor.<sup>4</sup> Chelex-100 resin (Bio-Rad Laboratories, Richmond, California) of 50-100 mesh was digested three times at room temperature with excess of 2N HNO<sub>3</sub> and washed thoroughly with distilled and deionized water. The resin, after digestion, was packed in 1-cm diameter glass tubing to give column length of 3 cm.

To determine the extraction efficiency, 25 ml of 1 mg/l zinc standard solution was passed through the column under a flow rate of 5 ml/min. After washing with 25 ml of water, the column was eluted with 5 ml of 2N HNO<sub>3</sub>. These volumes were selected to yield sufficient final material for accurate atomic absorption analysis. In fact, the column extraction efficiency was determined to be only 56.5% of added zinc. Riley and Taylor (addendum to 1968 paper) have noted that the acid Chelex-100 resin leaks zinc, and the effect would be severe when minor sample volumes are utilized. No attempt was made to utilize optimum values since, for these pore fluid samples, only a low concentration factor was required.

*Determination of Zinc in Interstitial Waters.*—25-ml portions of raw interstitial water samples

were percolated through the column under a flow rate of 5 ml/min. The retained zinc was subsequently eluted from the resin with 5 ml 2N HNO<sub>3</sub> after washing with 25 ml of distilled and deionized water. The final zinc concentrations were determined using a Perkin-Elmer 290 B atomic absorption spectrophotometer coupled to a Honeywell recorder. The eluents were compared with standards prepared in a similar matrix. Both standards and samples were introduced into the spectrophotometer via a suitably adapted syringe pump (Sage Instruments, Inc.). Use of this device minimized erratic data due to poor aspiration and minor solution viscosity differences.

The following instrument settings were used: grating, ultraviolet; analytical line, 2138 Å; slit, 7 Å; source, hollow cathode lamp; lamp current, 8 ma; air flow, 9.0; acetylene flow, 9.0; flame, oxidizing.

### Results and Conclusions

Data obtained for zinc for the glacial sediments ranged from 0.09 to 0.57 ± 0.005 mg/l zinc. The use of a simple chelating resin concentration step coupled with precise subsequent atomic absorption analysis has proved eminently suitable for pore fluid trace zinc analysis. No doubt this technique may be readily extended to other trace transition metals. The use of a syringe pump to give highly regulated flow rates is recommended for this work.

**Acknowledgements.**—This study was supported in part by Atomic Energy Commission Contract AT-(04-3)-310, PA-3, and National Science Foundation Grant GZ 1046. This is contribution No. 52 of the Institute of Marine Science.

### References

1. R.R. Brooks, B. J. Presley and I.R. Kaplan, *Geochim. Cosmochim. Acta.*, **32**, 397 (1968).
2. R.R. Brooks, B. J. Presley and I.R. Kaplan, *Talanta*, **14**, 809 (1967).
3. D.C. Burrell, *Atomic Absorption Newsletter*, **7**, 65 (1968).
4. J.P. Riley and D. Taylor, *Anal. Chim. Acta.*, **40**, 479 (1968).
5. W.S. Reeburgh, *Limnol. Oceanogr.*, **12**, 163 (1967).

Pakistan J. Sci. Ind. Res., **12**, 507-508 (1970)

## THE AGE OF KAWAHGAR FORMATION

M.H. KHAN

*Oil and Gas Development Corporation, Karachi*

(Received June 25, 1969)

In the Kawah Gar Hill, approximately two and a half miles south-east of Campbellpur, an apparently unfossiliferous sequence of clastic and carbonate rocks overlies the Giumal-Spiti (Lumshiwal\*) formation and is overlain unconformably by the Hill (Lockhart) limestone. This sequence of rocks was called 'Kawahgar Shales' by Cotter and 'Kawahgar Marls' by the geologists of the Attock Oil Company. Until recently the age of the Kawahgar formation was not known with certainty. Cotter (*op. cit.*) regarded this rock formation to be part of the Eocene succession. Some time ago the writer discovered the presence of unmistakable Upper Cretaceous foraminifera; *Globotruncana lapparenti*; *G. andori*; *G. arca* and *Hetrohelix globosa*. This discovery has established for the first time the definite presence of the late Cretaceous sediments in the Potwar area.

The Kawahgar formation attains its maximum development of 435 ft in the Kawah Gar Hill which is the type locality (Fig. 1). It consists of grey, weathering yellow, medium hard marls, which

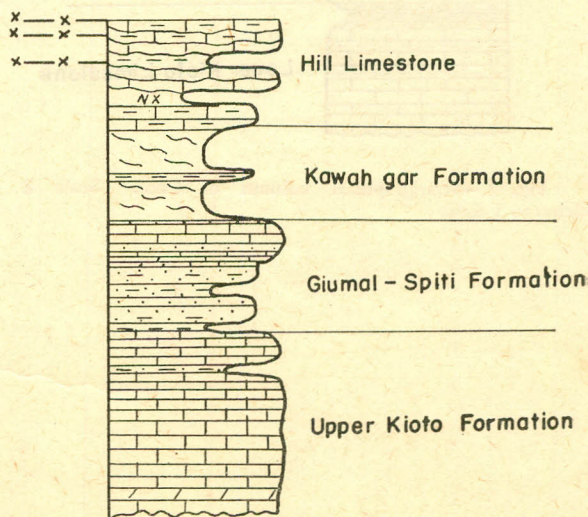


Fig. 1.—Stratigraphical column of Kawah Gar. Scale 8 inches to 1 mile.

\*The formation names in bracket are proposed by Stratigraphic Committee of Pakistan.

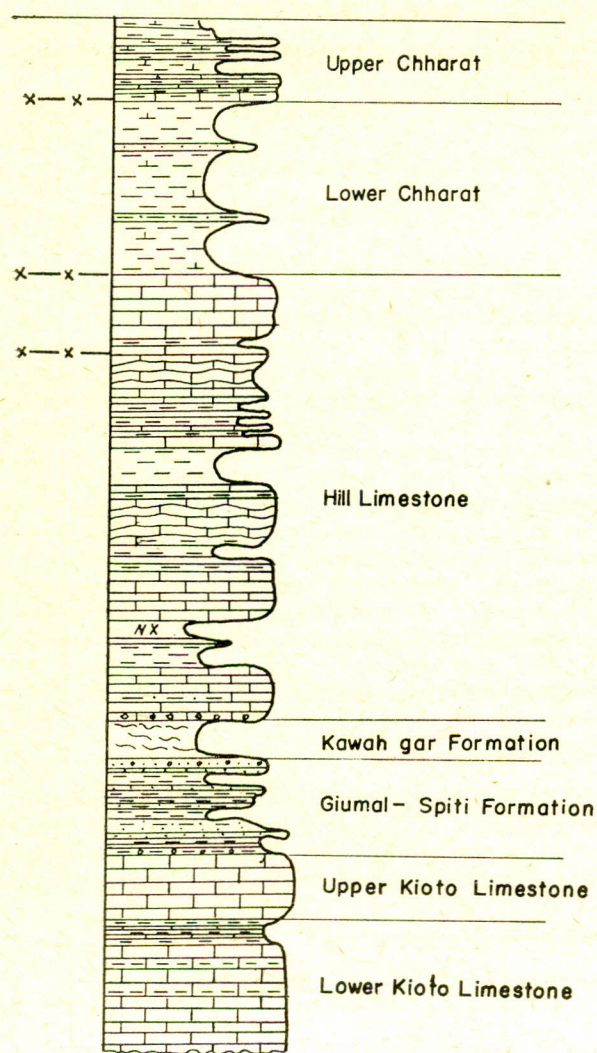


Fig. 2.—Stratigraphical column of Choi. Scale 8 inches to 1 mile.

exhibit well-developed slaty cleavages, and are interbedded with occasional thin bands of grey argillaceous limestone. The top of the formation is formed by 80 ft thick well-bedded, brown to yellow-brown, slightly argillaceous, sublithographic limestone. A good section of this formation is exposed about 1000 yd south-east of Jassian village where it starts in the Hill (Lockhart) limestone and runs southward across the Haro River through the Kawahgar formation upto its contact with the Giumal-Spiti (Lumshiwal) formation (from  $72^{\circ} 23' 52'' : 33^{\circ} 44' 45''$  to  $72^{\circ} 23' 52'' : 33^{\circ} 44' 37''$ ) and then starting from the top of the Giumal-Spiti (Lumshiwal) formation it follows a nala running south-east across the Kawah Gar Hill and finishes in the Upper Kioto (Sumna Suk) Limestone.

The Kawah Gar Hill is part of a recumbent anticlinal fold. The sequence near the village of Jassian is normal, but further east it becomes overturned. The contact between the Kawahgar formation and the overlying Hill (Lockhart) Limestone is not seen in this area and is probably faulted. In the Choi area (text fig. 2) a pronounced unconformity is marked by a ferruginous pisolite.

**Acknowledgement.**—The author is grateful to the Manager, Pakistan Petroleum Limited for permission to publish this note which is based on the field work carried out in 1960-61 in the Kala Chitta, Margala and Kawah Gar Hills by the author in conjunction with S. Manzur-ul-Hasan and M. J. W. Lofting, geologists of Pakistan Petroleum Limited at the time.

#### Reference

1. G. Dep. Cotter, *The Stratigraphy and Structure of the Attock District West of Longitude  $72^{\circ} 45'$* , Mem. Geol. Surv. India, LV, part 2, (1933).