Element partitioning in ferruginous and pyritic phosphorite from the continental margin off Morocco

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SUMMARY. Phosphorites from the continental shelf off Morocco have been analysed for major elements and Fe, Mn, V, Cu, Ni, Zn, As, Na, Sr, S, and for carbonate. In pyritic phosphorites Cu, Ni, Zn, and As are present mainly in minor pyrite and organic carbon. In ferruginous phosphorites As, Mn, and V are associated with goethite. In the ferruginous phosphorites Cu, Ni, and Zn may have been introduced in association with organic matter and pyrite during phosphorite formation and been retained during subsequent destruction of these phases by weathering. In all phosphorites Na and Sr are present mainly in carbonate-fluorapatite. Sulphur in the ferruginous phosphorites occurs only in carbonate-fluorapatite. In the pyritic samples it is partitioned between pyrite and francolite (carbonate-fluorapatite).

PHOSPHORITES have been defined as marine sedimentary deposits containing more than 18% P_2O_5 (Bushinsky, 1969). Francolite, a variety of apatite that contains more than 1% F and substantial amounts of CO_2 (McConnell, 1973) is almost always the major phosphorus phase.

Trace element concentrations in phosphorites are frequently higher than in other sedimentary and crustal rocks (Swaine, 1962; Mason, 1966; Tooms et al., 1969) and many of the elements enriched in phosphorites are also present in igneous and metamorphic apatites, where they may be structurally incorporated in high concentrations (Cruft, 1966; McConnell, 1973). The enrichment relative to crustal abundance and the frequent parallel enrichment in igneous and metamorphic apatites, together with the frequent inability to discern the trace element controls in phosphorites, has often led to the supposition that many trace elements occur within the structure of sedimentary francolite (Whippo and Murrowchick, 1967; Tooms et al., 1969; Cook, 1972).

This work examines this assumption for the elements Na, Sr, V, Mn, Zn, Cu, Ni, As, and S in phosphorites from the continental margin of Morocco.

Sample collection and description

Samples were dredged from the Moroccan continental margin during two cruises of the R.R.S. John Murray during 1968 and 1969 (fig. 1). Four types of phosphorite were recovered: glauconitic conglomerate, massive ferruginous phosphatic limestone containing iron oxide but no pyrite, and pyritic phosphatic limestone, both pelletal and non-pelletal, containing pyrite but virtually no free iron oxide. Whilst the glauconitic conglomerates are not considered here, most contained pebbles and cobbles of ferruginous phosphatic limestone, indistinguishable from those that occurred independently. A number of these were therefore sampled in order to supplement those occurring independently.

Excepting sample 966, the ferruginous and pyritic phosphorites were dredged from areas over 100 km apart. This difference, together with their different mineralogies, results in their separate consideration in this study. The pyritic samples occur both as pelletal and non-pelletal phosphorite; the former contain less calcite and more P_2O_5, Na, Sr, and total S than the latter but are otherwise similar. A distinction is therefore made between these samples when discussing these elements.

Whilst a number of these phosphatic limestones are not true phosphorites, in that they contain less than 18% P_2O_5 (see Table I) all are termed phosphorites for simplicity of presentation.

Mineralogy of phosphorites

The major mineral phases were identified by X-ray diffraction and thin-section examination. The d spacings attributed to carbonate-apatite within the samples agree well with the published figures for this mineral (Milton and Bennison, 1968; Cathcart, 1968). Calcite, dolomite, and quartz are present,

TABLE I. *Chemical analyses of Moroccan phosphorites*

Major elements:

Sample	CaO	P_2O_5	K_2O	Al_2O_3	MgO	SiO_2	Fe_2O_3	CO_2	*CO_3^{2-}	Cal.	Dol.	Total†
Iron-poor pelletal phosphorite												
139 (1)	48·8	25·2	0·13	0·30	1·10	2·4	0·82	12·3	8·1	13·0	2·8	96·38
139 (2)	48·6	24·0	0·15	0·40	0·85	3·0	0·97	12·6	8·6	16·4	2·1	95·35
966 (2)	50·3	29·3	0·12	0·45	0·90	2·3	0·78	7·6	8·2	4·1	1·8	97·77
982	48·6	25·8	0·10	0·30	0·90	2·3	0·57	11·3	8·3	8·0	1·8	92·90
1004	48·7	26·5	0·15	0·40	0·71	2·4	0·80	10·3	8·3	10·0	1·0	94·80
Iron-poor massive phosphorite												
135	47·8	18·6	0·17	0·30	0·85	3·9	0·57	18·8	8·5	30·4	2·5	94·54
136	51·2	19·8	0·11	0·35	0·90	1·9	0·42	17·2	8·1	33·0	2·3	96·17
959	48·7	16·0	0·12	0·30	1·20	3·3	0·43	21·4	8·7	38·4	4·1	94·10
988 (1)	50·6	15·9	0·19	0·50	0·95	2·5	1·75	12·3	8·7	42·9	3·0	87·87
988 (2)	50·0	20·4	0·10	0·30	0·65	1·7	0·67	18·3	8·3	29·6	1·2	97·13
1016	50·0	21·3	0·13	0·35	0·95	1·8	0·79	16·8	8·2	26·4	2·5	96·88
1022 (1)	49·1	20·6	0·11	0·30	0·65	1·5	0·26	17·8	8·9	25·2	1·2	95·00
1022 (2)	52·0	13·3	0·21	0·60	1·55	2·9	1·07	25·0	8·2	51·2	6·2	98·46
1038	48·9	21·5	0·13	0·35	0·90	2·0	0·64	17·7	8·2	23·9	2·3	96·32
Iron-rich phosphorite												
148	48·3	19·2	0·25	0·70	1·55	3·8	3·65	16·7	7·2	27·1	5·6	97·44
156 (1)	33·4	15·8	0·55	1·15	4·50	5·8	18·10	11·7	8·2	2·9	19·4	93·50
156 (2)	43·4	22·0	0·36	0·95	2·60	6·0	8·35	9·8	8·3	7·5	10·1	95·70
157	34·6	12·1	0·25	1·65	7·65	6·4	14·30	19·8	8·6	8·9	34·2	98·63
847 (1)	36·2	15·1	0·49	0·85	3·30	6·5	19·90	12·4	7·1	13·0	13·9	97·07
847 (2)	45·3	21·3	0·35	0·80	2·05	3·6	5·45	14·1	7·4	14·5	7·7	96·09
847 (3)	43·6	18·7	0·32	0·85	2·40	4·3	6·45	14·8	7·6	18·0	9·5	94·58
847 (4)	44·4	21·1	0·45	1·32	1·95	4·8	8·50	13·1	7·2	13·7	7·2	99·66
847 (5)	42·6	22·5	0·39	0·60	1·80	4·1	11·10	8·6	7·8	6·7	6·4	95·05
865	37·9	18·7	0·71	2·20	4·85	10·3	6·85	11·3	7·2	1·8	20·7	95·92
893	36·2	9·8	0·16	0·50	8·65	2·3	16·60	23·7	7·4	14·7	39·0	99·61
896 (1)	33·3	13·3	0·31	1·15	3·55	3·5	22·80	14·4	7·1	11·6	15·2	94·53
896 (2)	39·6	14·9	0·55	1·50	5·50	4·9	7·40	20·6	7·8	14·1	24·1	97·90
896 (3)	40·4	14·8	1·00	1·60	5·60	8·5	8·40	19·4	7·7	15·5	24·6	99·30
896 (4)	36·6	15·0	0·22	0·80	4·25	3·2	15·50	16·2	7·4	11·4	18·4	94·00
896 (5)	34·1	14·8	0·15	0·75	4·45	3·5	14·90	17·8	7·1	6·8	19·9	92·63
898 (1)	41·8	22·3	0·51	1·50	2·36	7·5	6·70	9·6	7·9	4·7	9·0	97·05
898 (2)	39·2	21·5	0·45	1·50	2·55	7·9	7·25	8·5	8·6	2·0	9·5	92·44
898 (3)	45·0	24·5	0·99	1·20	1·95	7·5	0·92	9·4	8·3	5·0	6·9	95·64
898 (4)	44·2	24·8	0·38	1·30	2·30	7·5	2·32	9·3	7·5	1·8	8·6	95·82
898 (5)	42·3	20·3	0·58	1·90	1·80	7·2	4·85	12·6	8·6	12·5	6·6	94·94
966 (1)	47·3	14·6	0·12	0·35	2·20	1·6	5·00	22·8	8·2	36·9	8·9	96·95

Fluorine, $H_2O^{\pm}$ not determined.   * Expressed on a pure francolite basis.   † Including organic C, Na_2O, SrO, S.

TABLE I (*cont.*):

Minor and trace elements:

| Sample	Org. C.	Total S.	S^{2-}	Na	Sr	As	Cu	Ni	Zn	Mn	V
Iron-poor pelletal phosphorite											
139 (1)	0·98	1·31	0·59	1·00	1860	22	20	28	53	65	29
139 (2)	0·73	1·19	0·50	0·99	1840	18	31	26	50	108	23
966 (2)	0·85	1·65	0·81	1·24	2130	25	24	46	82	65	34
982	0·59	1·23	0·49	0·91	2000	9	17	30	40	74	19
1004	0·76	1·15	0·39	0·94	2120	9	20	22	46	50	23
Iron-poor massive phosphorite											
135	0·35	0·86	0·33	0·82	1170	15	10	20	43	104	79
136	1·04	1·21	0·64	0·77	1130	<6	20	35	53	34	29
959	< 0·10	0·72	0·26	0·64	1130	10	11	15	23	73	63
988 (1)	0·30	0·73	0·27	0·76	1190	8	16	22	64	125	76
988 (2)	1·12	1·55	0·96	0·74	1300	30	17	51	50	64	20
1016	0·93	1·40	0·79	0·76	1450	31	22	45	66	55	38
1022 (1)	1·31	1·05	0·54	0·84	1460	<6	22	29	38	46	25
1022 (2)	0·22	0·61	0·23	0·68	1010	6	10	11	15	116	40
1038	0·75	1·53	0·92	0·81	1410	15	27	49	51	103	158
Iron-rich phosphorite											
148	0·34	0·65	—	0·62	1120	32	13	24	41	100	66
156 (1)	0·13	0·50	—	0·52	800	151	16	94	104	374	240
156 (2)	0·45	0·56	—	0·66	1300	64	17	32	40	213	120
157	0·21	0·30	—	0·47	780	100	14	51	77	486	184
847 (1)	0·18	0·46	—	0·47	740	145	21	49	61	193	134
847 (2)	0·20	0·62	—	0·69	1000	90	16	65	70	124	97
847 (3)	0·13	0·64	—	0·68	1100	92	19	47	70	172	64
847 (4)	0·13	0·58	—	0·70	1140	102	18	42	70	170	91
847 (5)	0·17	0·67	—	0·76	1130	91	14	35	62	127	139
865	0·17	0·56	—	0·75	1130	47	11	6	37	125	51
893	0·12	0·33	—	0·37	530	131	12	28	34	425	130
896 (1)	0·20	0·37	—	0·42	750	144	11	35	67	330	242
896 (2)	0·22	0·43	—	0·50	780	46	10	18	26	202	50
896 (3)	0·25	0·45	—	0·53	740	43	8	16	27	202	54
896 (4)	0·13	0·42	—	0·52	750	114	12	6	35	287	160
896 (5)	0·11	0·40	—	0·48	720	99	11	6	36	329	154
898 (1)	0·36	0·74	—	0·84	1250	95	23	112	83	71	256
898 (2)	0·28	0·70	—	0·85	1260	56	6	24	70	71	170
898 (3)	0·34	0·74	—	0·93	1390	<6	16	17	32	65	89
898 (4)	0·37	0·67	—	0·87	1220	27	13	39	45	61	129
898 (5)	0·21	0·80	—	0·81	1280	57	4	57	85	71	160
966 (1)	0·21	0·48	—	0·64	1160	75	10	12	15	239	50
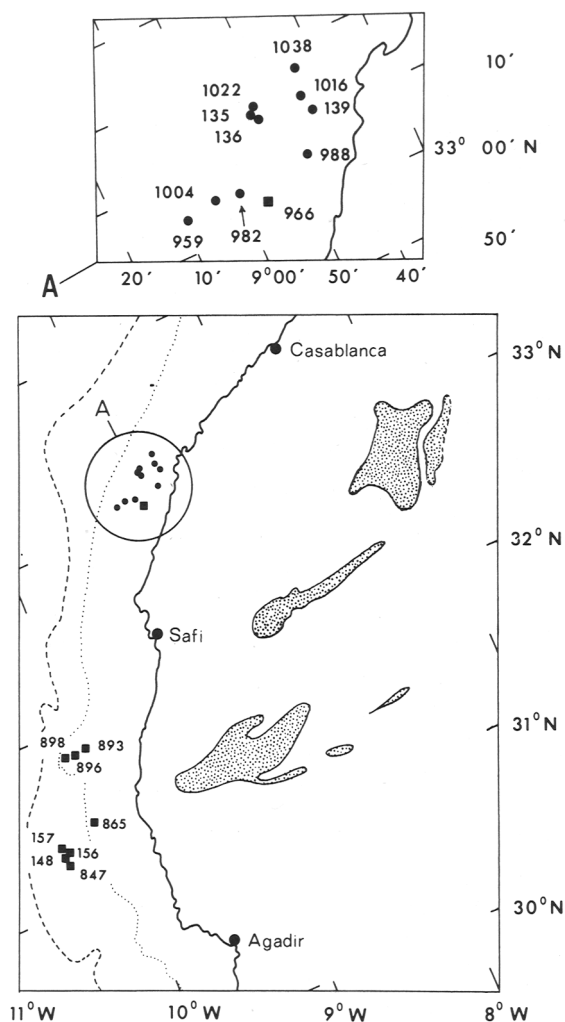
FIG. 1. Locations on the Moroccan continental shelf and slope from which phosphorite rock was obtained. The major onshore locations of phosphate are also shown. Iron-poor samples are represented by circles. Iron-rich samples are represented by squares.

often in considerable quantities, whilst some samples contain small quantities of illite. Ferruginous phosphorites contain goethite as the sole identifiable iron phase. Owing either to their low concentration or poor crystallinity, no other minerals have been identified.

Analytical methods. Carbon dioxide and organic carbon were determined either using a Leco Carbon Analyser or (for CO_2) the method of Bush (1970). Organic carbon was also determined using a chromate oxidation method. Sodium was determined by flame photometry. All other determina-

tions were made by X.R.F., with magnesium also being determined by atomic absorption spectrophotometry and phosphorus also being determined volumetrically. Carbonate structurally incorporated within carbonate-apatite was determined by the method of Gulbrandsen (1970).

Associations amongst the elements and phases have been elucidated by calculating Pearson correlation coefficients, and the use of reduced major axis regression.

For the purposes of estimating the contribution of carbonate minerals to the trace element composition of the samples, semi-quantitative calculations of their concentrations have been made from the major element data (Table I). Dolomite was calculated from total magnesium after correction for magnesium present in carbonate-apatite. Calcite was calculated from total calcium after correction for calcium present in carbonate-apatite and dolomite.

Interpretation of chemical data

For each of the elements Na, Sr, V, Mn, As, Zn, Cu, and Ni, Pearson correlation coefficients have been calculated between the element and all variables listed in Table I. Negative correlations and induced correlations between the above elements have been excluded as have coefficients that are significant at levels above 5%. The correlations are presented in Table II and graphically in fig. 2. These element associations are now discussed.

TABLE II. *Reduced major axis regression and correlation coefficients for Moroccan phosphorites*

Association	r	Significant at x%	Regression line Slope	Int.	Error int.
‡S–As*	0·65	2%	38·3	−6·5	9·0
‡S–As†	0·93	0·1%	32·8	−1·3	4·0
‡S–Cu	0·59	5%	18·9	8·6	4·7
‡S–Ni	0·98	0·1%	52·2	2·2	3·2
‡S–Zn	0·57	5%	95·2	−4·4	17·0
‡S–Org C	0·71	1%	0·68	0·064	0·16
‡Org C–Cu	0·59	5%	17·1	6·7	4·5
‡Org C–Ni	0·67	1%	35·4	5·6	8·6
‡(Org C + S)–Cu	0·64	2%	10·9	5·2	3·6
§Fe–As	0·88	0·1%	6·8	15	6·9
§Fe–Mn	0·75	0·1%	20·7	0·3	28
§Fe–V‖	0·54	1%	10·6	25	18
§Fe–V¶	0·86	0·1%	10·8	−4	15
§Na–P_2O_5	0·92	0·1%	0·039	−0·056	0·058
‡Na–P_2O_5	0·88	0·1%	0·035	0·115	0·093
§Sr–P_2O_5	0·88	0·1%	59·1	−64	108
‡Sr–P_2O_5	0·94	0·1%	87·7	−355	136
§S–P_2O_5	0·89	0·1%	0·034	−0·068	0·059

* All data points.   † Excluding As < 6 ppm.   ‡ Pyritic samples only. § Ferruginous samples only. ‖ All data points. ¶ Excluding samples 898(1)–898(5).

Na, Sr, SO₄, and CO₃. Sodium and strontium correlate well with phosphorous in all the Moroccan phosphorites and probably substitute for calcium in francolite. The axial intercepts of the regression lines show that only minor amounts of these elements are present in other phases. The large negative intercept for Sr shown by the pyritic phosphorites is due to an unusually high Sr/P ratio within the pelletal samples, owing to secondary enrichment, which is discussed later.
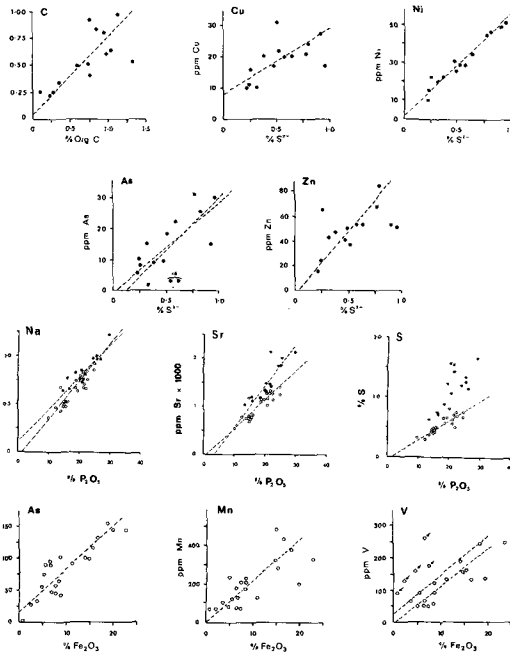

FIG. 2. Variation diagrams of major and trace elements in Moroccan phosphorites. Iron-rich samples are represented by open symbols. Iron-poor samples are represented by closed symbols. Pelletal samples are represented by diamonds.

The Na/P and Sr/P ratios are slightly but significantly greater in the pyritic phosphorites than in the ferruginous samples. These differences cannot be fully explained by the relative abundance of any phase other than francolite and are caused by the exposure of the two phosphorite types to different degrees of weathering (McArthur, 1978). The greater weathering undergone by the ferruginous phosphorites has slightly depleted them in Na, Sr, and CO₃ (and probably SO₄) relative to the pyritic phosphorites.

The greater Sr/P ratio in the pyritic pelletal phosphorites compared to the pyritic non-pelletal phosphorites is probably related to the way the pelletal samples formed. Summerhayes (1970) considers them to be intraformational conglomerates,

formed by the disaggregation and reworking within a sub-aqueous environment of partially indurated, phosphatized, lime-mud. The Sr/P ratio may have increased, at the time further phosphatization occurred, during reworking and re-exposure to the phosphatizing medium. However, no concomitant increase in the Na/P ratio has occurred. This may be because the replacement of Ca^{2+} by Na^+ requires a charge-balancing substitution of CO_3^{2-} or SO_4^{2-} for PO_4^{3-}, and is possibly subject to quantitative limits imposed by the crystal structure. Strontium suffers no such restrictions imposed by charge redistribution and may substitute more freely. Additional phosphatization of carbonate occurred during reworking, resulting in higher over-all phosphorus concentrations. Excepting for additional Sr replacement the existing francolite remained unchanged. The Sr/P ratio therefore increased, but the Na/P ratio did not.

In the ferruginous phosphorites no discrete sulphur-bearing minerals were found by X.R.D., electron microprobe, or thin section examination. Sulphur is therefore probably present as SO_4^{2-} within the apatite structure where it can substitute for PO_4^{3-} (McConnell, 1973). The significant S–P_2O_5 correlation and the almost zero intercept of the S–P_2O_5 regression line strongly support this view. This substitution probably occurs in the pyritic phosphorite, but the relationship is obscured by the presence of the pyrite.

The structural carbonate contents of these francolites (shown on a pure francolite basis in Table I) are very much higher than most reported values, although Parker and Siesser (1972) report similar concentrations in Agulhas Bank phosphorite.

The Moroccan francolite is clearly a highly substituted variety. The approximate composition is represented by sample no. 966(2), which contains only small amounts of impurities.

Cu, Ni, Zn, and As in pyritic phosphorites. The high correlation coefficients of Ni, Zn, and As with pyritic sulphur, together with axial intercepts that are zero (within the standard error of the intercept) suggest that these elements are present mainly in pyrite. Nickel correlates well with both organic carbon and pyritic sulphur, but the correlation with carbon is almost certainly an induced one, due to the high Ni–S and S–organic C correlation. Copper correlates equally well with organic carbon and pyritic sulphur, and slightly better with organic carbon+pyritic sulphur. This latter correlation also provides the lowest axial intercept of the regression line, and suggests that Cu is associated both with organic carbon and pyrite.

Because of the possibility of induced correlations caused by the large S–C correlation, however, the

associations chosen above are not definitive. In order to clarify them a number of sulphide inclusions were analysed by electron microprobe.

Electron probe analysis of sulphides

Sulphides occur as foraminiferal infillings and as dispersed sulphide blebs (fig. 3). Both types have a major element composition between $FeS_{1.8}$ and FeS_2. Within the foraminiferal sulphide Cu, Ni, Zn, and As are homogeneously distributed. Zinc occasionally spots out at concentration above 100 ppm. Analyses of ten random sites showed Ni to have an average concentration of 500 ppm, whilst Zn and Cu averages were below the instrumental detection limit of 100 ppm, and As below the detection limit of 250 ppm. Within the sulphide blebs Zn and Ni are inhomogeneously distributed and vary from less than 100 ppm to more than 5 %, with average concentrations of 800 ppm and 6000 ppm respectively. Copper is homogeneously distributed with an average concentration of 400 ppm. Arsenic was generally below detection.
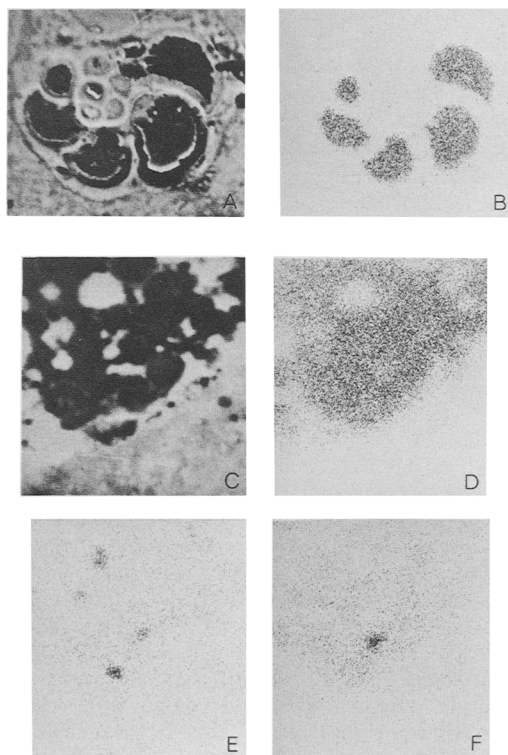
FIG. 3. Electron probe micrographs of sulphides. Foraminiferal infilling: backscattered electrons (A) and sulphur distribution (B). Sulphide blebs: backscattered electrons (C), sulphur (D), zinc (E), and nickel distributions (F).

By assuming that sulphides occur only as blebs with the average element concentrations given above, maximum values of the contribution of sulphide to the over-all element abundances may be calculated, of 65 ppm Ni, 9 ppm Zn, 5 ppm Cu, and 3 ppm As. With the exception of nickel, these concentrations fall well short of the mean concentrations of 31 ppm Ni, 48 ppm Zn, 19 ppm Cu, and 15 ppm As. The wide variability in the concentrations in the sulphide of Zn and Ni probably explains the disagreement between total sample mean abundance and the calculated sulphide contributions to these elements. Copper and arsenic are homogeneously distributed in both types of sulphide. The shortfall in Cu therefore probably represents Cu associated with organic carbon, which amounts to about 75 %. The shortfall in As is unexplained.

Manganese and vanadium do not correlate with any identifiable phase. The contents of silicates and carbonates can account for even the highest manganese concentration, but fail to account for more than half the mean vanadium concentration of 47 ppm. Vanadium may be present in francolite, or in association with organic material as occurs in Phosphoria Formation phosphorites. Which of these possibilities, if either, is responsible for the vanadium enrichment is not clear.

V, Mn, As, Cu, Ni, Zn in ferruginous phosphates. In these samples iron correlates well with As, V, and Mn (Table II, fig. 2). It seems likely that the greater part of these elements is associated with goethite. The correlation coefficient between Fe and V increases, and the axial intercept of the regression line decreases to zero (within the standard error of the intercept) if samples 898(1)–898(5) are excluded from the calculation. These samples occurred in one large conglomerate and appear to be somewhat enriched in V compared to the other ferruginous phosphorites, whilst conforming to the general $V-Fe_2O_3$ relationship. No explanation for this enrichment is apparent.

The axial intercept of 15 ppm As (the residual As) suggests that a significant fraction (15 %) of the As is present in other phases. No other identifiable phase, however, can contribute more than a small fraction of this residual As if normal concentrations of As are assumed. Copper, nickel, and zinc are present in high mean concentrations in the ferruginous phosphorite (Table I), but do not correlate with any identifiable phase. Their incorporation into carbonate-apatite seems unlikely (Cruft, 1966; Tooms *et al.*, 1969). The maximum contributions from carbonate and silicate phases, computed from average shale analyses given by Mason (1966), and Moroccan limestone analyses of Summerhayes (1970), are able to ac-

count for 60% of the Cu, 40% of the Ni, and 50% of the Zn. The remaining fraction of these elements, together with the residual As discussed above, may have been introduced into these phosphorites during their initial formation, in association with organic material and pyrite, phases that were subsequently destroyed by oxidation during re-working of the phosphorite into its present form. The ferruginous phosphorite has been subjected to substantially greater sub-aerial weathering than has the pyritic phosphorite (Summerhayes, 1970; McArthur, 1978) and is probably the reason for the absence of pyrite and appreciable organic carbon concentrations in the former.

In the ferruginous phosphorite, therefore, Mn and V are associated with Fe_2O_3, As is associated mainly with Fe_2O_3 with some having originally been introduced in association with pyrite, as was about half of the Cu, Ni, and Zn. Carbonates and silicates contribute the remainder of these elements.

Element sources in the Moroccan phosphorites. In the pyritic phosphorites the ratios to Al of Cu, Ni, Zn, and As are between eighteen and fifty times the ratios in average shale (Mason, 1966). Sulphide formation therefore probably occurred during early diagenesis whilst diffusional contact with a solution supply of these metals was possible. The Fe_2O_3/Al_2O_3 ratio is four times that for shales. The detrital component of the phosphorites may there-fore have contributed much of the iron. Metal diffusion, particularly of iron, implies a deposi-tional environment sufficiently reducing to main-tain metals in solution. It seems surprising that so little evidence remains for such an environment.

The lower trace element concentrations in the foraminiferal infilling compared to the blebs may be due to a more restricted access of metals in solution to the infilling compared to the more open sites of bleb formation.

The origin of the iron in the ferruginous phos-phates is unknown. The As/Fe_2O_3 ratio in these samples ($7 \cdot 5 \times 10^{-4}$) is similar to that in ferruginous phosphorite found in Florida ($5 \cdot 6 \times 10^{-4}$, Stow, 1969), the U.S.S.R. ($2 \cdot 6 - 16 \times 10^{-4}$, mean $6 \cdot 4 \times 10^{-4}$, Bliskovskiy *et al.*, 1968), and to the iron oxide component of marine sediments, ($5 - 10 \times 10^{-4}$, Neal, 1976; Calvert and Price, 1977) and suggests that no unusual processes are responsible for the iron content of these samples.

Element partitioning in other phosphates

The association of Zn, Cu, Ni, and As with sulphides, and Mn, V, and As, with goethite is by no means unusual, but reports of these associations in phosphorites are sparse. Tremearne and Jacob (1941) found no orderly relation between As and

sulphides or between As and iron in 210 samples, mainly from U.S. deposits, although an As-sulphide + organic carbon association was noted to occur in the 'mechanical fractions of certain phos-phates' from Wyoming and Idaho. Gulbrandsen (1966) and Krauskopf (1955) also note an associa-tion between organic carbon and As, Cu, Ni, Zn, and V in Phosphoria Formation phosphorite. A strong association between As and Fe_2O_3 has been found in Florida phosphorite (Stow, 1969) and in deposits in the U.S.S.R. (Bliskovskiy *et al.*, 1968). It is interesting that Stow (1969) found less than 3 ppm As in a suit of heavy minerals including pyrite and marcasite extracted from Florida phos-phorite.

No reports of a $Mn-Fe_2O_3$ association in phos-phorites is known to the writer, but would probably be seen if looked for in other ferruginous deposits.

Of the elements examined, only V is present in Moroccan phosphorite in concentrations larger than can be easily explained, and then only in five samples (898(1)–898(5)). Gulbrandsen observed similar anomalous concentrations in some Phos-phoria phosphorite and suggests that some V may replace P in apatite. Cook (1972) notes a corre-lation between V and P_2O_5 in Queensland phos-phorites, which he ascribes to substitution of V in apatite, although the data could equally be inter-preted as a difference between two distinct sample populations. Bliskovskiy (1969) in fact noted an antipathetic relationship between V and P_2O_5 in Russian deposits although again the comparison of separate deposits may be misleading.

It seems better to conclude that no evidence exists for V substituting in sedimentary marine apatite, but suggest that occasional anomalous V concentrations require further study.

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