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GEOCHEMICAL BEHAVIOUR OF VANADIUM IN IRON—TITANIUM OXIDES

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ABSTRACT

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The following geochemical rules-of-thumb seem to hold for vanadium:
(1) Magnetites as a group have higher V contents than either hematites or ilmenites.
(2) In magnetite—hematite pairs, however, the hematite has the higher V content.
(3) In magnetite—ilmenite pairs, the magnetite is usually richer in V than the ilmenite, although the enrichment factor is highly variable, between 1 and 20, and in one particular case even clearly < 1.
(4) In hematite—rutile pairs, the rutile strongly concentrates V. This behaviour of V is understandable from the interplay of two simple considerations, namely: (a) under most conditions in which magnetite and/or ilmenite are stable at high temperatures V is dominantly three-valent, and substitutes mainly for Fe^{3+}; and (b) when the oxygen fugacity is close to that defined by the magnetite—hematite equilibrium, V changes to valency 4+, and proxies mostly for Ti^{4+}, in hemo-ilmenites, ilmenohematites, or rutile.

INTRODUCTION

Data on the vanadium distribution between coexisting magnetite and ilmenite (e.g., Tugarinov et al., 1975; Wedepohl, 1978) show a wide scatter, although all published data so far indicate that magnetite concentrates V relative to ilmenite. A recent study (R.L. Hartstra, unpublished data, 1978), however, of a suite of magnetite—ilmenite pairs in metabauxites from Naxos shows the reverse trend, ilmenites being systematically higher in V than the coexisting magnetites (Fig. 1, crosses). As it seems highly unlikely that distribution coefficients would vary from 0.3 to more than 20 over a range of temperatures between 550 and 950° C, another explanation is presented here.

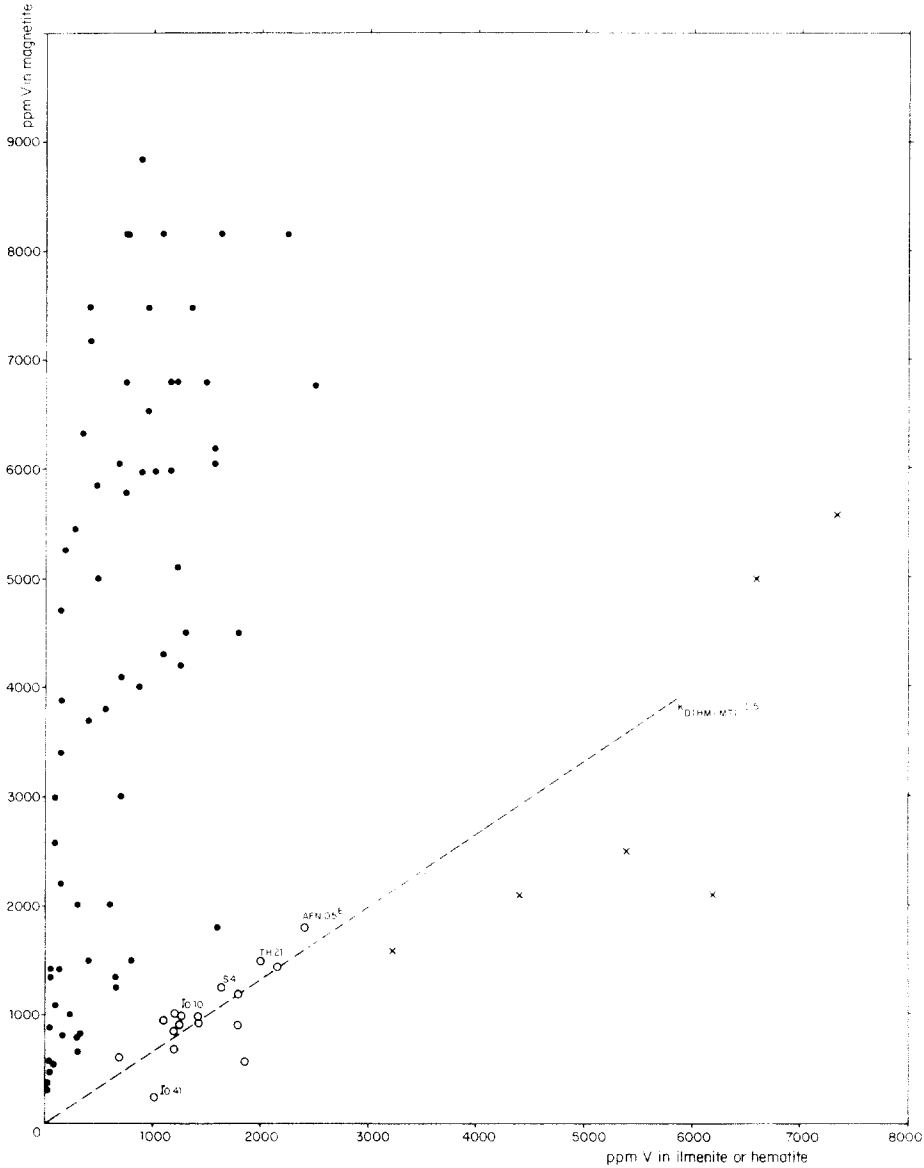

Fig. 1. Summary of vanadium distributions between coexisting magnetite—ilmenite pairs (*dots*), magnetite—hematite pairs (*open circles*), as well as the suite of magnetite—ilmenite pairs from metabauxites at Naxos (*crosses*). $K_{D(HM-MT)}$ is the distribution coefficient for the hematite—magnetite pair. Most data are from the literature (Duchesne, 1972; Tugarinov et al., 1975; Juopperi, 1977; Wedepohl, 1978). The magnetite—ilmenite pairs from Naxos are from R.L. Hartstra (unpublished data, 1978).

VANADIUM IN COEXISTING MINERAL PAIRS

Magnetite—ilmenite

Most data are from coexisting magnetites and ilmenites from gabbros, charnockites and high-temperature Fe ores. Results from a great number of papers (cited in Tugarinov et al., 1975; Wedepohl, 1978) are plotted in Fig. 1. A group of ilmenite—magnetite pairs from a series of metabauxite occurrences at Naxos, Greece, can be distinguished by their different geochemical behaviour. Although, in general, magnetites concentrate V with respect to ilmenites, the latter group shows the opposite behaviour. Even when ilmenite—magnetite pairs behave "normally" there is a wide scatter in the distribution coefficients. As has been shown by Duchesne (1972), the hematite contents and the V concentrations of ilmenites show a good correlation (Fig. 2); this means that the V distribution between coexisting ilmenites and magnetites often reflects the distribution between magnetites and *hematite*, which is in solid solution in the ilmenites. In many cases one can predict the V content of an ilmenite from the V content of the coexisting magnetite by the following formula:

$$(\text{mol fraction of Hm in Ilm}) \times \frac{3}{2} \times (\text{V content of Mt})$$

where Hm = hematite; Ilm = ilmenite; and Mt = magnetite. In this formula the factor $\frac{3}{2}$ stems from the fact that in hematite all the Fe-places are trivalent, whereas in magnetite only $\frac{2}{3}$ of the Fe is trivalent.

In order to demonstrate that under low oxygen fugacities V has a preference for magnetite over ilmenite, the following hydrothermal experiments were carried out. Two Au capsules, each 6 cm long, were filled with the following assemblage:

magnetite layer
layer of zircon grains
mixture of Ni + V_2O_5
layer of zircon grains
ilmenite layer

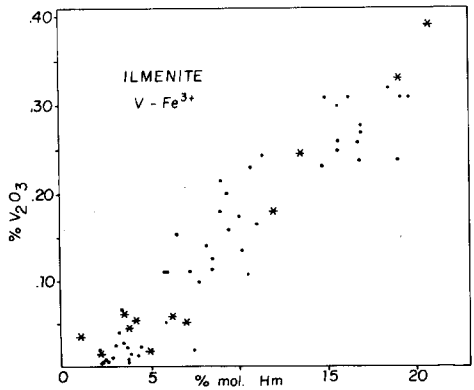

Fig. 2. Correlation between V and Fe^{3+} in magnetite—ilmenite pairs from Norway (Duchesne, 1972). (Hm = hematite.)

Water was added to these capsules before welding.

In order to make sure that neither the temperature gradient in the pressure vessel nor gravity were decisive factors in the resulting V distribution, one capsule was placed with the ilmenite at the top and the magnetite at the bottom, and the other with reversed positions for another run. Table I gives the results of both experiments, which were carried out at 600° C (bottom) to 550° C (top), at 1000 atm. water pressure; run duration was six weeks.

From the experiments it appears that under conditions corresponding to the equilibrium Ni—NiO, the V favours the magnetite over the coexisting ilmenite; in both positions the ilmenite loses V, whereas the V content of the magnetite increases. These experiments correspond to the situation as normally encountered in nature, namely that magnetite and ilmenite grow under conditions well below the hematite—magnetite equilibrium. At Naxos, however, conditions were close to the hematite—magnetite buffer curve, and part of the V was already in the tetravalent state; this explains why in this case the ilmenite takes up more V than the magnetite.

TABLE I

Experimentally produced vanadium distribution between magnetite and ilmenite

Run No.	Starting material	Vanadium content of starting material (ppm V)	Temperature traject (°C)	Time (weeks)	Product	Vanadium content of product (ppm V)
1283	ilmenite (Kragerö)	3,130	600—550	6	ilmenite	2,000
	magnetite (Normandy)	1,000			magnetite	2,500
1284	ilmenite (Kragerö)	3,130	600—550	6	ilmenite	2,000
	magnetite (Normandy)	1,000			magnetite	5,250

In run No. *1283* the ilmenite was at the top of the capsule (600° C), in run No. *1284* at the bottom (550° C). Both runs were carried out at 1 kbar pressure, with Ni—NiO buffer.

Magnetite—hematite

The number of published vanadium analyses of magnetite—hematite pairs is rather limited (see Fig. 1). Some additional analyses are reported in Table II. It seems that, without exception, the hematite phase always concentrates the V. The concentration factor is close to $\frac{3}{2}$, which is obviously the expression of the fact that the number of available sites (trivalent Fe-sites) in hematite is $\frac{3}{2}$ times the number of available sites in magnetite. By first approximation, crystal-chemical differences between trivalent sites in magnetite and in hematite can apparently be ignored as far as the site preference of V is concerned. The absolute level of the V concentrations is fairly low, if compared to most

TABLE II

Wet-chemical analyses of magnetite—hematite pairs

Sample No.	Site	Magnetite (ppm V)	Hematite (ppm V)	Rock description
Io *10*	Ios	1,000	1,250	Fe ore in glaucophanitic greenschist
Io *41*	Ios	250	1,000	Fe ore in glaucophanitic greenschist
S *4*	Syros	1,250	1,625	glaucophane schist with serpentinites
TH *21*	Thasos	1,500	2,000	staurolite—kyanite schist
AFN *05*E	Naxos	1,650	2,400	emery in amphibolite facies

The emery sample from Naxos was analyzed by microprobe.

magnetites without accompanying hematite. It may well be that under conditions corresponding to the hematite—magnetite equilibrium the availability of (trivalent) V is less than in most cases where magnetite forms under more reducing conditions.

Hematite—rutile

Three rutiles, coexisting with the new mineral schreyerite ($V_2Ti_3O_9$), have V_2O_3 concentrations between 1.67 and 1.90 wt.% (Medenbach and Schmetzer, 1978). A few other rutile analyses, mentioned in Deer et al. (1962), show measurable amounts of V. No analyses on the V distribution between coexisting hematite and rutile were found. As the pair hematite—rutile must form under conditions above the magnetite—hematite buffer curve, it can be expected that most of the V will be in the tetravalent state, and become concentrated in the rutile. Actually, this is borne out by the results of some microprobe and wet-chemical analyses (Table III) on hematite—rutile pairs from metamorphic rocks from the Cyclades, Greece. Whereas the hematites have low to very low V contents, the rutiles have, in fact, rather high V concentrations. An

TABLE III

Microprobe analyses of rutile—hematite and rutile—limonite pairs

Sample No.	Rutile (wt.% V_2O_3)	Hematite	Limonite	Rock description
125 F	0.73	n.d.		diasporite, Sikinos
IRA IA-*1*	0.52	n.d.		diasporite, Iraklia
IRA IA-*2*	0.75	$\leq$0.15		diasporite, Iraklia
Syros	0.12	0.16		glaucophane schist, Syros
135 A	0.63		0.18	diasporite, Sikinos
AF *138*D	0.66		n.d.	diasporite, Naxos

n.d. = not detected. Detection limit 0.15 wt.% V_2O_3. The Syros sample was analyzed by wet-chemical analysis.

experiment at 1 kbar and 750°C, buffered by hematite—magnetite, showed that rutile and V_2O_4 form a solid solution under these conditions. It should be mentioned here that the equilibrium between V_2O_3 and V_2O_4 should be rather pressure-sensitive ($\Delta V_S \approx 1.1$ J/bar for the stoichiometric reaction with 1 mol O_2); the fact that the rutile—hematite pair from Syros (Table III), in high-pressure glaucophane schists with jadeite—quartz, does not show a preferential uptake of V by rutile could be an indication of the pressure effect.

OXIDATION—REDUCTION IN VANADIUM OXIDES

Calculated $\log f_{O_2}$ —T curves for the V-oxides have been plotted in Fig. 3 [from data in Robie et al. (1978)], together with the magnetite—hematite and the Ni—NiO equilibrium. At 500°, 600°, 700° and 800°C (Fig. 3, crosses), hydrothermal experiments at 1 kbar showed that in none of the cases is V_2O_3

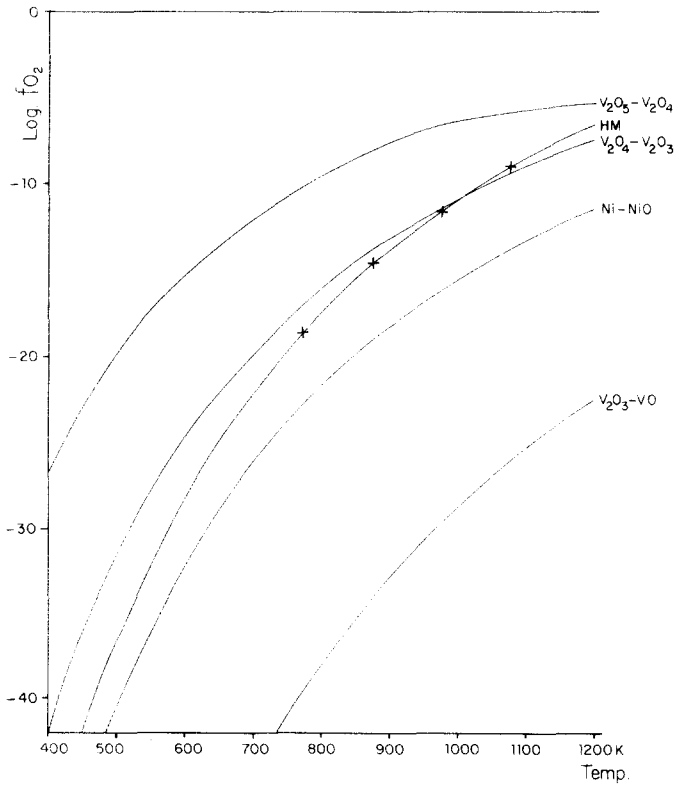

Fig. 3. Calculated redox equilibria among V oxides. Hematite—magnetite and the Ni—NiO buffer curves have also been indicated for reference. *Crosses* on the hematite—magnetite curve refer to experiments summarized in Table IV.

the stable V-oxide under the conditions imposed by the hematite—magnetite boundary curve (Table IV). Under these conditions either V_2O_4 or mixed oxides of V^{3+} and V^{4+} are stable. Thermodynamic data for V_2O_4 and/or V_2O_3 seem, therefore, to be in error, if it is assumed that the thermodynamic data for hematite and magnetite are correct.

The minimum shift in the equilibrium oxygen fugacity for the equilibrium V_2O_3—V_2O_4, which satisfies all the experimental data is a factor of ~ 10 in the oxygen fugacity, which corresponds to an increase of ~ 7 kJ/mol for $\Delta G_{V_2O_3}$, or a decrease of ~ 7 kJ/mol for $\Delta G_{V_2O_4}$ at temperatures around 1000°K. Another explanation may be that the thermodynamic properties of V_2O_3 and V_2O_4 are approximately correct, but that there exists a stability field (or stability fields) of mixed V-oxides (V_3O_5, V_4O_7, V_5O_9) in between them.

If it is assumed that activity coefficients of tetravalent V on Ti^{4+}-sites, and of trivalent V on Fe^{3+}-sites are not too different from unity, then the relative position of the different f_{O_2}—T curves has the following consequences.

Well below the hematite—magnetite boundary essentially all the V will be present in the trivalent form; since these are the conditions of formation for most ilmenite—magnetite pairs the magnetite will usually be strongly enriched in V relative to the ilmenite due to the close similarity between V^{3+} (ionic radius, 0.65 Å) and Fe^{3+} (ionic radius, 0.67 Å); when the magnetite—hematite boundary is approached, a large part of the V transforms to V^{4+}; and, in fact, experiments at the magnetite—hematite boundary with V_2O_3 as starting materials produced V_3O_5, V_4O_7 or V_5O_9 in which both V^{3+} and V^{4+} are present. Under similar geological conditions and geochemical environments, there will be less V available in the trivalent state for substitution on Fe^{3+}-sites, therefore the absolute amounts of V in magnetites and hematites become rather low, although the distribution clearly favours the hematite over the magnetite, by a factor of about $\frac{3}{2}$.

TABLE IV

Results of hydrothermal experiments on the stability of V-oxides

Run No.	Starting material	Buffer	Temperature (°C)	Time (days)	Product
1240	V_2O_5	NNO	700	14	V_2O_3
1241	V_2O_5	HM	700	14	V_2O_4
1270	V_2O_5	HM	800	8	V_2O_4
1271	V_2O_5	HM	600	32	V_2O_4
1272	V_2O_5	NNO	700	14	V_3O_5
1275	V_3O_5	HM	700	12	V_5O_9
1276	V_3O_5	HM	600	12	$V_3O_5 + V_4O_7$
1282	V_2O_5	HM	500	56	$VO_2 + VO_2 \cdot yH_2O$

All runs were carried out at 1 kbar H_2O pressure.
NNO = Ni—NiO buffer; HM = hematite—magnetite buffer.

If the oxygen fugacity is fairly close to the magnetite—hematite boundary, then the ilmenite will contain more V than the coexisting magnetite, because most of the V is present as V^{4+}, which can replace Ti^{4+} (ionic radius, V^{4+} = 0.61 Å; Ti^{4+} = 0.64 Å).

If the system can be properly calibrated, the distribution of V between magnetites and ilmenites will permit the construction of a continuous oxygen geobarometer in the neighbourhood of the magnetite—hematite boundary, as soon as we dispose of T—f_{O_2} data for the following oxidation exchange reaction:

$$V_2O_{3(Mt)} + \tfrac{1}{2}O_2 \rightleftharpoons V_2O_{4(Ilm)}$$

Even without such data it is already possible to state in a qualitative way that when magnetite is strongly enriched in V relative to the coexisting ilmenite, temperature and oxygen fugacity of formation have been well below the hematite—magnetite buffer curve; in the opposite case the conditions of formation must have been rather close to (and, of course, on the low oxygen fugacity side of) the hematite—magnetite equilibrium.

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