

A VANADIUM-TITANIUM CARBIDE INCLUSION IN GRAPHITE FROM HYDROTHERMAL EJECTA AT 13°N, EAST PACIFIC RISE

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ABSTRACT

An inclusion of vanadium-titanium carbide has been found in oceanic hydrothermal graphite by scanning electron microscopy; its composition was determined by electron microprobe. This represents a new find in the system TiC-VC, to which belongs khamrabaevite (Ti,V)C. The conditions of formation of the V-Ti carbide, corresponding to the iron-magnetite buffer, could be encountered during the serpentinization of basalt.

Keywords: carbide, electron microprobe, graphite, hydrothermal, khamrabaevite, oceanic, titanium, vanadium, 13°N, East Pacific Rise.

SOMMAIRE

Une inclusion de carbure de vanadium-titane a été trouvée par microscopie électronique à balayage dans du graphite hydrothermal océanique, et sa composition déterminée par microsonde électronique. Ceci représente une nouvelle occurrence dans le système TiC-VC, auquel appartient déjà la khamrabaevite (Ti,V)C. Les conditions de formation du carbure de V-Ti, correspondant au tampon fer-magnétite, pourraient se rencontrer au cours de la serpentinisation du basalte.

Mots-clés: carbure, microsonde électronique, graphite, hydrothermal, khamrabaevite, océanique, titane, vanadium, 13°N, ride Est-Pacifique,

INTRODUCTION

As a result of a study of graphite particles collected in sediment traps moored near active hydrothermal vents, using scanning electron microscopy (SEM) and electron microprobe (EMP), several kinds of associated over- and intergrown mineral species were found, notably sulfoantimonides (Jedwab & Boulègue 1984). However, one of these inclusions turned out to be a vanadium-titanium compound, included in, and outcropping from, a relatively large graphite particle (Figs. 1, 2). A semiquantitative analysis of this compound by SEM-EMP disclosed approxi-

mately equal amounts of the two metals (Table 1).

At the time of the discovery of this V-Ti inclusion, the mineralogy of the possible vanadium-titanium compounds seemed limited to the oxides: berdesinskiite V_2TiO_5 , kyzylkumite $V_2Ti_3O_9$ (monoclinic, black), schreyerite $V_2Ti_3O_9$ (monoclinic, red), and the oxyhydroxide tivanite $VTiO_3 \cdot OH$ (monoclinic). The latter is the only one in which the two metals occur in equal proportions (Grey & Nickel 1981). But the precise mineralogical identity of the compound was temporarily left unsettled, especially as it was represented by only one occurrence.

A casual reading of a paper by Novgorodova *et al.* (1984), describing the new mineral species khamrabaevite (Ti,V,Fe)C in basaltic porphyries in the Tshatkalskii Mountains, and granodiorites in the Zeratshanskii Mountains, both in Uzbek SSR (Khamrabaev 1964), shed new light on our find: the occurrence of a vanadium-titanium carbide in graphite was much more plausible than that of an oxide, from a chemical point of view. Indeed, the minerals associated with the Uzbek khamrabaevite include several highly reduced species (graphite, wüstite, cohenite, metallic iron, moissanite, suessite); vanadium-titanium oxides are absent. Our inclusion could thus possibly be a vanadium-titanium carbide and, more precisely, an intermediate member of the synthetically studied continuous TiC-VC solid-solution series (Goldschmidt 1967), of which the USSR khamrabaevite is a Ti-rich end member, containing some unaccounted-for iron (Table 1).

Owing to the present scarcity of observations on such mineral species, and the novel problems raised by its occurrence in a sediment trap, we felt it important to establish the nature of its anion(s) and its position in a mineralogical classification. The occurrence could be evidence of a previously unsuspected process in the oceanic basalts, or of a more varied chemistry of the reduced species found in connection with the graphite-coated vesicles and seams described in this environment (Mathez & Delaney 1981).

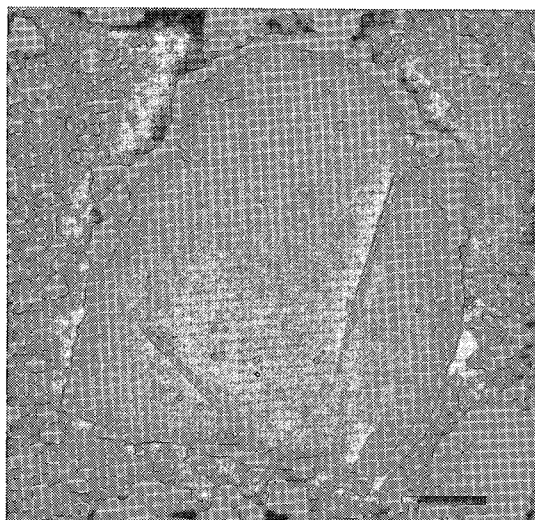


FIG. 1. Graphite particle on membrane filter. V-Ti inclusion appears as a white thorn at lower left corner. (SEM, secondary mode). Scale bar 10 μm .

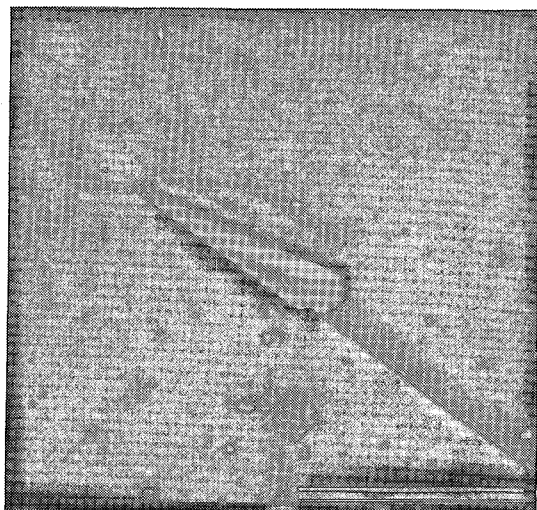


FIG. 2. V-Ti inclusion in line with a kink. Foliation in the host graphite is visible at the upper left corner. (SEM, secondary mode). Scale bar 5 μm .

MATERIALS STUDIED

The *vanadium-titanium inclusion* (1, Table 1) was casually detected by SEM-EMP in a large graphite flake in sample CL-1 from the Clipperton Cruise (1982) (Hekinian *et al.* 1983). A sediment trap was deployed on the East Pacific Ridge at 13°N, Station 1 for 10 days. Sample CL-1 is the aliquot of largest particles (> 1 mm) separated by the technique of

sediment settling from the sediments collected at this site.

Two samples of *reference hydrothermal graphite* (Table 2) were analyzed: the host graphite of the V-Ti inclusion (a, Table 2), which has been carbon-contaminated by extensive EMP analysis, and other graphite flakes from the same sample (b, Table 2). These graphite flakes, uncontaminated by extensive exposure in the electron microprobe, were selected on separate sediment mounts. Flakes of a *reference natural graphite* (Table 2) from Buckingham, Quebec, supplied by Ward (Rochester, N.Y.), also were analyzed.

For comparison with the vanadium-titanium inclusion, we analyzed: *reference khamrabaevite* (2, Table 1), from an unspecified locality in the USSR, provided by the Institute of Geology and Geophysics, Academy of Sciences, Uzbek SSR; polished sections of this sample were prepared at the Brussels Laboratoire de Géochimie; analytical grade powders of *synthetic TiC*, *VC*, and *VN* supplied by Johnson-Matthey (Royston, Great Britain), of *synthetic V₂O₅* supplied by BDH (Poole, Great Britain) and of *standard V metal* supplied by Merck (Darmstadt, FRG).

TABLE 1. CHEMICAL ANALYSES OF V-TI INCLUSION AND OF KHAMRABAEVITE

Element wt %	1	2	3
Ti	35.65±0.38	73.00±0.84	70.00
V	46.74±0.39	8.28±0.60	6.91
Fe	n.a.	0.56±0.12	1.75
Si	n.a.	n.a.	0.10
C	17.61	18.16	20.54

- 1: Vanadium-titanium inclusion in graphite. Carbon calculated by difference.
 2: Khamrabaevite (This work).
 3: Khamrabaevite (Novgorodova *et al.* 1984). Carbon calculated by difference. Recalculated to 100%.
 n.a.: not analyzed.

TABLE 2. CARBON PEAK-SHIFT MEASUREMENTS

Material	Origin	Analyst	Carbon K α Peak (Å)	$\Delta \lambda$ (Å)
Graphite	Buckingham	This work	44.9120±0.0036	0
"	synth.	Holliday	44.85	0
"	EPR.13°N	This work	(a) 44.8437±0.0036	-0.0684*
"	"	"	(b) 44.8833±0.0030	-0.0268*
(V,Ti)C	"	"	44.6836±0.0044	-0.02285*
VC	synth.	"	44.6206±0.0032	-0.02915**
"	"	Holliday	44.56	-0.29**
(Ti,V,Fe)C	Uzbek SSR	This work	44.5423±0.0037	-0.3698*
TiC	synth.	This work	44.5857±0.0025	-0.3464*
"	"	Holliday	44.54	-0.31**

- (a): Host graphite of the (V,Ti)C inclusion, contaminated by extensive analysis.
 (b): Uncontaminated graphite, from the same sample.
 *: in reference to the natural graphite from Buckingham.
 **: in reference to the synthetic graphite (Holliday 1967).

METHODS

The sample splits were filtered on NUCLEPORE 0.45 μm filters and fixed on glass slides as described in Jedwab (1979). The slides were then visually scanned under a light microscope (reflected and transmitted light, oil immersion), and the graphite particles were marked. Slide cut-outs were transferred for examination under the SEM-EMP.

The samples were analyzed under a JEOL Superprobe 733 (scanning electron microscope - electron microprobe) fitted with STE, TAP, LiF and PET crystals. WDS qualitative analyses for N, O and C were performed with the STE crystal at 5 kV, 1×10^{-9} amp. The actual $2d$ -value of the STE crystal is 100.4 Å, but the theoretical value of 100.7 Å has been adopted in the calculations for the sake of uniformity with the measurements by Holliday (1967). EDS qualitative analyses for $Z > 11$ were performed using the attached TRACOR 2000 at 20 kV, 1×10^{-9} amp and semiquantitative analytical values, again for $Z > 11$, were calculated using the SSQ program with ZAF correction by Chamber *et al.* (1978) and McCarthy (1979). The deconvolution for Ti-V interference was done using a program by J. Pinkster (Tracor Europa, Bilthoven, NL).

The measurement of C $K\alpha$ peak shifts was performed using repeated graphical recordings of the peak and background. The spectrometer and recorder scanning speeds were set to obtain a reading of 20 mm on paper for a wavelength difference of 0.4 Å. The peak position was determined at the half width of the peaks.

RESULTS

Morphological features

The graphite particle that hosts the inclusion is flat and approximately equidimensional. Its periphery is irregular, and the surface presents kinks and veins (Figs. 1, 2). The inclusion, which sticks out beyond the graphite and is in line with one of the major kinks, is an elongate, triangular body, with pinacoidal facets (Fig. 2). The dimensions are about $5 \times 1 \mu\text{m}$ (measured at the widest points). The inclusion dips below the surface of the graphite, as is shown by the morphology and also by the chemical V and Ti signals that can be obtained in the host graphite at some distance from the inclusion.

Chemical composition of the inclusion

The EDS spectrum shows the presence of major amounts of Ti and V. Fe and Si were not determined, since the whole set of particles from the filter is highly enriched in these elements, as well as in Cl, Ca and Zn. All these elements can be erased at once from the particle spectrum with a spectrum generated on

the filter of the host graphite, and adjusted on any of the extraneous elements. Semiquantitative analyses gave a composition that is definitely different from that of the USSR khamrabaevite (Table 1; Novgorodova *et al.* 1984). Our results for the type khamrabaevite compare satisfactorily with those given by Novgorodova *et al.* (1984).

The obvious absence of major amounts of sulfur in the EDS spectrum left carbon, nitrogen and oxygen as plausible candidates for the anion(s), but the metallic state could not be entirely ruled out at this stage. In view of the recent discovery of terrestrial osbornite TiN (Tatarintsev *et al.* 1987), nitrogen was sought in the V-Ti inclusion by EMP (WDS) analysis, using synthetic VN as a standard to adjust the operating conditions. No nitrogen signal above background was detected in the V-Ti compound by this technique. Thus the presence of this element can be excluded.

The vanadium $L\alpha$ line at 24.25 Å, which could partly interfere with the oxygen $K\alpha$ line at 23.62 Å, is hardly noticeable under the experimental conditions employed, as shown when using metallic vanadium and khamrabaevite as references. The spectrum for the V-Ti inclusion shows a weak oxygen signal, much weaker than that obtained on reference V_2O_5 .

The analysis for carbon in the inclusion showed the presence of major concentrations of this element. This ruled out the possibility of a purely metallic compound. However, when we tried to measure the respective intensities of carbon in the inclusion and in the host graphite, it appeared that the carbon signal detected on the inclusion was possibly due, at least in part, to aberrations in the electron optics. As a simulation experiment, we deposited micrometer-size metallic vanadium on flakes of Buckingham graphite, and indeed obtained noteworthy carbon signals, except for the largest vanadium particles (50 μm and up). The intensities of the carbon peaks could thus not be used to measure the carbon concentration in the graphite-hosted V-Ti inclusion.

We then tried to measure carbon $K\alpha$ peak shifts, for which good-quality data exist (Holliday 1967), and which have already been used by Mathez & Delaney (1981) in solving a similar problem. For the titanium and vanadium carbides, these shifts are sufficiently large to be significant, leading to the definitive determination of carbon in the V-Ti inclusion. Our measurements on natural graphite, synthetic TiC and VC, natural khamrabaevite, and the presently studied V-Ti inclusion are presented in Table 2 and Figure 3.

Our results for the synthetic materials are in good agreement with those of Holliday, and justify the approach adopted. However, a rather large discrepancy can be noted between the measurements

obtained on the Buckingham graphite and the EPR host-graphite [0.0 \AA versus -0.0684 \AA , Table 2 (a)], as well as between our values for the V-Ti inclusion compared to those for synthetic VC and khamrabaevite [-0.2285 \AA versus -0.29145 \AA and -0.3698 \AA , respectively: Table 2)]. These discrepancies may be due to the effect of contamination by instrumental carbon deposition on the peak shifts of TiC and VC, produced by the carbon deposited during the extensive analyses to which the sample had been previously subjected (Holliday 1967). The measured shift is thus the result of the (V,Ti)C shift minus the counteractive contamination carbon shift. As a simulation experiment, we measured the carbon peak shift on several other graphite particles from the sediment trap, which had never been subjected to such intensive analyses as the one hosting the V-Ti inclusion. This time, the shifts were lower than those observed on the "contaminated" graphite particle [0.0288 \AA , Table 2 (b)]. Thus, the discrepancies in the peak shifts are related to instrumental carbon contamination. This allows us to confirm the presence of carbon as the major anion in the V-Ti compound analyzed.

DISCUSSION AND CONCLUSIONS

Natural versus anthropogenic origin of the V-Ti inclusion

First of all, the origin of the particle should be briefly discussed, since it was collected in a trap open to loose particles of multiple origins, and since

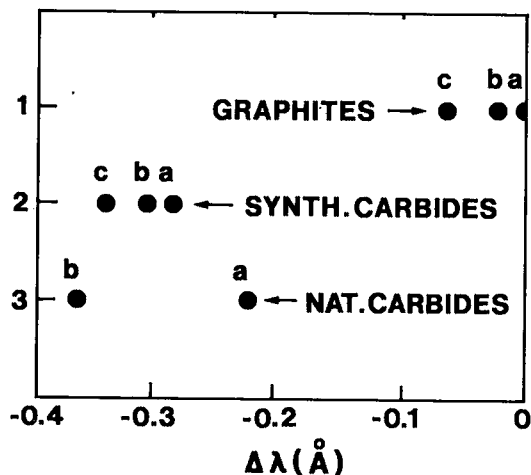


FIG. 3. Graphical representation of carbon $K\alpha$ peak shifts = $\Delta\lambda(\text{\AA})$ [see Table 2]. 1. Graphite samples: a: Buckingham and synthetic, b: EPR 13°N, uncontaminated, and c: EPR 13°N, contaminated. 2. Synthetic carbides: a. VC: this work and Holliday (1967), b. TiC: Holliday (1967), and c. TiC: this work. 3. Natural carbides: a. (V,Ti)C inclusion in graphite (EPR 13°N), and b. (Ti,V,Fe)C, khamrabaevite from Uzbek SSR.

vanadium and titanium carbides are resistant products of high technology. However, several arguments are in favor of a natural origin: 1) the particle is intimately included in a large flake of crystalline graphite, 2) it is associated with other graphite flakes overgrown with sulfosalts of Pb, Fe and Cu, and 3) V-Ti solid-solution carbides have never been prepared in commercial quantities and are not in regular use (J. Notton, pers. comm., 1988).

Chemical and mineralogical nature.

We may draw the following conclusions from the results of the chemical analyses, experiments and peak-shift measurements:

1. The V-Ti inclusion contains significant amounts of carbon, which cannot be determined quantitatively, owing to the background signal produced by the host graphite. But the presence of carbon and the absence of nitrogen and sulfur rule out the theoretically possible V-Ti metal, sulfide and nitride.
2. The inclusion contains small quantities of oxygen, but in insufficient amounts to form a pure oxide or oxyhydroxide. It is well known that the V and Ti carbides are easily contaminated by oxygen, and slowly form oxycarbides when exposed to air (Storms 1967).
3. However, the carbide nature of the inclusion does not solve the problem of the stoichiometry, and hence the place of this compound in a mineralogical or crystallographic classification, since several crystal phases and compositions are possible: VC, V_8C_7 , V_6C_5 , V_5C , V_4C_3 , V_2C_3 and V_2C (Storms 1967, Wells 1984). The situation is further complicated by the variable excesses or deficits of O and C that can be found in a given crystal phase, according to the temperatures of formation and bulk composition of the system (Storms 1967). Since the carbides of Ti and V define a complete solid-solution (Goldschmidt 1967), the relative proportions of these elements cannot be used to restrict the stoichiometric and crystallographic possibilities. In fact, Toth (1971) has insisted upon the difficulties in characterization of the refractory carbides, even when unlimited quantities of synthetic samples are available for structure determinations.

A clue to the most plausible composition may be found in the phase diagrams of the V-C and Ti-C systems (Storms 1967, Toth 1971). Two main forms exist, namely VC and V_2C , and the others are considered as mere polytypes, or as metal-deficient compounds. VC forms in the presence of large amounts of carbon (larger than 43 at.% C), and V_2C forms when this element is wanting. In the system Ti-C, the lower limit of TiC stability lies at 53 at.% C, below which the mixture Ti + TiC is stable. Although the ternary system Ti-V-C does not seem to have been studied (Goldschmidt 1967), it is reasonable to

envision that high-carbon systems would favor the formation of a (V,Ti)C phase, rather than a (V,Ti)₂C phase, especially as Ti₂C does not exist.

It is thus reasonable to hypothesize that the V-Ti carbide included in the large particle of graphite was formed in the high-carbon field, and consequently, that the inclusion belongs to the cubic (V,Ti)C group (Hägg compounds; see Wells 1984). The V-Ti inclusion thus represents an intermediate member of the system TiC-VC, and plausibly belongs crystallographically to the cubic system, as does khambaevite.

Conditions of formation

The V-Ti carbide we have found is intimately associated with graphite. We have previously presented data claiming that the graphite particles could have been formed during serpentinization in $f(\text{O}_2)$ conditions corresponding to the fayalite-magnetite-quartz (FMQ) buffer. These conditions are: $440 < 480^\circ\text{C}$; $260 < P < 500$ bars; $f(\text{O}_2) = 10^{-24.5}$ to 10^{-27} bars; $p\text{H}_2\text{O}/p\text{H}_2 = 100$ (Jedwab & Boulègue 1984; Boulègue & Jedwab 1985). This is in agreement with the extrapolation of recent results on the graphite-C-O-H fluid equilibrium (Ulmer & Luth 1988).

We think that there are two possible hypotheses that can explain the graphite-carbide association: (i) either they have been produced in the same conditions during serpentinization or (ii) the V-Ti carbide was present before the graphite, and the latter is the result of the transformation of amorphous carbon *via* carbide catalysis.

In order to check the validity of these hypotheses, we have first computed the $f(\text{O}_2)$ - T conditions in which a V-Ti carbide can be produced. Thermodynamic data for VC and TiC were obtained from Karapet'yans & Karapet'yans (1970), and enabled us to compute the following standard thermodynamic functions for a $\text{V}_{0.5}\text{-Ti}_{0.5}$ carbide:

$$\Delta H^\circ_{298} = -140.2 \text{ kJ mole}^{-1} \text{ (with } \Delta H_{\text{mixing}} = 0\text{);}$$

$$\Delta G^\circ_{298} = -142.7 \text{ kJ mole}^{-1}; \text{ C}^\circ p_{298} = 28.7 \text{ J K}^{-1} \text{ mole}^{-1}.$$

The $f(\text{O}_2)$ - T conditions were then calculated for the transformation of different V and Ti oxides and silicates reacting with graphite to give carbide, oxygen and by-products. In these calculations, we assumed constant heat capacities. The results are presented in the $f(\text{O}_2)$ - T diagram (Fig. 4). The $f(\text{O}_2)$ conditions needed for the formation of V-Ti carbide invariably are more reducing than the FMQ buffer. They are close to the iron-magnetite (FeM) buffer. Such conditions can be reached during serpentinization, as observed by Ramdohr (1967). In addition, we have observed native iron in association with SiO₂ in ejecta from hydrothermal vents (Jedwab &

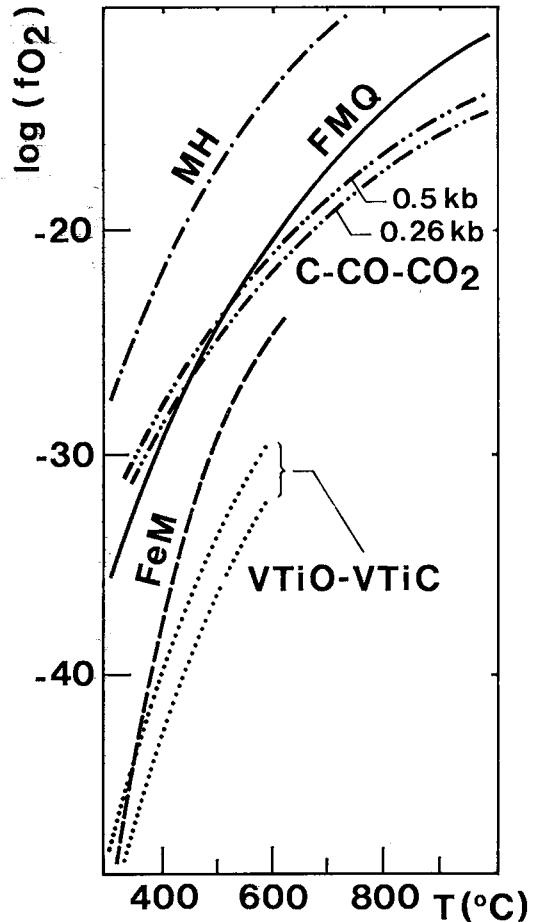


FIG. 4. $f(\text{O}_2)$ - T diagram for the formation of (V,Ti) carbide. VTiO-VTiC: domain of transformation of V and Ti oxides (and silicates) to $\text{V}_{0.5}\text{Ti}_{0.5}\text{C}$. FeM: iron-magnetite buffer, C-CO-CO₂: graphite-CO-CO₂ equilibrium for different pressures, FMQ: fayalite-magnetite-quartz buffer, and MH: magnetite-hematite buffer.

Boulègue 1984). Another relevant argument is the discovery of iron carbides (Fe₃C and Fe₂C) in serpentinized basalts from the Ural Mountains (Steinberg & Lagutina 1986). Hence it is possible to expect that a V-Ti carbide could be produced during serpentinization of basalt at mid-ocean ridges.

Similar conclusions were obtained by Novgorodova *et al.* (1984) concerning the occurrence of (Ti,V,Fe)C in basaltic porphyries, *i.e.*, FeM buffer, $T < 400\text{-}500^\circ\text{C}$; $P = 1\text{-}2$ kbars; $f(\text{O}_2) = 10^{-31}$ to 10^{-34} bars. These conditions suggest that the V-Ti carbide was produced during serpentinization, but under more highly reducing conditions than needed for

graphite. Such conditions may have led to the simultaneous synthesis of the graphite and the carbide, as suggested by the experimental results of Tagiri & Oba (1983). Another possibility is that the carbide was synthesized prior to the graphite, and it catalyzed the graphitization of amorphous carbon. This role is suggested by several experimental results (Fischbach 1971). Solid-phase catalysis of graphitization can occur by random burrowing of carbide particles through amorphous carbon, the most effective carbide catalysts being VC and TiC (Fischbach 1971). That this may have occurred in the case of the graphite particles is substantiated by the observation of a scar in the graphite, clearly associated with the presence of the V-Ti carbide. This scar may be the trail of the carbide particle burrowing through amorphous carbon, while catalyzing its graphitization.

This observation, as well as the results of Tagiri & Oba (1983), require that amorphous carbon be present in the basaltic rocks at 13°N, East Pacific Rise. This is supported by two sets of observations. Firstly, carbon deposition in cracks in basalt may result from the processes of lava emplacement (Mathez 1987). Secondly the lava at 13°N would be expected to be rich in carbon, since it corresponds to a Ti-K-enriched basalt, probably resulting from the mixing of a tholeiitic magma with an alkali-enriched magma (Hekinian *et al.* 1985), and such a lava would be expected to be richer in carbon (Pasteris 1981).

Both explanations for the presence of the V-Ti carbide-graphite association probably require pressures close to 1 kbar. If we consider the pressure in the hydrothermal system to be hydrostatic, only about 0.5 kbar can be reached, since the magma chamber is at about 2 km depth in the basalt (Avédik & Géli 1987). Higher pressures can be obtained if serpentinization is locally accompanied by self-sealing. This will lead to phase separation in the fluid, which may provide the energy to tear out particles from the rock, create new cracks and eject the particles with the hydrothermal fluid.

The discovery of a third natural member in the TiC-VC system [the two others are hongquuite TiC, probably meteoritic (see Yu Zuxiang 1984), and khamrabaevite] poses several interesting questions pertaining to other similar intercalated compounds that could be found in related environments, namely the carbides of Fe, Zr, Mo, W, Nb and Ta. With this possibility in mind, the old and still questionable finds of TaC in the Ural Mountains (Frondel 1962) deserve a reassessment, which we have undertaken.

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