Contributions to Mineralogy and Petrology

Nonstoichiometry and growth of some Fe carbides

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Abstract:	<p>Iron carbides containing from 31 to 17 atomic % carbon, with cohenite XRD structure and optical properties, were grown in experiments in Fe-Ni-S-C, Fe-Ni-C, and in Fe-C at 1, 6, and 7 GPa. X-ray cell volumes increase with C content. Compositions listed above vary considerably outside the nominal (Fe,Ni)₃C stoichiometry of cohenite/cementite. Cohenites coexisting with Fe-C liquid are carbon-poor. The Eckstrom-Adcock carbide, nominally Fe₇C₃, was found to show compositions from 29 to 36 atomic % C at 7 GPa in Fe-C. Both these materials are better regarded as solutions than as stoichiometric compounds, and their properties such as volume have compositional dependencies, as do the iron oxides, sulfides, silicides, and hydrides.</p> <p>The fraction of C dissolved in cohenite-saturated alloy is found to become smaller between 1 and 7 GPa. If this trend continues at higher pressures, the deep mantle should be easier to saturate with carbide than the shallow mantle, whether or not carbide is metastable as at ambient pressure.</p> <p>At temperatures below the cohenite-graphite peritectic, cohenite may grow as a compositionally zoned layer between Fe and graphite. The Eckstrom-Adcock carbide joins the assemblage at 7 GPa. Phases appear between Fe and C in an order consistent with metasomatic interface growth between chemically incompatible feed stocks. Diffusion across the carbide layer is not the growth-rate-limiting step. Carbon transport along the grain boundaries of solid Fe source stock at 1 GPa, to form C-saturated Fe alloy, is observed to be orders of magnitude faster than the cohenite layer growth. Growth stagnates too rapidly to be consistent with diffusion control. Furthermore lateral variations in carbide layer thickness, convoluted inert marker horizons, and variable compositional profiles within the layers suggest that there are local transport complexities not covered by one-dimensional diffusive metasomatic growth. In contrast to many transport phenomena which slow with pressure, at 7 GPa and 1162 °C, carbide growth without open grain boundaries is faster than at 1 GPa with fast grain boundary channels, again suggesting C transport is less of a constraint on growth than C supply. C supply at 7 GPa is enhanced by graphite metastability and</p>

	<p>the absence of fast grain boundary channels to divert C into the Fe instead of growing carbide.</p> <p>At both 1 and 7 GPa, the growth rate of carbide is found to systematically vary depending on which of two stock pieces of graphite are used to form the growth couple, suggesting that some property of each specific graphite, like C-release rate, possibly from amorphous binder material, may influence the cohenite growth process.</p> <p>At temperatures near and above the cohenite-graphite peritectic at 1-1.5 GPa, complex intergrowths involving Fe-C liquids and extensive thermal migration transport were encountered, eroding the organized spatial resolution and the range of cohenite compositions found grown below this peritectic from growth couples of crystalline Fe and graphite. The migration of graphite to a position in the metasomatic sequence between liquid and cohenite demonstrates that the solubility of graphite in liquid increases with temperature above the peritectic, whereas the solubility of graphite in cohenite below the peritectic decreases with temperature. The variable solubility of graphite in cohenite, shown by thermal migration, emphasizes that cohenite does have compositional variations.</p>
Response to Reviewers:	<p>Comments for the Author: (responses in red)</p> <p>Editor's comments: The authors are to be congratulated on submitting a well-written and intriguing manuscript. Both reviewers make minor, but interesting, suggestions for improvement, although neither have any significant comments. I'm therefore recommending that the paper return for minor revisions, with the expectation that it will be accepted. Best regards, Gordon Moore</p> <p>Reviewer #1: Review of "Nonstoichiometry and growth of some Fe carbides"</p> <p>This is a very tightly woven story, and I could not find any scientific errors in the paper, nor do there seem to be any segments of the paper that are not relevant to the whole story. It is not a good idea to pick at it because it has a certain flow that would easily be disrupted by too much editorial interference. So, my basic conclusion is that it should be mostly left alone and published as is.</p> <p>The cementite story presented here is quite interesting and provides a series of lessons to experimentalists about how to interpret experimental results that have thermal gradients, material migration from one end of samples to the other, and disequilibrium textures. In fact, the main subject of the study, the cementite itself, seems to be ultimately metastable, though it experiences local stability during the experiment by being located at the boundary of a pure iron ingot and a graphite reservoir. It maintains its stability for several days and grows as, in some cases, magnificent crystals which seem to mock the common idea (which I myself had sometimes espoused) that good crystals in an experiment should indicate the stability of a material. The cementite produced here can be grown in excellent quality crystals that will certainly find use in property measurements in the future.</p> <p>Several clever experimental tricks contribute to the story, including the addition of a passive layer to show that the cementite grows both into the carbon and into the iron, replacing both at the interface (the passive layer remains near the middle of the cementite layer, though disrupted from planarity). Inverting the initial sequence in the thermal gradient provides further information, as does a separate series of experiments with powdered starting materials.</p> <p>The paper is silent about the initiation of the growth process</p> <p>Indeed we were silent, perhaps minding A. Lincoln's maxim: "It is better to be silent and thought a fool than to speak and remove all doubt." Unfortunately the story that the reviewer spins is misdirected by our original version – we were not silent enough. In November we sent a revised version in which we reinterpreted the worms – no longer do we think that they are liquids. So the reviewer's alternate story, based on a liquid intermediary, needs to be changed to talk about 'fast channels' rather than liquids. Sorry about that. Judging by what amateurs we have proven to be at interpreting the metallographic textures we encountered, we prefer to remain silent. We do appreciate and agree with many of the points that went into the reviewer's alternative.</p> <p>but I would suggest the following: the first reaction between the graphite and iron</p>

stocks should be a thin melt layer at the boundary. Cementite is unlikely to grow into the Fe at this point because diffusion of C into Fe would first result in the formation of stable Fe-C solid solution, which would prevent further reaction. Instead, the cementite should grow into the carbon by addition of Fe, a stable process. The carbon that is displaced by this process goes into the melt which forms the "wormlike" features along grain boundaries throughout the Fe. Then, finally, the cementite that is found on the Fe side of the experiments is produced as an overgrowth, growing from the liquid (which could be more C-rich than the ultimately stable liquid) and not from the Fe itself. I basically think it's impossible to grow cementite directly by C diffusion into Fe. There is an experiment with 3 mm graphite stock where the cementite entirely disappears over a weekend. It is described on Page 35. To me this seems to provide another data point

Yes, another data point, but not for Figure 9, because the metastability and erosion of cohenite by virtue of Fe-saturation is different from bulk composition issues which preclude its long term existence whether or not it is metastable. Figure 9 tracks the former but the holiday weekend experiment HX-22 shows the latter.

for Figure 9A, an open square symbol at 139 hours and 0 microns thickness, to show the turnover in the layer thickness already partly shown by another point in the Figure for 5 mm graphite stock where the layer thickness begins to decrease with time. It shows that the layer first grows, then is resorbed but at different rates depending on the carbon source (note, I wonder what would have happened with the now discontinued Ultra Carbon U5, which was amorphous carbon stock). Good question. Since it is fairly well documented here that cementite is probably still metastable at 1 GPa, I wonder whether, given the ready availability of equation of state data for Fe, Fe₃C, graphite, and diamond, one could not easily decide whether it could possibly be stable at the 7 GPa or any other condition. Possible in theory but small differences in big numbers render the exercise uncertain until confirmed some other way.

Basically, the volume of formation would have to be negative or it could not possibly become more stable with pressure.

Many readers are going to interpret the stability diagrams as "phase diagrams" showing equilibrium. Can the authors refer to them consistently in the captions as "synthesis diagrams" "stability relations" or something like that? Agree. Have done.

If the diagram shows a graphite-saturated Fe phase along with a cementite phase, then it doesn't show a stable relation, of course - I think in most cases this does not happen in the paper and that the iron compositions shown are the ones that coexist with the cementite, is that correct? Yes. We have no graphite-saturated irons. But the figures should be carefully labeled and referred to to avoid confusing them with "equilibrium phase diagrams."

Altogether, the authors are to be congratulated on a nice paper that I found very interesting and I think many other readers who take the time to delve into the story should also find interesting.

More specific comments:

Abstract: "Into saturating Fe" might be more clear if changed to "into melting Fe." The actual saturation of the solid Fe seems to be the last and rate-limiting step of the whole process, also resulting in the consumption of all the cementite. Made a change, but not to melting because of our "worms ≠ liquid" revision.

Page 4: The detailed exposition of nonstoichiometry in cohenites (cementites) is one of the best new features of this paper, so is the determination of a unique composition at the peritectic melting point at 2 pressures.

Page 7: Given the detailed exposition of all the materials, I am curious to know what the "hard-fired MgO" is.

It is material fired to full density, having considerably more mechanical integrity than the more normal semi-sintered material in wider use.

Page 10: I am assuming the Figures will be color in the published version? Either that or the Figure captions should not refer to colors. ok

Page 23: Readers in industry, who are likely to be interested in this work, are going to start at the description of diamond nucleation as "hit or miss." There must be other

reasons for this experiment having such a rich yield of diamonds while no others did. When all the relevant experimental factors are carefully controlled in a regulated environment with strict protocols, diamond growth is very reproducible. This is generally possible in a facility that only grows diamonds, but is much harder to maintain in an academic environment with a wide variety of different activities in one location. No contest here, but what is the factor? We don't know.

Page 24: The hilarious and totally familiar description of the saw station with various carbons lying around is a perfect example of how academic laboratories rarely follow strict protocols. Indeed!

Page 27 The use of thermal migration to ascertain relative slopes in the binary diagram is really interesting and could be useful to many. I would like to have seen even more description of this, especially in the confusing case of the "inverted" cohenite appearances in some experiments. Glad it entertained. Paper a bit long as it is. Buchwald's references to the process in meteorites is very worth reading.

Page 35: A 'worm-track saturated charge' is still not at equilibrium. Equilibrium should be a single-composition liquid plus graphite, correct? No, the temperature of HX-22 was 1110 C, below the eutectic. Expect (and get) an Fe+cohenite assemblage. The cohenite was within the worms that eat their way into the Fe ingot. The metasomatic layer of cohenite disappeared with the graphite's demise.

Page 37: The inverted growth couple and the production of high-quality samples of the most Fe-rich cementite is a great outcome that would not be clearly understandable without the careful exposition throughout the paper. Thank you.

Reviewer #2: See attached file

Review of COMIPE 1278 Walker et al.

This paper reports several very interesting series of experiments on the growth of cohenite and other carbides from Fe and C sources at high pressures. The work highlights several observations: growth rates are higher at pressure (usually the opposite), cohenite and Eckstrom-Adcock carbide are both non-stoichiometric at the conditions of the experiments, and cohenite may be more stable at higher pressure due to the C contents of the gamma Fe phase decreasing at high P. These main findings are thoroughly discussed, leading to some very interesting conclusions about Fe-C systems that are relevant to planetary interiors. I have a number of suggestions and comments that might help to improve the paper. I think if these suggestions are followed the paper will be easier to read, and thus acceptable for publication in CMP.

General

- 1) Dasgupta and Walker 2008 use cohenite as an EMPA standard for C analysis – is it truly stoichiometric or is there a possibility it is also non-stoichiometric and how can one be certain? This seems like some circularity since the cohenite used in DW08 was synthesized under conditions where the authors here see non-stoichiometry. This seems like an important issue to be clear on because as written now it looks very circular.... Reassurances added.
- 2) When I first started reading the paper I thought the situation of Fe₃C non-stoichiometry is somewhat analogous to wustite non-stoichiometry and that therefore the authors should specify the conditions under which the non-stoichiometry (either Fe enriched or depleted) is allowed. By the end of the manuscript I think this has been done well.
- 3) The paper reads in some cases like a mystery novel which is great because is really grabs the reader – this is not a common in my experience and I think it is a terrific aspect of this paper. Who done it?
- 4) Is there a relation between growth rates and degree of non-stoichiometry? We have not directly determined this because we don't have much control on the growth rate except through T. But the 5-shooter experiments leading to figure 13 show that there is T control on the degree of nonstoichiometry. So the growth rate is tough to unwind from T as a control. We have not tried.
- 5) The depletions of C near cohenite, pointed out on page 13 might be attributed to kinetically controlled growth in the 1 GPa experiments. I don't quite see how to do that trick.
- 6) Is there any XRD data (single crystal?) that could show how the non-stoichiometry

works in the detailed structure of cohenite? Perhaps this is best left for future investigations, but it does make me wonder how the structure accommodates such a range of non-stoichiometry. Petch laid this out in 1944. C vacancies fit the case pretty well. Section on XRD volumes touching on this issue has been added. Need about 1 in 10 C atoms to be missing to cover what we see.

7) Is there any growth data for simple analogous systems like Fe-C that could be used as comparison to the 1 and 7 GPa results to assess which may be more expected (or anomalous?). Don't know of any.

Specific comments (there are no line numbers in the version I have so they are in order of appearance in each section)

Introduction

- Second line of Introduction: phantom "it" ok
 - What pressure range did Petch (1944) investigate – maybe give range in text? No pressure
 - Also what methods were available to Petch? Can they be stated? Covered in new XRD section.
 - "Eckstrom-Adcock carbide" is introduced here - maybe it can be defined (formula) here for the first time use? ok
 - Is "Ni-richness" a word – I know what you mean, but it seems wrong grammatically...
 - The end of the introduction needs some kind of general words about why these studies are of interest and what kinds of problems or issues that can be applied to. For example, the very last paragraph of the paper could be moved here to the introduction to help with the more general motivation of the paper and research.
- done

Starting materials

- I think you have done a good job of pointing out the differences in the C stock. However, I know from Fe metal and FeNi metal diffusion experiments we have done that the grain boundary scale can be variable? Yes it can be. How variable was it in the iron and could this have affected the PC vs. MA experimental outcomes? They are different sources of Fe (Johnson Matthey vs. Atomergic) and I wondered about this. Perhaps the C differences are so large that any small difference from the Fe source is masked? I believe we showed quite conclusively that the Fe has nothing to do with the rate change. So its variation of grain size doesn't matter, whatever it is.
- Line 6 of this paragraph refers to "Less certainty" – I think this needs to be explained a little better – certainty about what? changed
- Fe rods were cut down to what diameter for the MA runs? ~0.095"

Experimental methods for carbide growth couples

- There is a mix of inches and mm used in this section – does CMP have any guidelines for one or the other? I am happy with this as an experimentalist - we commonly switch back and forth without realizing it, but it does look funny on paper I have to admit. One reason I publish preferentially in Am. Min. and CMP is that they allow non-uniform units.
- Maybe this section should be split into two paragraphs – one for PC and one for MA? That would make more awkward the transition to the study where we mixed and matched sizes and materials to sort out whether the effect was in the Fe or the graphite.
- Maybe you can at least mention the size of the MA assembly used (truncation, etc.)? That information is not given anywhere. It was given. 6mm.
- How was the run duration arrived at? trial

Experimental growth couple results

- Again, I know what you mean using the phrase worm tracks, but is there a better phrase to use here? Suggestions will be respectfully entertained. I know worm tracks sounds corny but it captures what we need.
- Does this mean carbide might be produced interior to the interface along the tracks, too? Maybe hard to detect if it is.... Yes! Not hard to see. It is there. Figure 3C detail added to show it.
- Can the lateral variation in cohenite thickness observed be due to temperature gradients from center to edge of capsule? Wrong way around. Hotter edges should promote growth not retard it.
- Top of page 13: this description sounds analogous to the situation seen cases where

growth is kinetically controlled where the volume of matrix close to the growing crystal is depleted in a major component of the crystal again, I don't quite see this as applying here - the Fe had to get the C from across the cohenite as it is growing...diffusion controlled growth does not typically have such depletions...I think this is discussed and acknowledged in the paper but it does take some time to draw out this distinction.

- Top of page 16, there is a discussion about mobility of C and Fe. I think there is experimental evidence (maybe Brooker and Holloway) for extensive C mobility in PC experiments, and there have been studies of Fe mobility even in vapor phase by Palme and associates over the years (Dohmen?), so maybe no surprise that they are both pretty mobile... the issue is not just C mobility, but C vs Fe mobility

Carbide growth rates

- I checked the Watson and Watson paper and also the Richter et al. 92005) paper on metal-metal diffusion and found activation energies of 200-300 kJ/mole, so I am confused by this statement. Sorry, a misprint. Was supposed to be Mj/mol. Maybe you mean the entire H/RT term? Or maybe you mean the difference in activation energy at the two difference temperatures? But the error on those energies is pretty large since they are fits to diffusion data... ± 50 kJ/mole. Anyway it seems like this needs some clarification. Yes. Fixed, Thx.

- Bottom of page 20 to top of page 22: I think you are saying that the tracks make C leaky and therefore cause a slower growth rate? Is this right? yes

- Figure 11 scale units are in a different form than other figures (μ). Fixed

The search for equilibrium liquid-carbide-graphite-Fe phase relations at 1 GPa

- Page 25, midway down page – there is a description of cohenite stability being contentious – can you add a reference or two in here ? ok, done

- Figure 12 – needs scale bars. Objects described by size in caption

Equilibrium basis for growth couple evolution

- Figure 19 is missing scale bars, too, I think. Scale described in caption

Conclusions

- The very bottom of the page has a sentence that begins with “The increase in growth rate...” It might be better to say “The higher growth rate...” because there is a lengthy discussion as to whether the 1 GPa rates are anomalously slow or the 7 GPa rates are anomalously fast. I think you conclude that the 1 GPa rates are anomalously slow which means the 7 GPa rates are normal, and characterizing them as an increase may be slightly misleading. Ok, changed.

- Top of page 44: I think you mean 7 GPa here, not 70. Yup, I still think in kbar.

Kevin Richter Dec. 7, 2012

dw jan 21, 2013

Nonstoichiometry and growth of some Fe carbides

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Abstract: Iron carbides containing from 31 to 17 atomic % carbon, with cohenite XRD structure and optical properties, were grown in experiments in Fe-Ni-S-C, Fe-Ni-C, and in Fe-C at 1, 6, and 7 GPa. X-ray cell volumes increase with C content. Compositions listed above vary considerably outside the nominal (Fe,Ni)₃C stoichiometry of cohenite/cementite. Cohenites coexisting with Fe-C liquid are carbon-poor. The Eckstrom-Adcock carbide, nominally Fe₇C₃, was found to show compositions from 29 to 36 atomic % C at 7 GPa in Fe-C. Both these materials are better regarded as solutions than as stoichiometric compounds, and their properties such as volume have compositional dependencies, as do the iron oxides, sulfides, silicides, and hydrides.

The fraction of C dissolved in cohenite-saturated alloy is found to become smaller between 1 and 7 GPa. If this trend continues at higher pressures, the deep mantle should be easier to saturate with carbide than the shallow mantle, whether or not carbide is metastable as at ambient pressure.

At temperatures below the cohenite-graphite peritectic, cohenite may grow as a compositionally zoned layer between Fe and graphite. The Eckstrom-Adcock carbide joins the assemblage at 7 GPa. Phases appear between Fe and C in an order consistent with metasomatic interface growth between chemically incompatible feed stocks. Diffusion across the carbide layer is not the growth-rate-limiting step. Carbon transport along the grain boundaries of solid Fe source stock at 1 GPa, to form C-saturated Fe alloy, is observed to be orders of magnitude faster than the cohenite layer growth. Growth stagnates too rapidly to be consistent with diffusion control. Furthermore lateral variations in carbide layer thickness, convoluted inert marker horizons, and variable compositional profiles within the layers suggest that there are local transport complexities not covered by one-dimensional diffusive metasomatic growth. In contrast to many transport phenomena which slow with pressure, at 7 GPa and 1162 °C, carbide growth without open grain boundaries is faster than at 1 GPa with fast grain boundary channels, again suggesting C transport is less of a constraint on growth than C supply. C supply at 7 GPa is enhanced by graphite metastability and the absence of fast grain boundary channels to divert C into the Fe instead of growing carbide.

At both 1 and 7 GPa, the growth rate of carbide is found to systematically vary depending on which of two stock pieces of graphite are used to form the growth couple, suggesting that some property of each specific graphite, like C-release rate, possibly from amorphous binder material, may influence the cohenite growth process.

At temperatures near and above the cohenite-graphite peritectic at 1-1.5 GPa, complex intergrowths involving Fe-C liquids and extensive thermal migration transport were encountered, eroding the organized spatial resolution and the range of cohenite compositions found grown below this peritectic from growth couples of crystalline Fe and graphite. The migration of graphite to a position in the metasomatic sequence *between* liquid and cohenite demonstrates that the solubility of graphite in liquid increases with temperature above the peritectic, whereas the solubility of graphite in cohenite below the peritectic decreases with temperature. The variable solubility of graphite in cohenite, shown by thermal migration, emphasizes that cohenite does have compositional variations.

Introduction

Cohenite, nominally Fe_3C , is usually presumed to be stoichiometric. However the normal stoichiometry-fixing valency rules are difficult to apply to a compound of this composition; it is not clear what valencies to apply to Fe and C. This difficulty in understanding the stoichiometry is also apparently shown by cementite (metallurgical cohenite), as pointed out by Petch (1944) who suggested it might be better to interpret cementite as an intermetallic solution. In which case there is no compelling reason from valency for the compound to be stoichiometric. Petch (1944) surmised that variation in Fe/C might be responsible for the small shift to lower cell volumes he observed in cementites prepared at a range of increasingly higher temperatures saturated with austenite (γ Fe or mineralogical taenite). Any such compositional variation was not directly detectable with the bulk analytical chemistry methods available to Petch (1944). As Petch's systematic cell volume changes were rather small, most subsequent work has only obliquely raised the issue of nonstoichiometry in cohenite/cementite in passing over it (e.g. Darken and Gurry, 1951; Ban-ya et al., 1970; Chipman, 1972). We find evidence that cohenite and the Eckstrom-Adcock carbide, nominally Fe_7C_3 , can show considerable variation in their Fe/C ratio, perhaps even more than imagined by Petch (1944).

We studied the partitioning of Ni, Co, W, Pt, Re, and Os between liquids in the Fe-Ni-S-C system and Fe carbides of the cohenite structure (Buono, 2011; Buono et al., 2013). We discovered that there was rather a large range of cohenite compositions, more than the customary $(\text{Fe,Ni,Co})_3\text{C}$ stoichiometry shown by most naturally occurring cohenites and metallurgically grown cementites. Figure 1 shows the C and S atom % in both liquids and carbides found in our study, the balance of the compositions being Fe and Ni with trace Co, Pt, W, Re, and Os.

There is a broad cluster, 25 ± 3 atom % C, of cohenite compositions centered upon the customary 25 atom % C expected. However there are two other cohenites that have a much lower C content. The C-poor cohenites grow from the C-poorest liquid compositions, so it is unlikely that these Fe-Ni-rich carbides have their nonstoichiometric compositions as an artifact of random errors in microprobe analysis. XRD analyses of these two cohenites confirm that they have the XRD pattern of orthorhombic cohenite even though they are strongly C-deficient compared to stoichiometric Fe_3C cohenite. They are not the cubic Fe_{23}C_6 carbide haxonite reported by Scott (1971) from Toluca and other iron meteorites. Haxonites theoretically approach a lower limit of ~ 20 atom % C, whereas our carbides have distinctly less than 20 atom % C, have birefractance, and have an orthorhombic XRD pattern, that matches well with cohenite/cementite. Representative compositions from the range of cohenite and Eckstrom-Adcock carbides found by Buono (2011) and by this study are summarized in Table 1. The result of most interest is that both carbides show departures from stoichiometry which are beyond analytical uncertainty. Cohenite is found to be both C-rich and C-poor relative to Fe_3C whereas the Eckstrom-Adcock carbide is found to be either close to stoichiometric or C-rich compared to Fe_7C_3 .

The strongly Fe-enriched cohenites found by Buono (2011) appear to be separated by a small gap in composition from the more normal ones. These cohenites are also Ni-rich compared to the others. We sought to understand whether the anomalous cohenites were really a separate population and whether they form as the result of their growth at 6 GPa or of their Ni-richness. At 6 GPa with comparable, but Ni-free, liquids, our previous experience, Dasgupta et al. (2009), showed that Fe_7C_3 was the expected carbide. We attributed the presence here of cohenite instead of Fe_7C_3 to stabilization by Ni. It occurred to us that, the anomalies being extra-Ni-rich charges, Ni might stabilize a wider range of cohenite compositions as well. Thus our test was to attempt to grow a full range of cohenites at only 1 GPa in the Ni-free end-member Fe-C system. We have used the methods of combinatorial chemistry to grow the compounds formed between chemically incompatible feed stocks by placing them together as a reaction couple, in this case between crystalline Fe and graphite. This strategy should elicit the full range of reaction compositions possible. Executing this strategy at 1 GPa and Ni-free should remove high pressure and Ni from the list of potential causes for the range in stoichiometry if we succeed in growing cohenites of wide-ranging composition (as we did).

The recent rejuvenation of interest in the Fe carbides as potential constituents of solidifying planetary cores (Gao et al. 2008, 2011; Lord et al. 2009; Dasgupta et al., 2009; Nakajima et al. 2009, 2011; Mookherjee et al. 2011; Mookherjee, 2011; Buono, 2011; Buono et al. 2013) and as a potential host of carbon in the mantle (Dasgupta and Hirschmann, 2010; Dasgupta, 2013; Buono et al., 2013) makes the compositional variations shown to be possible in these phases of more interest than they might otherwise be. Physical properties [for instance volume] and partitioning behavior, prescribed for stoichiometric versions of these phases, may require modification with deviations from stoichiometry for application to core and mantle problems.

Starting materials

Rod stock of Fe and graphite was machined to closely fit within the open, cylindrical, hard ceramic sleeves used in our assemblies to maintain mechanical integrity of the planar interface between cylinder stock ends. For the piston-cylinder dimensions, Johnson-Matthey Puratronic Fe and National Carbon Spectroscopic grade graphite were generally used. These are designated “5mm” stock which is roughly their starting dimensions. A single bar of 5mm Puratronic Fe stock was used throughout. It is not clear whether a single bar of spectroscopic 5mm graphite was used, until serial #s greater than HX-14, when the issue of bar stock type was identified. All subsequent 5mm experiments used a single 5mm graphite bar which was used for most (but possibly not all, c.f. HX-12) previous 5mm experiments. For multi-anvil dimensions, different bar stocks were used, generally having 3mm original dimensions cut down to ~0.095” OD to fit the multi-anvil MgO sleeves. 3mm Fe stock was a single bar of Atomergic Grade 1 material, whereas all 3mm graphite stock was cut from a different (i.e. different from the 5mm stock) single bar of National Carbon spectroscopic grade material originally manufactured as smaller electrodes than the 5mm stock. When the issue of bar stock was identified, cross checks were run with the starting stocks used noted in Table 2. The bar stocks of Fe were both kamacite by X-ray diffraction. The bar stocks of graphite were all 2H polytype with an extra, small to moderate, X-ray diffraction “bulge” with d-spacing just larger than the basal (001) reflection, suggesting the presence of amorphous material. This variably-present “bulge” was detectable in

all the stock pieces we X-rayed, but was easily detected in some pieces of the most-used bar of 5mm graphite stock. The amorphous material may be a remnant from the rod binder.

Experimental Methods for carbide growth couples

Piston-cylinder and multi-anvil solid media devices were used to grow cohenite at the planar interface between cylinders of Fe and graphite placed end to end. Particular care was taken to note and record which cylinder was above the other in the loading process as this order was varied intentionally in selected experiments. These cylinders were generally constrained to form a planar interface at their end contacts through the expedient of limiting their deformational distortion by confining them in open-ended, hard ceramic hollow cylinders within the pressure media. For the piston-cylinder experiments at 1 GPa, the ceramic sleeve was fully dense Al_2O_3 of $\frac{1}{4}$ " OD, $\frac{3}{16}$ " ID, x $\frac{1}{4}$ " long. These sleeves fit within graphite heaters lodged within $\frac{1}{2}$ " sintered BaCO_3 pressure media. Experiments were run piston-in with a load determined from the friction correction procedure of Fram and Longhi (1991) using the same hard ceramic sleeves. Once an experiment was loaded and fully pressurized cold, temperature was increased to 1000 °C in ~1/2 hour where it was typically held overnight to sinter closed the pore spaces in the graphite and pressure media. Subsequently the sample was taken to the final temperature of cohenite growth, typically 1162 or 1110 °C, and held for periods of 1-17 days. For the multi-anvil experiments at 7 GPa, the ceramic sleeve was full density (hard-fired) MgO of $\frac{1}{8}$ " OD, 0.95" ID, x 3 mm long. The MgO sleeves were fit within LaCrO_3 heaters within castable ceramic pressure media octahedra with integral gasket fins [Aremco Ceramacast 584OF] inside clusters of 8 tungsten carbide cubes with 6 mm edge truncations. The 7 GPa pressure was achieved by application over ~10 hours of 225 tons of uniaxial force to a collection of wedges within a ring that drive the cubic WC anvils together [Walker et al., 1990]. Once slow pressurization was achieved, temperature was raised over the course of ~1/2 hour to 400 °C where the LaCrO_3 heaters were allowed to stabilize for at least an hour. The final temperature of carbide growth, 1110 °C, was achieved in about 10 minutes and held for 1-6 days. These standard operating procedures in this lab are detailed more fully in Dasgupta et al. (2009) and Buono (2011). Both types of experiment were controlled in temperature by W-Re type D thermocouples, except in a few experiments noted in Table 2 where Pt-10Rh type S thermocouples were used. Temperature

was dropped to about 100 °C in less than 15 seconds at the end of the heat treatment by cutting the power to the heater. Following power quenching the experiments were extracted from their apparatus and potted in epoxy, ground to expose the charge perpendicular to the Fe-graphite interface, and polished for optical, X-ray, and electron microprobe analysis. Carbide layers were observed and their thicknesses measured optically. Phase compositions were determined using a Cameca SX-100 electron microprobe at either the American Museum of Natural History or NASA Johnson Space Center, following the procedures of Dasgupta and Walker (2008). Synthetic, stoichiometric cohenite was used as the analytical standard. The standard cohenite was synthesized with piston-cylinder techniques in MgO from a stoichiometric Fe-C mix. As our results indicate that stoichiometric Fe_3C is within the range of permissible cohenites, and no Fe or graphite were detected in the standard, we feel that the range of carbide compositions discovered in this study is not undermined by uncertainty in the standard composition.

Experimental Growth Couple Results

Table 2 lists the run conditions, durations, and thicknesses of the carbide layers grown. The first two sections of Table 2 give results for carbide growth experiments at 1110 or 1162 ± 12 °C under piston-cylinder (first section) and multi-anvil conditions (second section). The third section gives results for piston-cylinder experiments at higher temperatures (1200-1250 °C) near or above the cohenite-graphite peritectic (close to, but above, 1225 °C), which are relevant to the nature of the phase relations and transport within the Fe-C system at 1-1.5 GPa, as discussed below.

A reflected light photomosaic of HX-8, a typical 1 GPa cohenite growth experiment at 1110 °C, is shown in Figure 2. This experiment began with the Fe above the graphite and this relationship is preserved. The changes introduced by the heat treatment are the growth of a layer of cohenite and the appearance of decorations on the grain boundaries of the Fe which would appear to be ‘worm tracks’. At highest magnification, lamellae of cohenite can be recognized within some of these tracked regions. These cohenite lamellae can also extend from the C-rich worm tracks into the relatively less C-rich iron crystals as seen in the Figure 3C red circle. The boundary between the C-rich tracks and the iron crystals is sharp, not diffuse. Our interpretation is that these ‘worm tracks’ represent the route taken by C along Fe grain boundaries in its transport from the graphite (through the cohenite layer) into the under-saturated mass of Fe.

These worm tracks are observed throughout the Fe, at all experimental durations observed with even the thinnest cohenite layers. The transport of C on the Fe grain boundaries is evidently orders of magnitude faster than the growth of the cohenite. C transport is not likely therefore to limit the growth of cohenite layers.

Additional features of note in Figure 2 include the dark pits in the cohenite layer. These correspond to plucks during polishing of individual single crystals of cohenite. The bireflectance of this material unambiguously shows that the crystals are indeed this coarse, spanning the full layer thickness. It should also be noted that the cohenite layer is not of uniform thickness. It feathers to minimum thickness near the hard ceramic capsule walls from its maximum near the central axis of the charge. The reason for this thickness variation is unknown, but minimum and maximum thicknesses corresponding to this variation, which is generally observed in all the charges, are recorded in Table 2. At a minimum, this thickness variation suggests that the cohenite growth and Fe-C transfer is not strictly a one dimensional process. Figure 3 shows the same sort of thickness variation in the much thicker cohenite layer of experiment HX-11, run for longer times at slightly higher temperature. Evidently the curious lateral variation in cohenite layer thickness is a persistent feature of these experiments.

Figure 4 shows the compositional variation across the cohenite layer in experiment HX-11 and into the Fe. The Fe has reached saturation in C with cohenite, having about 10 atomic % C throughout, with values to ~15 atomic % C in the worm tracks. The full range of cohenite stoichiometries seen by Buono (2011) and Buono et al. (2013) at 6 GPa in a range of Ni-bearing charges are not seen at 1 GPa in the Ni-free system in this one experiment, although the cohenite seen here is slightly C-deficient compared to stoichiometric. There is a small spatial zonation to the compositions which is the reverse of that which would make sense for their growth simply as a metasomatic reaction process (Thompson, 1959). These features are also seen in traverses across HX-8 (not shown). The cohenites near graphite should be more C-rich than those near Fe if there is a range of cohenites to sample. The reverse is seen. Again we have an indication that the growth process is not simple, even though the distribution of phases is broadly in accord with a metasomatic control of the phase distribution.

Figure 5 shows that the nature of the carbide layers changes when the growth process occurs at 7 GPa. Cohenite still grows but is not joined directly to graphite as at 1 GPa, but to a

new intermediate layer of the Eckstrom-Adcock (Fe_7C_3) carbide. This reflects the known increase of stability of this Fe-poor carbide at more than 5 GPa as found by many investigators including Shterenberg et al. (1975), Tsuzuki et al., 1984; Dasgupta et al. (2009), Nakajima et al. (2009), and Lord et al. (2009). It also shows that the stability field of cohenite has not been terminated by the increase in stability of Fe_7C_3 . The disposition of the phases is in accord with their compositional order in the composition space between Fe and C, consistent with a two-intermediate-phase metasomatic reaction process.

Additional features of note in Figure 5 are: a/ that the carbide thicknesses again feather towards their distal extremes as at 1 GPa, b/ that there are no ‘worm tracks’ suggesting that the grain boundaries have been sealed to no longer mediate C transport, and c/ that even so the growth rate of cohenite is $\sim 3\times$ faster than shown by HX-8 in Figure 3. HX-8 required 148 hours to grow 98 microns of cohenite instead of only 48 hours here. High pressure seems to favor more rapid carbide growth. We will consider below whether this is intrinsically a pressure effect, partly a temperature effect (1110 vs. 1162 °C), or a material stock effect, or all of these.

Figure 6 shows the results of microprobe analysis across the carbides and Fe metal of HX-14. Both carbides have only minor excursions from their nominal stoichiometries of Fe_7C_3 and Fe_3C to slight C-enrichment. As at 1 GPa, the cohenite is perplexingly marginally C-poorer close to the graphite adjacent to Fe_7C_3 than it is adjacent to the Fe.

Fe metal has slightly less C in solution at 1162 °C at cohenite saturation at 7 GPa (5-8 atomic %) than was the case at 1162 °C at 1 GPa (8-10 atomic %). This may be seen in Table 1 and by comparison of Figures 4 and 6. This anticipates the systematic result developed below in Figure 13B. The saturation level of carbon in Fe is of considerable interest for knowing how much carbon needs to be present to grow carbides in a planetary interior. The pressure sensitivity of this solubility is of particular interest in large planets. However little is known about the expected variation with pressure of the saturation level in Fe alloy. This value may be expected to vary with temperature and phase assemblage. Wood (1993) predicted that the Fe-cohenite eutectic should become more C-poor with pressure. This prediction was confirmed by Lord et al. (2009) for pressures above 20 GPa. A decreasing C content of the eutectic is simplest to understand if the C content of the saturated Fe alloy also becomes C-poorer at temperature near the eutectic. The experimental confirmation offered here for Fe saturation becoming C-poor with

pressure, makes the search for carbides in planetary interiors more likely to succeed. It should take less carbon to saturate γ Fe with carbide at higher pressure. If it should prove that cohenite is metastable with respect to saturated γ Fe and graphite at high pressures as well as ambient pressures (Darken and Gurry, 1951), our experimental result still stands. Fe saturated with cohenite becomes less C-rich with pressure whether or not this assemblage is metastable. The issue of whether this equilibrium applies to mantle petrogenesis depends on whether or not some more stable equilibrium is accessible. For instance, Fe produced in the mantle by whatever means will grow cohenite if it can access carbon in excess of the saturation value. Cohenite can grow on the surface of the Fe even if the carbon provided is less than the saturation value for the bulk material. Should graphite not be present, the more stable C-saturated-Fe/graphite equilibrium is not accessible and the Fe-cohenite assemblage could persist metastably.

By way of contrast, the central compositional profiles (shown in Figure 7) in the carbides of HX-16, a longer run at 7 GPa, are noticeably sloped. They are also sloped in a way that makes sense within the metasomatic framework. They are more carbon-rich as they approach the graphite. Both carbides begin their C-enrichment from near their nominally expected stoichiometric values of 25 and 30 mole %. The Fe present is still saturated with C at 7-8 atomic % as in HX-14, suggesting that the equilibrium value was reached in less time than the 48 hours for which HX-14 was run.

At both 1 and 7 GPa, some of our microprobe traverses across the carbides show strongly zoned compositional profiles in the carbide (e.g. HX-18, below, and HX-16) whereas some of the phase-zoned profiles are virtually unzoned in phase composition (e.g. HX-11 and HX-14). Different profiles in the same experiment may be more or less compositionally zoned [e.g. HX-8, and HX-16, Figure 7]. This is yet another piece of evidence that the Fe-C transport is not simple or one dimensional.

In order to gain insight into this complexity, or perhaps to further document it even without further insight, we performed an ‘inert marker’ experiment, HX-23. Al_2O_3 powder of 0.3 micron grain size was dusted onto the initial interface between Fe and graphite. If the Al_2O_3 powder layer can be found after the experiment, then relative motion of Fe and C with respect to the initial interface can be established. For instance if C were the only mobile element, Al_2O_3 would be found between the graphite and the cohenite. If only Fe were mobile then Al_2O_3 would

be recovered between the Fe and the cohenite. And if both Fe and C are mobile, then the Al_2O_3 is likely to wind up within the cohenite. We obtained a very clear result, the Al_2O_3 is found within the cohenite after the experiment, indicating that both Fe and C are mobile. Figure 8 shows micrographs of this recovery. Several features are of note.

The first feature of note is that a well-formed layer of cohenite did grow at the interface, undisrupted by the inert marker. The second is that the cohenite layer is thicker than expected from the Table 2 entries for other 1110 °C experiments. The third feature is that the cohenite layer thins to its distal portions but that the interfaces with Fe and graphite are very nearly planar [dashed lines]. The fourth feature is that the recovered layer of Al_2O_3 is convoluted in detail and stylolite-like in its overall presentation. This terminal geometric complexity is stunning considering the simplicity and planarity of the cohenite layer in which the Al_2O_3 is embedded and the simplicity and planarity of the initial configuration of the Al_2O_3 powder at the initial interface. The stylolite-like presentation can be appreciated better by noting the white arrows in the upper image of Figure 8. The arrows indicate the distance from the cohenite interface with either Fe or graphite to the Al_2O_3 . Note in particular the contrast in the arrows at a, and at b. The Al_2O_3 is closer to graphite at a and closer to Fe at b, taking stylolite-like steps from left to right across the image. Clearly the initial planarity of the Al_2O_3 has been lost on the micro scale [lower image] and on the meso scale [upper image]. It is difficult to contrive a simple scenario to explain this inert marker warpage inside a planar cohenite layer of large crystal size. Instead we restate the obvious, that the cohenite growth process is complex in detail, both in its chemical transport and its resulting documented geometry.

Carbide growth rates

Compared to the crystal sizes grown by Buono et al. (2013) in the presence of copious liquid, the cohenites in the first and second sections of Table 2 grew more slowly. An examination of the evolution of the cohenite layer thickness with time allows certain conclusions to be drawn about the control mechanisms involved. There are at least four identifiable factors influencing the thickness of layer growth. The first is that longer experiments grow thicker carbide layers. The second is that higher temperature makes growth faster, with plausible

activation energy for the variation. The third is that higher pressure experiments grow thicker layers in a given time for given starting materials. The fourth is that 5mm graphite stock grows layers about a factor of 2 faster than 3mm graphite stock, whereas no differences are observed for the different Fe stocks. These points may be understood by reference to Table 2 and Figures 9A and 9B.

The first two points, experiment duration and temperature dependence of carbide thickness, follow directly by inspection of Figure 9A. The curves for each temperature have positive, decreasing slope; thus indicating that the layer thickness increases with time, but more slowly as the layer thickens. The blue curve for 1162 °C is above the red curve for 1110 °C indicating temperature promotes faster layer growth. It is perhaps necessary to comment on the use of these curves at all, because the data are far from a perfect fit to them. These curves capture the suggestion that the carbide thickness increases at first and then levels off. [HX-12, the longest duration 1110 °C experiment, actually breaks the monotonic increase of carbide thickness with time at 1110 °C.] These curves and the data certainly are not linear nor are they $\sqrt{\text{time}}$ functions. So what are they? The carbide grows about 3-5 times faster at 1162 °C than it does at 1110 °C for the first 100 hrs or so. After that, rather less happens; the carbide growth slows considerably in each case. There is not enough precision of functional form or enough reproducibility to calculate precise activation energies from this growth rate difference between 1110 °C and 1162 °C. Increasing the growth rate 3-5 times over this temperature difference gives a formal activation energy in the neighborhood of $\frac{1}{2}$ of a Mj/mol which is comparable to the roughly $\frac{1}{3}$ of a Mj/mol found by Watson and Watson (2003) and Richter et al. (2005) for the diffusion of several trace siderophile elements in Fe-Ni alloys in this temperature range. So the initial growth rates at 1110 °C and 1162 °C do at least show a temperature dependence of the growth rate that is roughly consistent with what you might expect, if diffusion has some influence on the growth rate.

However satisfying this rough consistency may appear, it is difficult to reconcile the stagnating growth rate, or even negative excursions like HX-12, with a strictly diffusive model. Layer thickness should continue to increase until the reactants are consumed, albeit with slower rates as the layer growth proceeds. None of the data in Figure 9 are for experiments that have consumed one or the other, or both reactants. There is insufficient precision and duration in the

data to rule out the $\sqrt{t}$ layer thickness expected for diffusive growth. However it is difficult to make a case that $\sqrt{t}$ fits the data. Furthermore, diffusive growth makes no sense of the ‘wrong’ slopes of chemical variation across the carbides shown in Figures 4 and 6. Those ‘wrong’ slopes suggest that carbide is eroding, not growing. *How could that occur?* Darken and Gurry (1951) and Ban-ya et al. (1971) report negative free energies of formation of cohenite in this temperature range. So cohenite is expected to grow from pure Fe and graphite, as we observe. However Darken and Gurry (1951) deduced that the cohenite in equilibrium with C-saturated Fe was metastable with respect to graphite and its equilibrium with a slightly less C-rich C-saturated Fe alloy. Thus cohenite becomes metastable as the Fe alloy saturates with C. During our diffusion couple experiments, then, we have reason to expect combinatorial growth of cohenite at first from pure Fe, followed by growth stagnation, or even cohenite erosion, when cohenite becomes metastable, as Fe becomes C-saturated. Given that our 1 GPa experiments have a rapid transport route for C saturation which is irregularly distributed (worm tracks), it is perhaps unsurprising that the data in Figure 9A are as ragged as they are and that there is lateral variation in layer thickness. Different worm track distributions will make C saturation of the Fe shut down cohenite growth at different times in different stages and places of cohenite growth.

The third point, that pressure promotes growth rate, follows from inspection of Figure 9B. The green curve and red curve for 7 GPa growth are above the blue curve for 1 GPa growth at 1162 °C. The same 5mm graphite stock was used for the blue curve for 1 GPa and red curve for 7 GPa. It is interesting to note that the red and green 7 GPa curves of Figure 9B are much less ragged than the curves of Figure 9A, where worm tracks are present at 1 GPa. In the absence of these irregular channels, the progress towards Fe saturation with C proceeds in a more orderly, solid-state-diffusion-controlled manner. From this perspective, it may not be so much that growth rates are enhanced by pressure. Instead, pressure, is shutting down the erratic channels which short circuit C into the Fe and thus terminates cohenite stability and growth. So pressure may promote cohenite growth only indirectly by shutting down the diversionary channels that drain C into Fe rather than into cohenite. Clearly C transport is not the control on growth rate, or else growth would be expected to respond more favorably to the presence of a rapid transport medium like the worm tracks.

The fourth point, that graphite stock makes a difference but Fe does not, can be made most easily from Figure 10 and a comparison of HX-19 and HX-21 in Figure 9B, the two relatively short term experiments of 21.5 and 32.25 hours duration at 7 GPa. These experiments both used two starting layers of graphite, 5mm stock above and 3mm stock below, on either side of a single layer of Fe stock. In HX-19 the stock was 3mm Fe, whereas in HX-21 the stock was 5mm Fe machined to smaller size to fit the multi-anvil configuration. Both experiments fall along their respective Figure 9B trends for particular graphite stocks, indicating that the substitution of one piece of the Fe stock for another has no effect on the carbide growth achieved. By contrast, the 5mm graphite makes $\sim \times 2$ thicker carbides than the 3 mm graphite in each experiment, clearly showing the graphite stock effect is independent of the Fe stock. This is confirmed by a comparison of 1 GPa experiments HX-7 and HX-20 [open red symbol near origin of Figure 9A] which shows the same sense of growth retardation when 3mm graphite is substituted for 5mm graphite.

An exception to the rule that 3mm graphite retards cohenite growth is provided by HX-15 shown in Figure 11. This experiment was our first attempt to see if pressure or stock type was controlling the difference between the growth rates in piston-cylinder vs. multi-anvil experiments. We ran some 3mm multi-anvil stock in piston-cylinder configuration, but we did so without providing the supportive hard ceramic sleeve. Instead HX-15 was encapsulated entirely in semi-sintered MgO, with the result that substantial deformation of the charge took place with consequent degradation of the planar interface between Fe and graphite. The resulting deformed cohenite layer is strikingly irregular in thickness and much thicker than expected for the time spent at 1162 °C based on the other 1 GPa experiments. We interpret this anomalous thickness, which is omitted from Figure 9, to be a consequence of the distortional process which may stimulate the kinetics of the cohenite growth process. [The distortional enhancement of the cohenite growth process was successfully avoided in HX-21 by providing hard ceramic support around the 3mm graphite component of growth couples with 5mm Fe.]

Another exception to the rule that 3mm graphite retards cohenite growth is provided by HX-17. This experiment nucleated and grew abundant diamond within the carbide layer, as well as a large knot of diamond along one side of the carbide-graphite interface, although most of the graphite stock remained intact. The volume changes and distortions associated with the diamond

production may have provided deformational enhancement for the carbide growth process. HX-17 produced by far the thickest carbide layer observed - over 500 microns in 95 hours.

Furthermore the carbide layer produced is no longer neatly organized into paired carbide layers as seen in all other 7 GPa experiments. Because diamond nucleation is a hit or miss occurrence at the margin of its stability in these 7 GPa experiments, we pass over any further consideration of this chance anomaly - which is also omitted from Figure 9. It seems to provide another example of the importance of preserving the geometry of the growth process without mechanical distortion in order to get reproducible growth rates.

There is perhaps another lesson to be taken from the diamond-growing experiment HX-17, besides the effect of geometric distortion - which is real enough. It is that diamond can grow as it should in its stability field relative to graphite. But diamond does not always grow, because nucleation is a chance process. Metastable graphite may be preserved, as it was in most of our 7 GPa experiments. This metastable graphite may, however, more easily shed its C when metastable than when it is deep within the field of true graphite stability at 1 GPa. We developed a number of arguments, which we continue below, that C release rates by graphite provide control of cohenite layer growth rates. Furthermore we also argue that C transport rates do not control the layer growth, because they are observed to be much faster than the cohenite layer growth. Therefore the possibility that metastable graphite supplies C faster than stable graphite offers a supplemental explanation for the enhanced carbide layer growth rates at 7 GPa. This is in addition to the explanation put forth above that pressure suppresses grain boundary channeling or the alternative explanation that diffusion is enhanced with pressure. Reference to graphite instability is appealing because we do not think diffusion is the limit on growth in the first place, preferring the C-supply rate control on other grounds. Besides, diffusion is usually expected to slow with increasing pressure in metallic systems. The metastable-graphite-supplying-C-faster scenario is appealing because it avoids the physically implausible scenario of negative activation volumes for C diffusion.

Although there are the exceptions mentioned, there is still a clear systematic result in Figure 9 that different graphite stocks grow carbide layers by rates that differ by as much as a factor of 2 at both pressures investigated. Why? Both graphites were produced by National Carbon Corp. as spectroscopic grade material for analytical electrodes so that gross

contamination seems unlikely and none has been seen in energy-dispersive scans. They were produced as different sized electrodes, decades apart, several decades ago [pre-ZIP code] so that documentation may be difficult although some batch numbers remain. Optical examination of the polished graphite after the experiments showed no obvious difference in texture or grain size between the two batches. A range of grain size is noted in each batch. A coarse fraction, 10s to 100s of microns in characteristic dimensions, of about 75% of the material is bonded together by a much finer fraction whose textural properties are difficult to discern optically. XRD characterization for graphite polytype (2H) showed variable amounts of amorphous material that might be responsible for the growth rate differences observed. More amorphous material is found sporadically in the one 5mm bar stock used for most experiments, although the level found varies piece by piece.

The demonstrated existence of the graphite stock control on carbide growth rate may provide a possible explanation for the anomalous result seen in HX-12, an otherwise unremarkable experiment in the time series at 1110 °C, 1 GPa monitoring cohenite layer growth. HX-12 showed no particular anomalies of power consumption or deformation, and yet the amount of cohenite grown is about 1/2 that expected from the other experiments in the series using 5mm graphite stock. The population of worms in the HX-12 Fe is also less than expected suggesting a C supply problem. That we used 5mm stock for HX-12 is not in question, but it is not clear that we used the same bar as all the other 5mm graphite experiments because there was another bar available at the saw station where components were cut during the time of assembly of HX-12. We only became aware of the possible graphite effect for serial #s after HX-14, after which we exercised more inventory control on which exact bar of stock was used. It is possible that the HX-12 graphite stock was from the different 5mm bar which has been found to be low in amorphous material by XRD. It is also possible that it was the usual 5mm bar stock because that bar has been found to be heterogeneous in its amorphous peak intensity from piece to piece. The XRD fingerprint cannot be determined after an experiment because all trace of the amorphous peak disappears and some fraction of the 3R polytype develops. The initial structural state is evidently modified during the experiments.

The search for local equilibrium liquid-carbide-graphite-Fe phase relations at 1 GPa

Our initial attempt to grow spatially organized, compositionally zoned cohenites with the combinatorial chemistry strategy of diffusion couples met with qualified success. HX-1 run at 1150 °C, a temperature near that of most of the Buono et al. (2013) experiments, did indeed produce a layer of cohenite, but only ~10-25 microns thick. Evidently the absence of S introduced a paucity of liquid to mediate swift growth of crystals. To improve our opportunities to probe larger bands of zoned cohenite, we thought to overcome the slow-growth-kinetics barrier by raising temperature to some of the higher temperatures used by Buono et al. (2013) to grow their cohenites. Temperatures of 1200-1250 °C spectacularly changed the results of the experiments. Much larger cohenites were grown up to 1225 °C, above which temperature they disappeared completely at 1 GPa. Also, the spatial distribution of starting materials relative to products and the compositional organization of the cohenites was fundamentally changed at temperatures of 1200-1250 °C near the graphite-cohenite peritectic which must be between 1225 and 1250 °C at 1 GPa. These changes did little to help us understand the cohenite composition problem, but were informative about the phase relations and possible transport mechanisms operative in these experiments. We report these results and our interpretations below because they bear upon the stability and melting relations of cohenite, which are contentious. [Kopielovich (2011), for example, congruently melts cementite metastably, whereas Dasgupta and Walker (2008) incongruently melt cohenite stably.] But first we digress, and describe our attempt to establish some local equilibrium phase relations in the Fe-C system at 1 GPa, because these will be of some use in framing the interpretation of the higher temperature growth couple experiments. Our growth couple experiments at best reach local interface equilibria and steady state compositional variation, marking transport in progress. It is our immediate goal in this section to understand the equilibria toward which these steady states are evolving.

A new series of experiments was performed at 1062, 1110, 1162 and 1210 °C at 1 GPa using 10 different compositions with 1% increments from 1wt. % to 10 wt. % carbon.

Spectroscopic graphite powder [National Carbon, Grade SP-1, lot 322] was mixed into <10 micron grain size [Alfa-Aesar 99.9+%, lot G15G15] Fe powder. The 1 gram powder batches were mixed, without organic solvent or aggressive grinding, by spatula blending on glazed weighing paper followed by shaking in a glass vial followed by a second cycle of blending and

shaking, after which they were stored in tightly-stoppered glass shell vials until they were loaded into MgO experimental containers. The high purity [Ozark grade HP] semi-sintered MgO sample container was prepared for each multi-charged experiment from 3/8" rod stock. A well for the thermocouple was drilled along the rod axis about 1.5 mm into the rod end. The rod was then cut to 3/4" length to fit the lower inside diameter of a 1.25" long graphite heating tube that was inserted within a 3/4" OD BaCO₃ pressure medium wrapped in Pb foil to fit within a 3/4" WC-lined compound pressure vessel for piston-cylinder pressurization. The sample container was fashioned from the MgO blank with the thermocouple well by drilling from 5 to 7 holes, 3mm deep by 1.5mm diameter, parallel to the cylinder axis but arrayed around the thermocouple well, midway to the graphite heating tube. The resulting 5-7 petal rosette of sample holes arrayed around the thermocouple junction well was filled sequentially with 5-7 batches of sample powder. The first experiment, [HX-24] using 7 petals, displayed ring fractures leading to some apparent paths connecting samples to their neighbors. Little problem of material transfer was detected. However all experiments after HX-24 of this series used only 5-sample arrays, thus avoiding any incipient ring-diking through wider separation of the 5 sample wells. 5 samples in a charge made it possible to cover all 10 compositions at one temperature in just 2 experiments. Once the samples were loaded and inserted into the graphite tube, the upper part of the tube was filled with MgO rod stock with an axial thermocouple duct. The charge and its base plug were inserted in the pressure vessel, the thermocouple inserted, and thereafter the pressurization and heating schedules were the same as for the growth-couple experiment described above. Run durations at the experiment temperature after the sintering step at 1000 °C were 50-100 hours. Termination by quenching was followed by recovery of all 5-7 samples in their rosette array, potting in epoxy, and grinding and polishing for optical, XRD, and microprobe examination. Table 3 gives the experimental conditions and run products for this series of experiments. Figure 12 shows two typical clusters of run products from the highest and lowest temperatures studied. The multiple-sample charges allowed a rapid exploration across Fe-10wt% C composition space in search of the equilibrium assemblages. The fine grain size of the intimately mixed starting materials improved the chances of achieving more than surface equilibria and steady states.

Figure 13 gives an interpretive diagram for local equilibria within the Fe-rich portion of Fe-C that we believe to be relevant to our 1 GPa experiments tabulated in Table 3. Salient features of this phase diagram are that cohenite incongruently melts at a peritectic between

cohenite, graphite, and a more Fe-rich carbide liquid at temperature near but above 1210 °C. The cohenite-Fe eutectic is at a temperature near 1162 °C. This construction given in Figure 13 is consistent with the phase topology adopted by Wood (1993), Dasgupta and Walker (2008), and Lord et al. (2009) although it differs in details of temperatures and solubility curve slopes. The change in relations at 7 GPa is shown in red. The compositional limits of the Fe-alloy, liquid, cohenite, and Eckstrom-Adcock carbide solutions are more restricted in this diagram than the larger ranges reported in Table 1 from growth couple experiments. This restriction of composition in local equilibrium situations is to be expected. The results of our reaction couple experiments in Table 1 are at best steady state, rather than equilibrium to which Figure 13 approximately aspires. The growth experiments have access to more Fe-rich compositions in local surface equilibrium with C-undersaturated Fe alloy. The carbides so grown should be more Fe-rich than the equilibrium compositions. Likewise the growth experiments have access to graphites which are initially out of structural equilibrium and which evolve new polytypes and declining amorphous material. The initial graphites would certainly be expected to feed more C-rich carbides than the equilibrium values. So the growth experiments are expected to show more variation in the carbide compositions grown, which was the point of our strategy. Even so we do establish that the cohenites of Figure 13 and Table 3, which are expected to be more restricted in composition than the growth couples, are not just stoichiometric Fe_3C .

The principle point of contention with other literature, beyond its possible range of composition, is over whether cohenite, or cementite in the metallurgical literature, is metastable and whether it melts congruently. Opinion supporting metastable, congruently-melting cementite, relevant to steel making, can be found in the alternate diagrams given by Chipman (1972) or Kopielovich (2011). The issue of cohenite metastability at ambient pressure devolves back to Darken and Gurry (1951). We show cohenite growth, but not in the presence of saturated Fe and graphite. The bulk compositions make either cohenite with Fe or cohenite with graphite. One reactant or the other disappears in making the cohenite. Even if cohenite is metastable with respect to both saturated reactants, it grows before becoming metastable and in the process removes one of the phases that would render it to be metastable. Unless Fe or graphite can nucleate and grow, cohenite can show a persistent metastable equilibrium with either γFe or graphite, but not both. Our stagnating cohenite growth rates, when both remain present for a long time, and the wrong slopes to the compositional variation across the carbide layers, which

suggests their erosion instead of growth, are in accord with the view that cohenite may indeed still be metastable in the long term.

Local equilibrium basis for growth couple evolution

The growth couple experimental strategy employed can be analysed using the phase diagram in Figure 13A. We emphasize that this is a phase diagram for at most the local equilibria between coexisting phases. The global metastability of cohenite with respect to graphite and C-saturated Fe is ignored. The normal starting conditions are a cylindrical mass of Fe on top of a cylindrical mass of graphite [Fe/C denotes this stratigraphy]. Because there is a small temperature gradient in the charge from the thermocouple downwards through the charge, the Fe is a few degrees hotter than the graphite, their mutual planar interface being essentially isothermal. The green dashed line in Figure 14 gives the starting condition of the charge within the shaded box that shows the temperature and composition limits of the physical starting arrangement. Because the metasomatic reaction proceeds to make cohenite and to increase the C content within the Fe as C gets transported into the Fe, the situation evolves to the red final state of the system. (a) represents the C-bearing metallic Fe assemblage with the worm tracks which extends over some range of temperature within the Fe. (b) represents the isothermal interface between the cohenite and the Fe. (c) represents the cohenite+graphite isothermal interface, with the arrow pointing to the right to graphite which absorbs the remainder of the temperature drop of the assemblage at pure C composition, off-scale to the right. The (b-c) connector represents the small temperature drop and composition change across the cohenite layer. Although graphite usually is $\sim 1/4$ of the charge, and therefore the long-term equilibrium assemblage should be graphite+cohenite, C release and transport to the Fe is not rapid enough for this equilibrium to be achieved and Fe remains in the assemblage locally. C does not have sufficiently rapid access to lead to Fe's expected demise. This situation changes considerably as the temperature of the experiment is raised, as we discovered when trying to improve cohenite growth kinetics by raising temperature. We will consider this further below. In any event, the growth of cohenite at the expense of graphite and Fe, is a clear sign that cohenite is not metastable with respect to Fe and graphite under these conditions before Fe saturation with C is reached.

The importance of the excess C in our usual bulk compositions was demonstrated forcefully to us when we ran experiment HX-22 using 3mm graphite stock below the normal 5mm Fe stock in a piston-cylinder experiment. Was the slow layer growth shown by 3mm graphite stock at 7 GPa also found at 1 GPa? HX-20 had clearly already demonstrated that the growth rate for 3mm graphite stock was indeed slower than 5mm stock at 1 GPa. But one experiment was too few and that one was too short an experiment to distinguish linear from square root of time behavior. Thus the last tiny piece of the 3mm graphite stock that remained was coupled to the normal 5mm Fe stock and run for 139 hours in HX-22. From stock dimensions the bulk composition of HX-22 should have been 3.3 wt % C similar to HX-20. Figure 13 shows that this bulk composition should become Fe and cohenite, without graphite. Indeed no graphite remained. 139 hours were sufficient for the Fe to consume all the graphite and to develop a cohenite-bearing, worm-track-saturated charge. It is a sad experience to realize that your last piece of special graphite stock probably did make carbide like HX-20, and then had it erased by further interactions with the large Fe content of the charge over a long holiday weekend. Although we are therefore no longer able to explore whether that 3mm stock shows square root of time behavior at 1 GPa, we have the consolation that at least the results achieved by waiting too long match the expectations for the bulk composition. Sometimes one might be better content with a steady state.

Consider next the situation of a growth couple in which C is placed on top of Fe which is illustrated in Figure 15. Again the green is the initial condition and red is the final condition. (d) is the isothermal interface between the upper graphite and the cohenite growing beneath it. (e) shows that C penetrating the cohenite layer generated a cohenite+ γ Fe equilibrium at slightly lower temperature than (d). (f) represents the series of C-saturated Fe equilibria, without cohenite, generated to lower temperature as C penetrates the Fe. At each point within the (f) series, the Fe content of C increases to saturation with cohenite. Since it is the cohenite layer at (e) that supplies the C, there is no incentive to increase the C content beyond cohenite saturation and thus to actually grow new cohenite. The series of (f) Fe compositions projecting to lower temperatures become C-poor with depth because the solubility of C drops with temperature. This compositional gradient within the Fe sets up diffusional transport down the saturation gradient. C transported down the gradient brings cooler Fe up to the saturation value without growing cohenite until the physical limit of the bottom of the Fe is reached. Continued C transport on the

solubility gradient then precipitates cohenite with Fe at the bottom of the charge. This second spatial field of cohenite stability at the cold end of the charge is denoted by (g). Figure 16 shows that the expectations of Figure 15 are met in experiment HX-18 which started with C above Fe (C/Fe) in the growth couple, illustrating the usefulness of this analysis for unraveling the confusing relations encountered.

An additional benefit of the analysis of Figure 16 with the framework of Figure 15 is that the distal cohenite at g is predicted to be maximally Fe-rich compared to the cohenites at the graphite end d. Figure 17 and Table 1 show that this expectation is observed. The distal cohenites at g are C-poor compared to the cohenites at d. This inverted growth couple strategy maximizes the compositional and spatial separation of the cohenites grown.

Let us now consider what happens when higher temperature growth-couple experiments are performed. Figure 18 shows the situation relevant to two slightly different ranges at high temperature. Shaded region A shows temperatures near 1250 °C. Initial conditions of graphite over Fe or Fe over graphite are not distinguished because any experiment with graphite in excess of about 10% of the bulk composition will produce the same result no matter what the starting configuration. The reason for this is shown by the thin dashed red line that corresponds to a graphite-saturated liquid grading into an Fe-saturated liquid. Such paired liquids must inevitable be generated from adjacent Fe and graphite stocks at temperature range A. These liquids are not close to each other in composition and so are very corrosive to the adjacent crystalline stocks. As graphite is in excess in our experiments, the Fe is expected to lose the competition and disappear quickly into a liquid that retreats to the composition of graphite saturation as was demonstrated in previous experiments by Dasgupta and Walker (2008) who also showed that those graphite-saturated liquids are more Fe-rich than coexisting cohenites at cohenite's peritectic melting point. As long as the temperature range of the experiment exceeds the cohenite peritectic, no cohenite will be recovered as in region A. The graphite-saturated liquid solubility boundary has a steep positive slope. Thus, if graphite started at the top hot end of the charge, thermal migration would move it to the cold end by diffusive dissolution transfer (Pfann, 1957; Buchwald et al., 1985). If graphite started at the cold end, it would remain there as it converted the overlying Fe into carbide liquid. Thus we do not analyse the different stratigraphic starting configurations separately in A because they produce the same final result. This final result is what is found in

HX-3 seen in Figure 19. [The same result was found in HX-13 which experienced a thermocouple failure 2 weeks into a run and produced an unknown but high temperature in the experiment.]

Now consider the slightly cooler situation shown in Figure 18B where the temperature interval includes cohenite peritectic melting. The phase/temperature topology dictates that graphite should wind up as a layer between liquid and cohenite. HX-4 and HX-6 in Figure 19 show that this expectation is met whether the graphite starts above or below the Fe in the initial stratigraphy. Thermal migration moves an initially too low liquid up (HX-4) and moves an initially too high graphite down (HX-6). These derived stratigraphies rely on the positive-sloped, C-saturated liquid boundary and the negative-sloped, C-saturated cohenite boundary near the peritectic.

The expedient of raising temperature has indeed improved the grain size and layer thickness of the cohenites grown. HX-4 and HX-6 have produced mm scale cohenites that are order of magnitude bigger crystals and thicker layers than found in our series of layer growth experiments at 1162 °C. Perversely this achievement is completely counterproductive to our initial objective of finding and documenting new C-deficient cohenites. The cohenites grown at 1162 °C were arrayed between graphite and Fe or Fe+Fe-rich liquid. They were positioned to take maximum advantage of the metasomatic chemical potential gradients that would promote the most Fe-rich cohenites possible, disposed in a rational spatially resolved manner. Ironically, in the experiments of Figures 18 and 19 at higher temperatures, the huge cohenites grown are in equilibrium with just graphite and therefore in the least favorable position to lead to discovery of Fe-rich cohenite or any organized spatial variation of composition. As a consolation prize we may take comfort from our discovery of a route to synthesis of very large, fixed composition cohenite crystals which may be of some later use for physical property measurements.

Cohenite unit cell parameter variations with composition

The confirmation of the cohenite structure by X-ray diffraction provides an opportunity for examination of unit cell parameter variation with composition. Table 4 presents the refined values for cell parameters for cohenites synthesized for 110 and 118 hours at 1110 °C and 1 GPa

at the compositional extremes of graphite and iron saturation. The cell volume differences between these compositions of cohenite are not large, but they are resolvable. Figure 20 confirms that the graphite-saturated pattern is systematically shifted to lower 2θ and thus has a larger cell volume than the Fe-saturated material.

Figure 21 shows the cell parameters reported by Petch (1944) for cementites annealed at various temperatures in a matrix of Fe alloys. The cell volumes reported are slightly smaller than those we report, which are in turn smaller than one representative cohenite from the literature entered in Table 4 for comparison. It is not known if these absolute differences are meaningful or are an artifact of the various diffraction experiments and refinement techniques employed. Instead we examine the relative differences. The volumes Petch (1944) reports as a function of annealing temperature vary by 0.2%, which is similar to the volume variation of 0.27% we report with compositional change. This similarity suggests that the compositional range encountered in cementite by change of annealing temperature might be of the order of our variations, which are about 3 atomic % carbon, toward more carbon-deficient cohenites at higher temperature. The cementites annealed at high enough temperatures to coexist with γ Fe show systematic cell parameter variations. Those annealed at temperature below 700 °C in the presence of α Fe show little cell parameter change at all. In the high-temperature γ Fe+cementite field, cell volume decreases with temperature. This is not negative thermal expansion because all measurements are made at STP. If this cell volume decrease is compositional, as argued by Petch (1944), our results allow the interpretation that cohenite/cementite becomes more C-rich as annealing temperature with γ Fe falls. [i.e. The cementites become more nearly stoichiometric at lower temperature.] Petch (1944) had no knowledge of the actual Fe/C variations in his cementites because he had only bulk chemical analysis techniques which were compromised for microscopic carbide analysis by the difficulties in separating clean carbide without contaminant native Fe or C. However Petch (1944) argued that carbon vacancies in the solution were the most plausible mechanism for producing the compositional variations. Thus if one supposes carbon vacancies are easier to sustain at high temperature, Petch's argument would converge to the conclusion that cementites should approach stoichiometric at low temperature as their defect population diminishes. Indeed our work shown in Figure 13A above confirms Petch's (1944) proposition that Fe-saturated cohenites become less Fe-rich (less C-poor) as temperature falls.

Petch (1944) presented his cell volume variations as a function of annealing temperature in tabular form, stating that they were small but systematic. Figure 21 shows that there is another distinctive feature to his cell volume variations, upon which he did not comment. As volume of the cell decreases with temperature, so do the *a* and *c* parameters. Remarkably however the *b* parameter expands, contrary to the cell volume decrease. [Petch (1944) actually reported this as the *c* parameter, evidently having adopted the alternate Pbnm setting for space group 62. The literature is divided on the appropriate setting.] This distinctive feature of Petch's cementite unit cell variations with temperature of annealing is also found in our isothermal change of cell parameters with composition. Our larger C-saturated cohenite has, upon refinement, a smaller *b* than the smaller Fe-saturated material. This is consistent with the behavior of the (031) peaks in Figure 20 which show the smallest 2 theta offset because their d-spacing is most heavily influenced by the *b* parameter. Although this sense of smallness is marginally resolvable in our data, it is distinct enough to warrant comment compared to the easily resolved increases in the *a* and *c* parameters. This distinctive feature in the data reflects favorably upon Petch's analysis and its systematics and confirms his conclusion that compositional variations in cohenites are real, even if small. Our microprobe analyses in Table 1 suggest that transient compositional variations achievable during the growth process may be somewhat larger than those that result from strict constraint by metastable Fe+cohenite or graphite+cohenite coexistences, such as explored by Petch (1944) and by this study in Table 3. Under such saturation constraints, only about 10% of the carbon sites need to be vacant to produce the results seen by Petch (1944) and this study.

The curious contraction of the largest unit cell dimension, *b*, as the unit cell expands with increasing C content (through greater *a* and *c* expansion) brings the dimensions of the unit cell parameters of cohenite closer to one another. Conversely the Fe-rich cohenites expected in nature to coexist with Fe alloy in the mantle or the liquid of the core, are the most anisotropic dimensionally. It would be interesting to know what effect, if any, this dimensional change might have on nonstoichiometric cohenite physical and transport properties.

Conclusions

Growth couple experiments confirm that Ni-free cohenites can have both carbon-deficient and carbon excess stoichiometry at modest pressures. The growth of zoned cohenite layers between Fe and graphite at 1110-1162 °C, 1 GPa, show stagnating growth kinetics that are not rate limited by diffusion. The nature of the control is still obscure, possibly being a property of the release rate of C from graphite and of the fading of cohenite into metastability as the Fe alloy saturates with carbon (Darken and Gurry, 1951). The 7 GPa metasomatic layer growth is faster than at 1 GPa and includes an Fe₇C₃ layer between the graphite and Fe₃C, reflecting the known increased stability of this Fe-poor carbide at high pressure. This phase also shows significant departures from the nominally expected stoichiometry. The higher growth rate may reflect the marginal instability of graphite with respect to diamond at 7 GPa, thereby reducing the limits on C-supply-rate from graphite that are suspected of controlling layer growth rates. It may also reflect the suppression of grain boundary channeling which diverts C into Fe rather than into carbide. Effective application of the combinatorial method requires maintenance of spatial organization of charges. In Fe-C this proved to be a temperature-dependent challenge, and might prove to be either more or less challenging in other systems to be evaluated on a case by case basis. It is possible that further detailed combinatorial chemistry analysis will uncover surprises about the range of compositions possible in other compounds of supposedly fixed composition.

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Academic leaders sometimes pile their accomplishments into a remote spire of achievement at which students and colleagues may gaze from below. Illustrious academic leaders stimulate their students and colleagues to build their collective accomplishments into a broad pyramid from which all may gain a vista. We thank Ian Carmichael for providing the second style of leadership. We doubt that the mineral name cohenite ever passed Ian Carmichael's lips, much less did that of the Eckstrom-Adcock carbide. Nevertheless, in return for the stimulations that he provided to us, we dedicate this study of these phases to his memory, in the hope that his broad interests might have been tickled.

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FIGURE CAPTIONS

Figure 1 Composition of coexisting carbide and liquid in experiments of Buono et al. (2013).

Figure 2 Incident light photomosaic of HX-8 run for 148 hours at 1110 °C, 1 GPa. C-rich decorations on the grain boundaries of the Puratronic 5mm Fe, resembling ‘worm tracks’, are thought to be grain boundary routes through which C is introduced into the Fe and across the cohenite layer. There are decreasing temperatures towards the bottom of the charge of perhaps as much as 25 °C from the nominal temperature given by the thermocouple at the top of the charge.

Figure 3A. Incident light photomosaic of HX-11 run for 339 hours at 1162 °C, 1 GPa. The major difference between this experiment and HX-8 shown in Figure 2 is that the cohenite layer has thickened in this longer duration, higher temperature experiment. We return to the nature of this variation in thickness with time below. The worm tracks in the solid Fe have become slightly larger with time, and increased temperature, than they were in HX-8. White box is area of B.

Figure 3B. BSE image of interface region seen in white box of A. The worm tracks are more clearly visible by their chemical contrast with the Fe alloy. Their greater carbon content than the Fe appears darker gray, but not so dark as the cohenite layer which is still more C-rich. Dashed vertical line is trace of microprobe traverse across the cohenite layer and surroundings shown in Figure 4. Figure 3C. BSE of white box in B. Cohenite blades are clearly visible within both the Fe alloy and the worm tracks. The red circled area shows that these cohenite blades extend in optical continuity across the sharp interfaces between the Fe alloy and the carbon-rich material of the worm tracks.

Figure 4 Atomic % C as function of distance from graphite. Profile shown across cohenite layer into γ Fe metal, with lacework of C-rich grain boundaries. Both cohenite and γ Fe are more C-rich away from graphite than near it, a circumstance which is opposite to that expected for metasomatic growth through diffusive transport. Experiment HX-11 at 1162 °C, 1 GPa, for 339 hours.

Figure 5 Incident light photomicrograph above and BSE image below of experiment HX-14 run at 7 GPa, 1162 °C, for 48 hours. Metasomatic layers of two different carbides are present. There are no ‘worm tracks’ indicating that the fast grain boundary transport route has been sealed at

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4 *higher pressure. The growth rates of the carbide layers are substantially faster at 7 GPa than at*
5 *1 GPa, even though C transport was assisted at 1 GPa by the presence of a fast grain boundary*
6 *route.*
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10 *Figure 6 HX-14 microprobe traverse across pair of carbide layers into Fe metal. Experiment at*
11 *1162 °C, 7 GPa, for 48 hours. Traverse follows the dashed line in the BSE shown as lower panel*
12 *of Figure 5. There is little compositional variation within phases.*
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17 *Figure 7 HX-16, two microprobe traverses across a pair of carbide layers into Fe metal.*
18 *Experiment at 1162 °C, 7 GPa, for 149 hours. In the central portion of the Fe-graphite interface*
19 *the thicker carbides have compositional gradients. In the distal edge of this interface, carbides*
20 *are essentially unzoned as in HX-14 in Figure 6, suggesting that on the margins, transport has*
21 *ceased, whereas it is still in progress near the center of the interface.*
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27 *Figure 8 HX-23 Inert marker experiment at 1110 °C, 1 GPa, 150 hours. Upper image reflected*
28 *light photo micrograph in crossed polarizers illumination. Lower image a detail from the upper*
29 *with only the incident illumination polarized. Dotted lines in upper image indicate the thinning*
30 *of the cohenite layer to the left side of the image. The right side of this image is near the center of*
31 *the Fe/C interface where the cohenite is ~150 microns thick. Large single crystals are visible in*
32 *the cohenite illuminated by crossed polarization in the upper image. White circle in upper image*
33 *is enlarged in lower image to show the inert layer convolution in detail.*
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41 *Figure 9A and B Carbide thicknesses grown as a function of the time. Symbols are placed at the*
42 *maximum central carbide thicknesses and the tails on the symbols extend down to the minimum*
43 *thicknesses observed for the distal lateral edges of the layers. [A] shows experiments at 1 GPa at*
44 *two temperatures, 1162 and 1110 °C. The solid (blue) curve for 1162 °C is above the dashed*
45 *(red) curve for 1110 °C, so temperature increases carbide growth rate. [B] shows experiments at*
46 *1162 °C and two pressures. Growth rates at 7 GPa are faster than at 1 GPa even though there*
47 *are no worm tracks present as there are at 1 GPa. Different graphite stock bars make a factor of*
48 *~2 difference in growth rate. The pairs of symbols connected by dotted red vertical lines are two*
49 *materials run in the same experiment to eliminate P or T variations between experiments. The*
50 *5mm graphite stock consistently produces faster carbide growth. Comparison of the 7 GPa rate*
51 *does not depend on which bar of Fe used.*
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Figure 10. Incident illuminated photomicrograph of HX-19, 7 GPa, 1162 °C, 21.5hrs. 5mm graphite grows thicker carbide layers. The carbide on both sides of the Fe is cohenite with a layer of Eckstrom-Adcock carbide (invisible here) between it and graphite. The Eckstrom-Adcock carbide is 29-20 and 22-20 microns thick respectively against 5mm and 3mm graphite. The whole carbide layers composed of the 2 carbides (Σ carbides) is given in the figure as a range (e.g. 113-86 microns against the 5mm graphite stock) which is the variation from the center of the couple to the distal edge. The cohenite thickness in the center is then the difference between 113 and 29 microns, or 84 microns.

Figure 11 HX-15 run at 1 GPa, 1110 °C for 96.5 hours. This experiment did not have a hard ceramic shell and is the only one to show significant departure from a planar interface between Fe and graphite, possibly distorting during the experiment. The cohenite is $\sim 3\times$ thicker than expected for this duration even though it uses the 'slower' 3mm graphite stock. The cohenite is also decidedly ragged rather than being the usual well-formed layer.

Figures 12 A and B Left, center frame in each group shows 5-membered rosette of recovered samples within their 3/8" diameter, sintered MgO sample container. Pt marks a fiducial wire embedded within the sample holder to enable sample recognition after the experiment.

Remaining 5 frames are individual incident light photomicrographs of compositions from 1 wt. % to 7 wt. % carbon. [e.g. c1 = 1% C, c4 = 4% C, etc.]

(A) HX-33 1062 °C C1 is recovered as only Fe alloy, whereas C2-C5 are various mixtures of Fe-alloy and cohenite of constant composition with the cohenite proportion increasing with C content as expected. Note the distribution of cohenite is towards the central thermocouple well and the Fe alloy towards the warmer heater side of the individual sample holes. This suggests thermal migration (Buchwald et al., 1985) is operating on a carbon solubility gradient. Cohenite is known to be less soluble in γ Fe as temperature falls (Chipman, 1972). Thus diffusion within the variable composition alloy moves carbon to the cold end of the temperature gradient and Fe to the hot end where it accumulates as a single phase. Thermal migration requires variable temperature solubility, not that either phase be a liquid. The growth of cohenite and the disappearance of graphite could suggest that cohenite is no longer metastable at 1 GPa as it was at ambient pressure (Darken and Gurry, 1951). Or it could indicate that graphite's rapid consumption in these C-poor compositions, before Fe saturation is

reached, renders the Fe-graphite equilibrium inaccessible. In the absence of graphite it may be difficult to establish the graphite-saturated- γ Fe equilibrium that causes cohenite to be metastable.

(B) **HX-38 1210 °C** C1 is recovered as single-phase solid metal. C2 and C3 show two different iron-cohenite intergrowths. The coarse Fe-rich intergrowth on the cold side is interpreted as the quenching product of a coarse solid phase that grew dendrites of cohenite on quench. The C-rich intergrowth on the hot side is interpreted as a liquid phase that grew a fine grained cohenite-iron intergrowth on quench. C5 and C7 show cohenite and graphite intergrown. C5 also has a region of cohenite-metal intergrowth to the hot side that we interpret as a quenched liquid phase. The graphite in C7 is in the process of compacting to the hot side by the process of thermal migration. This indicates that graphite becomes less soluble in cohenite as temperature increases in this region. It follows that cohenite has a variable composition in coexistence with graphite, and that thermal migration is very sensitive to the small variations.

Figure 12C(a and b) Incident reflected light photomicrographs in partially crossed polarizer illumination of two compositions, C3 and C5, from Figure 12B. Liquid phase on the hot side of the thermal compaction process quenches to very coarse cohenite single crystal meshes, intergrown with microlamellar solid Fe. Detailed insert of the thermal migration boundary in 12C(b) shows that the cohenites in the C5 SOLIDS portion serve as a growth template for the coarse quench cohenite+Fe meshes. The optical continuity of the reflectance variations of the quench cohenites, seen to best effect in the left hand panels of each sub-figure, emphasizes their coarse grain size.

Figure 13 (A) Phase relations for conditions of local equilibrium in black relevant to 1 GPa 5-shooter experiments showing a stable field for cohenite, a range of cohenite compositions that are C-poor but with a wider range of compositions with increasing temperature until peritectic melting of cohenite to graphite plus liquid reduces the extent of cohenite variation to a single composition. Diamonds show the T and at. % C of the 1 GPa experimental phase compositions analyzed by electron microprobe used to constrain the local equilibria between coexisting phases. As explained in the text, cohenite may be metastable with respect to graphite plus C-saturated γ Fe. (B) Shown in red are phase relations shifted to 7 GPa with the introduction of a stability field for the variable composition Eckstrom-Adcock (E-A) carbide. γ Fe saturated with

cohenite becomes C-poor with higher pressure (blue dot→black dash→red solid lines), making cohenite saturation with pressure easier by occurring at lower carbon contents.

Figure 14 Phase relations in Fe-C with dotted (green) path showing the initial condition of our normal 1 GPa growth couple of Fe and C in a small thermal gradient outlined by the blue shaded region. The final conditions of the experiment, terminated before global cohenite+graphite equilibrium prevails from bulk composition considerations, is a sequence of local equilibria, **a**, **b**, and **c**, shown in dashed (red) path, described in the text, at temperatures all within 25-50 °C of the thermocouple temperature, but below it. HX-8 and HX-11 in Figures 2 and 3 are such run products.

Figure 15 Situation analogous to that of Figure 14 except the initial condition puts graphite at the warmer end of the charge, over Fe [C/Fe]. Dotted (green) is initial and dashed (red) is final condition.

Figure 16 Photomosaic of experiment HX-18 for comparison with the expectations of Figure 15. **d**, **e**, **f**, and **g** correspond to the same features in the very different presentations of this figure and Figure 15. The important observable that indicates the utility of the analysis of Figure 15, is that there are two spatially separated fields of cohenite growth, one quite far away from the graphite source of the C. Because the upper cohenite layer in this experiment plots on Figure 9, our conclusion that C transport has little to do with cohenite growth rates is reinforced. If C transport were a limit on growing the upper layer, then it would be difficult to understand how even more cohenite could grow much farther away. Big cohenite crystals (**g**) have grown here with Fe as a ragged 2-phase assemblage rather than as a well-formed layer, far from a distant C source.

Figure 17 Compositional traverse of phases in HX-18. There is a gap of several mm between the graphite and the distal end which is not faithfully represented by the X axis. The cohenites change composition significantly from **d** to **g**.

Figure 18 Phase relations for higher temperature growth couples A and B. Liquids generated at either end of the thin dashed horizontal lines are generated initially from the feedstock Fe and graphite. As they are quite separate in composition, each feedstock aggressively tries to make liquid carbide from the other. Graphite, being in excess in our experiments, wins. Configuration A is above the cohenite peritectic and produces no cohenite, as in HX-3 of Figure 19.

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4 Configuration B produces cohenite below the graphite. Figure 19 gives examples of B from
5 either C/Fe or Fe/C starting stratigraphy: HX-4 and HX-6. If the graphite-saturated cohenite
6 solubility curve were vertical, there would be no incentive for graphite and cohenite to trade
7 stratigraphic places in initial Fe/C experiments which should produce their first cohenite above
8 the graphite. Thermal migration is a very sensitive indicator that cohenite compositions are not
9 fixed.

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16 Figure 19 Reflected light photomosaics of charges from the third section of Table 2 at a range
17 of temperatures above or near the cohenite-graphite peritectic at 1-1.5 GPa. Each field of view
18 is about ¼" from top to bottom. Liquid Fe-C alloy is preserved as a quench intergrowth of Fe
19 and cohenite blades. C/Fe or Fe/C is the starting stock stratigraphy. HX-3 corresponds to Figure
20 18A. HX-4 and HX-6 correspond to Figure 18B with alternate starting stratigraphies both
21 producing the same final stratigraphy. In HX-3, thermal migration has completely transferred
22 the graphite from top to bottom by dissolution and reprecipitation during the experiment. In HX-
23 4, thermal migration has moved the graphite down to the level in contact with the cohenite that
24 grew on the bottom of the charge during the experiment. In HX-6, the cohenite has thermally
25 migrated downward on the negatively-sloped C-saturated cohenite solubility boundary to again
26 achieve the final liquid/graphite/cohenite stratigraphy.

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37 Figure 20 Partial X-ray diffraction pattern for cohenites synthesized at 1 GPa, 1110 °C.
38 The C-saturated material has a slightly larger unit cell as seen by its consistently smaller 2 theta
39 values for diffraction peaks. Peak fitting for refinement and display here is done using the
40 pseudo-Voigt option within the XFIT program. The 2 theta offset for the (031) peak is the
41 smallest, reflecting the larger influence of the **b** parameter size on the position of this peak and
42 the fact that refinement shows that the **b** parameter changes little or grows slightly as the unit
43 cell shrinks with compositional change to less carbon.

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51 Figure 21 Cementite/cohenite unit cell parameters as function of annealing temperature
52 with Fe plotted from data table presented by Petch (1944). Note anticorrelation of **b** parameter
53 variation with temperature compared to unit cell volume and to **a** and **c** parameter variations
54 with temperature.

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4 **TABLE CAPTIONS**
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7 *Table 1 Composition of selected cohenites, Eckstrom-Adcock carbides, and cohenite-saturated*
8 *(+/-liquid) Fe alloy. Note wide range of carbon compositions compared to the values of 25 and*
9 *30 atom % respectively for the stoichiometric carbides. 1 and 7 GPa experiments are for growth*
10 *couples, 6 GPa for partitioning equilibrium with liquid.*
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15 *Table 2 Experimental conditions and products of growth couple experiments.*
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18 *Table 3 Experimental results for attempts to explore local phase coexistences at 1 GPa. x*
19 *denotes phase presence (tr denotes appearance in trace quantities). Numbers in phase columns*
20 *are atomic % C.*
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24 *Table 4 X-ray diffraction results for selected cohenites.*
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Fig 1

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Fig 8

HX-23 details

Fig 9

Fig 10

Fig 11

Fig 12A

(A) HX-33 1 GPa 1062 °C 69 hrs

Fig 12B

(B) HX-38 1 GPa 1210 °C 50.5 hr

Fig 12C

Figure 13 [revised]

Fig 14

Fig 15

Fig 16

Fig 17

Fig 18

Fig 19

Fig 20

Fig 21

Table 1 Selected experimental phase compositions by electron microprobe analysis

Cohenite ('Fe ₃ C')				Atom %			
Expt #	System	GPa	T °C	Fe	Ni	C	sum
TT-716	Fe-Ni-C*	6	1150	71.7	2.1	26.1	99.93
TT-726	Fe-Ni-S-C*	6	1150	70.6	1.4	27.9	99.89
BB-937	Fe-Ni-S-C*	6	1150	75.6	0.7	23.2	99.60
TT-772	Fe-Ni-S-C*	6	1150	80.4	2.4	17.0	99.78
BB-934	Fe-Ni-S-C*	6	1250	80.8	2.5	16.6	99.92
HX-16 †	Fe-C near Fe	7	1162	76.0		22.6	98.61
HX-16 †	Fe-C near E-A	7	1162	72.8		27.6	100.41
HX-14	Fe-C	7	1162	73.8		25.9	99.68
HX-11	Fe-C	1	1162	75.4		23.6	98.97
HX-18 †	Fe-C, top	1	1110	69.0		31.3	100.29
HX-18 †	distal end (g)	1	1110	76.7		22.6	99.30
HX-8 †	Fe-C, center	1	1110	75.1		25.2	100.33
HX-8 †	lateral edge	1	1110	75.2		24.3	99.47
Eckstrom-Adcock Carbide ('Fe₇C₃')							
HX-16 †	Fe-C, graphite	7	1162	65.5		35.8	101.28
HX-16 †	Fe-C, cohenite	7	1162	70.5		29.2	99.70
HX-14	Fe-C	7	1162	68.5		31.1	99.60
Y Fe saturated with cohenite/liq							
HX-16	Fe-C	7	1162	93.1		6.0	99.05
HX-14	Fe-C	7	1162	93.6		6.3	99.86
HX-11	Fe-C	1	1162	88.6		10.1	98.65
HX-18 †	Fe-C top	1	1110	86.7		13.1	99.88
HX-18 †	distal end (g)	1	1110	92.1		7.5	99.60
HX-8 †	Fe-C center	1	1110	89.9		10.2	100.10
HX-8 †	lateral edge	1	1110	91.1		8.2	99.30

* From partitioning experiments of Buono et al. (2013)

† Two entries indicate compositional range found. [See Figures 2, 7, and 16.]

TABLE 2 Experimental conditions and products for growth couples

[illegible]

Table 3	Results for 1 GPa experiments not designed to be growth couples
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Expt #	T °C	hours	Wt % carbon	γ Fe	Liquid	Cohenite	Graphite
HX-38	1210	50.5	c1	5.8±0.9			
HX-38	1210	50.5	c2	8.5±0.4	15.5±0.3		
HX-38	1210	50.5	c3	7.4±1.5	14.9±2.4		
HX-38	1210	50.5	c5		18.7±0.9	24.1±.7	x
HX-38	1210	50.5	c7			25.7±.7	x
HX-28	1162	50	c1	7.4&3.7±0.2			
HX-28	1162	50	c2	8.9±0.3		22.9±0.3	
HX-28	1162	50	c3	9.4±0.6		23.3±0.3	
HX-28	1162	50	c4	?	?	23.0±0.2	
HX-28	1162	50	c5	?	?	22.3±0.1	
HX-29	1162	50	c6	x		23.4±0.3	
HX-29	1162	50	c7			25.2±0.2	tr
HX-29	1162	50	c8			25.5±0.2	x
HX-29	1162	50	c9			25.3±0.2	x
HX-29	1162	50	c10			25.3±0.2	x
HX-25	1110	90	c1	7.1&1.3±0.8			
HX-25	1110	90	c2	8.8±1.7		23.2±0.5	
HX-25	1110	90	c3	x		22.7±0.7	
HX-25	1110	90	c4	6.6±2.5		22.3±0.1	
HX-24	1110	54.5	c4	7.9±1.0		22.7±0.4	
HX-25	1110	90	c5	7.2±1.0		22.4±0.6	
HX-24	1110	54.5	c5	8.8±0.7		23.3±0.4	
HX-24	1110	54.5	c6			24.7±0.7	
HX-24	1110	54.5	c7			25.1±0.2	tr
HX-24	1110	54.5	c8			25.6±0.2	x
HX-24	1110	54.5	c9			25.0±1.4	x
HX-24	1110	54.5	c10			24.1±1.9	x
HX-33	1062	69	c1	3.7±0.2			
HX-33	1062	69	c2	4.8±1.1		24.1±0.4	
HX-33	1062	69	c3	4.7±0.2		24.1±0.3	
HX-33	1062	69	c4	5.3±1.0		25.0±0.7	
HX-33	1062	69	c5	4.1±0.4 (10%)		24.7±0.5	
HX-34	1062	100	c6			25.6±0.2	
HX-34	1062	100	c7			25.5±0.2	tr
HX-34	1062	100	c8			25.5±0.2	x
HX-34	1062	100	c9			25.4±0.3	x
HX-34	1062	100	c10			25.3±0.3	x

x=phase present ##.#±0.# is atomic % carbon, if phase present analysed tr=trace of phase present

Table 4 XRD results for various cohenite compositions

Cohenite cell parameters**, STP	<i>a</i> Å	+/- ⁴	<i>b</i> Å	+/- ⁴	<i>c</i> Å	+/- ⁴	vol Å ³	+/- ⁴
HX-32 ¹ C-saturated	5.0821	0.0016	6.7429	0.0053	4.5152	0.0009	154.73	0.10
HX-39 ² Fe-saturated	5.0739	0.0009	6.7462	0.0045	4.5103	0.0009	154.39	0.09
Petch (1944) annealed 680 °C	5.0785		6.7295		4.5142		154.28	
Petch (1944) annealed 900 °C	5.0735		6.7339		4.5074		153.99	
PDF 00-035-00772 ³	5.091		6.7434		4.526		155.38	

** Refinements of powder patterns collected with Rigaku Microfocus XRD Image Plate system. Scans and integration performed with AreaMax software. Peak fitting with XFIT software. Indexing with CELREF software and cell refinement done with UnitCell software. Pnma (S.G. 62) setting used. Herkimer quartz as standard.

¹ Cohenite grown from 8 wt.% C mix, 1110 °C, 1 GPa, 110 hr [comparable to HX24c8 = 25.6±0.2 at.% C]

² Cohenite grown from 5 wt.% C mix, 1110 °C, 1 GPa, 118 hr [comparable to HX25c5 = 22.3±0.6 at.% C]

³ Powder Diffraction File #035-0772, stoichiometric cohenite, from: Hendricks, S. (1930), *Z. Krist.*, **74**, 534

⁴ Uncertainty at the 95% confidence level.