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Do Fe-Ti-oxide magmas exist? Probably not! *Revision 1 (June 7, 2017)*

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ABSTRACT

Many Fe-Ti oxide bodies associated with anorthosite suites and with some tholeiitic plutonic bodies have cross-cutting relationships with their host rocks suggesting that they may have been emplaced as oxide melts. Pure Fe-Ti oxides melt at temperatures much higher than is considered to be geologically realistic, so various fluxes (mainly apatite, fluorine, or carbon) have been called upon to stabilize the melts down to plausible temperatures. This review traces our experimental attempts to test the effectiveness of proposed fluxes and therefore to demonstrate the existence of such melts at geologically realistic temperatures.

Neither F-apatite nor carbon act to stabilize Ti-rich Fe-Ti oxide melts at 1300ºC and below, and we conclude that - unless some totally unforeseen material does serve as a flux - Fe-Ti oxide magmas almost certainly do not exist. Although our data are not conclusive, it appears that increasing contents of FeO (and possibly TiO_2) and P_2O_5 mutually enhance their solubilities in silicate melts, allowing extensive build-up of those components in melts residual to anorthosite. We interpret that oxide orebodies form by gravitational accumulation of crystalline oxides from such liquids. Once those melts become saturated with either Fe-Ti oxides or apatite, both phases will tend to co-precipitate, thus explaining the common occurrence of apatite with oxide orebodies ("nelsonites". Cross-cutting oxide bodies were probably emplaced as crystalline oxides, possibly lubricated by small amounts of residual silicate liquid. Oxidation of the Fe_2TiO_4 component in initially ulvospinel-rich spinel and concomitant formation of ilmenite grains by granule-oxy-"exsolution" may have weakened the crystalline

oxide and facilitated its flow during emplacement.

It seems clear, though, that the presence of carbon does stabilize *Ti-poor* iron oxide melts to very low temperatures (at and even below 1000ºC), consistent with the (disputed!) magmatic origin of the magnetite lavas at El Laco, Chile.

Keywords: Fe-Ti oxides, oxide melts, oxide magmas, orebodies, immiscible melts, anorthosite suite, apatite, flux.

INTRODUCTION

Large bodies of Fe-Ti oxides (mainly titaniferous magnetite and ilmenite) are important sources of titanium and are also significant reserves of iron (see, for example, Gross, 1996; and especially the comprehensive reviews by Woodruff et al., 2013, and by Charlier et al., 2015). Their almost universal association with Proterozoic massif anorthosites strongly suggests a genetic relation to the anorthositic suite - anorthosites plus spatially- and temporally-associated rocks that go by a wide variety of names, including ferrodiorites (jotunites), syenites and monzodiorites (broadly mangerites), and high-K granites (charnockites). Many of these oxide bodies contain apatite in varying amounts, and the more apatite-rich ones are sometimes called "nelsonites" despite the fact that the type nelsonite is an ilmenite-apatite rock with essentially no magnetite (Watson, 1907, p. 300). It is probably fair to say that most workers today accept that the oxide bodies formed from melts residual to the anorthosites, but there is broad disagreement as to just how they formed and whether the oxides separated and were concentrated as **crystals** or as **immiscible oxide melts.** Some form "conformable layers...within oxide-rich gabbros", but many are "massive ore bodies that exhibit sharp, irregular contacts with surrounding ... anorthosites" (Ashwal, 1993, p. 157). It is the latter, cross-cutting type of occurrence that has led many workers to conclude that the oxides were emplaced as liquids, presumably liquids immiscible with a corresponding silicate melt. Asklund (1949) proposed that the *Ti-poor* oxides at Kiruna formed from an immiscible iron oxide-apatite melt. Buddington et al. (1955) considered the possibility that Fe-Ti oxide deposits may have formed as immiscible oxide liquids, but considered the evidence inconclusive. Perhaps the first worker to propose the

existence of **immiscible** Fe-Ti oxide liquids was Hargraves (1962, p. 175) who stated "Despite the lack of any sound experimental or theoretical foundation, immiscibility between silicate-rich and oxide-rich phases [context suggests this refers to melts] is suggested." Noting that the Allard Lake oxide ores typically contain 8-10 wt % apatite, Hargraves further suggested that significant amounts of apatite component had dissolved in the proposed oxide melt, thereby stabilizing it. Bateman (1951) had earlier suggested the existence of Fe-Ti- rich melts, but he viewed these as simply the residual melts after extensive silicate crystallization (evidently his interpretation of "petrogeny's residua system"), not melts immiscible with coexisting silicate liquids. It may be important here to emphasize that - like the data reviewed and presented here - this paper is mute on the possible importance of *silicate*-liquid immiscibility as a petrologic process. It is restricted to experimental evidence for and against the existence of Fe-Ti oxide melts - which by implication would have coexisted with one or more silicate liquids.

An apparent experimental foundation for the existence of immiscible oxide liquids was provided by Philpotts (1967) who heated a mixture of apatite, magnetite, and diorite in air to 1420 ºC and produced *three* immiscible liquids, one of which contained approximately two parts Fe_3O_4 component to one part apatite component (with a small silicate content as well). That composition is sometimes called the "nelsonite eutectic", and Philpotts' work continues to be cited by those favoring the immiscible-oxide-melt hypothesis despite the fact that this melt contains no TiO_2 (except a minute contribution from the diorite) and the temperature (1420 ºC) is approximately 200-250 ºC higher than modern geothermometry would suggest for the oxide bodies and associated silicate rocks. Possible evidence supporting this "eutectic" was provided by Kolker (1982) who showed that - while there is a wide range - in a number of nelsonites the ratio of modal oxides to apatite is broadly centered around 2:1.

The strongest evidence in favor of immiscible Fe-Ti oxide melts continues to be the clearly cross-cutting, dike-like, relationships between many oxide bodies and the host rocks (usually anorthosite). For example, in the authors' own experience, almost every geologist who has seen those relationships in the Laramie (Wyoming) anorthosite complex (Sybille Pit; Iron Mountain; Shanton deposit) has accepted that the oxides were emplaced as liquids. The only

voiced exception was Lew Ashwal, who argued for emplacement as a crystalline mush (see also Ashwal, 1978). Variations of that latter hypothesis have also been advocated by Emslie (1975), Duchesne (1996; 1999); Dymek and Owens (2002), and Charlier et al (2015).

Detailed mapping in the Laramie anorthosite complex by Eberle (1983) of the Iron Mountain deposit (which occurs within in the Chugwater anorthosite (Lindsley et al., 2010)) and by Bolsover (1986) of the Sybille Pit (which occurs within the Poe Mountain anorthosite (Scoates et al., 2010)) led both of them to conclude that the oxides had been emplaced by downward-intruding Fe-Ti oxide melts. They both also noted the presence of oxide-rich troctolitic rocks in these deposits, and suggested that those rocks might represent the complementary silicate melts from which the proposed immiscible oxide melts separated. Both the oxides and the troctolites contain distinct, but highly variable, amounts of apatite (Bolsover reported 0 to 56 volume % apatite in her samples). Bolsover described an exposure showing oxide-poor troctolite at the top, grading downwards to nearly pure Fe-Ti oxide ore at the base. A xenolith of anorthosite within the troctolite has a layer of nearly pure oxide on its upper surface. The outcrop presented clear evidence of gravity segregation of the denser oxides - regardless of whether they separated as crystals or as immiscible oxide melt. (This beautiful outcrop has sadly been mainly obliterated by "reclamation" of the Sybille Pit in the 1990s).

Oxide mineralogy. The dominant oxide mineral at both Iron Mountain and Sybille is titaniferous magnetite. In a few cases the magnetite host lacks ilmenite lamellae but contains separate (100) lamellae of ulvospinel and of green hercynitic spinel. However, in most samples the magnetite contains lamellae of ilmenite in (111), together with interstitial grains of ilmenite; hercynitic spinel occurs both as individual grains and as (100) lamellae in the magnetite. The ilmenite lamellae were interpreted as having formed by oxy-"exsolution" of ulvospinel component during cooling; there is a possibility that some or even all the separate ilmenite grains had also once been part of the spinel (forming by granule oxy-"exsolution"; Buddington and Lindsley, 1964). Bolsover noted a negative correlation between the relative modal abundance of ilmenite grains and the TiO_2 content of the magnetite, and suggested that the original oxide phase may have been a Fe_2TiO_4-rich spinel (having 5-10% $(Fe,Mg)Al_2O_4$ component), with little or no primary ilmenite present.

Based on the field evidence at Laramie, both Lindsley and Epler started out as definite advocates of the existence of immiscible Fe-Ti oxide melts. This paper, while partly a review, also presents a variety of information - previously unpublished or available only in abstract or thesis form (Epler, 1987; Lindsley and Philipp, 1993; Lindsley, 2003) - that forced our evolution from firm believers to definite skeptics of the immiscible oxide liquid hypothesis. While the arguments presented here are mainly directed at oxide bodies associated with Proterozoic anorthosite suites, they probably are also relevant to other deposits such as the numerous occurrences of Fe-Ti-V oxide ores in the Emeishan Large Igneous Province, China (Chung and Jahn, 1995; Zhou et al., 2002; Bai et al. 2016 and references therein); in the Bushveld complex (e.g., Reynolds, 1985), and possibly to ilmenite-rich occurrences such as Sept-Iles (e.g., Namur et al., 2010)

WEIDNER'S EXPERIMENTS IN THE SYSTEM FE-C-O

Both Eberle and Bolsover reported the presence of graphite in the ore deposits at Laramie; this was considered highly significant in light of some important experiments by Weidner (1982) in the system Fe-C-O. By adding carbon and at modest pressures (0.025 - 0.2 GPa), he was able to produce iron oxide melts below 1000ºC - temperatures hundreds of degrees lower than Philpott's and much more in keeping with temperatures inferred for the natural occurrences. Although Weidner's experiments did not include TiO_2, the temperatures were so low that even if the addition of TiO_2 raised the melting temperature by 100 degrees or so, the existence of Fe-Ti oxide melts in the presence of carbon and at geologically realistic temperatures seemed highly plausible.

EPLER'S EXPERIMENTS ON SAMPLES FROM THE SYBILLE DEPOSIT

In 1984, Epler and Lindsley performed experiments to test whether Fe-**Ti** oxide melts could form at geologically reasonable temperatures (Epler, 1987). Rather than simply adding TiO_2 to Weidner's experiments (in retrospect this might have been a better choice!), we decided

151 to use natural samples from the Sybille Pit. One was Bolsover's sample SCP-113 (hereafter
152 ORT), an oxide-rich troctolite containing titaniferous magnetite with (111) lamellae of ilmenite
153 and blebs of hercynitic spinel, separate ilmenite grains, olivine, and plagioclase, with minor
154 apatite. This sample was suggested by Bolsover (1986) as possibly representative of the
155 composition from which both silicate and Fe-Ti oxide melts had unmixed. The other (here
156 called ORE) was a sample of oxide ore containing ~85 % titaniferous magnetite with (100)
157 lamellae of both ulvospinel and hercynitic spinel and ~15% plagioclase and olivine). Both
158 samples were crushed and then ground in an agate mortar to produce powders with maximum
159 grain sizes of 20-30 microns. A portion of the ORT powder was then reduced at 1040ºC in a
160 CO-CO_2 mixture to produce an fO_2 value "within the fayalite stability field" (Epler, 1987).
161 Both reduced and unreduced ORT powders were used in the experiments. Because phosphate
162 and carbon had been proposed as possible fluxes for oxide melts, Epler added a natural
163 fluorapatite (Durango; Young et al., 1969), synthetic iron phosphate ($Fe_3(P_2O_7)_3$), oxalic acid
164 dihydrate, and/or graphite to many of his experiments.
165
166 **Experimental details.** Epler faced several experimental challenges. Available
167 geobarometry suggested emplacement pressures near 0.3 GPa for the Sybille deposit (e.g.,
168 Fuhrman et al. 1988), but at the time we believed that piston-cylinder experiments could not
169 reliably be conducted below 0.5 GPa, so he chose that pressure for his experiments.
170 Furthermore, we were still using ½" (12.5 mm) Boyd-England (1963) talc/boron nitride cells at
171 that time, and their geometry limited the *outer* diameter of the sample capsule to 2.4 mm.
172 Choice of sample capsule was limited because of the high Fe content of the samples. Silver is
173 essentially immiscible with iron, but its melting temperature is too low to be useful. Iron
174 capsules would have imposed an unrealistically low fO_2. The size constraint precluded use of
175 platinum-jacketed graphite capsules. Epler used platinum capsules, and since pure Pt readily
176 alloys with Fe, he painstakingly "pre-soaked" each capsule with iron (the amount determined by
177 trial and error) so as to minimize Fe loss or gain during the melting experiments (see Chen and
178 Lindsley, 1983). The experiments were carried out at 1060, 1100, 1150, and 1200ºC, a range
179 thought to include the likely temperatures of emplacement, and were quenched by turning off the
180 power to the assembly. As in all piston-cylinder experiments, "quench" is a relative term; Epler

estimated that the samples reached subsolidus temperatures in less than 3 seconds.

Epler's results.

The one experiment on ORT at 1060ºC appeared to be subsolidus, with no evidence for melting of either the silicate or oxide portion. However, the titaniferous magnetite and ilmenite in the starting material did homogenize to a single spinel in that experiment, thereby providing support for Bolsover's suggestion that there may have been only one primary oxide phase in the Sybille rocks. Although the Fe-Ti oxides homogenized, they did not increase significantly in grain size, in contrast to experiments conducted at higher temperatures.

All experiments at 1100ºC and above underwent partial melting, producing silicate melt that quenched to glass in 1100ºC experiments, but formed glass interlaced with feathery Fe-Ti oxide minerals in those performed at higher temperatures. All also produced primary Fe-Ti oxides showing a wide variety of textures, some of which were highly suggestive of having been immiscible droplets. Importantly, there was a significant increase in oxide grain size (2-3x or more) relative to the starting material. The experiments at 1100ºC also yielded primary olivine, which was absent from experiments at higher temperatures. Proportions of phases (Fig. 1) were determined by point-counting.

Textures. Oxide melts are essentially impossible to quench successfully to glass; they inevitably crystallize upon cooling. Therefore one must use indirect evidence - such as textures - to deduce the former existence of oxide melt at the temperature of an experiment. Some typical textures of Epler's experiments are shown in Figs. 2 A-F. Many oxides are at least partly rounded, and some even wrap around vesicles (Fig. 2D). Epler - with the agreement of his advisor - interpreted the oxide textures as indicating the presence of immiscible oxide melt droplets at the temperatures of the experiments. We interpreted the partial euhedral outlines of many grains as the result of quench overgrowth from the surrounding silicate melt during cooling of the experiment; in some experiments (e.g., Fig 2C, F), the scarcity of feathery oxides in the silicate glass immediately adjacent to primary oxide grains supported that hypothesis. We

interpreted the increase in grain size (over that of the starting material) as having resulted from the coalescence of melted oxide droplets, although we could not rule out simple grain ripening of unmelted oxides during the course of the experiment.

Oxide chemistry. Epler was very careful to point out that only the **textures** provided evidence for the formation of immiscible oxide melts in his experiments. If immiscible oxide and silicate melts did coexist, the chemical potentials of all components should have been the same in both melts at the temperatures of the experiment, although the amounts of "lithophile" elements like silica and alkalis in the oxide melts could be small. Compositions of the Fe-Ti oxides (Table 1) provide **no** chemical evidence for melting; the only elements present were those expected for crystalline oxide phases (Fe, Ti, Mg, Mn, Al, O). Even in experiments with added phosphate, there was no detectable P in the quenched oxides, nor was there any evidence for concentration of P and other "lithophile" elements around the perimeter of the oxide grains as might be expected if the oxide melt had successfully purged itself of those elements as it crystallized during quench. Thus if the oxides in Epler's experiments had been immiscible melts, *phosphorus did not serve as an important flux* in forming them. All phosphorus - whether initially present in the rock samples or added as apatite or as ($Fe_3(P_2O_7)_3$) - was concentrated in the silicate melts that coexisted with the oxides (Table 2).

Based on optical microscopy and backscattered electron imaging, the oxide phases appeared to be single-phase spinels. Epler's electron microprobe analyses (which report all Fe as FeO^T since he was unable to analyze directly for oxygen) would be consistent with this interpretation if 10 to 20% of the iron present were ferric iron. Neither Epler nor his advisor were concerned about this apparent fact at the time, but in retrospect it should have raised our suspicions, because it is highly unlikely that an immiscible oxide melt would have spinel stoichiometry. For example, in his study of melting in the FeO-Fe_2O_3-TiO_2 system, Taylor (1963) showed maximum temperatures along the magnetite-ulvospinel join, with lower temperature cotectics on both the higher FeO and higher TiO_2 sides of that join. One would expect that behavior to persist in more complex systems, and while it is statistically possible for an immiscible oxide melt to have spinel stoichiometry, it is extremely unlikely that a series of

melts at different temperatures and from different starting compositions would all do so, an idea that will be revisited later in this review. Epler's M.S thesis was enthusiastically accepted in 1987, and he moved on to other interests.

NEW EXPERIMENTS

While the textural evidence presented by Epler for oxide melts seemed convincing, one of us (DHL) was concerned about the lack of any *chemical* evidence. Why, for example, did the apparent oxide droplets show no detectable phosphorus, especially in the experiments with added apatite or iron phosphate? Were the mainly rounded "droplets" of oxide enclosed in silicate melt immiscible liquids - or simply non-euhedral crystalline oxides? This concern led to a series of new experiments that attempted to resolve this question.

Attempts to prove melting by density difference

DHL repeated some of Epler's experiments on ORE starting material having 5% added carbon, but with several differences. The new experiments used salt/Pyrex pressure cells (rather than talc/BN), and their larger furnace diameter (i.d. 6 mm rather than 3.2 mm) permitted the use of platinum-jacketed graphite capsules. A platinum ball ~ 0.5 mm in diameter was placed near the top of the capsule, but within the powdered sample. Because Pt is approximately 4 times as dense as Fe-Ti oxides, the Pt ball was expected to sink to the bottom of the capsule if the oxides in the sample melted. Experiments were done at 0.5 GPa and 1200ºC (at which temperature Epler reported apparent textural evidence for oxide melts); 1250ºC; 1300ºC; and even 1350ºC. **In no case did the platinum ball drop to the bottom of the capsule**! Unfortunately, while finding the ball at the bottom of the capsule would have been convincing evidence of melting in the sample, failure of the ball to move can only suggest but not prove lack of melting. The uncertainty was thus not resolved by this set of experiments.

Experiments on a different sample

Next came experiments on a natural sample (GM123) from Iron Mountain, Wyoming. It is mainly oxide (titaniferous magnetite, ilmenite, and green spinel) plus olivine; pyroxene and plagioclase are virtually absent(<1% each). As in the Pt-ball experiments, the capsules were platinum-jacketed graphite, which had the advantages of forcing graphite saturation on the sample and eliminating the need to pre-soak Pt capsules with Fe. As with Epler's experiments, the textures were mainly ambiguous, with poorly-quenched silicate glass containing oxide grains that were mainly rounded, but that did show hints of euhedral faces. Once again there was the question: had the oxides been liquid droplets, developing partial faces either upon rapid crystallization during quench or possibly by quench overgrowth from the surrounding silicate melt? Or had they remained unmelted, but for some reason mainly failed to develop euhedral faces during the course of the experiment?

One experiment (GM123-14), though, was especially enlightening. Natural fluorapatite (5.25 wt %) had been added to GM123 powder, so that if carbon, phosphate, or fluorine could flux oxide liquid, there was a good chance of producing an oxide melt. Pressure was 0.5 GPa, and the temperature was 1308ºC - admittedly high in terms of expected natural conditions, but by this stage DHL was desperate to produce an unequivocal Ti- rich oxide melt! The run products were poorly-quenched silicate glass, Fo_{63} olivine, and two oxide phases of distinctly different appearance and grain size. The coarser, dominant oxide phase (40-50 μm) was strongly reminiscent of those in Epler's experiments: partly rounded, partly euhedral, and with ~25 wt% TiO_2. It also had a brownish reflectivity similar to that of Fe_2TiO_4-rich magnetite-ulvospinel solid solutions. The second phase was much smaller (~3-10 μm), lacked the brown tint, and had a higher FeO^T and a much lower TiO_2 content (~3.3 wt. %; Table 3). Its texture was also ambiguous, ranging from rounded to subhedral. But importantly, its contents of SiO_2 (~0.8 wt%) and P_2O_5 (~0.08 wt %), while low, were distinctly higher than in the larger oxide grains. Did it represent a small amount of immiscible (but low-Ti) oxide liquid?! And if so, were the larger oxide grains spinel crystals that had coexisted with both silicate and FeO-rich liquids? Even if the FeO-rich oxide did represent a melt, its low TiO_2 content strongly suggests that such a melt could not be parental to TiO_2-rich oxides in nature. It also seemed possible that it might be a crystalline wüstite phase rather than a melt. Taylor (1964) showed that at 1300ºC

wüstite can coexist with Fe_2TiO_4-rich magnetite-ulvospinel solid solutions at log fO_2 values from ~-8.5 to -10.5 - a range broadly consistent with graphite saturation at 0.5 GPa.

Those questions were partly answered in 1992 when the Stony Brook electron microprobe was equipped with a detector crystal that permitted direct determination of oxygen. Re-analysis of larger oxide grains in GM123-14 showed 2.968 to 3.004 (average 2.992) cations per 4 oxygens - essentially perfect spinel stoichiometry (Table 3)! **This led to the conclusion that they had been crystalline spinels - not immiscible melt droplets - at the temperature of the experiment.** And since Epler's experiments were all performed at lower temperatures and produced similar textures and compositions, it seemed likely that the oxides in his experiments were also crystals rather than immiscible oxide melts, a conclusion further bolstered by the platinum-ball experiments described above. The new measurements on the low-TiO_2 oxide phase gave 0.88 cations per oxygen, slightly lower than the usual range for pure wüstites (0.90-0.95). Because of its relatively high contents of components like SiO_2, TiO_2, and Al_2O_3 (total 4-5 wt. %), it is interpreted as having been a melt rather than a crystalline wüstite phase. And if it was a melt, its low P_2O_5 content (0.08 wt.%) suggests that it was mainly fluxed by carbon rather than by the apatite added to this experiment.

Repeating Weidner's Fe-C-O experiments; adding TiO_2 and then phosphate

Because the only likely melts in our experiments to date were FeO-rich and TiO_2-poor, DHL decided to return to the simple system Fe-C-O, repeating Weidner's (1982) experiments but at 0.5 GPa. The experimental set-up was similar to that for sample GM123 (above). Even in that simple system, the presence of melt has to be inferred from textures, because it quenches to a wüstite-like oxide, never a glass. Weidner described in detail the textural features he interpreted as indicating oxide melt: "the quench liquids are ...vesiculated...and generally possess a meniscus" (1982, p. 559).

Lindsley and Philipp (1993) bracketed the reaction

331 Magnetite + graphite = FeO-rich melt + C-O vapor (1)
332
333 between 1025 and 1050ºC at 0.5 Gpa, in good agreement with Weidner's data at lower pressures.
334 Having convinced ourselves that we could recognize iron-oxide melt in this simple system, we
335 next added TiO_2 by replacing the pure magnetite with ulvospinel$_{20}$-magnetite$_{80}$ leading to the
336 reaction:
337
338 $Usp_{20}Mt_{80}$+ graphite = melt + Mt_{100-X}-Usp_X + C-O vapor (2)
339
340 where the proportion of melt and the value of X both increased with temperature: X ≅31
341 (1075ºC); X ≅37 (1100ºC); and X ≅52 (1150ºC). These samples were not microprobed; the
342 composition of the product spinel was estimated from its XRD patterns. From mass balance, we
343 concluded that the melt probably contained very little TiO_2.
344
345 The next step was to add apatite (or $Fe_3(P_2O_7)_3$) to test whether phosphate might increase
346 the solubility of Ti in the melt. The most informative of this set of experiments was that named
347 Usp70GrAp(4). The starting material was a mixture of 79 wt.% synthetic Usp_{70}-Mt_{30}, 4%
348 graphite, and 17% natural apatite (Durango); this was run at 0.5 GPa, 1250ºC for 19 hours.
349 Products were two oxides (the more abundant one was brownish in reflected light, the less
350 abundant one tended to be bright and interstitial), graphite, and apatite (Fig. 3A). XRD of the
351 product showed ~70 wt. % spinel (~Usp_{77} Mt_{23}); ~28% apatite; ~2% wüstite; plus a small
352 amount of graphite. The increase in the Ti content of the spinel is consistent with the notion
353 that it is mainly the Fe_3O_4 component that is reduced and enters any melt, with the bulk of the
354 spinel remaining crystalline; that melt would quench mainly to wüstite. An alternative
355 possibility is that the Fe_3O_4 component was directly reduced to wüstite, with no melting taking
356 place. However, semi-quantitative energy-dispersive analysis of the interstitial wüstite-like
357 phase shows 95 wt. % FeO^T ; 4% TiO_2; 0.5 % each of CaO and SiO_2, and possibly 0.1 % P_2O_5
358 (although that value must be very close to the detection limit; see Fig. 3B). It appears that the
359 interstitial oxide phase dissolved more Ca than P from the apatite. Its TiO_2 content seems

suspiciously high had that phase never been melted, but the solubility of TiO_2 in crystalline wüstite is not well known (see, for example, MacChesney and Muan, 1961). The SiO_2 content - which appears to be real - is intriguing because the experiment was nominally silica-free! Silica may have been introduced along with the natural apatite (Durango apatite occurs with quartz), or the source may have been the agate mortar used to homogenize the starting mix. Whatever the source, it is tempting to conclude that the trace of silica present was concentrated in the small amount of wüstite-like melt that formed during the experiment.

The presence of two oxide phases - one Ti-rich, the other Ti-poor in the quench products of experiments like GM123-14 and Usp_{70}GrAp(4) places important limits on interpretations of melting. There are three possibilities; the oxides represent: (1) Two immiscible oxide melts; (2) Two crystalline oxides; (3) One melt, one crystalline oxide. Case (1) seems unlikely; far from there being two coexisting melts in the pure Fe-Ti-O system at one atmosphere, there is a distinct **cotectic** between wüstite and the magnetite-ulvospinel join (Taylor, 1964), and there is no reason to suspect that elevated pressure or (relatively minor) addition of other components would so greatly change that behavior. Case (2) is not falsified by the available data - but it would mean that NO oxide melts were produced in these experiments - both of which were at temperatures higher than any of Epler's. That would mean there is **no** experimental evidence for the existence of Fe-Ti-oxide melts at and even above geologically plausible temperatures.

Thus case (3) is probably correct, and if so the much more likely melt candidate is the Ti-poor phase. First, the distinctly more abundant Ti-rich oxide in GM123-14 has spinel stoichiometry (Table 3) (this was later confirmed by microprobe analysis for Usp_{70}GrAp(4) as well, see below), which is most unlikely for a melt. Second, had it been a melt, it would probably have dissolved the rather small proportion of the wüstite-like, low-Ti phase, becoming displaced from the spinel join towards the wüstite-spinel cotectic and thereby losing spinel stoichiometry! Third, the Ti-rich phase has very low contents of "non-spinel" components like silica, P_2O_5, and CaO - components expected to be present in an oxide melt that coexisted stably with a silicate melt. In contrast, the wüstite-like phase departs from probable wüstite composition. It contains 3-4 wt. % of TiO_2, probably greater than the solubility of TiO_2 in

crystalline wüstite (MacChesney and Muan, 1961). Its contents of SiO_2 and P_2O_5, while low, are nevertheless distinctly higher than those in the high-Ti phase. Finally, formation of a wüstite-like melt would be quite compatible with the findings of Weidner (1982) in the Ti-free, but C-bearing system. For all these reasons we conclude that if *any* Fe-oxide-rich melt was produced in all our experiments, it quenched to the relatively minor, low-Ti, FeO-rich wüstite-like phase seen in experiments GM123-14 and Usp_{70}GrAp(4). Such a melt probably would not have formed as a separate phase in Epler's experiments, for it would have been dissolved into the abundant silicate melts present.

New electron microprobe data. Symmes' 1992 analyses of sample GM123-14 show that the high-Ti oxide phase has spinel stoichiometry, and it plots on a temperature maximum (Fig. 4) when projected onto Taylor's melting diagram (1963). While it is therefore unlikely to represent a melt composition, it is possible for an exceptional case to have done so. As a final check, we decided to re-analyze some of Epler's "oxide melts" (as interpreted from textures) for oxygen to determine whether they might also have spinel stoichiometry. Accordingly, we selected samples from a range of temperatures (1100, 1150, and 1200ºC) and starting materials (reduced and unreduced ORT; ORE) among Epler's experiments. We also analyzed sample Usp_{70}GrAp-4 and re-analyzed the Ti-rich phase of GM123-14 as a check. The results (Table 5) are all consistent with the oxide phases being essentially stoichiometric spinels, and as such plot on or near a thermal maximum in the FeO-Fe_2O_3-TiO_2 system (Fig. 5). We consider it most unlikely that they can represent quenched oxide melts - despite the textures we had originally interpreted as indicating melting.

Several things are worth noting. By far the greatest uncertainty in the analyses (Table 4) is in the measurement of oxygen, as shown by the large standard deviations for that element and also for FeO and Fe_2O_3, which are of course calculated using the oxygen values. The re-analysis for oxygen of GM123-14 barely overlaps (at the one-sigma level) with that of 1992 (Table 3; Fig. 4), further illustrating the difficulties in obtaining accurate analyses for oxygen. The results for experiment Usp_{70}GrAp-4 were initially surprising, as the oxide phase plots near $Usp_{70}Mt_{30}$ - essentially unchanged from the composition of the starting oxide (XRD had

suggested that it had changed ~$Usp_{77}Mt_{23}$). But XRD also suggested that the amount of the wüstite-like probable melt phase was only ~2%, and it seems possible that the microprobe analyses concentrated on mainly unreacted cores of zoned crystals, whereas the XRD would be mainly representative of reacted rims. It may be significant that Usp_{70}GrAp-4 is the only one of these experiments that lacked a coexisting silicate-melt phase - possibly those melts facilitated reaction rates in the other experiments.

One reviewer suggested that possibly the duration of our experiments was too short to produce oxide melt, but we consider this unlikely. First, the silicates did melt, and dissolved considerable portions of the oxides in the process. Second, the oxides produced in Epler's experiments **grew** in size (they were at least twice as large as the grains in the starting material) and thus had every opportunity to melt if oxide melt were the stable phase.

IMPLICATIONS

Despite all the efforts described above, we have found no good experimental evidence for the existence of *Ti-rich* Fe-Ti-oxide melts at geologically plausible temperatures. Addition of the fluxes proposed in the literature - apatite (phosphate; possibly fluorine) and carbon - failed to induce melting. Our conclusions are bolstered by the recent work of Wang et al. (2017), who successfully melted a mixture of one-third apatite, two-thirds Fe-Ti oxides at 1450º C and one atm. (thus even higher than Philpott's experiments!), but were unable to melt it at 1200º C and 0.3 GPa, even in the presence a vapor consisting of 8% H20 and 8% F. Thus neither of those volatiles served as a flux. It remains possible that there exists a completely unanticipated flux that stabilizes such melts, but until experimental evidence confirms such a *fluxus ex machina*, we conclude that high-Ti oxide melts do not exist in nature. How then do we explain the dike-like, apparently intrusive Fe-Ti oxide bodies so typical of anorthosite suites? We suggest that the answer lies partly in the *silicate* liquids produced in Epler's experiments (Table 2). Those liquids contain large amounts of normative magnetite and ilmenite, and clearly were in equilibrium with Fe-Ti oxides very similar to those found in nature. Furthermore, their compositions are broadly similar to some members of the anorthosite suite that are variously

called jotunites, ferrodiorites, and oxide-rich ferrodiorites, and that typically cross-cut massif anorthosites and are considered by many to represent magmas residual to the anorthosites themselves (for example, Mitchell, et al., 1996, their Table 2; Scoates et al., 2010, their Fig.16). One striking example is shown in Fig. 6, which compares the compositions of Epler's melt 64T at 1100ºC (see table 2) and that of a monzodiorite dike found near the Sybille Pit oxide deposit in the Laramie Anorthosite Complex (Fuhrman, 1986). We suggest that many of these dikes represent melts that are residual to *both* the anorthositic rocks *and* the associated oxide deposits. Importantly, Epler's experiments show that such melts can exist at plausible temperatures, despite their typically low SiO_2 content.

We must be careful not to over-interpret the significance of the compositions of those melts (since Epler's experiments were only designed to search for oxide melts), but it appears that increasing contents of P_2O_5 lead to increases in the solubility of both FeO^T and TiO_2 in the silicate melts (Table 2). Green and Watson (1982) and Tollari et al. (2006) show that SiO_2 and P_2O_5 vary antithetically in apatite-saturated silicate melts of a variety of compositions. Direct comparisons between their results and Epler's are difficult: while many of the Tollari et al. melts were saturated with Fe-Ti oxides *and* apatite, the experiments were conducted at 1 atm only. In contrast, Green and Watson's apatite-saturated experiments include pressures comparable to Epler's, but few if any were also saturated with Fe-Ti oxides. Only one of Epler's melts was apatite-saturated (64T, 1100ºC), but all coexisted with Fe-Ti oxides. While the underlying mechanisms are unclear, it appears that low SiO_2 contents of silicate melts are commonly associated with unusually high concentrations of FeO^T, TiO_2, and P_2O_5 (partly, of course, this is simply a zero-sum effect, but it appears to be more than that.) Does a lower silica content caused by higher P_2O_5 simply allow greater solubilities of iron and titanium? Do increasing amounts of FeO^T (and perhaps TiO_2) and P_2O_5 mutually enhance their solubilities in silicate melts? That would be intriguing, for it would mean that as a magma became saturated in, say, apatite, it would quickly become saturated in Fe-Ti oxides as well - and *vice versa*. That co-precipitation could help explain why oxide bodies are so often associated with abundant apatite - without any need to invoke a "nelsonite eutectic". Whatever the mechanism, it seems clear that the Fe-Ti oxide bodies formed from *silicate* melts rich in Fe, Ti, and P. Namur et al.

(2012) among others have suggested that Fe-Ti oxide bodies may have formed through fractional crystallization from the more mafic, silica-poor of two immiscible silicate melts. This is certainly possible, since studies of silicate liquid immiscibility show that Fe, Ti, and P are all concentrated in the conjugate melt having lower SiO_2 (for example, Naslund, 1983; Watson, 1976). However, it is not *necessary* to invoke silicate liquid immiscibility; Scoates and Lindsley (2000) and Whitaker et al (2007a,b) have shown that basaltic melts can evolve directly to low-silica residua enriched in Fe, Ti, and P at pressures near 1 GPa. Such pressures are probably high for the *emplacement* of anorthosite suites within the crust, but may well reflect the conditions under which the plagioclase originally accumulated near the crust-mantle boundary, as proposed in the two-stage model for anorthosite genesis (Morse, 1968; Emslie, 1985; Longhi and Ashwal, 1985).

If we accept that Fe-Ti oxide bodies were never liquid, but instead accumulated as crystals from Fe- and Ti-rich silicate melts (probably residual to anorthosites), how do we explain the strong field evidence that the oxide bodies cross-cut older rocks - including in many cases anorthosites themselves? It seems clear that the oxides were mobile in some fashion. We suggest two mechanisms. (1) The oxide cumulate may have been lubricated by a small amount of residual silicate liquid, most or all of which was squeezed out during emplacement. That squeeze-out would be represented by some of the "jotunitic" dikes so commonly associated with anorthosite complexes. (2) In many cases, the original oxide may have been mainly or entirely spinel, as suggested by Bolsover (1986) (and as supported by Epler's experiments (1987)) and by Pang et al. (2008). Yet commonly the oxide bodies also contain varying amounts of ilmenite, both as separate grains and as lamellae within Fe_3O_4-rich spinel. Buddington and Lindsley (1964) suggested that both types of ilmenite can form from oxidation of Fe_2TiO_4 component within the original spinel. At higher temperatures (say, >900ºC) the ilmenite migrates to form separate grains (the granule oxy-"exsolution" of Buddington and Lindsley), and we suggest that the oxide mass will be quite weak during this recrystallization process and able to flow readily. Indeed, deformation during flow may also aid in the separation of the oxide phases. We suggest that these two mechanisms may yield sufficient mobility to permit the oxides to cross-cut the host rocks - presumably intruding downward because of their greater

density (e.g., Saint-Urbain Fe-Ti oxide deposit, Morisset et al., 2010). Till and Moscowitz (2013) summarize available data on the deformation of magnetite. Even though the experiments were on pure Fe_3O_4 and were performed at lower temperatures than seem likely for granule oxy-"exsolution" of ilmenite from Fe-Ti spinel, they do show that magnetite is considerably weaker than plagioclase at a given T. Thus their study bolsters our suggestion that the (mainly crystalline) oxide accumulations were sufficiently weak to flow at high-subsolidus temperatures.

Why, then, do the oxides in many of our experiments show textures (rounded outlines) suggesting they had been melts? One possibility is suggested by silicate melting experiments done in iron capsules. By definition, the melts are saturated with metallic iron, and the melts typically have inclusions of iron. Those inclusions typically are rounded globules, suggesting texturally that they were immiscible droplets of iron melt suspended in the silicate! Yet the iron capsules themselves do not melt, showing that the temperature of the experiment was clearly below the melting point of iron metal. Either the globules had dissolved some unknown and undetectable flux, or they were crystals of iron having rounded surfaces. One experiment conducted by DHL was particularly instructive. It was performed in an incompletely filled iron capsule within an evacuated silica-glass tube, and a meniscus formed at the top of the silicate melt. Metallic iron particles completely within the melt had rounded outlines, while those at the meniscus *were rounded where in contact with the melt but had beautiful euhedral faces where in contact with the (tenuous) vapor phase*! It seems clear that the iron was crystalline but that contact with the melt inhibited formation of euhedral faces, presumably through a surface-energy effect. We suggest that there may have been a similar effect on the oxides in our experiments.

We realize that our experiments do not bear directly on the origin of ilmenite-rich oxide bodies such as those occurring in southeastern Canada, the Adirondacks, and the type nelsonites of Nelson County, Virginia. Those bodies generally have much higher Ti:Fe than those of this study, and their oxygen content is higher (typically the oxides are hemoilmenites with ~ 30% Fe_2O_3). And they are typically associated with andesine (K-rich feldspar in the unique case at Nelson County) rather than labradorite anorthosites, so there are clearly important differences relative to the rocks we have studied. Nevertheless, despite those differences, the

commonalities strongly suggest a broadly similar origin - for example, variations within the general outlines of the two-stage model (Morse, 1968; Emslie, 1985; Longhi and Ashwal, 1985) generally accepted for Proterozoic anorthosites. Explaining those differences is beyond the scope of this study, but one possibility is that the andesine anorthosite kindred may have assimilated more crustal material than have the labradorite anorthosites. For example, Frost et al. (2010) showed that the Snow Creek Anorthosite has assimilated more crustal material and has higher silica activity and fO_2 than the other plutons of the Laramie Anorthosite Complex in Wyoming; the dominant Fe-Ti oxide mineral in the Snow Creek is ilmenite or hemoilmenite, whereas the other anorthosites have mainly spinel. Whatever the reason for the differences, however, there remains no experimental evidence that the ilmenite-rich bodies were ever oxide melts.

Our experiments do support Weidner's finding (1982) that the presence of carbon greatly increases the stability of *Ti-poor* iron oxide melts - down into the "geologically plausible" range. If the Ti-poor "magnetite lava flows" at El Laco, Chile (Park, 1961; Naslund et al. 2002) , actually formed from an iron oxide magma (and this interpretation is hotly debated), the effects of carbon surely help provide an explanation for the existence of such melts - if not for the actual mechanism by which they have formed. Likewise, the Ti-poor "high iron melts" reported by Hurai et al. (1998) could also have been stabilized by carbon; those authors report abundant CO_2, both as bubbles in inclusions and dissolved in accompanying glass. However, if the two high-Ti (24% SiO_2, 43.9% TiO_2, and only 10.6 % FeO^T) globules reported by Hurai et al. were really melts, they are clearly something very new and unusual and deserve further study.

Perhaps the strongest evidence to date for the possible existence of very low-Si and Fe-Ti-rich melts comes from Kamenetsky et al. (2013), who reported droplets of silica-rich melt coexisting with droplets of silica-poor melt (SiO_2, 15–46; FeO, 15–22; TiO_2, 2–7; CaO, 11–27; P_2O_5, 5–30; wt. %) in a Siberian trap. However, these unusual compositions are most likely an anomaly, as they occur as millimeter-sized inclusions formed *within metallic iron droplets* where the trap encountered a coal seam, and thus at many orders of magnitude lower in fO_2 than for the rocks being considered here.

One of our reviewers noted that we had not considered the possible effect of water as a flux to stabilize Fe-Ti oxide melts, citing the work of Lester et al. (2013), who reported forming an immiscible melt having 72.8% FeO^T and only 7.14% SiO_2 at 1075ºC in the presence of a water-rich vapor. But that melt contains 16.6% sulfur, and *no* TiO_2, and thus is very different from the materials being considered here. Furthermore, there is compelling evidence that the orebodies and anorthosites in the Laramie Anorthosite Complex, at least, were strikingly dry. For the Sybille Pit, for example, Bolsover (1986) reported typically 0-3% "secondaries" that include biotite (Ti-rich and thus likely to be H_2O-poor), amphibole, and prehnite, even in samples that contain up to 35% silicates. But perhaps the most compelling argument for very dry conditions within the LAC is the first author's observation that, where water-rich granitic dikes cut the anorthositic rocks, those rocks are extensively altered for a distance of up to *ten times* the dike's thickness on either side: the dark gray to black plagioclase is bleached white, and the ferromagnesian minerals are largely converted to dark-green amphibole! Quite clearly the anorthositic rocks had seen very little water prior to intrusion of the granitic dike. The presence of graphite within the LAC orebodies (Eberle, 1983; Bolsover, 1985; Epler, 1987) and abundant "plumbago" deposits within and surrounding the LAC strongly suggests that any vapor originally present was rich in C-O rather than H_2O.

CONCLUSIONS

1. At present there is no plausible experimental evidence for the existence of Ti-rich Fe-Ti oxide melts at geologically reasonable temperatures. Neither apatite nor carbon are effective fluxes, although both have been proposed as the way such liquids could be stabilized. We conclude that cross-cutting oxide "dikes" were probably emplaced in the solid state, possibly lubricated by small amounts of residual silicate melt, and by recrystallization accompanying granule oxy-"exsolution" of ilmenite from Fe_2TiO_4-rich spinel.

2. Although our experimental data are not conclusive, we suggest that increasing contents of P_2O_5 and FeO (and possibly TiO_2) mutually enhance their solubility in *silicate* melts, allowing

those components to build up in melts residual to anorthosites. Once those melts become saturated with either apatite or a Fe-Ti oxide phase, the other phase will also crystallize, thereby explaining why varying amounts of apatite typically accompany Fe-Ti oxide orebodies.

3. We suggest that at least some of the "jotunitic" (low-Si, high-Fe and Ti) dikes associated with anorthosite suites may be doubly residual: residual first to nearby anorthosite, and second following the gravitational separation of crystalline Fe-Ti oxides that accumulated into the distinctive oxide bodies typically associated with anorthosites. Epler's experiments produced silicate liquids (similar in composition to many of those dikes) at temperatures as low as 1100ºC.

4. We have great admiration and affection for Tony Philpotts, but we respectfully suggest that it is past time for workers to stop referring to his 1967 experiments - with their unreasonably high temperatures and near-absence of titanium - as evidence for the existence of Fe-Ti oxide magmas in nature. They simply are not!

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Figure Captions

Fig. 1. Proportions (volume percent) of phases produced in Epler's melting experiments on ORT starting material (oxide-rich troctolite; Bolsover's sample SCP113). "T" indicates unreduced starting material; "TR" indicates starting material reduced at 1040ºC and at fO_2 "within the fayalite stability field". Components added: C, 4 wt. % synthetic carbon; "FeP", 5 wt. % ($Fe_3(P_2O_7)_3$); "Ap" 7 wt. % natural apatite from Durango, Mexico. Numerals correlate with experiments listed in Table 1.

Fig. 2. Photomicrographs (reflected light) of Epler's experimental products (all at 0.5 GPa). A, Experiment 25T (unreduced ORT, 1200ºC, 21.7 hours; 4 wt. % each of C and ($Fe_3(P_2O_7)_3$) added), showing typically ambiguous textures. Primary oxides (light) have both very rounded and euhedral boundaries with quenched silicate melt (medium gray with feathery quench oxides. We originally interpreted the textures to mean the oxides had been melts and that some euhedral faces formed during quench, both by rapid crystallization of the primary oxide and by

870 overgrowth of oxide components from the surrounding silicate melt. Dark gray, vesicles. B,
871 Experiment 61T (ORE with added oxalic acid, 1200ºC, duration not known). C, Experiment
872 38T (unreduced ORT, 1150ºC, 65.9 hours; 7 wt. % apatite added. Oxides (light gray) have
873 both euhedral and rounded outlines; darker material, silicate glass with abundant feathery quench
874 oxides; black, vesicles. D, Experiment 58D (ORE starting material at 1200ºC, 65.8 hours, no
875 added components). Both oxide grains (white) and poorly quenched silicate glass (darker with
876 feathery quench oxides) conform to the shape of the central vesicle. Both Epler and his advisor
877 considered this texture to be strong proof that the oxides were immiscible melts at the
878 temperature of the experiment. E, Experiment 56D (ORE starting material at 1200ºC, 4 wt. % C
879 added; water may have diffused into the charge from intentionally undried furnace parts).
880 Oxides (white) have ameboid outlines highly suggestive of melting. Darker gray is silicate
881 glass with quench oxides. F, enlargement of E, showing that quench oxides in interstitial
882 silicate glass are concentrated away from the primary oxides (large, white). Boundaries of the
883 primary oxides are uneven, suggesting that oxide components from the adjacent melt nucleated
884 on the primary oxides during quench. Scale bars are 50 μm.
885 Fig. 3. Results for experiment Usp_{70}GrAp(4) (1250ºC, 0.5 Gpa, 19 hours; see text). (A)
886 Backscattered electron image of polished surface. Very light gray, Fe-rich, Ti-poor oxide - now
887 mainly wüstite, but suspected of having been oxide melt (M); slightly darker gray, Ti-rich oxide,
888 believed to have been crystalline spinel (Sp); medium gray, apatite (Ap); black, graphite (Gr).
889 Accelerating voltage 20 kV. (B) energy-dispersive X-ray spectrum of suspected oxide melt
890 pocket shown by small square in (A). Any F present (possibly contributed by the fluorapatite)
891 is unfortunately masked by the Fe Lα peak near 0.7 keV.
892
893 Fig. 4. Liquidus (melting) diagram for oxides in the system FeO-Fe_2O_3-TiO_2 at one atm.
894 (modified from Taylor, 1964). Heavy dash-double-dot line shows compositional range of
895 stoichiometric spinels (magnetite-ulvospinel join) - a thermal maximum. Dash-single-dot line
896 shows the extent of the wüstite field at the liquidus (Darken and Gurry, 1946). Temperatures
897 drop off to cotectics (spinel-wüstite; spinel-rhombohedral phase) on either side of the spinel join.
898 GM123-14 High Ti, the Ti-rich oxide produced from an olivine-oxide rock from Iron Mountain,
899 Wyoming + 2% graphite + 5% apatite, 1308º C (see text for details). GM123-14 Low Ti is

interpreted as representing a likely oxide melt. Analyses (Table 3) by G. Symmes, Stony Brook microprobe in 1992. Size of symbols represents average of multiple analyses ± one standard deviation. Projection scheme: "FeO" = FeO + MnO + MgO + CaO; "Fe_2O_3" = Fe_2O_3 + Al_2O_3 + trace P_2O_5; "TiO_2" = TiO_2 + SiO_2 , all combined in *molar* proportions and then recalculated to *equivalent weight* percentages of FeO, Fe_2O_3, and TiO_2 to be compatible with Taylor's diagram.

Fig. 5. Enlargement of FeO-rich region of Fig. 4, showing projected compositions of oxides produced in attempted melting experiments, all at 5 GPa. Key: 54, 54T - oxide-rich troctolite (ORT; see Table 2) + 4% graphite, 1150º C. 37, 37TR - reduced ORT +7% apatite, 1150º C. 38, 38T, ORT + 7% apatite, 1150º C. 39, 39T - ORT + 5% "FeP", 1150º C. 61, ORE (see Table 2) with oxalic acid, 1200º C. 45, 45T - ORT + 5% "FeP", 1100º C. 64, 64T - ORT + 7% apatite, 1100º C (all re-analyzed from Epler, 1987). U_{70} - synthetic $Usp_{70}Mt_{30}$GrAp-4, 1250º C (see text for details). $Usp_{50}Mt_{50}$ is a synthetic spinel used as a working standard for the analyses. All Ti-rich samples are consistent with representing single-phase spinels, not melts. All analyses include direct measurement of oxygen, and size of symbols represents average of multiple analyses ± one standard deviation. GM123-14 (1992) and GM123-14 Low Ti, from Fig. 4; all others measured in 2016 at the American Museum of Natural History. Full analyses are given in Table 3 and Table 4. See caption for Fig. 4 for projection scheme.

Fig. 6. Log-log plot comparing compositions of Epler's silicate melt 64T (ORT with 7 wt. % apatite added; 1100ºC, 0.5 GPa, 70.5 hours; see Table 2) and a monzodiorite dike close to the Sybille Pit oxide deposit, Laramie Anorthosite Complex (Table 1-7, p. 66, Fuhrman, 1986). Units in wt %. Diagonal line shows 1:1 correspondence.

Table 1. Compositions of Fe-Ti oxides in Epler's experiments - interpreted by him as being quenched melts immiscible with the silicate melts in Table 2.

Table 2. Compositions of starting bulk composition and of silicate melts produced in Epler's experiments.

Table 3. Compositions of silicate melt and oxide phases in experiment GM123-14

930 Table 4. Compositions of several Fe-Ti oxides (initially interpreted as quenched melts) in
931 several experiments. All Ti-rich compositions approach spinel stoichiometry (3
932 cations/4 oxygens.)

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Table 1. Electron microprobe analyses of oxide phases in Epler's experiments (Epler, 1987, Tables 5-7)

Sample	42T	43T	47TR	48T	45T	64T	54T	39T	38T
Added comp.	none	none	none	4% C	5% "FeP"	7% Ap	4% C	5% "FeP"	7% Ap
Temp ^{o}C	1100	1100	1100	1100	1100	1100	1150	1150	1150
Duration (hrs.)	47.4	95.3	69.3	70.3	89.7	70.5	72.6	68.3	69.5
Wt %									
TiO_2	22.30	21.10	25.90	25.40	22.60	22.70	29.90	27.00	28.40
Al_2O_3	5.42	5.10	6.41	6.74	5.22	5.62	5.51	5.41	5.13
FeO^T	67.20	67.40	63.30	63.40	67.50	66.50	58.00	62.10	61.40
MgO	3.02	3.54	2.54	2.52	3.11	3.10	4.21	3.24	3.42
Total	97.94	97.14	98.15	98.06	98.43	97.92	97.62	97.75	98.35

Notes: ORT, Bolsover's oxide-rich troctolite SCP-113. xxT indicates experiments on unreduced ORT sta
reduced at 1040^{o}C and at fO_2 "within the fayalite stability field". FeO^T, total iron expresse
Added components are: C, synthetic graphite. "FeP", synthetic $Fe_4(P_2O_7)_3$. Ap, fluorapati
Si and P were searched for by energy-dispersive analysis and X-ray imaging, but not dete

37TR	20TR	22T	21TR	25T	24TR	36TR
7% Ap	none	4% C	4% C	4% C; 5% "FeP"	5% "FeP"	7% Ap
1150	1200	1200	1200	1200	1200	1200
70.2	26	27	21.8	21.7	30.6	47.2
29.00	26.70	27.20	29.00	29.10	29.10	29.20
5.61	6.32	6.84	6.34	7.50	6.01	5.63
60.30	60.50	59.40	58.30	61.20	58.90	57.60
3.83	4.03	4.04	4.24	3.73	3.60	5.81
98.74	97.55	97.48	97.88	101.53	97.61	98.24

rting material. xxTR indicates experiments on ORT that had been
d as FeO.

te from Durango, Mexico.

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Table 2. Electron microprobe analyses of bulk rock and silicate melts[a] in Epler's experiments using ORT starting

Sample	SCP113	42T	43T	47TR	48T	45T	64T	54T	39T	38T
Added comp.	"LiB"[b]	none	none	none	4% C	5% "FeP"	7% Ap	4% C	5% "FeP"	7% Ap
Temp °C	1050	1100	1100	1100	1100	1100	1100	1150	1150	1150
Duration (hrs.)	0.5	47.4	95.3	69.3	70.3	89.7	70.5	72.6	68.3	69.5
Wt %										
SiO_2	21.90	42.80	43.70	41.10	39.50	35.70	36.50	32.40	29.70	25.00
TiO_2	14.00	4.04	4.43	3.30	3.56	4.30	4.17	7.79	6.21	8.56
Al_2O_3	8.65	11.87	11.90	13.00	12.00	9.75	9.98	10.40	8.79	8.74
FeO^T	41.90	23.60	21.30	25.30	27.80	27.70	26.20	32.70	35.30	32.70
MnO	0.40	0.31	0.31	0.32	0.37	0.36	0.33	0.33	0.33	0.31
MgO	5.28	3.47	4.12	2.98	3.11	5.20	4.60	5.51	5.16	4.68
CaO	3.02	7.26	7.20	7.74	7.59	5.56	10.50	4.86	4.64	9.41
Na_2O	1.31	2.17	2.44	2.79	2.47	1.94	2.05	1.80	1.77	1.34
K_2O	0.24	0.60	0.61	0.59	0.49	0.44	0.47	0.39	0.35	0.27
P_2O_5	0.42	0.94	0.98	0.99	0.78	5.64	3.78	0.64	4.83	4.38
Total	97.00	97.06	96.99	98.11	97.67	96.59	98.58	96.82	97.08	95.39

Notes: ORT, Bolsover's oxide-rich troctolite SCP-113. xxT indicates experiments on unreduced ORT starting m
reduced at 1040°C and at fO_2 "within the fayalite stability field". "LiB", 50% lithium metaborate ac
omits Li, B. C, synthetic graphite. "FeP", synthetic $Fe_4(P_2O_7)_3$. Ap, fluorapatite from Durango, M

[a]Melts produced at 1150 and 1200°C quenched to fine-grained intergrowths of silicate glass plus feathery quenc
in an attempt to obtain representative melt compositions.

[b]Normalized to 97% to facilitate comparison to other analyses.

[c]Evidently Na and K were lost during either the experiment or the analysis.

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g material (Epler, 1987, Tables 3-4)

37TR 7% Ap	20TR none	22T 4% C	21TR 4% C	25T 4% C; 5% "FeP"	24TR 5% "FeP"	36TR[c] 7% Ap
1150	1200	1200	1200	1200	1200	1200
70.2	26	27	21.8	21.7	30.6	47.2
27.10	31.30	30.80	31.30	26.10	26.20	20.00
7.63	8.64	7.03	8.89	10.40	9.51	13.20
8.74	11.80	8.88	10.00	9.43	9.38	11.60
31.20	35.20	37.20	35.50	36.70	38.20	32.10
0.33	0.37	0.37	0.39	0.36	0.41	0.34
4.56	4.97	5.29	5.23	4.88	5.15	4.45
10.30	4.30	4.42	4.71	3.87	4.08	7.37
1.27	1.29	1.78	1.71	1.34	1.61	0.94
0.34	0.30	0.37	0.39	0.30	0.32	0.22
4.91	0.54	0.63	0.63	3.52	2.78	3.59
96.38	98.71	96.77	98.75	96.90	97.64	93.81

aterial. xxTR indicates experiments on ORT that had been
dded as a flux to make a glass; reported bulk rock analysis
Mexico. FeO^T, total iron expressed as FeO.
ch-formed oxides. Analyses used an enlarged beam

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Table 3 Analyses of Experiment GM123-14 (0.5 GPa, 1308°C, 24 hours)

	Wyo(1990)[a]		Wyo(1990)[a]		SB (1992)[c]		AMNH (2016)[e]	
	Silicate melt		**Large Oxides**		**Large Oxides**		**Large Oxides**	
Wt. %	Avg of 2	Std Dev	Avg of 6	Std Dev	Avg of 9	Std Dev	Avg of 20	Std Dev
SiO_2	30.161	0.211	0.20	0.10	0.15	0.01	0.15	0.02
TiO_2	1.035	0.005	24.95	0.35	25.31	0.08	25.36	0.25
Al_2O_3	0.375	0.041	3.85	0.08	3.78	0.03	3.82	0.04
Fe_2O_3					19.12	1.24	16.27	1.58
FeO					43.29	1.20	45.97	1.58
FeO^T	44.114	0.203	60.03	0.30	(60.49)		(60.60)	
MnO	0.185	0.262	0.45	0.07	0.31	0.04	0.35	0.03
MgO	19.285	0.556	7.06	0.20	7.03	0.04	7.18	0.07
CaO	n.a.		n.a.		n.a.		0.08	0.02
P_2O_5	3.544	0.018	0.03	0.06	0.01	0.01	0.01	0.01
Tot	98.697	0.681	96.56	0.40	98.98	0.23	99.19	0.31
At. Fract.								
Si	0.1278	0.0003	0.0011	0.0005	0.0007	0.0001	0.0007	0.0001
Ti	0.0033	0.0000	0.0984	0.0010	0.0959	0.0003	0.0960	0.0007
Al	0.0019	0.0002	0.0239	0.0004	0.0224	0.0003	0.0227	0.0003
Fe^T	0.1563	0.0007	0.2636	0.0022	0.2548	0.0010	0.2553	0.0015
Mn	0.0007	0.0009	0.0020	0.0003	0.0013	0.0002	0.0015	0.0001
Mg	0.1218	0.0024	0.0553	0.0014	0.0528	0.0003	0.0539	0.0005
CaO	n.a.		n.a.		n.a.		0.0004	0.0001
P	0.0127	0.0000	0.0002	0.0003	0.0000	0.0001	0.0000	0.0000
O	[b]0.5756	0.0002	[b]0.5560	0.0003	[d]0.5720	0.0012	[d]0.5694	0.0140
Tot	1.0000		1.0001		1.0000		0.9999	
			Cats/4 Oxy		Cats/4 Oxy		Cats/4 Oxy	
Si			0.0076	0.0037	0.0051	0.0005	0.0052	0.0006
Ti			0.7083	0.0069	0.6704	0.0024	0.6747	0.0053
Al			0.0239	0.0004	0.1567	0.0024	0.1594	0.0021
Fe^{3+}					0.5066	0.0302	0.4317	0.0404
Fe^{2+}			b1.8967	0.0162	1.2754	0.0392	1.3615	0.0521
Mn			0.0144	0.0022	0.0092	0.0012	0.0104	0.0007
Mg			0.3976	0.0101	0.3689	0.0028	0.3787	0.0038
Ca			n.a.		n.a.		0.0300	0.0008
P			0.0012	0.0020	0.0003	0.0004	0.0003	0.0003
Tot Cations			3.1975	0.0035	2.9925	0.0138	3.0249	0.0171

Starting material: 92.6 wt % GM123 (an oxide-olivine rock with minor pyroxene and plagioclase from Iron Mount
2.1% graphite, 5.3 % Durango apatite. n.a. not analyzed for.

[a]Analyses by Susan Swapp, University of Wyoming electron microprobe

[b]Oxygen by stoichiometry, assuming all Fe^{2+}

[c]Analyses by Gregory Symmes, Stony Brook electron microprobe

[d]Oxygen determined directly

[e]Analyses by A. Fiege and D. H. Lindsley, American Museum of Natural History electron microprobe

SB (1992)[c]	
'"Low-Ti" Oxides	
Avg of 2	Std Dev
0.80	0.11
3.29	0.08
0.67	0.02
19.34	0.87
74.06	1.48
(91.46)	
0.21	0.03
1.69	0.31
n.a.	
0.08	0.04
100.14	0.44
0.0045	0.0006
0.0139	0.0003
0.0044	0.0001
0.4305	0.0025
0.0010	0.0001
0.0142	0.0026
n.a.	
0.0004	0.0002
[d]0.5310	0.0006
1.0000	
Cats/1 Oxy	
0.0085	0.0011
0.0262	0.0006
0.0083	0.0002
0.1542	0.0071
0.6564	0.0128
0.0019	0.0002
0.0267	0.0049
n.a.	
0.0005	0.0007
0.8827	0.0022

tain, Wyoming) plus

Table 4. Summary of electron microprobe andalyses of Fe-Ti oxides, Oct. 2016. Oxygen measured directly

Sample	45T	64T	54T	39T	38T	37TR
Added Comp.	5% "FeP"	7% Ap	4% C	5% "FeP"	7% Ap	7% Ap
P, GPa	0.5	0.5	0.5	0.5	0.5	0.5
Temp ^{o}C	1100	1100	1150	1150	1150	1150
Duration (hrs.)	89.7	70.5	72.6	68.3	69.5	70.2
Wt. %	**Avg . of 20**	**Avg. of 18**	**Avg. of 21**	**Avg. of 19**	**Avg. of 20**	**Avg. of 20**
SiO_2	0.15(5)	0.14(3)	0.09(5)	0.08(2)	0.06(1)	0.07(1)
TiO_2	22.37(25)	22.22(29)	29.647(33)	26.76(21)	28.25(29)	28.92(22)
Al_2O_3	4.95(4)	5.28(4)	5.21(5)	5.11(6)	4.94(5)	5.21(4)
Fe_2O_3	19.06(1.20)	23.68(1.77)	5.20(2.20)	14.17(2.09)	10.36(1.90)	5.93(3.00)
FeO	48.36(1.30)	44.10(1.77)	52.95(2.08)	49.34(1.85)	50.99(1.83)	54.41(2.84)
MnO	0.31(2)	0.32(2)	0.37(3)	0.29(2)	0.33(3)	0.34(3)
MgO	3.17(6)	3.16(4)	4.41(5)	3.28(5)	3.63(4)	3.67(5)
CaO	0.07(2)	0.13(4)	0.05(2)	0.04(1)	0.04(2)	0.09(3)
P_2O_5	0.04(2)	0.02(1)	0.00(1)	0.02(1)	0.01(1)	0.01(1)
Tot	98.48(29)	99.04(49)	98.63(45)	99.10(35)	98.61(33)	98.64(29)
Atomic Fraction						
Si	0.0007(2)	0.0007(2)	0.0005(2)	0.0005(1)	0.0003(1)	0.0004(1)
Ti	0.0877(8)	0.0861(9)	0.1141(9)	0.1034(8)	0.1095(9)	0.1121(9)
Al	0.0304(3)	0.0320(2)	0.0314(3)	0.0309(4)	0.0300(3)	0.0316(3)
Fe^{T}	0.2856(15)	0.2818(12)	0.2494(16)	0.2668(10)	0.2599(15)	0.2575(19)
Mn	0.0014(1)	0.0014(1)	0.0016(1)	0.0013(1)	0.0014(1)	0.0015(1)
Mg	0.0247(5)	0.0243(3)	0.0336(4)	0.0252(4)	0.0279(3)	0.0282(4)
CaO	0.0004(1)	0.0007(2)	0.0002(1)	0.0002(1)	0.0002(1)	0.0005(1)
P	0.0002(1)	0.0001(0)	0.0000(0)	0.0001(0)	0.0000(0)	0.0001(0)
O	0.5720(13)	0.5759(15)	0.5724(20)	0.5749(16)	0.5740(17)	0.5714(26)
Cats/4 Oxygens						
Si	0.005(1)	0.005(1)	0.003(2)	0.003(1)	0.002(0)	0.003(0)
Ti	0.613(5)	0.598(7)	0.797(7)	0.719(7)	0.763(7)	0.785(9)
Al	0.213(2)	0.222(2)	0.220(3)	0.215(3)	0.209(3)	0.221(3)
Fe^{T}	1.997(15)	1.958(13)	1.743(17)	1.856(11)	1.811(15)	1.803(22)
Mn	0.010(1)	0.010(1)	0.011(1)	0.009(1)	0.010(1)	0.010(1)
Mg	0.172(4)	0.169(2)	0.235(3)	0.175(3)	0.195(3)	0.197(3)
Ca	0.003(1)	0.005(2)	0.002(1)	0.001(1)	0.002(0)	0.003(1)
P	0.001(0)	0.001(0)	0.000(0)	0.000(0)	0.000(0)	0.000(0)
Tot Cations	3.014(16)	2.967(18)	3.012(24)	2.980(19)	2.992(20)	3.023(32)

Analyses by A. Fiege and D. H. Lindsley, American Museum of Natural History. Oxygen determined directly.
Standards: Fe, Ti, O: Synthetic $Usp_{50}Mt_{50}$; Mg, Si, Ca: diopside; Al: orthoclase; P; berlinite. Numbers in () sh
Detection limits (ppm): O, 2700; Mg, 260; Al, 290; Si, 220; P, 170; Ca, 160; Ti, 800; Mn, 530; Fe, 770
ORT, Bolsover's oxide-rich troctolite SCP-113. xxT indicates experiments on unreduced ORT starting mater
reduced at 1040^{o}C and at fO_2 "within the fayalite stability field". ORE, see text. Fe^{T}, total i
Added components are: C, synthetic graphite. "FeP", synthetic $Fe_4(P_2O_7)_3$. Ap, fluorapatit

61 ORE	$Usp_{70}GrAp(4)$	GM123-14	$Usp_{50}Mt_{50}$
oxalic acid	4% C 16% Ap	2.1% C 5.3% Ap	(Synthetic) working standard)
0.5	0.5	0.5	
1200	1250	1308	
unk	15	24	
Avg. of 20	**Avg. of 20**	**Avg. of 20**	**Avg. of 10**
0.09(2)	0.07(2)	0.15(2)	0.29(1)
27.54(28)	25.30(28)	25.36(25)	17.39(32)
5.13(7)	0.00(0)	3.82(4)	0.00(0)
15.74(2.63)	24.24(1.56)	16.27(1.58)	32.41(2.16)
4.96(2.45)	49.57(1.64)	45.97(1.58)	49.37(2.19)
0.39(3)	0.02(2)	0.35(3)	0.01(2)
3.07(5)	0.04(1)	7.18(7)	0.02(2)
0.03(1)	0.40(11)	0.08(2)	0.02(1)
0.03(1)	0.05(6)	0.01(1)	0.03(1)
98.98(49)	99.68(50)	99.32(36)	99.53(31)
0.0005(1)	0.0004(1)	0.0007(1)	0.0016(1)
0.1062(9)	0.1020(17)	0.0877(8)	0.0877(8)
0.0310(5)	0.0000(0)	0.0229(3)	0.0000(0)
0.2622(15)	0.3202(21)	0.2553(15)	0.3541(71)
0.0017(1)	0.0001(1)	0.0015(1)	0.0001(1)
0.0235(4)	0.0003(1)	0.0539(1)	0.0001(1)
0.0002(1)	0.0023(6)	0.0004(1)	0.0001(1)
0.0001(1)	0.0002(3)	0.0000(0)	0.0001(0)
0.5779(22)	0.5769(16)	0.5695(14)	0.5714(34)
0.003(1)	0.003(1)	0.005(1)	0.011(1)
0.736(8)	0.708(4)	0.675(5)	0.500(6)
0.215(4)	0.000(0)	0.159(21)	0.000(0)
1.815(17)	2.220(21)	1.793(14)	2.507(31)
0.012(1)	0.000(0)	0.010(1)	0.000(1)
0.163(3)	0.002(1)	0.379(4)	0.001(1)
0.001(0)	0.016(4)	0.003(1)	0.001(1)
0.000(0)	0.001(2)	0.000(0)	0.001(0)
2.944(27)	2.950(19)	3.025(17)	3.021(28)

Conditions, 15 kV, 20 nA. Beam 5 microns.
ɔw standard deviation in the last decimal place(s).

ial. xxTR indicates experiments on ORT that had been
iron.

e from Durango, Mexico.

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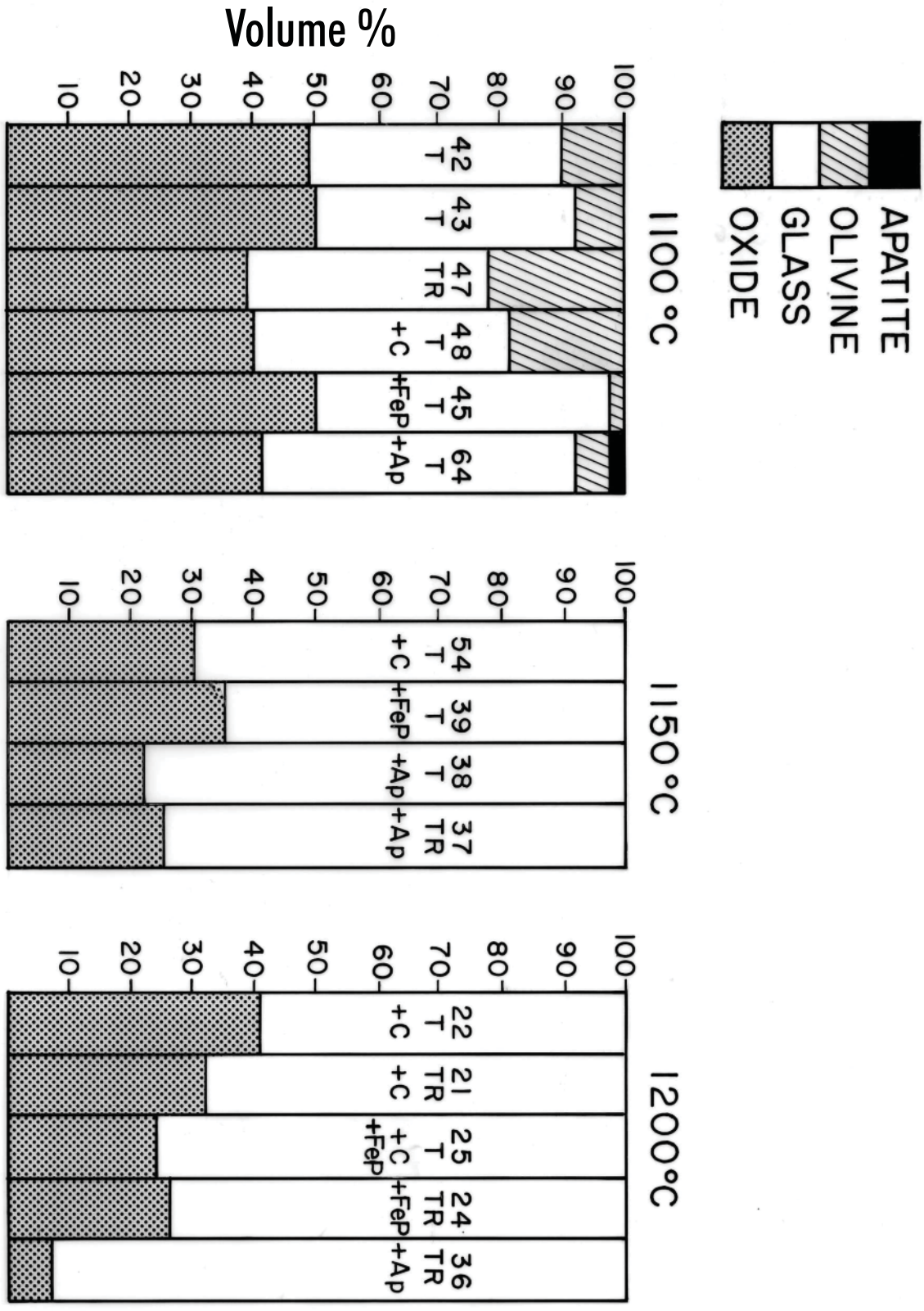

Fig. 1

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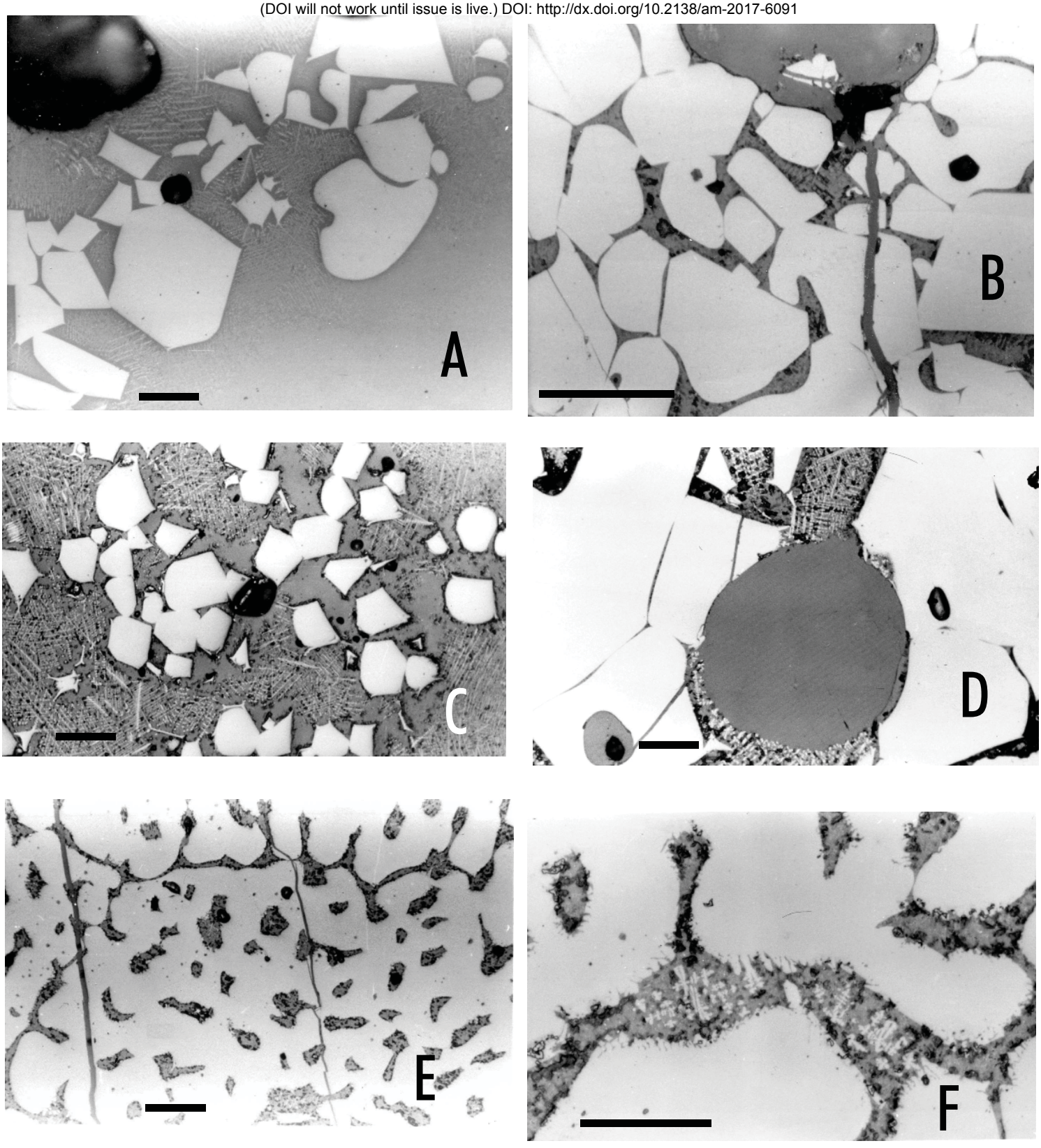

Lindsley-Epler Fig. 2

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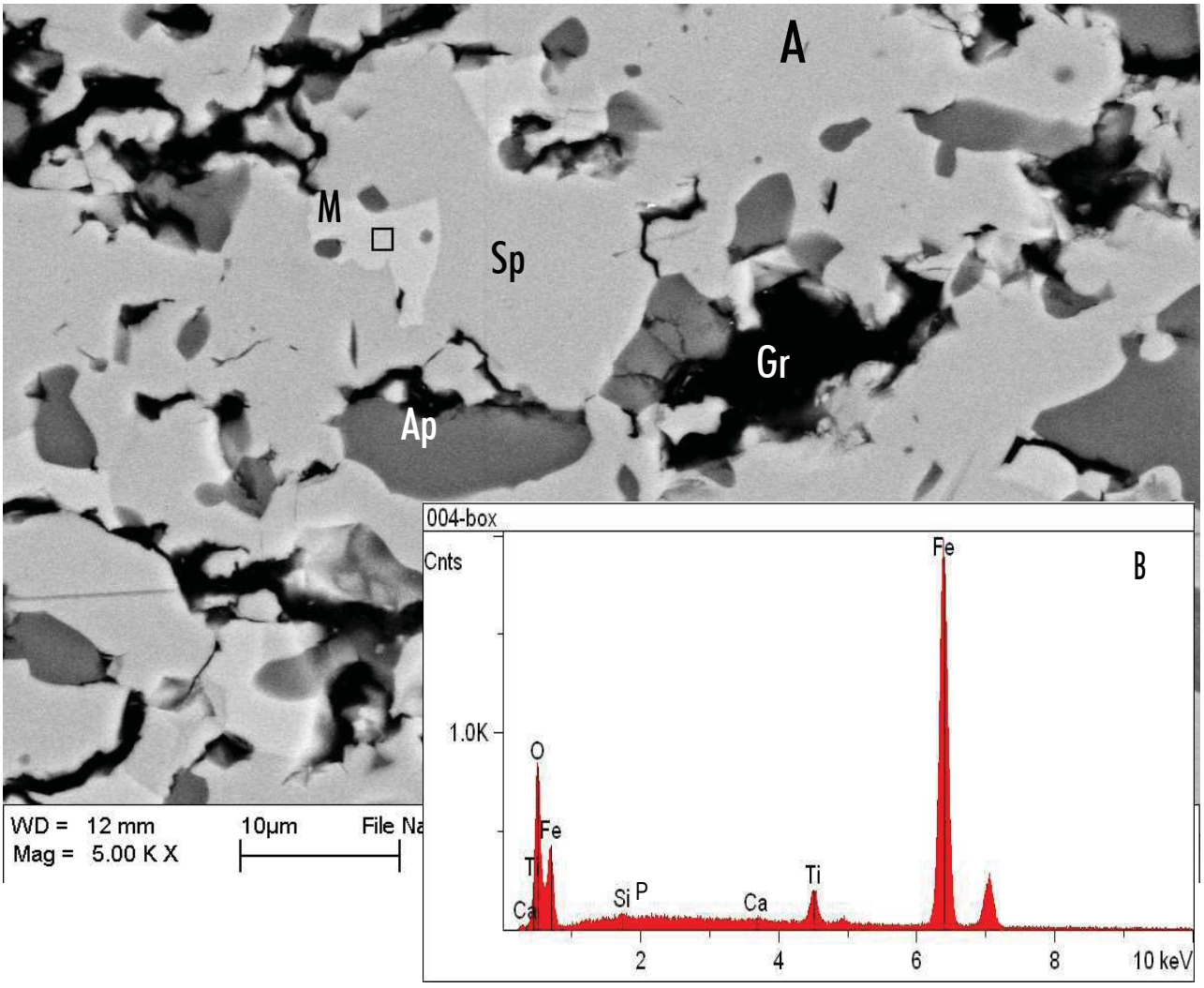

Lindsley-Epler Fig. 3

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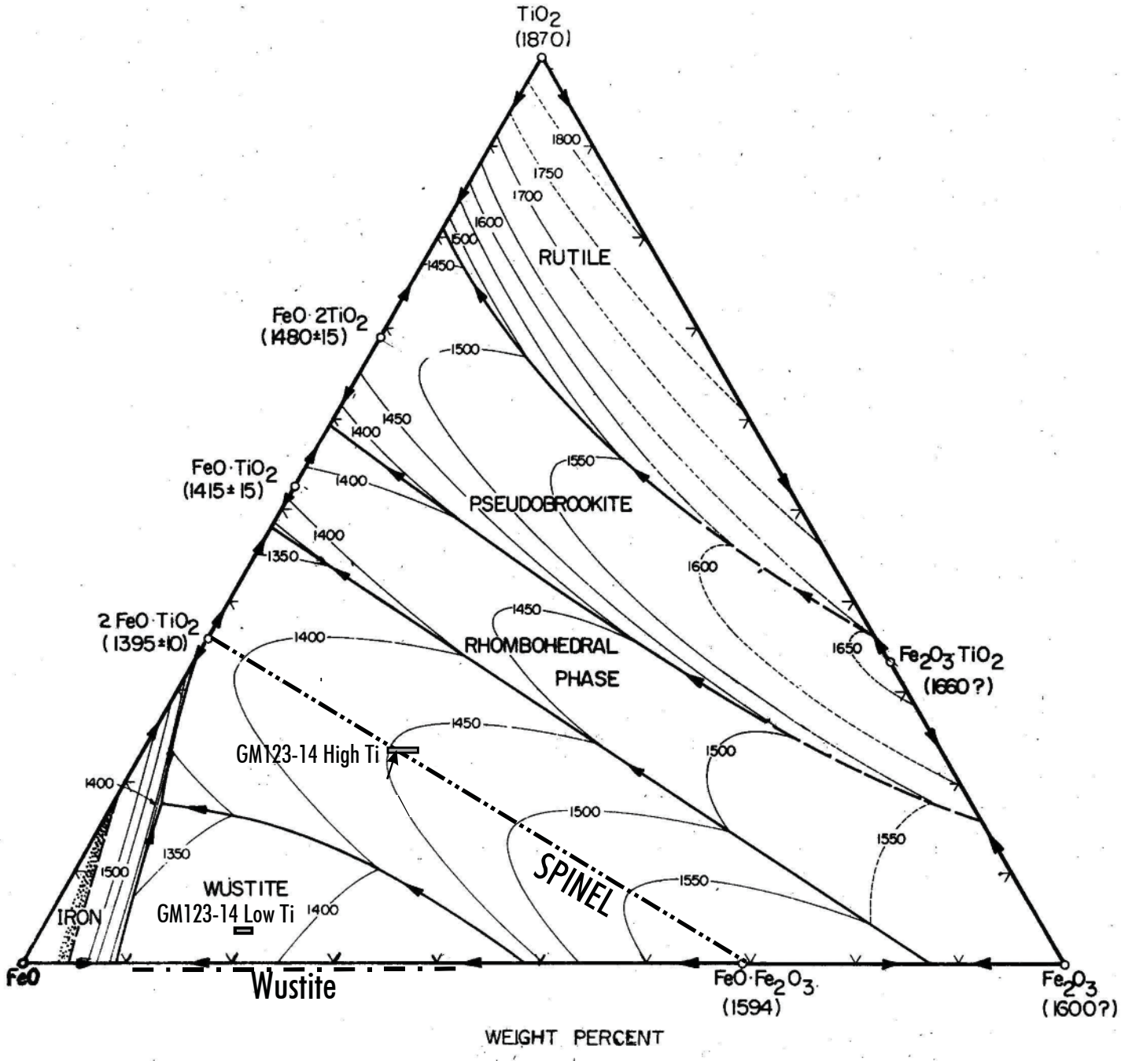

Lindsley-Epler Fig. 4

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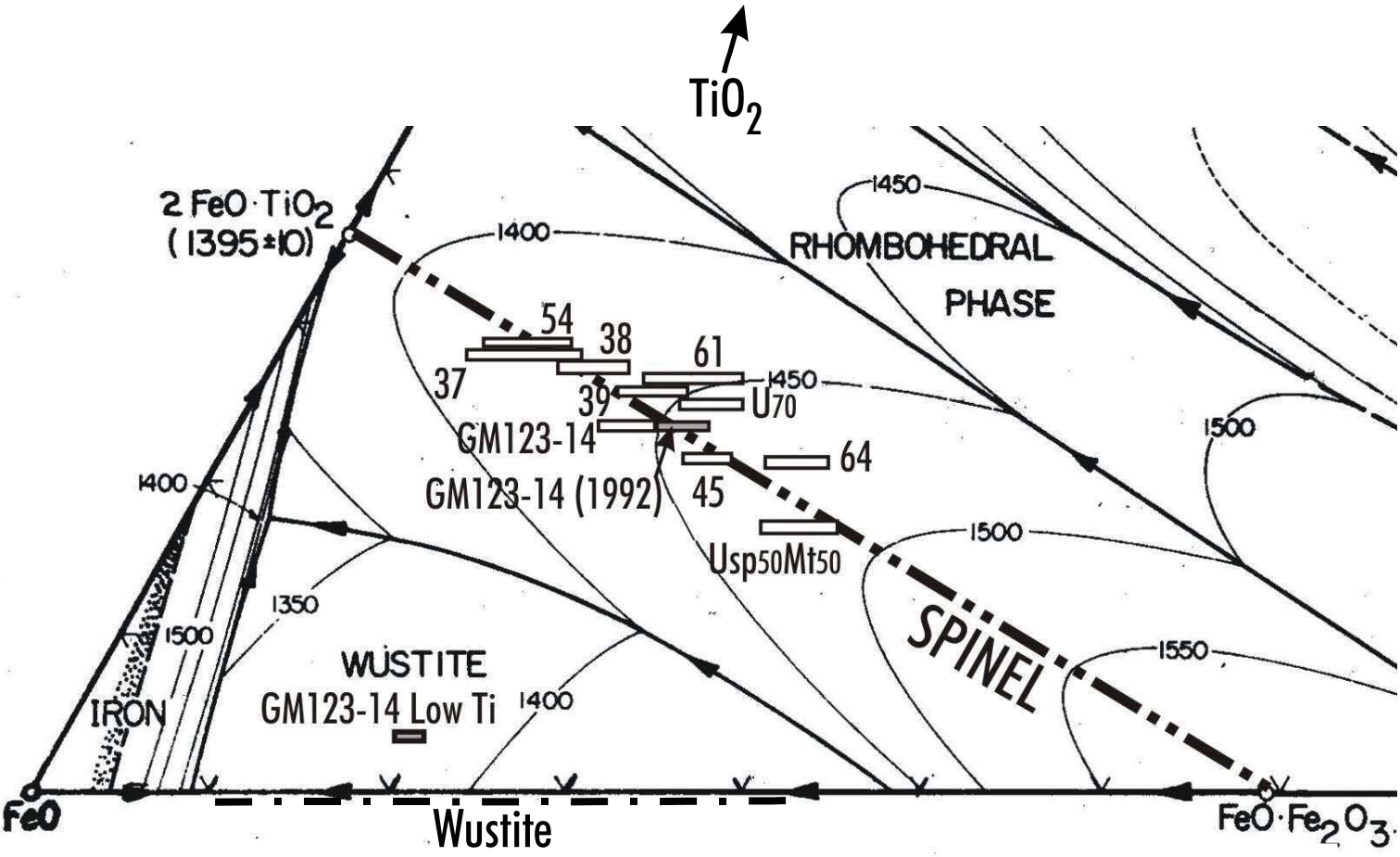

Lindsley-Epler Fig. 5

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