Chapter 2

The Petrologic Nature of the "Medellín Dunite" Revisited: An Algebraic Approach and Proposal of a New Definition of the Geological Body

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Abstract The "Medellín Dunite", the main ultramafic body of the Central Cordillera of Colombia, constitutes a fragment of oceanic lithospheric mantle formed at a back-arc basin/incipient arc scenario emplaced onto the western continental margin of Pangaea during Triassic time. This body has been classically, and is still considered, mainly of dunite composition. However, in spite of two subsequent metamorphic imprints that obscure the primary mantle mineralogical composition, there is petrographic and geochemical evidence that points to a harzburgitic nature of the unit. In order to overcome the petrographic effects of medium-T metamorphism, metasomatism, and serpentinization, we analyzed published and new major-element geochemical data by means of algebraic methods to approximate the mantle mineralogical composition of ultramafic rocks. The restored mantle mineralogy clearly indicates that the body is mainly of harzburgitic composition, and therefore we propose that the term "Medellín Dunite" should no longer be applied to avoid terminological confusion. Furthermore, a phase-relation approach in simple systems for the metamorphic evolution allows identifying the main reason for the contradictory terminology used so far: olivine is paragenetic (stable) with tremolite and talc during medium-T (ca. 600 °C) metamorphic imprint undergone by the body. During this initial metamorphic event, characterized by full hydration (as opposed to the late-stage serpentinization), mantle pyroxenes reacted out and medium-T olivine formed while high-T olivine persisted metastably as a likely consequence of moderate temperature and sluggish diffusion kinetics. On the other hand, we analyze two likely geodynamic scenarios to provide a common context of metamorphism for the ultramafic body and associated metabasites (Aburrá Ophiolite): (i) ocean-floor metamorphism and (ii) intra-backarc subduction-initiation metamorphism. The latter allows a new tectonic view of the Aburrá Ophiolite, formed by tectonic units from the upper and down going plates on a nascent active plate margin. For all these reasons, we propose the new term "Medellín Metaharzburgitic Unit" in order to combine in a single term the original high-T mantle composition, its subsequent metamorphic transformation and the independent tectonic character of the ultramafic body.

Keywords: Medellín Dunite, Medellín Metaharzburgitic Unit, metaharzburgite, phase relations, ophiolite.

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Resumen La "Dunita de Medellín", principal cuerpo ultramáfico de la cordillera Central de Colombia, constituye un fragmento de manto litosférico oceánico formado en un ambiente de cuenca de retroarco/arco incipiente emplazado sobre el margen continental occidental de Pangea durante el periodo Triásico. Este cuerpo es y ha sido clásicamente considerado de composición esencialmente dunítica. Sin embargo, y a pesar de dos eventos metamórficos subsecuentes sufridos que han enmascarado su composición mineralógica mantélica primaria, existe evidencia petrográfica y geoquímica que indica una naturaleza harzburgítica generalizada de la unidad. Para evitar los efectos petrográficos del metamorfismo de T-media, metasomatismo y serpentinización, analizamos datos geoquímicos publicados y nuevos de rocas ultramáficas mediante métodos algebraicos para deducir su composición mineralógica mantélica primaria. La mineralogía mantélica reconstruida claramente indica que el cuerpo es principalmente de composición harzburgítica y, por tanto, proponemos que el término "Dunita de Medellín" no debe aplicarse en el futuro para evitar confusiones terminológicas. Aún más, un análisis de las relaciones de fases en sistemas simples durante la evolución metamórfica sufrida permite identificar la razón principal por la cual se ha llegado a esta terminología contradictoria: el olivino es paragenético (estable) con tremolita y talco durante el evento metamórfico generalizado de T-media (ca. 600 °C) sufrido por el cuerpo. Durante este evento metamórfico inicial, caracterizado por hidratación completa (a diferencia de la serpentinización tardía), se consumieron los piroxenos primarios mantélicos y se formó olivino, en tanto que el olivino de T-alta persistió de forma metaestable probablemente como consecuencia de una cinética de difusión lenta a temperatura moderada. Por otro lado, analizamos dos posibles ambientes geodinámicos para ofrecer un contexto común para el metamorfismo del cuerpo ultramáfico y las rocas básicas asociadas (Ofiolita de Aburrá): (i) metamorfismo de fondo oceánico y (ii) metamorfismo de inicio de subducción intra cuenca de retroarco. Este último modelo permite una nueva conceptualización tectónica de la Ofiolita de Aburrá, conformada por unidades tectónicas pertenecientes al techo y muro del incipiente margen de placa activo. Por todo ello, proponemos el nuevo término "Unidad Metaharzburgítica de Medellín" para unir en una sola expresión la composición mantélica original de T-alta, la subsiguiente transformación metamórfica y la naturaleza tectónica independiente del cuerpo ultramáfico.

Palabras clave: Dunita de Medellín, Unidad Metaharzburgítica de Medellín, metaharzburgita, relaciones de fases, ofiolita.

1. The Origin and Evolution of the Concept "Medellín Dunite" and Its Metamorphic Imprint

Ultramafic bodies with variable extent of metamorphic imprint and serpentinization are found in the Central Cordillera of Colombia. The largest of these bodies, and probably the largest one in the entire Andes, crops out to the east and north of the Aburrá valley and Medellín. This body, generally termed as the "Medellín Dunite", is composed of three outcrops separated by the Santa Elena Creek and the Medellín River (Figure 1). The whole body trends N–NW and is 35 km long and 5 km wide, with a total area of about 71 km². In the first modern geological study of the region (Botero, 1963), the ultramafic rocks were termed "Medellín Serpentinites", made of serpentinites containing 15– 35 % of olivine. Botero (1963) considered these rocks to have formed as an almost crystalline ultramafic magma "intrusion" into the surrounding metamorphic rocks, in particular amphibolites that developed a strong foliation/lineation of hornblende and plagioclase upon the proposed intrusion. With the advent of plate-tectonics theory, the emplacement of the ultramafic rocks was attributed to a probable Cretaceous obduction of oceanic mantle over Paleozoic metamorphic rocks (mostly amphibolites) (Restrepo, 1986; Restrepo & Toussaint, 1973, 1974).

As new petrographic studies became available, it was apparent that the amount of olivine in the ultramafic rocks was higher than reported by Botero (1963) and that the rock ensemble should not be termed "Medellín Serpentinites". Álvarez (1982, 1987) considered that the body represents the solid residue of partial melting of the mantle in the transition zone of an oceanic lithosphere and ascribed the strong banding of the rocks and oriented olivine fabrics to ductile mantle deformation. This led



Figure 1. (a) Topography of northwestern South America (National Geographic MapMaker Interactive, http://mapmaker.nationalgeographic.org/) with indication of Eastern, Central, and Western Cordilleras (EC, CC, and WC, respectively) and the area shown in Figure 1b. (b) Geological sketch map of the Central Cordillera of Colombia (adapted from Nivia et al., 2016) with indication of map in Figure 1c. (c) Simplified geological map of the Medellín region compiled after Botero (1963), Rendón (1999), Correa–Martínez & Martens (2000), Rodríguez et al. (2005), Restrepo et al. (2012), and Rodríguez & Correa–Martínez (2015). The question marks indicate possible extension of the La Espadera–Chupadero and Santa Elena Amphibolites. The location of samples studied in this paper (Table 1) is indicated. Pg– Paleogene; K–Cretaceous; PZ–Paleozoic; T–Triassic.

this author to name the body "Medellín Dunite Tectonite". Metamorphic minerals such as tremolite, chlorite, talc, and serpentine were related to a late low-temperature alteration event which included metasomatic formation of Al-rich minerals (essentially, chlorite). Restrepo & Toussaint (1984) followed Álvarez (1982) and formally used the term "Medellín Dunite", though these authors emphasized that, even if pyroxenes were not generally present, tremolite and chlorite aggregates replace probable former pyroxene(s) and, consequently, indicated that at least some rocks may not have a dunitic composition. Notably, these authors considered tremolite and chlorite the result of a regional metamorphic event affecting the unit. Álvarez (1987) presented 14 whole-rock chemical analyses of the ultramafic rocks and used Coleman's (1977) SiO₂ versus FeO*/(FeO* + MgO) diagram to show that the samples plot between the fields of dunite and harzburgite. He emphasized that the bulk composition of the dunite tectonite is relatively restricted and that it compares well, except for Al_2O_3 contents, with ophiolitic dunites reported by Coleman (1977). The observations of Álvarez (1982, 1987) and Restrepo & Toussaint (1984) influenced other workers to name the body as "dunite" almost ever since their work.

Thus, González (2001), in the memoir of the Mapa geológico del departamento de Antioquia, used the term "Medellín Dunite" and emphasized the olivine–rich primary composition (with relicts of Cr–spinel) transformed to variable extent to serpentine group minerals, tremolite, chlorite, talc, magnetite, and carbonates. Similarly, Rodríguez et al. (2005), in the memoir of the Geological Map of East Medellín (sheet 147; 1:100 000), introduce the term "Medellín Serpentinized Dunite" to emphasize the variable extent of serpentinization. These authors

recognized the relict high-T banding as a preferential orientation for serpentinization and formation of tremolite and talc. In their modal analyses of 45 samples (800 points per thin section) Rodríguez et al. (2005) identified olivine (up to 76 mode %), chromian-spinel, tremolite, talc, chrysotile, antigorite, carbonates, chlorite, and magnetite, but no pyroxene. These authors presented whole-rock major elements analyses of 12 samples and follow Álvarez's (1987) conclusion that the composition of the body is similar to dunitic rocks of ophiolitic complexes as defined by Coleman (1977). Because these authors considered that the composition of the ultramafic rocks is dunitic, i.e., poor in SiO₂, Al₂O₂, and CaO, the formation of secondary minerals such as talc, chlorite, and amphibole was associated with metasomatic transformations triggered by addition of these elements from external sources. They also indicate that MgOloss likely took place during serpentinization.

Correa-Martínez & Nilson (2003) and Correa-Martínez (2007) reported very local occurrences of unaltered and altered harzburgite and wehrlite and considered that the unit forms part of the Aburrá Ophiolite of Correa-Martínez & Martens (2000; see section 2 for details). However, these authors report that most of the body corresponds to massive dunites, with only minor harzburgitic rocks classified as I- and II-type harzburgites with preserved and altered orthopyroxene, respectively. These rocks present variable amounts of serpentine, tremolite, talc, and carbonates that are considered secondary minerals formed after primary mantle minerals. Correa-Martínez & Nilson (2003), Correa-Martínez et al. (2004), Proenza et al. (2004), and Correa-Martínez (2007) concluded that the body formed in a suprasubduction environment (back-arc basin). Correa-Martínez & Nilson (2003) and Proenza et al. (2004) still retained the term "Medellín Dunite", but Correa-Martínez (2007) dropped this term and proposed "Medellín Ultramafic Massif" to emphasize that, in spite of a predominance of dunitic composition, the unit contains minor amounts of harzburgite, ultramafic dikes, and wehrlite (in addition to chromitite). Though the last author did not present major-element bulk-rock chemical analyses of the ultramafic rocks, four unpublished analyses obtained during her PhD thesis are presented in this paper (see below).

Pereira et al. (2006) and Restrepo (2008) published bulk– rock major–element analyses of 2 and 6 samples, respectively. Even if small in number, they show a relatively large chemical spread that suggests varied lithology. Restrepo (2008) analyzed samples from the main body and from other smaller bodies, some of which may not be related to the former. Both Pereira et al. (2006) and Restrepo (2008) use the term "Medellín Dunite". Interestingly, however, Restrepo (2008) highlights the (very) local presence of fresh and tremolite + talc–altered orthopyroxene in samples from Chupadero Creek, San Pedro, and the southern part of the body and suggested that, if ubiquitous tremolite formed at the expense of clinopyroxene the body may correspond to the mantle section of a lherzolite–harzburgite ophiolite type (following the nomenclature of Nicolas & Boudier, 2003). Moreover, Restrepo (2008) emphasized that because the body suffered medium grade metamorphism (tremolite + chlorite \pm talc \pm anthophyllite–bearing assemblages) the correct definition of the body should be "Medellín Metadunite".

Hernández-González (2014) presented 4 chemical analyses of serpentinized samples and recognized the presence of dunite, harzburgite, and lherzolite, the latter based on one chemical analysis of Restrepo (2008) that is probably carbonated (as discussed below). This author used the term "Medellín Metaperidotite", but did not offer a comprehensive treatment of metamorphism. A suprasubduction environment of formation is proposed, probably a back-arc basin. Recently, González-Ospina (2016) published chemical analyses of 9 samples. This author indicated that the geochemical characteristics of most samples conform to an island arc environment of formation, assigned a (serpentinized) dunitic composition based on petrographic analyses, and retained the term "Medellín Dunite". However, the calculated CIPW norm of the samples clearly points to harzburgitic composition (the abundance of normative hypersthene ranges from 42 to 24%; see Table 6.5 in González–Ospina, 2016).

In summary, the term "Medellín Dunite" is strongly rooted in the Colombian geological literature and is still used in spite of petrographic (i.e., presence of tremolite) and geochemical (i.e., large variability in major element composition) indications that the unit does not comprise mainly dunite. Except Correa–Martínez & Nilson (2003), Correa–Martínez (2007), and Restrepo (2008), previous authors have not addressed this fundamental contradiction. Also, except Restrepo (2008), the evaluation and terminological significance of the metamorphic imprint of the "Medellín Dunite" has not been discussed. However, it is of paramount importance to give its proper name to each rock (paraphrasing the influential paper by Streckeisen, 1976).

In this paper, we address the terminological issue of the "Medellín Dunite". In the first part of the paper, we use published and new chemical analyses to show the petrological nature of the body. In the second part, we will focus on the origin of the most important and paradoxical characteristic of these ultramafic rocks: why olivine has generally resisted metamorphic overprinting. We show that the body originally was harzburgitic and should no longer be termed "Medellín Dunite" in order to avoid terminological confusion. Furthermore, since metamorphic conditions attained by these rocks are the reason for the presence of olivine, we propose the term "Medellín Metaharzburgitic Unit", which will be used henceforth in this paper.

2. Geologic Setting

The bedrock geology of the Central Cordillera of Colombia is essentially made of low-, medium-, and high-grade metasedimentary and metaigneous rocks and post-metamorphic igneous intrusions and volcanic and sedimentary sequences of mainly

Permian - Triassic to Late Cretaceous age (Rodríguez et al., 2005, and references therein). To the west, the lithological ensemble is cut by a number of strike-slip faults grouped in the Romeral-Cauca Fault System, including the San Jerónimo and Cauca–Almaguer Faults that separate these complexes from the Western Cordillera (Cretaceous Oceanic Colombian-Caribbean Plateau Basalt Province). To the east, the Otú-Pericos Fault separates the ensemble from the Chibcha Terrane, located in the eastern flank of the Central Cordillera, and the Eastern Cordillera (Mesozoic continental passive margin) (Maya & González, 1995). Roughly, metamorphic ages in the Central Cordillera follow an east-west younging trend, including the Grenvillian Chibcha Terrane, the Permian – Triassic Tahamí Terrane, the small Devonian Anacona Terrane, the volcanicsedimentary slightly metamorphic to non-metamorphic Cretaceous Quebradagrande Complex, and the Cretaceous Arquía Complex, while plutonic intrusions are of Triassic, Jurassic, and, mainly, mid-late Cretaceous age (Cochrane et al., 2014; Jaramillo et al., 2017; Martens et al., 2014; Maya & González, 1995; Ordóñez-Carmona, 2001; Restrepo et al., 1991; Spikings et al., 2015; Toussaint & Restrepo, 1989; Villagómez et al., 2011; Vinasco et al., 2006). Recently, an eastern fragment of the Tahamí Terrane has been dated Jurassic, emphasizing the need of further geochronologic work to better define terranes and terrane boundaries (Blanco-Quintero et al., 2014). In this work we follow Restrepo (2008) and consider that the Medellín Metaharzburgitic Unit forms part of the Tahamí Terrane. This terrane is roughly equivalent to the "Polymetamorphic Complex of the Central Cordillera" of Restrepo & Toussaint (1984) and the "Cajamarca Complex" of Maya & González (1995).

The metamorphic rocks in the Medellín region (Aburrá valley) are mostly metabasite and, to a lesser extent, low-, medium-, and high-grade metasedimentary and metagranitic rocks, including muscovite-quartz schist, migmatite, and biotite gneiss (e.g., Figure 1; Restrepo, 2008; Restrepo & Toussaint, 1984; Rodríguez et al., 2005) that were grouped initially in the "Ayurá-Montebello Group" by Botero (1963) and more commonly in the "Cajamarca Complex" after Maya & González (1995). Metamorphic ages are essentially Permian - Triassic (Bustamante et al., 1999; Cochrane et al., 2014; Martens et al., 2014; Ordóñez-Carmona, 2001; Restrepo et al., 1991, 2011; Vinasco et al., 2006). Since Restrepo & Toussaint (1984) defined the term Medellín Amphibolite to name the amphibolitic body of the basal part of Ayurá-Montebello Group/Cajamarca Complex in the region, different metabasite units have been separated from this geologic unit, making the term Medellín Amphibolite no longer valid. Correa-Martínez & Martens (2000) and Correa-Martínez et al. (2005) defined four units, the Medellín, El Retiro, and Boquerón Amphibolites and the El Picacho Metagabbros, the latter including plagiogranite bodies. Restrepo (2008) defined two main units: the Santa Elena Amphibolites, which bear intercalations of Las Peñas Paragneiss, and the La

Espadera-Chupadero Amphibolites, the latter grouped with the Picacho Metagabbros as the Picacho Metabasites. For the El Retiro Amphibolites, Restrepo (2008) suggested that they could constitute the southern extension of the Santa Elena Amphibolites, but recent U-Pb zircon ages provided by Cochrane et al. (2014) and Restrepo et al. (2012) indicate that there is no relation. Amphibolites are (almost) totally recrystallized, while igneous relict textures are present in metagabbros, in particular in banded varieties (El Picacho). Metamorphic recrystallization yielded relatively homogeneous amphibole + plagioclase ± clinopyroxene-bearing assemblages denoting medium grade, conditions. Garnet is locally present in the Santa Elena Amphibolites. Correa-Martínez (2007) calculated 6.5-9 kbar for the garnetbearing samples, and ca. 5 kbar for other samples of the Santa Elena Amphibolites. The pressure calculation of other metabasite units has not been addressed. However, Correa-Martínez (2007) indicates that metamorphic pressure in the El Picacho and Boquerón Metagabbros is <2 kbar. Since these rocks are probably related to the La Espadera-Chupadero Amphibolites (see below), similar pressures could be anticipated.

The contacts between units are generally obscured by strike-slip faults, such as the Rodas Fault that separates the Medellín Metaharzburgitic Unit from the Santa Elena Amphibolites (Figure 1). Restrepo & Toussaint (1974) and Restrepo (2008) claimed that the Medellín Metaharzburgitic Unit overrides the La Espadera-Chupadero Amphibolites (Figure 2a), which in turn would override the Santa Elena Amphibolites. Restrepo (2008) suggested that the La Espadera-Chupadero Amphibolites formed the metamorphic sole of the ophiolite. The structural position of other metabasite units is uncertain. The fabric of the Santa Elena Amphibolites is complex, with development of at least two syn-metamorphic foliations and associated folding (Martens, 2003; Rodríguez et al., 2005). In all other metabasite units the fabric is simpler, with development of a single foliation, often mylonitic (Correa-Martínez, 2007). In this regard, mid-Cretaceous U-Pb zircon ages from the Santa Elena Amphibolites and related rocks (Restrepo et al., 2012), similar to metamorphic ages of the Arquía Complex, challenge the present view of the structural architecture and tectonics of the region. On the other hand, if La Espadera-Chupadero Amphibolites forms the metamorphic sole of the ophiolite, the proposal of a "normal" (i.e., Penrose-type) ophiolitic sequence would be defeated (see section 8).

All metabasite rocks are of oceanic origin and likely formed in a back–arc basin (Correa–Martínez, 2007; Correa–Martínez & Martens, 2000; Correa–Martínez et al., 2005). Correa–Martínez & Martens (2000) proposed that, in addition to the "Medellín Dunite", at least the El Picacho Metagabbros forms part of an ophiolitic complex, termed the Aburrá Ophiolite. Correa– Martínez (2007) expanded the concept to all other metabasite units in the region, including the Santa Elena Amphibolites and the El Picacho and Boquerón Metagabbros, which were consid-



Figure 2. (a) Panoramic view of the Medellín Metaharzburgitic Unit on top of the La Espadera–Chupadero Amphibolites at Chupadero Creek. **(b)** Typical outcrop aspect of ultramafic rocks showing massive structure. **(c)** Detail of massive ultramafic rock showing foliated structure on weathered surface. **(d)** Foliated ultramafic rock showing probable altered orthopyroxene porphyroclasts. **(e)** Banded structure with variable amount of probable pyroxene. **(f)** Detail of foliated ultramafic rock with orthopyroxene porphyroclasts. **(g)** Magnesite veins in altered ultramafic rocks.

ered to form part of the volcanic and plutonic crustal sections, respectively, of the Aburrá Ophiolite. U–Pb zircon data from a plagiogranite sample and a margarite–bearing metagabbro– pegmatite yielded concordant 216.6 \pm 0.4 Ma and 228 \pm 0.92 Ma ages, respectively (Correa–Martínez, 2007; Restrepo et al., 2007). The 216.6 \pm 0.4 Ma age is considered by Correa–Martínez (2007) as the timing of syn–oceanic shearing, metamorphism, and partial melting of the El Picacho Metagabbros and, hence, the minimum age of ophiolite formation. Restrepo et al. (2007) indicate that 228 \pm 0.92 Ma is the timing of the late stages of magmatism or, more unlikely, of a metasomatic overprinting.

However, Restrepo (2008) established geochemical contrasts between the Santa Elena (MORB–like) and other metabasite units (IAT–like), and considered the former as older than, and not–related to, the Aburrá Ophiolite. Following this author, the Santa Elena Amphibolites are related to the medium– to high–grade metasedimentary rocks of the Tahamí Terrane that form the basement overridden by the Medellín Metaharzburgitic Unit. Only the La Espadera–Chupadero Amphibolites and the El Picacho Metagabbros were considered as the basaltic and plutonic parts of the ophiolitic sequence by Restrepo (2008). This is in agreement with the mid–Cretaceous age (Restrepo et al., 2012), the more complex deformation and the higher metamorphic pressure of the Santa Elena Amphibolites.

The Medellín Metaharzburgitic Unit and other minor bodies occur to the east of the Medellín (Figure 1). As described above, the body is apparently made mainly of "dunite", with minor harzburgite, wehrlite, and ultramafic dykes (Correa-Martínez, 2007). Ductile deformation is generally weak, showing metamorphic massive non-oriented to oriented fabrics that overprint previous high-temperature mantle foliation, local banding, and porphyroclastic fabrics (Figure 2b-f). This metamorphic event is characterized by the generalized development of Tr + Tlc + $Chl \pm recrystallized$ olivine and will be termed in this paper as Tr + Tlc + Ol event (in this paper, mineral abbreviations are from Whitney & Evans, 2010). Previous high-temperature deformation is more common and intense towards the base of the main body in contact with country-rock amphibolites, where the extent of serpentinization is lower (Correa-Martínez, 2007). However, strong deformation in this part of the body is indicated by strongly oriented chlorite-actinolite schists formed at intermediate temperature after metasomatic transformation of ultramafic rocks (Correa-Martínez, 2007; Restrepo, 2008; Rodríguez et al., 2005). It hence seems that, at least more intensely at the base of the unit, the Tr + Tlc + Ol event is related to strong deformation. This event is overprinted by late serpentinization, carbonation (Figure 2g), and talc–forming episodes. The unit contains podiform chromite deposits. The composition and texture of the original chromite and olivine are strongly affected by the Tr + Tlc + Ol metamorphic event and late serpentinization. However, relict compositions point to formation in a back–arc basin (Correa–Martínez, 2007; Hernández–González, 2014; Proenza et al., 2004).

3. Mineral Assemblages and Textures

Most rocks of the Medellín Metaharzburgitic Unit lack pyroxenes and preserve only primary olivine with a variable extent of replacement by serpentine-group minerals and iddingsite (a very fine-grained mixture of chlorite group and smectite group minerals and iron oxi-hydroxides). They also contain chromian-spinel with moderate to strong transformation to ferrian-chromite and replacement by magnetite and chlorite. The primary fabric is defined by orientation of medium- to coarsegrained olivine and medium- to fine-grained spinel parallel to mineralogical banding and extent of serpentinization/weathering. Olivine is granular to elongated, and shows evidence of ductile/cataclastic mylonitic deformation, with undulose extinction and development of subgrains and recrystallization (Alvarez, 1982, 1987; Correa–Martínez, 2007; Restrepo, 2008; Rodríguez et al., 2005). Correa-Martínez (2007) indicates that mylonitic deformation is more intense towards the base, near the contact with amphibolites. Accessory chromian-spinel is equant to holly-leaf textured.

The rocks contain secondary minerals, which include tremolite, talc, chlorite, serpentine group minerals, magnetite, iddingsite and, locally, carbonates, that formed at various stages during the thermal evolution of the body. Serpentinization follows and crosscuts the primary foliation. Olivine is commonly replaced by lizardite-like serpentine (mesh texture) and masses of variably intersected sheet crystals of antigorite (Figure 3a), indicating mild deformation during serpentinization. Chrysotile and asbestoid aggregates occur in fractures, which also host garnierite (Restrepo, 2008). Serpentine group minerals occur associated with fine-grained magnetite and, locally, talc and carbonates, the latter more common in discordant veinlets that may contain serpentine and magnetite (Figure 3b). Chlorite is present as alteration haloes around chromian spinel altered to ferrian chromite/magnetite and as isolated grains/aggregates in the matrix associated with tremolite, talc, and serpentine.

Tremolite is fine-to-coarse grained. It is generally decussate (Figure 3a, 3c) but is locally oriented following post-high-



Figure 3. Optical images (cross-polarized light) of metaharzburgitic rocks. **(a)** Large mantle olivine grains (partly affected by late serpentinization) and tremolite. **(b)** Fine carbonate (magnesite?) vein in strongly serpentinized sample. **(c)** Tremolite + talc + olivine + chlorite in close association. **(d)** Relict(?) grain of clinopyroxene (refractive indexes oriented almost parallel to the polarizers in order to better see the exfoliation planes) in a matrix of olivine from a sample taken close to the base of the unit. **(e)** Large orthopyroxene porphyroclast showing kink bands and recrystalized grains in a matrix of deformed recrystallized olivine. **(f)** Detail of (e) showing clinopyroxene exsolutions (lamellae) within orthopyroxene and newly formed tremolite.

temperature fabrics. It locally occurs in aggregates (Figure 3a, 3c) and it forms intergrowths with neoformed olivine (Restrepo, 2008). A similar textural scenario applies to talc, which commonly occurs associated with tremolite (Figure 3c). However, replacement of tremolite by talc is not uncommon and late talc

locally crosscuts serpentine, suggesting that talc formed at various stages along the metamorphic evolution.

Clinopyroxene is extremely rare. It occurs as distinct finegrained crystals in the matrix (Figure 3d). González–Ospina (2016) indicated up to 4 mode % in samples B–1–A and LP–1 at vereda Chachafruto (Bello) and Medellín–Las Palmas road (Las Palmas), respectively. In all cases the identification has been made by means of optical microscopy, and chemical analyses are needed to allow classification, as far as subcalcic ("augitic") compositions are typical of primary mantle mineralogy while diopside would indicate metamorphic growth at low temperature. The clinopyroxene–bearing samples are moderately to highly serpentinized and show similar textures and all common minerals of "dunites", including olivine, chromian spinel, tremolite, talc, chlorite, and serpentine. This suggests that clinopyroxene may have formed part of the primary mantle assemblage, an inference anticipated by Restrepo (2008) based on the generalized presence of tremolite in "dunites".

To date, fresh orthopyroxene has been reported only in the Chupadero Creek locality (Restrepo, 2008). It amounts 10-15 modal % (Restrepo, 2008); similar amount is reported by Correa-Martínez (2007) and occurs as porphyroclasts up to 12 mm long that show exsolution lamellae of clinopyroxene and intense ductile and cataclastic deformation parallel to the main foliation with development of undulose extinction, kink bands, subgrains and grain recovery (Figure 3e, 3f). The groundmass is made of fine- to medium-grained recrystallized olivine indicating similar intense deformation and recrystallization. The extent of medium temperature metamorphic imprint is mild but, importantly, tremolite grains formed at the rims of orthopyroxene and within deformed crystals with clinopyroxene exsolution lamellae (Figure 3f; Correa-Martínez, 2007). This is interpreted as a result of very limited fluid infiltration during tremolite growth after exsolution of clinopyroxene (see below), but it nonetheless indicates stability of the assemblage Ol-Opx-Tr at high temperature. In this regard, the widespread presence of tremolite in "dunites" can be explained, at least in part, if high-Ca orthopyroxene formed part of the rocks in significant amount, pointing to generalized non-dunitic composition of the body. If this holds true, the former presence of clinopyroxene can be anticipated, for high-Ca orthopyroxene is only possible if subcalcic augitic clinopyroxene forms part of the primary mineral assemblage (e.g., Lindsley, 1983). In fact, distinct fine- to medium-grained talc + tremolite aggregates and bastite (a very fine-grained mixture of, mostly, serpentine group minerals) occur in some rare samples where the former presence of orthopyroxene porphyroblast/clast is inferred, located in Chupadero Creek, San Pedro, and the southern part of the body (Figure 2d-f; Correa-Martínez, 2007; Restrepo, 2008). Except for the Tlc + Tr and bastite pseudomorphs, all other mineralogical and textural relations described above for "dunites" are observed in these samples, strengthening the view that "dunites" contained orthopyroxene previous to the Tr + Tlc + Ol metamorphic event. It follows that temperature (and fluid flow) was intense enough as to assure element mobility and widespread metamorphic recrystallization during the Tr

+ Tlc + Ol event in order to completely erase orthopyroxene porphyroclast–replacement textures in common "dunites".

Nevertheless, dunite bands several centimetres in thickness are locally present (Correa–Martínez, 2007). This type of rock is clearly distinct from common "dunites". In addition to trace amounts of spinel, tremolite, talc, and sulfides, it is made almost exclusively of variably serpentinized coarse–grained flattened olivine (98–99 mode %) that shows significant recovery with common triple junctions (Correa–Martínez, 2007).

The varied mineralogical nature of blastesis and replacement events mentioned above indicates contrasted P-T-hydration/carbonation conditions. Our observations suggest the following general textural sequence of metamorphic imprint (with or without associated deformation) Ol + Opx + Tr (only locally preserved) > Ol + Tr + Tlc + Chl > Tlc + Atg/Lz + Chl> Atg/Lz + Chl > Tlc/carbonates (though carbonates may have formed during much of the metamorphic/metasomatic imprint), implying cooling from high-T mantle conditions. This sequence can be simplified in two distinct thermal + hydration events, one characterized by generalized Tr + Tlc + Ol (containing newly formed olivine) at medium to high temperature, as indicated by the widespread occurrence of this assemblage in the body, followed by generalized partial serpentinization to variable extent (except in some serpentinites sensu stricto lacking olivine) which locally includes talc-forming events. These observations agree with descriptions and interpretations by Restrepo (2008). This author concurs with the idea that at least part of olivine recrystallized during amphibolite-facies metamorphic imprint at temperature likely higher than 670 °C. Restrepo (2008) included tremolite and anthophyllite in his argument. However, even if the anthophyllite-bearing Media Luna metaultramafic rocks forms a distinct body, the high temperature of the Tr + Tlc + Olevent is warranted, as will be discussed below (see section 7.1).

4. Geochemical and Algebraic Methods

We will follow here a bulk-rock major element geochemical approach. Whole-rock composition are taken from the literature (Figure 1; Table 1; Álvarez, 1987; Botero, 1963; González-Ospina, 2016; Hernández–González, 2014; Pereira et al., 2006; Restrepo, 2008; Rodríguez et al., 2005). Of the 6 analyses presented by Restrepo (2008) we have considered only samples JJ1296–B (Las Palmas) and JJ1422–B (Chupadero Creek, with relict orthopyroxene) and have excluded other samples because they were taken from bodies that may not form part of the main Medellín body (e.g., Media Luna; Figure 1). For the same reason, we have excluded sample 724A of Botero (1963). In addition, we also use unpublished data of Ana María CORREA-MARTÍNEZ obtained during her PhD thesis and published here for the first time (Figure 1; Table 1). These samples were analyzed at the ACME Laboratory, Canada by means of inductively coupled plasma optical emission spectrometry

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 Table 1. Whole-rock composition of samples from the Medellín Metaharzburgitic Unit.

Sampla	SiO	TiO	41.0	CrO	FoO*	MnO	MaO		No O	KO	P O	I 0I**	Total	Publication
	30.40	0.00	Al ₂ O ₃	0.00	6.87	0.10	10 75	0.70	0.03	N ₂ O	1 ₂ 0 ₅	7 70	10tai	This study
AC52R	39.40	0.00	0.51	0.09	7.46	0.10	42.75	0.70	0.03	0.00	0.00	12.40	98.55	This study
AC52B	20.44	0.00	0.55	0.12	7.40	0.10	43.99	0.05	0.01	0.00	0.00	12.40	90.20	This study
AC39B	39.44 40.00	0.00	1.20	0.09	7.01	0.11	37.60 42.50	1.12	0.02	0.00	0.00	6 10	98.00	This study
AC35A	40.00	0.02	1.29	0.08	/.10	0.11	42.50	1.13	0.02	0.00	0.00	0.10	98.41	This study
630-A	38.30	0.01	2.81		0.01	0.03	40.97	1.75	0.47	0.01		8.70	98.84	Botero (1963)
665-A	45.14	0.01	8.90	0.21	6.91	0.02	30.61	1.75	0.41	0.01		9.01	102.77	Botero (1963)
166960	39.82	0.00	0.76	0.21	8.14	0.13	42.75	1.13	0.02	0.00		4.91	97.87	Alvarez (1987)
166961	38.05	0.00	0.76	0.26	7.37	0.10	39.30	1.69	0.01	0.00		10.51	98.05	Alvarez (1987)
166962	39.74	0.00	0.81	0.27	7.91	0.10	39.71	1.69	0.03	0.00		8.26	98.52	Alvarez (1987)
166965	36.26	0.00	0.64	0.10	9.54	0.14	42.55	1.69	0.02	0.00		7.07	98.01	Alvarez (1987)
166966	38.60	0.00	0.64	0.34	7.63	0.10	38.09	2.25	0.04	0.00		10.63	98.32	Alvarez (1987)
166967	34.62	0.00	1.19	0.12	8.59	0.13	42.14	1.13	0.01	0.00		10.39	98.32	Alvarez (1987)
166968	35.30	0.00	0.21	0.07	8.70	0.12	45.18	0.56	0.01	0.00		7.60	97.76	Alvarez (1987)
166970	35.90	0.00	0.53	0.17	7.22	0.13	42.35	0.84	0.01	0.00		10.78	97.93	Alvarez (1987)
166971	38.54	0.00	1.30	0.26	7.30	0.10	41.53	0.84	0.01	0.00		8.71	98.59	Álvarez (1987)
166972	38.46	0.00	0.32	0.16	7.90	0.10	38.50	1.13	0.02	0.00		11.36	97.94	Álvarez (1987)
166973	37.32	0.00	0.10	0.26	7.12	0.10	40.12	1.69	0.04	0.00		11.28	98.02	Álvarez (1987)
174567	30.12	0.00	9.25	0.19	13.47	0.13	30.00	4.90	0.35	0.02		7.00	95.43	Álvarez (1987)
174569	31.06	0.00	4.06	0.29	10.17	0.09	43.74	0.08	0.01	0.01		9.36	98.87	Álvarez (1987)
174572	32.82	0.00	7.31	0.45	9.98	0.10	38.61	0.01	0.01	0.01		8.93	98.23	Álvarez (1987)
705612	35.60	0.02	0.29	0.28	7.77	0.12	45.27	0.11	0.26	0.03		9.68	99.43	Rodríguez et al. (2005)
705731	40.70	0.03	0.62	0.32	7.88	0.12	42.40	0.56	0.20	0.02		6.37	99.21	Rodríguez et al. (2005)
705535	40.40	0.01	0.60	0.13	7.66	0.12	42.48	0.71	0.08	0.02		6.71	98.93	Rodríguez et al. (2005)
705544	40.20	0.03	1.25	0.36	7.53	0.09	38.51	0.04	0.09	0.02		11.13	99.25	Rodríguez et al. (2005)
705730	40.30	0.02	0.74	0.26	8.08	0.10	39.65	0.04	0.03	0.01		9.74	98.98	Rodríguez et al. (2005)
705570	36.10	0.02	0.04	0.09	8.32	0.12	43.92	0.36	0.08	0.02		9.28	98.35	Rodríguez et al. (2005)
705574	38.80	0.02	0.75	0.17	7.23	0.11	42.53	0.77	0.11	0.01		8.56	99.06	Rodríguez et al. (2005)
705576	39.10	0.03	0.71	0.17	7.77	0.11	43.49	0.83	0.09	0.01		6.46	98.78	Rodríguez et al. (2005)
705584	40.70	0.02	1.48	0.23	7.46	0.11	39.15	2.94	0.17	0.02		7.36	99.64	Rodríguez et al. (2005)
705590	37.70	0.04	0.94	0.23	7.60	0.15	41.48	0.57	0.06	0.01		10.55	99.32	Rodríguez et al. (2005)
705602	38.80	0.02	0.49	0.15	6.87	0.10	44.02	0.40	0.06	0.01		7.96	98.88	Rodríguez et al. (2005)
705603	38.50	0.02	0.60	0.18	7.71	0.11	42.02	0.77	0.06	0.01		9.26	99.24	Rodríguez et al. (2005)
Of-10	34.96	0.08	2.24	0.34	9.29	0.15	42.23	0.08	0.20	0.03		9.92	99.52	Pereira et al. (2006)
Of-10A	36.91	0.04	0.79	0.11	9.03	0.13	43.26	0.32	0.20	0.03		8.60	99.42	Pereira et al. (2006)
JJ1296-B	40.91	0.02	1.20	0.35	6.57	0.11	38.95	2.21	0.14	0.07		9.24	99.77	Restrepo (2008)
JJ1422-B	38.85	0.02	1.06	0.29	7.31	0.11	40.13	0.95	0.07	0.02		11.20	100.01	Restrepo (2008)
SP-001	38.93	0.04	0.77	0.23	6.82	0.12	39.92	0.53				11.29	98.64	Hernández–González (2014)
LP-7	31.18	0.30	5.27	0.22	9.72	0.12	37.20	0.07				9.79	93.86	Hernández–González (2014)
LP-4	40.60	0.06	0.96	1.87	7.22	0.12	40.36	0.74				8.63	100.55	Hernández–González (2014)
LP-1	39.59	0.02	0.84	0.33	7.75	0.13	41.20	0.57				8.17	98.59	Hernández–González (2014)
B-1-A	42.86		1.17	0.29	10.82	0.14	33.65	1.03	0.04			8.77	98.78	González–Ospina (2016)
G-1-A	43.11		0.42	0.38	6.87	0.14	39.97	0.34				7.96	99.20	González–Ospina (2016)
G-1-C	42.48		0.98	0.43	7.24	0.12	43.34	1.44				3.10	99.14	González–Ospina (2016)
LP2-A	41.75		0.66	0.36	11.61	0.13	40.67	0.42				3.06	98.66	González–Ospina (2016)
SH-1-(A)-A	42.10		1.15	0.41	6.96	0.13	42.45	1.50				4.50	99.19	González–Ospina (2016)
SH-1-(A)-B	42.36	0.02	0.96	0.47	7.74	0.14	43.34	0.31				3.79	99.13	González–Ospina (2016)
SH-1-(B)-B	43.04	0.04	1.41	0.47	7.22	0.12	41.07	0.71				5.14	99.22	González–Ospina (2016)
SH-1-(B)-C	42.13		0.92	0.43	7.43	0.14	42.96	1.66	0.02			3.43	99.13	González–Ospina (2016)
SP-2-A	42.62	0.02	1.17	0.36	12.81	0.14	40.55	0.57				2.03	100.28	González–Ospina (2016)

Source: Samples labels and analyses of Álvarez (1987) were taken from Rodríguez et al. (2005).

* Total Fe expressed as FeO.

** LOI—Loss on ignition.

(ICP–OES) using a Jarrel Ash Atomcomp model 975. Because of the lack of chemical analyses, other types of rock, such as wehrlite and ultramafic dikes described by Correa–Martínez (2007), are not considered. The total number of analyzed samples considered here is 49. In all cases, iron is treated as Fe²⁺_{total}. Mass loss on ignition (LOI) is treated as H₂O, though, as described in the original papers and discussed below, part of the measurements should be considered CO₂ since carbonates are present in (at least some of) the analyzed samples. The amount of analyzed H₂O/LOI ranges between 2.03 and 12.70 wt %. Taking into account that a fully serpentinized peridotite yields ca. 12–13 wt % H₂O, these values indicate variable extent of serpentinization (± carbonation).

In order to give each sample its proper name following the IUGS classification scheme, petrographic amounts of high T mantle minerals must be measured (e.g., Le Bas & Streckeisen, 1991; Le Maitre, 2002). However, because metamorphism and serpentinization (± carbonation) have commonly replaced pyroxene(s) and only olivine is generally present, the application of this petrographic scheme leads to the conclusion that the rocks are dunitic. But the metamorphic mineralogy of the samples indicates that, by no means, all samples are dunitic, for talc and tremolite cannot form in a dunite in such a high amount (up to 20 modal % summing–up both phases) as recorded in many samples. A similar conclusion was reached by Correa–Martínez (2007) after recognizing the presence of bastite (alteration of orthopyroxene).

However, it is important to quantitatively assess the high-T mantle mineralogy of the geological body in order to show whether it is dunitic or not. A geochemical method that allows applying such a classification scheme to altered samples, and that offers insight into the nature of alteration, involves algebraic mapping of the bulk rock compositions in transformed n-dimensional composition spaces defined ad hoc for the problem under consideration (see, for example, Spear et al., 1982; Thompson, 1982; Torres-Roldán et al., 2000). In this task, components are generally expressed in molar units, for wt % units depend on the molar weight of components rather than on true atomic/molecular abundance. However, oxy-equivalent (gram-oxygen) units are in particular convenient for reconstructing mineralogical composition, since this measure of component abundance has the advantage of being an estimate of the volume of solids in which oxygen is the only major anion (Brady & Stout, 1980; Thompson, 1982). The general composition space considered here is 9-dimensional, as defined by the chemical components SiO₂-TiO₂-Al₂O₃-Cr₂O₃-FeO-MnO-MgO-CaO-H₂O (Na₂O, K₂O, and P_2O_5 are neglected due to their low amounts in the samples considered; note, also, that because independent Fe₂O₂ and FeO estimates are known for only a few samples, they are not considered as independent components and total iron is expressed as FeO). The definition of the new set of 9 chemical species is flexible, but we will concentrate on new system components that allow obtaining meaningful graphical representations. These are obtained after projection onto selected (hyper–) planes of the 9–dimensional composition space from particular phases (minerals and fluids) and along mathematical operators (simple and coupled exchange vectors) that allow condensation of the composition space. This is convenient for visualization of the whole 9–dimensional chemical system in appropriate diagrams, though the information contained in the new components that are affected by the exchange vectors is complex and, in cases, not straight forward (see below for clarification).

The procedure followed here makes use of barycentric, rather than Cartesian, coordinates, because the focus is put in component/mineral proportions rather than absolute abundances. The projected barycentric diagrams have the advantage of considering all 9 variables at a time. In this regard, this method supersedes binary Cartesian diagrams relating the absolute amount of components (e.g., the Harker diagrams of Figure 4) or component ratios (e.g., the MgO/SiO₂ – Al₂O₃/SiO₂ diagram of Figure 5) where only 2 or 4 chemical components, respectively, are considered while all other components are neglected. We have performed the corresponding calculations and 3D and 2D projections using software CSpace (Torres–Roldán et al., 2000), that makes use of the singular value decomposition technique for solving linear equations (Fisher, 1989, 1993).

Appropriate diagrams for describing ultramafic compositions correspond to the 3D CaO-MgO-Al₂O₃-SiO₂ (CMAS) and 2D CaO-MgO-SiO₂ (CMS) molar plots and the 3D Ol-Opx-Cpx-Spl and 2D Ol-Opx-Cpx oxy-equivalent plots, all projected from the phases and exchange vectors indicated in Figures 6–12. Figure 10 (Ol-Opx-Cpx oxy-equivalent plot, projected from spinel) shows the reconstructed high-T mantle mineral composition of the studied samples in the petrographic classification scheme of ultramafic rocks by Le Maitre (2002). Figure 12 (Ol-Opx-Cpx oxy-equivalent plot, projected from chlorite) shows the phase relations appropriate for the Tr + Tlc + Ol metamorphic event.

In restoring of the mineralogy of metamorphic/serpentinized ultramafic rocks at high–T mantle conditions, H_2O component can be dropped from consideration in the manipulation of the composition space, as long as H_2O content at high–T subsolidus conditions adjacent to the site of generation of oceanic lithospheric mantle can be effectively considered 0. However, this does not hold true during cooling at mantle conditions in the oceanic realm, when H_2O infiltrates the rocks and causes growth of hydrated minerals. For this reason, and in order to evaluate the effects of metamorphism/alteration, component H_2O is considered and hydrated minerals such as tremolite, talc, anthophyllite, antigorite/lizardite, brucite, and clinohumite are projected in the molar and oxy–equivalent diagrams. On the other hand, because of the lack of CO_2 estima-



Figure 4. Harker diagrams for the Medellín Metaharzburgitic Unit (anhydrous basis). Samples with high Al₂O₃ are labeled in the SiO₂ versus Al₂O₃ diagram and indicated with grey bands in the rest of the diagrams for reference. Also for reference, the projection of forsterite, enstatite, diopside, and spinel is indicated.

tions in the studied samples, carbonates cannot be projected. However, they are plotted as if they were CO_2 -free chemical species (for this reason the labels appear within brackets). In spite of this deficiency, the consideration of these species in the diagrams is valuable because it allows evaluation of the effects of carbonation.

Further details of the procedure followed for each diagram are described below when required.

5. General Geochemical Features of the Medellín Metaharzburgitic Unit

On anhydrous basis (Figure 4), the compositional range of the Medellín Metaharzburgitic Unit is 34.13-48.14 wt % SiO₂, 0.00– 0.36 wt % TiO₂, 0.05–10.48 wt % Al₂O₃, 7.28–15.26 wt % FeO₍₋total), 0.02–0.17 wt % MnO, 32.65-51.34 wt % MgO, 0.01-5.55 wt % CaO, 0.01-0.52 wt % Na₂O, 0.00-0.08 wt % K₂O, 0.00 wt % P₂O₅. The amount of Cr ranges between 500 and 12 770 ppm and Mg# (molar MgO/(MgO + FeO)) ranges between 0.80 and 0.92. It is obvious that some samples are problematic in terms of comparison with "normal" peridotite composition, particularly in terms of Al₂O₃ contents above 4 wt % (Figure 4).

Five samples are clear outliers: samples 174569, 174572, and 174567 from Álvarez (1987) yielded 4.55, 8.23, and 10.48 wt % Al₂O₃, respectively, sample LP–7 from Hernández– González (2014) yielded 6.28, and sample 665–A from Botero (1963) yielded 9.49 wt % Al₂O₃. Sample LP–7, taken from the Medellín–airport road (Las Palmas region) is rich in olivine and relatively rich in chromian spinel (>5%, totally altered to ferrian–chromite/magnetite and chlorite) and in Fe–Ni–Cu– sulfides and Ni–Fe arsenides and sulfoarsenides (Hernández– González, 2014). This author classifies the rock as a dunite. Álvarez (1987) identified the high–Al contents of some of his samples and considered it the result of metasomatism, but did not go further in the problem. Botero (1963) does not comment on the issue. Nevertheless, even if all these samples clearly are not of peridotite composition, they will be considered below.

On the other hand, samples with relatively high MgO and low SiO_2 within the group of seemingly normal peridotitic composition compare with dunitic (sensu lato) compositions, but samples with relatively high SiO_2 , Al_2O_3 , and CaO, and relatively low MgO, suggest instead non–dunitic compositions (Figure 4).

A complementary geochemical view of the samples can be gained by means of inspecting chemical ratios rather than abso-



Figure 5. MgO/SiO₂ (wt %) versus Al₂O₃/SiO₂ (wt %) diagram for the Medellín Metaharzburgitic Unit. The samples indicated with labels correspond to Al-rich non-peridotite compositions of Botero (1963), Álvarez (1987), and Hernández-González (2014) indicated in Figure 4. The terrestrial array of mantle peridotites is after Jagoutz et al. (1979) and Hart & Zindler (1986) and primitive mantle (PM) is from McDonough & Sun (1995). Samples of serpentinite/hydrated peridotite derived from harzburgite from abyssal (Paulick et al., 2006), mantle wedge (Kodolányi et al., 2012; Pearce et al., 2000), and oceanic fracture zone (Chen et al., 2015; Niu, 2004; Pearce et al., 2000) settings are plotted for comparison. Mg-end members of phases of interest, anorthite, and the region of MORB are also indicated (note that spinel plots at infinity).

lute component concentrations. In terms of major element composition, perhaps the most widely used and informative plot is the MgO/SiO₂ (wt %) versus Al₂O₃/SiO₂ (wt %) diagram of Figure 5. In this diagram many samples plot close to the so–called "terrestrial array", defined by the composition of unaltered mantle peridotites with Al₂O₃/SiO₂ < 0.1 (Hart & Zindler, 1986; Jagoutz et al., 1979). These samples should be considered essentially unaltered peridotites that are strongly depleted relative to the composition of the primitive mantle, suggesting one or more partial melting and melt extraction events (Restrepo, 2008). To be noted is that, in terms of major elements, these samples are similar in composition to both drilled/dredged samples of mantle wedge and abyssal harzburgites worldwide (Figure 5).

However, the scattering of "normal" peridotitic samples with $Al_2O_3/SiO_2 < 0.1$ in terms of MgO/SiO₂ is noticeable, suggesting that metasomatic processes related to magmatic percolation/impregnation/refertilization and/or seawater alteration/ serpentinization and/or carbonation have largely transformed the original mantle bulk compositions. Among this group of samples, those with lower MgO/SiO₂ were most likely affected by seawater alteration/serpentinization, which typically involves MgO–loss (by dissolution of brucite as a result of low–temperature alteration/weathering; e.g., Boschi et al., 2017; Milliken et al., 1996; Niu, 2004; Snow & Dick, 1995; and references therein) and/or SiO₂–gain (due reaction with fluids containing aqueous silica during serpentinization at high fluid/ rock ratios; e.g., Bonnemains et al., 2017; Malvoisin, 2015; and references therein). However, pre–alteration magmatic impregnation/refertilization cannot be ruled out (Figure 5; Kodolányi et al., 2012; Paulick et al., 2006; Pearce et al., 2000).

On the other hand, the samples within this group of $Al_2O_2/$ $SiO_2 < 0.1$ that plot above the terrestrial array indicate SiO_2 -loss and/or MgO-gain, which can hardly be related to early magmatic impregnation and late serpentinization processes. Carbonation, however, can potentially explain these geochemical characteristics, as long as precipitation of magnesite and/or dolomite (and/or hydrous Mg-carbonates) increases the MgO/SiO2 ratio and does not affect Al₂O₃/SiO₂. The presence of carbonates is generally indicated in papers dealing with the Medellín Metaharzburgitic Unit though, to our knowledge, its nature (calcite and/or dolomite and/or magnesite and/or hydrous carbonates) has not being reported except for microscopic to macroscopic veins of calcite reported by Rodríguez et al. (2005) and small magnesite stockworks in Niquía mentioned by Correa-Martínez (2007). However, one of us (Jorge Julián RESTREPO) has collected altered samples with typical clayey magnesite. Therefore, it appears that, at least magnesite, is present in the unit, as otherwise would be expected in serpentinized and metamorphic metaultramafic rocks (e.g., Evans, 1977; O'Hanley, 1996; Trommsdorff & Connolly, 1990). In order to assess the original geochemical composition

of carbonate–bearing samples, the bulk compositions should be restored substracting the amount of CaO and MgO "stored" in dolomite/calcite and magnesite/dolomite, respectively (\pm hydrous carbonates). However, because CO₂ has not been analyzed and the nature of the carbonates present has not been identified in the studied samples, the restoration of bulk compositions of the potentially carbonated samples with high MgO/SiO₂ cannot be carried out.

Finally, the MgO/SiO₂ (wt %) versus Al₂O₃/SiO₂ (wt %) diagram of Figure 5 shows that some samples of Botero (1963), Álvarez (1987), and Hernández–González (2014) have non–peridotitic compositions (Al₂O₃/SiO₂ > 0.1) that can hardly be interpreted as a result of metasomatism/alteration during serpentinization/sea water alteration or carbonation. Their large amount in Al₂O₃ (Figure 4) points to either a non–peridotitic sensu stricto composition likely rich in spinel (e.g., LP–7 from Hernández–González, 2014) and/or the presence of plagioclase.

In spite of metasomatic alterations and (local) presence of non-peridotitic compositions, such a varied geochemistry illustrated in Figures 4, 5 points to a varied mineralogy of the high–T mantle protoliths, rather than to a simple dunitic composition of the Medellín Metaharzburgitic Unit. An attempt to "restore" the high–T mantle mineralogy of the Medellín Metaharzburgitic Unit is presented below.

6. The Restored High–T Mantle Mineralogy of the Medellín Metaharzburgitic Unit

6.1. The CMAS Diagram

The bulk rock compositions are first mapped in the 9-dimensional composition space defined by the new components SiO_2 , Al_2O_3 , MgO, CaO, TiO_2MgO(Al_2O_3), Cr_2O_3(Al_2O_3), FeO(MgO)_1, MnO(MgO)_1, and pure H2O-fluid expressed in molar units. This procedure allows projection onto the SiO₂, Al₂O₃, MgO, and CaO tetrahedron along simple and coupled exchange vectors, resulting in condensation of the composition space. Note that the information contained in the new components CaO, MgO, Al₂O₃, and SiO₂ that are affected by the exchange vectors do not correspond to that of the original components. For this reason, the new components are termed C, M, A, and S, and the resulting diagram is termed CMAS. Also note that in this particular case CaO and SiO, are not affected by the projection (i.e., exchange vectors do not add extra components to these components), but M and A represent in fact new complex components, i.e., MgO + MnO + FeO-TiO, and $Al_2O_3 + Cr_2O_3 + TiO_2$ (old variables), respectively. This procedure is justified because Mg-Mn-Fe and Al-Cr are exchanged in all mineral structures considered (i.e., Cpx, Opx, Tr, Ol, Tlc, etc.), following the indicated simple exchange vectors,

while Ti + Mg exchanges with 2Al (coupled exchange vector) in the structure of spinel. Note that not only Al and Mg are involved in the latter exchange, but also Cr, Fe, and Mn as long as the vectors $Cr_2O_3(Al_2O_3)_{-1}$, FeO(MgO)_1, and MnO(MgO)_1 are considered. For this reason, the Ti–spinel exchange vector $(TiO_2MgO(Al_2O_3)_{-1})$ accounts, in fact, for a complex exchange vector $(TiO_2(Fe,Mn,Mg)O((Al,Cr)_2O_3)_{-1})$ that includes all significant potential compositional variations of Fe³⁺–free spinel. This implies that projected spinel corresponds to a mixture of Cr–, Mg–, Fe–, Mn– and Ti–spinel end–members, including, ulvospinel, and chromite. The same concept applies to other phases, namely olivine (forsterite–fayalite), orthopyroxene (enstatite–ferrosilite and Al–Cr–Ti–end–members), and all other phases projected except quartz and anorthite.

The resulting tetrahedral CMAS diagram is presented in Figure 6. The space defined by the Ol–Opx–Cpx–Spl tie–tet-rahedron (in white) marks the locus of Spl–bearing anhydrous ultramafic rocks. The high–A samples (labeled in Figure 6) correspond to the samples with Al–rich non–peridotitic composition indicated in Figure 5. A group of low–A samples plots within the Ol–Opx–Cpx–Spl tie–tetrahedron comparable to "normal" peridotitic compositions. However, another group plots outside it, away from the Opx apex, which is obvious-ly not permitted in pristine Spl–bearing anhydrous peridotitic compositions. This latter group of samples (labeled in Figure 6) roughly corresponds to samples with MgO/SiO₂ higher than the terrestrial array in Figure 5.

6.2. The CMS Diagram Projected from Spinel

Details in a 3D diagram are not easily appreciated. For this reason, it is convenient to reduce the dimension of the diagram in order to generate a 2D triangular representation. This can be accomplished projecting form a given phase, in this case spinel, onto the CMS plane. This is done in Figure 7 and implies recasting sample compositions in a 9–dimensional new set of components including spinel (MgAl₂O₄) instead of Al₂O₃ (all other components used above to generate the CMAS diagram are retained). Note that the use of exchange vectors applies as above, so that the new components M and A do not represent exclusively old components MgO and Al₂O₃ and projection phase spinel and projected phases correspond to a mixture of Cr–, Mg–, Fe–, Mn–, and Ti end–members.

Projection from spinel implicitly requires that the rock samples plotted in the diagram contain this phase. If this is not so, the conclusions reached are flawed. This may (or may not) apply to the Al–rich samples of the data base. All other samples, however, are expected to be Spl–bearing at high–T mantle conditions, as recorded by relict spinel and newly formed ferrian–chromite and magnetite (e.g., Correa–Martínez, 2007; Hernández–González, 2014; Proenza et al., 2004). Hence, the space defined by the Ol–Opx–Cpx tie–triangle (white in Figure 7) marks the locus





 $\begin{array}{l} \mbox{Projection points}\\ \mbox{H}_2O\\ \mbox{Exchange vectors}\\ \mbox{TiMgAI}_2\\ \mbox{FeMg}_1\\ \mbox{CrAI}_1\\ \mbox{MnMg}_1\\ \mbox{Fe}=\mbox{Fe}^{2*} \mbox{ total} \end{array}$

Figure 6. Samples of the Medellín Metaharzburgitic Unit plotted in the CMAS diagram. Note that projection from H₂O is not needed to illustrate the phase relations at high mantle temperature (Ol–Opx–Cpx–Spl tetrahedron), but it has been done so for convenience in order to represent the locus of hydrated phases produced during the Tr + Tlc + Ol metamorphic and late serpentinization events. Also, carbonates are indicated between brackets as far as CO₂ contents are not available for the studied samples and, hence, this component is not considered in the transformation of coordinates. The labeled samples correspond to the non–peridotite compositions indicated in Figures 4, 5. See text for further explanation.

of Spl-bearing anhydrous ultramafic rocks. This diagram more clearly depicts the distribution of rocks. Samples rich in Al (labeled) are no longer commented, for they are not of normal peridotitic composition. The rest of samples distribute across the Ol–Cpx tie–line, indicating that some samples bear "negative" calculated orthopyroxene (see below and Figures 8–10). Clearly, these samples are affected by SiO₂–loss and/or MgO–(\pm FeO \pm MnO)–gain. Lines are drawn that describe the expected chemical behavior in case of addition of carbonates. The results point to addition of magnesite rather than dolomite or calcite. Only Al–rich non–peridotitic sample 174567 may have been affected by dolomite addition, though this conclusion is uncertain as far as it relies in the unknown presence of spinel in this sample.

6.3. The Ol-Opx-Cpx-Spl Diagram and Ol-Opx-Cpx Diagram Projected from Spinel

The bulk compositions of the samples can be recasted to directly reflect their high–T mantle mineralogy. This is done defining four new components, Fo, En, Di, Spl that, together with the exchange vectors used for the construction of the CMAS and CMS diagrams, represent in fact Ol, Opx, Cpx, and Spl solid solutions. However, instead of following the common practice of defining these components with molecular formulas based on 4, 3 (or 6), 6, and 4 oxygens, respectively (e.g., Putirka et al., 2011), it is more convenient to define all four chemical species as having the same number of oxygens (no matter what the number). As justified above (see section 4), this allows a better approximation of calculated mineral abundance to real mineral volume proportions. For this particular case, the calculated molar and oxy-equivalent contents of Ol, Opx, Cpx, and Spl are similar, for they have similar oxygen content in their molecular formulas. However, this is not the case if species with contrasted oxygen contents are used (e.g., amounts of SiO₂-quartz-versus KAlSi₂O₈ -orthoclase- in granites). This and the use of an appropriate set of projection phases and exchange vectors are important issues that should be seriously considered in classifying altered



Figure 7. Samples of the Medellín Metaharzburgitic Unit plotted in the CMS diagram projected from spinel. Arrows indicate the expected geochemical behavior upon carbonation. See Figure 6 and text for further explanation.

rocks using modal–abundance diagrams (e.g., Streckeisen diagrams). Thus, while this procedure using oxy–equivalent units was followed by Cárdenas–Párraga et al. (2017) for serpentinites of Cuba, Blanco–Quintero et al. (2011), Putirka et al. (2011), and Hernández–González (2014) used molar rather than oxy–equivalent units of Ol, Opx, Cpx, and Spl.

The result of the described procedure in oxy-equivalent units is represented in the Ol-Opx-Cpx-Spl and Ol-Opx-Cpx diagrams of Figures 8–10, the latter two projected from spinel. All issues considered so far can be more clearly appreciated in these diagrams, including the outlier nature of Al-rich rocks, the projection of low-Al samples of non-normal peridotite composition outside the Ol-Opx-Cpx-Spl tie-tetrahedron and Ol-Opx-Cpx tie-triangle and the potential carbonation of these samples by means of addition of magnesite. However, two additional aspects illustrated in these figures are of interest. First, some of the samples within the group of normal peridotite composition are likely carbonated by means of addition of dolomite and/or calcite. This is indicated by the displacements towards the Ol-Cpx tie-line, which is more clearly appreciated in Figure 10 containing the modal classification scheme of Le Maitre (2002). In this classification scheme, potentially carbonated samples plot rather away from

the harzburgite field and classify as lherzolite, an unlikely picture given the residual nature of the Medellín Metaharzburgitic Unit (Figure 5; Correa–Martínez, 2007).

A second point of major interest is that most samples of normal peridotite composition plot within the field of harzburgite, not dunite. Moreover, even if the lack of CO₂ analysis prevents the restoration of the composition of carbonated samples, it can be deduced that the samples that bear negative Opx (most likely affected by magnesite carbonation) and the samples that plot within the lherzolite field (potentially dolomite/calcite-carbonated) should probably have harzburgitic composition previous to carbonate alteration. Furthermore, at least some of the samples that properly plot within the harzburgite and dunite fields of Figure 10 are also likely affected by subtle carbonation. This implies that the original composition of these samples should plot displaced towards the Opx apex, and that samples that plot within the dunite field would, in fact, be of harzburgite composition. On the other hand, the bulk composition of the Cpx-bearing sample B-1-A of González-Ospina (2016) lies close to the harzburgite-lherzolite boundary, suggesting that clinopyroxene is a relict high-T phase (though metamorphic recrystallization/ growth is also possible; see below). This suggests that many other samples may have contained clinopyroxene previous to metamorphism/serpentinization.

Another issue is that of samples plotting below the terrestrial array of mantle peridotites and that likely have undergone SiO_2 -gain and/or MgO-loss during serpentinization (Figure 5). These samples correspond to those that plot closer to the Opx apex in Figures 8–10 within the harzburgite field. After eventual restoration of their composition previous to SiO_2 -gain and/or MgO-loss these samples would plot closer to the olivine apex.

Therefore, if our inferences hold true, the pre-serpentinization and pre-carbonation scatter of samples would contract significantly within the Ol-Opx-Cpx diagram, and we speculate that most samples of the Medellín Metaharzburgitic Unit had a relatively restricted composition within the field of harzburgite, as indicated in Figure 10. This picture of the Medellín Metaharzburgitic Unit as being essentially composed of relatively restricted harzburgite composition is not to say, of course, that dunite and, eventually, lherzolite do not exist in the body. Though scarce, dunite is present as thin bands within harzburgite and as envelopes around chromitite bodies (Correa-Martínez, 2007; Hernández-González, 2014) and some samples may indeed contain enough clinopyroxene as to be termed lherzolite. But the amount of these rocks in the unit seems small. We consequently propose that the "Medellín Dunite" should no longer be termed "dunite", for it introduces major confusion in the description of this geologic body. The "Medellín Ultramafic Massif", as proposed by Correa-Martínez (2007), would more closely correspond to the presented evidence.

Botero (1963)

Álvarez (1987)

▲ Restrepo (2008)

□ This work

Projection points

Exchange vectors

Rodríguez et al. (2005)

Hernández–González (2014)

González-Ospina (2016)

Pereira et al. (2006)

 \diamond

⊳

H₂O

TiMgAL₂ CrAL₁ FeMg₋₁ MnMg₋₁ Fe = Fe^{2+} total



Figure 8. Samples of the Medellín Metaharzburgitic Unit plotted in the Ol-Opx-Cpx-Spl diagram in oxy-equivalent units. Arrows indicate the projection of quartz and brucite/periclase and the effects of carbonation. See Figure 6 and text for further explanation.

7. Altered or Metamorphosed Mantle? Another Key Terminological Issue

7.1. The Mineralogy of the Medellín Metaharzburgitic Unit during Medium-T Metamorphic Conditions

Dragged/drilled samples of present–day abyssal and forearc/ backarc lithospheric sections show that shallow oceanic mantle undergoes cooling and hydration upon drift from spreading centers (e.g., Bach et al., 2006; Kimball et al., 1985). A variety of new hydrated minerals are hence developed during eventual influx of seawater along fractures. The most common transformation is serpentinization, which takes place at temperature lower than ca. 500 °C down to ambient surface temperature. Full serpentinization of a harzburgitic composition made of Mg₂SiO₄ (Ol) and MgSiO₃ (Opx) in equimolar amounts needs up to 13 wt % H₂O, which translates into 28.6 mole % abundance (Figure 11a). Somewhat higher amounts of H₂O are needed if the molar olivine/orthopyroxene ratio is greater than 1, because brucite (Mg(OH)₂) is formed in addition to serpentine (Mg₃Si₂O₅(OH)₄), reaching up to 16.1 wt % H₂O for 100% Mg₂SiO₄ dunitic composition (which translates into 33.3 mole % H₂O; Figure 11a). Such a flux of external H₂O is not readily available to relatively large sections of the oceanic mantle, and full hydration is only generally reached at location of intense deformation, such as along transform faults/fracture zones, oceanic core–complex fault systems, and lithosphere bending–related faulting at subduction zones (Guillot et al., 2015 and references therein). Hence, most mantle sections are only partly serpentinized and, for this reason, such rocks are generally considered "serpentinized peridotite" or "hydrated peridotite", not serpentinites sensu stricto, in an attempt to emphasize the variable extent of alteration and, importantly, that the event has not fully transformed the protholith into a new rock.

It is to be noted that full serpentinization of peridotite allows H_2O to coexist with solid phases after consumption of high–T mantle minerals (e.g., Atg/Lz–Tlc–H₂O and Atg–Brc–H₂O assemblages colored in blue in Figure 11a), while partial serpentinization does not. In this case, reactions triggered by fluid infiltration consume all H_2O and produce stable assemblages



Figure 9. Samples of the Medellín Metaharzburgitic Unit plotted in the Ol-Opx-Cpx projected from spinel in oxy-equivalent units. Note the area of potentially carbonated (dolomite and/or calcite addition) samples within the group of samples of normal peridotite composition. See Figures 6, 8, and text for further explanation.

made only of solids including those stable at high temperature (e.g., Atg/Lz–Brc–Ol, Atg/Lz–Tlc–Ol, and Tlc–Ol–Opx in the orange region of Figure 11a). In complex natural chemical systems, however, the equilibrium composition of these minerals differs at high– and low–T conditions, but the chemical differences can be subtle (e.g., Mg/(Mg + Fe) and Ni contents in olivine, Ca contents in orthopyroxene) or large (e.g., Al content in orthopyroxene, Al, Ca, and Na content in clinopyroxene). Coupled with the low temperature of transformation, that hampers reaction kinetics and intra–crystalline diffusion, this fact explains the relict presence of high–T mantle mineral composition in partially serpentinized rocks.

A quite different scenario occurs when the temperature of shallow oceanic mantle is higher than 500 °C, above the stability field of antigorite. At these conditions, hydration reactions trigger the formation of other minerals, such as tremolite and talc, which bear much less H₂O (ca. 2 and ca. 4.5 wt %, respectively) than serpentine-group minerals and brucite. The lack of the latter minerals in peridotitic compositions at intermediate temperature conditions allows topological relations that make the maximum hydration of peridotite to involve less than 10 mole % H₂O (i.e., less than 1/3 of the amount needed for full serpentinization). Typically, the amount of H₂O needed for saturation (full hydration) in the simple MgO-SiO₂-H₂O system is less than 5 and close to 0 mole % in harzburgitic and dunitic compositions, respectively (Figure 11b). Hence, during cooling and hydration of shallow oceanic mantle at temperature higher than the stability field of antigorite, the amount of H₂O needed to fully saturate a peridotite rock and to transform it into a new fully hydrated metamorphic rock is much less than the amount needed at conditions of serpentinization. In short, a new fully hydrated rock is more easily formed at intermediate (and high)

V Botero (1963)

Álvarez (1987)

▲ Restrepo (2008)

□ This work

Projection points

Exchange vectors

⊳

Spl

HO

 $TiMgAI_{\cdot 2}$ $CrAI_{\cdot 1}$ $FeMg_{\cdot 1}$ $MnMg_{\cdot 1}$ $Fe = Fe^{2^+} total$

Rodríguez et al. (2005)

Pereira et al. (2006)

Hernández–González (2014)
 González–Ospina (2016)

Botero (1963)

Álvarez (1987) Rodríguez et al. (2005)

Pereira et al. (2006)

Hernández–González (2014) González-Ospina (2016)

Restrepo (2008)

This work

Projection points

Exchange vectors

 ∇

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⊳

Spl

НÖ

TiMgAl.2

CrAL₁

FeMg. MnMg. $Fe = Fe^{2+}$ tota



Figure 10. Samples of the Medellín Metaharzburgitic Unit plotted in the Ol-Opx-Cpx projected from spinel in oxy-equivalent units. The fields of ultramafic rocks of Le Maitre (2002) are indicated. Note that most samples of normal peridotite composition are harzburgite. See Figures 6, 8, 9, and text for further explanation.

temperature than at low temperature upon fluid infiltration (see, for example, Schmädicke, 2000, for moderate- to high-T metamorphic ultramafic rocks).

As for serpentinization, it should be no surprise that high-T mantle minerals coexist metastably with newly formed hydrated minerals at intermediate temperature conditions. At the condition of full hydration, H₂O coexist with solid phases but reactions triggered upon infiltration do not consume all mantle minerals. This is illustrated for the simple MgO-SiO₂-H₂O (MSH) system by the blue Tlc-Ol-H₂O assemblage of Figure 11b. The extreme case is dunite made of 100% olivine in this system, that does not react upon fluid infiltration and no hydrated phase is formed, allowing the stable coexistence of olivine and fluid (i.e., Ol-H₂O tie-line of Figure 11b). Hence, as opposed to serpentinization, olivine in this type of rock is a stable metamorphic mineral and not the result of limited availability of external H₂O. Moreover, during partial hydration due to limited availability of external H₂O, reactions completely consume H₂O and produce stable assemblages made of solids only, including those stable at high temperature (illustrated by the assemblage Tlc-Ol-Opx in the orange region of Figure 11b, MSH system). Partial replacement due to limited availability of H₂O is, likely, the most feasible interpretation for (i) the presence of olivine, orthopyroxene, tremolite, and talc in samples of the San Pedro locality, where the amount of orthopyroxene is small (ca. 2%), and (ii) the rather small amount of tremolite in the fresh orthopyroxene-bearing sample of Chupadero Creek, where talc is not present (Figure 3f). Hence, at least part of the typical high-T mantle mineralogy of ultramafic rocks characterizes intermediate temperature conditions, though the corresponding equilibrium compositions of the minerals are different. As indicated above for serpentinization, the chemGARCIA–CASCO et al.



Figure 11. Hydration in the MgO–SiO₂–H₂O system. Phase relations appropriate for **(a)** serpentinization upon fluid infiltration at low-temperature and **(b)** talc formation at intermediate temperature compatible with the stability of Tr + Tlc + Ol of Figures 12, 13. Upon fluid infiltration, the bulk compositions (dunite, harzburgite, and orthopyroxenite) are displaced towards H_2O -fluid (Fl) until the line of maximum hydration is reached if enough H_2O is available from external sources; otherwise the bulk composition is displaced to an intermediate temperature in fully hydrated rocks and that orthopyroxene is stable in partly hydrated rocks at low and intermediate temperature (i.e., the orange fields of the fluid–absent assemblage Ol + Opx + Tlc where ultramafic rocks totally consume infiltrated H_2O at these conditions). At intermediate temperature, brucite is not stable in peridotitic compositions.

ical differences can be small or large, depending of the solid solution involved but, because temperature is closer to the original mantle temperature, the chemical gap is narrower. This, together with sluggish kinetic factors at moderate temperature, explains the metastable persistence of high–T olivine in fully and partly hydrated metaultramafic rocks.

In conclusion, the name applied to a fully-hydrated intermediate-temperature ultramafic rock should not be biased by the fact that its mineral assemblage contains minerals that characterize its high-T mantle mineralogy, even if the compositions of these minerals have been partly preserved due to sluggish kinetic factors (this concept also applies to any rock formed at high temperature). In our case, the presence of ubiquitous olivine in the Medellín Metaharzburgitic Unit is the consequence of the metamorphic conditions attained (see below) and not necessarily of limited supply of fluid (full hydration was likely attained at intermediate temperature), rendering the term "dunite" incorrect.

During the Tr + Tlc + Ol metamorphic event of the Medellín Metaharzburgitic Unit, compatible with Tlc–Ol–H₂O assemblage of Figure 11b, the equilibrium assemblage in fully hydrated (i.e., maximum hydration) harzburgitic compositions is Tr + Tlc + Ol + Chl + H₂O. This assemblage is shown in the Ol– Opx–Cpx phase diagram projected from chlorite of Figure 12. In the simple CaO–MgO–SiO₂–H₂O system, the corresponding assemblage under the condition of maximum hydration is Tr + Tlc + Ol + H₂O, which is stable at temperature higher than 500 °C and below 650 °C at the moderate to low pressures expected for a shallow suboceanic mantle (Figure 13; Spear, 1995). The presence of widespread chlorite, particularly as concordant deformed bands of tremolite + chlorite schists at the base of the unit in contact with the La Espadera–Chupadero amphibolitic sole, is consistent with this temperature interval, suggesting roughly co–facial assemblages of ultramafic and metabasite rocks at intermediate temperature conditions.

To be noted is that all assemblages indicated in Figure 12 contain chlorite and H₂O (projection points), and that chlorite, instead of spinel, is used as a projection point due to the instability of this phase at temperature lower than ca. 800 °C (Figure 13). This has the effect of modifying the projection of bulk compositions compared to previous diagrams projected from spinel. While most samples undergo subtle displacements because of their low-Al content, the Al-rich samples of non-peridotitic composition are strongly modified. Even if subtle, this effect invalidates the application of the classification scheme of Le Maitre (2002), but it has been retained in Figure 12 for reference. Also, note that at these conditions serpentine-group minerals and orthopyroxene are not stable under the condition of maximum hydration, though Ol and Cpx are (depending on bulk composition). The topology shown (colored tie-triangles) defines all the stable assemblages at these conditions. In addition to the predicted Tr + Tlc + Ol assemblage that characterize almost all rocks of the Medellín Metaharzburgitic Unit, the topology indicates that Ol + Tr + Cpx may characterize some of the analyzed samples. The common lack of Cpx points, in fact, to calcite/dolomite carbonation. In this regard, the bulk



Figure 12. Samples of the Medellín Metaharzburgitic Unit plotted in the Ol–Opx–Cpx projected from chlorite in oxy–equivalent units. Projection from chlorite prevents using the classification scheme of Le Maitre (2002), which is indicated only for reference. Most samples should have developed the Ol + Tr + Tlc assemblage during the Tr + Tlc + Ol metamorphic event, including the carbonated samples (+ magnesite ± dolomite/calcite) some of which plot in the Ol + Cpx + Brc and Ol + Tr + Cpx fields (see text for further explanation). Anthophyllite and antigorite/lizardite are not stable at these conditions.

composition of the Cpx-bearing sample of González–Ospina (2016) is harzburgitic and not compatible with metamorphic clinopyroxene at these conditions (Figure 12), pointing to a relict high–T mantle nature of this phase in this sample.

No matter whether the metasomatic transformation of samples affected by SiO_2 -gain and/or MgO-loss (Figure 5; samples with higher calculated Opx in Figures 8–10) took place during the Tr + Tlc + Ol metamorphic event or during late serpentinization, these samples should have developed the same Tr + Tlc + Ol assemblage of non-altered harzburgite at medium temperature conditions, as predicted in the phase diagram of Figure 12 (note vector "seawater/serpentinization alteration" pointing

away from brucite in this figure). On the other hand, the case of the samples affected by SiO_2 -loss and/or MgO-gain (Figure 5; samples with negative calculated Opx in Figures 8–10) is more complex. If this alteration is due to true SiO_2 -loss and/or MgO-gain involving no carbonation, these samples should contain brucite, i.e., Ol + Cpx + Brc if developed during the Tr + Tlc + Ol event (Figures 12, 13) or Brc + Atg + Cpx if developed during the late serpentinization event (Figure 13). But, if this alteration is apparent and simply due to the effect of magnesite carbonation with little or no true SiO_2 -loss and/or MgO-gain (note vector "magnesite carbonation" towards brucite in Figure 12), the corresponding samples would not have developed the predicted Ol + Cpx + Brc assemblage, but Tr + Tlc + Ol, as other samples discussed above. The fact that the assemblage Ol + Cpx + Brc has not been described in the unit and that Tr + Tlc + Ol-bearing samples contain carbonate strengthens magnesite carbonation as a main process underwent by rocks in the unit. Similarly, the samples that have undergone potential dolomite/ calcite carbonation (Figure 9) would have developed Ol + Tr + Cpx (Figure 12), which is not generally described in the unit. In other words, the silicate mineralogy of carbonated samples during the Tr + Tlc + Ol event would have consisted of this assemblage, which explains the widespread development of this silicate assemblage and the lack of brucite- and clinopyroxenebearing assemblages in the Medellín Metaharzburgitic Unit, even if the composition of many samples project erroneously (as a result of not considering component CO₂ and CO₂-bearing phases) in fields appropriate for their development (note the "likely field of Medellín harzburgite" in Figures 10, 12).

It is apparent that most samples of the Medellín Metaharzburgitic Unit should have developed Tr + Tlc + Ol at intermediate-T metamorphic conditions. Besides the presence of fine-grained recrystallized olivine in many samples, a major point of concern here is that the textural relations of olivine do not generally indicate metamorphic growth and, instead, resembles relict mantle olivine. In order to solve this problem, it should be noted that the influx of external H₂O would have fully consumed Opx (and Cpx, if present) under the condition of maximum hydration, but only a small part of olivine would have been involved in recrystallization as long as this mineral is stable at intermediate-T conditions. As indicated above, it is certainly true that the composition of mantle olivine (in terms of Mg#) should have been readjusted, either by intracrystalline volume-diffusion and/or dissolution-precipitation processes. However, a broad formation of new composition of olivine should not be expected, as the difference in composition of high-T and medium-T olivine is small (basically, a slight change in molar MgO/(MgO + FeO)) and intracrystalline volume diffusion in large relict olivine grains is a sluggish process at medium temperature conditions (Chakraborty, 1997, 2010, and references therein), preventing widespread compositional re-homogenization in larger grains and allowing high-T mantle olivine to persist metastably (see discussion above). Even if detailed petrological work is needed to demonstrate this scenario, we speculate that a significant amount of olivine with slight different compositions developed during the Tr + Tlc + Ol metamorphic event. In this regard, the rock should be termed Tlc + Tr + Ol metaharzburgite, raising the question of the use of metamorphic versus common igneous terminology.

7.2. A Note on IUGS Rules

The recommendations of the IUGS Subcommission on the Systematics of Metamorphic Rocks (Schmid et al., 2007) indicate that only metamorphic ultramafic rocks containing olivine, and/ or pyroxene and/or hornblende such as peridotite, harzburgite, lherzolite, wehrlite, websterite, pyroxenite, and hornblendite should be termed on the basis of mineral content as given by Le Maitre (2002). However, this rule does not apply for other types of rock containing lower temperature minerals, and terms like metaharzburgite, metaperidotite, or metadunite are permitted, implying that the protolith was a harzburgite, peridotite, or dunite and having no implications about the mineral content or structure of the rock, which may or may not have been substantially changed from that of the protolith. In this regard, terms like Tr + Tlc + Ol metaharzburgite are not only permitted, but desirable. Furthermore, the IUGS rules also indicate that the prefix meta "should, of course, only be applied to a protolith name when the protolith can be fully identified by some means". In this respect, our harzburgite compositions deduced by algebraic means perfectly fit the rules.

The IUGS rules recall that the term "ultramafic" refers to the predominance of mafic minerals in a rock and that this adjectival term may be used to name a rock, such as ultramafic Tr + Tlc + Ol granofels, which can also be used to term the studied rocks. However, we prefer to use this adjectival term to describe the geologic unit, not to name rocks. In this regard, our term Medellín Metaharzburgitic Unit, predominantly consisting of harzburgitic granofels and, to a lesser extent of dunitic granofels, does not violate the rules.

7.3. Late Serpentinization

Eventual late hydration during cooling after the Tr + Tlc +Ol metamorphic event allowed serpentinization (Figure 13). Provided that external H₂O is available for full saturation of the rocks at all stages during cooling, the expected sequence of mineral assemblage development is illustrated in Figure 13 as colored tie-triangles. At temperature lower than the Tr + Tlc + Ol event Tr + Tlc is not stable and, for the common harzburgitic composition of the Medellín Metaharzburgitic Unit, talc should have been consumed upon reaction with olivine and initial growth of antigorite. The same applies to Tr + Ol at still lower temperature, and tremolite should have been totally consumed upon reaction with olivine and growth of diopside and additional antigorite. Since tremolite and talc persist, it must be concluded that H₂O availability for full saturation of the rocks during the serpentinization event was limited (Figure 11a). Interestingly, the topology at lower temperature predicts the generalized presence of brucite together with antigorite/ lizardite, even though brucite has not been reported in the Medellín Metaharzburgitic Unit. This is also a likely consequence of limited availability of fluid (see the orange field within the Tlc-Opx-Ol tie-triangle of Figure 11a; see also, for example, Fyfe et al., 1978, their Figure 7.4). However, perhaps a detailed study focused on the metamorphic evolution of the unit would



SiO₂-MgO-CaO-H₂O system (H₂O-saturated diagrams only)

Figure 13. P–T diagram showing relevant reactions (after Spear, 1995) in the CaO–MgO–SiO₂–H₂O system and associated phase diagrams in oxy-equivalent units projected from spinel and chlorite to the right and left of the maximum stability limit of chlorite (light blue curve, schematic), respectively. Note that the phase diagrams do not represent H₂O–subsaturated assemblages. The classification scheme of Le Maitre (2002) is indicated in the diagrams for reference. The assemblages expected for the common harzburgitic composition of the Medellín Metaharzburgitic Unit are indicated (mustard color). Most samples should have developed the sequence of assemblages Ol + En + Tr (partly hydrated sample in Figure 3f) > Tr + Tlc + Ol (Tr + Tlc + Ol metamorphic event, red star) > Ol + Tr + Atg > Ol + Atg + Cpx and finally Atg/Lz + Cpx + Brc (late serpentinization event). The lack of late Cpx and Brc suggests H₂O–subsaturated conditions at this stage. Arrows indicate schematic P–T paths expected for a) static hydrothermal (ocean–floor) metamorphism of oceanic mantle that undergoes extension (i.e., decompression) and cooling in a subduction–initiation related setting. See Figure 14 and text for further explanation.

"discover" this predicted mineral in fully serpentinized samples. Similarly, metamorphic clinopyroxene is predicted below ca. 450 °C. As noted above, the fact that tremolite has been preserved due to limited availability of H_2O for full saturation of the rocks explains this observation, though it should be stressed that the presence of this mineral, together with brucite, is predicted in fully serpentinized samples (Figure 13).

The late talc–forming event recorded in some samples (e.g., Rodríguez et al., 2005) can be explained as a result of the open–system behavior at low temperature. Indeed, talc is expected to form in rocks that underwent intense SiO_2 –gain and/or MgO–loss, as can be deduced in the three phase diagrams below the

antigorite stability field of Figure 13 (i.e., the Atg/Lz–Tr–Tlc assemblage). Note that this process also helps to explain the lack of brucite and clinopyroxene below 450 °C.

8. Tectonic Implications of the Tr–Tlc– Ol Event

Mantle sections of onshore ophiolitic tectonic units do not generally show Tr + Tlc + Ol assemblages of regional extent. They generally show low-T serpentine \pm talc \pm brucite assemblages and only local development of higher-T tremolite. Given the regional extent of the Tr + Tlc +Ol-forming metamorphic im-



Figure 14. Alternative schematic tectonic interpretations of the Aburrá Ophiolite (general geodynamic setting after Spikings et al., 2015). **(a)** Formation in a back-arc scenario followed by static hydrothermal metamorphism, perhaps in a transform-fault setting, which developed Tr + Tlc + Ol assemblage and late serpentinization (path a in Figure 13). **(b)** Subduction initiation in a back-arc setting, likely at a transform-fault, triggered prograde metamorphism of the underriding oceanic crust (La Espadera-Chupadero and El Picacho Metabasites) and extension (decompression), cooling, and hydration of upper-plate mantle (i.e., the Medellín Metaharzburgitic Unit; path b in Figure 13). In both cases, the "Aburrá Ophiolite" would be eventually emplaced onto the Tahamí Terrane upon closure of the back-arc basin.

print in the whole Medellín Metaharzburgitic Unit, we propose that a distinct medium-temperature hydration event took place in the geologic evolution of the associated mantle lithosphere.

This proposal is not to say that the unit underwent prograde metamorphism. As proved by textural analysis, this distinct medium-T metamorphic imprint took place during cooling. However, such event must have to do with an episode of generalized infiltration of H₂O in a broad region. Two main tectonic scenarios (Figure 14) are envisaged in a back-arc region where the protoliths of the Medellín Metaharzburgitic Unit likely formed (Correa-Martínez, 2007; Correa-Martínez & Nilson, 2003; Correa-Martínez et al., 2004; Proenza et al., 2004) in the context of a Permian - Triassic geodynamic evolution of the northwestern corner of Gondwana characterized by the formation of a continental volcanic arc and late extension and rifting of continental crust while the paleo-Pacific ocean subducted below Gondwana (e.g., Cochrane et al., 2014; Riel et al., 2018; Spikings et al., 2015, and references therein). A first scenario is a fracture zone in the back-arc (Figure 14a), where the corresponding shallow mantle would have been relatively hot because ca. 600 °C characterizes the Tr-Tlc + Ol event. Hence, the fracture zone should be relatively close to the spreading ridge where the ultramafic

rocks formed (i.e., the precise location may have been a transform-fault sensu stricto). It should be noted that a fracture zone is a first-order mechanical discontinuity in the lithosphere that may help the process of closure of a back-arc basin and obduction of oceanic mantle onto continental margins (e.g., Stern, 2004). In this context, obduction of Tr + Tlc + Ol metamorphic rocks over the Tahamí Terrane is a likely hypothesis. However, this setting can hardly explain (i) amphibolite facies metamorphic conditions in the basaltic crustal section of the Aburrá Ophiolite (i.e., La Espadera-Chupadero Amphibolites), (ii) prograde metamorphism and generalized hydration plus coeval intense deformation of this basaltic (and plutonic) section, (iii) the tectonic location of the basaltic section below the associated mantle (i.e., Medellín Metaharzburgitic Unit), and (iv) the fact that the metamorphic assemblages of the mantle and basaltic sections of the Aburrá Ophiolite indicate metamorphism at roughly similar temperature, an unexpected feature for a 5-15 km thick crust + mantle section that experiences cooling upon drifting from the corresponding ridge.

Obduction of the Aburrá Ophiolite was only possible after closure of the back-arc basin, implying subduction of a fragment of the back-arc lithosphere and offering an alternative scenario

for metamorphism, hydration, and deformation of all types of rock. Upon subduction initiation, a first frequent step in the obduction process, relatively cold mafic-sedimentary oceanic crust is dragged down into the mantle, resulting in prograde metamorphism and accretion as a medium- to high-grade metamorphic sole made of metabasic and metasedimentary oceanic rocks that may undergo partial melting during emplacement below the ambient hanging-wall mantle (e.g., Boudier et al., 1988; Lázaro et al., 2013; Robertson, 2004; Stern, 2004; Wakabayashi & Dilek, 2003). During this process, the overriding mantle adjacent to the slab experiences extension (i.e., decompression, as a result of trench retreat, e.g., Stern, 2004), cooling (as a result of heat transfer to the underlying crustal section), and hydration (as a result of slab devolatilization). Intense deformation is expected in the volcanic and, to a lesser extent, plutonic crustal section adjacent to the slab-mantle interface, while the mantle section remains relatively less affected by deformation except at its base close to the accreted crust. This general scenario is consistent with observations in the Aburrá Ophiolite. The La Espadera-Chupadero metamorphic sole (Restrepo, 2008) likely developed upon subduction initiation after heating (prograde metamorphism) of the back-arc crust dragged down below the Medellín Metaharzburgitic Unit, which experienced contemporaneous cooling and uplift (Figure 14b). This scenario explains the observed contrasted thermal evolution of the crustal and mantle sections of the Aburrá Ophiolite (i.e., one is heated while the other cools) and the arrival of both sections to roughly co-facial metamorphic conditions. Similar medium-grade metamorphism of ultramafic bodies and associated metabasites worldwide are also explained in the context of subduction, though much higher pressures are observed if accretion takes place at the mature stages of subduction (e.g., Khedr & Arai, 2010). It should be noted, however, that in this model the ultramafic body and amphibolites form part of the overriding and downgoing plates, respectively (Figure 14b), implying that the obducted "ophiolite" (i.e., the Aburrá Ophiolite) does not represent fragments of a former coherent oceanic lithosphere. In this regard, it should not be considered as characterized by the typical Penrose pseudostratigraphy, though the crustal and mantle sections would certainly be closely and, henceforth, petrogenetically related (Figure 14).

It could be argued that both scenarios discussed above are not contradictory and can be merged into a single model, or that a different scenario is possible. However, given the scarcity of detailed structural and petrological data we cannot go further in the analysis of potential geodynamic scenarios in the present contribution. Future work should concentrate in detailed textural–chemical relations (using, for example, XR and EBSD maps), calculation of P–T conditions, structural relations, and geochronology of the different rock types related to the Aburrá Ophiolite. In any case, we note that the term Medellín Metaharzburgitic Unit is still even more appropriate, for it strengthens the view of a distinct tectonic unit affected by geodynamic processes that distorted the mantle geotherm (onset of subduction?), allowed cooling and hydration at medium temperature, and finally resulted in the tectonic emplacement of the ophiolite in the continental margin of Pangea (Figure 14).

9. Conclusions

The rocks that form the Medellín Metaharzburgitic Unit are mostly metaharzburgite and, to a lesser extent metadunite, bearing relict mantle-derived olivine and spinel-group minerals (plus local orthopyroxene), but much of the mineral assemblage is metamorphic made of olivine, tremolite, chlorite, talc, and spinel-group minerals, in addition to lower grade serpentine-group minerals. These associations are not co-facial. The assemblage chlorite + tremolite + talc + olivine indicates medium-grade conditions (ca. 600 °C) at indeterminate to low pressure. However, if anthophyllite forms part of the assemblage, relatively low pressure is anticipated (<6 kbar). The widespread presence of tremolite, talc, and chlorite indicates a distinct thermal/hydration event in the metamorphic evolution of the unit. This metamorphic imprint can be the result of cooling and hydration of oceanic mantle in a back-arc setting before the tectonic processes that finally led to the obduction of the metaharzburgitic unit onto the continental margin of western Pangea. Roughly co-facial metamorphism and strong deformation in associated metabasite rocks point, however, to a complex scenario that likely involved subduction initiation.

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Explanation of Acronyms, Abbreviations, and Symbols:

AtgAntigoriteIATIsland-arc tholeAthAnthophylliteICP-OESInductively coup	iite pled plasma optical pmetry
AthAnthophylliteICP-OESInductively coup	oled plasma optical metry
	ometry
Brc Brucite emission spectro	2
Cal Calcite LOI Loss on ignition	
Chl Chlorite Lz Lizardite	
Chu Clinohumite Mgs Magnesite	
CIPW Cross, Iddings, Pierson, and Washington MORB Mid-ocean ridge	e basalt
CMAS CaO-MgO-Al ₂ O ₃ -SiO ₂ Ol Olivine	
CMS CaO-MgO-SiO ₂ Opx Orthopyroxene	
CNPq Conselho Nacional de Desenvolvimento P Pressure	
Científico e Tecnológico Per Periclase	
Cpx Clinopyroxene Qz Quartz	
Di Diopside Spl Spinel	
Dol Dolomite Tlc Talc	
En Enstatite T Temperature	
Fl H ₂ O-fluid Tr Tremolite	
Fo Forsterite * Total Fe express	ed as FeO
** LOI Loss on ignition	

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