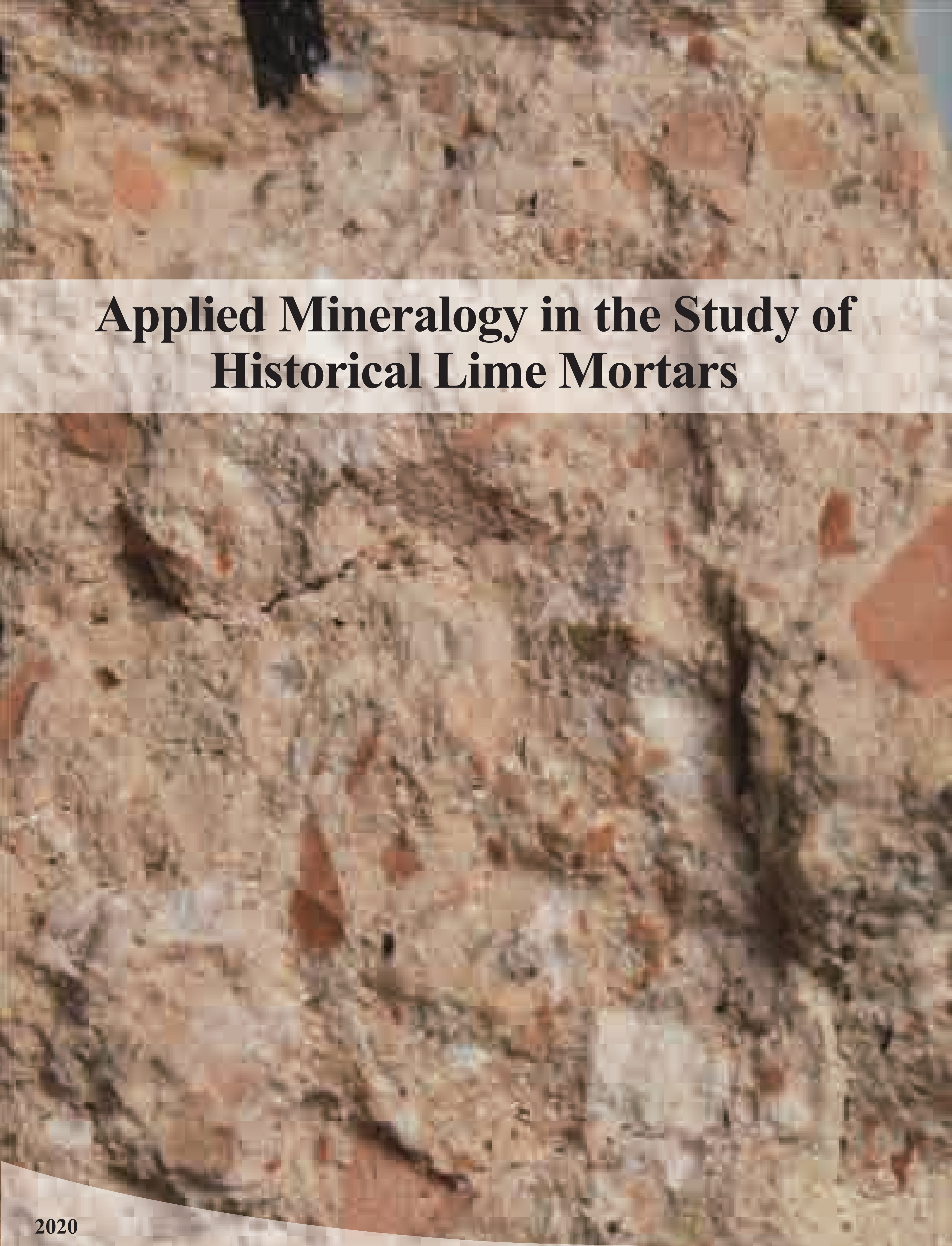

Applied Mineralogy in the Study of Historical Lime Mortars

2020

PhD Thesis

Graciela Ponce Antón

eman ta zabal zazu
Universidad del País Vasco
Euskal Herriko Unibertsitatea

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The pictures on the cover, back cover and spine correspond to lime mortar samples from the cisterns of Irulegi Castle, Amaiur Castle and Portilla Castle, respectively.

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Reserve your right to think, for even to think wrongly is better than not to think at all.

[Defiende tu derecho a pensar, porque incluso pensar de manera errónea es mejor que no pensar.]

Hypatia of Alexandria
ca. 370-415 AD

Acknowledgements
Agradecimientos

El desarrollo de una tesis doctoral nos va empujando hacia un inevitable e inconsciente aislamiento; sin embargo, nunca imaginé que el final de mi tesis doctoral sería escrito durante la cuarentena de una pandemia. COVID-19. Semanas de confinamiento, nerviosismo, incertidumbre y profunda reflexión.

El recuerdo de mi primer dictado me ha acompañado en cada etapa de mi vida, aunque especialmente durante el doctorado, ya que plasma la frustración generada cuando las cosas no salen bien o, mejor dicho, cuando no salen como una hubiera querido. La perfección, una quimera que siempre me ahoga en un vaso vacío.

Ese primer dictado dio paso a otro, y así hasta hacer de la escritura mi más admirado modo de expresión. Sin embargo, en estos algo más de cuatro años he tenido que aprender un nuevo lenguaje, una nueva forma de escribir. Como bien dijo una vez alguien muy querido, he tenido que aprender a *desescribir*. Atrás quedaron las oraciones sin fin, ésas que dejan a una sin aliento, para dar paso a las frases cortas, claras y concisas que exige la escritura académica y científica. Escribir y reescribir en busca de la idea, el concepto, pues lo que en la mente parece cristalino puede vislumbrarse amorfo sobre el papel.

En estas líneas he encontrado el lugar donde dar rienda suelta a la palabra y, valiéndome de ellas, quisiera agradecer a todas aquellas personas que, de una manera u otra, me han acompañado en este apasionante viaje.

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Como peregrina en el camino nunca me hubo de faltar valeriana, amapola, romero, incienso, espliego y jazmín para calmar mis sentidos.

«Oratio vultus animi est»

« Je te le redis, et n'aie plus peur du contraire; si c´était la coutume d'envoyer les petites filles à l'école et de leur enseigner méthodiquement les sciences, comme on le fait pour les garçons, elles apprendraient les difficultés de tous les arts et de toutes les sciences tout aussi bien qu'eux ».

[Te lo vuelvo a decir, y no temas más de lo contrario, que si la costumbre fuera mandar a las niñas a la escuela y enseñarles las ciencias con método, como se hace con los niños, aprenderían y entenderían las dificultades y sutilezas de todas las artes y ciencias tan bien como ellos.]

Christine de Pisan
La Cité des Dames, 1405, Livre I, XXVII

On left, the three Ladies visit Christine in her studio. On right, City Construction. From *La Cité des Dames*, Livre I. National Library of France, Paris. Ms 607, fol.2 r. Master of La Cité des Dames, ca. 1407-149.

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Foreword

This PhD thesis has been accomplished with the research grant from the Basque Country Government PRE-2015-1-0235 in the Department of Mineralogy and Petrology of the University of the Basque Country (UPV/EHU) under the supervision of Dr Maria Cruz Zuluaga and Dr Luis Angel Ortega.

During the research project, a one-month stay was spent in the Department of Mineralogy and Petrology at the University of Granada (Spain) from 1st October until 31st October 2017 to improve formation studies and to acquire knowledge on the study of physical properties of mortars.

The present PhD thesis aims for the 'International Doctorate' distinction, for which a three-months stay was spent in the Department of Geology and Mineralogy at the Åbo Akademi University in Turku (Finland) from 15th February until 16th May 2018.

Most of the results obtained during the research project have been published in JCR-SCI journals even though this dissertation includes unpublished data. The published works are listed below-.

Ponce-Antón, G., Zuluaga, M. C., Ortega, L. A., & Agirre Mauleon, J., 2020. Petrographic and Chemical–Mineralogical Characterization of Mortars from the Cistern at Amaiur Castle (Navarre, Spain). *Minerals*, 10 (4), 311.

Ponce-Antón, G., Zuluaga, M. C., Ortega, L. A., & Mauleon, J. A., 2020. Multi-analytical approach for chemical-mineralogical characterization of reaction rims in the lime mortars from Amaiur Castle (Navarre, Spain). *Microchemical Journal*, 152, 104303.

Ponce-Antón, G., Arizzi, A., Zuluaga, M. C., Cultrone, G., Ortega, L. A., & Agirre Mauleon, J., 2019. Mineralogical, Textural and Physical Characterisation to Determine Deterioration Susceptibility of Irulegi Castle Lime Mortars (Navarre, Spain). *Materials*, 12 (4), 584.

Ponce-Antón, G., Ortega, L. A., Zuluaga, M. C., Alonso-Olazabal, A., & Solaun, J. L., 2018. Hydrotalcite and Hydrocalumite in Mortar Binders from the Medieval Castle of Portilla (Álava, North Spain): Accurate Mineralogical Control to Achieve More Reliable Chronological Ages. *Minerals*, 8(8), 326.

In addition, in this period the following contributions were presented in scientific meetings:

Ponce-Antón, G., Zuluaga, M.C., Ortega, L.A. Petrographic and chemical-mineralogical characterization of plaster and mortar from the Renaissance cistern at Amaiur Castle (Navarre, Spain). *HMC 2019: 5th Historic Mortars Conference*, Pamplona, Spain, 19-21 June 2019.

Alonso-Olazabal, A.; Ortega, L.A.; Zuluaga, M.C.; **Ponce-Antón, G**.; Jiménez Echevarría, J.; Alonso Fernández, C. Roman mortars of floor substrates and walls from Arroyo de la Dehesa de Velasco site: petrographic and mineralogical characterization. *HMC 2019: 5th Historic Mortars Conference*, Pamplona, Spain, 19-21 June 2019.

Ponce-Antón, G.; Zuluaga, M.C.; Ortega, L.A.; Agirre Mauleon, J. XRD, SEM-EDS and µ-Raman spectroscopy for chemical-mineralogical characterisation of reactivity rims in the lime mortars from Amaiur Castle (Navarre, Spain). *TechnArt 2019*, Bruges, Belgium, 7-10 May 2019.

Ponce-Antón, G.; Lindroos, A.; Ringbom, Å.; Ortega, L.A.; Zuluaga, M.C.; Hajdas, I.; Olsen, J.; Agirre Mauleon, J. Comparison of sample preparation methods for radiocarbon dating of mortars. Case study of Irulegi Castle (Navarre, Spain). *MoDIM 2018: Mortar Dating International Meeting*, Bordeaux, France, 25-27 Octobre 2018.

Ponce-Antón, G, Ortega, L.A.; Zuluaga, M.C.; Alonso-Olazabal, Agirre Mauleon, J. Caracterización Arqueométrica de los Morteros del Castillo de Amaiur (Navarra). *XXXVI Reunión de la Sociedad Española de Mineralogía (SEM)*, Oviedo, Spain, 5-7 July 2017.

Resumen

Los morteros constituyen uno de los materiales de construcción más antiguos, utilizados principalmente para conectar elementos de mampostería pero también como soporte para mosaicos y pavimentos o como revoco para proteger y decorar paredes (Borges et al., 2014; Moropoulou et al., 2000).

Un mortero es un material artificial, principalmente compuesto por una mezcla de uno o más conglomerantes (e.g., cal, yeso) y áridos inorgánicos que mezclados con agua, en proporciones adecuadas, dan lugar a un material plástico y trabajable con propiedades de unión. El conglomerante constituye la fase de unión, proporcionando cohesión a través de transformaciones químicas que dan como resultado nuevos compuestos, mientras que los áridos proporcionan estabilidad a la mezcla. Asimismo, para proporcionar propiedades específicas al mortero, diferentes tipos de aditivos orgánicos e inorgánicos pueden ser incorporados a la mezcla.

El empleo de la cal como conglomerante se remonta al Neolítico, aunque el uso de morteros de cal *sensu stricto* tuvo lugar en la Antigua Grecia. Los morteros helenos se caracterizan por una cuidada selección y mezcla de los componentes, así como por una cuidada técnica de aplicación del mismo. Los griegos introdujeron el uso de revestimientos y las técnicas de pulimentado y aplicación en multicapa del mortero. A su vez, los romanos heredaron el conocimiento tecnológico de los griegos en la manufactura de los morteros de cal y mejoraron tanto los procesos de fabricación como las técnicas de aplicación, dando lugar a morteros de gran calidad (Álvarez Galindo et al., 1995; Furlan & Bissenger, 1975; Garofano et al., 2014; Malinowski, 1961, 1979, 1981; Reller et al., 1992). Cabe destacar que en el antiguo Egipto el empleo de la cal como conglomerante fue particularmente escaso, probablemente debido a la escasa disponibilidad de la madera necesaria como combustible para la calcinación de la caliza. Por ello, los egipcios adquirieron un amplio conocimiento en la fabricación de morteros de yeso convirtiéndose así en el tipo de mortero más utilizado en esta época (Álvarez Galindo et al., 1995; Furlan & Bissenger, 1975; Ghorab, 1986; Hewlett, 1998; Martinet, 1992; Ragai, 1988, 1989). Con la caída del Impero Romano, también se perdieron los procedimientos de elaboración de los morteros que no sólo variarían de un lugar a otro y de una época a otra, sino también entre construcciones contemporáneas. La disminución en la calidad de los morteros en la Edad Media se debe al escaso cuidado en la selección de las materias primas y producción de la cal, a la inadecuada proporción y homogeneidad de la mezcla, así como al escaso cuidado en la aplicación final del mortero. Durante la Edad Media no hubo ninguna mejora técnica notable en la elaboración de los morteros; sin embargo, a partir del siglo XII las calidades mejoraron (Álvarez Galindo et al., 1995; Furlan & Bissenger, 1975; Gutiérrez-Solana et al., 1989). El siglo XVIII se caracterizó por el descubrimiento de cales hidráulicas modernas, mientras que el siglo XIX lo hizo por el descubrimiento del cemento Portland (Álvarez Galindo et al., 1995; Ashurst, 1983; Furlan & Bissenger, 1975; Rassineux, 1989).

La elaboración básica de un mortero comienza con el calcinado de la caliza en un horno de cal. En el proceso de calcinación el carbonato cálcico [$CaCO_3$] se descompone liberando dióxido de carbono [CO_2] y formando óxido de calcio [CaO] o cal viva que, posteriormente, es apagada con agua para dar lugar a la formación de hidróxido de calcio [$Ca(OH)_2$]. A continuación, la portlandita o cal apagada es mezclada con áridos y agua para obtener el mortero. El fraguado del mortero tiene lugar por la reacción de la portlandita con el dióxido de carbono atmosférico, formándose nuevamente calcita [$CaCO_3$] (Boynton, 1980). Durante este proceso de carbonatación, el ^{14}C atmosférico es incorporado a la estructura de calcita.

Las materias primas empleadas en la elaboración de los morteros históricos, tanto los áridos como los materiales necesarios para la producción de cal, se tomaban principalmente

de las zonas cercanas a la construcción y, por tanto, están fundamentalmente condicionadas por los materiales geológicos circundantes.

La elaboración básica de un mortero de cal sólo requiere de cal, áridos y agua; sin embargo, estos morteros constituyen un sistema complejo. La amplia variedad de materiales geológicos posibles para su elaboración resulta en diferentes tipos de morteros y, por lo tanto, en una gran variedad de composiciones químicas y mineralógicas.

Cuando se emplean dolomías [$CaMg(CO_3)_2$] o calizas magnesianas como materia prima para la producción de la cal, en el proceso de calcinación se forma una mezcla de cal viva [CaO] y periclasa [MgO] que dará lugar, en el proceso de apagado, a la formación de portlandita [$Ca(OH)_2$] y brucita [$Mg (OH)_2$]. Por lo tanto, al final del proceso de manufactura del mortero el conglomerante no sólo estaría formado por calcita, sino también por una amplia variedad de fases carbonatadas de calcio y magnesio en cantidades variables (Ponce-Antón et al., 2018; Schork, 2012). La dedolomitización de los áridos dolomíticos, con la subsecuente formación de zonas de reacción, produce la incorporación adicional de magnesio al sistema, favoreciendo así la formación de fases carbonatadas de magnesio en el conglomerante (Ponce-Antón et al., 2020). La disponibilidad de magnesio y aluminio en el sistema puede favorecer la formación de hidróxidos dobles laminares (HDL), fases minerales caracterizadas por mostrar propiedades de intercambio iónico. (Evans & Slade, 2006; Forano et al., 2006; Gácsi et al., 2016; Guo & Reardon, 2012; Mills et al., 2012; Miyata, 1980, 1983; Miyata & Okada, 1977; Rosenberg & Armstrong, 2005; Sipos, 2009).

La calcinación de calizas impuras con un contenido en arcilla inferior al 6 % da lugar a la producción de cal aérea, mientras que la calcinación de calizas con un contenido en sílice y alúmina de hasta el 25% produce una cal hidráulica (Henry & Stewart, 2011). El fraguado de la cal hidráulica se produce principalmente por la reacción de la cal con el agua en lugar de con el dióxido de carbono, como ocurre con la cal aérea. Los silicatos y aluminatos reaccionan con la cal en presencia de agua dando lugar a la formación de una amplia familia de silicatos y silicoaluminatos hidratados estables (fases hidráulicas) que confieren hidraulicidad al mortero (Rizzo et al., 2008; Walker and Pavía, 2011). Aunque la producción de cal hidráulica comenzó en el siglo XVIII, desde la antigüedad se han empleado aditivos puzzolánicos (e.g., ladrillos triturados, arcillas calcinadas o material volcánico) para proporcionar hidraulicidad a las mezclas elaboradas con cal aérea, ya que estos materiales reactivos están fundamentalmente compuestos por fases silíceas y aluminosilicatadas (Arizzi & Cultrone, 2012; Baronio & Binda, 1997; Baronio et al., 1997; Stefanidou & Papayianni, 2005; Walker & Pavía, 2011). El material volcánico empleado como aditivo por los griegos es conocido como *Tierra de Santorini*, de la isla griega de Santorini, mientras que los romanos empleaban ceniza volcánica de la región de Pozzuoli, dando lugar al término genérico de *puzolana* para describir a aquellos materiales silíceos o aluminosilicatados reactivos que confieren hidraulicidad al mortero (Álvarez Galindo et al., 1995). Los morteros hidráulicos han sido comúnmente empleados en la construcción de aljibes, estructuras en continuo contacto con el agua, ya que la hidraulicidad del mortero está estrictamente relacionada con su impermeabilidad (Mays et al., 2013; Rizzo et al., 2008; Stefanidou et al., 2014).

Durante la manufactura del mortero pueden tener lugar reacciones álcali-árido (AAR), resultado de la reacción entre los áridos y la cal, entre las cuales se describen las reacciones álcali-sílice (ASR), álcali-silicato (ASSR) y álcali-carbonato (ACR), y que dan lugar a la formación de zonas de reacción en el borde de los áridos (Bonazza et al, 2014; da Fonseca et al., 2018; Galí et al., 2001; García et al., 2003; Hobbs, 1988; Katayama, 2004; Shrimer, 2005).

La disponibilidad de materias primas para la manufactura de los morteros, su fácil elaboración y su durabilidad han hecho de los morteros de cal un material ubicuo en los yacimientos arqueológicos, convirtiéndose así en una importante fuente de información (Boaretto & Poduska, 2013; Kingery et al., 1988). Determinar la cronología de los edificios históricos es uno de los objetivos principales de la arqueología de la arquitectura. Ante la ausencia de registros escritos u otras evidencias arqueológicas que permitan establecer el momento de construcción del edificio, los morteros de cal constituyen un potencial material para evaluar su cronología. El ^{14}C atmosférico es fijado en la estructura de la calcita del conglomerante durante el fraguado del mortero, por lo que la datación por radiocarbono del conglomerante reflejará el momento de construcción del edificio. El estudio de morteros de cal como registro temporal se lleva a cabo desde la década de 1960 (Labeyrie and Delibrias, 1964; Stuiver and Smith, 1965) y desde entonces se han desarrollado varias metodologías y procedimientos de preparación de muestra para aislar la calcita formada durante el fraguado y evitar cualquier contaminación por otras fuentes de carbono (e.g., Folk and Valastro, 1976; Heinemeier et al., 1997; Heinemeier et al., 2010; Lindroos et al., 2007; Marzaioli et al., 2011; Nawrocka et al., 2005; Nonni et al., 2013; Ortega et al., 2012; Ponce-Antón et al., 2018; Sonninen & Jungner, 2001; Van Strydonck et al., 1992).

Dado que los edificios históricos son importantes vestigios del pasado, la caracterización de los morteros de cal históricos también proporciona valiosa información sobre el conocimiento tecnológico en los métodos de elaboración y técnicas de aplicación en el pasado, permitiendo aumentar el conocimiento de la Cultura Material (Izzo et al., 2016; Pecchioni et al., 2006). Desde el descubrimiento del cemento Portland en el siglo XIX, su extendido uso en sustitución de los morteros de cal condujo a la pérdida del conocimiento en los procedimientos de elaboración y aplicación de los mismos (Veiga et al., 2010; Hewlett, 1998; Singh et al., 2015). Además, este tipo de materiales muestra una gran incompatibilidad con los morteros de cal y el resto de materiales de construcción tradicionales tanto desde un punto de vista químico, físico como mecánico debido a su alto contenido en sales solubles, alta impermeabilidad al agua, alto coeficiente de expansión térmica o a la alta resistencia mecánica (Callebaut et al., 2001; Collepardi, 1990; Veiga et al., 2010; Elert et al., 2002; Hansen et al., 2008; Hartshorn et al., 1999; Henry & Stewart, 2011; Holmes & Wingate, 2002; Lanas & Alvarez, 2003; Mosquera et al., 2006; Veniale et al., 2003). Esta incompatibilidad puede causar daños irreversibles, por lo que se desaconseja su uso en la restauración del patrimonio.

La conservación y mejora del Patrimonio Construido requiere de materiales y técnicas adecuadas (ICOMOS, 1975). Sin embargo, los edificios históricos no están tan bien documentados como los modernos, por lo que la caracterización de los morteros históricos es esencial para asegurar un trabajo de conservación adecuado (Groot et al., 2007; Rossi-Doria, 1986; Schueremans, 2011; Van Balen et al., 2005). Desde la adopción de la Carta de Venecia en 1964 y la fundación del Consejo Internacional de Monumentos y Sitios (ICOMOS) en 1975, tanto la caracterización de los morteros de cal históricos como el uso de morteros a base de cal en la conservación de edificios históricos ha ido en aumento. Previamente a la realización de cualquier trabajo de reparación, es necesario realizar la caracterización del mortero de cal histórico en términos de caracterización mineralógica, química, física y mecánica que permita conocer la microtextura del mortero, la naturaleza del agregado y composición del conglomerante, la relación conglomerante/árido, la distribución del tamaño de grano del árido o la porosidad y distribución del tamaño de poro (Schueremans et al., 2011; Groot et al., 2007). Por lo tanto, un buen conocimiento de las características intrínsecas de los morteros históricos es esencial para diseñar un mortero de reparación adecuado que asegure la compatibilidad entre el mortero de reparación y el mortero original, garantizando así la conservación del Patrimonio Construido (Borges et al., 2014; Lanas and Alvarez-Galindo, 2003; Luque et al. 2010; Sandrolini and Franzoni, 2010).

Por otro lado, las características intrínsecas de cada mortero también determinarán su susceptibilidad al deterioro (Ordoñez et al., 1997; Ponce-Antón et al., 2019; Török and Vásárhelyi, 2010). Los morteros de cal históricos son uno de los materiales de construcción más porosos, por lo que la caracterización de su sistema poroso (e.g., tamaño, interconexión y distribución de poro) es esencial para evaluar su susceptibilidad al deterioro (Charola and

Lazzarini, 1986; Hall & Hoff, 2002). El sistema poroso juega un papel importante en la meteorización del mortero ya que determina la circulación y retención de agua dentro del material, haciendo también necesario el estudio de su comportamiento hídrico (Arizzi and Cultrone, 2014; Cultrone et al., 2012; Groot et al., 2007; Molina et al., 2011; Whiteley et al., 1977).

El agua, ya sea en forma líquida o de vapor (e.g., lluvia o humedad), constituye uno de los agentes de meteorización más activos para el patrimonio, dado que favorece los procesos de deterioro químico y físico de los materiales (Kühnel, 2002; Martys and Ferraris, 1997; Van Hees et al,. 2004; Veniale et al., 2008). Cuando el mortero se encuentra expuesto a temperaturas por debajo de los 0 ºC y sus poros están saturados o llenos de agua, ésta cristaliza en hielo aumentando su volumen y provocando, tras varios ciclos de expansión-contracción, el agrietamiento del mortero (Esbert et al., 1991). Por otro lado, el agua meteórica no sólo puede incorporar al interior del mortero especies gaseosas solubles como el CO_2, favoreciendo la disolución parcial de los carbonatos, sino también sales solubles que por evaporación del agua cristalizan y contribuyen al agrietamiento del material (Coussy, 2006; Langmuir, 1997; Marchand et al., 1995;Scherer, 1999; Winkler, 1987). Las condiciones ambientales a las que están expuestos los morteros condicionarán la presencia de agua y, por lo tanto, su proceso de deterioro (Arizzi et al., 2012; Arizzi et al., 2015; Borges et al., 2014; Charola et al., 2004; Cultrone and Sebastian, 2008; Izaguirre et al., 2010).

Así mismo, las condiciones de humedad relativa y temperatura, conocidas como condiciones termo-higrométricas, también influirán en la cristalización de las sales (Benavente et al., 2011; Grossi et al., 2011; Menéndez, 2018). En este sentido, es posible relacionar los tipos climáticos de Kóppen-Geiger con la potencial cristalización de sales, lo que ha dado lugar al desarrollo de métodos de estimación y cuantificación de los daños producidos por su cristalización, de acuerdo con las condiciones climáticas a las que está expuesto el material (Brimblecombe, 2010; Grossi et al., 2011, Menéndez, 2017, 2018). La clasificación climática de Köppen-Geiger define diferentes tipos de clima basándose en los valores medios mensuales de temperatura y precipitación y su influencia en la distribución de la vegetación y la actividad humana (Essenwanger, 2001). De esta manera, los materiales expuestos en áreas con el tipo de clima Cfb (clima oceánico templado totalmente húmedo) son los más susceptibles al daño por cristalización de sales (Brimblecombe, 2010; Grossi et al., 2011; Menéndez, 2017).

La presente tesis doctoral tiene como objetivo contribuir a una mejor comprensión y conservación del Patrimonio Arquitectónico a través de la mineralogía aplicada en el estudio de morteros de cal históricos. Para lograr el objetivo de esta tesis doctoral, se han establecido los siguientes tres objetivos específicos:

1) Evaluar la datación por radiocarbono de morteros de cal históricos a través de una caracterización mineralógica precisa del conglomerante del mortero.

La caracterización mineralógica precisa del conglomerante del mortero permite establecer la distribución del tamaño de partícula de las fases minerales de las que está compuesto y, por lo tanto, permite seleccionar una fracción granulométrica adecuada para su datación por radiocarbono. Para este fin, se ha seguido el procedimiento de extracción descrito por Ortega et al. (2012).

2) Evaluar la susceptibilidad de los morteros de cal históricos al deterioro.

Determinar la susceptibilidad al deterioro de los morteros de cal históricos, no sólo teniendo en cuenta sus características intrínsecas, sino también las condiciones climáticas a las que están expuestos, proporcionará importante información para el diseño de morteros de reparación compatibles.

3) Aproximarse al conocimiento tecnológico relacionado con los procesos de elaboración y técnicas de aplicación de los morteros de cal históricos.

Para abordar estos objetivos, se han estudiado morteros de cal históricos de diferentes estructuras del Castillo de Portilla (Álava), el Castillo de Irulegi (Navarra) y el Castillo de Amaiur (Navarra) en el norte de España.

El muestreo ha sido el primer paso fundamental para realizar una adecuada caracterización de los morteros de cal históricos. Durante el muestreo se han evitado las zonas intervenidas en trabajos de restauración previos para así garantizar la recolección de muestras de morteros históricos originales. La profundidad de muestreo también es un factor importante a considerar, tanto para garantizar el estudio de las características originales de los morteros como para garantizar los resultados de datación por radiocarbono. Por un lado, se ha evitado tomar muestras superficiales con el fin de obtener muestras lo más inalteradas posible, ya que al estar expuestas a los factores ambientales se encuentran más deterioradas. Las muestras superficiales también se han evitado con el fin de impedir la presencia de carbonatos secundarios, formados como resultado de la meteorización del mortero, que darían lugar a resultados de datación por radiocarbono rejuvenecidos. Por otro lado, se ha evitado tomar muestras en las zonas internas de los muros ya que en las zonas internas el mortero carbonata más tarde y, por lo tanto, su datación también daría lugar a edades rejuvenecidas.

Los morteros de cal se han estudiado desde un enfoque multianalítico que ha incluido la microscopía digital, microscopía óptica de polarización, Microscopía Electrónica de Barrido (MEB), Microanálisis por Dispersión de Energías de Rayos-X (EDX), Difracción de Rayos X (DRX), Catodoluminiscencia (CL), Microespectroscopia Raman, Espectroscopía Infrarroja por Transformada de Fourier (FTIR), Análisis Termogravimétrico (TGA), Fluorescencia de Rayos X (FRX), cálculo del índice de hidraulicidad, test de carbonatación y también Espectrometría de Masas con Acelerador (AMS), Porosimetría de Inyección de Mercurio (PIM), ensayos hídricos y de velocidad de pulso ultrasónico y colorimetría.

Los resultados obtenidos han permitido observar que la naturaleza de los áridos de los morteros estudiados difieren en cada edificio histórico. Además, se ha observado que la naturaleza de los áridos también varía según las estructuras del edificio, en función de los requisitos específicos de construcción, como es el caso de los aljibes. Todo ello indica una selección específica de las materias primas.

La preparación de muestra para la datación por radiocarbono de morteros mediante el proceso de sedimentación así como una rigurosa caracterización mineralógica del conglomerante del mortero, han sido esenciales para lograr edades de radiocarbono fidedignas. La caracterización mineralógica del conglomerante, ha permitido detectar fases minerales hidratadas de magnesio en el conglomerante de los morteros del Castillo de Portilla y el Castillo de Amaiur. Entre las fases minerales hidratadas de magnesio detectadas, se ha demostrado que las fases de hidróxidos dobles laminares (HDL) constituyen un contaminante para la datación por radiocarbono de los morteros de cal.

Los resultados obtenidos también han proporcionado información sobre el conocimiento tecnológico, tanto en la elaboración como en las técnicas de aplicación de los morteros de cal históricos. La caracterización de los morteros de cal del Castillo de Amaiur apunta al empleo del método tradicional de mezcla en caliente en la elaboración de los morteros, lo que habría favorecido la formación de una zona de reacción en el borde de los áridos, así como al empleo de la técnica de aplicación en multicapa en los morteros del tanque del aljibe del castillo. Por otro lado, para conferir hidraulicidad a los morteros del tanque del aljibe, y así lograr la impermeabilización de la estructura, se emplearon áridos de rocas aluminosilicatadas, fragmentos cerámicos así como cera de abeja a modo de aditivo orgánico.

La caracterización de los morteros de cal históricos también ha permitido evaluar su susceptibilidad al deterioro. La alta porosidad y capacidad de absorción de agua, la baja interconexión de poros o la dificultad de secado han sido las principales causas de la susceptibilidad al deterioro de los morteros. Las condiciones ambientales a las que están expuestos los morteros de cal estudiados favorecen su meteorización, haciéndolos susceptibles a posibles daños por agua y sales. Además, el presente estudio sienta las bases para el diseño de morteros de reparación que garanticen la conservación del Castillo de Amaiur y el Castillo de Irulegi en futuros trabajos de restauración.

Summary

The present PhD thesis approaches the study of the historical lime mortars from different structures at Portilla Castle (Alava), Irulegi Castle (Navarre) and Amaiur Castle (Navarre) in northern Spain through applied mineralogy.

Lime mortars have been studied by a multi-analytical approach that comprises digital and optical microscopy, Scanning Electron Microscopy, Energy-dispersive X-ray Spectroscopy, X-ray Diffraction, Cathodoluminescence, Raman Microspectroscopy, Fourier Transform Infrared Spectroscopy, Thermogravimetric Analysis, X-ray Fluorescence, Hydraulicity analyses, Carbonation test and also Accelerator Mass Spectrometry, Mercury Intrusion Porosimetry, Hydric and Ultrasonic Pulse Velocity tests and Colourimetry analyses.

Although the basic manufacture of lime mortars only requires lime, aggregates and water, it results in a wide range of mortar types and therefore, in a huge variety of chemical and mineralogical compositions. These variations in mortar composition are related to the raw material used for mortar manufacture, which is mainly conditioned by the surrounding geological materials. It was observed that the aggregates nature in the studied mortars differed in each historical building. Furthermore, it has been seen that aggregates nature also vary depending on the building structures, based on the specific construction requirements, as is the case of cisterns. This points to a specific selection of the raw materials.

Lime mortars are an important source of information at archaeological sites and are therefore a suitable material to establish the chronology of historical buildings. The atmospheric ^{14}C is fixed in the structure of binder calcite during mortar setting and thus the radiocarbon dating of mortar binder will reflect the time when the building was constructed. Sample preparation for mortar radiocarbon dating by the settling process and the accurate mineralogical characterization of mortar binder have been essential to achieve more reliable radiocarbon ages. Through the mineralogical characterization of mortar binder, magnesium hydrated mineral phases have been detected in the binder of Portilla Castle and Amaiur Castle lime mortars. Among the magnesium hydrated mineral phases detected, it has been demonstrated that the layered double hydroxides phases (LDHs) constituted a potential contaminant mineral phase for lime mortar radiocarbon dating.

The obtained results also provided valuable information about technological knowledge in both historical lime mortar manufacture and application techniques. The characterization of Amaiur Castle lime mortars points to the use of the traditional hot-mixing method in the manufacture of mortars, which favoured the formation of a reaction zone around the edge of aggregates. The multi-layering application technique was used in the construction of the Amaiur Castle cistern tank. Ceramic fragments and silico-aluminous rocks aggregates were used as well as the beeswax organic additive in the last pigmented layer of the plaster to confer hydraulicity to the lime mortars of the cistern tank and thus achieve the waterproofing of the structure.

Characterization of historical lime mortars has succeeded in assessing their susceptibility to deterioration. The high porosity and water absorption capacity, poor pore interconnection or difficulty in drying have been the main causes for mortar deterioration susceptibility. Environmental conditions to which the studied lime mortars are exposed also favour mortar weathering, making them susceptible to potential water and salts damage. Furthermore, the characterization of historical lime mortars is also essential to design a suitable repair mortar compatible with the original mortar to ensure historical building conservation. The present study lays the foundations for the design of repair mortars that ensure the conservation of Amaiur Castle and Irulegi Castle in future restoration works.

1. Introduction

1. Introduction

1.1. Historical Background of Lime Mortars

Mortars are one the oldest building materials and have been mainly used to connect masonry elements, but also as supporting materials for mosaics or pavements and as plasters to protect and/or decorate the walls (Borges et al., 2014; Moropoulou et al., 2000).

Mortars are artificial materials primarily composed by one or more inorganic binder, aggregates and other kinds of organic and/or inorganic additives proportionally mixed with water to give rise to a plastic and workable material with bonding properties. Binder constitutes the phase joining the elements in the mixture, providing cohesion through chemical transformations that result in new compounds. Clay, gypsum and lime are the most common binders in historic mortars. Aggregates are inorganic materials whose function is to stabilize the mixture. Aggregates are essentially rocks naturally shattered (e.g. river sands and pebbles) or artificially crushed, but reused components such as ceramic fragments or leftover old mortars have also been used. Aspects such as aggregate size or shape will affect mortar properties. Additives are natural organic and/or inorganic compounds that added to the mixture provide specific properties to the mortars. For historical mortar manufacture, the raw materials, both aggregates and the raw material needed for lime production, were commonly taken from areas near the construction. Therefore, variations in mortar composition will be conditioned by local geology.

The use of lime as a binder goes back to the Neolithic, when the oldest structures with lime are those of Nevari Çori (Turkey) in 10,000-8000 BC and Jericho City (West Bank) in 7000 BC (Furlan and Bissenger, 1975; Malinowski, 1981; Reller et al., 1992).

Nevertheless, the use of lime mortar *sensu stricto* took place in Ancient Greece (Furlan and Bissenger, 1975; Malinowski, 1981). Hellenic mortars are composed by lime and fine sand and are characterized by the careful selection and mixing of mortar components as well as by the careful application technique. At the end of the 2nd century-beginning of the 1st century BC the Greeks began using it as a plaster, also introducing the mortar polishing and multilayer application techniques (Furlan and Bissenger, 1975; Malinowski, 1961, 1979, 1981). Greeks used the “Santorini Earth” additive, a volcanic rock obtained from Santorini Island, to obtain hydraulic mortars and in the absence of volcanic rock crushed bricks were used (Álvarez Galindo et al., 1995).

Romans inherited Hellenic technological knowledge in lime mortar manufacture, improving later both mortar manufacture and application techniques. In the mortars of Ancient Rome, fired clays and volcanic rock from the Pozzuoli deposits, which would give rise to the term *pozzolana*, were added to the lime to obtain hydraulic mortars. The high quality of Roman mortars was based on the careful selection of materials (of aggregates, the raw material for lime production and the use of specific additives), accurate lime production (both during the calcination process and in the slaking process), homogeneity and proportionality of the mixtures and on the careful final mortar application (Álvarez Galindo et al., 1995; Furlan and Bissenger, 1975; Garofano et al., 2014; Malinowski, 1961). According to Roman literature, to obtain high quality lime the calcination of very pure limestone or with a low silica and alumina content was necessary and impure limestones were rejected (Furlan and Bissenger, 1975; Rassineux, 1989).

In Ancient Egypt the use of lime as a binder was particularly scarce, although some works have described the use of lime in Egyptian mortars (Boynton, 1980; Ritchie, 1990; Sersale, 1991). The scarce use of lime mortars in Ancient Egypt could be due to the scarcity of wood in the region, the raw material required as fuel for limestone calcination (Álvarez Galindo et al., 1995; Martinet, 1992). Therefore, the Egyptians acquired extensive knowledge of the manufacture of gypsum mortars, which became the most widely used type in Ancient Egypt (Furlan and Bissenger, 1975; Ghorab, 1986; Hewlett, 1998; Ragai, 1988, 1989).

In the Middle Ages the quality of the mortars decreases, owing to the loss of Roman procedures. Since the fall of the Roman Empire, each country / region followed its own development path, losing the global technical vision that ruled until then. This also affected mortar manufacturing, which changed not only from one place to another and from one time to another, but also between contemporary constructions (Furlan, 1990; Gutiérrez-Solana et al., 1989). Mortar quality decreased due to the lack of care in the choice of aggregates and lime production (both in raw material selection and in the calcination and slaking process), the absence of homogeneous and proportional mixtures and the less careful application of the final mortar (Álvarez Galindo et al., 1995). From the 12th century, mixtures become more homogeneous and the quality of the binders improves again (Furlan and Bissenger, 1975). Nevertheless, in the Middle Ages there was no notable technical improvement in mortar manufacture (Álvarez Galindo et al., 1995).

In the 18th century, the manufacture of modern hydraulic lime began (Álvarez Galindo et al., 1995). For the production of hydraulic lime, limestone blended with clay or limestones with clay content were used (Furlan and Bissenger, 1975; Rassineux, 1989).

The 19th century was characterized by the appearance of Portland cement, named for its similarity with Portland Stone from the Isle of Portland, England. In 1824 the first type of Portland cement was patented, artificial cement obtained by the slow calcination of limestone and clay. In the manufacture of this cement, the limestone was calcined at low temperature and the resulting quicklime is mixed with clay, hydrated and carefully mixed. The resulting mixture is calcined, and then again crumbled and calcined. From 1850 the limestone and clay were ground in a humid mill and subsequently calcined at temperatures between 1300 ºC and 1500 ºC. The resulting quicklime is chemically bonded with the clay, forming a clinker. The clinker was ground and calcined again, and once cooled a small amount of gypsum ($CaSO_4 \cdot ½H_2O$) was added (Álvarez Galindo et al., 1995; Ashurst, 1983; Furlan and Bissenger, 1975).

1.2. Historical Lime Mortar Production

The availability of raw materials for mortar production, their ease of manufacture and their durability has contributed to making lime mortars a ubiquitous material at archaeological sites, thus becoming an important source of information (Boaretto and Poduska, 2013; Kingery et al., 1988).

The basic mortar manufacturing, also known as the lime cycle, begins with the burning of limestone in a limekiln. In the calcination process the calcium carbonate [$CaCO_3$] of the limestone breaks down releasing carbon dioxide [CO_2] to give rise to calcium oxide [CaO] or quicklime. This quicklime is slaked with water forming portlandite [$Ca(OH)_2$]. Portlandite is mixed with aggregates and water to obtain the mortar. The mortar setting takes place by the reaction of the portlandite with atmospheric carbon dioxide, forming again calcite [$CaCO_3$] in the carbonation process (Boynton, 1980). The atmospheric ^{14}C is incorporated into the calcite structure during the carbonation process.

When dolostones [$CaMg(CO_3)_2$] and/or magnesium limestones are used as a raw material in the production of lime the occurred cycle differs from the typical lime cycle (Ponce-Antón et al., 2018; Schork, 2012). By burning a dolostone or a magnesium limestone the resulting lime is composed by a mixture of periclase [MgO] and quicklime [CaO] and thus, as a result of the slaking process portlandite [$Ca(OH)_2$] and brucite [$Mg(OH)_2$] will be formed. Consequently, at the end of the manufacturing process not only calcite is formed but also a wide variety of calcium and magnesium carbonates phases in varying amounts.

By the calcination of limestones with a clay content < 6 %, aerial lime, also called non-hydraulic lime, is obtained. Nevertheless, if limestone blended with clays or limestone containing < 25 % silica and alumina impurities are calcined, a hydraulic lime is obtained (Henry and Stewart, 2011). The hardening of hydraulic lime takes place mainly by the reaction of lime with water instead of with carbon dioxide as happens in aerial lime. The siliceous and/or silico-aluminous phases from the silico-aluminous materials react with slaked lime in the presence of water and form a wide family of stable silicate and/or aluminium silicate hydrated products that confer hydraulic properties to the mortar (Rizzo et al., 2008; Walker and Pavía, 2011). Thus, hydraulic lime can set under water. The amount of silicates and aluminates in the mixture will determine the amount of silicate and/or aluminium silicate hydrated products (hydraulic phases) and thus, the hydraulicity degree of mortar (Henry and Stewart, 2011).

Although modern hydraulic lime production began in the 18th century, the lime used in ancient mortars would have had slightly hydraulic properties since impure limestones also would have been used for lime production (Maurenbrecher, 2004; Vicat, 1997). However, the ancient masons provided hydraulic property to non-hydraulic lime by adding to the mixture pozzolanic components, reactive materials (e.g. crushed bricks, burnt clays or volcanic materials) mainly composed of siliceous and/or silico-aluminous phases necessary for the formation of silicate and/or aluminium silicate hydrated products (Arizzi and Cultrone, 2012; Baronio and Binda, 1997; Baronio et al., 1997; Stefanidou and Papayianni, 2005; Walker and Pavía, 2011).

Hydraulic mortars have been frequently used in the construction of ancient cisterns, the essential structures for water storage, since mortar hydraulicity is strictly related to mortar impermeability and therefore to their resistance to moisture (Mays et al., 2013; Rizzo et al., 2008; Stefanidou et al., 2014).

As a result of a reaction between the siliceous and/or silico-aluminous phases and lime on the edge of pozzolanas, a reaction rim can also be formed (Bonazza et al., 2014). These reactions are known as alkali-silica reaction (ASR) and alkali-silicate reaction (ASSR), a specific type of ASR, respectively (da Fonseca et al., 2018; Hobbs, 1988; Katayama, 2004). The ASR and ASSR have been described within the alkali-aggregate reaction (AAR) a general term that refers to all reactions between the aggregates and the alkalis of binder (Shrimer, 2005). Besides, within the AAR, the alkali-carbonate reaction (ACR) has also been described, such as dedolomitization, a partial dissolution of dolomite that can also give rise to a reaction zone on the edge of aggregate (Galí et al., 2001; García et al., 2003; Shrimer, 2005).

As aforementioned, calcite is not the only carbonate formed during the mortar manufacturing process but also a wide variety of calcium and magnesium carbonates phases can be formed (Ponce-Antón et al., 2018). Aggregate dedolomitization and formation of reaction zones in the dolomitic aggregates lead to higher magnesium content in the system favouring the formation of other magnesium carbonate phases in the binder (Ponce-Antón et al., 2020). When available aluminum is present in the putty and it is combined with magnesium, the formation of hydrotalcite [$Mg_6Al_2(CO_3)(OH)_{16}\cdot 4(H_2O)$] could take place, as well as the formation of hydrocalumite [$Ca_4Al_2(Cl,CO_3,OH)_2(OH)_{12}\cdot 4H_2O$], the calcium analogue of hydrotalcite (Guo and Reardon, 2012; Miyata, 1980; Miyata and Okada, 1977; Rosenberg and Armstrong, 2005; Sipos, 2009). Hydrotalcite and hydrocalumite belong to layered double hydroxide phases (LDHs) that are characterized by showing ion-exchange properties (Evans and Slade, 2006; Forano et al., 2006; Gácsi et al., 2016; Mills et al., 2012; Miyata, 1983).

1.3. Building Heritage: Chronology, Technology and Conservation

Determining the chronology of historical buildings is one of the main goals of building archaeology and, in the absence of written records or other archaeological evidence to establish the first construction period of historical buildings, historical lime mortars become a suitable material for dating.

Lime mortars are a suitable material for dating since they can reflect the building construction time. As noted in Section 1.1 the ^{14}C present in the atmosphere is fixed in the structure of binder calcite during the carbonation process of mortar and therefore the chronology of the building could be known by dating the binder calcite. Radiocarbon dating of historical lime mortars has been carried out since the 1960s (Labeyrie and Delibrias, 1964; Stuiver and Smith, 1965). Thereafter, several methodologies and sample preparation procedures have been developed in order to isolate the calcite formed during mortar hardening and to avoid any other carbon contamination (e.g. Folk and Valastro, 1976; Hajdas et al., 2017; Heinemeier et al., 1997; Heinemeier et al., 2010; Lindroos et al., 2007; Marzaioli et al., 2011; Nawrocka et al., 2005; Nonni et al., 2013; Ortega et al., 2012; Ponce-Antón et al., 2018; Sonninen and Jungner, 2001; Van Strydonck et al., 1992). Besides, isolated lime lumps also have been used for radiocarbon dating (Van Strydonck et al., 1992; Lindroos et al., 2007; Pesce et al., 2009; Pesce et al., 2012). Since calcite is not the only carbonate formed during the mortar manufacturing process, an accurate mineralogical characterization of each studied sample ensuring the selection of the adequate binder grain-size is essential to obtain reliable radiocarbon dates (Ortega et al., 2012; Ponce-Antón et al., 2018). Recently it has been shown that the presence of LDHs in mortar binder constitutes a potential contaminant for lime mortar radiocarbon dating (Ponce-Antón et al., 2018) due to the high CO_3^{2-} anion capture capacity of the LDHs (Miyata, 1983).

Historical buildings are important vestiges of the past and the characterization of historical lime mortars can also provide valuable information about the technological knowledge of the ancient masons, thus improving knowledge of Material Culture (Izzo et al., 2016; Pecchioni et al., 2006). The characterization of lime mortars not only allows to identify the raw materials used in their manufacture but also to assess the traditional production technology and application practices. The lack of knowledge of ancient methods hampers the design of compatible repair mortars (Bonazza et al., 2013). Therefore, the characterization of lime mortars constitutes the basis of suitable heritage conservation work. The presence of reaction zones at the edge of carbonated aggregates has been related to the use of the hot-mixing method in the mortar manufacturing process (Ponce-Antón et al., 2020). The hot-mixing method is a traditional method in which the quicklime is mixed with the aggregates and then slaked and was principally used for mortar manufacture in cold weather or winter work (Copsey, 2019; Forster, 2004; Henry and Stewart, 2011). Mortar manufacture by the hot-mixing method is relatively quick and reduces storage problems (Forster, 2004; Valek and Matas, 2012).

To ensure Built Heritage conservation and enhancement, suitable materials and techniques are required (ICOMOS, 1975). Nevertheless, historic buildings are not as well documented as modern buildings and therefore the characterization of the historical mortar is essential for designing a repair mortar compatible with the historical mortar (Groot et al., 2007; Rossi-Doria, 1986; Schueremans, 2011; Van Balen et al., 2005).

Until the 19th century, the construction of buildings was carried out mainly with lime mortar. However, thereafter lime mortars were gradually replaced by the already widely used Portland cement-based mortars and consequently knowledge of the characteristics and production techniques of lime mortars was lost (Veiga et al., 2010; Hewlett, 1998; Singh et al., 2015). Portland cement-based mortars display great incompatibilities with lime mortars and other traditional masonry elements from a chemical, physical and mechanical point of view (Elert et al., 2002; Hansen et al., 2008; Lanas and Alvarez, 2003). These incompatibilities reside in the high mechanical strength, high thermal expansion coefficient, high water impermeability (both in liquid and vapour form) and the high soluble salt content of cement-based mortars (Hartshorn et al., 1999; Henry and Stewart, 2011; Holmes and Wingate, 2002; Mosquera et al., 2006; Veniale et al., 2003). Therefore, cement-based mortars are considered unsuitable as repair mortar for heritage restoration since they have led to adverse interactions with the lime mortars and other traditional building materials, causing in some cases irreversible damage (Callebaut et al., 2001; Collepardi, 1990; Veiga et al., 2010; Veniale et al., 2003).

However, since the adoption of the Venice Charter in 1964 and the foundation of the International Council on Monuments and Sites (ICOMOS) in 1975, the characterization of historical lime mortars and the use of lime-based mortars for historical building conservation has been increasing. Before performing any repair work, it is necessary to conduct the characterization of historic lime mortar in terms of mineralogical, chemical and physical features, such are the microtexture, aggregate nature and binder composition, binder/aggregate ratio, aggregate grain size distribution, porosity and pore size distribution (Schueremans et al., 2011; Groot et al., 2007). Therefore, good knowledge of the intrinsic features of historic lime mortars is essential to design the most suitable repair mortar, ensuring compatibility between the new and original mortar and avoiding future damage to guarantee Built Heritage conservation (Borges et al., 2014; Lanas and Alvarez-Galindo, 2003; Luque et al., 2010; Sandrolini and Franzoni, 2010).

The intrinsic features of each mortar will also determine their susceptibility to deterioration (Ordoñez et al., 1997; Ponce-Antón et al., 2019; Török and Vásárhelyi, 2010). In this respect, mortar characterization through the porous system (e.g., pore size, interconnection and distribution) is essential to assess mortar durability (Charola and Lazzarini, 1986; Hall and Hoff, 2002). The porous system plays an important role in mortar weathering since it determines water circulation and retention within the material, which makes necessary the study of the hydric behaviour of mortar (Arizzi and Cultrone, 2014; Cultrone et al., 2012; Groot et al., 2007; Molina et al., 2011; Whiteley et al., 1977).

Water either in liquid or vapour form (e.g. rainfall and/or humidity) constitutes one of the most active weathering agents for architectural heritage since it favours physical and chemical processes in the building materials leading in some cases to irreversible damage (Kühnel, 2002; Martys and Ferraris, 1997; Van Hees et al., 2004; Veniale et al., 2008). When mortar is exposed to temperatures below freezing and its pores are full of water, it crystallizes into ice increasing its volume and causing, after several expansion and contraction cycles, the cracking of mortar (Esbert et al., 1991). Besides, meteoric water could not only incorporate into the material gaseous species such as soluble CO_2 that favours the partial dissolution of carbonates but also salts that may crystallize after water evaporation contributing to mortar weathering (Coussy, 2006; Langmuir, 1997; Scherer, 1999; Winkler, 1987). Therefore, the environmental conditions to which mortars are exposed will control mortar deterioration processes due to water (Arizzi et al., 2012; Arizzi et al., 2015; Borges et al., 2014; Charola et al., 2004; Cultrone and Sebastian, 2008; Izaguirre et al., 2010).

Environmental conditions will also will control the crystallization of salts. Related to relative humidity and temperature (thermo-hygrometric conditions), the crystallization of different salts can take place favouring salt weathering (Benavente et al., 2011; Grossi et al., 2011; Menéndez, 2018). Since salt crystallization-dissolution cycles causes serious damage to building materials, methods have been developed in order to estimate and quantify the evolution of salt weathering depending on the local environmental conditions to which the materials are exposed, even relating salt weathering with the Kóppen-Geiger climate types (Grossi et al., 2011; Menéndez, 2017, 2018).

2. Objectives of the Research

2. Objectives of the Research

This PhD thesis aims to contribute towards a better understanding and conservation of Architectural Heritage through applied mineralogy in the study of historical lime mortars.

To achieve the aim of this PhD thesis the following three specific objectives have been set:

1) To assess the radiocarbon dating of historical lime mortars through accurate mineralogical characterization of mortar binder.

   Accurate mineralogical characterization of mortar binder can establish the particle size distribution of the mineral phases of which the binder is composed and thus allow a suitable granulometric fraction to be selected for its radiocarbon dating. To this end, the extraction procedure described by Ortega et al. (2012) has been followed.

2) To assess the susceptibility of historical lime mortars to deterioration.

   Determining the susceptibility to deterioration of historical lime mortars not only taking into account their intrinsic features but also the climate conditions to which they are exposed will provide valuable information for the design of compatible repair mortars.

3) To approach technological knowledge related to the manufacturing processes and application techniques of historical lime mortars.

To address these objectives, lime mortars from three historic buildings have been studied through different case studies, by combining a series of mineralogical, chemical and physical analytical techniques (Section 3).

3. Materials and Methods

3.1. Materials

To conduct the present PhD thesis, historical lime mortars from three different historical buildings have been analysed and studied. Historical lime mortars come from different structures at Portilla Castle (Alava), Irulegi Castle (Navarre) and Amaiur Castle (Navarre) in northern Spain (Figs. 1 and 2). At Portilla Castle the samples were collected from the Tower Keep, East Tower and West Tower (Appendix I.1). Samples at Irulegi Castle were collected from the Tower Keep and from the West perimeter wall (Appendices I.2 and II.1). At Amaiur Castle, samples were collected from the 14th-15th century wall, from the cistern and the rounded structures of the 16th century bastion, from the diamond-shaped structures of the 17th century bastion and from the fill between the 13th-14th and 14th-15th century walls (Appendices II.2, III.1 and III.2).

A total of thirty-five samples of historic lime mortars have been used to achieve the objectives proposed for this thesis (Section 2). Seven lime mortar samples were taken from Portilla Castle (Fig. 3a), nine samples from Irulegi Castle (Fig. 3b) and nineteen samples from Amaiur Castle (Fig. 3c).

Sampling has been a fundamental step to perform successful characterization of the historical lime mortars (Fig. 4). One of the main goals during the sampling has been to avoid the repaired areas in previous restoration works in order to ensure sample collection of historical mortars and not of repair materials. Another goal during sampling has been related to the depth of the sampling. Very superficial sampling would fail to obtain samples that ensured characterizing the original features of the historical mortars since outermost zones can be the most deteriorated due to exposure to environmental factors.

Sampling has also been essential to perform the radiocarbon dating of mortars. To ensure a reliable historical age, the sampling points were selected not only avoiding the external parts of the walls but also the deeper parts. Superficial samples were discarded to ensure mortar samples as unaltered possible since the secondary carbonates formed as a result of mortar weathering would yield younger radiocarbon results. Samples from the inner part of the wall were also avoided since mortar carbonation in deeper parts takes place later and thus also would yield younger radiocarbon results.

Figure 1. Geographic location of Portilla Castle (Alava, Spain), Irulegi Castle (Navarre, Spain) and Amaiur Castle (Navarre, Spain). Modified from Ponce-Antón et al. (2018).

Figure 2. Historical buildings to which the studied lime mortar samples belong. (a) Portilla Castle. (b) Irulegi Castle. (c, d) Amaiur Castle.

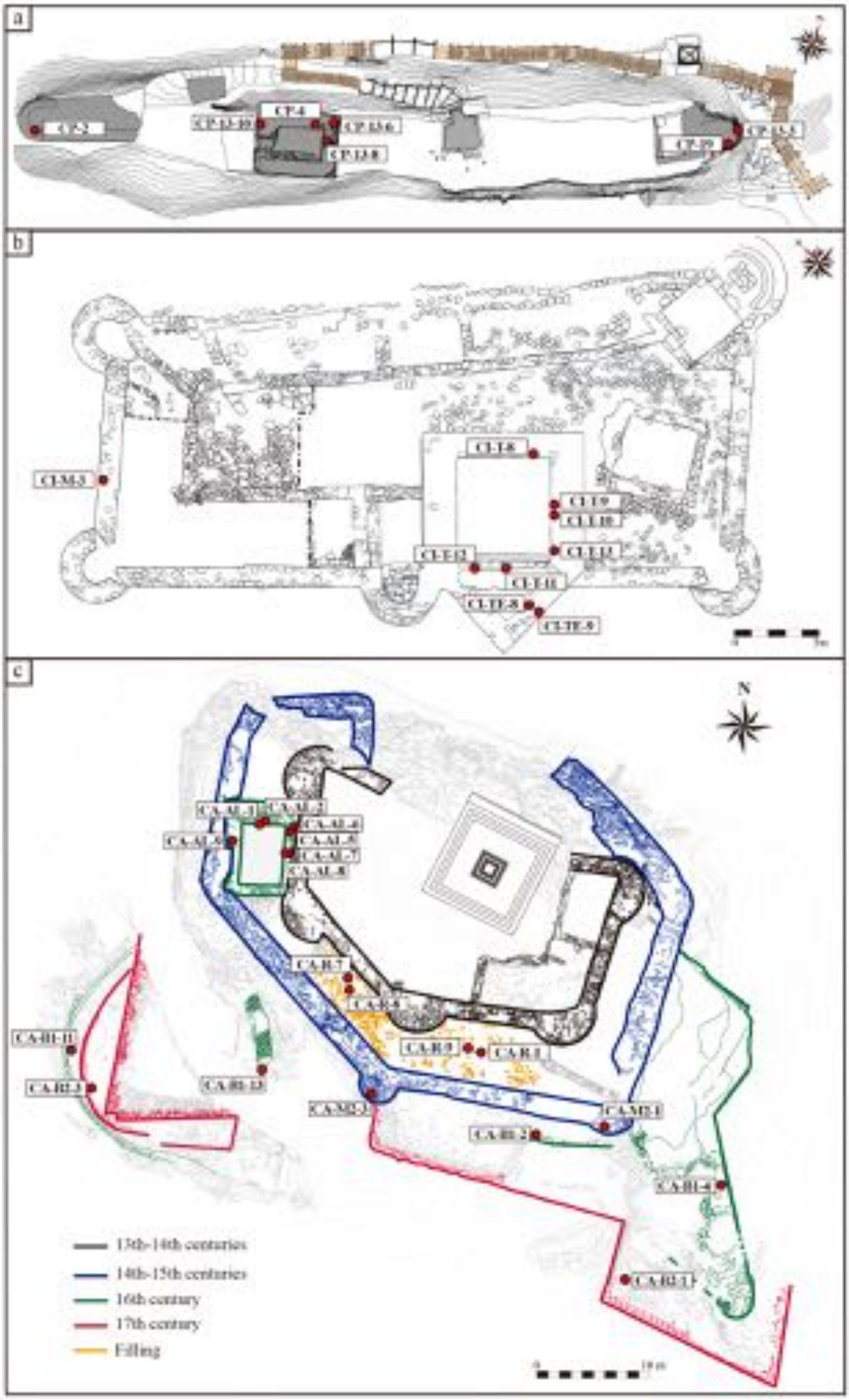

Figure 3. Location of the lime mortar samples at (a) Portilla Castle, (b) Irulegi Castle and (c) Amaiur Castle, modified from Ponce-Antón et al. (2020).

Figure 4. Collecting samples of the historical lime mortars at different archaeological sites.

3.2. Methods

Textural, mineralogical, chemical and physical analyses were conducted in order to characterize the historic lime mortars. The performed techniques are summarized in Figure 5.

Digital Microscopy

Macroscopic high-resolution analysis was carried out on the polished surface of hand mortar sample using a Dino-Lite Premier AM7013MZT digital handheld microscope equipped with a Microtouch II sensor with adjustable polarizer with up to 200× magnification working distance. Measurement and calibration were made with DinoCapture 2.0 software.

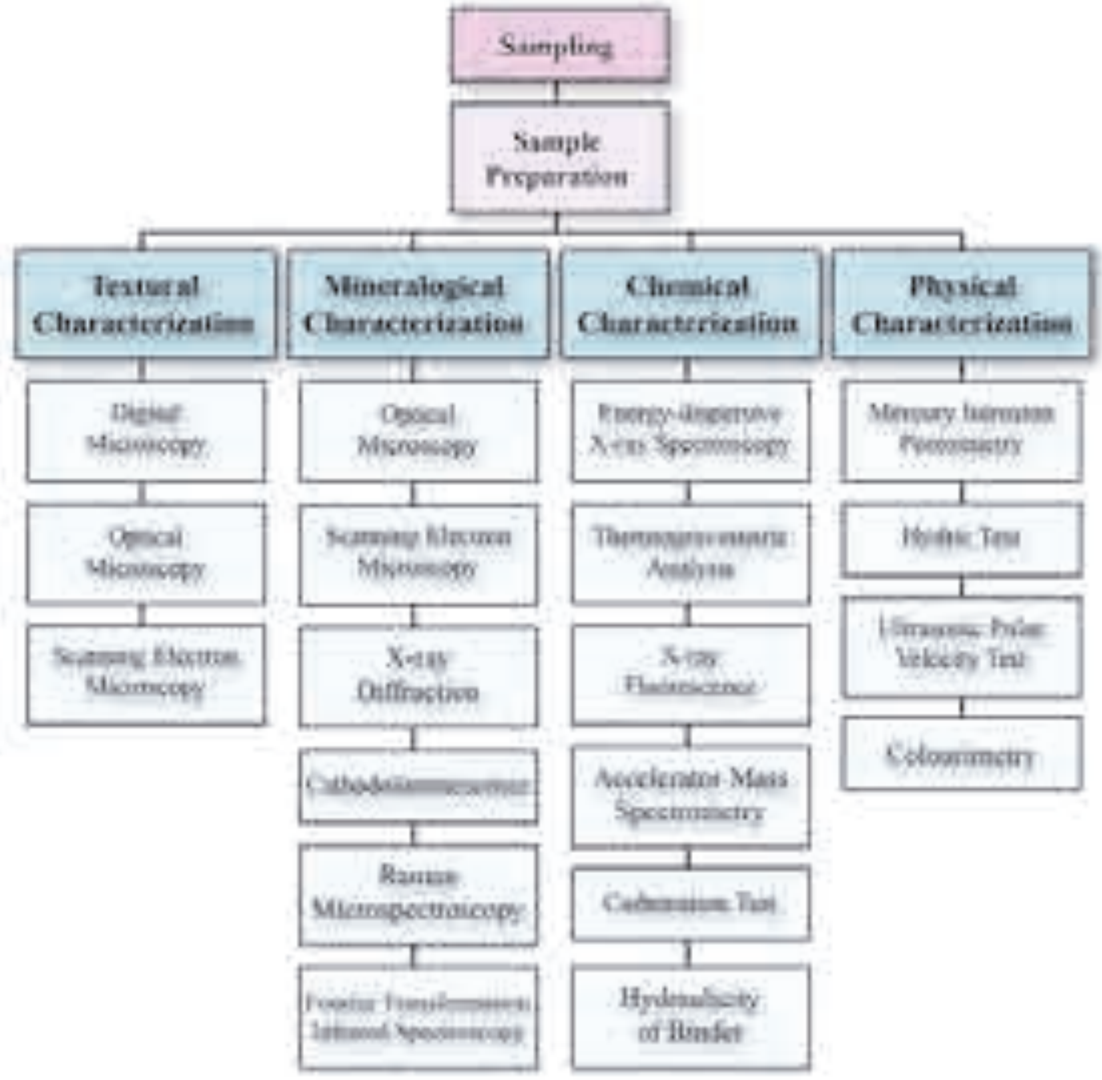

Figure 5. Diagram showing the different analytical techniques used for the textural, mineralogical, chemical and physical characterization of the historic lime mortars.

Optical Microscopy

The mineralogical nature of mortar components was determined on mortar polished thin-sections using a Nikon Eclipse LV100POL optical polarizing microscope equipped with DS F-I1 digital camera and a DS L-2 control unit in both plane and crossed-polarized light modes.

Scanning Electron Microscopy (SEM)

Scanning electron microscopic analyses were carried out on polished thin sections by means of a JEOL JSM-7000F Schottky-type field emission scanning electron microscope (JEOL, Tokyo, Japan). The backscattered electron (BSE) resolution was 3 nm at 15 kV and 10mm working distance.

Energy-dispersive X-ray Spectroscopy (EDX)

Energy-dispersive X-ray spectroscopic analyses were carried out on polished thin sections by means of a JEOL JSM-7000F Schottky-type field emission scanning electron microscope (JEOL, Tokyo, Japan) equipped with an INCA EDX detector X-sight Series Si (Li) Oxford pentaFET microanalysis system.

The EDX mapping measurements were performed on polished thin sections using an EVO 40 scanning electron microscope (Carl Zeiss STS, Germany) coupled to an X-Max energy dispersive X-ray spectrometer (Oxford Instruments, Abingdon, Oxfordshire, UK). The EDX analyses were carried out using a working distance of 8–10 mm, an I Probe of 400 pA, an acceleration potential of 20 kV and 10 scans. Samples were carbon-coated to eliminate charging effects. SEM-EDS measurements were carried out to determine the elemental distribution images in the cross-section of the reaction zone.

X-ray Diffraction (XRD)

The mineralogical phases of both bulk mortar, binder fractions were determined by X-ray diffraction in a powder sample using a Philips X'Pert diffractometer (Malvern PANalytical, Almelo, The Netherlands) equipped with a monocromatic Cu-k$_{\alpha1}$ X-radiation (λ = 1.5405 Å) operating at 40 kV and 20 mA analysis conditions. The data collection was performed by a continuous scan in the range from 5 to 70° 2θ, at an acquisition rate of 0.02° per second. Mineral phase identifications and semi-quantitative calculation were performed with X'Pert HighScore Plus 3.0 software (Malvern PANalytical, Almelo, The Neatherlands) on the basis of the characteristic space of each mineral by reconstructing mineral profiles of the compounds and comparing the experimental peaks with experimental patterns of ICDD and ICSD diffraction databases.

Cathodoluminescence (CL)

Cathodoluminescence was performed in powder sample using a Technosyn Cold Cathode unit–luminescence 8200 MK II attached to an Olympus BH–II microscope equipped with an Olympus Camedia C 7070 camera.

Raman Microspectroscopy

Micro-Raman analyses were performed by means of Renishaw inVia confocal microRaman spectrometer (Renishaw, Gloucestershire, UK) coupled to a DMLM Leica microscope provided with 5×, 20×, 50× and 100× long working distance lenses using 785 nm (NIR) excitation laser. Laser was set at low power (not more than 1mW at the sample) in order to avoid thermal photodecomposition. Spectra were acquired between 1000 and 1120 cm^{-1} with a 1 cm^{-1} resolution and a good signal-noise ratio. Data acquisition was carried out using Renishaw's WireTM 3.2 software package. The interpretation of Raman results was carried out by comparison of acquired Raman spectra with Raman spectra of pure standard compounds collected in the e-VISNICH dispersive Raman database. In order to obtain Raman mapping, the StreamLine technique was used. Internal calibrations and daily calibration with a silicon chip ensured measurement quality.

Fourier Transform Infrared Spectroscopy (FTIR)

Fourier Transform Infrared Spectroscopy by the potassium bromide pellet technique was carried out to determine the nature of the organic compounds using a JASCO 4200 FTIR spectrometer (JASCO INTERNATIONAL CO., Hachioji, Tokyo, Japan) and acquiring spectra between 400 and 4000 cm^{-1}.

To improve the FTIR signal of the organic components an extraction was conducted using 200 µL of dichloromethane organic solvent

Thermogravimetric Analysis (TGA)

Thermogravimetric analyses were performed using a TA SDT 2960 TG-DSC simultaneous instrument (TA Instruments, New Castle, USA). A 5 mg to 7 mg of samples were heated in Pt crucibles at 2 °C min^{-1} from room temperature to 900 °C under a dry oxidizing atmosphere.

X-ray Fluorescence (XRF)

Elemental chemical composition of major elements of bulk mortar was determined in powder sample using a Wavelength Dispersive X-ray Fluorescence (WDXRF) PANalytical Axios Advanced PW4400 XRF spectrometer with 4 kW Rh anode SST-mAX X-ray tube (Malvern PANalytical, Almelo, The Netherlands). Detection limits for major elements are in the range of 0.01 wt %. Fused beads were obtained after melting the powder bulk mortar sample with lithium borate flux (Spectromelt A12, Merck) in approximate 20:1 proportions at ~1200 °C for 3 min in Pt/Au crucibles using a PANalytical Perl'X3 fusion machine. The loss on ignition (LOI) was calculated after heating the powder bulk mortar sample at 1050 °C for one hour.

Accelerator Mass Spectrometry (AMS)

Radiocarbon dating of samples was performed by means of Accelerator Mass Spectrometry. Radiocarbon dating of mortars was performed in the Laboratory for Ion Beam Physics ETH (Zurich, Switzerland) following the procedure described by Hajdas (2008) and in Beta Analytic Inc. (Miami, FL, USA). A charcoal fragment and a tooth found embedded in a mortar sample was dated in the Aarhus AMS Centre (AARAMS), Aarhus University (Aarhus, Denmark). Charcoal was pretreated following the acid-alkali-acid (AAA) method prior to conversion to CO_2 (Bird et al., 1999). To extract the collagen from the tooth to perform the AMS analysis a precleaned ultra-filters of the Millipore Amicon Ultra-4 type with MW=30 kDa were used (Brown et al., 1988).

The ^{14}C ages are reported in conventional radiocarbon years BP (Before Present = AD 1950) according to the international convention (Stuiver and Polach, 1977). Calculated ^{14}C ages were corrected for natural isotopic fractionation based on the $^{14}C/^{13}C$ ratio measurement to be equivalent to the standard $\delta^{13}C$ value of -25‰ VPDB. IntCal13 atmospheric calibration curve (Reimer et al., 2013) was used to calibrate the conventional ^{14}C ages to calendar ages by means of OxCal v4.2.3 calibration software (Bronk Ramsey, 2017). The calibrated age ranges are reported at the 95.4 % confidence level (2σ) calculated by the probability method.

Carbonation Test

The carbonation test was carried out using a phenolphthalein indicator solution (2% in ethanol) for the visual assessment of the carbonation degree of mortar.

Hydraulicity of Binder

To assess the hydraulicity of binder the Hydraulicity Index (HI) (Eq. 1) and Cementation Index (CI) (Eq. 2) were calculated according to Boynton formula (Boynton, 1980; Vicat, 1997). Indices were calculated as below:

$$\mathrm{HI} = \frac{SiO_2 + Al_2O_3}{\mathrm{CaO+MgO}}$$

$$\mathrm{CI} = \frac{2.8SiO_2 + 1.1Al_2O_3 + 0.7Fe_2O_3}{\mathrm{CaO+1.4MgO}}$$

Mercury Intrusion Porosimetry (MIP)

The pore size distribution and the pore volume (open porosity, (P_{MIP})) were determined using a Poremaster-60 GT porosimeter (Quantachrome Instruments), with a maximum injection pressure of 414 MPa, measuring the pore diameter in a range of 0.003 to 360 µm. Mortar fragments of ca. 1 cm^3 were oven-dried for 24 h at 60 °C before the analysis.

Hydric Tests (HT)

To assess the parameters associated to fluid uptake and circulation through the mortar porous system hydric tests were carried out. Measurements were performed under controlled thermo-hygrometric conditions at 25 °C and 50% relative humidity on mortar samples of 3 cm^3 in size, previously oven-dried at 80 °C for 24 h. Due to the archaeological nature of the samples, the hydric assays were performed on no more than two or three samples per mortar type.

The free water absorption (A_b), forced water absorption (A_f, under vacuum) and absorption coefficient (C_a) were determined following the UNE-EN 13755 standard. The degree of pore interconnection (A_x) and the saturation coefficient (S) were also determined. These hydric parameters were calculated as follows:

$$A_b = \frac{M_L - M_0}{M_0} \cdot 100$$

where M_0 is the mass of the dried sample and M_L is the mass of the sample saturated under water at atmospheric pressure (until constant mass is reached),

$$A_f = \frac{M_S - M_0}{M_0} \cdot 100$$

$$A_x = \frac{A_f - A_b}{A_f} \cdot 100$$

$$C_a = \frac{A_b}{\sqrt{t}}$$

where M_S is the mass of the sample saturated with water under vacuum. The absorption coefficient (C_a) is determined as the slope of the curve representing the weight increase as a function of the square root of time 4 min after the beginning of the test.

$$S = \frac{M_{48h} - M_0}{M_s - M_0} \cdot 100,$$

where M_{48h} is the mass of the sample after 48 h immersion in water at atmospheric pressure.

Drying index (D_i) is defined as the definite integral of the drying curve from the beginning (t_0) to the end (t_f) times of the test in which M_t represents a decreasing water weight content starting from the saturation values (under vacuum) as a function of time. The D_i was measured according to the NORMAL 29/88:

$$D_i = \frac{\int_{t0}^{tf} f\,(Mt)\,dt}{M_S \cdot t_f}$$

The capillarity coefficient (C_c) and the capillarity height (H_c) of samples were calculated according to the UNE-EN 1925 standard:

$$Cc = \frac{Mt - M_0}{A \cdot \sqrt{t}},$$

Where M_t is the amount of water absorbed at time t and A is the surface of the sample in contact with the water:

$$H_c = \frac{h}{\sqrt{t}}$$

where h is the height of water rise by capillarity at time t.

Finally, UNE-EN 1936 standard was used to determine the open porosity (P_{HT}) and skeletal (ρ_{Hsk}) and bulk (ρ_{Hb}) densities as follows:

$$P_{HT} = \frac{Ms - M_0}{Ms - M_H} \cdot 100$$

$$\rho_{Hsk} = \frac{M_0}{M_0 - M_H}$$

$$\rho_{Hb} = \frac{M_0}{M_S - M_H},$$

where M_H is the mass of the sample saturated with water under vacuum and weighted in water.

Ultrasonic Pulse Velocity Test (UPVT)

Ultrasonic pulse velocity test stand out for their non-destructive nature. Ultrasonic signals allow to evaluate features concerning the porosity or the anisotropies in the mortar (Malhotra and Carino, 2004).

Ultrasonic wave propagation was measured using a Controls 58-E4800 ultrasonic pulse velocity tester with a non-polarised piezoelectric couple transducers of 54 MHz. A viscoelastic couplant gel (Transonic gel) was used to ensure a good contact between the transducers and the mortar sample. Measurements were performed under controlled thermo-hygrometric conditions at 25 °C and relative humidity of 50% on samples of 3 cm^3 in size. Samples were previously oven-dried at 80 °C for 24 h. The propagation velocity of ultrasonic primary wave (V_p) was calculated following the ASTM D 2845-05 standard and the V_p values were used to calculate the structural anisotropy (ΔM) as follows:

$$V_p = \frac{L}{T}$$

where V is the pulse-propagation velocity in m/s, L is the pulse-travel distance m and T is the effective pulse-travel time in s,

$$\Delta M = \left(1 - \frac{2V_{pmin}}{V_{pmax} + V_{pmean}}\right) \cdot 100,$$

where V_{pmax} is the mean maximum velocity, V_{pmin} is the mean minimum velocity and V_{pmean} is the mean intermediate velocity in each of the three orthogonal directions.

Colourimetry

The colour of samples was measured according to the CIELAB colour space according to the UNE-EN 15886 standard. Konica-Minolta CM-700d portable spectrophotometer was used to measure the lightness (L*) and chromatic (a*and b*) parameters under measurement conditions of 8 mm diameter, 10° view angle, D65 standard illuminant, with SCI/SCE modes and 400–700 nm wavelength range. Colour measurements were performed in five different points for each mortar sample to calculate the mean value of each parameter.

Digital and optical microscopy was performed at the Department of Mineralogy and Petrology at the University of the Basque Country (UPV/EHU).

Polished thin-sections were made in the Sample Preparation Laboratory of the Department of Mineralogy and Petrology at the University of the Basque Country (UPV/EHU).

The CL analyses were performed in the Geology and Mineralogy Department at the Åbo Akademi University (Turku, Finland) and in the Department of Mineralogy and Petrology at the University of the Basque Country (UPV/EHU).

The XRD, XRF, SEM-EDX, FTIR and Raman microspectroscopy analyses were conducted in the Materials and Surface Unit and the Raman-LASPEA laboratory in the Advanced Research Facilities (SGIker) of the University of the Basque Country (UPV/EHU).

The TGA were performed in the Department of Organic Chemistry at the University of the Basque Country (UPV/EHU).

The AMS analyses of mortar samples were carried out in the Laboratory for Ion Beam Physics ETH (Zurich, Switzerland) and in Beta Analytic Inc. (Miami, FL, USA) whereas AMS analyses of a charcoal fragment and tooth were performed in the Aarhus AMS Centre (AARAMS), Aarhus University (Aarhus, Denmark).

Powder sample preparation for chemical-mineralogical analyses was done in the Clay Minerals Laboratory at the University of the Basque Country (UPV/EHU) (Leioa, Spain). Sample preparation for mortar radiocarbon dating was also performed in the Geology and Mineralogy Laboratory at the Åbo Akademi University (Turku, Finland).

The MIP analyses were carried out in the Thermal Analysis and Porous Solids Unit in the Area of Scientific Instrumentation at the University of Alicante.

The HT, UPVT and colorimetry measurements were performed in the Department of Mineralogy and Petrology at the University of Granada.

Sample preparation for the HT, UPVT and colorimetry measurements was carried out in the Sample Preparation Laboratory of the Department of Mineralogy and Petrology at the University of the Basque Country (UPV/EHU).

4. Geological Setting

4. Geological Setting

Historical buildings to which the studied lime mortars belong are located in the north of the Iberian Peninsula (Fig. 1).

Geologically, Portilla Castle is located on the southern edge of the Basque-Cantabrian Basin (Fig. 1). The Basque-Cantabrian Basin is bounded by the Basque Massifs (Cinco Villas and Alduides) to the east, by the Asturian Massif to the west and by the Ebro and Duero Basins through the Sierra de Cantabria-Montes Obarenes Thrust to the south (Fig. 2). The Basque-Cantabrian Basin is constituted by Mesozoic and Cenozoic materials. Within the Basque-Cantabrian Basin, Portilla Castle is located in the west of the Sierra de Portilla on the north flank of the Ocio Anticline (Figs. 3 and 4). The Ocio Anticline is a north-vergent dome-anticline with a partial thrust in the inverted northern flank, located in the outermost area of the folded band of the Sierra de Cantabria. The regional geology of the area in which Portilla Castle is located consists of sedimentary materials from the Upper Triassic to Holocene (Fig. 3). Triassic is represented by clays, gypsum and halite (Keuper Facies). Jurassic is very poorly represented and mainly constituted by calcareous breccia, dolostones and limestones. Cretaceous is mainly represented by carbonated materials, limestones and marls and to a lesser extent by sandstone and dolostones. While the Paleogene and Neogene materials are characterized by conglomerates and sands; gravels, sands, silts and clays characterize the Quaternary materials (Garrote Ruiz et al., 1994; Martín-Alafont et al., 1978; Portero Ruiz et al., 1979). Portilla Castle is built on Paleocene limestones, dolostones and sandy limestone and/or sandstone intercalations (Fig. 4).

Figure 1. Simplified geological map showing the Basque-Cantabrian Basin, Jaca-Pamplona Basin and Pyrenees. Modified from Silva-Casal et al. (2019).

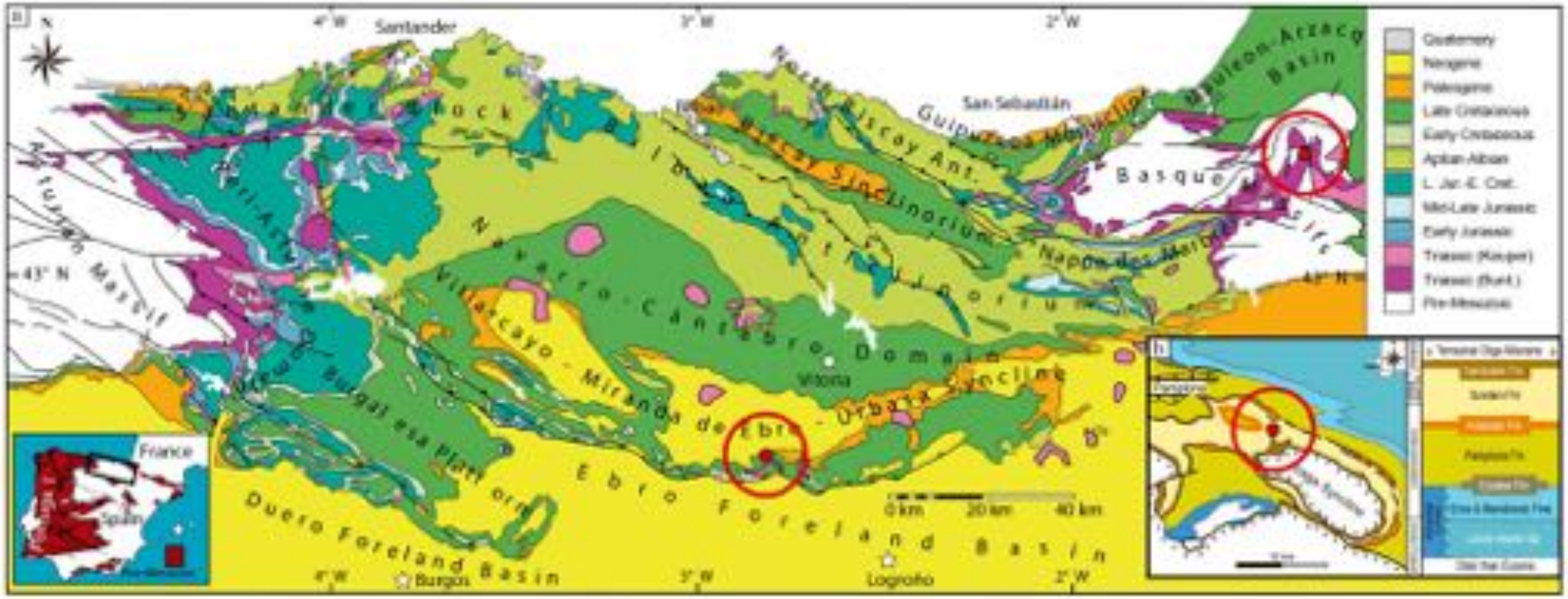

Figure 2. Geological Sketch map showing the Basque-Cantabrian Basin, Jaca-Pamplona Basin, Pyrenees and Ebro and Duero Basins. Modified from (a) Abalos (2016) and (b) Astibia et al. (2016).

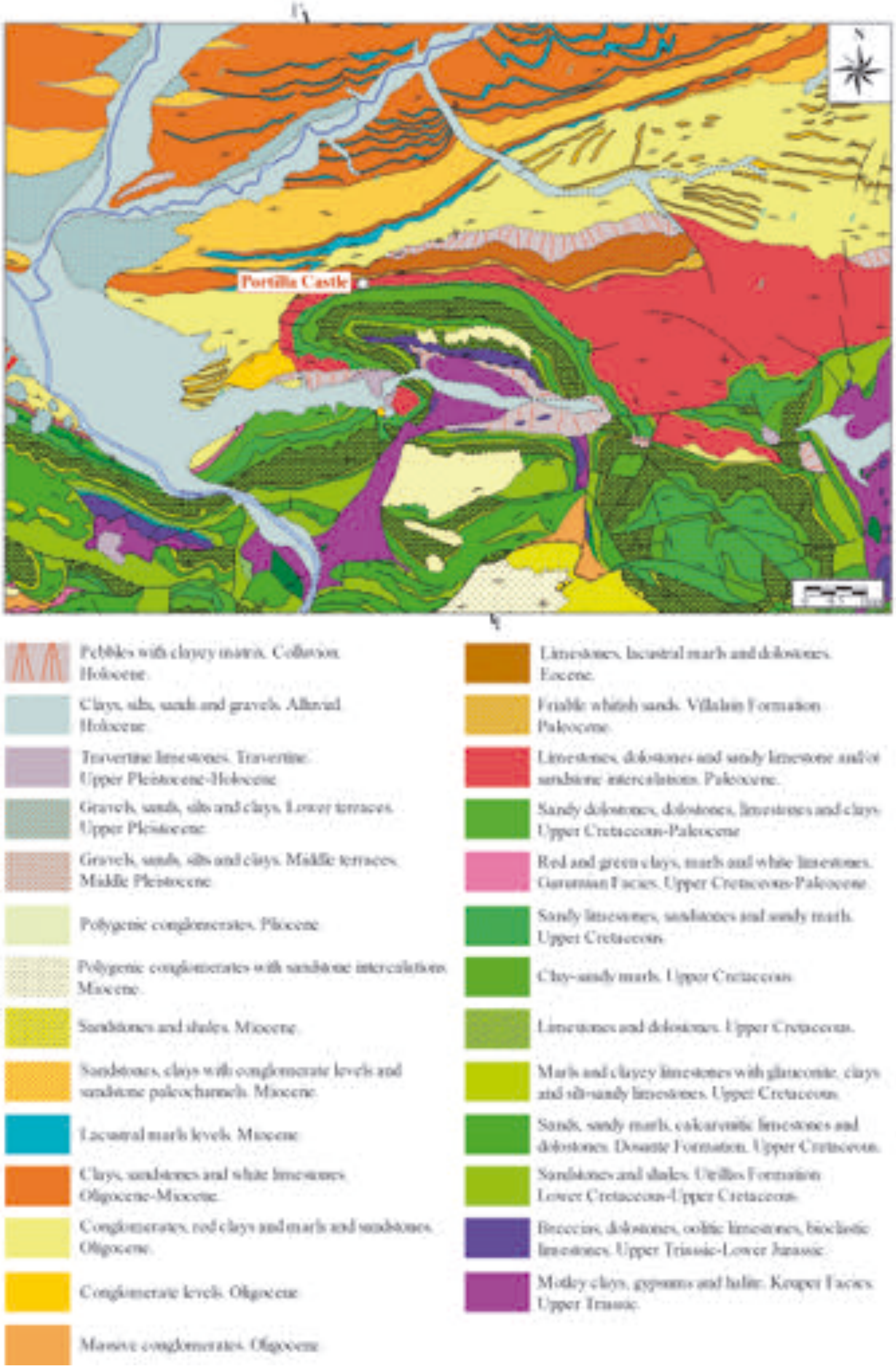

Figure 3. Geological map showing the regional geological materials of the area in which Portilla Castle is located. Modified from GEODE, Digital Geological Cartography of IGME.

Figure 4. Geological cross-section of Section I-I´ in Figure 3. On the right, Portilla Castle's location on top of the north flank of the Ocio Anticline. Modified from Garrote Ruiz et al. (1993).

Irulegi Castle is located in the western zone of the Jaca-Pamplona Basin (Fig. 1). The boundaries of the Jaca-Pamplona Basin are defined to the north by east-west structures originated by the Roncesvalles Thrust, by the Ebro Basin through the Sierra de Alaiz Thrust to the south, by the Pyrenean structures to the east and by the Estella Fault to the west (Fig. 2). The oldest materials that outcrop in this area correspond to limestones, dolomites and sandy limestones of the Cretaceous in platform facies. The Eocene outcrops on these materials, mainly characterized by limestones and platform or distal ramp marls to the south and by turbidites formed by marls, sandstones and limestones to the north. Quaternary materials are represented by fluvial, sandy and conglomeratic materials. Sedimentary materials from the Middle Eocene to Holocene dominate the regional geology of the area in which Irulegi Castle is located (Fig. 5). Eocene materials are represented by sandstones, calcareous breccias, calcarenites and marls, and the Oligocene by sandstones and silts. The Pleistocene is characterized by terraces of gravels, sands, silts and clays and the Holocene by clays, silts, sand and gravel alluvial materials (del Valle de Lersundi, 1978; García de Domingo et al., 1993; García Sansegundo et al., 1993; Puig de Fábregas et al., 1978). Irulegi Castle is built on the Upper Eocene marls and sandstones

Amaiur Castle is geologically located at the western end of the Pyrenean Axial Zone, part of the Western Pyrenees Domain and the Basque Massifs (Figs. 1 and 2). In this area, a wide representation of Paleozoic materials outcrops as well as Triassic Mesozoic materials, while the Quaternary materials are scarcely represented. The Paleozoic is represented by materials from the Ordovician to the Carboniferous, characterized by metamorphic materials, mainly by schist and quartzites, and scarcely represented limestones and dolomites. The Permian is represented by a great complex lithofacies formed by a sequence of carbonated breccias, slate breccias, limestones and sandtones. The Triassic is characterized by conglomerates and red sands of the Buntsandstein Facies, by dolomitic limestones and dolostones of the Muschelkalk Facies and by the mottled clays with gypsum levels of the Keuper Facies. Subvolcanic basic rocks known as ophites outcrop associated with the Keuper Facies. Quaternary materials are represented by alluvial clays, silts, sand and gravel and colluvial pebbles of the Holocene (Galán Pérez et al., 2002; Juch et al., 1974). All the materials described above outcrop in the area where Amaiur Castle is located (Fig. 6). Amaiur Castle is built on the Triassic limestones and dolostones.

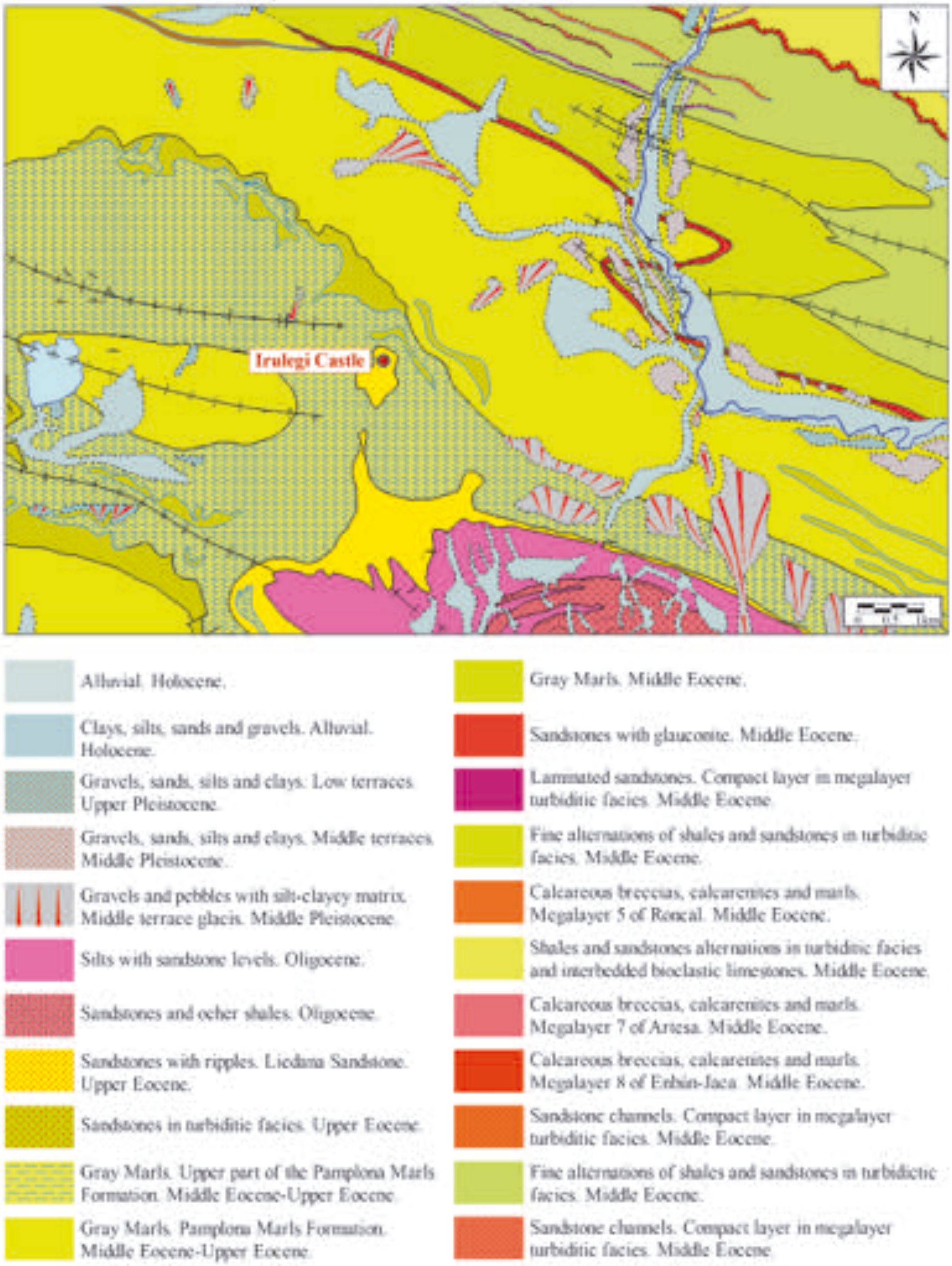

Figure 5. Geological map showing the regional geological materials of the area in which Irulegi Castle is located. Modified from GEODE, Digital Geological Cartography of IGME.

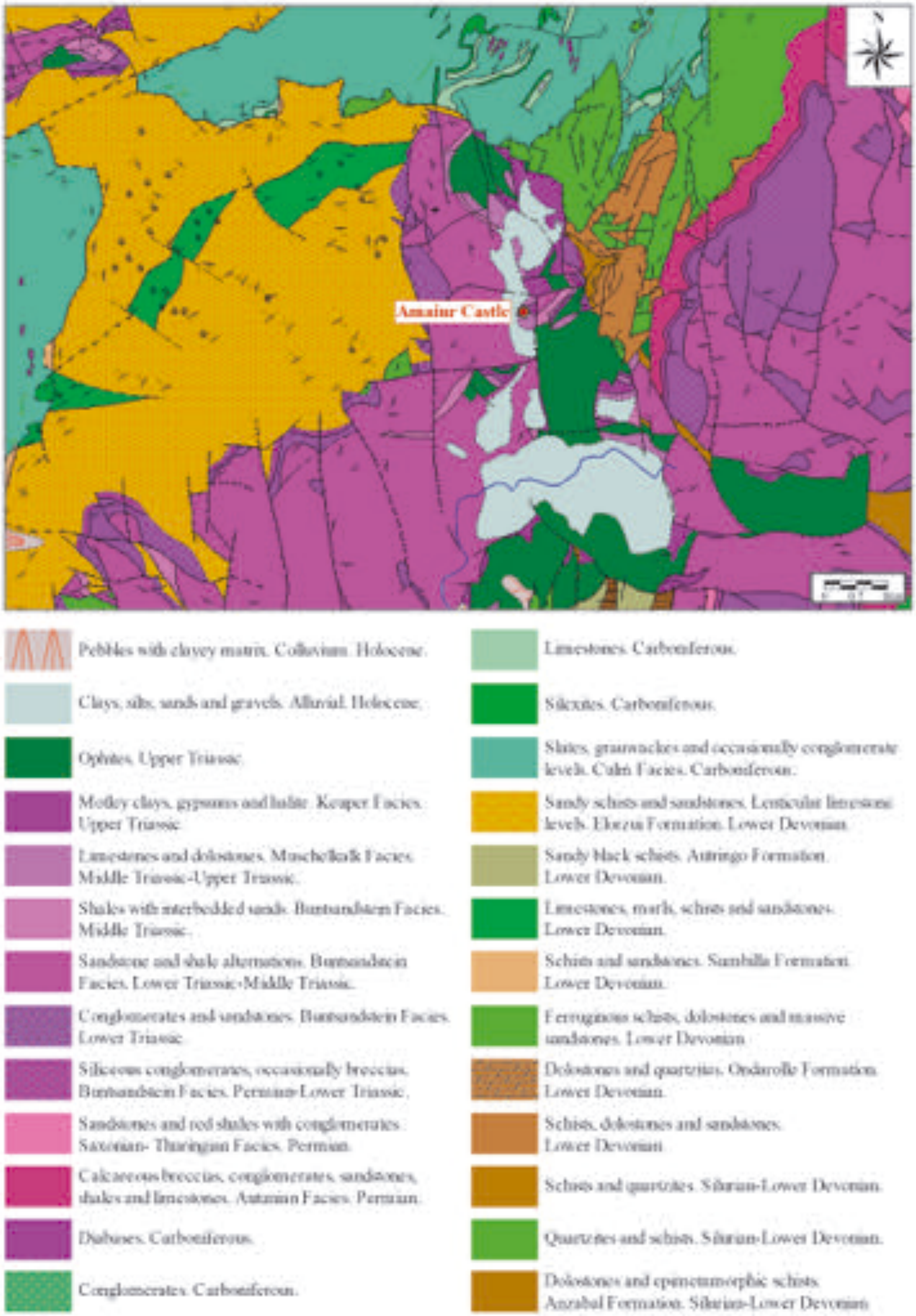

Figure 6. Geological map showing the regional geological materials of the area in which Amaiur Castle is located. Modified from GEODE, Digital Geological Cartography of IGME.

5. Concluding Remarks

5. Concluding Remarks

The basic manufacture of a mortar only requires three components: lime, aggregates and water. However, mortars constitute a complex system. The variety of available raw materials for the production of lime and aggregates, mostly conditioned by local geology, results in a wide range of mortar types and therefore, a huge variety of chemical and mineralogical compositions as well as physical and textural features.

The main results of this research have been discussed throughout the six main chapters presented as an appendix section (following the Regulations Governing the Management of Doctoral Studies). However, some concluding remarks will be conducted.

Regarding the mixing proportions of historical lime mortar, the proportions found in the studied historical lime mortars are in accordance with those described in the literature. Several authors have found that the binder/aggregate ratio in historical lime mortars was often of 1:1 or 1:2 (e.g. Elsen, 2006; Holmes and Wingate, 2002; Leslie and Hughes, 2002). Historical lime mortars from Portilla Castle, Irulegi Castle and Amaiur Castle show a binder/aggregate ratio between 1:2 and 1:1, except in the inner layer of the cistern plaster at Amaiur Castle which shows a binder/aggregate ratio of 2:1.

Petrographic studies also show that raw materials used as aggregates in the manufacture of the lime mortars at Portilla Castle, Irulegi Castle and Amaiur Castle came from the surrounding geological materials (Section 4). Aggregates in the Portilla Castle mortars could be related to Cretaceous and Paleogene sandstones and carbonated rocks, those in Irulegi Castle mortars to Eocene calcarenites, sandstones and marls, and those in Amaiur Castle mortars to Paleozoic metamorphic materials and to Triassic dolostones and subvolcanic basic rocks.

The presence of hydrotalcite [$Mg_6Al_2(CO_3)(OH)_{16}\cdot4(H_2O)$] and hydrocalumite [$Ca_4Al_2(Cl,CO_3,OH)_2(OH)_{12}\cdot4H_2O$] in the binder of Portilla Castle mortars pointed to the use of impure limestones and/or partially dolomitized limestones for the production of lime (Ponce-Antón et al., 2018, Appendix I.1). Remains of unburned or partially burned rock fragments also could allow to identify the raw material used for lime production if the fragment preserved the original texture of the rock, allowing its identification in the surrounding geological materials. The partially burned rock fragments found in the lime mortar at Portilla Castle correspond to oolitic limestone fragments, which are related to Upper Triassic-Lower Jurassic materials outcropping in the surrounding geology (Fig. 3 in Section 4 and Fig. 4b in Appendix I.1). Therefore, these characteristics would point to the use of Upper Cretaceous limestones and/or Upper Triassic-Lower Jurassic limestones for lime production at Portilla Castle. The identification of hydrotalcite in the binder at Amaiur Castle mortars also points to the use of impure limestones or partially dolomitized limestones as raw materials for lime production. Besides, hydromagnesite also was identified in the binder of a few samples (Appendices II.2, III.1 and III.2). Hydromagnesite can be formed in mortars made with dolomitic lime but has not always been identified (Arizzi and Cultrone, 2012b; Bruni et al., 1998; Dheilly et al., 1999; Montoya et al., 2003). The dedolomitization of the dolomitic aggregates in Amaiur Castle mortars added a greater amount of magnesium to the system, hindering the determination of the amount of magnesium from the lime used in the mixture. This input of magnesium to the system could have favoured the formation of a greater amount of hydrotalcite than detected in the binder of Portilla Castle mortars, besides the formation of hydromagnesite. This magnesium input into the system could have made the system work as it would have done using a dolomitic lime and thus, having used dolostones for the lime production. Nevertheless, in the current stage of research it is difficult to define the type of raw material used for lime production at Amaiur Castle. However, the absence of magnesium phases in the binder of the Irulegi Castle mortars could indicate the use of limestones with low magnesium content for lime production, pointing to the Middle Eocene limestones that outcrop in the surrounding geological materials. Nevertheless, the use of Upper Cretaceous limestone cannot be ruled out.

Furthermore, the presence of magnesium in the lime due to the use of impure limestones for lime production as well as the use of reactive aggregates in the mixture could have furnished the binder of ancient mortars with a feeble hydraulic nature (Henry and Stewart, 2011; Maurenbrecher, 2004; Pavía et al., 2005; Pavia and Caro, 2008; Vicat, 1997). Besides, the hot-mixing method also could have favoured the activation of a weak pozzolanic potential of some of these reactive aggregates (Henry and Stewart, 2011). Both of these aspects were involved in the mortars from Amaiur Castle.

Furthermore, the environmental conditions in which historical lime mortars are located will condition their deterioration process. According to the Koppen-Geiger climate classification, the areas that the studied materials come from (Fig. 1) are characterized by: (a) warm-summer Mediterranean climate, a temperate climate with dry and temperate summer (Csb) at Portilla Castle, (b) temperate oceanic climate, a temperate fully humid climate with two dry months and temperate summer (Cf2b) at Irulegi Castle, (c) temperate oceanic climate, a temperate fully humid climate without a dry season and temperate summer (Cfb) at Amaiur Castle (Chazarra Bernabe et al., 2018; AEMET and IM, 2011). Köppen-Geiger climate classification establishes different climate types based on the monthly average values of precipitation and temperature according to their influence on vegetation distribution and human activity (Essenwanger, 2001). Table 1 shows annual average thermo-hygrometric and rainfall data in the studied areas.

Table 1. Annual average thermo-hygrometric and rainfall data at Portilla Castle, Irulegi Castle and Amaiur Castle (Arizkun; Beortegi GN; Euskalmet; Gorramendi). KGC = Köppen-Geiger climate, T= temperature, T_{min} = minimum temperature, T_{max} = maximum temperature, RH = relative humidity, RH_{max} = maximum relative humidity, PCPT: precipitation.

	KGC	T (ºC)	T_{min} (ºC)	Absolute T_{min} (ºC)	T_{max} (ºC)	Absolute T_{max} (ºC)	RH (%)	RH_{max} (%)	PCPT (mm)
Portilla Castle	Csb	12.9	7.8	-	18.8	-	76.2	82	635
Irulegi Castle	Cf2b	11.8	6.5	-12.4	17.8	39.9	75.8	85	858
Amaiur Castle	Cfb	12.9	7.5	-19	18.5	41	83.4	86	2040

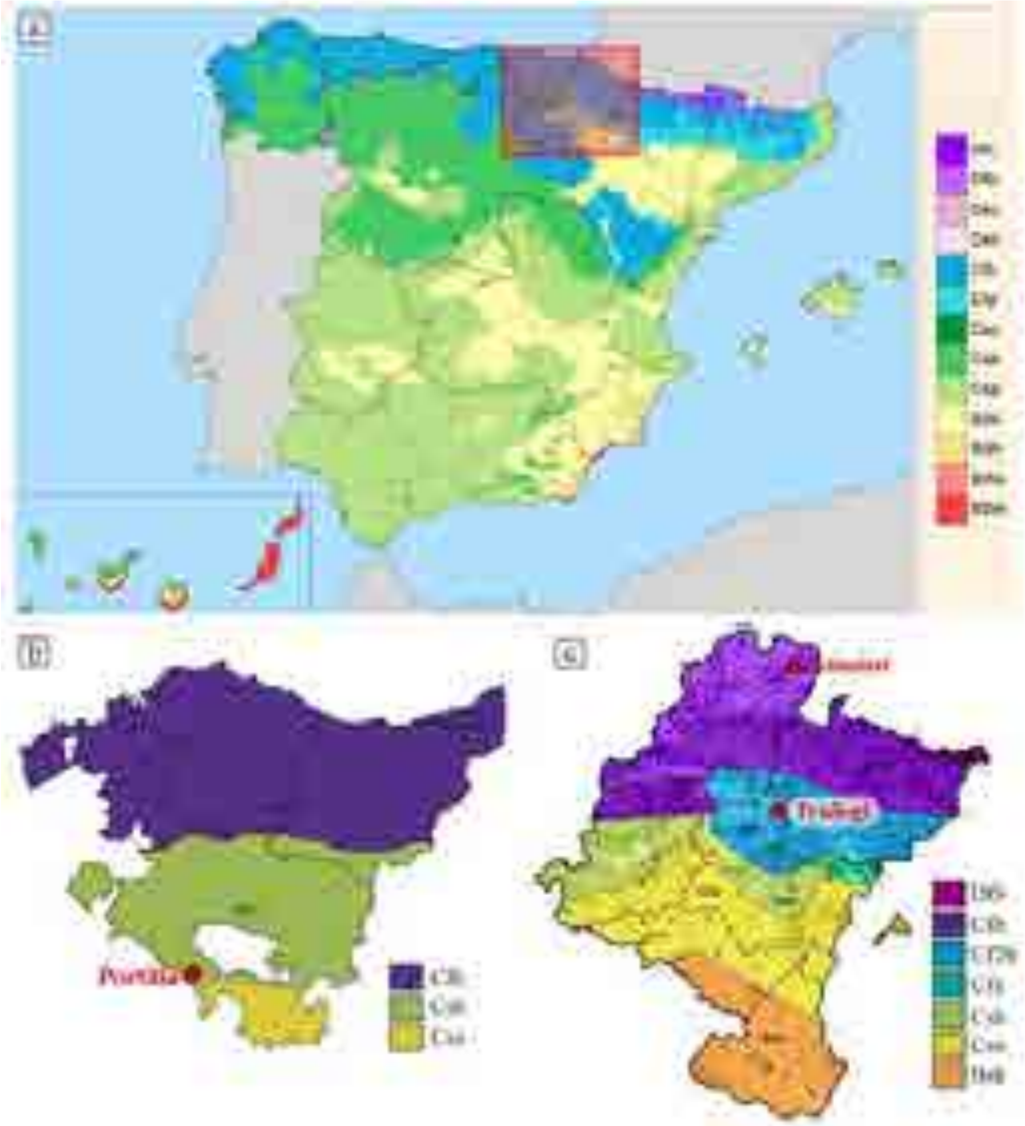

Figure 12. Köppen-Geiger climate types areas in which the studied materials are located. (a) Köppen-Geiger climate types in peninsular and insular Spain. Modified by Chazarra Bernabe et al. (2018). (b) Köppen-Geiger climate types in the Basque Country. Modified by Euskalmet-b. (c) Köppen-Geiger climate types in Navarre. Modified by AEMET (2020). Dfb: Warm-summer humid continental climate; Cfb: Temperate oceanic climate; Cf2b: Temperate oceanic climate with two dry months; Cfa: Humid subtropical climate; Csa: Hot-summer Mediterranean climate; Csb: Warm-summer Mediterranean climate; BsK: Cold semi-arid (steppe) climate.

Historic lime mortars are one of the most porous building materials, making them susceptible to water damage (both in liquid or vapour form) (Van Hees et al., 2004). At relative humidity values between 65% and 95% water coexists in vapour and liquid form remaining continuously within the pores and thus favouring mortar deterioration (Thomson et al., 2007). Nevertheless, water causes lime mortar deterioration, not only owing to both chemical damage by dissolution and physical damage by water crystallization into ice, but also due to soluble salt attack (Coussy, 2006; Langmuir, 1997; Marchand et al., 1995; Scherer, 1999). Environmental conditions also determine the crystallization of different salts favouring mortar deterioration by salt weathering (Grossi et al., 2011, Menéndez 2017, 2018). Temperature and relative humidity (thermo-hygrometric conditions) are the main environmental factors that control the crystallization of different salts (Benavente et al., 2011;

Grossi et al., 2011; Menéndez, 2018). In this regard, it is possible to relate the Kóppen-Geiger climate types with the salt weathering, leading to the development of methods that estimate and quantify the evolution of salt weathering according to the local environmental conditions to which the material is exposed (Brimblecombe, 2010; Grossi et al., 2011, Menéndez, 2017, 2018). In temperate areas in damp conditions close to relative humidity values of 75%, salt crystallization would be favoured, causing building material weathering (Grossi et al., 2011; Menéndez, 2017). According to Brimblecombe (2010) and Grossi et al. (2011) materials in areas with the Cfb climate type are the most susceptible to salt damage. Irulegi Castle and Amaiur Castle are located in areas with this temperate fully humid climate (Cf2b and Cfb, respectively), characterized by mean relative humidity values above 75%. Portilla Castle is located in an area with a drier climate (Csb); however, the mean relative humidity values also exceed 75% (Fig. 1 and Table 1). Therefore, lime mortars at Portilla Castle, Irulegi Castle and Amaiur Castle are susceptible to potential salt weathering.

Environmental conditions in the areas where the studied historical lime mortars are located make it necessary to perform future tests related to salt crystallization for better assessment of mortar deterioration by salt weathering.

6. Conclusions

6.1. General Conclusions

The present PhD thesis has contributed to historical building chronology, technological knowledge in historical lime mortar manufacture and mortar application techniques, and the susceptibility to deterioration of historical lime mortars. Results achieved in the present doctoral thesis have led to the following conclusions:

6.1.1. Characteristics of Historical Lime Mortars

- Lime mortars from Portilla Castle, Irulegi Castle and Amaiur Castle show a heterogeneous binder-matrix supported texture with aggregates embedded in a micritic calcite matrix. However, the studied mortars show aggregates of different nature depending on each historical building. Aggregates in Portilla Castle lime mortars are mainly formed by limestone fragments, some partially dolomitized, and quartz grains. In the Irulegi Castle mortars the aggregates are quartz grains, sandstone, marl and calcarenite fragments and large variety of bioclast fragments whereas in some Tower Keep mortars reused mortar fragments are also observed. Aggregates of the lime mortars from the different structures at Amaiur Castle mainly consist of dolostone fragments and minor amounts of sandstone and ceramic fragments, while the mortars from the cistern tank are mainly formed by siliceous and silico-aluminous aggregates like phyllite, schist, quartzite, sandstone, and subvolcanic rock sands and pebbles, ceramic fragments and quartz grains. Hematite inorganic additive and beeswax organic additive have been found in the pigmented layer of the cistern plaster.

- Aggregates in Amaiur Castle lime mortars are characterized by a reaction zone. The reaction zone in dolomitic aggregates is formed by two reaction rims on the edge of the aggregates and a halo within the binder resulting from an alkali-aggregate reaction (AAR) that led to aggregate dedolomitization. The reaction zone around ceramic fragments and silico-aluminous rock aggregates was result of an alkali silicate reaction (ASSR).

- Magnesium hydrated mineral phases have been detected in the binder of Portilla Castle and Amaiur Castle lime mortars. The layered double hydroxides phases (LDHs) of hydrotalcite and hydrocalumite have been detected in the binder of Portilla Castle mortars whereas hydrotalcite and pyroaurite LDHs have been detected in the binder of Amaiur Castle mortars. Furthermore, in the binder of Amaiur Castle mortars, hydromagnesite was also found whereas amesite, a magnesium aluminosilicate hydrated (M-A-S-H) phase, was found in the binder of cistern tank mortars.

- Raw materials used as aggregates in the manufacture of studied lime mortars came from the surrounding geological materials. Aggregates in the Portilla Castle lime mortars are related to Upper Cretaceous and Paleogene sandstones and carbonated rocks, those in Irulegi Castle mortars to Eocene calcarenites, sandstones and marls, and those in Amaiur Castle lime mortars to Paleozoic metamorphic materials and to Triassic dolostones and subvolcanic basic rocks. The presence of magnesium phases in the binder of both Portilla Castle and Amaiur Castle lime mortars points to the use of impure limestone and/or partially dolomitized limestones as raw material for lime production.

6.1.2. Chronological Considerations

- The sample preparation procedure for radiocarbon dating of lime mortars is essential to achieve reliable radiocarbon ages. The settling process has proved to be more efficient than the sieving process since it avoids the presence of mechanical particles of geogenic origin. In order to obtain an accurate binder grain size fraction for radiocarbon dating of lime mortars, an additional step in the extraction procedure described by Ortega et al. (2012) has been included.

- Accurate mineralogical characterization of lime mortar is able to identify the binder mineral phases and establish their particle size distribution, and thus enables the selection of the most suitable granulometric fraction for radiocarbon dating of mortar.

- This study has demonstrated that the presence of layered double hydroxides phases (LDHs) in the mortar binder constitute a potential contaminant mineral phases for lime mortar radiocarbon dating.

- Sample preparation and mineralogical study of binder should be designed for each specific case in order to select the most suitable binder grain-size fraction in each mortar sample.

6.1.3. Approach to Technological Knowledge

- Mineralogical and chemical characterization of lime mortars from Amaiur Castle point to the use of the traditional hot-mixing method in the mortar manufacture, a method that might have been appropriate for the damp and cold area in which the castle is located.

- Amaiur Castle cistern shows three types of lime mortars related to their specific function within the structure: lime mortars from the barrel vault, structural lime mortars in the tank, and plaster. The different nature of aggregates used in the manufacture of different lime mortars indicates the specific selection of raw materials according to specific requirements for cistern construction.

- A multi-layering application technique was performed for the construction of the cistern tank in Amaiur Castle. Tank structural mortar is formed by two/three layers, with a decrease in grain size and an improvement in sorting of aggregates from the inner part to the outer part. The plaster is formed by two layers, an inner layer and an outer pigmented layer.

- Ceramic fragments and silico-aluminous rocks were used as aggregates in the mortar manufacture to confer hydraulicity to the structural lime mortars in the cistern tank at Amaiur Castle and achieve the waterproofing of the structure. The beeswax organic additive was added to confer impermeability to the pigmented layer of the cistern plaster.

6.1.4. Deterioration Susceptibility of Historical Lime Mortars

- Lime mortars from the southeast and southwest faces of the Tower Keep at Irulegi Castle are more susceptible to deterioration due to their high porosity and water absorption capacity.

- Lime mortars from different areas of Amaiur Castle structures are also susceptible to deterioration. The poor pore interconnection of mortars from the SW structure of the 16th century bastion and the SE mortars of the 17th century diamond-shaped structure makes them more susceptible to decay. Water absorption capacity of both lunette and barrel vault base lime mortars could affect the preservation of the only currently preserved cistern vault remains. Filling mortars from the south-west area are more susceptible to deterioration since they show higher porosity and water absorption capacity, poor pore interconnection and difficulty in drying. Differences in aggregate size, pore system and hydric behaviour between the filling mortar in the south-west area and the south-east suggest at least two different filling periods.

- Temperature variation, high humidity and frequent rainfall to which the lime mortars at the Portilla Castle, Irulegi Castle and Amaiur Castle are exposed throughout the year make these historical lime mortars susceptible to potential water and salts damages.

- The present study describes the characteristic of the original lime mortars at Irulegi Castle and Amaiur Castle, thus providing a valuable reference for a suitable formulation of compatible repair mortar to ensure architectural heritage conservation in future restoration works at Amaiur Castle and Irulegi Castle.

6.2. Future Perspectives

This PhD thesis leaves open issues for future research work to address, such as:

- Wider studies about the provenance of the raw materials would be necessary to obtain more information about the materials used to manufacture the lime mortars at Portilla Castle, Irulegi Castle and Amaiur Castle, as well as to determine the possible locations of the quarries where they were extracted. At the same time, more information about lime production could also be obtained.

- Temperature variation, high humidity and frequent rainfall to which lime mortars at Portilla Castle, Irulegi Castle and Amaiur Castle are exposed make it necessary to perform decay tests that include salt crystallization, wet and dry cycles, rainfall exposure and freeze-thaw cycles, for better assessment of historical lime mortar deterioration.

- Changes in the Amaiur Castle defences led to the construction of different structures in different periods resulting in mortars with diverse characteristics. Therefore, studies on mortar mechanical properties would provide valuable information on potential differences in material strength according to the evolution in the defensive structures.

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