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## UNIVERSITÀ DEGLI STUDI DI TORINO

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# Petrographic characterization of historic mortar as a tool in archaeologic study: examples from two medieval castles of Aosta Valley, Northwestern Italy

#### 4 Abstract

In the present work is reported the study of historical mortars sampled in the two medieval castles
of Châtel Argent and Quart (Aosta Valley, NW Italy), which in recent years are subject to restoration
projects.

8 All the samples were subjected to a petrographic analyses with an optical microscope, in order to 9 recognize and compare the minerals constituting the main aggregates with the geological formations 10 surrounding the areas where the castles stand.

Four mortar samples were analyzed for each castle with the scanning electron microscope (SEM-EDS system). This procedure allows us to know the composition of the binder (not distinguishable on the basis of a petrographic analyses under an optical microscope), to calculate indices related to the composition of the binder, to analyze the composition of the main minerals present in the aggregate.

16 Then, compositional X-ray maps were performed, in order to investigate the relative abundances of

17 the different elements and calculate other important information of the mortars such as the hydraulic

18 index, the porosity distribution and the abundance of aggregate with respect to the binder.

The analytical protocol allowed us to define not only the characteristics of the individual mortars, but also to detect the area of provenance of the raw materials used for their realization, guiding the choice of the best materials for future restoration operations.

22 **Key word:** historic mortar, hydraulic index, binder, SEM – EDS facility, X-ray maps, provenance.

#### 23 **1. Introduction**

Mortars, since ancient times, are an artificial and man-made product made up of natural materials usually obtained by the firing of carbonate or gypsum. By this process, the binder forms and, only after the mixing with aggregate and water, it hardens becoming a mortar (Pecchioni et al., 2018).

The use of mortars seems to have origin in prehistoric times. The discovery probably occurred as the result of an accidental event: the firing of a carbonate rock. It would have been reduced to a powder by heating (calcination process) then extinguished with water and hardened in the air (Schiele and Berens, 1976).

In ancient times, people used different types of both binders and mortars for different purposes;
these materials were known in Asia, Mesopotamia, the Near East and Egypt (Elsen, 2006). The

Minoan civilization handed down to the Greeks the art of lime production that was in turn transmitted to the Etruscans (Moropoulou et al., 2000). The Romans increased the Greeks knowledge of mortars and began to spread out the use of these materials, improving their physical and chemical characteristics (Lezzerini et al., 2017, Miriello et al., 2010). Thanks to the Romans, their writings and the study of the several Roman buildings still in good conditions, the advanced techniques of mortar production are nowadays known.

However, during history and especially in the Middle Ages, the techniques of building constructions changed considerably. Mortars with a totally different composition from the Roman parameters were found especially in Italy, France and England (Rampazzi et al., 2016). In the medieval period, moreover, it seems that organic additives such as animal fat, linseed oil, albumen, blood and natural resins were used (Rapp, 2009).

44 Currently, according to NORMA UNI 10924, 2001, mortars are defined as a mixture of binders 45 (organic or inorganic), aggregates (mainly of fine grain size) and water, to which it is possible to add 46 one or more organic or inorganic additives, in order to improve and/or control the laying conditions 47 of the mix, their physical characteristics (e.g., porosity, water permeability) and mechanical 48 characteristics as resistance, deformability, adherence to surfaces, etc.

The presence and the abundance of MgO compared to CaO is an important aspect to be analyzed. In fact, magnesian mortars tend to have more shrinkage porosity due to the drying process that causes stress around the smallest pores and defines the cracking in the mortar (Sherer, 1990). Magnesian mortars are also characterized by very low mechanical strength also because of internal stresses and shrinkage (Arizzi and Cultrone, 2012).

The petrographic study of mortars, in particular of aggregates, when compared with regional geology, allows us to obtain important information on the source areas of the raw materials with which they were made. Mortars characterization has been performed by combining macroscopic observations, minero-petrographic and micro-chemical techniques as shown in several works focused on this topic (Cantù et al., 2015; Lezzerini et al., 2018; Pecchioni et al., 2018; Riccardi et al., 2007).

In this article a petrographic approach was adopted involving optical microscopy (OM) and Electron
 Microscopy with X-ray analysis (SEM-EDS system) to characterize the mortars of two medieval
 castles used as military and lookout fortresses and therefore placed in tactical and inaccessible
 mountainous positions located in the Aosta Valley (NW Italy).

#### 64 **2. Historic framework**

65 2.1 Châtel-Argent Castle

The Castle of Châtel Argent, also called Castle of Villeneuve, is located on a rocky terrace at the 66 valley outlet, to the orographic right of the Dora Baltea River, in the territory of the village of 67 Villeneuve (Figure 1a). The surviving structure dates back to the 13th century, but there is evidence 68 69 that the spur from the important strategic position on which it stands has been used since ancient 70 times, especially by the Romans (De Gattis and Cortellazzo, 2008). Châtel-Argent represents the classic fortified complex, which probably over the centuries was increasingly expanded in the territory 71 72 and enriched with works, defensive or not. To date, in the Châtel-Argent complex, the remains of a building and a cistern dating back to the 13th century and a better-preserved portion consisting of a 73 74 cylindrical tower 16 m high and with a diameter of 9.5 m are recognizable.

#### 75 2.2 Quart Castle

76 The Quart Castle is located in a lookout position, on a steep promontory at the beginning on the left 77 bank of the Dora Baltea River, in the Aosta Valley (Figure 1b). The castle consists of several buildings placed on different levels that were built in different eras and it seems that the first works 78 79 began between the 11th and 12th centuries (Appolonia et al., 2006). The functions of this fortress 80 diversified over time also by means of the different families who took charge of it over the centuries. 81 Since its primitive phase the castle, used for defensive purposes, as a residence and 82 territorial/organizational reference point for an agro-pastoral activity, was always a power center of 83 several noble families. Only at the beginning of the 19th century the castle was sold to the 84 municipality of Quart and in the mid-20th century it became the property of the regional administration of the Aosta Valley (Appolonia et al., 2006). 85



86 **Figure 1**: Châtel Argent Castle (a); Quart Castle (b).

87

#### 3. Geological setting of Aosta Valley

The two castles of Châtel Argent and Quart are located respectively upstream and downstream of Aosta town, the regional capital of Aosta Valley. The city of Aosta is placed in the middle of the Alpine orogenic chain and is geologically located within the Combin Zone (De Giusti et al., 2004; **Figure 2**) which represents the metamorphic product of the Piemonte-Liguria Ocean originally interposed in the Mesozoic age between the Paleo-European and Insubric continental margins (e.g., Dal Piaz, 1999; Beltrando et al., 2010). The Piemonte Zone includes two main tectonic units, called Zermatt-

Saas Zone (lower) and Combin Zone (upper). The Zermatt-Saas Zone is dominated by ophiolites 94 deriving from a basic and ultra-basic protolite. The metamorphic evolution is characterized by a first 95 event developed under eclogitic facies of the Eocene age, followed by a retrograde event in 96 97 greenschist facies conditions (Ernst and Dal Piaz, 1978; Beltrando et al., 2010). The upper Piemonte 98 nappe (Combin Zone) consists mainly of Mesozoic metasediments (calcschist and impure marble) interbedded with tabular levels of metabasites (prasinite) and slices of serpentinite and minor meta-99 100 gabbro. The Combin Zone shows metamorphic relict in blueschist facies conditions, strongly retrogressed to greenschist facies in the Eocene-Oligocene age (Dal Piaz 1999; De Giusti et al., 101 102 2004). Near the city of Aosta, other important geological units of the Alpine chain also outcrop. They 103 consist of different varieties of continental crust rocks such as the klippe of Monte Emilius 104 (equilibrated in eclogitic facies), the nappes of Dent Blanche and Mont Mary (metamorphosed in greenschist facies) belonging to the Austroalpine domain (Dal Piaz, 1999). The Dent Blanche nappe 105 consists of a lower unit (Arolla Gneiss) of prevalent orthogneiss metamorphosed under greeenschist 106 107 facies conditions and an upper unit (Valpelline Serie) formed by high grade metapelite and metabasite of pre-Alpine age. In the easternmost portion of the Aosta Valley the Sesia Lanzo Zone 108 109 crops out, a unit of continental crust metamorphosed into eclogitic facies in the Alpine age and partially retrocessed to greenschist facies (Dal Piaz et al., 1972). The Pennidic Domain consists of 110 the internal crystalline massifs of Gran Paradiso (GP) and Monte Rosa (MR) Massifs, both 111 metamorphosed in eclogitic conditions, in addition to the different units of the Gran St. Bernard (GSB) 112 Nappe, metamorphosed in blueschist facies conditions, and the Houillère Zone equilibrated in 113 114 greenschist facies. These units are mainly made up of mono- and poly-metamorphic micaschist and ortho-derivate with minor metabasite and marble, which represent the metamorphic product of 115 116 original Mesozoic covering sequences (e.g., De Giusti et al., 2004; Malusà et al., 2005). Finally, in 117 the outermost position of the Pennidic domain, the Sion – Courmayeur Zone crops out (Elter and 118 Elter, 1965), consisting of two main geological units: the Roignais-Versoyen Unit and the Brèches de Tarentaise Unit. The first is composed of oceanic metasediments, metabasites and serpentinized 119 Iherzolites of Mesozoic age. The latter consists of carbonate and pelitic metasediments with bodies 120 121 of polygenic breccias, and are interpreted as a high-pressure metamorphosed flysch deposited in the oceanic trench during Alpine convergence (Loprieno et al., 2011). 122

The Aosta Valley geology is completed by the Mont Blanc massif, a crustal unit of Helvetic Domain,with the related covers from the Meso-Cenozoic age.

As regards the lithologies on which the castles of Châtel-Argent and Quart insist, we refer to the 1: 50,000 cartography of each area (De Giusti et al., 2004; Polino et al., 2015, with Ref.). The Châtel Argent Castle stands on a marble ridge, interlayed within a body of calcschists belonging to the basal portions of the Combin Zone. The Quart Castle is located in an area where the lower unit of Mont Mary out crops, which is part of the upper nappes of the Austroalpine Domain. The unit in question is described as consisting of schists with quartz, biotite, garnet ± muscovite. In the area also occurs

- 131 a level of carbonate cover, consisting of meta-dolostone (Roisan Zone), which detach two sub-units
- 132 of the Mont Mary with Arolla unit.



Figure 2: Geological-structural map of Aosta Valley. AB: Arcesaz-Brusson; AR: Arolla Series; DK: Dioritic-Kinzigitic Zone;
 E: Emilius; GM: Gneiss Minuti Complex; GNM: Gran Nomenon; GR: Glacier Refray; GP: Gran Paradiso; GSB: Gran St.
 Bernard Nappe; HE: Helvetic; ME: Mount Emilius; MR: Monte Rosa; MM: Mont Mary; P: Pillonet; UE: Ultra Helvetic; V:
 Valpelline; ZH: Zone Houillère; ZP: Piemonte Zone; ZSC: Sion-Courmayeur Zone (Modified by Martinotti et al., 2011).

#### 137 **4. Materials and methods**

The thirty-six samples were analyzed for this work. Twenty of these were sampled in the Quart Castle, while sixteen were sampled at the Châtel Argent Castle. **Figure 3a** and **Figure 3b** shows

140 the sampling site, while **Table 1** the intended use of the samples.



Figure 3: Planimetry of Châtel Argent Castle; the acronyms show the sampling points (a) (modified by Appolonia et al., 2010) and planimetry of Quart Castle (b); the acronyms show the sampling points (modified by Appolonia et al., 2006).

Châtel	Argent Castle	Q	uart Castle
Sample	Type of survey	Sample	Type of survey
ACK01	Lime fragment with coal	ADY01	Plaster upper balcony (150 cm, date about 1400-1500)
ACK02	Lime inside the kiln	ADY02	Plaster balcony in front of access stairs (135 cm)
ACK03	Lime inside the kiln	ADY03	Upper balcony (260 cm)
ACK04	Lime inside the kiln	ADY04	Plastering upper balcony, 1st floor scaffold
ACK05	Lime cooling zone	ADY05	Plaster over door, external main hall (338 cm)
ACK06	Lime cooling zone	ADY06	Inside window, outside main hall (150 cm)
ACK07	Lime cooling zone	ADY07	Plaster left arch of Savoia building
ACK08	Sample of Bardiglio Marble	ADY08	Plaster room 26 (150 cm)
ACK09	Smooth surface mortar	ADY09	Plaster pre-Montiglio
ACK10	North wall below ACK09	ADY10	Plaster under window
ACK11	Smooth surface mortar	ADY11	Pink plaster
ACK12	West wall	ADY12	Donjon Plaster
ACK13	Tower, west side	ADY13	Donjon plaster, burned
ACK14	Tower, smooth surface mortar	ADY15	Donjon plaster (1556)
ACK15	Smooth surface mortar	ADY16	Mortar Pre-Savoia passage, room 27 and 28
ACK16	Just below ACK15	ADY17	Plaster, Savoia room 28
ACK17	Wall near tank entrance	ADY18	Ancient mortar, arcade room 28
		ADY19	Window draft, outside room 28
		ADY20	Stillness near the ceiling, room 27
		ADY21	Tough mortar, room 27

**Table 1**: Sample and type of survey respectively for Châtel Argent Castle (on the left) and Quart Castle (on the right).

All the samples were subjected to a petrographic analysis with an optical microscope, through which 144 145 the main minerals making up the aggregate were recognized. It was performed using a Leitz Laborlux 11 Pol microscope with a 10x Leitz wetzlar periplan eyepiece. In addition to the 146 petrographic analyses, four mortar samples were analyzed for each castle using a scanning electron 147 microscope (SEM-EDS system) and a X-ray powder diffractometer. This procedure allowed to: 1) -148 149 know the composition of the binder (which is not distinguishable on the basis of an optical microscope 150 analysis); 2) - analyze the composition of the main minerals present in the samples; 3) - identify the 151 composition and the petrographic nature of some elements of the aggregate that are not easily 152 recognizable under the optical microscope. For 2 samples (ACK17 sample from Châtel Argent Castle 153 and ADY17 sample from Quart Castle) a set of compositional maps were performed, in order to analyze the relative abundances of the different elements and calculate other important information 154 of the mortars, such as porosity, the abundance of aggregate with respect to the binder and the 155 distribution of the aggregate within the binder. 156

#### 157 4.1 COMPOSITION OF THE MINERALOGICAL PHASES

The data concerning the chemical composition of the mineralogical phases of the mortars were analyzed with a JEOL IT300 LV SEM equipped with a X-Act3 SDD-EDX detector. The operating conditions were potential difference = 15Kv, beam current = 800pA, working distance = 10mm, counting times = 25s. Cobalt was used as a reference standard and the analyzed sections were previously polished and metallized with graphite. The mineral analyses were acquired using the INCA 300 operating system of Oxford Instruments and were recalculated using the MINSORT software (Petrakakis and Dietrich, 1985). The values reported in the text of the various elements making up the mineralogical phases are to be considered expressed in atoms per unit of formula (a.p.u.f.). The acronyms of the minerals used in the text are taken from Whitney and Evans (2010).

168 In order to confirm the obtained classification, the mineralogical composition of the binder was 169 checked by X-ray powder diffraction (XRPD) analyses. XRPD evaluation was conducted on 170 representative samples of both Castles. XRPD patterns were collected by using an Analytical Rigaku 171 "Miniflex II" equipped with an D/teX Ultra: silicon strip detector powder diffractometer using Cu Ka radiation generated at 30 kV and 15 mA. The 20 range was from 4° to 70°. For the measurement, 172 around 1 g of sample was ground in an agate mortar, and the appropriate amount of powder (from 173 174 both matrix and inclusion) was placed in a quartz sample holder and compressed with a glass slide. 175 The MD Jade 9 software was used for the evaluation of the diffraction patterns and the identification of the mineralogical phases. 176

#### 177 4.2 X-RAY MAPS

178 The maps were acquired by means of the SEM-EDS system installed in the laboratories of the 179 Department of Earth Sciences in Turin using the AZTEC operating system of Oxford Instruments. Digital maps are made up of numerical matrices where in each pixel the number of X-rays detected 180 for a particular characteristic energy interval for each mapped element is reported. TruMap © 181 software has developed an algorithm for automatic peak deconvolution and background removal, 182 thus allowing the real-time acquisition of compositional maps where each pixel corresponds to an X-183 ray spectrum with a net peak. This allows the easy processing of the map using the QUANTMAP©, 184 which by processing the maps with a set of pre-acquired standards allows to obtain quantitative 185 maps. The maps can be expressed as apparent concentration, percent by weight, atomic percent 186 and percent of oxides. 187

The operating conditions were as follows: beam acceleration = 15 KeV, working distance = 10 mm, probe current = 5 nA. Using a process time of 1  $\mu$ s these conditions have made it possible to reach approximately 100,000 counts per second (CPS) with a dead time of 30%. The maps were acquired at a fixed magnification of 50x. A dwell time of 7 ms was used which implies a total acquisition time of about 16 h for 8 frames scanned with a spatial resolution of 1024 X 768 pixels for a total of about 6.5 MPixel on 40 mm<sup>2</sup>.

Each set of X-ray maps was corrected for instrument probe current drift due to long acquisition times
by performing an automated measurement on a reference sample of known coordinates (x, y and z)
at pre-set time intervals of 1 hour.

With these maps it was possible to: 1) - evaluate the porosity, the distribution of the aggregate within the binder and identify its mineral phases; 2) - perform a mapping to identify the value of the Hydraulic 199 Index of the two mortars; 3) - obtain a modal map of the mineral phases and other components200 present in the mortar.

#### 201 **5. Results**

#### 202 5.1 Petrography

In the following a petrographic description of the main features of the analyzed mortars is reported.
In **Table 2** the main minerals and rock fragments that make up the aggregate are detailed for each sample.

Samples	Quartz	White Mica	Biotite	K-Feldspar	Plagioclase	Amphibole	Carbonate	Quartzite	Gneiss	Marble	Impure marble	Calcschist	Micaschist	Biotite bearing micaschist	Chlorite-schist	Graphite-schist	Serpentinite	Granitic Rock
АСКО2	х	х		х	х			х										
АСК03	х	х		х				х	х		х			х				
АСКО4	х	х		х		х		х					х					
АСК05	х	х		х	х		х	х	х	х	х		х			х		
АСКО6	х	х		х	х				х		х			х		х		
АСК07	х	х		х	х	х	х	х	х		х	х		х		х		
ACK08											х							
ACK09	х	х		х				х	х			х			х			х
ACK10	х	х		х		х		х	х	х	х	х	х			х		
ACK11	x	х		x	х		х	х	х		х	X					х	
ACK12	x	x		X			X			X	X	x				х		
ACK13	x	x		x		v	x	X	x	x	x	x	X			v		
ACK14 ACK15	×	×		×		X	×	~	x	X	x	~	v			x		
ACK15 ACK16	x	×	x	×	x		x	x	x	x	x	^	x			x		x
ACK17	x	x	X	x	Χ	x	x	x	x	Χ	X		Λ			Χ		X
ADY01	x	x		x	x	x	x		~	х		х	х			х		х
ADY02	х	х		х	х	х	х	х	х	х		х				х		х
ADY03	х	х		х	х	х		х		х	х		х		х	х		х
ADY04	x	х	х	х	х	х	х	х	х	х	х		х			х		х
ADY05	x	х	х	х	х	х	х			х	х				х	х		
ADY06	х			х		х		х	х	х	х		х			х		х
ADY07	х			х	х	х		х	х	х	х		х	х		х		
ADY08	х	х		х	х		х	х	х	х	х				х	х		
ADY09	х	х			х	х			х	х				х		х		
ADY10	х	х	х	х	х	х	х		х	х	х	х	х	х	х	х		х
ADY11	х		х	х	х	х	х	х	х	х		х			х			х
ADY12	х	х		х	х	х	х	х	х	х		х			х	х	х	х
ADY13	х	х		х	х		х	х		х	х	х				х	х	х

ADY15	х	х		х	х	х	х	х		х	х		х					
ADY16	х	х	х	х	х				х					х				х
ADY17	х	х	х	х		х	х	х	х	х	х			х	х	х		х
ADY18	х	х		х	х	х			х									
ADY19	х	х	х	х		х		х	х				х	х				
ADY20	х			х	х	х	х		х	х		х		х		х	х	
ADY21	х	х	х	х		х			х					х				

Table 2: Minerals and rocks present in Châtel Argent Castle samples (ACK) and in Quart Castle samples (ADY)
 respectively.

The aggregate has a granulometric distribution from serial to poorly classified. In almost all sections a bimodal particle size dispersion is observable. The smaller-grained portion of aggregate has dimensions ranging from submillimetric to about 2.5 mm and shapes from irregular to elongated and edges from sub-angular to sub-rounded, while the greater-grained portion is between 9 mm and 15 mm.

213 The composition is always heterogeneous, but with a silicate prevalence. In all sections there are 214 clasts of quartz, especially in the fine-grained fraction of the aggregate. The edges can be both 215 angular and rounded (Figure 4a). The most common rock fragments, in addition to single quartz 216 crystals, are guartzites, with a fine and very fine grain. The guartzite elements appear for the most 217 part with sub-spherical shapes and rounded edges. Very common are also the elements of white mica, which often occur in single crystals with a lamellar habit in the fine-grained fraction of the 218 aggregate. Less abundant are biotite and chlorite. Both in the fine-grained and in the coarse fraction 219 220 of the aggregate, there are elements of more or less altered feldspar with very fine-grained felts (Figure 4a). Locally, the polysynthetic twinning of plagioclase is recognized, or the Carlsbad twinning 221 of potassium feldspar. Rock fragments of gneiss are frequently present (Figure 4b) composed 222 mainly of fine-grained quartz and white mica oriented and distributed in levels that often envelop 223 224 potassium feldspar porphyroclasts, often altered and medium-grained. Gneisses and quartzites usually constitute the elements of the aggregate with a coarser grain and have sub-angular and 225 226 rounded edges (Figure 4c).

There are normally coarse-grained elements of impure marble composed of fine-grained carbonate crystals and minor quartz and fine-grained white mica oriented in discontinuous and not very thick levels. Frequently there are elements of the aggregate consisting of calcschist composed of finegrained carbonate crystals, fine-grained white mica arranged in oriented levels of submillimeter and continuous thickness and less fine-grained quartz (**Figure 4b**).

Many samples include monocrystalline carbonate fragments that make up the fine-grained aggregate elements (**Figure 4b**). They often have angular or sub-angular edges and are interpreted as fragments of vein calcite added to the mixture. In some sections there are lithic elements of prasinite consisting of plagioclase, epidote, chlorite and actinolite, and elements of serpentinite

consisting of serpentine and lesser magnetite (Figure 4d). Almost all sections contain graphitic 236 schists, composed of thin and dense layers of white mica, graphite, and lesser quartz (Figure 5a). 237

238 Finally, there are lithic elements with a granite composition consisting of quartz, feldspar, and 239 plagioclase as well as rare, isolated crystals of pyroxene and pleochroic amphibole from yellow to 240 brown.



241 242

Figure 4: Micrographs of mortars: a) Crossed polarized light of ACK05 sample under optical microscope low resolution; b) 243 Crossed polarized light of ADY02 sample; c) Plane polarized light of ACK05 sample: note the intense secondary porosity 244 and the lower primary porosity; d) Photograph at SEM-EDS of ADY17 sample.

245 All sections show a slightly pervasive closed primary porosity (probably due to the use of excess water in the mixture, which creates bubbles) with rounded pores and dimensions ranging from sub-246 millimeter to a maximum of about 1.5 mm. In some samples these pores appear to be filled with re-247 precipitated minerals, probably of calcite composition. The secondary porosity, on the other hand, is 248 249 due to shrinkage or degradation and proves to be more pervasive. Often this porosity develops from 250 the primary one and determines the low degree of conservation of the mortars. In many cases the secondary porosity occurs along the edges of the aggregate elements, weakening the mechanical 251 properties of the mortar (Figure 4c). In some sections, the secondary porosity presents fractures 252 253 affecting the entire sample with spacing in the order of magnitude of 2 mm wide. Even along these fractures, precipitation recrystallization can be noted in some cases. The total porosity is estimated 254 255 between 7% and 15% by volume.

In all samples some lumps are present. These are residues of raw material of the binder that did not react during cooking. They appear with rounded shapes and with sub-rounded to rounded edges, with dimensions ranging from submillimetric to about 3-4 mm. They have mostly homogeneous colours, dark brown or dark hazelnut, but especially in cases where the lumps are fractured (**Figure 5b**), they tend to be more intense in colour just along the edges, due to an incomplete reaction with the binder during cooking.

The ACK17 sample comes from a wall near the entrance to the castle cistern. The main feature of 262 this sample is the presence of numerous inclusions consisting of fusion slag. These slags are formed 263 by irregular fragments ranging in size from millimeters to micrometres in which a glassy portion is 264 265 identified whithin skeletal crystals of wustite and olivine with a fayalite composition (Figure 5c). From their shapes and sizes, it can be deduced that they are slag generated during the iron extraction 266 process, which in medieval times took place through the use of low-fire furnace that could reach 267 1200 °C. These elements were probably added to the mixture to make the binder no more aerial but 268 hydraulic (see the SEM analyses) and thus make the mortar more resistant. This has also been 269 achieved by adding artificial "cocciopesto" elements to the aggregate obtained from the mechanical 270 271 crushing of bricks and other ceramic material, which at a macroscopic observation are brick red 272 coloured. Finally, skeletal inclusions are worthy of note and are interpreted as remains of fossil coal combustion (Figure 5d). 273



Figure 5: a) SEM photograph of the ADY04 sample; b) Plane polarized light microphotograph of ACK15 sample: note the intense fracturing of the lump; c) SEM photograph of ACK17 sample note the foundry waste with eutectic point structures;
 d) SEM photograph of sample ACK17; note the remnant fossil coal combustion.

#### 277 5.2 Mineral chemistry

• Pyroxenes:

The pyroxenes come from single crystals present in the aggregate of the ACK04 and ACK12 samples from Châtel Argent and the ADY04 and ADY17 samples from the Quart Castle. The analyses were calculated on the basis of 6 oxygens and are available in supplementary materials (**Table S1**).

The pyroxenes were projected on the classification diagram of Morimoto (1988) (**Figure 6a**), and all show a calcitic composition. In particular, the samples fall into the fields of diopside-augite and pigeonite.



286

Figure 6: Different diagrams of samples of Châtel Argent and Quart Castle. a) Pyroxene ternary diagram (modified by
 Morimoto, 1988). En= Enstatite, Fs= Ferrosilite, Di= Diopside, Hd= Hedembergite, Wo= Wollastonite; b) Amphiboles; c)
 Feldspar diagram; d) Dioctahedral micas diagram.

290 The pyroxenes analyzed were therefore all calcic, while the typical sodium-calcium pyroxenes of the basic rocks equilibrated in eclogitic conditions of the Piemonte Zone and the sodium pyroxenes of 291 the ortho-derivatives of the Sesia Lanzo Zone are missing. This data is consistent with the location 292 occupied by the two castles studied, both placed to the west of the outcrop areas of the main eclogitic 293 294 units of Aosta Valley. For the mortars of the Quart Castle, the pyroxenes identified could derive from 295 the dismantling of basic rocks of a high metamorphic grade from the Valpelline Series: the attribution of the pyroxenes found in the mortars of the Châtel Argent Castle is more difficult. In this case it can 296 be assumed that it comes from basic/ultrabasic rocks of the Versoven Zone or from basic lenses of 297 298 the polymetamorphic basement of the Gran St. Bernard multi-nappes system.

299 • Amphiboles:

The amphiboles derive from the ACK10 sample from the Châtel Argent site and from samples ADY04, ADY10 and ADY17 from the Quart Castle. The analyses were calculated on the basis of 23 oxygens and are available in the supplementary materials (**Table S2**). 303 The diagram which correlates the Na content of the M4 site, and the AI IV content was reported (Figure 6b). The amphibole of the ACK10 sample shows a composition that falls within the field of 304 305 hornblende. The compositions of the ADY04 sample plot into the field of actinolite. The amphibole of the ADY10 sample shows different compositions, which fall into the fields of actinolite and 306 hornblende, while those of the amphibole of the ADY17 sample plots into the fields of the barrosite 307 and of the tschermackite. All the amphiboles analyzed can therefore be classified as calcium or 308 309 sodium-calcium amphiboles with a composition ranging from tremolitic to pargasitic, reflecting conditions of medium-low pressure and variable temperature from low to medium metamorphic 310 degree. Amphiboles of this type are present in numerous units of both oceanic and continental origin 311 312 cropping out in the Aosta Valley, which have undergone a pervasive metamorphic retrogression 313 under low pressure conditions, possibly with late heating. On the other hand, sodium amphiboles, 314 characteristic of high pressures conditions, were absent. This data is consistent with the position occupied by the two castles studied, both located to the west of the outcrop areas of the main oceanic 315 316 units of Aosta Valley, which suffered eclogitic facies conditions.

317 •Feldspars:

The feldspars analyzed come from the ACK04, ACK10, ACK12 and ACK17 samples from Châtel Argent Castle and from the ADY04, ADY10 and ADY17 samples from the Quart Castle and refer to aggregate elements consisting of lithic fragments, or single clasts of feldspar. The analyses were calculated on the basis of 8 oxygens and are available in supplementary materials (**Table S3**) and are represented in the diagram of **Figure 6c**.

323 The composition of feldspars is variable and can be summarized in three categories:

Albite: all the analyses carried out on the ACK04 and ACK17 samples plot into this field, together
with some of the ACK10 and ACK12 samples and the ADY04, ADY10 and ADY17 samples. These
compositions are typical of Aosta Valley rocks of greenschist metamorphic grade originating from
both the basic and pelitic protolites.

Orthoclase: an analysis of the ADY04 sample falls on the vertex of the field, while the feldspar of
the ACK10, ACK12 and ADY10 samples are arranged along the Ab-Or side, with approximately a
maximum 7% of albitic molecule. The presence of K-feldspar can be attributed to orthogneiss
dismantling materials (in most cases) widespread in the continental units of Gran Paradiso, Monte
Rosa and Gran St. Bernard or granite (most likely coming from the erosion of the Mont Blanc
granites).

Labradorite: the analyses of the ADY10 and ADY17 samples plot on the Ab-An side between 52 %
and 60% of anorthitic molecule. Intermediate composition plagioclases could come from basic rocks
or from high temperature units, such as the Valpelline Series.

337 • Dioctahedral micas:

- The dioctahedral micas come from single crystals dispersed in the binder and from micas present in lithic fragments in the aggregate of samples ACK04, ACK10, ACK12 and ACK17 of the Châtel Argent
- Castle and of the samples ADY04, ADY10 and ADY17 of the Quart Castle. The analyses were
- calculated on the basis of 22 oxygens and are available in supplementary materials (**Table S4**).
- Almost all of the micas analyzed appear to belong to the family of potassic micas (muscovites), while only a few samples belong to the family of paragonitic micas.
- The micas of the ACK04, ACK10, ACK12 and ACK17 samples are reported in the diagram Al tot / Si (**Figure 6d**), which allows a subdivision in almost pure muscovite and in terms close to the phengite composition. The analyses are distributed approximately along the Muscovite-Phengite junction.
- 348 The micas analyzed therefore reflect high pressure metamorphic conditions, typical of the continental
- 349 crust units outcropping in Aosta Valley and, in particular, in the eclogitic facies units such as the
- 350 Gran Paradiso massif and those in blueschist facies of the Gran St. Bernard multi-nappe system.
- 351 •*Trioctahedral micas:*
- 352 The trioctahedral micas come from single crystals occurring in the aggregate of samples ADY04,
- ADY10 and ADY17 of the Quart Castle. The analyses were calculated on the basis of 22 oxygens and are available in supplementary materials (**Table S5**).
- The biotites likely come from high temperature metamorphic lithotypes, such as the kinzigites of the Valpelline Series.

#### 357 **5.3 Analyses of binders**

- The composition of the binders was performed on six thin sections: three relating to the Châtel Argent Castle (ACK10, ACK12 and ACK17) and three relating to the Quart Castle (ADY04, ADY10 and ADY17). The following description of the binders has been divided according to their use, so as to
- highlight the differences in composition. The results are expressed as wt%.
- The first group of binders comes from Quart Castle. All three analyzed samples derive from plasters, the analyses of their binders can be consulted in **Table 3**.

Sample	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	CaO	H.I.
ADY04_1	3.15	1.34	0.00	42.59	52.67	0.047
ADY04_2	5.89	2.35	0.00	39.43	51.15	0.091
ADY04_3	1.03	0.00	0.00	42.26	46.71	0.010
ADY04_4	2.43	1.16	1.08	42.68	52.65	0.049
ADY04_5	3.27	1.76	0.72	44.75	48.97	0.061
ADY04_6	3.61	1.08	0.00	36.65	58.36	0.049
ADY04_7	1.26	0.00	0.00	37.42	61.32	0.013
ADY04_8	4.72	1.29	0.00	41.96	51.71	0.064
ADY04_9	3.52	1.36	0.69	43.37	50.37	0.059

ADY04_10	2.47	0.00	0.00	47.12	49.88	0.025
ADY10_1	6.27	3.31	1.27	33.39	53.18	0.125
ADY10_2	3.30	0.00	0.00	37.58	57.44	0.035
ADY10_3	3.53	0.00	0.00	35.29	59.51	0.037
ADY10_4	2.70	1.14	0.00	33.00	61.16	0.041
ADY10_5	1.86	0.00	0.00	40.04	50.38	0.019
ADY10_6	2.92	2.82	0.00	42.04	50.38	0.062
ADY10_7	2.98	1.10	0.00	36.77	56.54	0.044
ADY10_8	2.85	1.17	0.00	38.39	55.11	0.043
ADY10_9	3.00	1.18	1.54	36.14	56.28	0.062
ADY10_10	2.46	0.00	0.00	39.20	56.01	0.026
ADY17_1	8.88	1.95	0.82	44.79	45.55	0.132
ADY17_2	4.03	1.16	0.00	39.51	55.30	0.055
ADY17_3	3.45	1.54	0.00	41.45	53.56	0.053
ADY17_4	8.97	0.96	0.00	42.05	48.03	0.110
ADY17_5	6.88	2.63	1.12	40.87	47.82	0.120
ADY17_6	7.75	1.35	0.00	41.52	49.37	0.100
ADY17_7	1.82	0.54	0.00	12.90	84.50	0.024
ADY17_8	1.31	0.00	0.00	11.18	86.67	0.013
ADY17_9	0.93	0.00	0.00	13.79	84.98	0.009
ADY17_10	6.88	0.00	0.00	24.43	68.69	0.074
ADY17_11	3.99	0.00	0.00	27.17	68.48	0.042
ADY17_12	6.22	0.91	0.00	49.85	42.61	0.077
ADY17_13	4.42	0.00	0.00	49.06	46.51	0.046
ADY17_14	4.31	1.21	0.00	40.48	53.67	0.059
ADY17 15	3.91	1.01	0.00	38.18	56.90	0.052

Table 3: Analyses of binders from the plasters of Quart Castle. Acronyms represent percentage weight of oxides and H.I.
 the Hydraulic Index.

366 In most cases, the binder is magnesian and therefore with a high MgO component that varies 367 between 24.43% and 49.85%, while the calcic component varies between 42.61% and 68.69%. Only three samples show a MgO percentage between 11.18% and 13.79%, while the CaO percentage 368 varies between 84.50% and 86.67%. SiO<sub>2</sub> values are low and vary between 0.93% and 8.97%, Al<sub>2</sub>O<sub>3</sub>, 369 not always present, has values between 0.91% and 3.31%, while Fe<sub>2</sub>O<sub>3</sub>, is in most cases absent, 370 371 reaches up to 1.54%. The Hydraulic Index (H.I.) identifies an aerial binder (see Table 3) with values 372 ranging from 0.010 to 0.091 for mainly samples. Only five samples from ADY17 sample show H.I. 373 values between 0.100 and 0.132 which identifies weakly hydraulic binders.

The ADY04 samples have a homogeneous binder, which generally shows a composition made up in a minimal part also of potassium (maximum 1.75%).

ADY10 section has different sites that present higher values of SiO<sub>2</sub>, while CaO and MgO values are
 almost stable.

Numerous sites were analysed in the ADY17 section and many of them present different ranges of values, expecially the SiO<sub>2</sub> ones. The second group of binders comes from Châtel Argent Castle. The ACK10 and ACK12 samples come from the external walls of the castle, while the ACK17 sample comes from the masonry of the water tank inside the external walls. The analyses of their binders are reported in **Table 4**.

Sample	SiO₂	<i>Al</i> <sub>2</sub> <i>O</i> <sub>3</sub>	<i>Fe</i> <sub>2</sub> <i>O</i> <sub>3</sub>	MgO	CaO	H.I.
ACK10_1	22.54	6.38	2.79	3.69	63.12	0.475
ACK10_2	21.37	7.31	2.57	5.03	61.74	0.468
ACK10_3	24.02	5.43	2.39	5.27	61.40	0.478
ACK10_4	25.18	5.89	1.42	6.05	58.68	0.502
ACK10_5	15.45	4.11	3.61	5.00	71.05	0.305
ACK10_6	19.57	7.25	2.15	3.29	66.00	0.418
ACK12_1	4.20	0.00	0.00	3.39	92.41	0.044
ACK12_2	4.97	0.99	0.00	3.12	90.93	0.063
ACK12_3	9.98	3.48	1.38	4.31	80.40	0.175
ACK12_4	9.54	4.39	2.88	6.38	76.61	0.203
ACK12_5	9.40	2.99	1.35	3.09	83.17	0.159
ACK12_6	11.55	5.60	1.25	3.51	76.80	0.229
ACK12_7	6.95	1.33	0.95	5.61	85.15	0.102
ACK12_8	10.38	2.22	0.89	6.04	80.09	0.157
ACK12_9	6.63	2.15	0.92	2.62	87.00	0.108
ACK17_1	40.14	8.88	2.42	4.23	44.33	1.059
ACK17_2	36.18	8.14	6.25	3.95	45.48	1.023
ACK17_3	39.12	8.55	2.20	4.72	45.41	0.995
ACK17_4	36.98	10.21	2.15	3.67	46.99	0.974
ACK17_5	31.29	10.07	2.06	8.52	48.05	0.768
ACK17 6	32.42	8.24	3.82	5.45	49.14	0.815

Table 4: Analyses of binders from the plasters of Châtel Argent Castle. Acronyms represent percentage weight of oxides
 and H.I. the Hydraulic Index.

385 For the ACK10 and ACK12 samples the composition is generally calcic (the values of CaO vary from 386 58.68% to 92.41%), with SiO<sub>2</sub> values ranging from 4.20% to 25.18%, MgO between 2.62% and 387 6.38%. Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> are present in most of the analyses in guantities respectively between 1.33% and 7.31% and between 0.89% and 3.61%. The ACK17 sample shows a marly composition 388 (respectively with values between 44.33% - 49.14% for CaO and 31.29% - 40.14% for SiO<sub>2</sub>) with 389 lower MgO (3.95%-8.52%), Al<sub>2</sub>O<sub>3</sub> between 8.14% and 10.21% and Fe<sub>2</sub>O<sub>3</sub> between 2.06% and 390 6.25%. The Hydraulic Index varies for the different sections. In the ACK10 sample the binder has an 391 average value ranging from properly hydraulic (H.I. = 0.305) to eminently hydraulic (H.I. = 0.502) 392 and shows a coarse grain (up to about 50 µm) with an important microporosity. 393

The ACK12 sample shows two different binders, distributed in bands. One has a micritic grain and a lower Hydraulic Index, with values ranging from 0.044 to 0.063 and is identified as an aerial binder, while the other has a microsparitic appearance (with greater grain), where white mica crystals are abundant and with values of H.I. ranging from 0.102 to 0.229 (medium to properly hydraulic binder).

The binder of the ACK17 sample has an uneven grain and is microfractured. Its Hydraulic Index is high and varies from 0.768 to 1.059, identifying no longer as lime, but as cement. The presence of a high amount of silicon in its composition was probably intended to allow the mortar to have a 401 hydraulic setting process considered for its use in the water tank. In this case the binder shows an402 important shrinkage microporosity.

403 XRPD analyses performed on two representative samples (ADY10 and ACK17) confirmed the 404 overall mineralogical pattern identified by the SEM-EDS facility for both castles (Figure 7a and Figure 405 7b). In particular, in the Quart Castle sample the occurrence of dolomite is reported, absent in the 406 Châtel Argent Castle sample. The occurrence of akermanite in the ACK17 can be related to the 407 activation of reaction between blastofurnace slag and carbonate minerals (calcite or dolomite) during 408 the baking process.



409

410 Figure 7: XRPD analyses of ADY10 sample (a) and ACK17 sample (b).

#### 411 **5.4 X-ray maps**

The overall observation of the maps made it possible to provide some information relating to the various components of the mortar investigated. For example, the binder / aggregate ratio, the shape and distribution of the elements of the aggregate, the shape and distribution of porosity can be appreciated.

416 In **Figure 8** the quantitative maps of the main oxides (SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, CaO, MgO, Na<sub>2</sub>O, K<sub>2</sub>O) of the ADY17 section are represented, divided into discrete classes with false colours. The data are 417 reported as Wt % of the oxide. The comparison of the maps allows to identify the different mineral 418 419 phases that make up the aggregate of the mortar. The main distinguishable phases are (in order of abundance): quartz, albite, potassium feldspar, calcite, dolomite, white mica, chlorite and titanite. All 420 clasts show an average size below 1 mm and a fairly homogeneous grain, with some larger lithic 421 clasts. Their shape is generally rounded and sub-spherical. Among the feldspar there are both albite 422 and K-feldspar. Phyllosilicates (white mica and chlorite) are relatively abundant. 423



Figure 8: Quantitative maps of the main oxides found in the ADY17 section of Quart Castle. The legend refers to intervals
 of discrete percentage expressed in false colours. Ab= Albite, Cal= Calcite, Chl= Chlorite, Dol= Dolomite, Kfs= K-feldspar,
 Pg= Paragonite, Ms= Muscovite, Qz= Quartz (Mineral abbreviations according to Whitney and Evans, 2010).

427 As regards the binder, it can be observed that its composition is slightly inhomogeneous and 428 composed mainly of CaO and MgO.

- 429 Figure 9, on the other hand, shows the quantitative maps of the main oxides (SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, MgO,
- 430 CaO, Na<sub>2</sub>O, FeO) of the ACK17 section. This section shows the particularity of being made up of an

aggregate composed of natural materials (silicate mineralogical phases) and artificial materials with 431 pozzolanic behavior, such as the slag from iron processing (aggregates of fayalite, wustite and glass 432 that are clearly distinguishable in the map of the iron) and fragments of cocciopesto, easily 433 recognizable by comparing the maps of silicon and aluminum. The main components of the 434 aggregate are (in order of abundance): cocciopesto, quartz, albite, melt waste, combustion residues 435 (coal), chlorite, light mica and rare carbonate. From the comparison between the various maps, it 436 can be seen that the larger lithic clasts are made up of schists fragments composed by white mica, 437 chlorite and quartz (in the central portion on the right of the map), followed by albite, which is present 438 439 in submillimeter clasts and quartz in very small fragments.

The binder is mainly calcic with a minor magnesium component of the previous section, while the presence of phyllosilicates is clearly visible. There are also abundant shrinkage microfractures, which appear to be filled with re-precipitated carbonate. On the other hand, primary porosity ispractically absent.



Figure 9: Quantitative maps of main oxides found in the ACK17 section of Châtel Argent Castle. The legend refers to
 ranges of discrete percentages expressed in false colours. Ab= Albite, Cal= Calcite, Chl= Chlorite, Fa= Fayalite, Ms=
 Muscovite, Qz= Quartz (Mineral abbreviations according to Whitney and Evans, 2010).

- The modal compositional maps sections and their relative legends expressed in false colours are shown in **Figure 10** (ADY17) and **Figure 11** (ACK17), processed through the MultiSpec© program
- 449 (Multispectral Image Data Analysis System) (Biehl and Landgrebe, 2002).



450 **Figure 10**: Modal compositional map of ADY17 section of Quart Castle.



451 **Figure 11**: Modal compositional map of ACK17 section of Châtel Argent Castle.

This maps processing allows to calculate the percentage quantity of the single phases present in the samples, which in this case are respectively reported in **Table 5** (relative to the data of the ADY17 section) and **Table 6** (relative to the data of the section ACK17).

455 It can be noted that in both sections the binder is the most abundant phase, with a value of 38.21% for the ADY17 section and 60.86% in the ACK17 section. Another interesting information that this 456 processing method can provide is the percentage value of the porosity. For the ADY17 sample it is 457 around 7.31%, while for the ACK17 it stands at 3.93%. From the observation of the two modal maps, 458 it can also be deduced that in the first case the primary porosity is concentrated in subspherical 459 pores of irregular shapes and not communicating with each other, in the second case mainly 460 secondary porosity occurs, due to shrinkage phenomena. The percentage of inert material is equal 461 to 54.48 for the ADY 17 section and 35.21 for the ACK 17 section. From here it can be deduced that 462

the binder / aggregate ratio is 0.70 for the mortar of the Quart Castle, a very low value, also considered that it is a plaster mortar and 1.73 for the mortar of the of Châtel Argent Castle.

Class	Percent
Quartz	24.74
Albite	9.27
K-feldspar	2.29
Chlorite	1.73
Muscovite	8.26
Calcite	7.32
Dolomite	0.86
Porosity	7.31
Binder	38.21
Total	100.00

**Table 5**: Values percentages of the phases present in section ADY17 of Quart Castle.

Class	Percent
Fayalite	1.31
Quartz	2.48
Chlorite	1.16
Albite	1.96
Carbonate	0.20
Muscovite	0.93
Coal	0.86
Cocciopesto	24.94
Porosity	3.93
Binder	60.86
Total	100.00

466 **Table 6**: Values percentages of the phases present in section ACK17 of Châtel Argent Castle.

The aggregate component of the ADY17 mortar consists mainly of quartz with a percentage of 27.74%, there are also albite at 9.27%, muscovite at 8.26% and calcite at 7.32%, in low quantities

there are also potassium feldspar (2.29%), chlorite (1.73%) and dolomite (0.86%).

For the mortar of the ACK17 sample, the aggregate is mainly formed by fragments of cocciopesto with a value of 24.94%, followed in very low percentages by quartz (2.48%), albite (1.96%) an amorphous phase (glass) (1.38%) and fayalite (1.31%) which together constitute the smelting slag from iron processing (2.69%), followed by chlorite with a value of 1.16%, muscovite (0.93%), remains of coal (0.86%) and carbonate (0.20%).

#### 475 **5.5 Hydraulic index map**

476 An important parameter to which reference for the analysis of mortars is the Hydraulic Index (H.I.).

- 477 This index is strictly related to the quantity of clayey minerals or hydraulicizing materials that are part
- 478 of the starting composition of the binder. It is identified by the formula:

479 
$$I = \frac{SiO_2 + Al_2O_3 + Fe_2O_3}{CaO + MgO}$$

The numerator indicates the acid components of the binder, while those with the denominator, its basic components. Based on the value of the Hydraulic Index, the binders can be distinguished according to the following classification (**Table 7**) by Mariani (1976):

Lime	Weakly	Medium	Properly	Eminently	(Cements)
	Hydraulic	Hydraulic	Hydraulic	Hydraulic	
Hydraulic Index	0.10-0.16	0.16-0.31	0.31-0.42	0.42-0.50	0.50-0.65
Table 7: Classification	of binders, by Mar	riani (1976).			

484 Figure 12 and Figure 13 show the maps of the Hydraulic Index, respectively, of sections ADY17 and ACK17. The maps were constructed by means of a simple algebraic operation, using the 485 486 numerical matrices of the quantitative maps of Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> at numerator and the acquired 487 maps of CaO and MgO at denominator. In this way, the complete quantification point by point of 488 each EDS spectrum (expressed as oxides) of the map was performed, in order to calculate the 489 distribution of the Hydraulic Index (H.I.), with its statistical error, within the mapped area. The values obtained were then divided into discrete classes, reported in the legend and graphed using false 490 colours. It can be noted that the intervals of the selected classes are not constant but reflect the one 491 492 generally used for the classification of mortars reported in Table 7.



493 Figure 12: Map of Hydraulic Index value of ADY17 section (Quart Castle).

483



494 Figure 13: Map of Hydraulic Index value of ACK17 section (Châtel Argent Castle).

The value of the Hydraulic Index is uniform and ranges between 0.00 and 0.10 for the ADY17 section, allowing to deduce that the binder is very homogeneous and of the aerial type (H.I. < 0.10). Those values are concordant with the values got through the microprobe analyses which are between 0.009 and 0.132 (**Table 3**). This indicates that in the preparation of the binder, in the specific case of magnesian composition due to the composition reported in **Table 3**, no hydraulic additives were added and therefore the setting took place through the typical exchange reaction between the CO<sub>2</sub> of the atmosphere and the H<sub>2</sub>O of the binder: 503 As for the ACK17 section, the value of the Hydraulic Index is more inhomogeneous, indicating that 504 the binder also has a heterogeneous composition, perhaps accentuated by its coarser grain.

The calculated Hydraulic Index resulted between of 0.50 and 1.50 values, corresponding to a binder that ranges from eminently hydraulic to decidedly cement and concordant with the values analyzed through the microprobe analysis which are between 0.768 and 1.059 (**Table 4**). A deliberate selection of the aggregate nature and grading to contribute to mortar impermeability was also applied for the cistern in Amaiur Castle (Navarre, Spain), where ceramic and silico-aluminous rock fragments were used as aggregates tank to confer hydraulicity to the mortars (Ponce-Anton et al., 2020).

511 The presence of an important microfracturing is also highlighted by the widespread red veins 512 (carbonate in composition) due to the cementitious character of the binder and therefore less plastic 513 than less hydraulic binders.

#### 514 **6.** Discussion

515 In this paper an analytical protocol based on a complete minero-petrographic approach for the study 516 of medieval castles mortars from Aosta Valley (NW Italy) is reported. This method requires time to 517 collect X-ray maps of the sections to be analyzed, and then to process the collected data; but it allow 518 to define different features of a mortar as the chemical composition of aggregates and binder 519 (reported as Wt % of single oxides present), the percentage of porosity and its distribution, and the 520 aggregates/binders ratios. The aggregate is defined by the petrographic approach through the study of rocks fragments and minerals, so the mineral phases compositions are characterized by the EDS 521 analyses, in such a way to define the area of provenance of the raw materials used to make the 522 mortars. 523

524 Similar analytic approach was reported by Carò et al. (2008), which studied plasters and mortars 525 from medieval Lardirago Castle (Pavia, northern Italy) by means of petrographical and chemical 526 analyses. Similar conclusions were reported. Two main types of binders were available: pure lime 527 and magnesian lime; neither hydraulic binders nor additives have been employed. The most ancient 528 building phase, which dates back to the 12th century, is characterized by the use of magnesian limes 529 for both plaster and mortar mixtures. The mineral composition of the aggregate correspond to lithic 530 sand of fluvial origin.

According to the data reported in the previous chapters, the mortars of the two castles under analysisdiffer on several aspects.

The mortars sampled from the Châtel Argent Castle (ACK) generally show a higher quantity of binder than the one present in the mortars from the Quart Castle. In fact, the former has a binder / aggregate ratio (B / A) generally of 1/3 and in some cases of 1/2 or 1/4. The mortars from Quart Castle (ADY) show an B / A ratio generally around 1/5, except for some sections that have values of 1/4 or 1/6.

The two binders are also very different compositionally: in particular the composition of the binder 537 used in the mortars of the Châtel Argent Castle (from the end of the 13th century) was calcic, with 538 values of CaO that varies from 58,68% to 92.41%, while the MgO values varies from 2.62% and 539 540 6.38%. In the Quart Castle mortar (sample) (from the end of the 12th century) the composition of the 541 binder was magnesian, with CaO values varies from 42.61% and 68.69% and MgO values between 24.43% and 49.85%. This diversity could be explained by petrographic considerations. The Quart 542 543 Castle is in fact located a few hundred meters from strongly tectonized meta-dolostone belonging to the Roisan Zone, corresponding to the Mesozoic cover of the Mont Mary nappe and outcropping 544 along the bed of the Bouthier Stream. It is therefore possible that the workers of the time used this 545 546 material to prepare the binder used in the Castle.

The use of magnesian mortars in medieval times was rather limited. For example, the ancient mortar employed in the medieval port of Genova were found to be produced with magnesian lime (Mannoni, 1988). In many other cases the mortar binder used in medieval castles of Aragon (Ponce-Antón et al., 2021) and Andalusia (Cosano et al., 2021) was found to be made of lime.

The total porosity varies between percentage values of 7% and 15% for the Châtel Argent Castle 551 sections represented by mostly primary and close porosity due to bubbles of air present in the 552 553 mixture, and between 8% and 20% for the Quart Castle sections, where the secondary porosity due 554 to shrinkage are more common and sometimes it is spread to the entire section. In the Quart Castle 555 samples, the primary porosity is also relevant and it can contribute to develop a serious secondary 556 porosity. The presence of higher MgO values in the Quart Castle samples tend to reduce the strength in the mortar because of the behavior of the magnesian binder during the drying process, which 557 create a capillary stress around the primary porosity and produce the shrinkage. A high degree of 558 pore interconnection, high desorption index and the presence of high pore volume in the 0.01 µm to 559 560 1 µm size range affect the mortar durability since pores retain water longer inside the mortar.

561

#### 6.1 Petrographic considerations and geological correlations

The mineralogical composition of the aggregate of the two different sites studied and some of its characteristics reflect the lithologies found in the areas adjacent to the two castles.

In particular, it can be noted that biotite is generally present in the samples of the Quart Castle and only in one sample of the Châtel Argent Castle. Precisely, biotite in the Aosta Valley can be easily traced back to the dismantling of the kinzigites belonging to the Valpelline Series, dismantled and transported downstream by the Buthier Stream, a left tributary of the Dora Baltea River, where it flows into the city of Aosta, that is just upstream of the site where the Quart Castle is located (**Figure 14**).

- 570 The few glaucophane crystals present in the sections of the Quart Castle could derive from the 571 eclogitic units that outcrop south of Quart on the orographic right of the Dora Baltea River, as well
- as the clasts of serpentinite and prasinite (**Figure 14**).



Figure 14: Extract from the Geotectonic Map of the Aosta Valley (modified by De Giusti et al., 2004). The Quart Castle is
identified with the yellow rhombus. The unit of the Valpelline Series include n.42 which identifies the kinzigites (light brown)
togheter with n.43 orthoterivates in pink; the eclogitic units of the Zermatt-Saas zone (ZS) are indicated with the n.37.

In all the analyzed samples there are often single feldspar crystals, which together with the white mica and quartz crystals probably derive from the dismantling of more or less metamorphosed continental crust units. The potassium feldspar inclusions, in particular, could derive from the dismantling of orthogneiss, such as those of the Gran Paradiso massif outcropping in the Valsavaranche Valley, or of granite, probably deriving from the erosion of the granite of Mont Blanc massif. The lithic clasts with a granite composition found in some sections, especially those sampled in the Quart Castle, could also derive from this last massif.

- Plagioclases with a labradorite composition can refer to basic rocks or to units of high metamorphic grade. Also, in this case there is a congruence between the data found from the analyses of the Quart Castle binder and the location of the castle. In the unit of the Valpelline Series in fact high temperature basic masses occur.
- A lithology frequently present in the samples from both castles are the graphitic-schists, which appear to be present in greater quantities and in greater dimensions in the mortars of Châtel Argent Castle and in smaller quantities and of much smaller dimensions in those of the Quart Castle. These lithic fragments most likely derive from the dismantling of graphitic-schists belonging to the units of

the Houillère Zone out cropping just upstream of the site where the Châtel Argent Castle is located (**Figure 15**). In this case, also the petrographic analysis of the aggregate is consistent with the regional geology of the areas surrounding the buildings studied. The calcschist are probably referable to the Mesozoic covers of oceanic crust of the Piemonte Zone (**Figure 15**).



595 **Figure 15**: Extract from Geotectonic Map of the Aosta Valley (modified by De Giusti et al., 2004). The Châtel Argent Castle 596 is identified with the yellow rhombus. The n. 31 identifies the Briaçonnais Unit of Permo-Carboniferous age containing 597 graphitic-schists, while the n. 35 identifies the units of origin of calcschists.

#### 598 **7. Conclusions**

599 On the basis of the petrographic and mineralogical analyses, it can be concluded that the aggregate

used in medieval times to make the bedding mortars and plasters used in the two historic buildingscan be classified as river sand, coming from alluvial deposits of the Dora Baltea River located in the

602 immediate proximity to the sites where the two castles stand.

Only in limited quantities were used materials from crushed rocks, such as the inclusions of calcite

from vein observed in numerous samples analyzed or, in the only case of the ACK17 sample from

- 605 Châtel Argent Castle, of artificial materials with pozzolanic behavior, such as the inclusions of
- 606 cocciopesto and melting slag.

The possible finding of raw materials to be used for potential restoration works must therefore be sought in the vicinity of historical sites. In particular, in the case of the Quart Castle: 609 - In fluvial sands located at the confluence of the Buthier Stream in the Dora Baltea River, which are

- 610 characterized by rock fragments coming from the Valpelline Series and calcschist from the Piemonte
- 611 Zone.
- 612 In the case of the Châtel Argent Castle:

In fluvial sands located just downstream of the confluence of the Dora di Rhemes and Savara
 streams into the Dora Baltea River, rich in clasts deriving from the dismantling of the units of the
 External Brianconnais Zone and of the calcschists of the Piemonte Zone.

In conclusion, it can be stated that the petrographic observation accompanied by an in-depth analysis using scanning electron microscopy and attached electron microprobe has resulted in an analytical approach useful for the characterization of historical mortars, defining the basins of origin of the raw materials used for the realization of the same, and therefore guiding the choice of the best materials for future restoration operations.

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#### 627 References

Appolonia, L., De Gattis, G., Fioravanti, P., Pizzi, L., Vaudan, D., Zidda, G., Bedini, E., Bertone, A.,
Cortellazzo, M., Hurni, J. P., Lupo, M., Orcel, C., Tercier, J., 2006. Il Castello di Quart. Bollettino
Soprintendenza per i beni e le attività culturali della Valle d'Aosta n.2. ©RAVA, pp. 71-122.
<a href="https://gestionewww.regione.vda.it/cultura/pubblicazioni/bollettino/n 2/default\_i.aspx">https://gestionewww.regione.vda.it/cultura/pubblicazioni/bollettino/n 2/default\_i.aspx</a>.

Appolonia, L., Vaudan, D., Glarey, A., 2010. Il castello di Châtel-Argent a Villeneuve: il contributo
allo studio dei materiali in relazione alla fornace da calce. Bollettino Soprintendenza per i beni e le
attività culturali della Valle d'Aosta n.6. ©RAVA, pp. 108-111.
https://gestionewww.regione.vda.it/cultura/pubblicazioni/bollettino/n\_6/default\_i.aspx

Arizzi, A., Cultrone, G., 2012. The difference in behaviour between calcitic and dolomitic lime mortars
set under dry conditions: The relationship between textural and physical–mechanical properties.
Cement and Concrete Research. 42, 818-826. https://doi.org/10.1016/j.cemconres.2012.03.008.

Beltrando, M., Compagnoni, R., Lombardo, B., 2010. (Ultra) High-pressure metamorphism and
orogenesis: an Alpine perspective. Gondwana Research. 18, 147-166.
<u>https://doi.org/10.1016/j.gr.2010.01.009</u>

Biehl, L., Landgrebe, D. A., 2002. MultiSpec: a tool for multispectral-hyperspectral image data
analysis. Computer & Geosciences. 38, 1153-1159. <u>https://doi.org/10.1016/S0098-3004(02)00033-</u>
X

- Cantù, M., Giacometti, F., Landi, A. G., Riccardi, M. P., Tarantino, S. C., Grimoldi, A., 2015.
  Characterization of XVIIIth century earthen mortars from Cremona (Northern Italy): Insights on a
  manufacturing tradition. Materials Characterization. 103, 81-89.
  https://doi.org/10.1016/j.matchar.2015.03.018
- 649 Cosano, D., Esquivel, D., Jimenez-Sanchidrian, C., Ruiz, J.R., 2021. Analysis of mortars from the 650 castle keep in Priego de Cordoba (Spain). Vibrational Spectroscopy, 112, 103184.
- Carò, F., Riccardi, M.P., Mazzilli Savini, M.T., 2008. Characterization of plasters and mortars as a
  tool in archaeological studies: the case of Lardirago Castle in Pavia, Northern Italy, Archaeometry
  50, 1, 85–100.
- Dal Piaz, G. V., 1999. The Austroalpine–Piedmont nappe stack and the puzzle of Alpine Tethys.
  Memorie di Scienze Geologiche. 51(1), 155-176.
- Dal Piaz, G. V., Hunziker, J. C., Martinotti, G., 1972. La Zona Sesia Lanzo e l'evoluzione tettonometamorfica delle Alpi nordoccidentali interne. Memorie Società Geologica Italiana. 11, 433-466.
- De Gattis, G., Cortellazzo, M., 2008. Indagini archeologiche al sito fortificato di Châtel-Argent
  (Villeneuve) tra tarda antichità e Medioevo. Bollettino Soprintendenza per i beni e le attività culturali
  della Valle d'Aosta n.4. ©RAVA, pp. 203-211.
  https://www.regione.vda.it/cultura/pubblicazioni/bollettino/n 4/default i.aspx
- De Giusti, F., Dal Piaz, G. V., Massironi, M., Schiavo, A., 2004. Carta geotettonica della Valle d'Aosta. Memorie di Scienze Geologiche. 55, 129-149.
- Elsen, J., 2006. Microscopy of historic mortars a review. Cement and Concrete Research. 36(8),
  1416-1424. <u>https://doi.org/10.1016/j.cemconres.2005.12.006</u>
- Elter, G., Elter, P., 1965. Carta geologica della regione del Piccolo S. Bernardo (versante italiano):
   note illustrative. Memorie Istituto Geologico Mineralogico Università di Padova. Societa Cooperativa
   Tipografica, Padova. 25, 1-53.
- Ernst, W. G., Dal Piaz, G. V., 1978. Mineral parageneses of eclogitic rocks and related mafic schists
  of the Piemonte ophiolite nappe, Breuil St. Jacques area, Italian Western Alps. American
  Mineralogist, 63(7-8), 621-640.
- Lezzerini, M., Ramacciotti, M., Cantini, F., Fatighenti, B., Antonelli, F., Pecchioni, E., Fratini, F.,
- Cantisani, E., Giamello, M., 2017. Archaeometric study of natural hydraulic mortars: the case of the
  Late Roman Villa dell'Oratorio (Florence, Italy). Archaeological and Anthropological Sciences. 9,
  603-615. <a href="https://doi.org/10.1007/s12520-016-0404-2">https://doi.org/10.1007/s12520-016-0404-2</a>
- Lezzerini, M., Raneri, S., Pagnotta, S., Columbu, S., Gallello, G., 2018. Archaeometric study of
  mortars from the Pisa's Cathedral Square (Italy). Measurement. 126, 322-331.
  <a href="https://doi.org/10.1016/j.measurement.2018.05.057">https://doi.org/10.1016/j.measurement.2018.05.057</a>
- Loprieno, A., Bousquet, R., Bucher, S., Ceriani, S., Dalla Torre, F. H., Fugenschuh, B., Schmid, S.
  M., 2011. The Valais units in Savoy (France): a key area for understanding the palaeogeography
  and the tectonic evolution of the Western Alps. International Journal of Earth Sciences. 100, 963–
  92. <u>https://doi.org/10.1007/s00531-010-0595-1</u>
- Malusà, G., Polino, R., Martin, S., 2005. The Gran San Bernardo nappe in the Aosta Valley (Western
  Alps): a composite stack of distinct continental crust units. Bulletin de la Société Géologique de
  France. 176(5), 417-431. https://doi.org/10.2113/176.5.417

- Mannoni, T., 1988. Ricerche sulle malte genovesi alla «porcellana», Atti del Convegno di Studi «Le
  Scienze, le Istituzioni, gli Operatori alla soglia degli anni '90», Bressanone, 137-142.
- Mariani, E., 1976. I leganti aerei e idraulici. Ed. Ambrosiana, Milano.

Martinotti, G., Giordan, D., Giardino, M., Ratto, S., 2011. Controlling factors for deep-seated
 gravitational slope deformation (DSGSD) in the Aosta Valley (NW Alps, Italy). Jaboyedoff, M. (ed.)
 Slope Tectonics. Geological Society London Special Publications. 351(1), 113–131.
 <a href="http://dx.doi.org/10.1144/SP351.6">http://dx.doi.org/10.1144/SP351.6</a>

- Miriello, D., Barca, D., Bloise, A., Ciarallo, A., Crisci, G. M., De Rose, T., Gattuso, C., Gazineo, F.,
  La Russa, M. F., 2010. Characterisation of archaeological mortars from Pompeii (Campania, Italy)
  and identification of construction phases by compositional data analysis. Journal of Archaeological
  Science. 37(9), 2207-2223. https://doi.org/10.1016/j.jas.2010.03.019
- 697 Morimoto, N., 1988. Nomenclature of Pyroxenes. Mineralogy and Petrology. 39, 55–76. 698 <u>https://doi.org/10.1007/BF01226262</u>
- Moropoulou, A., Bakolas, A., Bisbikou, K., 2000. Investigation of the technology of historic mortars.
  Journal of Cultural Heritage. 1, 45-58. <u>https://doi.org/10.1016/S1296-2074(99)00118-1</u>
- NORMA UNI 10924, 2001. Malte per elementi costruttivi e decorativi: classificazione e terminologia.
   Ed UNI (Ente Nazionale Italiano Unificazione) Milano.
- Pecchioni, E., Fratini, F., Cantisani, E., 2018. Le malte antiche e moderne tra tradizione ed innovazione, second ed. Pàtron, Bologna.
- Petrakakis, K., Dietrich, H., 1985. MINSORT: a program for the processing and archivation of
  microprobe analyses of silicate and oxide minerals. Neues Jahrbuch für Mineralogie, Monatshefte.
  74(8), 379-384.
- Polino, R., Bonetto, F., Carraro, F., Gianotti, F., Gouffon, Y., Malusà, M.G., Martin, S., Perello, P.,
  Schiavo, A., 2015. Note Illustrative della Carta Geologica d'Italia alla scala 1:50.000 Foglio
  090AOSTA. ISPRA, Roma.
- Ponce-Antón G., Zuluaga M.C., Ortega, L.A., Mauleon, J.A., 2020. Petrographic and Chemical–
  Mineralogical Characterization of Mortars from the Cistern at Amaiur Castle (Navarre, Spain).
  Minerals, 10, 311.
- Ponce-Antón, G., Arizzi, A., Cultrone, G., Zuluaga, M.C.I., Ortega, L.A., Mauleon, J.A., 2021.
  Investigating the manufacturing technology and durability of lime mortars from Amaiur Castle
  (Navarre, Spain): A chemical–mineralogical and physical study. Construction and Building Materials
  299.
- Rampazzi, L., Colombini, M., Conti, C., Corti, C., Lluveras-Tenorio, A., Sansonetti, A., Zanaboni, M.,
  2016. Technology of Medieval Mortars: An Investigation into the Use of Organic Additives.
  Archaeometry, Wiley. 58, 115-130. <u>https://doi.org/10.1111/arcm.12155</u>
- Rapp, G., 2009. Archaeomineralogy, second ed. Natural Sciences in Archaeology, Springer-Verlag
  Berlin Heidelberg. doi:10.1007/978-3-540-78594-1.

723 Riccardi, M. P., Lezzerini, M., Carò, F., Franzini, M., Messiga, B., 2007. Microtextural and 724 microchemical studies of hydraulic ancient mortars: Two analytical approaches to understand pre-725 industrial technology process. Journal of Cultural heritage. 8, 350-360. https://doi.org/10.1016/j.culher.2007.04.005 726

- Scherer, G.W., 1990. Theory of drying. Journal of the American Ceramic Society. 73(1) 3-14.
   <a href="https://doi.org/10.1111/j.1151-2916.1990.tb05082.x">https://doi.org/10.1111/j.1151-2916.1990.tb05082.x</a>
- Schiele, E., Berens, L.W., 1976. La Calce. Calcare, calce viva, idrato di calcio. Ed. Tecniche ET,Milano.
- 731 Whitney, D.L., Evans, B.W., 2010. Abbreviations for Names of Rock-Forming Minerals. American
- 732 Mineralogist. 95, 185-187. <u>http://dx.doi.org/10.2138/am.2010.3371</u>

Pyroxen	e											
SAMPLE	АСКО4		ACK12	ADY04				ADY17				
SiO2	53,16	52,34	52,20	47,94	46,53	46,47	47,94	51,83	50,20	51,94	52,03	50,86
Al2O3	4,23	3,53	6,72	9,71	11,05	11,00	10,14	2,08	2,70	1,94	1,89	2,97
FeO	1,67	9,78	14,71	19,28	19,84	19,92	17,29	13,39	15,19	12,77	13,46	14,25
MgO	15,89	13,58	13,39	10,39	9,93	9,90	11,59	10,86	11,20	11,15	11,21	11,34
CaO	25,06	20,78	12,23	11,35	11,08	11,16	11,62	21,46	20,34	21,85	21,06	20,23
Na2O	0,00	0,00	0,76	1,33	1,56	1,54	1,42	0,39	0,37	0,35	0,34	0,35
	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****
Total	100,01	100,01	100,01	100,00	99,99	99,99	100,00	100,01	100,00	100,00	99,99	100,00
Si	1,925	1,943	1,929	1,814	1,758	1,757	1,795	1,967	1,907	1,967	1,973	1,928
ALIV	0,075	0,057	0,071	0,186	0,242	0,243	0,205	0,033	0,060	0,033	0,027	0,066
Fe 3+	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,032	0,000	0,000	0,006
Al VI	0,105	0,098	0,221	0,246	0,251	0,247	0,242	0,060	0,060	0,054	0,057	0,066
Fe 3+	0,000	0,000	0,000	0,037	0,105	0,109	0,066	0,002	0,060	0,005	0,000	0,032
Fe 2+	0,050	0,260	0,297	0,354	0,311	0,311	0,293	0,382	0,335	0,366	0,380	0,354
Mg	0,845	0,643	0,482	0,362	0,333	0,333	0,399	0,556	0,545	0,576	0,563	0,548
Fe 2+	0,001	0,044	0,158	0,219	0,211	0,210	0,183	0,040	0,055	0,034	0,047	0,060
Ма	0,012	0,109	0,256	0,224	0,226	0,225	0,248	0,059	0,090	0,054	0,070	0,093
Ca	0,972	0,827	0,484	0,460	0,449	0,452	0,466	0,872	0,828	0,887	0,855	0,822
Na	0,000	0,000	0,054	0,098	0,114	0,113	0,103	0,029	0,027	0,026	0,025	0,026
т	2,000	2,000	2,000	2,000	2,000	2,000	2,000	2,000	2,000	2,000	2,000	2,000
M(1)	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000
M(2)	0,985	0,980	0,952	1,000	1,000	1,000	1,000	1,000	1,000	1,000	0,998	1,000
Xmq	0,944	0,712	0,619	0,506	0,517	0,517	0,576	0,592	0,619	0,612	0,598	0,607

**Table S1**: Representative microprobe analyses of pyroxenes of Châtel Argent Castle (ACK04 and ACK12) and Quart Castle (ADY04 and ADY17). The chemical composition of minerals is expressed as weight% oxides. The structural formulae, reported as number of cations per formula unit (a.p.f.u.), were recalculated on the basis of 6 oxygens. T= Tetrahedral site, M(1)= Octahedral site, M(2)= distorted 6- or 8-fold site, Xmg= Mg/(Mg+Fe<sup>2+</sup>+Fe<sup>3+</sup>).

Amphib	ole											
SAMPLE	ACK10	ADY04		ADY10								
SiO2	52,40	56,86	56,25	56,11	55,73	55,96	51,68	53,70	52,72	46,67	46,54	46,73
Al2O3	5,62	0,62	1,76	1,63	1,97	1,80	3,97	3,58	4,81	9,14	9,88	9,91
FeO	15,13	10,11	11,21	10,47	11,79	11,03	15,49	15,32	14,75	19,81	18,48	18,45
MgO	13,26	17,97	16,44	17,58	16,54	17,11	14,21	13,90	13,81	10,47	9,91	10,04
CaO	10,25	11,93	11,56	11,35	11,07	11,11	11,57	9,79	10,19	10,54	11,17	11,19
Na2O	1,32	0,51	0,78	0,87	0,89	0,99	1,05	1,72	1,72	1,20	1,71	1,41
К2О	0,02	0,00	0,00	0,00	0,00	0,00	0,04	0,00	0,00	0,18	0,31	0,27
	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****
Total	98,00	98,00	98,01	98,00	98,00	98,00	98,02	98,00	98,00	98,01	98,00	98,00
Si	7,487	8,000	7,955	7,914	7,903	7,911	7,424	7,653	7,505	6,781	6,843	6,842
Al IV	0,513	0,000	0,045	0,086	0,097	0,089	0,576	0,347	0,495	1,219	1,157	1,158
Al VI	0,432	0,103	0,249	0,185	0,232	0,211	0,096	0,254	0,313	0,347	0,555	0,551
Fe 3+	0,444	0,036	0,000	0,000	0,000	0,000	0,620	0,567	0,599	1,176	0,536	0,644
Mg	2,824	3,770	3,465	3,697	3,497	3,606	3,044	2,952	2,931	2,267	2,172	2,190
Fe 2+	1,300	1,091	1,286	1,118	1,271	1,183	1,240	1,227	1,157	1,210	1,737	1,615
Fe 2+	0,065	0,063	0,040	0,116	0,128	0,121	0,000	0,031	0,000	0,021	0,000	0,000
Са	1,569	1,798	1,751	1,715	1,682	1,683	1,780	1,495	1,555	1,642	1,760	1,756
Na	0,366	0,139	0,209	0,169	0,190	0,196	0,220	0,474	0,445	0,337	0,240	0,244
Na	0,000	0,000	0,006	0,070	0,055	0,075	0,072	0,000	0,028	0,000	0,246	0,156
Κ	0,004	0,000	0,000	0,000	0,000	0,000	0,007	0,000	0,000	0,033	0,059	0,051
Xmg	0,674	0,766	0,723	0,750	0,714	0,735	0,711	0,701	0,717	0,648	0,556	0,576
Fe2O3	4,214	0,344	0,000	0,000	0,000	0,000	5,855	5,396	5,701	10,970	4,944	5,965
FeO	11,648	10,010	11,440	10,680	12,030	11,250	10,531	10,775	9,920	10,339	14,411	13,453

Amphib	ole	-						
SAMPLE	ADY10	ADY17						
SiO2	46,75	48,83	50,70	49,74	43,25	43,23	43,21	42,93
Al2O3	10,28	9,25	6,86	9,19	13,22	13,18	13,35	13,06
FeO	18,18	16,57	15,67	16,12	17,98	18,17	17,93	18,70
MgO	9,83	11,52	13,06	11,44	9,03	8,87	8,85	8,71
CaO	11,13	9,00	9,51	8,53	11,56	11,51	11,61	11,53
Na2O	1,46	2,72	2,20	2,98	1,43	1,44	1,45	1,50
К2О	0,37	0,11	0,00	0,00	1,53	1,60	1,60	1,57
	*****	*****	*****	*****	*****	*****	*****	*****
Total	98,00	98,00	98,00	98,00	98,00	98,00	98,00	98,00
Si	6,850	6,995	7,214	7,098	6,438	6,446	6,447	6,419
Al IV	1,150	1,005	0,786	0,902	1,562	1,554	1,553	1,581
Al VI	0,625	0,556	0,365	0,644	0,758	0,763	0,794	0,720
Fe 3+	0,545	0,912	0,915	0,827	0,411	0,391	0,323	0,432
Mq	2,147	2,459	2,771	2,433	2,003	1,972	1,968	1,942
Fe 2+	1,683	1,073	0,950	1,096	1,828	1,874	1,915	1,906
Fe 2+	0.000	0,000	0,000	0,000	0,000	0,000	0,000	0,000
Ca	1.748	1,381	1,449	1,303	1,845	1,840	1,856	1,848
Na	0,252	0,619	0,551	0,697	0,155	0,160	0,144	0,152
Na	0 163	0.137	0.057	0.128	0.258	0.256	0.276	0.282
K	0,070	0,020	0,000	0,000	0,290	0,304	0,304	0,299
Xmg	0,561	0,700	0,745	0,689	0,523	0,513	0,507	0,505
Fe2O3	5,044	8,632	8,717	7,864	3,746	3,560	2,934	3,918
FeO	14,011	9,143	8,147	9,374	14,979	15,337	15,660	15,555

**Table S2**: Representative microprobe analyses of amphiboles of Châtel Argent Castle (ACK10) and Quart Castle (ADY04, ADY10 and ADY17). The chemical composition of minerals is expressed as weight% oxides. The structural formulae, reported as number of cations per formula unit (a.p.f.u.), were recalculated on the basis of 23 oxygens. Xmg= Mg/(Mg+Fe<sup>2+</sup>+Fe<sup>3+</sup>).

Feldspa	r											
SAMPLE	АСКО4				ACK10						ACK12	
SiO2	69,34	69,17	68,70	69,10	69,18	69,31	69,44	69,19	68,96	69,30	68,91	69,07
Al2O3	19,45	19,43	19,62	19,56	19,43	19,28	19,39	19,43	19,52	19,33	19,62	19,40
CaO	0,00	0,00	0,30	0,00	0,00	0,00	0,00	0,00	0,23	0,00	0,20	0,00
Na2O	11,09	11,40	11,38	11,34	11,39	11,41	11,17	11,38	11,29	11,37	11,28	11,53
К2О	0,12	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****
Total	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,01	100,00
Si	3,017	3,012	2,996	3,008	3,012	3,017	3,019	3,012	3,004	3,016	3,002	3,009
Al	0,997	0,997	1,008	1,004	0,997	0,989	0,994	0,997	1,002	0,992	1,007	0,996
Са	0,000	0,000	0,014	0,000	0,000	0,000	0,000	0,000	0,011	0,000	0,009	0,000
Na	0,935	0,962	0,963	0,957	0,961	0,963	0,942	0,961	0,954	0,960	0,953	0,974
К	0,007	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000
Ζ	4,014	4,009	4,004	4,012	4,009	4,007	4,013	4,009	4,007	4,008	4,009	4,006
X	0,942	0,962	0,977	0,957	0,961	0,963	0,942	0,961	0,964	0,960	0,962	0,974
An	0,000	0,000	0,014	0,000	0,000	0,000	0,000	0,000	0,011	0,000	0,010	0,000
Ab	0,993	1,000	0,986	1,000	1,000	1,000	1,000	1,000	0,989	1,000	0,990	1,000
Or	0,007	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000

Feldspai	r											
SAMPLE	ACK12						ACK17	ADY04				
SiO2	68,76	69,20	69,35	69,31	69,22	69,35	69,20	66,62	68,92	69,41	68,56	68,98
Al2O3	19,78	19,45	19,40	19,37	19,42	19,43	19,24	23,42	19,42	19,36	19,81	19,59
CaO	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,77	0,15	0,00	0,11	0,00
Na2O	11,47	11,35	11,26	11,32	11,36	11,23	11,54	9,19	11,51	11,23	11,51	11,44
К2О	0,00	0,00	0,00	0,00	0,00	0,00	0,02	0,00	0,00	0,00	0,00	0,00
	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****
Total	100,01	100,00	100,01	100,00	100,00	100,01	100,00	100,00	100,00	100,00	99,99	100,01
Si	2,996	3,012	3,017	3,016	3,013	3,016	3,015	2,891	3,005	3,019	2,990	3,004
Al	1,016	0,998	0,995	0,993	0,996	0,996	0,988	1,198	0,998	0,992	1,018	1,006
Са	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,036	0,007	0,000	0,005	0,000
Na	0,969	0,958	0,950	0,955	0,959	0,947	0,975	0,773	0,973	0,947	0,973	0,966
κ	0,000	0,000	0,000	0,000	0,000	0,000	0,001	0,000	0,000	0,000	0,000	0,000
Ζ	4,012	4,010	4,011	4,010	4,009	4,012	4,003	4,088	4,003	4,011	4,009	4,010
X	0,969	0,958	0,950	0,955	0,959	0,947	0,976	0,809	0,980	0,947	0,978	0,966
An	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,044	0,007	0,000	0,005	0,000
Ab	1,000	1,000	1,000	1,000	1,000	1,000	0,999	0,956	0,993	1,000	0,995	1,000
Or	0,000	0,000	0,000	0,000	0,000	0,000	0,001	0,000	0,000	0,000	0,000	0,000

Feldspar												
SAMPLE	ADY04	ADY10							ADY17			
SiO2	68,96	68,89	68,76	69,42	68,70	68,47	55,88	56,77	69,12	68,94	53,46	54,60
Al2O3	19,41	19,54	19,51	19,36	19,77	20,15	25,22	24,83	19,24	18,91	29,98	29,12
CaO	0,00	0,00	0,35	0,00	0,53	0,62	12,64	12,19	0,00	0,54	12,18	11,17
Na2O	11,63	11,57	11,39	11,21	11,00	10,77	6,26	6,21	11,64	11,61	4,38	5,11
К2О	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****
Total	100,00	100,00	100,01	99,99	100,00	100,01	100,00	100,00	100,00	100,00	100,00	100,00
Si	3,006	3,003	2,999	3,019	2,994	2,982	2,541	2,573	3,013	3,011	2,413	2,459
Al	0,997	1,004	1,003	0,992	1,015	1,034	1,351	1,326	0,988	0,974	1,595	1,546
Са	0,000	0,000	0,016	0,000	0,025	0,029	0,616	0,592	0,000	0,025	0,589	0,539
Na	0,983	0,978	0,963	0,945	0,929	0,910	0,552	0,546	0,984	0,983	0,383	0,446
К	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000
Ζ	4,004	4,007	4,002	4,012	4,009	4,017	3,892	3,899	4,001	3,985	4,008	4,005
Х	0,983	0,978	0,980	0,945	0,954	0,938	1,168	1,138	0,984	1,009	0,972	0,985
An	0,000	0,000	0,017	0,000	0,026	0,031	0,527	0,520	0,000	0,025	0,606	0,547
ab	1,000	1,000	0,983	1,000	0,974	0,969	0,473	0,480	1,000	0,975	0,394	0,453
Or	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000

Feldspa	r										
SAMPLE	ACK10		ACK12				ADY04	ADY10			
<b>C</b> :00	65.60			66.00	65.00	65.00	65.07	66.40	cc 07	66.00	65.00
5102	65,69	65,92	65,92	66,08	65,92	65,90	65,97	66,40	66,07	66,08	65,90
Al2O3	18,47	18,57	18,42	18,51	18,44	18,31	18,57	18,28	18,52	18,43	18,59
CaO	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
Na2O	0,73	0,46	0,27	0,59	0,49	0,60	0,00	0,35	0,30	0,32	0,50
К2О	15,11	15,05	15,39	14,82	15,15	15,19	15,46	14,97	15,10	15,17	15,01
	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****
Total	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	99,99	100,00	100,00
Si	3,014	3,018	3,022	3,022	3,021	3,022	3,022	3,035	3,024	3,026	3,017
Al	0,999	1,002	0,995	0,998	0,996	0,990	1,003	0,985	0,999	0,994	1,003
Са	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000
Na	0,065	0,041	0,024	0,052	0,044	0,053	0,000	0,031	0,027	0,028	0,044
К	0,884	0,879	0,900	0,865	0,886	0,889	0,904	0,873	0,882	0,886	0,877
Ζ	4,012	4,021	4,018	4,020	4,017	4,012	4,025	4,020	4,023	4,020	4,021
х	0,949	0,920	0,924	0,917	0,929	0,942	0,904	0,904	0,908	0,914	0,921
An	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000
Δh	0.068	0.044	0.026	0.057	0.047	0.057	0.000	0.034	0.029	0.031	0.048
Or	0.932	0.956	0.974	0.943	0.953	0.943	1.000	0.966	0.971	0.969	0.952

**Table S3**: Representative microprobe analyses of feldspars of Châtel Argent Castle (ACK04, ACK10, ACK12 and ACK17) and Quart Castle (ADY04, ADY10 and ADY17). The chemical composition of minerals is expressed as weight% oxides. The structural formulae, reported as number of cations per formula unit (a.p.f.u.), were recalculated on the basis of 8 oxygens. Z= Tetrahedral site, X= large, irregularly coordinated site. An= Anorthite Ab= Albite, Or= Orthoclase (Mineral abbreviations according to Whitney and Evans, 2010).

Dioctahedı	ral micas											
SAMPLE	АСКО4					ACK10						
									- /			
SiO2	48,19	47,30	55,33	54,26	53,82	51,45	53,81	51,40	51,02	49,95	52,04	48,21
Al2O3	27,41	21,79	24,13	26,24	26,65	27,36	26,86	27,42	27,48	31,04	27,92	34,65
FeO	3,08	6,23	0,00	0,00	0,00	2,99	1,03	2,94	3,20	1,84	2,54	0,88
MgO	1,02	4,88	5,29	4,87	4,47	2,82	4,04	3,14	3,10	2,20	2,96	1,23
CaO	0,00	1,02	0,39	0,00	0,00	0,47	0,00	0,00	0,00	0,00	0,00	0,00
Na2O	4,13	9,52	0,32	0,00	0,00	0,33	0,00	0,00	0,00	0,48	0,00	0,65
К2О	11,17	4,27	9,54	9,62	10,06	9,58	9,27	10,11	10,20	9,49	9,54	9,38
	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****
Total	95,00	95,00	95,00	95,00	95,00	95,00	95,00	95,00	95,00	95,00	95,00	95,00
Si	6,623	6,559	7,245	7,093	7,055	6,864	7,051	6,860	6,826	6,616	6,894	6,356
ALIV	1,377	1,441	0,755	0,907	0,945	1,136	0,949	1,140	1,174	1,384	1,106	1,644
ALVI	3.064	2.120	2.968	3.135	3.171	3.165	3.199	3.172	3.160	3.460	3.254	3.741
Fe	0.354	0.723	0.000	0.000	0.000	0.334	0.112	0.328	0.358	0.204	0.281	0.097
Mq	0,208	1,010	1,033	0,950	0,874	0,561	0,789	0,624	0,618	0,435	0,585	0,243
5												
Са	0,000	0,151	0,055	0,000	0,000	0,068	0,000	0,000	0,000	0,000	0,000	0,000
Na	1,101	2,560	0,082	0,000	0,000	0,086	0,000	0,000	0,000	0,122	0,000	0,165
К	1,959	0,755	1,593	1,605	1,682	1,630	1,550	1,721	1,742	1,604	1,612	1,577
7	8 000	<u> 000</u>	<u> 000</u>	8 000	8 000	8 000	8 000	8 000	8 000	8 000	8 000	8 000
2	3,000	2 952	8,000 4 001	0,000 4 094	8,000 4.046	4,000	8,000 4 100	8,000 4 1 2 4	0,000 4 126	4,000	8,000 4 120	0,000 4 001
Ŷ	3,020	5,052	4,001	4,064	4,040	4,000	4,100	4,124	4,150	4,099	4,120	4,001
X	3,060	3,400	1,730	1,605	1,082	1,784	1,550	1,/21	1,/42	1,725	1,012	1,742
Xmg	0,371	0,583	1,000	1,000	1,000	0,627	0,875	0,656	0,633	0,681	0,676	0,714
Ms	0,640	0,218	0,921	1,000	1,000	0,914	1,000	1,000	1,000	0,929	1,000	0,905
pg	0,360	0,739	0,047	0,000	0,000	0,048	0,000	0,000	0,000	0,071	0,000	0,095
та	0,000	0,044	0,032	0,000	0,000	0,038	0,000	0,000	0,000	0,000	0,000	0,000

Dioctahedr	al micas											
SAMPLE	ACK10	ACK12										ACK17
SiO2	49,63	51,09	53,76	49,36	52,90	53,30	47,41	47,60	46,93	53,03	54,21	52,33
Al2O3	28,09	29,84	25,46	32,95	27,06	25,52	39,74	39,42	38,31	27,68	26,23	25,57
FeO	5,09	0,47	1,07	0,38	0,73	1,14	0,00	0,30	0,00	0,00	1,65	3,48
MgO	2,07	3,39	4,83	2,18	4,21	4,76	0,00	0,00	0,52	4,16	4,05	2,91
CaO	0,00	0,00	0,00	0,00	0,00	0,00	0,39	0,00	1,81	0,00	0,00	1,49
Na2O	0,67	0,62	0,00	0,90	0,53	0,30	6,68	7,43	7,16	0,44	0,00	3,36
К2О	9,44	9,60	9,88	9,22	9,58	9,98	0,78	0,25	0,27	9,69	8,86	5,87
	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****	
Total	95,00	95,00	95,00	95,00	95,00	95,00	95,00	95,00	95,00	95,00	95,00	95,00
Si	6,701	6,727	7,086	6,490	6,963	7,046	6,048	6,071	6,024	6,952	7,105	6,947
ALIV	1,299	1,273	0,914	1,510	1,037	0,954	1,952	1,929	1,976	1,048	0,895	1,053
Al VI	3,171	3,357	3,040	3,597	3,160	3,022	4,022	3,996	3,818	3,230	3,156	2,949
Fe	0,575	0,051	0,118	0,042	0,081	0,126	0,000	0,032	0,000	0,000	0,181	0,386
Mg	0,417	0,666	0,948	0,428	0,826	0,938	0,000	0,000	0,100	0,813	0,791	0,575
Са	0,000	0,000	0,000	0,000	0,000	0,000	0,053	0,000	0,248	0,000	0,000	0,212
Na	0,174	0,158	0,000	0,230	0,136	0,078	1,652	1,837	1,783	0,111	0,000	0,866
К	1,627	1,612	1,661	1,547	1,608	1,682	0,127	0,040	0,044	1,621	1,482	0,994
Ζ	8,000	8,000	8,000	8,000	8,000	8,000	8,000	8,000	8,000	8,000	8,000	8,000
Ŷ	4,163	4,074	4,107	4,067	4,067	4,086	4,022	4,028	3,918	4,043	4,128	3,910
X	1,801	1,769	1,661	1,777	1,744	1,760	1,832	1,877	2,074	1,732	1,482	2,072
Xmg	0,420	0,929	0,889	0,911	0,911	0,882	0,000	0,000	1,000	1,000	0,814	0,598
Ms	0,903	0,911	1,000	0,871	0,922	0,956	0,069	0,021	0,021	0,936	1,000	0,480
Pg	0,097	0,089	0,000	0,129	0,078	0,044	0,902	0,979	0,859	0,064	0,000	0,418
Mrg	0,000	0,000	0,000	0,000	0,000	0,000	0,029	0,000	0,120	0,000	0,000	0,102

Dioctahedra	l micas											
SAMPLE	ADY04											
SiO2	51,32	50,84	50,96	49,04	53,99	50,55	52,54	51,00	48,83	48,43	49,37	47,45
TiO2	0,34	0,33	0,00	0,00	0,29	0,52	0,30	0,29	0,00	0,00	0,39	0,00
Al2O3	27,87	28,20	28,57	27,38	25,58	27,49	27,62	29,35	34,37	33,92	33,30	38,74
FeO	2,94	2,99	2,75	4,93	2,50	3,45	2,00	2,59	1,26	2,50	1,38	0,80
MgO	2,60	2,60	2,57	3,44	3,17	2,77	3,41	2,57	1,17	1,46	1,28	0,48
CaO	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
Na2O	0,43	0,40	0,45	0,00	0,00	0,00	0,38	0,52	1,36	2,95	0,76	6,90
К2О	9,50	9,63	9,71	10,21	9,47	10,21	8,75	8,67	8,01	5,74	8,52	0,64
	*****	*****	*****	*****	* * * * * *	*****	*****	*****	*****	*****	*****	*****
Total	95,00	95,00	95,00	95,00	95,00	95,00	95,00	95,00	95,00	95,00	95,00	95,00
Si	6,833	6,781	6,787	6,650	7,134	6,780	6,918	6,745	6,407	6,356	6,487	6,074
Al IV	1,167	1,219	1,213	1,350	0,866	1,220	1,082	1,255	1,593	1,644	1,513	1,926
Al VI	3,206	3,214	3,271	3,025	3,118	3,126	3,205	3,319	3,724	3,603	3,644	3,918
Ti	0,034	0,033	0,000	0,000	0,028	0,053	0,030	0,028	0,000	0,000	0,038	0,000
Fe	0,327	0,334	0,306	0,559	0,276	0,387	0,221	0,287	0,139	0,274	0,151	0,085
Mg	0,517	0,518	0,511	0,695	0,625	0,555	0,670	0,508	0,229	0,286	0,251	0,092
Са	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000
Na	0,110	0,103	0,115	0,000	0,000	0,000	0,097	0,134	0,346	0,752	0,194	1,712
Κ	1,614	1,639	1,650	1,767	1,597	1,747	1,470	1,463	1,341	0,961	1,428	0,104
Ζ	8,000	8,000	8,000	8,000	8,000	8,000	8,000	8,000	8,000	8,000	8,000	8,000
Ŷ	4,084	4,098	4,088	4,279	4,047	4,120	4,125	4,141	4,091	4,164	4,085	4,096
X	1,724	1,742	1,765	1,767	1,597	1,747	1,567	1,597	1,687	1,713	1,622	1,816
Xmg	0,613	0,608	0,626	0,554	0,694	0,589	0,752	0,639	0,622	0,511	0,624	0,520
Ms	0.936	0.941	0,935	1.000	1.000	1.000	0.938	0.916	0.795	0.561	0.881	0.057
Pa	0.064	0.059	0.065	0.000	0.000	0.000	0,062	0.084	0,205	0.439	0,119	0.943
. g Mra	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000

Dioctahedr	al micas											
SAMPLE	ADY10								ADY17			
SiO2	52,46	52,41	52,07	49,92	47,07	47,19	48,07	47,25	50,32	49,94	51,96	50,09
TiO2	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,39	0,34	0,00
Al2O3	26,10	26,29	26,35	25,17	35,99	35,89	34,91	34,09	26,81	31,40	28,80	33,15
FeO	2,31	2,14	2,35	6,03	1,24	1,05	1,10	2,38	5,05	1,78	1,94	0,90
MgO	3,81	3,81	3,78	3,14	0,67	0,58	0,78	1,59	2,70	2,18	2,94	0,00
CaO	0,00	0,00	0,00	0,82	0,00	0,00	0,00	0,00	0,00	0,00	0,00	1,47
Na2O	0,29	0,29	0,32	0,00	1,03	0,98	1,08	0,76	0,37	0,53	0,29	2,38
К2О	10,02	10,07	10,13	9,92	9,01	9,31	9,06	8,94	9,75	8,79	8,73	7,00
	* * * * * *	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****
Total	95,00	95,00	95,00	95,00	95,00	95,00	95,00	95,00	95,00	95,00	95,00	95,00
Si	6,980	6,968	6,938	6,810	6,218	6,237	6,341	6,279	6,798	6,586	6,837	6,563
ALIV	1,020	1,032	1,062	1,190	1,782	1,763	1,659	1,721	1,202	1,414	1,163	1,437
Al VI	3,073	3,088	3,077	2,856	3,821	3,827	3,769	3,618	3,066	3,466	3,303	3,683
Ti	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,039	0,034	0,000
Fe	0,257	0,238	0,261	0,688	0,136	0,117	0,122	0,264	0,571	0,196	0,213	0,099
Mg	0,755	0,755	0,751	0,639	0,133	0,114	0,153	0,314	0,543	0,428	0,576	0,000
Са	0,000	0,000	0,000	0,119	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,207
Na	0,076	0,073	0,083	0,000	0,263	0,251	0,277	0,196	0,097	0,136	0,075	0,606
К	1,701	1,708	1,722	1,726	1,518	1,570	1,525	1,515	1,680	1,478	1,466	1,170
Ζ	8,000	8,000	8,000	8,000	8,000	8,000	8,000	8,000	8,000	8,000	8,000	8,000
Y	4,085	4,081	4,090	4,184	4,090	4,058	4,044	4,196	4,180	4,128	4,126	3,782
X	1,777	1,782	1,805	1,845	1,781	1,820	1,802	1,711	1,777	1,614	1,541	1,983
Xmg	0,746	0,761	0,742	0,482	0,493	0,495	0,558	0,544	0,488	0,686	0,730	0,000
		0.070		0.00-	0.070	0.000	0.010	0.000		0.040	0.074	0 - 00
Ms	0,957	0,959	0,954	0,935	0,852	0,862	0,846	0,886	0,945	0,916	0,951	0,590
Pg	0,043	0,041	0,046	0,000	0,148	0,138	0,154	0,114	0,055	0,084	0,049	0,306
Mrg	0,000	0,000	0,000	0,065	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,104

**Table S4**: Representative microprobe analyses of dioctahedral micas of Châtel Argent Castle (ACK04, ACK10, ACK12) and Quart Castle (ADY04, ADY10). The chemical composition of minerals is expressed as weight% oxides. The structural formulae, reported as number of cations per formula unit (a.p.f.u.), were recalculated on the basis of 22 oxygens. X= Interlayer site, Z= Tetrahedral site, Y= Octahedral site, Xmg= Mg/(Mg+Fe<sup>2+</sup>+Fe<sup>3+</sup>). Ms= Muscovite, Pg= Paragonite, Mrg= Margarite (Mineral abbreviations according to Whitney and Evans, 2010).

Trioctahe	edral micas					
SAMPLE	ADY04	ADY10			ADY17	
SiO2	39,80	36,25	36,06	36,05	37,03	36,75
TiO2	1,76	4,44	4,40	4,39	4,98	4,83
Al2O3	15,84	17,44	17,54	17,31	17,63	17,31
FeO	15,70	18,60	19,10	19,55	16,08	15,96
MgO	14,72	10,25	10,40	9,65	11,21	12,34
Na2O	0,00	0,00	0,00	0,00	0,00	0,00
К2О	8,19	9,02	8,51	9,06	9,06	8,82
	*****	*****	*****	*****	*****	*****
Total	96,00	96,00	96,00	96,00	96,00	96,00
Si	5,817	5,440	5,410	5,439	5,480	5,436
Al IV	2,183	2,560	2,590	2,561	2,520	2,564
Al VI	0,545	0,525	0,511	0,517	0,555	0,454
Ti	0,193	0,501	0,496	0,498	0,555	0,537
Fe	1,918	2,334	2,397	2,466	1,990	1,974
Mg	3,206	2,294	2,325	2,170	2,473	2,720
Са	0,000	0,000	0,000	0,000	0,000	0,000
Na	0,000	0,000	0,000	0,000	0,000	0,000
К	1,527	1,728	1,628	1,744	1,711	1,665
Ζ	8,000	8,000	8,000	8,000	8,000	8,000
Y	5,863	5,653	5,729	5,652	5,573	5,685
X	1,527	1,728	1,628	1,744	1,711	1,665
Xmg	0,626	0,496	0,492	0,468	0,554	0,580

**Table S5**: Representative microprobe analyses of trioctahedral micas of Quart Castle (ADY04, ADY10 and ADY17). The<br/>chemical composition of minerals is expressed as weight% oxides. The structural formulae, reported as number of cations<br/>per formula unit (a.p.f.u.), were recalculated on the basis of 22 oxygens. X= Interlayer site, Z= Tetrahedral site, Y=<br/>Octahedral site, Xmg= Mg/(Mg+Fe<sup>2+</sup>+Fe<sup>3+</sup>).

### Petrographic characterization of historic mortar as a tool in archeologic study: examples from two medieval castles of Aosta Valley, Northwestern Italy

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#### **Consent for publication**

All authors gave consent for publication on the Resources Policy

#### **Authors' contributions**

Field work: EM, ES; conceptualization: EM, ES, AB, FG, LA, AB and AG; data collection:

EM, ES and LA; data analysis: EM, ES, FG, LA, AB and AG; archaeological framework: EM,

LA and AG; writing original draft: EM and ES; figures draft and editing: EM and ES;

validation: EM, ES, FG, LA, AB and AG; writing, review and editing: EM, ES, FG, LA, AB

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#### **Competing interests**

The authors declare that they have no competing interests.

#### **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.