

Kinetics of Grain Size Reduction in Minerals Undergoing Ball Milling

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Abstract This work focuses on the grain size reduction induced by ball milling in individual minerals and binary mixtures containing quartz and a softer mineral. All the investigated minerals and mineral mixtures undergo a significant monotonic grain size decrease upon mechanical processing. The rate at which the process occurs in individual minerals decreases with the hardness of the mineral phase. Hardness is shown to play a crucial role also in the case of mineral mixtures. The final grain size attainable by the softer mineral as well as the rate of the grain size reduction process depend, indeed, on the amount of quartz in the mixture. A kinetic model allows rationalizing the observed behaviour based on the intensity of mechanical stresses generated during individual impacts.

Keywords Minerals processing · Ball milling · Nanocrystalline minerals · Nanostructural refinement

1 Introduction

Human beings have often got the impression that history runs in cycles [1, 2]. Undeniably, history seems to repeat itself and, indeed, the existence of cyclical patterns in history has deeply rooted in many different cultures and civilizations all around the world. Dating approximately from 4000 to

1500 BC, Hindu holy scriptures hand down a cosmology that operates within vast time cycles [3]. Philosophers from ancient Greece postulated as well the changing of cosmic cycles [4]. From Heraclitus and Empedocles to Plato, Aristotle and Polybius, Greeks understood human and cosmic history to be organized in cycles [4]. The idea of historical cycles was revived in Italy during Renaissance. A common thread connects Niccolò Machiavelli [5] and Giambattista Vico, who proposed, in the eighteenth century, to divide history into three ages [6]. Similar ideas have been discussed in the 20th century by Spengler, Toynbee and Braudel [7].

Mechanochemistry does not seem to escape to this logic. According to Takacs' studies [8], this important branch of Chemistry developed according to recurring waves of interest. From the unconscious activation of physical and chemical processes through the use of simple tools such as mortar and pestle, the art of crushing and blending solid materials has slowly evolved to become a crucial field of investigation able to attract interest from different areas of science and technology [8]. The gradual maturation of mechanochemistry into a scientific research subject started with the first systematic studies of W. Spring and M. Carey Lea at the end of nineteenth century. Research in the field progressively expanded under the push of researchers like W. F. Ostwald, K. Peters, and F. M. Flavitsky at the beginning of the twentieth century. Starting from 1950s, the grinding of minerals, inorganic compounds, and polymers was carefully investigated, among others, by P. A. Reh binder and N. K. Baramboin. During 1950s and 1960s, several research groups dedicated to mechanochemistry were established in the Soviet Union and Eastern Europe. In this respect, P. A. Thiessen and his research activity in Berlin, East Germany, deserve a special mention for the influence he had on tribochemistry and triboemission [9]. Shortly after, other research groups were established in the Soviet Union under the leadership of V.V. Boldyrev and E. G. Avvakumov in

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Novosibirsk, P. Yu. Butyagin in Moscow, and S. N. Zhurkov in Leningrad [10].

While research in mechanochemistry progressed steadily since 1950s in the Soviet Union and Eastern Europe, the first worldwide wave of interest arrived only starting from 1966, when J. Benjamin and co-workers fabricated the first oxide-dispersion-strengthened Ni superalloy for the International Nickel Company [11]. Since then, mechanical alloying became an irreplaceable method of powder metallurgy, attracting increasing attention on the physical and chemical transformations induced by mechanical forces [12]. In 1980s, the discovery of mechanically activated amorphization in intermetallics and elemental metal mixtures prompted the second surge of interest, which involved the whole materials science community [12]. The third wave of interest is currently ongoing. Starting approximately from 2010, mechanochemical methods have expanded to inorganic and organic synthesis, which resulted in a further, huge increase in the relevant scientific community [13–18].

Prof. Kapur [19, 20], in honour of whom this *festschrift* is brought out, has been one of the protagonists of the research in mechanical processing between 1970 and 2000. During this period, he has been giving outstanding contributions to mineral processing, extractive metallurgy and waste recycling. Among the others, he helped us to deepen the understanding of grinding kinetics and comminution in tumbling mills and high-pressure grinding rolls. It is on a similar subject that this work is focused on, namely on the kinetics of grain size reduction in mineral phases subjected to mechanical processing by ball milling (BM).

BM is a well-established powder processing method based on the occurrence of impacts between milling tools [12, 14, 15]. During each impact, a small amount of powder gets trapped between the colliding surfaces. Powder particles undergo dynamic compaction at relatively high strain rates, which results in the generation of non-hydrostatic mechanical stresses at the points of contact between particles. In the case of brittle materials such as minerals, mechanical loading can be severe enough to induce the breakage of particles and the reduction of grain size [12, 14, 15, 21]. Although the microstructural refinement is well known to take place, its kinetics, and the factors controlling it, are not yet satisfactorily understood.

The present study aims precisely at throwing new light on the process of grain size reduction in brittle phases. To this aim, we focused on the behaviour under BM of different minerals and mineral mixtures. The subject is commonly investigated taking advantage of the well-known population balance

framework, a modelling approach that relies upon the partition of particle and grain size distributions into suitable size classes, with fragmentation and coarsening described in terms of mass transfer between the classes [22–27]. To this aim, several measures must be taken to have a rigorous input for the model. In particular, a rigorous experimentally established protocol should be adopted to keep the population balance minimalistic and pseudo-elementary as far as possible [26, 27]. This is the best way, indeed, to predicting and optimizing comminution processes in powder processing [26, 27].

Nevertheless, in this work, we deliberately make a different choice in the attempt of highlighting the main result of our study without making the underlying modelling uselessly complex. In particular, we show that experimental evidence can be rationalized using a simple kinetic model based on the statistical nature of the mechanical processing by BM. The kinetic model itself uses population balances to define the fractions of powder that exhibit a different degree of microstructural refinement. However, we have referred in the model the average grain size, thus avoiding a more detailed description of grain size reduction based on population balance. It would more rigorous, but, in the absence of detailed experimental information, it could also be misleading. The simpler approach is enough to allow us to highlight how the reduction of grain size depends on the hardness of the mineral phase.

2 Experimental Methods

Experiments were carried out using commercial powders of talc (T), gypsum (G), halite (H), calcite (C), fluorite (F), apatite (A), magnetite (M), orthoclase (O) and quartz (Q) with 99.9% purity. The different mineral phases were suitably chosen to have a significant change of Vickers hardness, H_v , from one to another. The H_v values are shown in Table 1.

BM experiments were conducted using 10 cm³ of powders. Powders were placed inside a hardened-steel vial together with a single stainless steel ball of 12 g, and the vial was sealed in air. Then, the vial was clamped on the mechanical arm of a SPEX Mixer/Mill 8000 and swung at a frequency of 14.6 Hz. At the end of each BM run, powders were collected from the vial, and the vial was cleaned and refilled with a fresh amount of pristine powder.

The selected working conditions result in almost completely inelastic impacts between ball and vial. Accordingly, we measured an average impact frequency, f , of about 29.2 Hz and an average impact velocity of about

Table 1 Vickers hardness, H_v (kg mm⁻²) of the minerals used in BM experiments

	T	G	H	C	F	A	M	O	Q
H_v	45	63	88	104	195	661	690	721	1211

4.1 m s^{-1} [28–30]. Under these conditions, the total number of impacts, m , can be readily calculated by the product $f \cdot t$ between the impact frequency and the milling time, t [28–30].

Experiments were performed using powders of pure minerals as well as quartz-based binary mixtures. Quartz was chosen because it is the hardest mineral among the ones we selected. Binary mixtures of different compositions were prepared by varying the volume fraction of quartz, χ , between 0 and 0.4 with the aim of investigating the effect of hardness on the grain size reduction process.

Structure and microstructure of initial and processed powders were characterized by X-ray diffraction (XRD). XRD patterns were analysed using the Rietveld method [31]. To this aim, we used the software for Rietveld refinement known as MAUD (material analysis using diffraction) [32, 33], which is generally regarded as a powerful tool to simulate crystallographic structures and microstructures for different classes of materials. Accordingly, a set of mathematical model functions are used to generate simulated XRD profiles of individual crystallographic phases and the total diffraction pattern. Then, the differences between the simulated and measured XRD profiles are calculated. Such differences are squared, suitably weighted and, eventually, summed. A least-squares minimization algorithm is utilized to minimize the differences between model functions and experimental points based on the set of active best-fitting parameters, which are related to the crystallographic and microstructural features of the solids considered. Active parameters are refined through repeated cycles of refinement.

3 Kinetic Model

The kinetics of grain size refinement can be described using a phenomenological model expressly developed to take into account the statistical nature of the mechanical processing by BM [30, 34–36]. The rapid motion of the vial results in the effective stirring of powders. As a consequence, powders can be expected to keep a high degree of homogeneity throughout the mechanical processing. In combination with the periodic displacement of the ball inside the vial, stirring also guarantees that impacts involve powders on a stochastic basis. Similarly, it can be also expected that the amount of powder involved in impacts is always the same. Colliding media are expected to trap the powder following an approximately stochastic dynamic.

Experimental evidence suggests that only a small fraction of the volume of trapped powder is effectively processed during each impact [30, 34–36]. We assume that the impact induces critical loading conditions (CLCs) severe enough to activate the process of grain size reduction only in a small sub-volume v of the powder compressed during

the impact. As in the case of the powder amount trapped at impact, it is also reasonable to assume that v remains approximately constant throughout the mechanical processing. The volume fraction of powder that undergoes CLCs during each impact is $k = v/V$, where V is the total volume of powder inside the vial.

As described in detail elsewhere [24, 26–28], the evidence that k is much smaller than 1 allows expressing the volume fraction of powder subjected to CLCs i times after m impacts as

$$\chi_i(m) = \frac{(km)^i}{i!} e^{-km}. \quad (1)$$

The condition $\sum_i \chi_i(m) = 1$ is always fulfilled. Equation 1 represents the master equation of our kinetic model. If we assume that the powder fraction $\chi_i(m)$ that has undergone i CLCs is characterized by a grain size L_i , the average grain size L exhibited by the processed powder can be set equal to

$$L = \sum_{i=0}^m \chi_i(m) L_i. \quad (2)$$

Equation 2 can be interpreted as the weighed sum of the grain sizes L_i pertaining to the volume fractions $\chi_i(m)$. It expresses the change of the average grain size that can be measured by experimental methods based on the investigation of samples representative of the whole powder charge subjected to BM. This is the case of XRD analysis, in principle. Therefore, Eq. 2 also represents the equation to be used to best fit the experimental information on grain size obtained by XRD.

Equation 2 shows that the average grain size L depends on the spectrum of L_i values that, in turn, can be expected to change with the severity of CLCs. In particular, if CLCs are relatively mild, we can expect that the grain size changes gradually. Specifically, we can write that $L_0 > L_1 > L_2 > \dots > L_i > \dots$. Conversely, if CLCs are really severe, we can expect that the grain size changes abruptly from the initial value, L_0 , to the minimum possible value, L_f . In other words, $L_0 \neq L_1 = L_2 = \dots = L_i = \dots = L_f$. Under these conditions, Eq. 2 can be remarkably simplified. Taking into account Eq. 1, it can be rewritten as

$$L = L_0 e^{-km} + L_f (1 - e^{-km}). \quad (3)$$

Accordingly, the quantity k can be also regarded as the rate constant of the grain size reduction process. Equation 3 can be rewritten as a function of time, t , a much more common reference quantity for kinetics. Since the total number of impacts, m , is simply the result of the product between the frequency of impacts, f , and time, the new equation is

$$L = L_0 e^{-kft} + L_f (1 - e^{-kft}). \tag{4}$$

Accordingly, the rate constant for the kinetics referred to time is equal to kf . In the following, we show that Eqs. 3 and 4 can be profitably used to best fit the experimental data.

4 Results and Discussion

The experimental estimates of the average grain size L obtained by the Rietveld analysis of XRD patterns are shown in Fig. 1 as a function of time, t .

It can be seen that L decreases smoothly in all the cases examined. The minerals tend to reach asymptotically a final grain size value, L_f , which is different for different minerals. The decreasing trends are similar, but there is a clear change in the rate from one mineral to another. In particular, grain size reduction is faster for softer minerals.

The different experimental datasets were best fitted using Eq. 3. As shown in Fig. 1, the model curve overlaps very well with the experimental points in all the cases. This allows a reliable estimate of the model quantities L_f and k . Their values are reported in Table 2.

While no clear trend is discernible for the final grain size L_f , the apparent rate constant k tends to decrease with the hardness of the mineral phase. This can be seen from Fig. 2, where L_f is plotted as a function of the Vickers hardness, H_v . While this seems to contradict general expectations according to which the harder is the material, the smaller is the final grains size attainable during BM, our data are quite scattered. In this regard, we can only call attention on two different aspect. First, all L_f values fall in the very narrow range from 20 to 40 nm. Therefore, we can expect that any further increase in the accuracy with which XRD patterns are collected and the grain size is estimated can result, in principle, in a reduction of the data scattering, maybe revealing an appreciable trend. Second, expectations are based on the well-known relationship between brittleness and size reduction. Normally, the more brittle is the material an object is made of, the smaller are the fragments that can be obtained by repeated fracture. However, the case of grain size is different. On the one hand, the grain can be reduced in size because of the sudden application of intense mechanical stresses. On the other hand, relaxation processes following the initial stage can also lead to grain re-orientation and coalescence depending on the physical properties of the material. It follows that only a more complex and thorough investigation can clarify the observed behaviour. Nevertheless, the decrease in k with H_v still suggests that hardness can play a key role in the grain size reduction process.

To further elucidate the effect of hardness on the grain size reduction process, we investigated the behaviour of binary mixtures containing quartz, the hardest mineral phase we have considered. The results obtained are summarized in Fig. 3, where the average grain size, L is plotted as a function of the

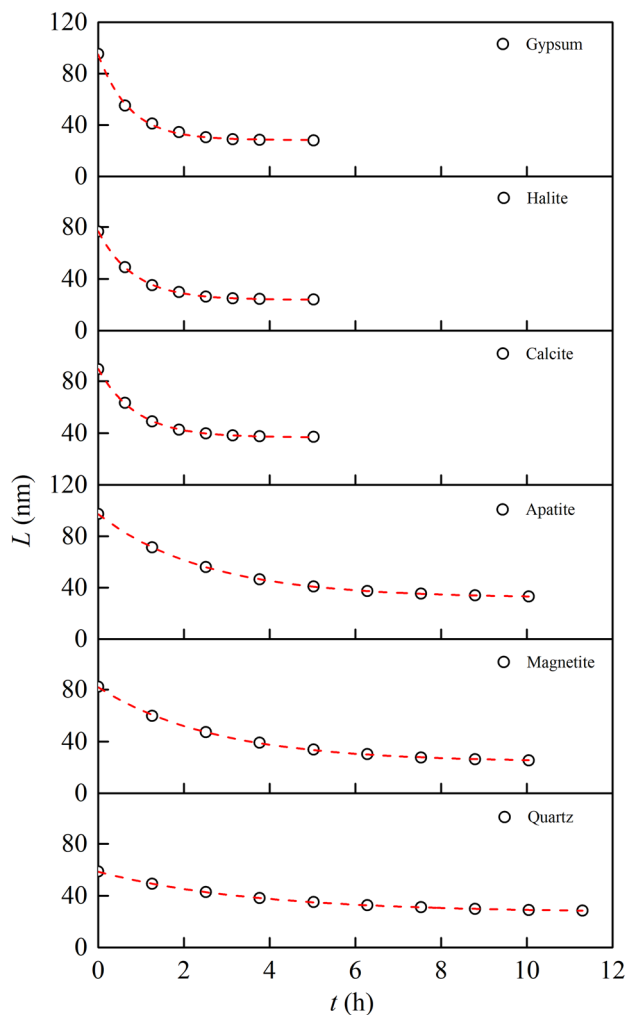


Fig. 1 Grain size, L , as a function of time, t , for the different pure mineral phases. Best-fitted curves are shown

Table 2 The final grain size, L_f (nm), and the apparent rate constant of grain size reduction, k

	T	G	H	C	F	A	M	O	Q
L_f	37.8	28.4	23.9	36.7	22.4	32.1	24.2	21.0	27.1
k	0.120	0.131	0.114	0.107	0.092	0.038	0.035	0.035	0.026

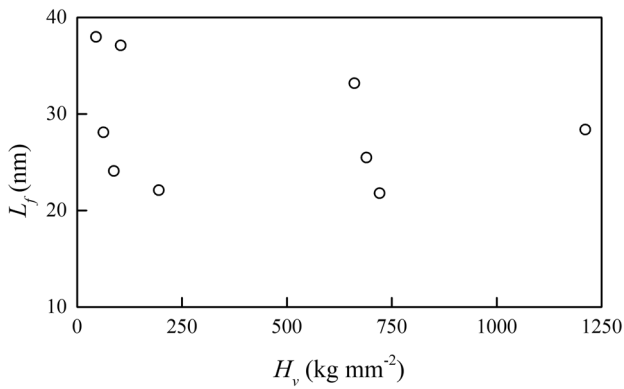


Fig. 2 The final grain size, L_f , as a function of the Vickers hardness, H_v , for the different minerals examined

number of impacts, m . For convenience, only the data of three representative cases are shown, namely the ones obtained from Q–T, Q–F and Q–O mixtures.

As in the case of pure mineral phases, L undergoes a smooth, monotonic decrease with m . However, we have also observed a clear effect of the mixture composition. In particular, the final grain sizes, L_f , and the apparent rate constants of the grain size reduction process, k , respectively, decrease and increase with the volume fraction of Q in the mixture, χ . Accordingly, the presence of Q in the mixture

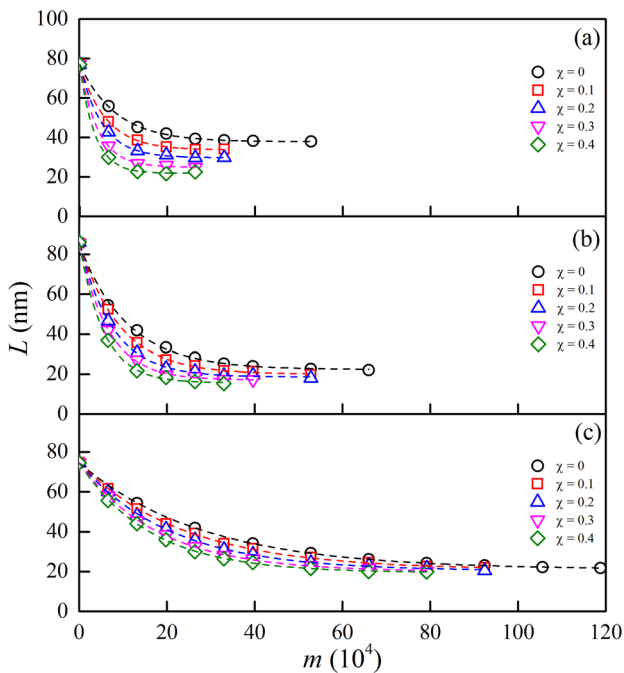


Fig. 3 The average grain size, L , as a function of the number of impacts, m . Data refer to **(a)** Q–T, **(b)** Q–F, and **(c)** Q–O binary mixtures. Best-fitted curves are shown

allows the other mineral phase to reach a finer final grain size at a higher rate.

It appears from Fig. 3 that Eq. 3 is, again, able to best fit very well the experimental datasets. The model curves overlap the data and, again, the model quantities L_f and k can be reliably estimated.

The L_f and k estimates obtained are plotted in Fig. 4 as a function of χ .

We can see that any increase in χ induces a proportional change of both L_f and k . Specifically, L_f decreases linearly and k increases linearly. Therefore, we can safely conclude that the presence of quartz (i) enables a more effective refinement of grain size, allowing the attainment of smaller L_f values and (ii) makes the grain size reduction process definitely faster. This holds true for all the different Q-based binary mixtures examined. Mixing the hardest mineral with softer ones results, for these, in a more effective microstructural refinement.

Aimed at quantitatively evaluating the effects stemming from the presence of quartz in the mixtures, we have best fitted with a line the experimental datasets describing the change of L_f and k with χ for all the different quartz-based mixtures. Being the plots almost perfectly linear, we have obtained a reliable estimate of the line slopes, s_{L_f} and s_k , which measure the rate of change of, respectively, L_f and k with χ . The obtained s_{L_f} and s_k values are shown in Fig. 5 as a function of the logarithm of the difference in Vickers hardness, ΔH_v , between Q and the second mineral in the mixture.

The plots clearly show that the difference in hardness between the mineral phases deeply affects the grain size reduction process. The larger the difference, the more effective the mechanical processing in reducing the grain size of the softer mineral. These findings are in line with those

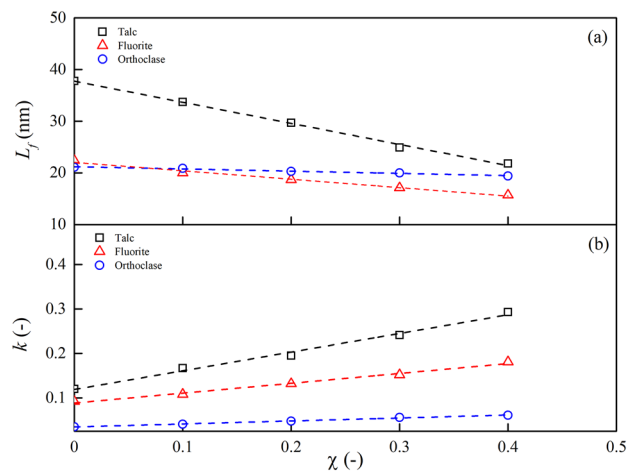


Fig. 4 **a** The final grain size, L_f , and **b** the apparent rate constant of the grain size reduction process, k , as a function of the volume fraction of Q in the mixture, χ . Data refer to Q–T, Q–F and Q–O binary mixtures. Best-fitted lines are shown

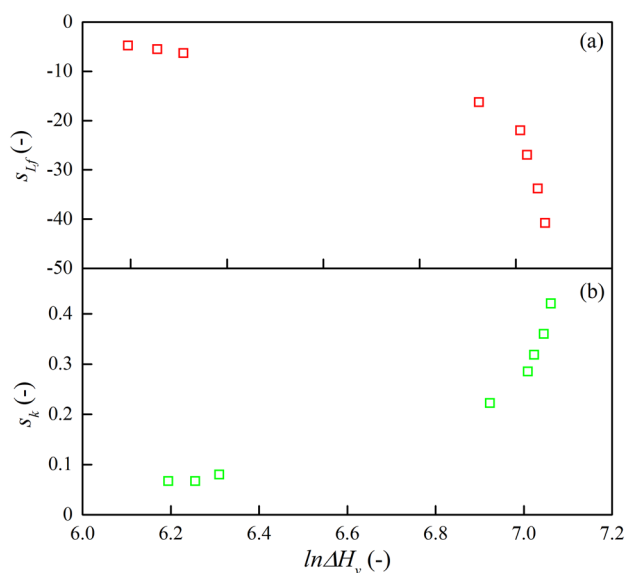


Fig. 5 **a** The rate of change of L_f , s_{L_f} , with χ and **b** the rate of change of k , s_k , with χ as a function of the logarithm of the difference in Vickers hardness, ΔH_v , between quartz and the other mineral in mixture. Data refer to all the different quartz-based binary mixtures examined

regarding metals and metal mixtures [34, 35]. Also for such systems, indeed, hardness has been shown to affect the rate of grain size reduction and the minimum grain size value attainable.

In our opinion, the observed microstructural evolution of mineral phases can be related to the severity of CLCs. For pure minerals, it is reasonable to expect that the volume of powder affected by CLCs per impact, v , decreases as the hardness of the mineral increases. It is well-known, indeed, that the intensity of mechanical stresses required to induce a disordering of the crystalline lattice on the microscopic scale, and the formation of smaller grains, increases with the hardness of the mineral. Therefore, we can reasonably expect that the apparent rate constant k of the grain size reduction process cannot but be lower for the harder mineral, which is precisely what we observe. From the softest mineral, T, to the hardest one, Q, the quantity k decreases smoothly.

What is surprising is that, for any given mineral phase mixed with Q, k increases with the volume fraction of Q in the mixture, χ . Logic suggests that, in any given mixture, any addition of Q reduces the amount of the softer mineral that can be involved in individual impacts. This simply means that there is less mineral that can be effectively processed during individual impacts, which should result in a decrease in k values with χ . Instead, we observe the opposite.

This unexpected behaviour can be rationalized if we accept the idea that the presence of Q particles in the mixture

allows an intensification of CLCs during individual impacts. In this respect, it is worth recalling that, during individual impacts, powder particles are compressed at relatively high strain rates and force chains establish along the network formed by the points of contact between the powder particles [37, 38]. Force chains are defined as the chains of powder particles that enable the transfer of force from one particle to another [37, 38]. Forces between compressed powder particles are heterogeneously distributed and it is the size and structure of the resulting force chains that affect shear resistance, sound propagation and the extent of mechanical deformation at the level of individual particles [37, 38]. As mechanical stresses between two particles in contact become higher than the yield stress of the mineral phase, the particles break and disordering processes can take place on the microscopic scale. Soft minerals exhibit a relatively low yield stress, and we cannot expect that local mechanical stresses build up significantly. Correspondingly, we cannot expect that severe CLCs occur.

Conversely, the presence of hard Q particles dispersed among the particles of the softer mineral can allow the generation of much more intense force chains able to impose more severe local deformation conditions. It follows that the severity of CLCs increases with the amount of Q in the mixture and, consequently, the volume of softer mineral exposed to the CLCs required to induce the reduction of grain size increases. Then, the enhancement of CLC severity not only can explain the increase in k values, but also the observed decrease in the final grain size, L_f . More severe deformation conditions could, indeed, result in a more effective disordering of the crystalline lattice, eventually determining the formation of smaller grains.

5 Conclusions

We carried out a systematic study of the grain size reduction process in minerals and mineral mixtures subjected to mechanical processing by BM. Experiments were performed using minerals with very different hardness with the aim of investigating how hardness can affect the final grain size attainable by BM and the rate at which microstructural refinement proceeds. Experimental findings allow concluding that hardness has, indeed, marked effects on the grain size reduction process in terms of final grain size and rate.

In the case of pure minerals, we observed a clear correlation between rate of grain size reduction and hardness of the mineral phase subjected to BM. In particular, the grain size reduction process is slower for the minerals with higher hardness.

Q-based mineral mixtures exhibit an evident dependence of final grain size and rate on the amount of Q present in the mixture. Due to such compositional effects, the final grain

size of the softer mineral phase decreases as the relative amount of Q, the hardest mineral we used, increases. Similarly, the rate of the grain size reduction process increases with the relative amount of Q in the mixture.

We provided a quantitative description of the grain size reduction process using a kinetic model that takes into account the statistical nature of the mechanical processing by BM. Based on the results obtained, we explained the observed grain size reduction processes based on the severity of deformation conditions imposed by local mechanical stresses generated during individual impacts. Specifically, it seems that the presence of hard particles can induce the intensification of the force chains responsible, eventually, for the reduction of grain size. Hardness is shown to play a key role.

Our results on mineral phases agree remarkably well with previous ones obtained for metallic phases. This suggests that the dependence of microstructural refinement on the mechanical properties of the processed material represents a general feature of mechanically activated transformations.

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