

LASER μ -RAMAN INVESTIGATION OF GREEK BAUXITES FROM THE PARNASSOS-GHIONA ACTIVE MINING AREA

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Abstract

Bauxite samples collected with permission from currently active mining areas in the Parnassos-Ghiona Mts district were studied using both conventional (optical microscopy and powder XRD) and, for the first time in the literature, micro-scale advanced non-destructive spectroscopic techniques, in particular Laser μ -Raman. The results showed that the different bauxite types (diasporic or boehmitic) can easily be identified regardless of sample type (porous white-grey or massive red-brown) by recording spectra in the low-wavenumber region ($250\text{ cm}^{-1} - 600\text{ cm}^{-1}$) where distinct bands of the natural AlOOH polymorphs are easily discernible (448 cm^{-1} for diasporite and 362 cm^{-1} for boehmite). The method described herein could equally be applied in the laboratory as well as in-situ at the mines for quick and accurate phase determination, in order to bypass the laborious and time-consuming indirect bulk techniques (such as XRD) routinely used to this date.

Key words: Raman, Diasporite, Boehmite, Bauxite, Greece.

Περίληψη

*Δείγματα βωξίτη τα οποία αποκτήθηκαν από εταιρείες που εμφανίζουν ενεργή μεταλλευτική δραστηριότητα στην περιοχή Παρνασσού-Γκιώνας χαρακτηρίστηκαν αρχικά με τη χρήση συμβατικών μεθόδων (οπτικό μικροσκόπιο, περίθλαση ακτίνων X) και στη συνέχεια μελετήθηκαν χρησιμοποιώντας, για πρώτη φορά στη διεθνή βιβλιογραφία, προηγμένες μη-καταστροφικές φασματοσκοπικές τεχνικές σε μικροκλίμακα (Laser μ -Raman). Τα αποτελέσματα της παρούσας μελέτης έδειξαν πως ο τύπος του βωξίτη (διασπορικός ή μπειμιτικός) μπορεί εύκολα να προσδιοριστεί, ανεξάρτητα από το είδος του δείγματος (πορώδες λευκό-τεφρό ή και συμπαγές ερυθρό-φαιό), μέσω της καταγραφής του φάσματός του στην περιοχή χαμηλών ενεργειών ($250\text{ cm}^{-1} - 600\text{ cm}^{-1}$) όπου και είναι ευδιάκριτες συγκεκριμένες Raman ταινίες των πολύμορφων του AlOOH (448 cm^{-1} για το διάσπορο και 362 cm^{-1} για τον μπειμίτη). Η παραπάνω μικρο-μέθοδος θα μπορούσε να εφαρμοσθεί για τον άμεσο προσδιορισμό των ορυκτολογικών φάσεων τόσο στο εργαστήριο όσο και επιτόπου στα μεταλλεία, έτσι ώστε να αποφευχθούν έμμεσες και χρονοβόρες ολικές τεχνικές οι οποίες χρησιμοποιούνται έως και σήμερα (όπως π.χ. η περίθλαση ακτίνων X).
Λέξεις κλειδιά: Φασματοσκοπία, Διάσπορο, Μπειμίτης, Αιματίτης, Ανατάσης.*

1. Introduction

In 2005, Greece was the twelfth bauxite producer in the world with a total production of 2.2×10^6 tonnes (USGS – Mineral Commodity Summaries, January 2006). The bauxite reserves in Greece are estimated to be 600×10^6 tonnes. It is now established that the Greek mining industry controls the most significant bauxite reserves in the EU (USGS – 2005 Minerals Yearbook). The overall production is mainly related to exploitation of bauxite deposits situated within the Parnassos-Ghiona geotectonic zone (central Greece) by three mining companies (Aluminium de Grèce S.A., S&B Industrial Minerals S.A., Elmin S.A.). Almost 72 % of the current Greek aluminium market is covered by domestic production (USGS – 2005 Minerals Yearbook). Most of the raw material is processed by Aluminium de Grèce at its metallurgical plant at Antikyra, Corinthiakos gulf, for the production of alumina and metallic aluminium to be used in industry and constructions. The remainder of the raw bauxite and associated metallurgical products are exported generating an annual income of ~25 and ~165 million € respectively, according to Greek Mining Enterprises Association.

Numerous geological studies have been published about the Parnassos-Ghiona allochthonous karst-type bauxite deposits (Aronis 1955, Papastamatiou 1960, Papastamatiou 1964, Bárdossy and Mack 1967, Nia 1971, Valeton, 1972, Maksimović and Papastamatiou 1973, Papastavrou 1974, Mack and Petrascheck 1978, Nicolas and Bildgen 1979, Combes *et al.* 1981, Bárdossy 1982, Biermann 1983, Combes and Andreou 1983, Arp 1985, Papastavrou 1986, Valeton *et al.* 1987, Petrascheck 1989, Valeton 1991, Vgenopoulos and Daskalakis 1991, Economopoulos and Vgenopoulos 1998). These ores are hosted within Mesozoic carbonate formations (Fig. 1). The Parnassos-Ghiona geotectonic zone is characterised by nearly continuous sedimentation of epicontinental reef-like carbonates from the Upper Triassic to the Upper Cretaceous (Valeton *et al.* 1987). In this carbonate sequence three bauxite horizons (from bottom to top: B₁, B₂ and B₃) can be distinguished and they were caused by epirogenic emersion phases and formation of coastal karst reliefs (Valeton *et al.* 1987, Petrascheck 1989). Horizon B₁ is hosted in the calcareous Middle-Upper Jurassic units, horizon B₂ in the calcareous Upper/Jurassic – Lower Cretaceous units (Tithonian and Neokomian respectively), whereas horizon B₃ is hosted in the calcareous Upper Cretaceous units (Cenomanian – Turonian).

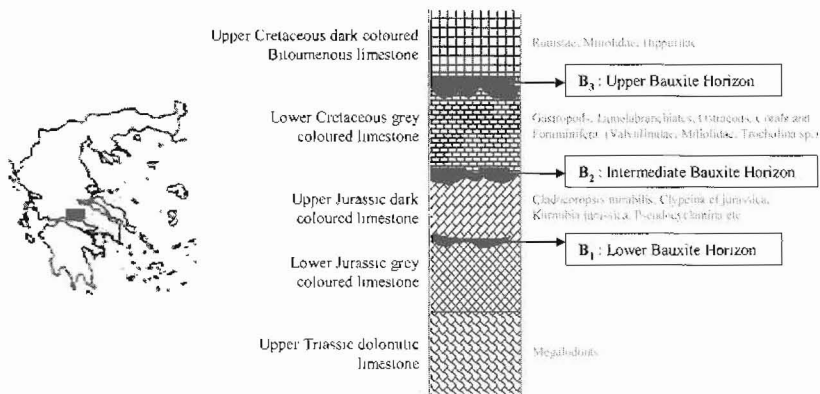


Figure 1 - Stratigraphic position of bauxite horizons B₁, B₂ and B₃ intercalated with shallow-water Jurassic to Cretaceous limestones of the Parnassos-Ghiona zone (modified, from Valeton *et al.* 1987)

The main mineralogical and geochemical characteristics of the Parnassos-Ghiona bauxites have been described by several authors using conventional methods such as optical microscopy, SEM-EPMA, XRD, XRF, Fire-Assay/AAS/ICP and TGA/DTA (Kiskyras 1960, Nia 1968, Bárdossy and Pantó 1971, Ochsenkühn and Parissakis 1977, Augustithis *et al.* 1978, Combes 1979, Biermann 1983, Arp 1985, Paspaliaris 1985, Kritsotakis *et al.* 1986, Papastavrou and Perdikatis

1987, Economopoulou-Kyriakopoulou 1991, Laskou 1991, Perdikatsis 1992, Ochsenkühn-Petropoulou and Ochsenkühn 1995, Laskou 2001, Laskou and Andreou 2003, Laskou 2005, Solymár *et al.* 2005, Laskou and Economou 2006). More detailed characterization techniques, and particularly TEM and INAA, have also been used (Bárdossy and Mack 1967, Laskou and Economou 1991, Ochsenkühn-Petropoulou and Ochsenkühn 1995, Ochsenkühn *et al.* 1995, Lymperopoulou 1996, Ochsenkühn *et al.* 2002). It is evident that the only non-bulk (micro- and nano-scale) instrumental methodology used so far, for the study of Parnassos-Ghiona bauxites, concerns some electron microscopy techniques (TEM and SEM-EPMA). Here, we present, for the first time in the literature, the application of micro-scale, non-destructive, advanced spectroscopic techniques such as laser μ -Raman in the characterisation of typical bauxite samples from the Parnassos-Ghiona active mining area. We demonstrate that this method can equally be applied in the laboratory as well as *in-situ* at the mines (e.g. by using portable spectrometers) for quick and accurate phase determination, thus bypassing laborious and time-consuming indirect bulk techniques (such as XRD) routinely used to this date.

2. Materials and Methods

The investigated bauxite samples were collected during the period March 2006 – September 2006 from mining sites (Fig. 2) of the three Greek companies (Aluminium de Grèce S.A. indicated as “ALM”, Elmin S.A. indicated as “ELM” and S&B Industrial Minerals S.A. indicated as “SAB”, Table 1) exploiting bauxite in the Parnassos-Ghiona area (central Greece).



Figure 2 – Bauxite underground works of Aluminium de Grèce at Pera-Lakkos site, Parnassos-Ghiona area

The present investigation is focused on the analysis of bauxite samples from the 2nd (intermediate) and the 3rd (upper) bauxite horizon (Fig. 1, Table 1). All bauxites samples (both white-grey and red-brown) were initially investigated in polished-thin sections using transmitted and reflected light optical microscopy. The mineralogical composition was also examined using powder X-ray diffraction (XRD) on a Siemens D5005 (Bruker AXS) diffractometer using $\text{CuK}\alpha$ -radiation. The Laser μ -Raman spectra were obtained on the polished-thin sections using a Renishaw Ramascope RM 1000 equipment with a HeNe laser at 633 nm, a spectrometer with a grating of 1800 lines/mm, and a CCD Peltier-cooled detector. The laser beam diameter was adjusted depending on resolution requirements. In any case its maximum energy did not exceed 4 mW.

3. Results and discussion

The microscopic and XRD studies have shown that the major mineral phases in the investigated bauxite samples from the Parnassos-Ghiona deposits are the two common AlOOH polymorphs diaspore and boehmite, the typical $\text{Fe}^{(II)}$ oxide and oxyhydroxide hematite and goethite, and the TiO_2 polymorph anatase. Iron sulphides (such as pyrite) are frequently present. Microscopic

images (reflected light) of the most common in appearance (red-brown diasporic) bauxite samples are presented in Figure 3. Patches and veins of metallic minerals consisting of iron oxides and sulphides (lighter areas) are included in diasporic matrix (darker areas containing also pisoliths). Most of the characteristic bauxitic pisoliths contain both diaspore and finely dispersed hematite.

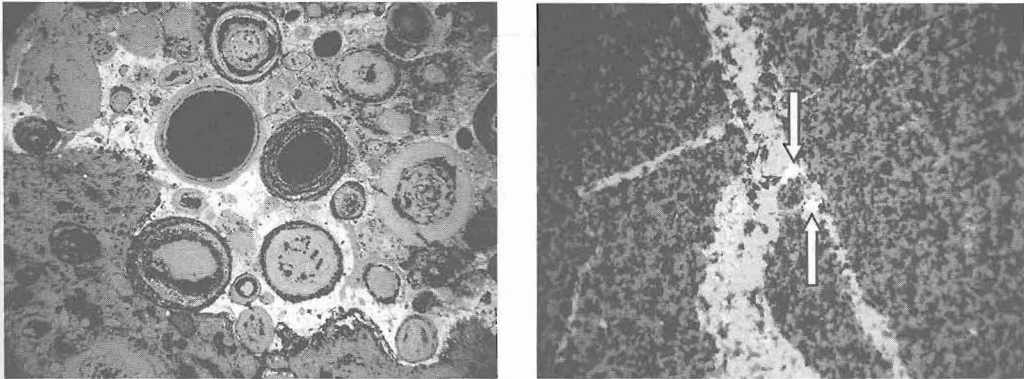


Figure 3 – Representative microscopic images ($\times 100$ and $\times 200$) from typical red-brown diasporic bauxite samples using reflected light (lighter areas = Fe-oxides, arrows = sulphides)

Typical XRD patterns of diasporic and boehmitic samples are shown in Figure 4 whereas the complete data are included in Table 1. It should be emphasized that the diasporic bauxite appears both in the form of porous white-grey (high quality) and red-brown samples, while boehmitic bauxite only in the form of massive red-brown samples.

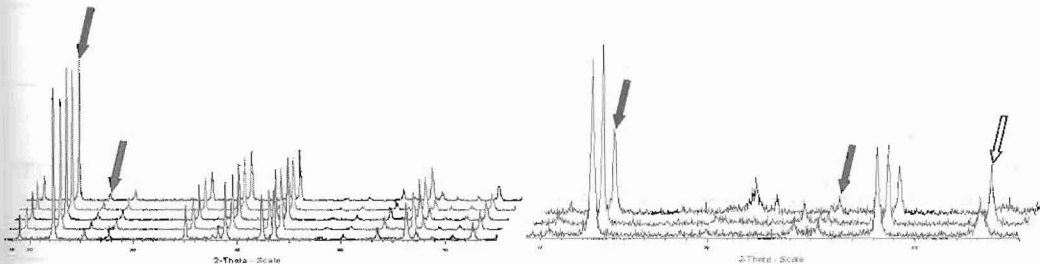


Figure 4 – Powder XRD patterns of white-grey diasporic and red-brown boehmitic bauxite samples. In the first case the diaspore and anatase strongest reflections at 22.26 (3.99) and 25.35 (3.51) 2θ (d in Å) are indicated by black and grey arrows respectively, whereas in the second case boehmite, anatase and hematite strongest reflections at 14.48 (6.11), 25.35 (3.51) and 33.27 (2.69) 2θ (d in Å) are indicated by black, grey and white arrows respectively

Conventional chemical methods are not recommended to characterize AlOOH polymorphs in bauxite samples. Thus powder XRD is fundamentally used in laboratory conditions. However it is rather difficult to use XRD for *in-situ* measurements in the field and in underground mining areas because portable XRD equipments are not greatly commercialized up to now. Therefore, it is important to suggest convenient spectroscopic methods, such as Laser μ -Raman, which can be easily used for phase determination in any case. The instrument is a bench system capable of confocal imaging with high spectral and spatial resolution. Representative Laser μ -Raman spectra of diasporic bauxite samples investigated during the present study (both white-grey and red-brown), together with standard Raman spectra from the Mineral Spectroscopy Server of CalTech (© Prof. G. Rossman 2006), are shown in Fig. 6. It should be noted that the spectra were obtained by focusing the laser beam on the diasporic matrix away from microscopically detectable metallic minerals including anatase grains. The diaspore bands are observed in the low-wavenumber region, namely between 200 cm^{-1} and 600 cm^{-1} . The most prominent are the 705 cm^{-1} , 446 cm^{-1}

Table 1 – Summary of the XRD mineralogical analyses

	Sample	Description	Major Minerals
DIASPORIC	ALM0306_PL1_B1 (3 rd horizon)	Red-brown to pale-brown, Massive	Diaspore, Hematite, Kaolinite
	ALM0306_PL1_B3 (3 rd horizon)	Red-brown, massive	Diaspore, Hematite, Anatase
	ALM0306_PL1_B4 (3 rd horizon)	Red-brown, slightly porous	Diaspore, Hematite, Goethite, Kaolinite
	ELM0206_DV_B1 (2 nd horizon)	Red-brown, massive	Diaspore, Anatase, Magnetite, Maghemite, Kaolinite
	SAB0306_ASV (3 rd horizon)	Red-brown, massive	Diaspore, Hematite, Anatase
	ALM0306_PL1_BS2 (3 rd horizon)	White-grey-yellow, highly porous	Diaspore, Anatase
	ALM0306_PL1_WB (3 rd horizon)	White-grey to pale-pink, highly porous	Diaspore, Anatase
	ELM0206_SK_B1a (3 rd horizon)	White-grey, highly porous	Diaspore, Anatase
	ELM0206_SK_B1b (3 rd horizon)	White-grey-yellow, highly porous	Diaspore, Anatase
	ALM0306_PL1_BIW (3 rd horizon)	White-grey, porous	Diaspore, Anatase
	ALM0306_BIW (3 rd horizon)	White-grey to pale-brown, highly porous	Diaspore, Anatase
	ELM0206_SK_B2 (3 rd horizon)	White-grey to yellow- brown, highly porous	Diaspore, Anatase, Goethite
	BOEHMITIC	ALM0306_PL1_B2 (3 rd horizon)	Red-brown, massive
ELM0206_KV_B1 (2 nd horizon)		Red-brown, massive	Boehmite, Hematite, Kaolinite
ELM0206_2H1 (2 nd horizon)		Red-brown-orange, massive	Boehmite, Goethite, Kaolinite
SAB0306_SKR (2 nd horizon)		Red-brown, massive	Boehmite, Hematite

and 260 cm^{-1} , which are assigned to symmetric stretching modes (Ruan *et al.* 2001). In the porous white-grey bauxite samples the main diaspore band appears at 448 cm^{-1} (solid arrow in Fig. 5), which is assigned to Al-O-Al stretching bend, and it is in good agreement with the results from the literature (Ruan *et al.* 2001, see Fig. 6). A number of strong peaks are also observed in the band

range between 1000 and 2000 cm^{-1} which are attributed to fluorescence from the 633 nm He-Ne laser. Fluorescence peaks are wavelength-dependent and they should disappear when another laser is used, such as a Nd:YAG laser at 1064 nm. In synthetic diaspore a number of broad bands are observed with the 1064nm laser in the 2800-3700 cm^{-1} region, attributed to the $\nu(\text{OH})$ stretching. These bands were not observed in our spectra. The massive red-brown samples along with diaspore contain hematite (empty arrows in Fig. 5) with Raman bands at 612 cm^{-1} , 496 cm^{-1} , 412 cm^{-1} , 293 cm^{-1} and 225 cm^{-1} (Faria *et al.* 1997, Bersani *et al.* 1999, Chamritski and Burns 2005, Zoppi *et al.* 2005, Zoppi *et al.* 2006).

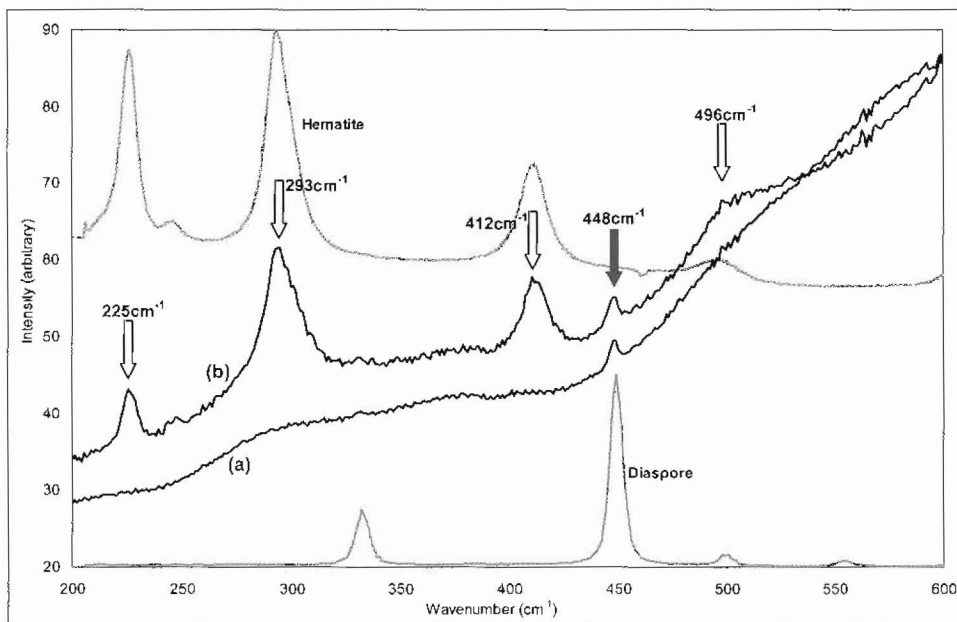


Figure 5 – Representative Laser μ -Raman spectra of diasporic bauxite samples in the low-wavenumber region (a: porous white-grey and b: massive red-brown). The lower spectrum corresponds to the Mineral Spectroscopy Server diaspore and the upper to standard hematite

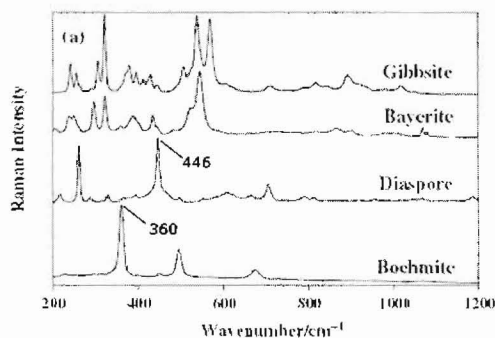


Figure 6 – Raman spectra of different AlOOH polymorphs (Ruan *et al.* 2001). It is clearly marked the difference of the diasporic Raman band at 446 cm^{-1} from the one of the boehmitic at 360 cm^{-1} , at the low-wavenumber region between 250 cm^{-1} and 600 cm^{-1}

Representative Laser μ -Raman spectra of boehmitic bauxite samples (massive red-brown) are shown in Figure 7 (low-energy region). According to literature, the more intense boehmite peaks at the low-wavenumber region are at 674 cm^{-1} , 495 cm^{-1} and 360 cm^{-1} and they correspond to the

hydroxyl translational modes. In our samples we observe the 362 cm^{-1} band (Ruan *et al.* 2001, see Fig. 6). The spectrum (a) from Figure 7 corresponds to the boehmitic matrix of the sample, at an area where metallic minerals, such as rounded hematite aggregates were not optically visible. This band (solid arrow in Fig. 7) is observed between the 412 cm^{-1} and 293 cm^{-1} hematite bands and it could be used as a rule of thumb to easily distinguish it from the diasporic peak which is observed outside these hematite peaks (Faria *et al.* 1997, Bersani *et al.* 1999, Chamritski and Burns 2005, Zoppi *et al.* 2005, Zoppi *et al.* 2006).

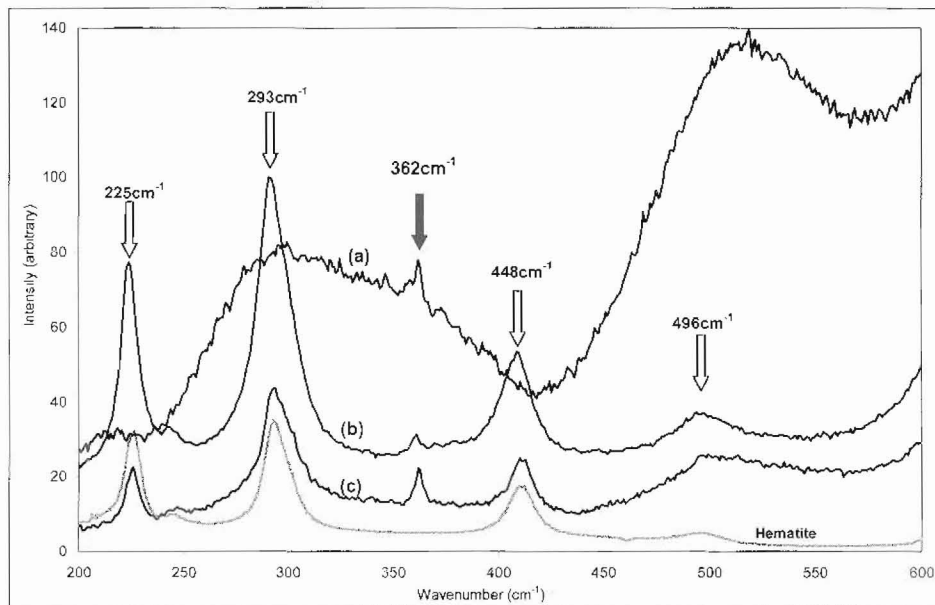


Figure 7 – Representative Laser μ -Raman spectra of boehmitic bauxite samples in the low-wavenumber region (a, b, c: massive red-brown). The lower spectrum corresponds to the Mineral Spectroscopy Server hematite

At this point one could refer that the hematite Raman bands differ evidently to that of goethite, which may also be present in massive red-brown bauxites (either diasporic or boehmitic). In this case, the AlOOH polymorph bands (either at 448 cm^{-1} or 362 cm^{-1}) are most probably expected to be distinguishable at the opposite sides of the main goethite band around 385 cm^{-1} (Faria *et al.* 1997, Bersani *et al.* 1999). Furthermore, it is also expected that diasporic and boehmitic low-wavenumber Raman bands will be apparent if kaolinite is present, under the laser beam spot, inasmuch as the main –very intense– kaolinite band appears at 140 cm^{-1} (Johnston *et al.* 1984, Frost *et al.* 1993).

Table 2 – Summary of the Laser μ -Raman data

	Raman bands (cm^{-1})	
	AlOOH polymorphs	Hematite ($\alpha\text{-Fe}_2\text{O}_3$)
Diasporic Type		
White-grey bauxites	448	-
Red-brown bauxites	448	412, 293, 225
Boehmitic Type		
Red-brown bauxites	362	612, 412, 293, 225

Concluding, the results of the present study suggest that Laser μ -Raman spectroscopy could be applied for the fast determination of the AlOOH polymorphs and, as a consequence, the "type" of bauxite of the Parnassos-Ghiona active mining area (central Greece). In the case of the white-grey (high-quality) diasporic bauxite there is a clear diasporic Raman band at 448 cm^{-1} to be used as the characteristic band, while in the case of the typical red-brown diasporic bauxite the same band is accompanied by the unavoidable bands of hematite (Table 2). For the red-brown boehmitic bauxite, the main Raman band of boehmite appears at 362 cm^{-1} , between two major hematite bands. It is therefore demonstrated that both diasporic and boehmitic bauxites can easily be characterized by recording Raman spectra in the $250\text{ cm}^{-1} - 600\text{ cm}^{-1}$ region. In this low-wavenumber region the bands of the AlOOH polymorphs do not interfere with bands from other bauxite minerals. A portable Raman system with a CCD acquisition camera and with a laser operating at the wavelength of 1064 nm could be used to rapidly acquire the narrow spectra range between 250 cm^{-1} and 600 cm^{-1} . The He-Ne laser with a wavelength of 633 nm introduces significant fluorescence which might suppress the Raman peaks and make them invisible. However, it still can be used when the CCD is centred to cover the low wavenumber region but it may require longer integration times. The use of a powder XRD or of another time-consuming technique is not necessary in order to distinguish the type of bauxite (diasporic or boehmitic). This could be particularly useful in characterising similar in appearance samples such as the massive red-brown samples (e.g. SAB0306_ASV and SAB0306_SKR, see Table 1) which could be of diasporic or boehmitic type. Future work could employ direct tests on site with a portable Raman system that has the above characteristics. Furthermore, one could proceed into calibrating a portable system to acquire quantitative or semi-quantitative information for precise quality assessment during production.

4. Acknowledgments

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