Cent. Eur. J. Geosci. • 4(2) • 2012 • 219-224
DOI: 10.2478/s13533-011-0048-9

VERSITA

Central European Journal of **Geosciences**

Design of two crushing devices for release of the fluid inclusion volatiles

Short communication

Yuri V. Dublyansky *

Institut für Geologie und Paläontologie, Leopold-Franzens-Universität, Innrain 52, 6020 Innsbruck, Austria

Received 4 October 2011; accepted 3 December 2011

Abstract: Two crushing cells have been described for the release of volatiles from fluid inclusions in minerals in vacuum, static gas, and gas-flow applications. To minimize the adsorption of released volatiles on the freshly created mineral surfaces, both devices employed heated crushing. In the MTSN (Museo Tridentine di Scienze Naturali) crusher, samples were disintegrated by a piston driven by an induction coil. For efficient crushing, the electromagnet operated in dynamic impulse mode. In the LFU (Leopold-Franzens-Universität) crusher, the sample was disintegrated through the combined action of compression (manually operated hydraulic ram) and attrition. Crushers are able to be used in off-line and on-line modes, in gas chromatographic and mass spectrometric analyses.

Keywords: fluid inclusions • gas chromatography • mass spectrometry • volatiles

The chemical and isotopic composition of volatiles trapped in fluid inclusions is important information sought in a wide variety of fluid inclusion studies. Gas chromatography (GS) and isotopic-ratio mass spectrometry (IRMS) are the two methodologies most frequently used for analysis of fluid inclusion volatiles. For analysis, volatiles need to be quantitatively released from the sample mineral. The two methods most frequently used for this purpose are thermal decrepitation and crushing; both of which have specific advantages and drawbacks which have been thoroughly discussed elsewhere [1–4]. In many applications, the method of heated crushing was found to give optimal results [5, 6].

Although the task of releasing fluid inclusion contents by mechanical destruction of samples appears trivial, a multitude of different designs of crushing devices can be found in the literature. Examples include: crushing of a sample in an evacuated steel tube [7]; off-line grinding system with stainless steel balls [8]; piston-cylinder/hydraulic ram design [9]; grinding using a steel ball in an evacuated vessel on a shaking table [10]; "peppermill" design [11]; and, the electromagnetic crushing stage [6].

In this short communication, two designs of crushing stages are presented, which have been tested, used, and proved successful in a number of research projects over the last 5 years. The designs are complementary and are able to be adopted for different applications.

MTSN – crushing cell for non-polar volatiles

The MTSN crushing cell was designed and tested while the author worked at the Museo Tridentino di Scienze Naturali (Trento, Italy). The design is therefore designated MTSN. Although recent advances in the applica-

*E-mail: Juri.Dublyansky@uibk.ac.at

tion of techniques for rapid on-line analysis of very small amounts of volatiles released from fluid inclusions are encouraging [12–15], there is a continued need for the off-line collection and treatment of fluid inclusion volatiles (e.g. separation of gases and conversion of various H-C-O-N-S compounds into gases suitable for analysis in IRMS: CO_2, H_2, N_2, and SO_2). The MTSN crushing cell is designed primarily, although not exclusively, for these off-line applications.

Electromagnetic crushing

An induction coil was used by Dennis *et al.* (2001) [6] to lift and drop a piston, hanging on a spring just clear of the sample in an evacuated tube. In contrast, in the MTSN crusher the electromagnet operated in a dynamic impulse mode. The crusher cell consisted of the base, the piston tube, and the piston (Fig. 1). The sample was placed on the anvil-plate mounted in the base of the cell. The piston was then inserted into the piston tube and the latter was attached to the base by means of a flange connection. The assembled crusher cell was positioned vertically and an induction coil was placed on the piston tube. Controlled by a custom-designed power supply unit (Fig. 2), the solenoid generated short impulses of a strong magnetic field. Each impulse threw the piston upwards, but ceased before the piston was able to reach the top of the piston tube. A steel spring mounted on the upward-facing end of the piston provided the rebound, causing the piston to accelerate downwards, and hit the sample. Impulses were repeated at approximately 1 Hz.

Crusher cell

The base of the crusher is made from a standard knife-edge flange (Varian ConFlat FO27 50000 NCE; 2.75″). The anvil-plate, made of hardened steel is press-fitted into the well machined in the base (Fig. 1), while the piston is made of hardened steel. The upper part of the piston is tapered to decrease the pneumatic resistance, and the lower working surface of the piston is machined as a 120°-cone and the anvil plate in the base of the crusher cell is shaped accordingly. This creates a shear component on impact with the mineral grains, which improves crushing, and also serves for self-centering of the piston.

The piston tube is sealed at its upper end and is welded to a second knife-edge flange on its lower side. The basal and upper parts of the crusher cell are connected using bolts and a custom-made Teflon gasket. The latter has an internal diameter corresponding to the diameter of the piston tube, so that it fills the gap between the flanges completely and prevents accumulation of uncrushed mineral grains. The internal, wetted surface of

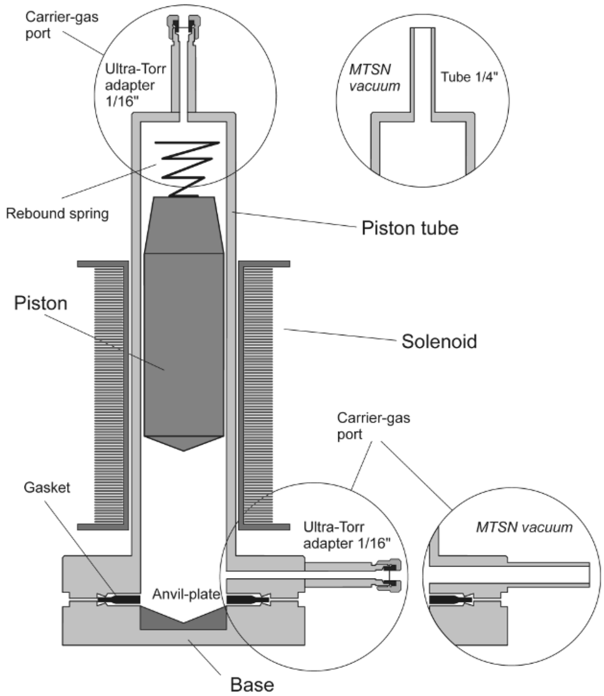

Figure 1. Schematics of the MTSN crusher. Modification of ports for gas-flow and vacuum applications are shown in circles.

the cell is ca. 215 cm^2; the volume (with inserted piston) is ca. 40 cm^3.

In order to minimize adsorption of gases on the metal surface and on the freshly crushed material, the cell is placed in a heater block, with another heater mounted on the piston tube above the solenoid. The temperature of the heater blocks is controlled by a pair of Jumo ecoTRON M thermostats with PT100 sensors.

The efficiency of crushing in this cell depends on a number of factors including the energy of the magnetic impulses; the mass of the piston; the position of the magnet relative to the piston; the elasticity of the rebound spring; the length of the piston tube; and the pneumatic resistance (the latter is only relevant for non-vacuum applications). These parameters have been optimized experimentally. The MTSN crusher has two modifications adjusted for two operational modes: vacuum/static gas and gas-flow.

Modification MTSN vacuum/static gas

Vacuum outlet ports of the crusher cell represent a 1/4″ o.d. stainless steel tube welded to the lid of the piston tube and to the side of the flange (Fig. 1). One port is connected to a vacuum line by means of 1/4″ Swagelock connectors.The second port is able to be sealed, connected to a gas line, or fitted with a detachable septum port. The relatively wide bores (4.4 mm) allow for efficient evacua-

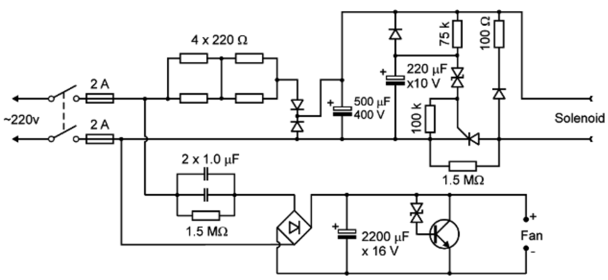

Figure 2. Circuit diagram of the transformerless power supplies for solenoid and cooler fan.

tion of the crusher cell. This modification can also be used for crushing in a static gas medium. Under this scheme, post evacuation and purging, the crusher is filled with inert incondensable gas (e.g. He) in which the released fluid inclusion volatiles are diluted. Aliquots of this mixture can be removed by a gas syringe and introduced into the GC line. The gas can then be transferred into a vacuum line for manipulations preceding the IRMS analyses (separation of volatiles, conversion of gases into analyzable form, etc.).

Modification MTSN gas-flow

Two carrier-gas ports have been fitted, made of the Swagelock Ultra-Torr adapters (1/16"Ultra-Torr Fitting x 1/4" tube stub), and welded to the body of the crusher cell. The Ultra-Torr fitting allows easy connection of the tubing without instruments (finger-tight). This crusher cell can be directly integrated into the GC or IRMS analytical lines [15]. It can also be used in the dual gas flow-vacuum schemes of the off-line gas recovery [16, 17].

Other configurations of inlet- and outlet ports may be designed to accommodate specific analytical schemes and requirements.

Electromagnet control/power supply

The circuit diagram of the control block for impulse operation of the induction coil is shown in Fig. 2. The circuit comprises two branches, one of which represents a transformerless resistive power supply for the solenoid and another is the capacitive power supply for cooling fan of the control block.

Additional features

Particle filter

Operation of the crusher cell produces fine dust, which can contaminate the vacuum line, tubing and equipment. To prevent this from occurring, an in-line particle filter (e.g., Swagelock FW Series, with the desired nominal pore size) is mounted near the crusher's outlet port.

Septum port

To provide an option for express calibration (MTSN gas-flow) and withdrawal of gas by a syringe (MTSN vacuum/static gas), a removable septum port may be mounted on one of the inlet ports. A septum port can be consrtucted from either a 1/4" Ultra-Torr Vacuum Union Tee or a 1/4" Swagelcok Union Tee (with Teflon ferules) fitting.

LFU - crushing cell for polar volatiles

As water is a polar molecule, it is readily absorbed on the inner metal surface of the crusher and on the crushed material. This may cause problems in IRMS analyses, particularly when very small amounts of water are involved (for example, as little as 0.2 μL of water; [14]). Adsorption of even minute amounts of this water may lead to significant distortion of measured δD and $\delta^{18}O$ values. Adsorption was the most likely factor for largely unsuccessful early attempts at using crushing to extract fluid-inclusion water for stable isotope analyses [6].

The need to address these issues led to the design of another crusher [14]. The LFU (Leopold Franzens Univeristät) crushing cell was designed to optimize the balance between the volume (which must be sufficient to allow crushing of cm^3-sized samples) and the inner surface (which should be kept at a minimum). The compromise is a cell with an internal surface of ca. 26 cm^2 (i.e. almost 10 times less than that of the MTSN crusher). The crushing cell consists of a base, an upper part, and a plunger (Fig. 3).

Working elements of the crusher (i.e. elements between which the sample is actually crushed) have matching convex and concave surfaces (Fig. 4). The perfect match between these surfaces allows crushing of even very small samples. Two types of the working elements were tested, one by leuco-sapphire (most suitable for hard minerals such as quartz, topaz, olivine, etc.) and a second by hardened steel (for softer mineralssuch as calcite and fluorite). The working surfaces were either rough (600 grit; sapphire) or polished (steel). The lateral surfaces of the upper working element were polished, which was necessary for a gas-tight seal with the upper part of the crusher (via a custom-designed Teflon gasket; Fig. 5). The upper working element was mounted coaxially on the plunger and the lower working element was press-fitted into the base of the crusher. The basal and the upper parts of the crusher were connected using a knife-edge flange and a Teflon gasket. All wetted surfaces of the crushing cell (except for the working surfaces of the sapphire working elements) were polished to diminish adsorption of water.

The carrier gas was admitted into and out of the crusher cell through two ports equipped with Swagelok Ultra-Torr® connectors, allowing easy instrument-less connec-

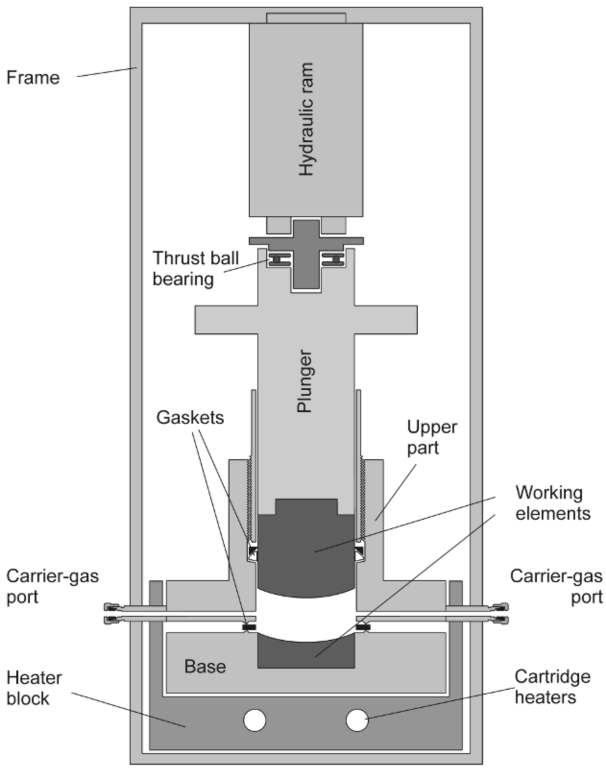

Figure 3. Schematics of the LFU crusher. Septum port is not shown. Geometry of the working elements and the gas-tight seal between plunger and upper tube is shown in Figs. 5.

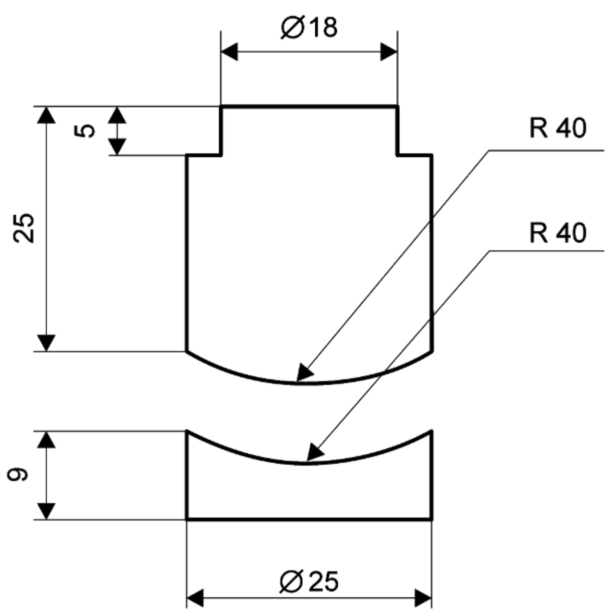

Figure 4. Working elements of the LFU crusher. Material: leucosapphire or hardened steel.

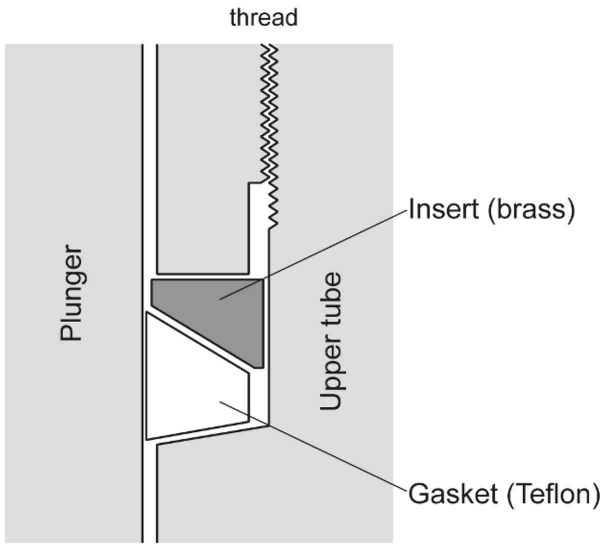

Figure 5. Schematic cross-section of the seal between the plunger and the upper tube.

tion of the tubing. The third port was equipped with a septum, and through this the port reference water or gas could be injected. The cap of the septum port had a finned design to enhance heat removal. The standard 11.5 mm diameter septum was able to be easily exchanged. BTO X-145 septa (Thermo Fisher Scientific) gave the best results in terms of longevity, withstanding several hundreds of injections.

Dennis, *et al.* (2001) [6] demonstrated that the adsorption of fluid inclusion water on the freshly crushed calcite lead to significant isotopic fractionation, and recommended removing water at elevated temperatures (ca. 150°C). Accordingly, the assembled LFU crusher was placed in a well in an aluminum heater block equipped with two cartridge heaters. The temperature was controlled by means of a Jumo ecoTRON M thermostat and a PT100 sensor.

The heater block was mounted on a frame. A small (length 7 cm; diameter 3.5 cm) manually operated hydraulic ram was attached to the upper part of the frame. The ram contacted the plunger through a thrust ball bearing which allowed axial rotation of the plunger. Rotation, done manually, induced attrition of the sample in addition to compression crushing.

The current design allows crushing of samples ranging in size from individual mm-sized grains up to ca. 1 cm^3. With increasing sample size, the efficiency of crushing deteriorates. The efficiency was assessed through multiple crushes of calcite samples of different weights. Samples smaller than ca. 0.5 g were crushed to fine powder (<250 μm) almost quantitatively (>95 %). The efficiency of crushing of larger samples (up to 2.5 g) depends on

Table 1. Comparison of properties of the MTSN and the LFU crushers.

Crusher	MTSN	LFU
Best suited for	Non-polar gases, off-line applications	Water and non-polar gases, on-line applications
Working medium	Vacuum or inert gas (He, Ar)	Inert gas flow (He, Ar)
Wetted surface (cm^2)	215	26*
Internal volume (cm^3)	40	3-4*
Max sample weight (g)	6.0	2.5
Time of crushing (min)**	3 to 20	0.5 to 2
Preferred initial sample state (grain size)	0.25 mm to 20 mm-sized fragments	3 mm to 20 mm-sized fragments

Notes: * - changes during crusher operation; ** - depends on sample weight.

the type (the surface finish) of the working elements. The yield of the <250 μm-grains is 25% to 40% for the steel working elements (polished working surfaces) and ranges between 40% and 75% for the sapphire working element (600 grit surfaces). Although the efficiency of crushing of other minerals has not been tested systematically, based on the current study, it appears to be satisfactory. For instance, small samples of quartz and olivine (ca. 0.2 g) were crushed quantitatively (>95%) in the crusher with the sapphire working elements. One property which has been noted for the LFU crusher is that it is more efficient when the loaded sample consists of fragments ranging from 3 mm to 20 mm in size. Crushing of samples consisting of uniform fractions of smaller grains can be less efficient as the grains self-organize in a "sand bed" in which adjacent grains are protected from crushing by their neighbors.

Comparison of the MTSN and LFU crushers

The major advantages of the MTSN design are the high efficiency of crushing, the possibility of crushing larger samples, and the possibility of being able to crush relatively fine-grained sand samples. The sample is able to be reduced to fine particle sizes, so that virtually no uncrushed fragments (>100 μm) remain. However, because of the relatively large inner volume of the MTSN crusher cell, the gas-flow configuration volatiles released from inclusions are strongly diluted by the carried gas. Therefore, pre-concentration or cryo-focusing must be employed down the line when using the MTSN crusher in the gas-flow applications. In contrast, the LFU crusher is designed for on-line gas-flow applications, and is best suited for analyses of small, volatile-rich samples. The most important properties of the two crushers are compared in Table 1.

A common feature of both crushers is the very simple and inexpensive maintenance, consisting of periodical changes of Teflon gaskets (after 30 to 50 analyses) and septa (after several hundreds of injections). The Teflon gasket sealing the gap between the plunger and the upper tube (Fig. 5) withstands several years of operations.

Example applications

MTSN crusher

The crusher has recently been used by teams at Hydroisotop GmbH, Germany and the Institute of Geological Sciences, University of Bern, Switzerland for quantitative GC analyses (O_2, N_2, CO_2, CH_4, C_2-C_6) and IRMS analyses of certain gas species ($\delta^{13}C$ in CO_2 and C_1-C_4; δ^2H in H_2 and CH_4) within a project aimed at characterization of paleofluids at the prospective nuclear waste disposal site Olkiluoto, Finland [18]. The crusher has also been used for quantitative GC analysis of quartz, which is being evaluated as potential high-purity raw material for the glass industry [19].

LFU crusher

The crusher was successfully used for GC analyses of different minerals (carbonates, quartz, fluorite, and olivine) at the Institute of Geology, Geophysics and Mineralogy, Russian Academy of Sciences, Novosibirsk, Russia. Over the last four years the crusher has been routinely used as an element of the dedicated analytical line built at Innsbruck University for IRMS analyses of paleowater trapped in fluid inclusions in speleothems. This analysis provides important paleoclimatic and paleohydrogeological information [14, 20].

Acknowledgements

The work was funded through project NEXTEC (at Museo Tridentino di Scienze Naturali, Trento, Italy) and a FWF project P182070 and a TWF support (at Leopold-Franzens-Universität, Innsbruck, Austria).

References

[1] Roedder E. Fluid Inclusions in Minerals. Rev. Mineral., Miner. Soc. Amer., 12, 1984

[2] Salvi S., William-Jones A. Bulk analyses of volatiles in fluid inclusions. In: Samson I., Anderson A., Marshall D. (Eds.) Fluid Inclusions. Analysis and Interpretation. Short Course Series Volume 32, Mineralogical Association of Canada, Vancouver, Canada, 2003, 247-278.

[3] Dallai L., Lucchini L., Sharp Z. Techniques for stable isotope analysis of fluid and gaseous inclusions. In: de Groot P. (Ed.) Handbook of Stable Isotope Analytical Techniques, vol. 1, Elsevier, 2004, 62-87.

[4] Mironova O. Volatile Components of Natural Fluids: Evidence from Inclusions in Minerals: Methods and Results. *Geochem. Int.+*, 2010, 48, 1, 83–90. DOI: 10.1134/S0016702910010052

[5] Bray C.J., Spooner E.T.C., Thomas A.V., Fluid inclusion volatile analysis by heated crushing, on-line gas chromatography; application to Archean fluids. *J. Geochem. Explor.*, 1991, 42, 1, 167-193.

[6] Dennis P., Rowe P., Atkinson T. The recovery and isotopic measurements of water from fluid inclusions in speleothems. *Geochim. Cosmochim. Ac.*, 2001, 65, 6, 871-884. DOI:10.1016/S0016-7037(00)00576-7

[7] Demèny A., Siklosy Z. Combination of off-line preparation and continuous flow mass spectrometry: D/H analyses of inclusion waters. Rapid Commun. Mass Sp., 2008, 22, 1329-1334. DOI: 10.1002/rcm.3473.

[8] Petersilie I., Sørensen H. Hydrocarbon gases and bituminous substances in rocks from the Ilímaussaq alkaline intrusion, south Greenland. *Lithos*, 1970, 3, 59-76.

[9] Andrawes F., Gibson E. Release and analysis of gases from geological samples. *Am. Mineral.*, 1979, 64, 453-463.

[10] Ohba T., Matsuo S. Precise determination of hydrogen and oxygen isotope ratios of water in fluid inclusions of quartz and halite. *Geochem. J.*, 1988, 22, 2, 55-68.

[11] Simon K. Does δD from fluid inclusion in quartz reflect the original hydrothermal fluid? *Chem. Geol.*, 2001, 177, 3-4, 483-495. DOI:10.1016/S0009-2541(00)00417-4

[12] Norman D., Blamey N. Quantitative analysis of fluid inclusion volatiles by a two mass spectrometer system. In: Noronha F., Dòria A., Guedes A. (Eds.) European Current Research on Fluid Inclusions (ECROFI-XVI), Faculdade de Ciências do Porto, Departamento de Geologia, Porto, Portugal, 2001, 341-344.

[13] Vonhof H., van Breukelen M., Postma O., Rowe P., Atkinson T., Kroon D. A continuous-flow crushing device for on-line δ^2H analysis of fluid inclusion water in speleothems. *Rapid Commun. Mass Sp.*, 2006, 20, 2553–2558. DOI: 10.1002/rcm.2618

[14] Dublyansky Y., Spötl C. Hydrogen and oxygen isotopes of water from inclusions in minerals: design of a new crushing system and on-line CF-IRMS analysis. *Rapid Commun. Mass Sp.*, 2009, 23, 2605-2613. DOI: 10.1002/rcm.4155

[15] Lüders V., Plessen B. Carbon and nitrogen isotope measurements of gas-bearing fluid inclusions. In: Bakker R., Baumgartner M., Doppler G. (Eds.) European Current Research on Fluid Inclusions (ECROFI-XXI), Montanuniversität Leoben, Austria, 2011, 130-131.

[16] Dublyansky Y. Development of methods for recovery of waters from fluid inclusions for stable isotope analysis. In: Strauch G., Weise S. (Eds.) Proceedings of the VIII-th Isotope Workshop of the European Society for Isotope Research, UFZ Centre for Environmental Research Leipzig-Halle, Leipzig, Germany, 2005, 43-47.

[17] Zhang R., Schwarcz H., Ford D., Serefiddin Schroeder F., Beddows P. An absolute paleotemperature record from 10 to 6 Ka inferred from fluid inclusion D/H ratios of a stalagmite from Vancouver Island, British Columbia, Canada. *Geochim. Cosmochim. Ac.*, 2008, 72, 4, 1014–1026. DOI:10.1016/j.gca.2007.12.002

[18] Eichinger F., Meier D., Hämmerli J., Diamond L. Stable Isotope Signatures of Gases Liberated from Fluid Inclusions in Bedrock at Olkiluoto. Working Report 2010-88. Hydroisotop GmbH, Germany/RWI, Institute of Geological Sciences University of Bern, Switzerland, 2010

[19] Morteani G., Eichinger F., Götze J., Tarantola A., Müller W. in press. Evaluation of the potential of the pegmatitic quartz veins of the Sierra de Comechigones (Argentina) as a source of high purity quartz by a combination of LA-ICP-MS, ICP, cathodoluminescence, gas chromatography, fluid inclusion analysis, Raman and FTIR spectroscopy. Special Contribution to the Freiberger Forschungsforum 2011, Springer, Berlin, Germany.

[20] Dublyansky Y., Spötl C. Evidence for a hypogene paleohydrogeological event at the prospective nuclear waste disposal site Yucca Mountain, Nevada, USA, revealed by the isotope composition of fluid-inclusion water. *Earth Planet Sc. Lett.*, 2010, 289, 583-594. DOI:10.1016/j.epsl.2009.11.061