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Recognising anthropogenic modification of the subsurface in the geological record

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Abstract

Humankind, in its technological development, is increasingly utilising both mineral resources from Earth's interior and developing the rock mass as a resource in itself. In this paper we review the types of anthropogenic intrusion, at different depth ranges, that can modify the physical structure and chemistry of the subsurface. Using examples from across the world, but with emphasis on the UK, and physical models of the induced modifications, we predict what kind of subsurface signatures a geologist of the future might recognise as anthropogenic, including boreholes, tunnels and caverns, waste and resource storage facilities, mineral workings and military test traces. The potential of these anthropogenic signatures to be discriminated from natural analogues is discussed against known or modelled processes of deterioration and transformation over geological timescales of millennia or longer.

Keywords: Anthropocene, Borehole, Landfill, Mining, Tunnel, Weapons

1. Introduction

A key stage in the development and ultimate success of *Homo sapiens* has been the capability to utilise the subsurface as a resource. Initially this was dominated by small-scale shallow mining of metals. Major underground development came with the Industrial Revolution, which saw markedly increased and extended mineral working. New technologies, including steam engines used to pump water from mine workings, allowed mining to extend to greater depths (Fig. 1). There was great expansion of coal working, to fuel steam engines, this becoming the volumetrically dominant global mining activity.

London, which by the mid-19th century was the largest city in the world, saw the extensive development of the shallow subsurface to support building construction, transport infrastructure and utilities (Fig. 2a; Price *et al*. 2016). The opening of the first London Underground station in 1863 is seen by Williams *et al*. (2014, in press) as a key indicator of the technological evolution of cities, allowing outward expansion of the conurbation. Arguably of greater importance was development between 1859 and 1865 of 160 km of intercepting sewers, fed by 720 km of main sewers and 21,000 km of smaller local sewers. This provided the model by which subsequent megacities have developed.

Technological development during the 20th century saw new use of underground rock masses (Fig. 2b; Price *et al*. 2016). These include disposal and storage facilities for wastes or resources such as radioactive waste (radwaste), CO_2 Carbon Capture and Storage (CCS), underground gas storage, compressed air energy storage, geothermal energy, subsurface development of habitations and laboratories (Fig. 1; Evans *et al*. 2009) and modification through warfare and weapons testing. Table 1 compares the ranges of anthropogenic intrusions, from the near surface to thousands of metres depth. Shallow excavations remain the most extensive category of subsurface use by both area and volume.

The scale of intrusion of the underground rock mass through discrete developments is now significant as a planetary phenomenon, and this study explores aspects of the scale and permanence of these developments:

(1) to what extent will infrastructure associated with these developments provide a lasting (on geological timescales of millennia or longer) signature of anthropogenic activities?

(2) how far does anthropogenic influence of the rock mass extend beyond the rock directly excavated?

(3) can these far-field physical and chemical alterations of the rock mass be unequivocally distinguished from natural processes?

Subsurface modification includes the construction of voids, the propagation of fractures associated with these voids and the migration of materials to form vein-fill or cements between pores. The types and nature of the voids, discussed by Zalasiewicz *et al*. (2014) in the context of characterisation of the Anthropocene, are summarised in Table 1. Earthworks associated with surface construction and landfill sites, both associated with distinctive artificial deposits readily identifiable as anthropogenic, and diffuse infiltration of contaminants (nitrates, heavy metals or organic pollutants) into groundwater from the ground surface, are not considered here.

2. Structural impacts of subsurface modification as distinctive anthropogenic features

Anthropogenic (induced) seismicity has many causes: mining of minerals, particularly coal; solution mining, especially of salt; oil and gas field depletion; hydraulic fracturing ('fracking') of low-permeability rocks to extract gas and oil; reservoir impoundment; enhanced geothermal operations; and academic research boreholes (Davies *et al*. 2013, Mitchell & Green 2017). The seismicity commonly results from reactivation of pre-existing 'natural' faults. Accepted criteria for recognising that fault reactivation is anthropogenic depends on knowledge of the timing and spatial relationships of the seismicity and of the injection procedures (Davis & Frohlich 1993). Hence, far-future recognition that a component of displacement is anthropogenic would be difficult, if not impossible. Here, we investigate fracture patterns that may be of uniquely anthropogenic in origin, summarised in Table 2.

2.1 Structural or mechanical loading by earthworks

Mechanical compaction applies mechanical energy to densify a soil, changing its bulk density. On a larger scale, extensive urban development can increase consolidation of subsurface deposits and enhance subsidence rates, particularly in coastal deltas. In extreme cases, dam construction, with reservoir impoundment and suddenly increased water-loading of the ground surface, can induce earthquakes (Gupta 1985).

In the future it would be exceptionally difficult to differentiate between the effect of mechanical compaction or structural loading by human constructions and that of natural burial consolidation (e.g. uneven glacial loading). Similarly, recognition of an anthropogenic origin for components of displacement on a fault would be difficult, if not impossible, unless observed at the time of deformation.

2.2 Structural disturbance by boreholes and hydrocarbon wells

Drilling-induced disturbance associated with boreholes is typically minor, on the scale of a few millimetres (Kelsall *et al*. 1983), though fractures may extend up to 0.2 m from boreholes (Fig. 3). Weak materials such as chalk and sand can flow into a well-bore, and sandstones can be affected by fracturing and borehole breakouts (Doornof *et al*. 2006).

On a larger scale, hydrocarbon and groundwater extraction can cause consolidation, e.g. the subsidence of Venice in the 1940s to 1970s resulted from consolidation of underlying deposits following extraction of groundwater and natural gas, resulting in pore space collapse, grain fracture, the closing of open fractures or initiation of new fractures (Doornhof *et al*. 2006); groundwater abstraction has resulted in a similar situation in London (Bonì *et al*. 2016). The flexure of the overburden due to hydrocarbon extraction generates shear stresses that can cause slip along weak shale strata (Davies *et al*. 2013).

Injection of CO_2 as part of a CCS facility can result in increased seismicity and subsidence of the Earth's surface (Cox *et al*. 1996). Fluid injection to enhance secondary oil recovery or dispose of extracted saline waters reduces consolidation effects, but can cause fault reactivation (Davies *et al*. 2013; Elsworth *et al*. 2016). Enhanced geothermal and hydrocarbon extraction involves creation of fracture networks through fracking. The fracturing operation for hydrocarbons commonly involves detonation of explosives perforating the well in controlled orientations to produce finger-like fractures up to 2.5 cm diameter and extending up to 0.6 m into the shale rock (Cuss *et al*. 2015). Hydraulic fractures are then induced by pumping saline water under high pressure, which can reactivate faults that cross or are within hundreds of metres of the wellbore (Davies *et al*. 2013). There remains some uncertainty regarding the morphology and development of fracture networks generated during shale gas production (Cuss *et al*. 2015). However, stimulated fractures are expected to propagate along planes in the lowest energy orientation, generally orthogonal to the maximum horizontal stress (Gale *et al*. 2007, Davies *et al*. 2012), as indirectly observed from microseismic hypocentre location and seismic anisotropy analysis (Simon 2005).

Natural hydraulic fractures are common, ranging from cm-scale sand-filled injectites up to hundreds of metres in height (Hurst *et al*. 2012). Natural hydraulic fracture pipes cluster into pipe-like features that may propagate upwards by >1 km. Stimulated hydraulic fracture pipes have a maximum upwards propagation recorded to date of ~600 m, although most are <100m (Davies *et al*. 2012).

Methane extraction from unworked coal (Davidson *et al*. 1995) involves drilling boreholes down to the seam, with permeability enhancement through: (a) fracking to develop new cracks or open existing joints (known as 'cleat') within the coal; (b) blasting; (c) injection of CO_2 or N_2; or (d) chemical reactions, such as the introduction of weak hydrochloric acid. Alternatively, *in situ* Underground Coal Gasification (UCG) involves injection of a water/oxygen mixture via a borehole, igniting and partially combusting the coal and extracting the gasification products (syngas). This process forms cavities, which as with coal mining, can cause subsidence that could propagate to the surface.

Enhancement of groundwater borehole yields can cause permanent changes to the subsurface. Groundwater abstraction in carbonate aquifers (e.g. chalk) is highly dependent on fractures, which often have limited connectivity and extent. The productivities of boreholes drilled in chalk are improved by introduction of hydrochloric acid under pressure, which enhances weaknesses in the rock and promotes fracture development (Banks *et al*. 1993).

2.3 Structural disturbance of tunnels and caverns

When a shaft, tunnel or storage facility is excavated into a rock mass it produces an Excavation Damaged Zone (EDZ), reflecting stress redistribution around the opening, damage by the excavation process and weathering associated with rock-groundwater interaction (Kelsall *et al*. 1983). The EDZ includes fracturing of originally intact rock, opening or closing of pre-existing fractures or loosening of crystal structures, particularly in salt. Blasting disturbs the walls of an excavation more than mechanical processes, but typically only to a depth of 1 m from the face (Fig. 4a). In fractured rock, Kelsall *et al*. (1983) show the EDZ resulting from stress relief typically ranges from 0.3–0.7 times the excavation radius. The fracture distribution around the tunnel (Fig. 4b) is similar in geometry to that generated by much smaller-diameter boreholes (Blümling *et al*. 2007). More extensive subsidence results from collapse of the generated voids. Such collapse structures in natural systems, such as dissolution of salt or gypsum, commonly generate laterally extensive breccias.

2.4 Structural impacts from Geological Disposal Facility (GDF) construction

The EDZ extent is influenced by natural fractures or heterogeneities, the initial stress field, bulk material properties and the geometry of the excavation (Blümling *et al*. 2007). The resulting distribution and longevity of fractures will vary depending on context, but excavation activity in more plastic materials may not be preserved, while in brittle shales or crystalline rocks (Martino & Chandler 2004, Cai & Kaiser 2005) an EDZ may remain detectable on longer timescales.

Experiments in Underground Research Laboratories give insight into the physical damage generated during excavation of a GDF. Indurated argillaceous rocks at the Tournemire research site, southern France, described by De Windt *et al*. (1999), show natural sub-vertical fracturing including mm-scale microfissures and cm-scale fractures sealed with calcite sourced from adjacent shales, and dm- to m-scale faults, including fault breccia. Tunnel construction generated additional mm- to cm-scale fractures within a 2 m-thick EDZ. These induced fractures lack calcite sealing or pyrite alteration, though currently show macroscopic gypsum crystal growth on fracture planes.

Observations at the HADES test facility, Belgium, indicate the potential transient nature of anthropogenic fractures in more plastic materials. Excavation of horizontal galleries through clays generates large shear planes, with a geometry reflecting stress redistribution (Mertens *et al.* 2004). Here, the clay tends to self-seal, with a reduction in fracture transmissivity through time (Blümling *et al*. 2007).

2.5 Deformation associated with subsurface solid mineral workings

Collapse of mine workings can deform adjacent bedrock, the first report of induced seismicity due to coal mining dating to 1738 at South Stanford Colliery, England (Li *et al*. 2007). Deformation of the overlying rock mass is dependent upon the mineral extraction technique used (Waters *et al*. 1996; Table 1). At very shallow depths (<10 m), extraction was historically undertaken using bell pits. This involved sinking many narrow (~1 m) shafts and working the coal for up 20 m diameter, after which the roof would become unstable, producing a crown-hole or subsidence hollow (Edmonds 1988, Fig. 5). The pillar-and-stall method allowed minerals to be extracted (notably coal) to greater depths of ~30 m by driving a grid of narrow roadways through the mineral seam, leaving pillars to support the roof (Figs 5 & 6). In West Yorkshire, UK, such workings extended up to 200 m from the shaft, with room sizes up to 5 m and extraction ratios of <70% (Bell 1978). The pillars can support open voids for many decades after working stops. However, pillar failure through ‘robbing’ on retreat from the workings, or subsequent loading, results in roof collapse (Figs 5 & 6), which can reach the ground surface, as a crown-hole (Edmonds 1988). The remaining grid-like pattern of coal and intervening stowed waste is uniquely an anthropogenic signature (Fig. 6). To mitigate the risk of surface subsidence, voids can be grout-filled (Fig. 3).

Longwall mining, which involves the void roof being temporarily supported by props that are moved forwards as the face is advanced, permits the total extraction of coal from a panel (Fig. 5). The Commission on Energy and the Environment (1981) detailed the method, which originated in Shropshire in the 17th century, and in the UK typically ranged to 100–1000 m deep in panels 50–250 m long. The process produces a zone of sagging, fracturing and general subsidence within days after coal extraction, with residual subsidence completed after ~2 years. The zone of disturbance has an 'angle of draw' extending ~35° outwards from the workings to the surface (Bowell *et al*. 1999, Fig. 5). The worked-out coal seam can often be recognised as chaotic beds of broken shale and coal fragments where the coal was formerly present.

Analysis of mining-induced seismicity in China by Li *et al*. (2007) shows that fracture initiation, propagation and rock mass movement typically occurs along pre-existing fracture planes. Here, rockbursts occur at >200 m depth, becoming increasingly common with greater mining depths. Fractures develop in the roof rock above the mined area in response to flexure under gravity load and these fractures may propagate to the surface. The floor deforms and fractures during mining, resulting in local floor heave (Fig. 5), which can also induce seismicity typically within 1000 m depth below the active mining. Underground coal fires (accidental or to extract coal gas) can also cause roof collapse and surface subsidence, the adjacent shales typically being reddened with most organic carbon content lost. Whilst induced seismicity may result from mining activity, it seems unlikely that future geologists would be able to differentiate between slip resulting from natural and human-induced events. Although such modern structures are associated with brittle and open fractures and loose collapse debris, with time the fractures will become mineralised and the debris will form breccias.

The development of chimneys of collapsed material or more regional sagging due to subsurface extraction of coal, either through mining or UCG, can have natural analogues in lithologies prone to dissolution, e.g. gypsum or limestone, in which dissolution creates the voids that result in comparable collapse structures (e.g. Edmonds 1988). Although natural subsidence hollows may look superficially similar to these crown-holes, development of such structures in dominantly siliciclastic successions associated with coal workings indicates an anthropogenic origin.

Where excavated evaporite workings are abandoned, within months they reseal as the surrounding salt flows into the cavity, e.g. Boulby Potash mine (Yorkshire, UK). In such circumstances, it may be difficult to detect prior mining activities unless there is a corresponding surface expression, though entombed artefacts will commonly be well-preserved.

2.6 Structural effects of subsurface weapon detonations

Subsurface detonation of nuclear devices produces very high temperatures and pressures generated over a fraction of a second. This causes the nuclear device and associated hardware and the rock mass adjacent to the charge to be vaporised or melted; a strong shockwave travels outwards, crushing and fracturing nearby rock (US Congress 1989; Fig. 7a).

The effects of underground detonations reflect explosion depth, the yield of the device and local lithology (McEwan 1988). Uncontained subsurface explosions at shallow depths will penetrate to the ground surface (Hawkins & Wohletz 1996), producing a conical crater, tens to hundreds of metres in diameter and depth, surrounded by ejecta. After the explosion, the central cavity may collapse to form a debris chimney, which if it reaches the ground surface forms a bowl-shaped subsidence crater that may be tens of metres to nearly a kilometre wide and several tens of metres deep (Fig. 7b). Typically, the chimney diameter is 10–20% greater than the cavity diameter (McEwan 1988). A broader area of subsidence can extend some hundreds of metres from the test site, with local reactivation of faults (Hawkins & Wohletz 1996).

A detonation at greater depths may be evident at the surface as a shallow crater, a mound or by consolidation of surface strata (McEwan 1988). In deep constrained detonations there are four commonly recognised zones (Fig. 7a) (Adushkin & Spivak 1994; Hawkins & Wohletz 1996), with the range of detonation effects in rock (r), scaled to the explosive yield of the detonation in kilotons: (a) the cavity, potentially floored by molten rock with a void radius of r = 4 to 12 m/kton $^{1/3}$; (b) the crushed zone surrounding the cavity in which the rock mass has lost all of its former integrity and with r = 30 to 40 m/kton $^{1/3}$; (c) the cracked zone in which the rock mass contains radial and concentric fractures (Fig. 7c), with r = 80 to 120 m/kton $^{1/3}$; and (d) the zone of irreversible strain with deformation modifying porosity/permeability and material strength, with r = 800 to 1100 m/kton $^{1/3}$.

In the USA, Shoemaker (1959) directly compared the Teapot Ess Crater (Nevada), generated by an uncontained subsurface detonation of a 1.2 kton nuclear device 20 m below ground surface, and the Meteor Crater (Arizona), formed by a bolide impact ~50,000 years ago (Fig. 8). The impact origin of the bolide structure is demonstrated by the ‘high-shock’ mineral coesite within the crater (Chao *et al*. 1960). However, the generation of similar minerals is expected in the case of nuclear explosion and Shoemaker (1959) noted that nearly all the major structural features at Meteor Crater (Fig. 8a), are reproduced at Teapot Ess (Fig. 8b). Comparable structures include inverted bedrock stratigraphy within debris ranging from micron to >30 m diameter, in turn resting on older disturbed strata dipping at moderate to steep angles in the wall of the crater and locally overturned near the debris contact. A further crater nearby (Jangle U, Fig. 8c), created by a nuclear device of the same yield but at shallower depths of ~5 m, is structurally distinct, having an anticline rim, as opposed to a syncline seen at Teapot Ess, though an anticlinal rim was also recognised at a shallow meteorite impact site near Odessa (Texas) (Shoemaker 1959).

3. Chemical alteration of the subsurface as a distinctive anthropogenic feature

Anthropogenic geochemical or mineralogical modification of the subsurface rock mass can result from: a) the migration of leachates from wastes within a void; b) the interaction of wastes with any containing barrier; c) the alteration of construction materials used to support and line voids; or d) injection of novel minerals or mineral assemblages directly into the rock mass. The leachates include dissolved minerals that may precipitate within fractures and pore spaces within the rock mass.

In Table 3 the effects of geochemical or mineralogical modification are summarised for a number of important construction materials and settings, including: bricks, concrete, drilling fluids and infrastructure associated with boreholes and wells, rockmass adjacent to a Geological Disposal Facility (GDF), rockmass part of a Carbon Capture and Storage (CCS) site, mining leachate, and rocks and soils adjacent to zones of atomic weapon detonation.

3.1 Deterioration of brick-built structures

Bricks are commonly used in deep basements and older tunnels, their durability reflecting their composition and the processing of raw materials. Brick-clays typically comprise quartz, clay minerals (illite in combination with kaolinite, chlorite or smectite), and variably subordinate feldspars, carbonates, Fe-bearing minerals and organic materials (Dunham 1992). Fired bricks are heated to crystallize high-temperature mineral phases. The length and temperature of firing determines brick durability, strength, subsequent water absorption and hence expansion and deterioration, with bricks fired at low temperatures being least durable (Hughes & Bargh 1982). However, fired bricks rich in sodium and potassium or illite-rich clay tend to expand when wet and the presence of calcite, dolomite, pyrite, and siderite is associated with development of cracks, spalls and pops (Hughes & Bargh 1982). Bricks can suffer salt deterioration resulting in efflorescence with resultant volume increases causing degradation (Sena da Fonseca *et al*. 2013). Lime present in calcareous fired bricks can modify to portlandite in the presence of water, causing volume increase and 'lime blowing' (Elert *et al*. 2003).

The oldest fired bricks from Babylonia date around 4000 BCE (Rapp 2009). This suggests, despite their progressive deterioration, recognition of bricks as anthropogenic structures is likely to persist for many millennia into the future.

However, in contrast to slow thermal processes attained naturally, brick clays are heated rapidly and for short durations and may not contain geologically stable mineral assemblages (Dunham 1992) that could ensure preservation in their current state over millions of years.

3.2 Mineralisation and chemical alteration of concrete

Concrete, commonly used in modern shallow (e.g. spread footing) and deep (e.g. piled) foundations, to line and protect excavations such as tunnels, and as a grout to infill voids, may decompose to affect the host rocks. Boreholes differ in this respect and consequently are described later.

The main phases present in hydrated Portland cement are ~micron-scale particles of portlandite ($Ca(OH)_2$), Ca silicate hydrates (e.g. jennite and tobermorite), Ca aluminate hydrates and Ca sulpho-aluminate hydrates, e.g. ettringite (Gherardi *et al*. 2012, Rochelle & Milodowski 2013, Waters & Zalasiewicz 2018).

Construction of sub-surface structures can modify and divert groundwater flow (Attard *et al*. 2016) with geochemical impacts. For example, carbonate-rich water derived directly from leaky water mains or the leaching of lime mortars and cement-grouting ('concrete carbonation') results in hyperalkaline groundwater formation (pH >10). During carbonation, phases react (Table 3) to form $CaCO_3$ (calcite, aragonite or vaterite depending on the degree of supersaturation), SiO_2, and gibbsite (Gherardi *et al*. 2012, Rochelle & Milodowski 2013), initial decreasing porosity. After >~100 years porosity increases due to loss of primary cement phases and re-dissolution of secondary minerals, e.g. zeolites (Gherardi *et al*. 2012). Ultimately, on a millennial timescale, the altered cement is a carbonated, low-porosity layer comprising a mineralogy (e.g. calcite, aragonite, quartz, illite, dawsonite) that is naturally common (Waters & Zalasiewicz 2018). This suggests that far-future, recognition of an anthropogenic source would be difficult mineralogically, although macroscopic structural fabrics may persist, and novel geochemical or isotopic fingerprints may still be observable long into the future.

Rapidly growing calcium carbonate speleothems have been observed in domestic cellars (Sundqvist *et al*. 2005), and both abandoned and active railway tunnels (Field *et al*. 2016), underground aqueducts (Pons-Branchu *et al*. 2015) and dam site tunnels (Liu & He 1998), but do not extend beyond the void.

Natural mineral systems similar to Portland cement are very rare, limited to low-temperature serpentinisation of ultrabasic rocks or retrograde alteration of marble, impure limestones, calcareous shales and carbonaceous sediments such as coal within high temperature-low pressure metamorphic aureoles around igneous intrusions (Alexander 1992). Natural Ca silicate hydrate phases show similar reactions as cement/concrete, but over ~10,000 year timescales, involving conversion to $CaCO_3$ and SiO_2 and formation of a well-defined reaction front associated with localised Ca migration, increase in matrix porosity and cracking (Milodowski *et al*. 2009, Rochelle & Milodowski 2013). A close analogue at Maqarin, Jordan, involves bituminous biomicrites and calcareous mudstones heated by combusting bitumen in a hyperalkaline groundwater system (pH 12.5). It forms a plume ~500 m from the ‘cement zone’ (Savage 2011), buffered by naturally occurring cement minerals, mainly portlandite but also ettringite and tobermorite (Khoury *et al*. 1992). CO_2, and

H_2O release causes brecciation of rocks overlying the area of combustion, possibly distinguishing this natural system from most anthropogenic cement sources.

3.3 Chemical and mineralogical changes associated specifically with boreholes

Boreholes can include complex associations of clay or cement grouts, steel or plastic casing, with injection of drilling muds and fracturing fluids into adjacent rocks and soils extending the geochemical fingerprint of drilling activity well beyond the borehole itself.

Clays, mainly bentonite, or cement grouts are widely used in the construction, geotechnical and water well industries to plug boreholes (Daemen 1996). When pumped down a well-bore to seal it, cement filtrates containing dissolved $CaCO_3$ and sulphate can be forced at high differential pressure into, and re-precipitate within, the surrounding rocks (Hodgkinson & Hughes 1999). Portland-type cements (described above) have been used for only ~200 years, so there is uncertainty as to the long-term alteration of boreholes cement plugs (Rochelle & Milodowski 2013).

Drilling boreholes involves pumping bentonite-rich “drilling muds” down the borehole. In chalk rocks, Hilbrecht & Meyer (1989) recorded injectites of drilling mud and rock cuttings that superficially appear similar to natural marl and solution seams, but may be distinguished by the presence of flow structures, abrasion of cuttings, wedge-shape geometries with sharp tops and bases locally cross-cutting sedimentary bedding and the absence of trace fossils, stylolites and concretions. Drilling muds may also contain water-emulsifying, suspending and filtration-control agents, clay-barite suspensions, salts (sodium chloride and calcium chloride), various detergents, flocculants, organic polymers and bentonite (Caenn *et al*. 2011) that may leave a diagnostic geochemical signal. Extraction of conventional oil can also be enhanced through the injection of NaOH/KOH-type alkaline fluids (pH 12-13) (Savage 2011). Such drilling muds and solutions may temporarily leak into formation waters, but because of the potential damage to aquifers and the cost of lost drilling materials, such penetration into subsurface strata is typically kept to a minimum.

A typical hydrocarbon well on completion comprises a steel casing, separated from surrounding rock by a cement grout, and a cement plug sealing. The steel can vary in the type and degree of corrosion (Enning & Garrelfs 2014): (a) Oxygen and moisture near the ground surface will oxidise the steel casing with time; (b) absence of oxygen and pH >6 – the corrosion of iron is insignificant and is expected to last for centuries; (c) CO_2-rich, O_2-poor (anticipated during concrete alteration) – siderite ($FeCO_3$) coating initially forms on the casing; (d) anoxic conditions (expected in oil and gas pipelines) – sulphate-reducing bacteria can significantly accelerate corrosion (anaerobic biocorrosion), resulting in iron sulphide precipitation.

Plastic casing/liners are common in monitoring wells. Chemical degradation of plastic polymers at depth in geological strata is poorly known, but may result from alteration of molecular bonds driven by heat or hydrolysis at very high or very low pH (Zalasiewicz *et al*. 2016). Ultimately over geological timescales plastics will likely alter to hydrocarbons, expelled as oil and gas and leaving a carbonised film on a mould of the plastic artefact.

High-viscosity fracturing fluids associated with fracking (Ferrer & Thurman 2015) typically comprise polymer-based gels and chemical additives, including gelling agents (Guar/xantham gum or hydroxyethyl cellulose), crosslinkers (borate salts), breakers (ammonium persulphate, magnesium peroxide), friction reducers (polyacrylamide, petroleum distillate), surfactants (ethanol, isopropyl alcohol, 2-butoxyethanol), biocides (glutaraldehyde, 2,2-dibromo-3-nitrilopropionamide (DBNPA)), scale inhibitors (ethylene glycol), corrosion inhibitors (isopropanol, acetaldehyde) and oxygen scavengers (ammonium bisulphite). The organic polymers and chemicals may have only short to intermediate residence on grain surfaces or as a filtrate in shales whereas, proppants used to keep the fractures open (Fig. 9) will leave permanent injectite fabrics (Legarth *et al*. 2005). Superficially, the injectite structures are comparable to natural neptunean dykes, but the presence of the proppants, typically synthetic ceramic spheres, or natural sand of provenance that cannot be traced back to a source within the depositional basin, indicates an anthropogenic origin. Short-term, artificial hydraulic fractures lack the calcite cement seen commonly in natural fractures, though subsequent mobility of Portland cement from the well will ultimately produce a likely source of calcite fill of the hydraulic fractures.

Over-pressurisation during Underground Coal Gasification can drive a plume of benzene, volatile organic carbons and inorganic contaminants, leached from the residual ash, into regional aquifers (Burton *et al*. 2013). It is unclear if this would produce a geochemical signal that would differ from natural combustion of coal.

Deep (> 500 m) “closed” groundwater systems, with very slow groundwater flow and limited or no connection to the surface and potable water aquifers (Hickey 1989), have been used since the 1950s for hazardous waste disposal through boreholes, e.g. radioactive, toxic or other heavily contaminated substances. Pressure changes mean that contaminated formation fluids can penetrate other parts of the groundwater system (Lesage *et al*. 1991).

3.4 Temporal chemical and mineralogical changes to a Geological Disposal Facility (GDF)

Globally, many GDF schemes are under construction or proposed, but completed underground storage of radioactive wastes is limited to Asse II and Morsleben former salt mines (Germany) and near Carlsbad (New Mexico, USA) and active sites to Onkalo (Finland) and Forsmark (Sweden). The intention is for radwaste to be ‘contained and isolated’ until it has similar radioactivity to naturally occurring materials, generally within hundreds of thousands of years. Repository evolution is therefore generally considered over ~1 million year timescales. Existing and proposed repository designs show considerable variability, so long-term evolution is likely to differ substantially between sites and be highly dependent on the choice of barriers, host rock, repository geometry, thermal footprint, groundwater behaviour and type of waste. However, there has been much study of the long-term progression of specific processes, including evidence derived from natural analogues.

In most cases, the radwaste would be stored in cement or vitrified form and associated containment structures would be recognisably anthropogenic in origin. Alexander & McKinley (1999) describe various alteration scenarios. To slow devitrification in the

Swedish disposal concept, the waste is contained in copper canisters filled with lead and a surrounding bentonite buffer, with *in situ* corrosive penetration timescales of 10−100 million years. In Switzerland, more corrosive higher sulphate groundwaters and greater pressures necessitated a stainless steel flask (a redox buffer) surrounded by bentonite (a pH buffer) to ensure low radionuclide solubility. Alteration of the bentonite barrier, mainly montmorillonite with minor calcite, pyrite and siderite, progresses very slowly, with significant alteration to illite not expected within the first million years and complete alteration to take 10−100 million years. The steel canisters by contrast are likely to have a lifetime of 10,000 years. Devitrification/dissolution of the glass is expected to take ~100,000−10 million years after canister failure and exposure to groundwater, yielding radionuclide-bearing colloids.

Fluids produced by cement dissolution (section 3.2) could migrate into the host geology as a 'hyperalkaline plume' or ‘alkaline-disturbed zone’ (Berry *et al*. 1999). This would result in significant dissolution, mainly of aluminosilicates, followed by precipitation of amorphous calcium aluminosilicate hydrate phases crystallizing as zeolites and feldspars as the final product of mineralisation (Eikenberg & Lichtner 1992, Savage & Rochelle 1993, Hodgkinson & Hughes 1999, Moyce *et al*. 2014, Milodowski *et al*. 2015). Modelled over 50,000 years, the zone of alteration can extend up to 3 km from the site (Eikenberg & Lichtner 1992).

A GDF will be associated with a thermal footprint generated by the radwaste; repository design is optimised to achieve a ‘desired’ temperature. Clay mineral stability at elevated temperatures is of particular importance. Above 100 °C, smectite fully alters to illite over timescales of <1 million years, while high pH conditions associated with a repository containing cementitious materials could potentially accelerate the transformation, even at lower temperatures (Horseman & McEwen 1996). Weaver (1979) considered that illitization could begin within a few years at temperatures as low as 40 ^{o}C in saturated conditions and moderate (50–100 ^{o}C) temperature increases, particularly in the presence of organic material, and will cause kaolinite to form in sandy beds. Chlorite can form by the alteration of other clay minerals at temperatures as low as 70 ^{o}C and at ~200 °C chlorite may grow in fractures and voids. However, if shales have been subjected to temperatures of 200–300 ^{o}C for millions of years, as with many Lower Palaeozoic rocks, the heat generated by radwaste is unlikely to cause any major chemical or mineralogical change.

To understand the potential for migration, should radionuclides become mobile, there has been research on natural nuclear fission reactors, e.g. the uranium-rich 2.0 Ga old site at Oklo, Gabon described by Gauthier-Lafaye *et al*. (1996). Here, 90% of the uranium remained *in situ* after criticality (the point at which a nuclear reaction is self-sustaining), with limited dissolution and chemical mobility of some elements (most actinides, some REE, Y and Zr). Uranium mineralisation, associated with calcite, organic matter and sulphides, occurs in dense networks of bedding-parallel microfractures. During criticality the intense hydrothermal alteration of the host sandstone extended ~50 m beyond the centre of the natural reactor, with replacement of the sandstone by newly crystallized Mg-chlorite, Al-chlorite and illite. The resultant volume decrease caused a collapse of the host rock both above and below the natural reactor and the associated fractures acted as pathways for the hydrothermal fluids. The study of anthropogenic nuclear accident sites such as Hanford (USA), Chernobyl (Ukraine), and Fukishima (Japan) indicates that some elements have mobilised, e.g. at Hanford, caesium is estimated to have migrated up to 40 m below the storage tanks (Serne *et al*. 2001, McKinley *et al*. 2001).

3.5 Chemical alteration associated with CCS gas sites

Carbon Capture and Storage (CCS) technology involves injection of CO_2 into porous and permeable strata at depths likely to be >~800 m, resulting in a phase change to a supercritical fluid with <0.3% of the volume of the gaseous form (Rochelle *et al*. 1999). Once injected, trapping of CO_2 is expected via four primary mechanisms (IPCC 2005, Fig. 10 and Table 3): (a) Immediately after injection, the CO_2 will be stored as a free phase within the host rock through structural traps, e.g. within an anticline; (b) CO_2 dissolution into the local formation water initiates a variety of geochemical reactions (Rochelle *et al*. 2004) – Simulations suggest that a supercritical CO_2 bubble develops in a 5 m radius around a well after 10 years of injection, surrounded by a two-phase zone of ~650 m radius (André *et al*. 2007); (c) residual trapping along the migration path of CO_2; and (d) mineral trapping, caused by interaction of supercritical CO_2 with the reservoir rock, may provide a permanent CO_2 sink and can lead to partial dissolution of feldspars, dolomite and anhydrite and precipitation of clays and calcite (Rochelle *et al*. 1999, 2004).

The Bravo Dome CO_2 field, New Mexico, provides a natural analogue in which CO_2 is considered to have degassed from magma entering the reservoir <50,000 years ago (Rochelle *et al*. 2004), with resultant dissolution of anhydrite, gypsum, dolomite, K-feldspar and plagioclase and late-stage precipitation of kaolinite, zeolites and gibbsite, particularly along fault planes (Pearce *et al*. 1996). For rocks with saline pore fluids, dawsonite can be an important secondary phase, along with quartz and occasionally Ca−Mg−Fe carbonates, e.g. the Bowden-Gunnedah-Sydney, eastern Australia (Baker *et al*. 1995).

CCS sites will exhibit many of the features present in naturally occurring CO_2 accumulations. CO_2-rich gas discoveries at the Fizzy Horst, Southern North Sea, demonstrate the potential for CO_2 to be contained in the subsurface over long timescales (~50 Ma) (Underhill *et al*. 2015). Within the first few hundred years, it may be possible to differentiate human-made storage sites from natural accumulations, simply by detection of the ongoing pressure-pulse generated by CO_2 injection (Noy *et al*. 2012). On longer timescales, isotopic signatures may indicate an anthropogenic origin. For example, for Fizzy Horst, Heinemann *et al*. (2013) used carbon and oxygen isotopic compositions to differentiate between dolomite generated before and after the CO_2-rich gas was introduced to the reservoir, the novel dolomite being generated by the reaction of CO_2-bearing brines and silicate minerals. In Fizzy Horst the carbonate mineral dawsonite, distinctively a product of high CO_2 concentrations, has formed in only trace amounts (0.4 ± 0.3 % solid volume) even after >50 Ma (Wilkinson *et al*. 2009). Hence, the majority of injected CO_2 is unlikely to be stored by chemical mineralisation (Wilkinson *et al*. 2009; Fig. 10b). On intermediate timescales (~1000 years), anthropogenic CO_2 will be most apparent by its physical presence, either as a distinct phase, in solution or as a result of potential leakage to the seafloor.

Cold-water geysers at Green River (Utah), provide a natural analogue of the potential long-term fate of anthropogenic CO_2 stored in geological reservoirs migrating to the surface (Assayag *et al.* 2009), potentially evident in the form of chimneys. The geysers show helium and carbon isotopic ratios suggesting that the CO_2 is derived from crustal sources. Trace impurities within captured CO_2, such as SO_2 and NO_x, could indicate an anthropogenic source.

3.6 Leachates from underground mining activity

Acid mine drainage is highly aggressive to native rocks (Simate & Ndlovu 2014). A study by Bowell *et al*. (1999) showed that underground metal mine workings typically contain water with high Total Dissolved Solids >1000 mg/l, and in some coal mines sulphate is commonly >2000 mg/l. Water contaminated by natural interaction with minerals can have widely variable pH. The Levant mine, Cornwall, has acidic groundwater, pH 2-4, and high levels of Fe, Al, Cu, Zn and SO_4^{2-}, whereas in Yerrington pit, Nevada, mine water is neutral and has low metal content despite reacting with sulphide-bearing host rocks.

Acid Mine Drainage (AMD) in metal or coal mines, reviewed by Akcil & Koldas (2006), is caused by mining introducing an oxidizing environment, with oxidation of FeS_2 generating both the acidity of the mine waters and the supply of large quantities of Fe and sulphate-forming ochre precipitates, but relatively low concentrations of toxic heavy metals. Where neutralization occurs, metals and sulphates are precipitated forming a range of minerals dominated by iron oxyhydroxides, oxysulphates such as ferrihydrite ($Fe(OH)_3$), goethite ($FeOOH$) and iron sulphate polymorphs. AMD can generate very soon after mining commences and persist long after the operations cease (potentially thousands of years if unremediated). AMD can migrate extremely quickly through flooded mine workings, and on intermediate timescales migrate through natural, or mining-induced fractures and disconformities. In an underground mine, oxidation can be reduced by keeping the former workings flooded, with isolation of pollution sources through the use of plugs (bulkheads) to reduce the flow of water through parts of the mine where contamination is high.

3.7 Mineralogical expression of nuclear detonations

Nuclear testing has produced a durable, but localised lithological expression through the conversion of sand into a glass-like substance known in the USA as 'trinitite' (Eby *et al*. 2010) and in Kazakhstan as 'kharitonchik'. Trinitite is the complex product of surface detonations, and the glass may be vesicular, similar to natural volcanic scoria, but showing compositional heterogeneity at the tens to hundreds of micrometres scale, with unmelted quartz grains, parts of the nuclear device present as explosion-generated metallic chondrules and radionuclides that are distinctively anthropogenic (Eby *et al*. 2010). Trinitite from surface explosions generates glass beads similar to tektites produced during meteorite impact explosions (Eby *et al*. 2010). Nickel-iron crystalline debris and minute spherules, typical of a meteorite impact (Shoemaker 1959), contrast to the products of nuclear detonations described above. Radioactive gases may also diffuse through pore spaces and unsealed fractures of the overlying rock in underground explosions producing a marked radiogenic signal. However, a more immediately apparent marker resulting from nuclear activities is the isotopic 'bomb-spike' signature deposited from both local and global fallout, reviewed in the context as a potential marker for the Anthropocene by Waters *et al*. (2015).

4. Conclusions

Many of the physical and chemical products of human subsurface intrusion either do not extend far from the source of intrusion, lack long-term persistence as a signal (Fig. 11) or are not sufficiently distinctive from the products of natural processes to make them uniquely recognisable as of anthropogenic origin. But the scope and complexity of the signals have increased greatly over recent decades, both in areal extent and with increasing depths, and seem set to be a fundamental component of our technological expansion. There will be some clues to the geologist of the far-future, when historical knowledge records may not be preserved, that will help resolve the origin.

- Infrastructure associated with subsurface developments over the short term will leave a clear expression of anthropogenic intrusion. Over geological timescales of millennia and longer, the anthropogenic materials associated with such infrastructure will alter diagenetically to minerals that may be common in nature, but the physical form of the intrusion will likely be fossilized as a permanent signal.

- Chemical alteration of bricks is not expected to extend beyond the immediate vicinity of the structures and their likely durability for millions of years into the future is both untested and unmodelled.

- Cement and concrete, when initially introduced into the subsurface in tunnel or cavern linings or as a grout in boreholes, comprise phases which are relatively rare in nature; where found naturally the presence of brecciation above deposits indicates a natural origin. In the presence of acidic groundwaters, cement and concrete will produce contaminant plumes which may migrate in groundwaters some distances from the source, eventually within hundreds or thousands of years reacting to form naturally common minerals, in which the anthropogenic origin may be determined through complex geochemical or isotopic signatures.

- Steel may in favourable conditions persist for centuries, but over geological timescales will alter to iron oxides, carbonates or sulphides depending upon the redox environment, potentially fossilizing the infrastructure morphology.

- Rates of chemical degradation of plastic polymers in the subsurface is poorly known, but on geological timescales will likely leave a carbonised film on a mould of the plastic artefact.

- The generation of crush zones and radial and concentric fractures associated with subsurface detonations (Fig. 4a), at sub-metre-scale as part of the early phase of fracking or tunnel excavation, and at the hundreds of metres-scale through deep subsurface nuclear explosions (Fig. 7), has no direct natural analogue. However, shallow subsurface nuclear detonations produce craters similar in geometry to bolide impacts (Fig. 8) and both can contain the mineral coesite. Glass associated with subsurface nuclear detonations will be recognisable through extremely small-scale compositional heterogeneity and incorporation of vaporised metals from the site infrastructure.

- Drilling disturbance adjacent to boreholes is typically less than the diameter of the borehole itself (Fig. 3), whereas excavation of shafts, tunnels or underground storage facilities can generate Excavation Damaged Zones with fracturing induced up to 1.4 times the void diameter (Fig. 4). Such mechanical processes do not greatly extend the lateral influence of the bores or larger excavations (Fig. 11), but chemically and mineralogically distinctive drilling muds may penetrate a short distance into the surrounding bedrock.

- Hydraulic fracturing induced as part of enhanced geothermal and hydrocarbon extraction operations can produce fracture pipes or networks on hundreds of metres-scale. Though, superficially similar to natural structures, discrimination will be possible on short to intermediate timescales through organic chemicals used to extract hydrocarbons, or permanently through the presence of proppants injected to keep fractures open.

- The origin of collapse structures would be mainly resolvable by the nature of the host rocks: subsidence in mainly siliciclastic rocks with coal seams or mineral veins is likely to be associated with anthropogenic void generation and collapse; collapse structures in carbonates- and evaporate-rich successions could be equivocal in origin, but a natural source would be assumed unless infrastructure associated with mining or brine dissolution was present.

- The chemically disturbed zone around a Geological Disposal Facility could extend several hundred metres, and the hyperalkaline plume well beyond that. Thermal alteration of the host rock around a repository, in which temperatures associated with high level waste is unlikely to exceed 100 °C and low and intermediate wastes a few tens of degrees above ambient temperatures, may be very difficult to distinguish from mineral and chemical alterations resulting from natural diagenesis and low grade metamorphism of mudrocks. The most distinctive feature will be the vitrified radwaste and containment structures.

- Long-term containment of CO_2 in rocks can result in the interaction with the reservoir rock, leading to partial dissolution of some minerals and precipitation of others. These features can be seen in naturally occurring CO_2 accumulations, though carbon and oxygen isotopic composition and SO_2 and NO_x impurities may indicate an anthropogenic origin. However, differentiation from natural accumulations will be most clearly made by the discovery of infrastructure related to injection activities, such as boreholes.

- Subsurface mineral extraction can be associated with groundwaters rich in dissolved metals and sulphates and Acid Mine Drainage (AMD) with precipitates of iron hydroxides and sulphates, may not clearly be recognisable as of anthropogenic origin when found in rocks, even if AMD precipitates can be a distinctive indicator of oxidizing environment in mineral workings when seen in surface springs.

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Figures

Fig. 1. Approximate depth ranges of typical anthropogenic structures discussed in this study (modified from Evans *et al*. 2009).

Fig. 2. Schematic representation of historical development of the subsurface in a city: (a) during the Victorian era, and (b) its evolution to multiple historical and current uses. From Price *et al*. (2016), reproduced with permission.

Fig. 3. Excavation near Stoke-on-Trent, UK, revealing a former void associated with old coal workings, subsequently infilled with injection grout to stabilise the ground above the workings. The feeder injection borehole, also grout-filled, is associated with a 0.2 m wide zone of closely spaced fractures appearing to be associated with the intrusion by the borehole. Widely spaced fractures evident in the sandstone present in the roof of the former (labelled on the image) coal seam are probably formed by collapse of open voids following coal extraction and before grout injection. Photo taken by Allott & Lomax (reproduced in Wilson *et al.* 1992).

Fig. 4. (**a**) Example of radial fracture pattern (~0.5 m in diameter) with central pulverised core (~50 mm diameter) associated with blasting during construction of a cutting in basalt, near Arteara, Gran Canaria (Spain). Photo taken by C.N. Waters; (**b**) Schematic failure pattern in transversely isotropic hard clay (from Blümling *et al*. 2007). Red marks the tunnel circumference; damage in the sidewalls is generally limited to tensional circumferential cracks (in green); compressive zones (in blue) may be prone to slabbing or breakout notches if stresses are sufficiently high.

Fig 5. Schematic cross-section showing the types of subsidence associated with different coal mining methods (from Waters *et al*. 1996).

Fig. 6. View of a former pillar-and-stall workings for coal, subsequently re-excavated. The coal seam, seen at the base of the backwall, forms pillars present as the dark areas of the excavation floor. The infilled waste materials, mainly shale, form the paler areas between the pillars. A rubble-filled void in the backwall shows the development of a choked chimney. Photo taken by C.N. Waters (BGS © NERC).

Fig. 7. Schematic illustration of the development of cavities, fractures and collapse structures as a consequence of a confined underground nuclear weapon detonation: (**a**) and (**b**) in profile (from Houser 1969) showing initial maintenance of the explosion cavity (a) until the main collapse occurs after several seconds, culminating in surface subsidence (b) and (**c**) in plan (from Barosh 1968) showing radial, concentric and linear fracture patterns.

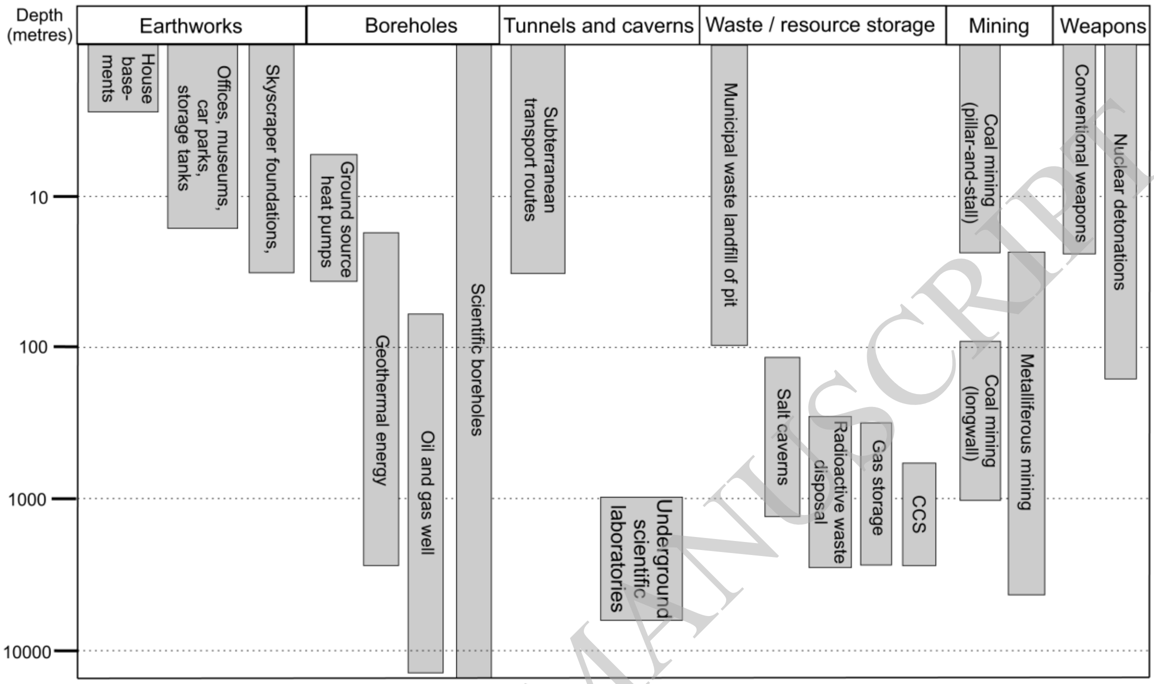
Fig 8. Comparison of crater structures associated with (**a**) meteorite impact at Meteor Crater; (**b**) comparatively deep unconfined nuclear detonation at Teapot Ess; (**c**) comparatively shallow unconfined nuclear detonation at Jangle U (Shoemaker 1959).

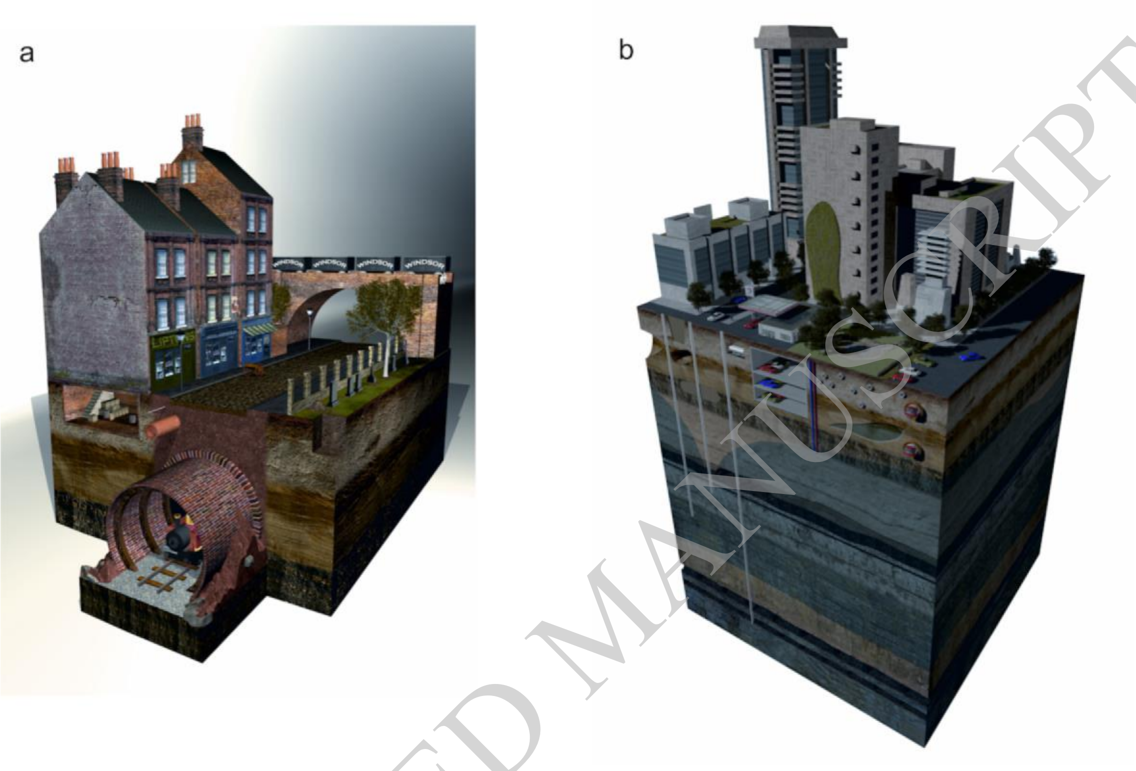
Fig. 9. Schematic view of secondary effects associated with hydraulic fracture that may be observed as of anthropogenic origin (from Legarth *et al*. 2005).

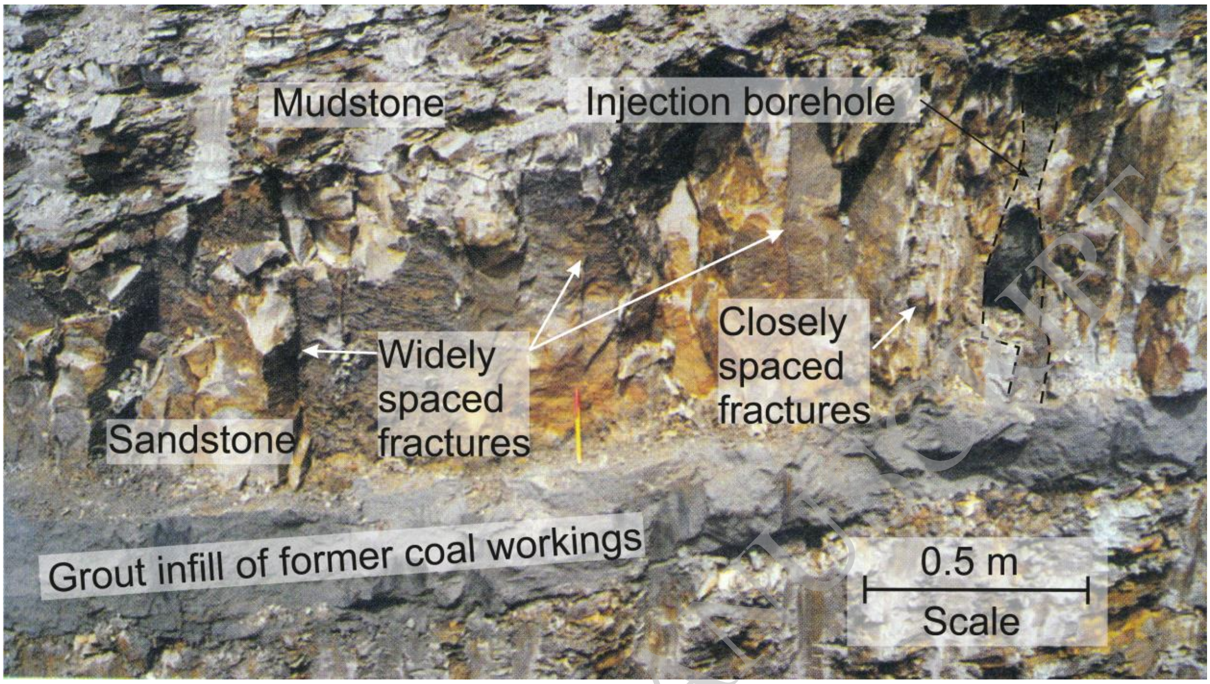
Fig. 10. (**a**) Components of the CCS storage system showing interaction of the CO_2 plume with formation waters and the CO_2 bubble with the host and cap rock

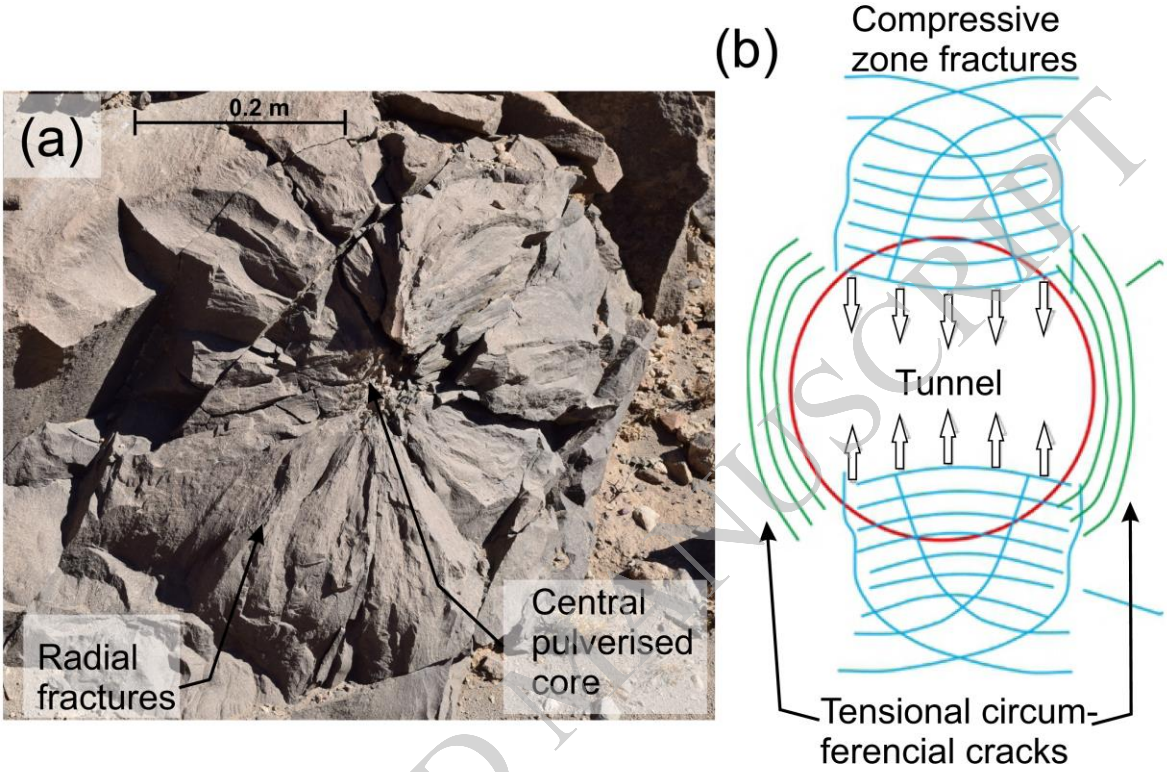
(schematic cross-section from Rochelle *et al*. 2004); (**b**) Trapping mechanisms of CO_2 with time (IPCC 2005).

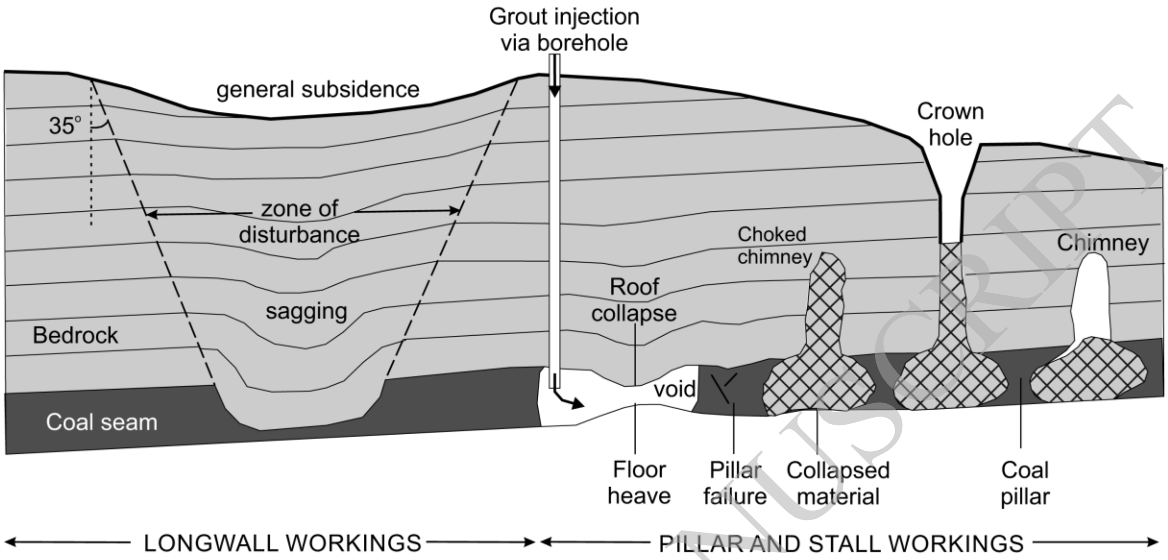
Fig. 11. Maximum persistence of key subsurface physical and chemical signals and their likely maximum distance of migration beyond the source anthropogenic feature. CCS: Carbon Capture and Storage; EDZ: Excavation Damaged Zone; GDF: Geological Disposal Facility.

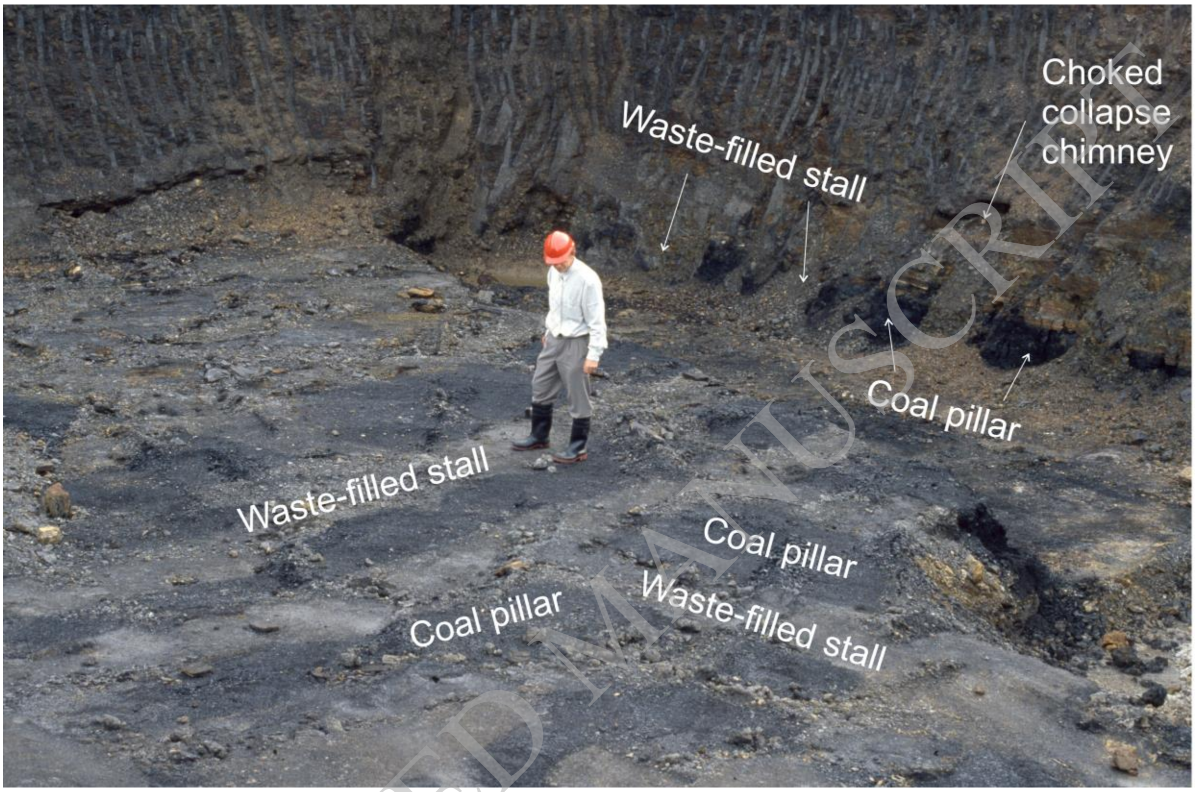

Depth (metres)
Earthworks
Boreholes
Tunnels and caverns
Waste / resource storage
Mining
Weapons
10
100
1000
10000
House base-ments
Offices, museums, car parks, storage tanks
Skyscraper foundations,
Ground source heat pumps
Geothermal energy
Oil and gas well
Scientific boreholes
Subterranean transport routes
Underground scientific laboratories
Municipal waste landfill of pit
Salt caverns
Radioactive waste disposal
Gas storage
CCS
Coal mining (pillar-and-stall)
Coal mining (longwall)
Metalliferous mining
Conventional weapons
Nuclear detonations

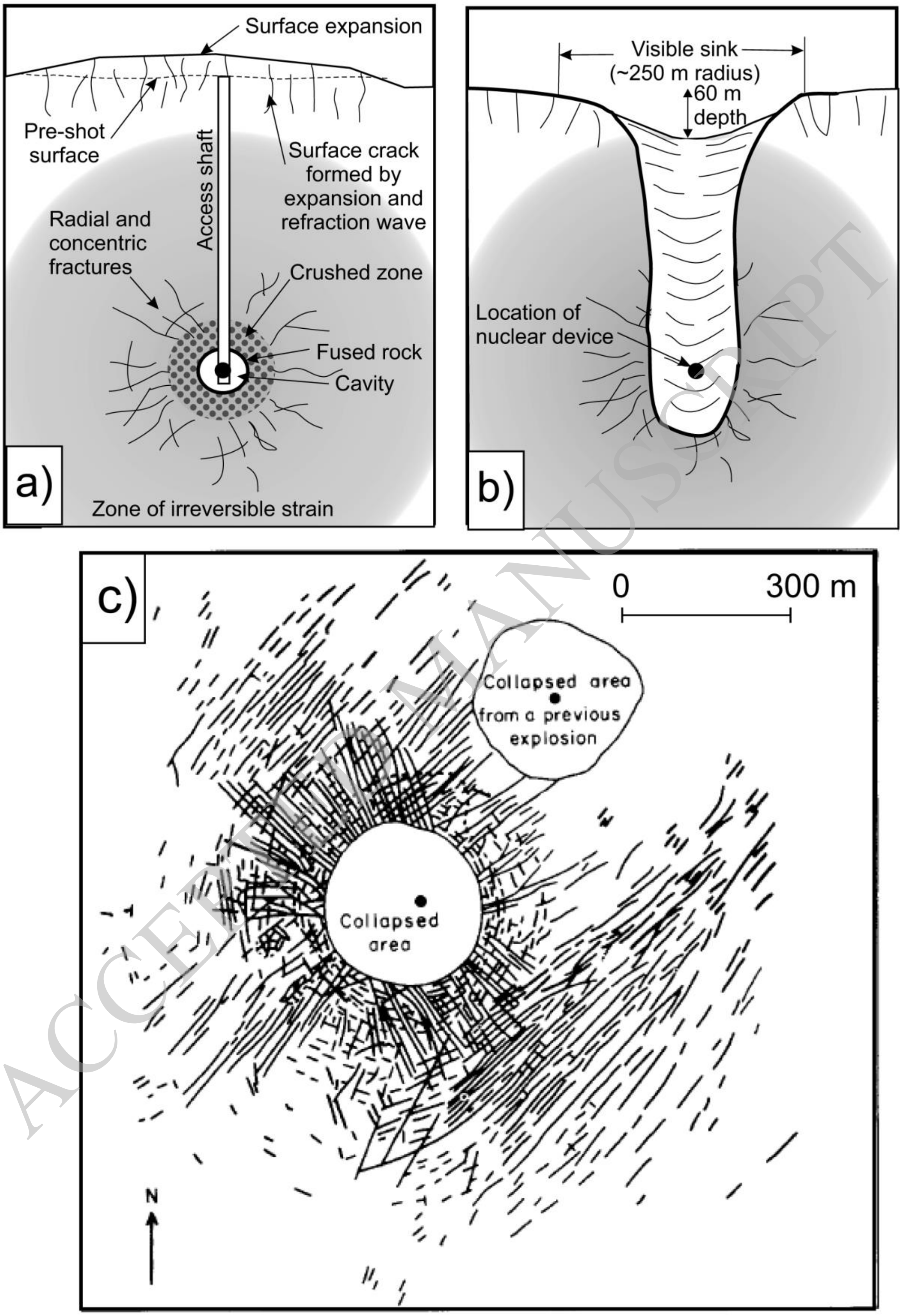

a
WINDSOR
WINDSOR
WINDSOR
WINDSOR
b

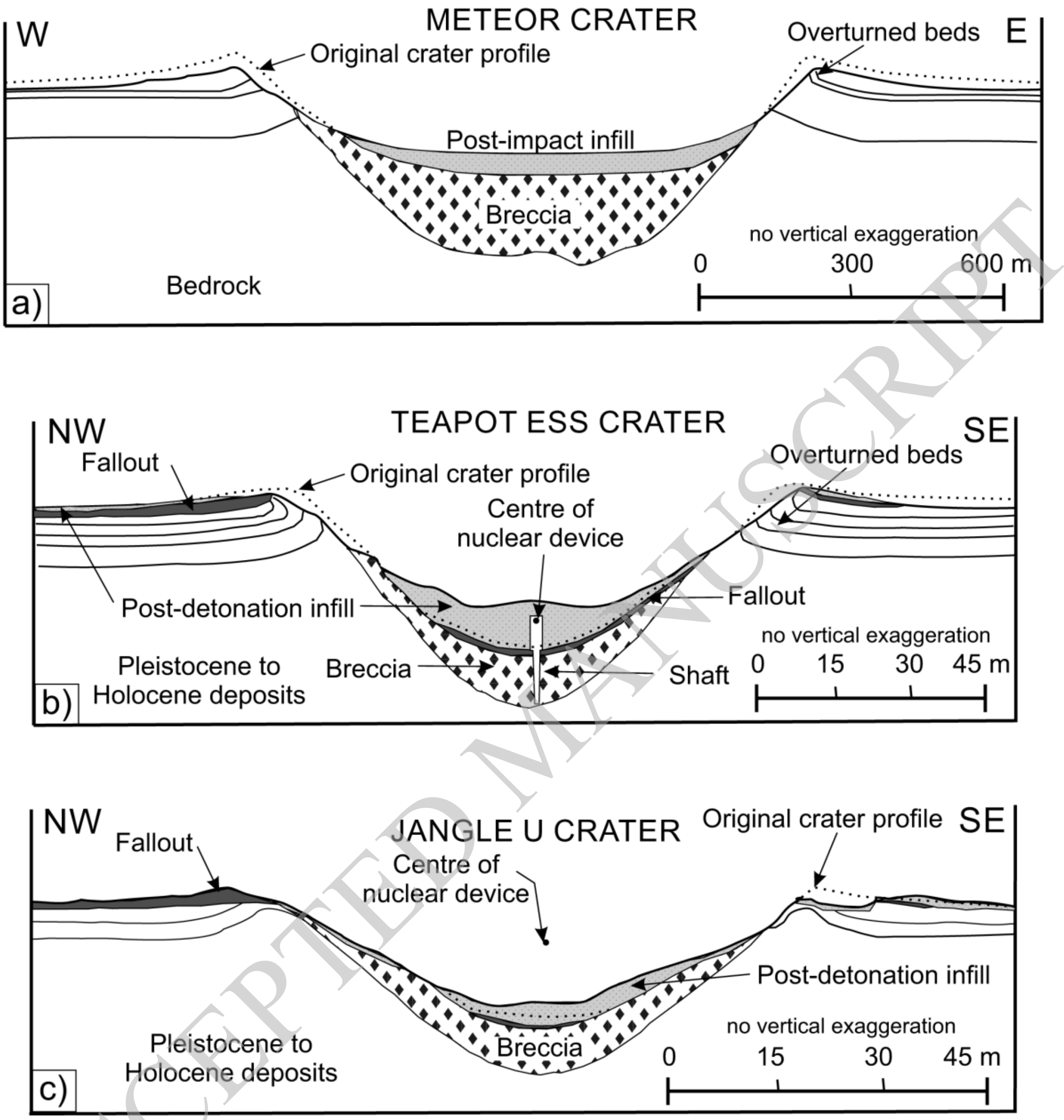

Mudstone
Injection borehole
Widely spaced fractures
Closely spaced fractures
Sandstone
Grout infill of former coal workings
0.5 m
Scale

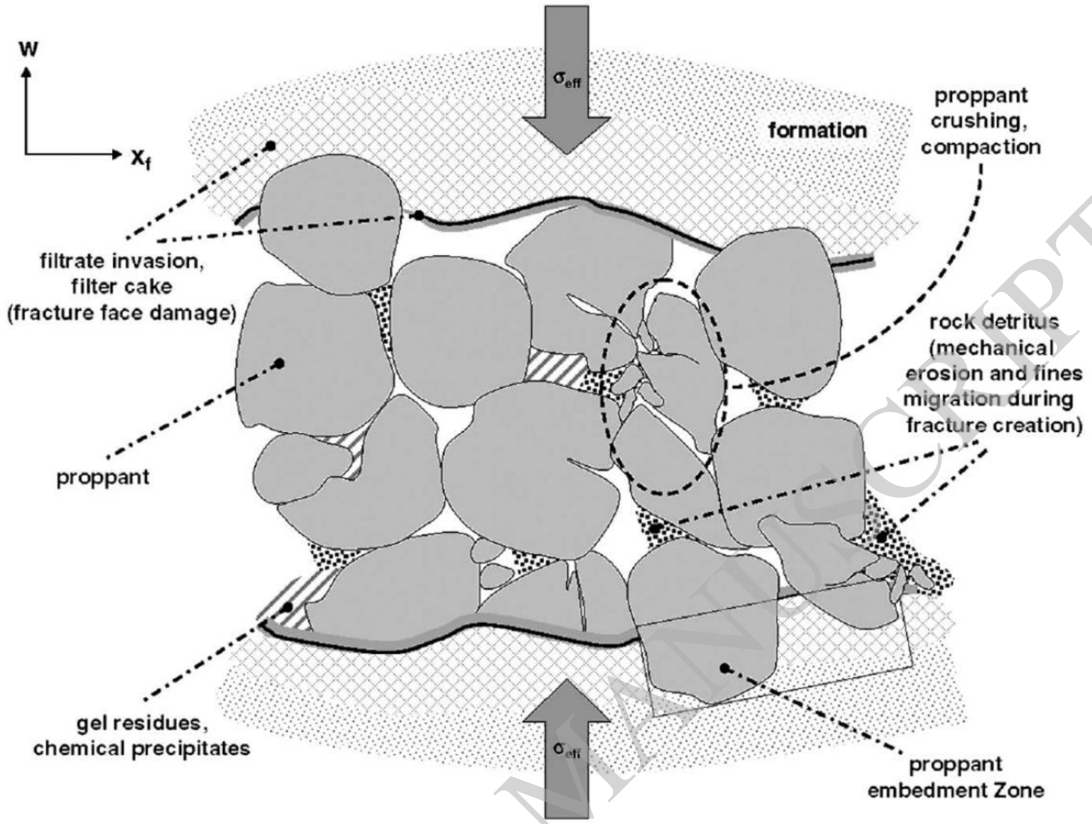

(a)
0.2 m
Radial fractures
Central pulverised core
(b)
Compressive zone fractures
Tunnel
Tensional circum-ferencial cracks

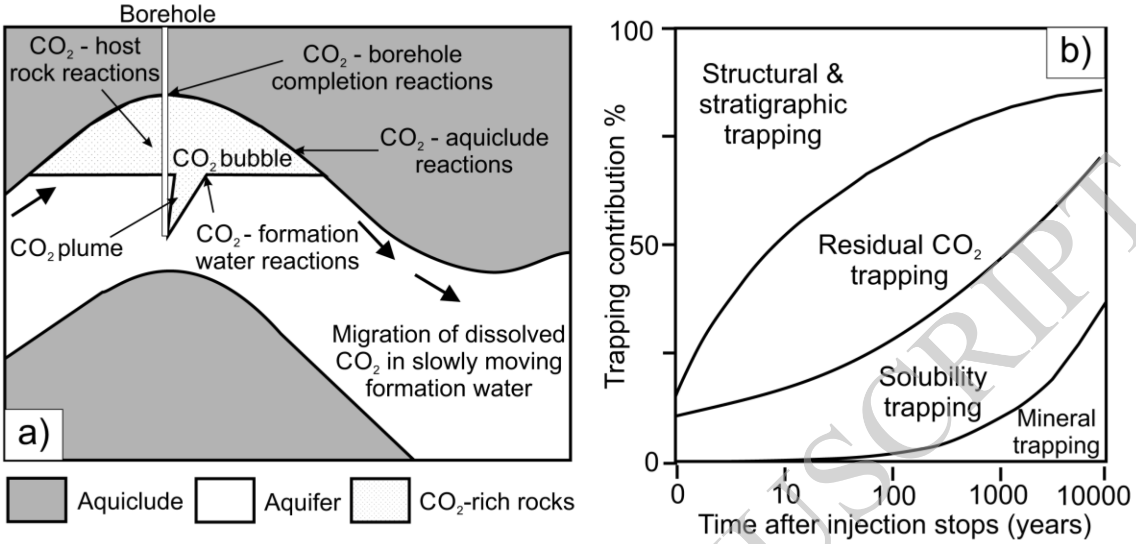

Grout injection
via borehole
general subsidence
35°
zone of
disturbance
sagging
Bedrock
Coal seam
Roof
collapse
void
Choked
chimney
Crown
hole
Chimney
Floor
heave
Pillar
failure
Collapsed
material
Coal
pillar
LONGWALL WORKINGS
PILLAR AND STALL WORKINGS

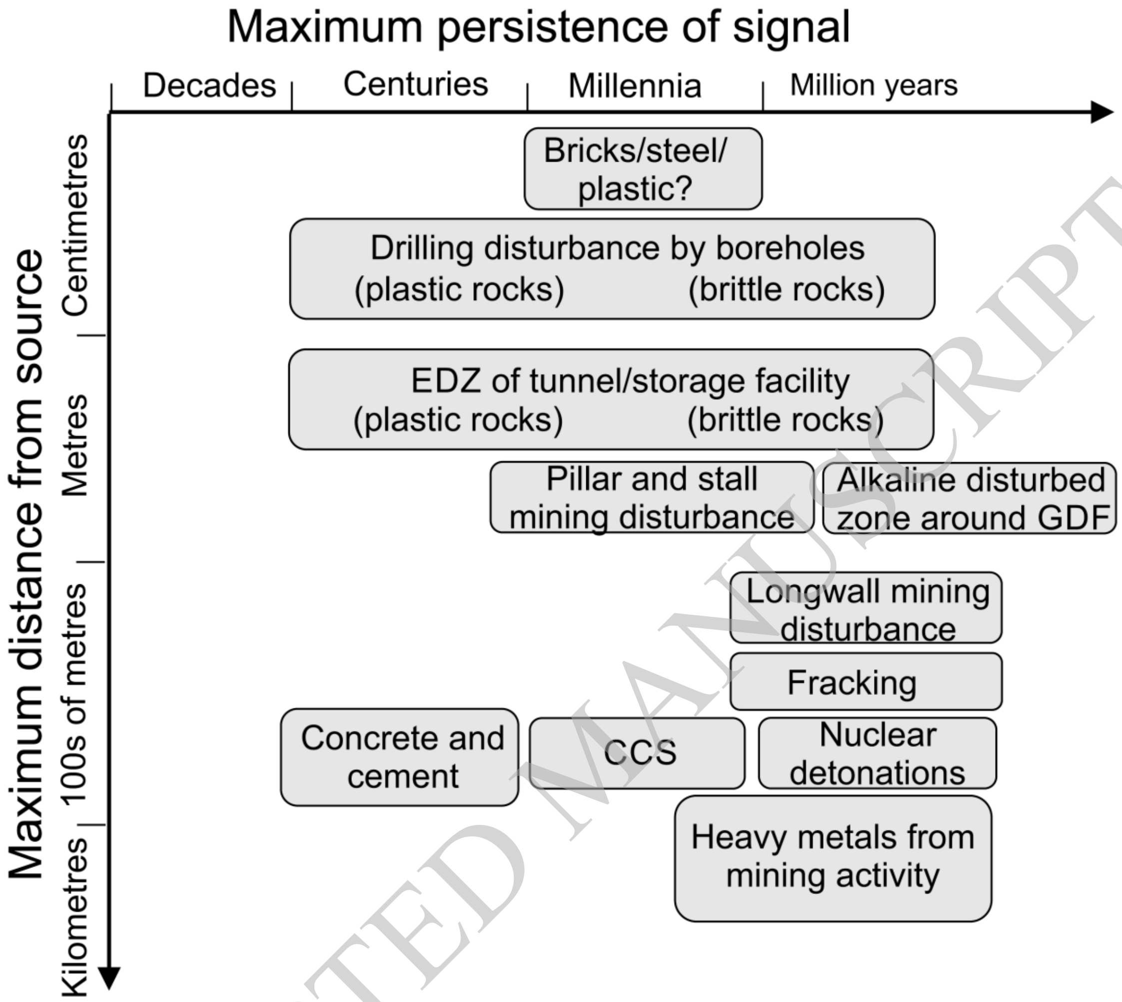

Choked collapse chimney
Waste-filled stall
Coal pillar
Waste-filled stall
Coal pillar
Coal pillar
Waste-filled stall


Surface expansion
Pre-shot surface
Access shaft
Surface crack formed by expansion and refraction wave
Radial and concentric fractures
Crushed zone
Fused rock
Cavity
a)
Zone of irreversible strain
Visible sink (~250 m radius)
60 m depth
Location of nuclear device
b)
c)
0
300 m
Collapsed area from a previous explosion
Collapsed area
N


W
METEOR CRATER
E
Original crater profile
Overturned beds
Post-impact infill
Breccia
no vertical exaggeration
0
300
600 m
Bedrock
a)
NW
TEAPOT ESS CRATER
SE
Fallout
Original crater profile
Overturned beds
Centre of nuclear device
Post-detonation infill
Fallout
no vertical exaggeration
0
15
30
45 m
Pleistocene to Holocene deposits
Breccia
Shaft
b)
NW
Fallout
JANGLE U CRATER
Original crater profile
SE
Centre of nuclear device
Post-detonation infill
no vertical exaggeration
0
15
30
45 m
Pleistocene to Holocene deposits
Breccia
c)


w
x_f
σ_{eff}
formation
proppant crushing, compaction
filtrate invasion, filter cake (fracture face damage)
rock detritus (mechanical erosion and fines migration during fracture creation)
proppant
gel residues, chemical precipitates
σ_{eff}
proppant embedment Zone


Borehole
CO$_2$ - host rock reactions
CO$_2$ - borehole completion reactions
CO$_2$ - aquiclude reactions
CO$_2$ bubble
CO$_2$ plume
CO$_2$ - formation water reactions
Migration of dissolved CO$_2$ in slowly moving formation water
a)
Aquiclude
Aquifer
CO$_2$-rich rocks
b)
Structural & stratigraphic trapping
Residual CO$_2$ trapping
Solubility trapping
Mineral trapping
Trapping contribution %
100
50
0
0
10
100
1000
10000
Time after injection stops (years)


Maximum persistence of signal
Decades
Centuries
Millennia
Million years
Maximum distance from source
Centimetres
Metres
100s of metres
Kilometres
Bricks/steel/ plastic?
Drilling disturbance by boreholes (plastic rocks) (brittle rocks)
EDZ of tunnel/storage facility (plastic rocks) (brittle rocks)
Pillar and stall mining disturbance
Alkaline disturbed zone around GDF
Longwall mining disturbance
Fracking
Concrete and cement
CCS
Nuclear detonations
Heavy metals from mining activity

Subsurface modification type	**Depth range**	**Typical anthropogenic materials**
Earthworks	**<10m:** basements, spread foundations, utility and sewerage networks; **>10m–<150m:** piled foundations, deep basements, transportation networks	Brick, earthenware (pre-1950); concrete, plastic, geotextiles (post-1950); wire cables, steel
Boreholes and hydrocarbon wells	**>3m–<100m:** ground investigation boreholes; **>15m–<100m:** ground source heat pumps; **<12300m:** scientific boreholes and hydrocarbon wells (e.g. Z-44 Chayvo well, Russia)	Steel casing, cement and grout; plastic casing/ liners in monitoring wells; drilling muds, sand and gravel packing in uncased hydrocarbon wells
Tunnels and caverns	**<50m:** transport	Brick or bolted cast iron segmental lining (pre-1950); concrete lining (post-1950)
Waste and resource storage facilities	**>200–<1000m:** Geological Disposal Facility (GDF); **>800m–<3000m:** Carbon Capture and Storage (CCS)	**GDF:** waste (possibly as glass), metal container (Cu or Pb), cement or bentonite plug or seal, backfill
Mineral workings	**<10m:** coal bell pits; **<30m:** coal pillar-and-stall; **>100–<1000m:** coal longwall mining; **<4000m:** gold mining	Props, corrugated iron shuttering and linings, stowed wastes
Weapon detonation	**<2850m:** nuclear detonation, e.g. Nefte-yugamsk, Russia	Melt of nuclear device and associated hardware and adjacent rock/ sediment

Table 1. Typical types of anthropogenic subsurface modifications, their depth of influence and associated material types.

Type	Magnitude of effect (m)	Mechanical alteration processes and effects	Natural analogue	References
Earthworks	10^{-3} to 10^{2}	• Mechanical compaction of sediment or weak rock. • Induced seismicity and consolidation through loading, e.g. dam construction.	Glacial/ sediment loading	Gupta (1985)
Boreholes and wells	10^{-3} to 10^{-2} (mechanical fractures) 10^{-3} to 10^{3} (hydraulic fractures)	• Production and partial or complete infill of discontinuities adjacent to boreholes and wells from mechanical disturbance and/or hydraulic fracture to increase permeability (Fig. 1). • Fault reactivation, subsidence during pore-fluid extraction and induced seismicity. • Consolidation from pore-fluid extraction; can be countered by swelling from injection of drilling fluids. • Fracture enhancement through acidulation in carbonate aquifers.	Natural hydraulic fractures, sand-filled injectites and fracture pipes	Banks *et al*. (1993), Cox *et al*. (1996), Cuss *et al*. (2015), Davidson *et al*. (1995), Davies *et al*. (2012, 2013), Doornhoff *et al*. (2006), Gale *et al*. (2007, 2014), Kelsall *et al*. (1983), Simon (2005)
Tunnels and caverns	10^{-3} to 10^{3}	• Excavation Damage Zone (EDZ) resulting in opening or closing of fractures and rock-crystal realignment (e.g. salt mining). Extent of EDZ from cavity excavation is typically 0.3 to 0.7 excavation radius (Fig. 2). • Ground subsidence.	Natural dissolution collapse structures	Blümling *et al*. (2007), Kelsall *et al*. (1983)
Geological Disposal Facility	10^{-3} to 10^{0}	• EDZ extent influenced by presence of natural fractures, initial stress field, bulk materials properties and geometry of excavation. • EDZ resulting in opening of natural sub-vertical fractures; fractures may self-seal if excavated material deforms plastically with increasing stress. • Creation of shear zones.	Natural nuclear fission reactors, e.g. Oklo (Gabon)	Blümling *et al*. (2007), Cai & Kaiser (2005), De Windt *et al*. (1999), Martino & Chandler (2004), Mertens *et al*. (2004)
Solid mineral workings	10^{-3} to 10^{4}	• Subsidence whose magnitude and style depends on rock physical properties, seam/ore thickness, overburden thickness, groundwater conditions and excavation style (Figs 3 & 4). • Partial or complete fill of mining-induced voids with artificial cement (grout). • Fault reactivation and induced seismicity through roof collapse/ floor heave. • Opening of discontinuities including fractures.	Natural dissolution collapse structures	Bell (1978), Bowell *et al*. (1999), Commission on Energy and the Environment (1981), Li *et al*. (2007), Waters *et al*. (1996)
Munition detonation	10^{-3} to 10^{3}	• Induced seismicity resulting in rock fracture and crushing (Fig. 5). Zones of rock crushing rock cracking and zone of irreversible strain. • Creation of voids (radii 4 – 12 m/kton$^{1/3}$) and debris chimneys (Fig. 5). • Temperature effects include partial or complete rock melting; magnitude decreases from detonation zone. • Inverted bedrock stratigraphy in deep subsurface detonation (Fig. 6). • Consolidation and subsidence (deep subsurface detonation).	Meteorite impact, e.g. Meteor Crater (Arizona)	Adushkin & Spivak (1994), Hawkins & Wohletz (1996), McEwan (1988), Shoemaker (1959), US Congress (1989)

Table 2. Mechanical effects of anthropogenic subsurface modification. The magnitude, style and extent of the example effects is in part dependent on the properties of the excavated material, including its consolidation characteristics, stiffness and drained and/or undrained shear strength behaviour, which is in turn influenced by its past, present and future stress condition.

Material type	Chemical alteration processes and effects	Natural analogue	References
Bricks	• Swelling on absorption of water (bricks include swelling clays, lime and elements including Na and K). • Swelling due to salt efflorescence. Conditioning factors: mineralogical composition, method of manufacture, firing temperature and duration	Thermally metamorphosed sandy clay	Dunham (1992), Elert *et al*. 2003, Hughes & Bargh (1982), Sena da Fonseca *et al*. (2013)
Concrete	• Cement mineralogical changes include precipitation of gypsum, carbonation produces carbonate minerals and leached ions e.g. Portlandite → $CaCO_3$, Ca -silicate hydrates → $CaCO_3$ + SiO_2, Ca-aluminate hydrates → $CaCO_3$ + gibbsite ($CaCO_3$ = calcite, aragonite or vaterite depending on supersaturation of fluid). • Short-term (<10^2 yr) porosity decrease associated with mineral-phase transformation, followed by porosity increase due to loss of primary cement and re-dissolution of secondary minerals, e.g. zeolite. On 10^3 yr timescale alteration product is carbonated, low-porosity layer like that occurring naturally. • Leaching from lime mortars and cement-grouting increases groundwater pH. • Rapid growth of speleothems in cellars and tunnels. Portland cement has generally been in wide use for ~10^2 yr so its long-term durability and preservation potential is uncertain.	Low-temperature serpentinisation of ultrabasic rocks; high temperature-low pressure metamorphic aureoles in calcareous or carbonaceous sediments	Alexander (1992), Attard *et al*. (2016), Gheradi *et al*. (2012), Liu & He (1998), Milodowski *et al*. (2009), Rochelle & Milodowski (2013), Waters & Zalasiewicz (2018)
Drilling fluids and structures in wells and pipes	• Circulation of bentonite-rich drilling fluid and concrete grout used to seal wells may result in injection of $CaCO_3$ and sulphate into surrounding fractured rock. • Drilling mud injectites distinguished by presence of flow structures, abraded cuttings, wedge-shaped geometries with sharp tops and bases, cross-cutting bedding relationships and absence of trace fossils, stylolites and concretions. • Drilling muds may contain water-emulsifying, suspending and filtration-control agents, a suspension of clay and barite, salts (sodium chloride and calcium chloride), various detergents and flocculants and organic polymers. • Accelerated corrosion of steel drill casing through oxidation produces iron oxides, or precipitation of siderite or iron sulphide in O_2-poor environment. • Potential chemical degradation of plastic polymers in pipes and liners by molecular alteration by hydrolysis or heating in conditions of high or low pH. • Introduction of polymer-based drilling fluids and chemical additives and proppants designed to keep open fractures. • Contamination from Underground Coal Gasification or waste disposal via bore.	Natural hydraulic fractures; natural neptunean dykes	Burton *et al*. (2013), Caenn *et al*. (2011), Daemen (1996), Enning & Garrelfs (2014), Hilbecht & Meyer (1989), Hodgkinson & Hughes (1999), Legarth *et al*. (2005), Rochelle & Milodowski (2013), Savage (2011)

Material type	**Chemical alteration processes and effects**	**Natural analogue**	**References**
Rocks adjacent to Geological Disposal Facility	• Caverns filled in part with radioactive waste stored in concrete cells or vitrified form, in turn placed in copper cannister filled with lead (Swedish method), or in steel cannister (Swiss method) and surrounded by bentonite. Bentonite buffer designed not to significantly degrade within the first 10^6 yr of operation. Steel cannisters may degrade within 10^4 yr of operation and de-vitrification of glass between ~10^5 and 10^7 yr. • Fluid could be produced from cement dissolution, resulting in an alkaline plume migrating into bedrock, in turn causing mineral dissolution and precipitation of amorphous Ca-aluminosilicate mineral phases. • Elevated temperature-induced clay-mineral phase transition, e.g. >100°C smectite is modelled to transform to illite in <1x10^6 yr.	Low grade metamorphism of mudrocks; Natural nuclear fission reactors, e.g. Oklo (Gabon)	Alexander & McKinley (1999), Berry *et al*. (1999) Eikenberg & Lichtner (1992), Hodgkinson & Hughes (1999), Milodowski *et al*. (2015), Savage & Rochelle (1993), Weaver (1979)
Rocks part of Carbon Capture and Storage	• Trapping of CO_2 as a free phase in geological structural traps. • Dissolving CO_2 into local groundwater to form a supercritical CO_2 plume reaching 5 m radius around the injection well after 10^1 yr and a two phase zone of ~650 m radius. • Residual trapping along the migration path of CO_2. • Mineral trapping through dissolution of mineral phases, e.g. feldspar, dolomite and anhydrite, and precipitation of clay and calcite phases.	Bravo Dome CO_2 field, New Mexico; Fizzy Horst, Southern North Sea	André *et al*. (2007), IPCC (2005), Rochelle *et al*. (1999, 2004)
Mining leachate	• Production of acidic groundwater commonly from oxidation of FeO_2 and subsequent incorporation of dissolved metals including Fe^{3+}. • Subsequent precipitation of minerals dominated by iron oxyhydroxides, oxysulphates such as ferrihydrite ($Fe(OH)_3$), goethite (FeOOH) and iron sulphate polymorphs.	Natural oxidation of sulphide-bearing rocks	Akcil & Koldas (2006), Bowell *et al*. (1999)
Rocks/soils at atomic weapon test sites	• Production of durable, but localised conversion of sand into a glass-like substance known variably as trinitite and kharitonchik, with unmelted quartz grains, metallic chondrules and radionuclides.	Meteorite impact sites	Eby *et al*. (2010), Shoemaker (1959)

Table 3. Chemical and mineralogical changes brought about by anthropogenic modification of the subsurface.