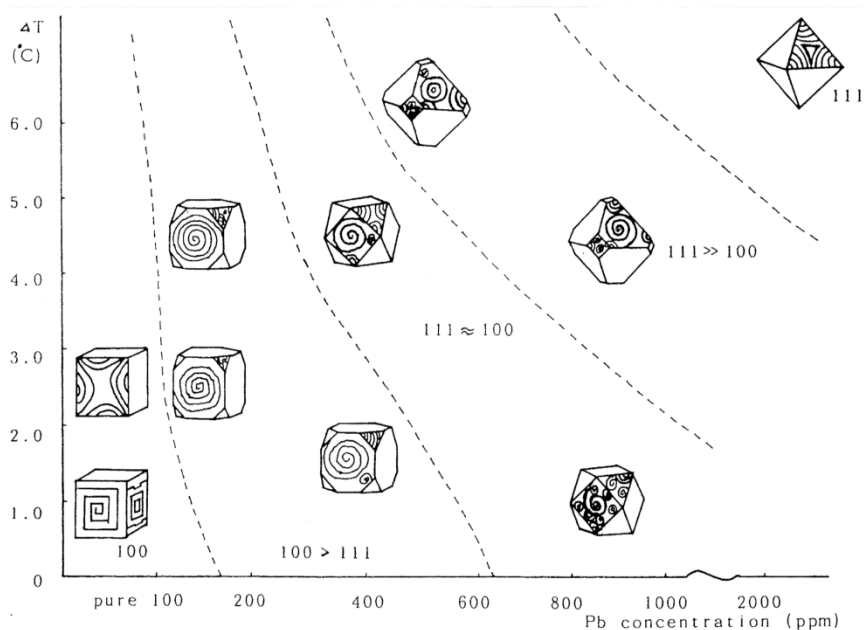


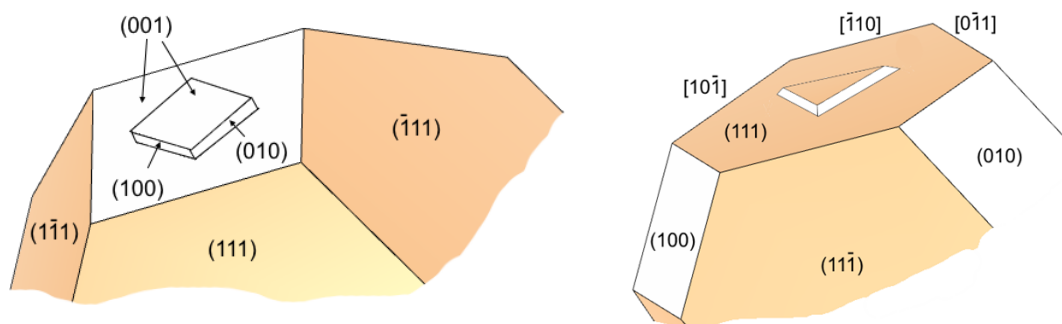
## Supporting Information



**Fig. 1 (S.I.)** Morphodrome of KCl crystals growing at different supersaturation values and under different Pb concentration (ppm) in solution. This is the original Figure that can be found in the paper: Lian, L.; Tsukamoto, K.; Sunagawa, I.; J. Crystal Growth 1990, 99, 150. Surface patterns are drawn in detail on different as grown surfaces.  $\sigma$  (%) represents the supersaturation, while  $\Delta T$  is the corresponding temperature difference from the equilibrium (saturation) temperature.

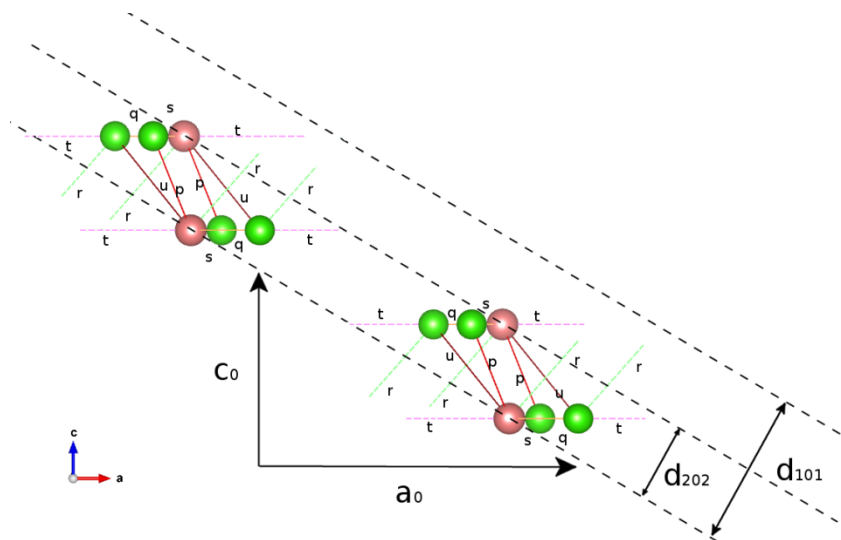
Fig. 1 in the main text has been inspired from Fig. 1 (S.I.) and redrawn for the sake of clarity.

### Surface patterns of KCl (cube + octahedron) grown in the presence of Pb.

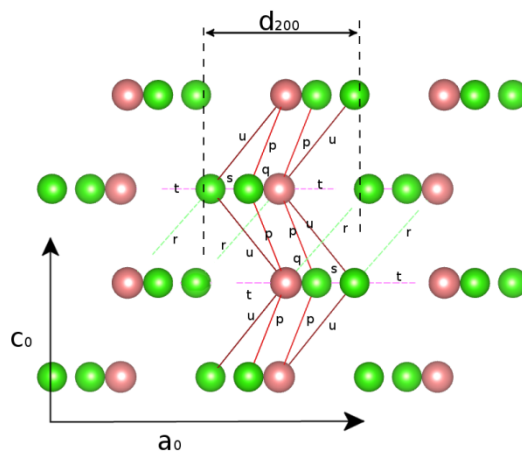


**Fig. 2 (S.I.)** Sketch of the surface patterns observed on KCl crystals grown in the presence of Pb, as shown in Fig. 4. Left side: the cube face, let's say (001), is limited by four equivalent  $\langle 110 \rangle$  edges and is populated by growth islands limited by macrosteps having the structure of the cube faces (100) and (010), while the terrace of the island has the structure of the (001) substrate. Right side: onto a (111) octahedron face, limited by six equivalent  $\langle \bar{1}10 \rangle$  edges, the growth islands are defined by macrosteps having the structure of the faces (100), (010) and (001); the terrace of the island has the structure of the underlying (111) face. White color stays for cubic surface structure, while orange color stays for the octahedral one.

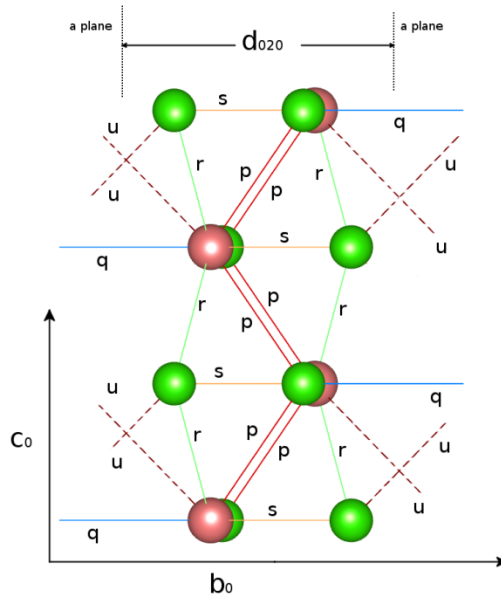
### Surface structures of some crystal forms of Cotunnite-PbCl<sub>2</sub>



**Fig. 3a (S.I.)** Projection along the [010] direction of the  $\text{PbCl}_2$  structure. The composition of a slice with thickness  $d_{202}$  shows that the PBCs running along the [010] direction are not connected within the slice thickness. Since the slices of thickness  $d_{101}$  are not allowed, owing to the extinction rules, the character of the corresponding  $\{101\}$  form is decidedly stepped. According to the Hartman-Perdok method,  $\{101\}$  is a S form. Chlorine atoms- green color



**Fig. 3b (S.I.)** Projection along the [010] direction of the  $\text{PbCl}_2$  structure. The composition of a slice with thickness  $d_{200}$ , allowed by the extinction rules, shows that the PBCs running along the [010] direction are connected within the slice thickness. Thus, according to the Hartman-Perdok method,  $\{100\}$  is a F (flat) form. Nevertheless, the figure shows that the  $\{100\}$  surface profile is markedly wavy, even if the face character allows that this form can grow layer by layer (of minimum thickness  $d_{200}$ ). Chlorine atoms- green color



**Fig. 4 (S.I.)** Projection along the [100] direction of the  $\text{PbCl}_2$  structure. The composition of a slice with thickness  $d_{020}$  shows that the PBCs running along the [100] direction are strongly connected, within the slice thickness, by  $2p(2.873 \text{ \AA})$  and  $2r(3.072 \text{ \AA})$  bonds. Each  $d_{020}$  slice is confined within two  $a$ -glide planes, which render non-polar the  $\{010\}$  surfaces that, in turn, do not need to be reconstructed. Chlorine atoms- green color.

The reference frame we adopted for  $\text{PbCl}_2$ , in order to improve the PBC analysis carried out by Woensdregt – Hartman (1988), was that determined by Y. Z. Nozik, L.E. Fykin, L.A. Muradyan, Soviet Phys. Crystallography 21 (1976) 38-40; Krystallographia, 21 (1976) 76-79

Then, we used, for  $\text{PbCl}_2$ :  $a_0 = 7.615 \text{ \AA}$ ,  $b_0 = 9.022 \text{ \AA}$ ,  $c_0 = 4.514 \text{ \AA}$ , associated to the orthorhombic space group  $Pnam$  and to the following atomic positions

atom	Fractional coordinate ( $x/a_0$ )	Fractional coordinate ( $y/b_0$ )	Fractional coordinate ( $z/c_0$ )
Pb	0.2607	0.0955	0.25
Cl <sub>1</sub>	0.8575	0.0745	0.25
Cl <sub>2</sub>	0.4773	0.8379	0.25

The symmetry operations related to the  $Pnam$  setting were:  $x,y,z$ ;  $-x, -y, (\frac{1}{2}+z)$ ;  $(\frac{1}{2}+x), (\frac{1}{2}-y), z$ ;  $(\frac{1}{2}-x), (\frac{1}{2}+y), (\frac{1}{2}+z)$ . The glide planes  $n$  and  $a$  are located at  $x=(1/4), (3/4)$  and  $y=(1/4), (3/4)$ , respectively. The mirror planes  $m$  are located at  $z=(1/4), (3/4)$ .

To help the reader, in the following Table the atoms belonging to the  $\text{PbCl}_2$  elementary cell are labelled, along with their fractional coordinates.

	x	y	z		$(\frac{1}{2}+x)$	$(\frac{1}{2}-y)$	z
Pb <sub>1</sub>	0.2607	0.0955	0.25	Pb <sub>3</sub>	0.7607	0.4045	0.25
Cl <sub>11</sub>	0.8575	0.0745	0.25	Cl <sub>13</sub>	0.3575	0.4225	0.25
Cl <sub>21</sub>	0.4773	0.8379	0.25	Cl <sub>23</sub>	0.9773	0.6621	0.25
	$-x$	$-y$	$(\frac{1}{2}+z)$		$(\frac{1}{2}-x)$	$(\frac{1}{2}+y)$	$(\frac{1}{2}+z)$
Pb <sub>2</sub>	0.7393	0.9045	0.75	Pb <sub>4</sub>	0.2393	0.5955	0.75

Cl <sub>12</sub>	0.1425	0.9255	0.75	Cl <sub>14</sub>	0.6425	0.5745	0.75
Cl <sub>22</sub>	0.5227	0.1621	0.75	Cl <sub>24</sub>	0.0227	0.3379	0.75

In the following Table, the interatomic Pb-Cl bonds are labelled along with their length (Å). Besides the label  $\delta_i$ , the symbols used by Woensdregt –Hartman are also indicated (in parentheses).

Bond label	Bond length (Å)	Atoms involved	Bond disposition
$\delta_1$ (s)	2.845	Pb <sub>1</sub> - Cl <sub>21</sub> [0 $\bar{1}$ 0] Pb <sub>2</sub> [0 $\bar{1}$ 0] - Cl <sub>22</sub> Pb <sub>4</sub> - Cl <sub>24</sub> Pb <sub>3</sub> - Cl <sub>23</sub>	z = 1/4 z = 3/4 z = 3/4 z = 1/4
$\delta_2$ (p)	2.873	Pb <sub>2</sub> - Cl <sub>11</sub> [010] Pb <sub>3</sub> - Cl <sub>14</sub> Pb <sub>4</sub> - Cl <sub>13</sub> Pb <sub>1</sub> - Cl <sub>12</sub> [0 $\bar{1}$ 0]	all bonds connect atoms at z = 1/4 with atoms at z = 3/4
$\delta_3$ (q)	3.066	Pb <sub>1</sub> - Cl <sub>13</sub> Pb <sub>4</sub> - Cl <sub>12</sub> Pb <sub>3</sub> - Cl <sub>11</sub> Pb <sub>2</sub> - Cl <sub>14</sub>	z = 1/4 z = 3/4 z = 1/4 z = 3/4
$\delta_4$ (r)	3.072	Pb <sub>2</sub> - Cl <sub>21</sub> Pb <sub>3</sub> - Cl <sub>24</sub> [100] Pb <sub>1</sub> - Cl <sub>22</sub> Pb <sub>4</sub> - Cl <sub>23</sub> [ $\bar{1}$ 00]	all bonds connect atoms at z = 1/4 with atoms at z = 3/4
$\delta_5$ (t)	3.076	Pb <sub>1</sub> - Cl <sub>11</sub> [ $\bar{1}$ 00] Pb <sub>2</sub> - Cl <sub>12</sub> [100] Pb <sub>3</sub> - Cl <sub>13</sub> Pb <sub>4</sub> - Cl <sub>14</sub>	z = 1/4 z = 3/4 z = 1/4 z = 3/4
$\delta_6$ (u)	3.628	Pb <sub>1</sub> - Cl <sub>24</sub> Pb <sub>4</sub> - Cl <sub>21</sub> Pb <sub>3</sub> - Cl <sub>22</sub> Pb <sub>2</sub> - Cl <sub>23</sub>	all bonds connect atoms at z = 1/4 with atoms at z = 3/4

### Laurionite PbCl(OH)

We used, for PbCl(OH) :  $a_0 = 9.6987$  Å,  $b_0 = 4.0203$  Å,  $c_0 = 7.111$  Å, associated to the orthorhombic space group *Pcmn* and to the following atomic positions

atom	Fractional coordinate (x/a <sub>0</sub> )	Fractional coordinate (y/b <sub>0</sub> )	Fractional coordinate (z/c <sub>0</sub> )
Pb	0.0877	0.25	0.79736
O	0.0422	0.25	0.12230
H	0.1100	0.25	0.22300
Cl	0.8202	0.25	0.55640

The symmetry operations related to the *Pcmn* setting were:  $x, y, z$ ;  $-x, (\frac{1}{2}+y), -z$ ;  $(\frac{1}{2}+x), (\frac{1}{2}+y), (\frac{1}{2}-z)$ ;  $(\frac{1}{2}-x), (\frac{1}{2}-y), (\frac{1}{2}+z)$ . The glide planes *c* and *n* are located at  $x=(1/4), (3/4)$  and  $z=(1/4), (3/4)$ , respectively. The mirror planes *m* are located at  $y=(1/4), (3/4)$ .

